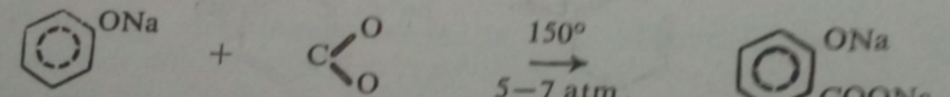
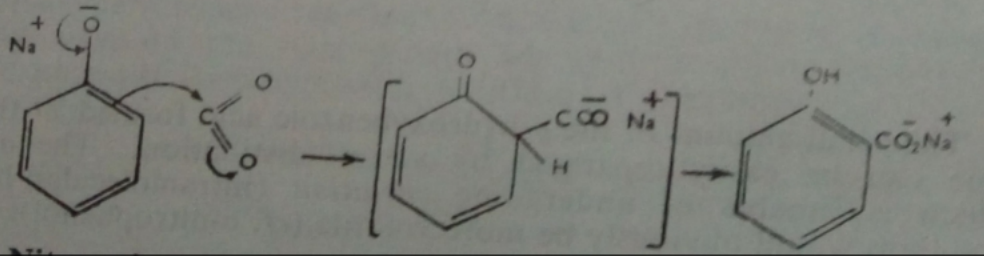
(*vii*) **Kolbe reaction**. When a sodium phenoxide is treated with carbon dioxide gas under pressure, a carboxyl group is introduced, preferably in *ortho* position to the -OH group, into the aromatic nucleus. For example,



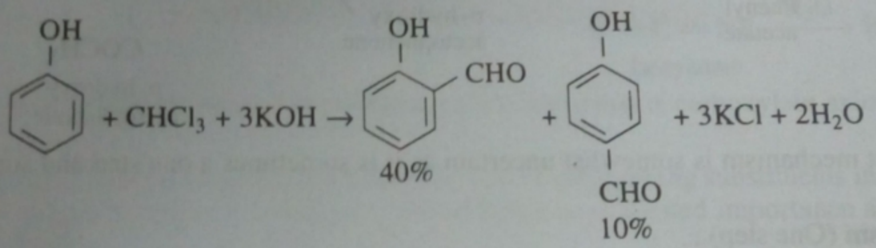
Sodium phenoxide

Sodium salicylate (main product)

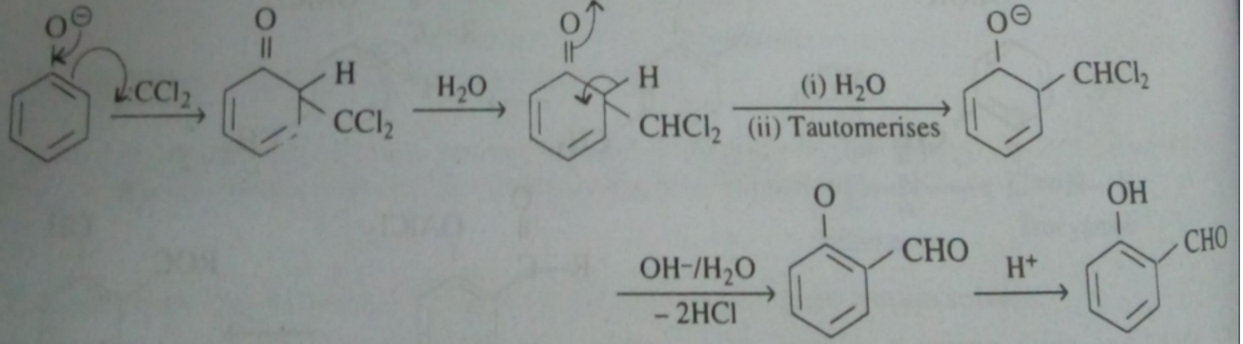
The mechanism of this reaction is believed to involve an electrophilic attack by carbon dioxide on the highly reactive ring, as illustrated below :



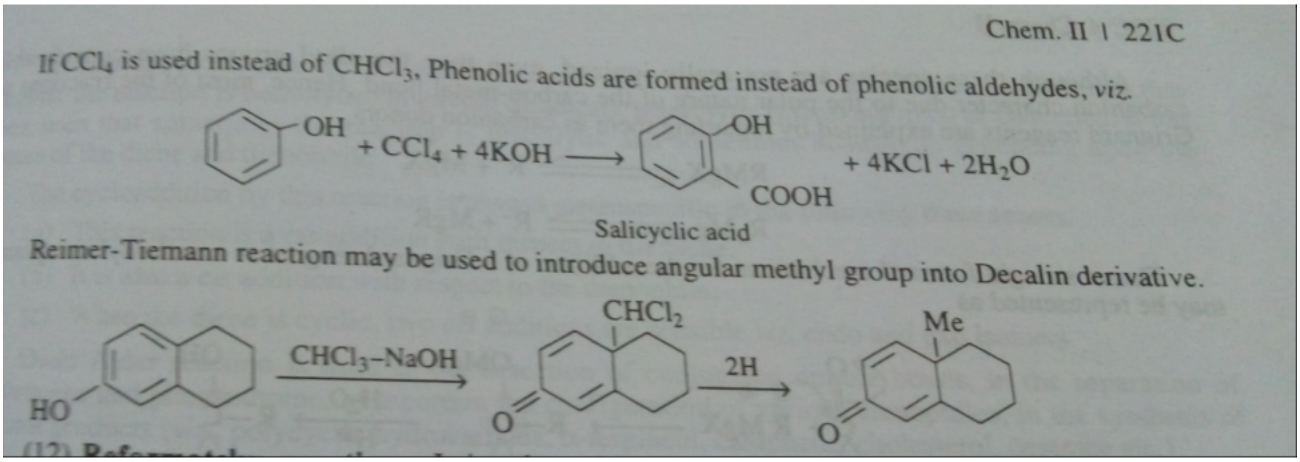
(11) **Reimer-Tiemann reaction**—This reaction consists in the conversion of phenols into phenolic aldehydes by treatment with alkaline chloroform solution



The reaction occur through dichlorocarbene which is generated by the action of alkali of chloroform.



Presence of –I groups such as CN, COOH etc. (*m*-orienting) inhibits the reaction.



If CCl_4 is used instead of $CHCl_3$, Phenolic acids are formed instead of phenolic aldehydes, *viz.*

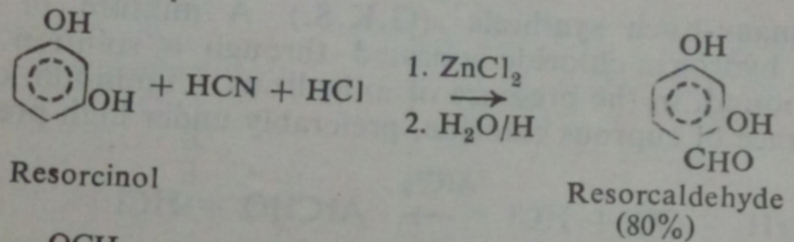
Salicyclic acid

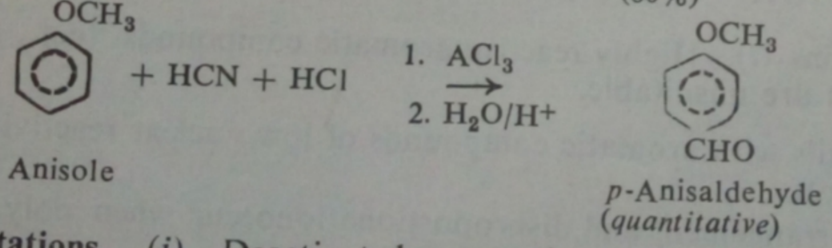
Reimer-Tiemann reaction may be used to introduce angular methyl group into Decalin derivative.

3. Gattermann's aldehyde synthesis. It consists in treating the aromatic substrate with a mixture of hydrogen cyanide and hydrogen chloride, in the presence of anhydrous aluminium chloride or zinc chloride (*cf.* G.K.S.)

$$\text{Ar—H} + \text{HCN} + \text{HCl} \xrightarrow[\text{2. } H_2O]{\text{1. } AlCl_3} \text{ArCHO}$$

Alternatively, a mixture of zinc cyanide and hydrogen chloride, in place of hydrogen cyanide, hydrogen chloride and zinc chloride, 's used. This method, unlike the Gattermann-Koch synthesis, is very successful with reactive aromatic substrates like phenols and phenolic ethers. For example.





Limitations. (*i*) Deactivated aromatic compounds (*e.g.*, $ArNO_2$) fail to react.

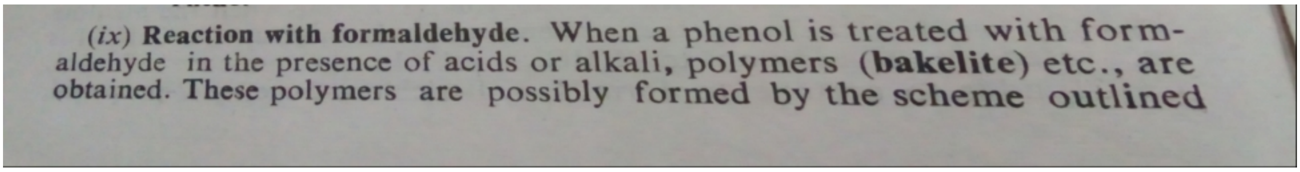
(*ii*) Aromatic compounds of moderate nuclear reactivity (*e.g* , C_6H_5Cl) give low yields.

Mechanism. It is believed to involve *electrophilic substitution* of he aromatic substrate, as shown below :

$$HC{\equiv}N + HCl \xrightarrow{AlCl_3} HC{\equiv}\overset{+}{N}H\ Al\overset{-}{Cl}_4$$

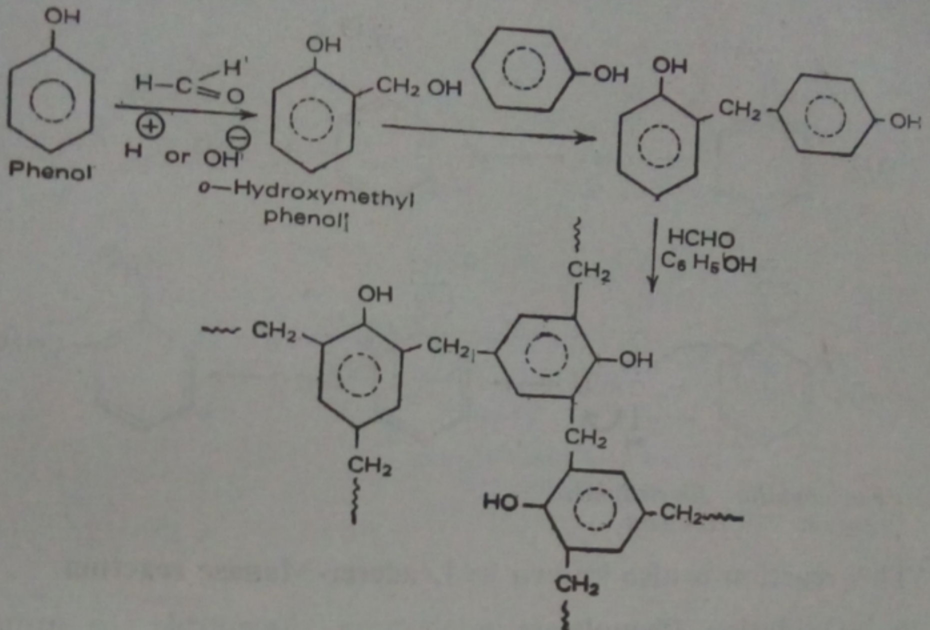
$$HC{\equiv}\overset{+}{N}H \leftrightarrow H\overset{+}{C}{=}NH$$

$$\mathrm{Ar{-}H} \xrightarrow[\text{2. } -\mathrm{H}^+]{\text{1. } \mathrm{H\overset{+}{C}{=}NH}} [\mathrm{Ar{-}CH{=}NH}] \xrightarrow{\mathrm{H_3\overset{+}{O}}} \mathrm{ArCHO}$$



(ix) **Reaction with formaldehyde**. When a phenol is treated with formaldehyde in the presence of acids or alkali, polymers (**bakelite**) etc., are obtained. These polymers are possibly formed by the scheme outlined

below in the case of reaction of the phenol with formaldehyde.

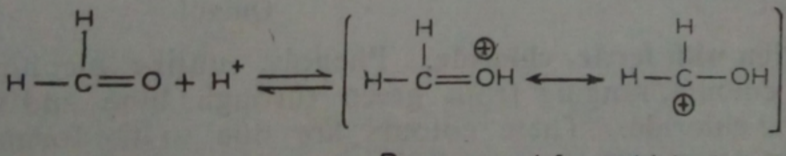


This proeess can continue to yield a product of high molecular weight. The final product would contain many cross-links (hence the rigid structure of the polymer) because each phenol molecule has three vulnerable positions.

The formation of *o*-hydroxymethylphenol in the above sequence is essentially an electrophilic substitution on the aromatic ring by the electron-deficient carbon of formaldehyde or a nucleophilic addition of the benzene ring to the carbonyl group of formaldehyde. While the acid catalyses the reaction by protonating formaldehyde and increasing the electron-deficiency of the carbonyl carbon, the base converts the phenol into the more reactive phenoxide ion.

Acid catalysed reaction :

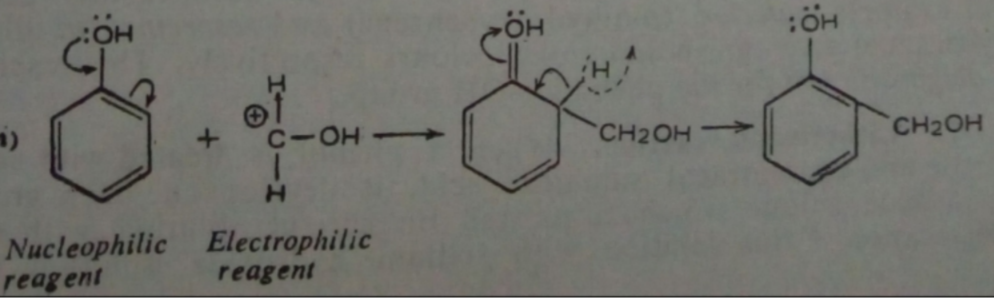
(*i*)



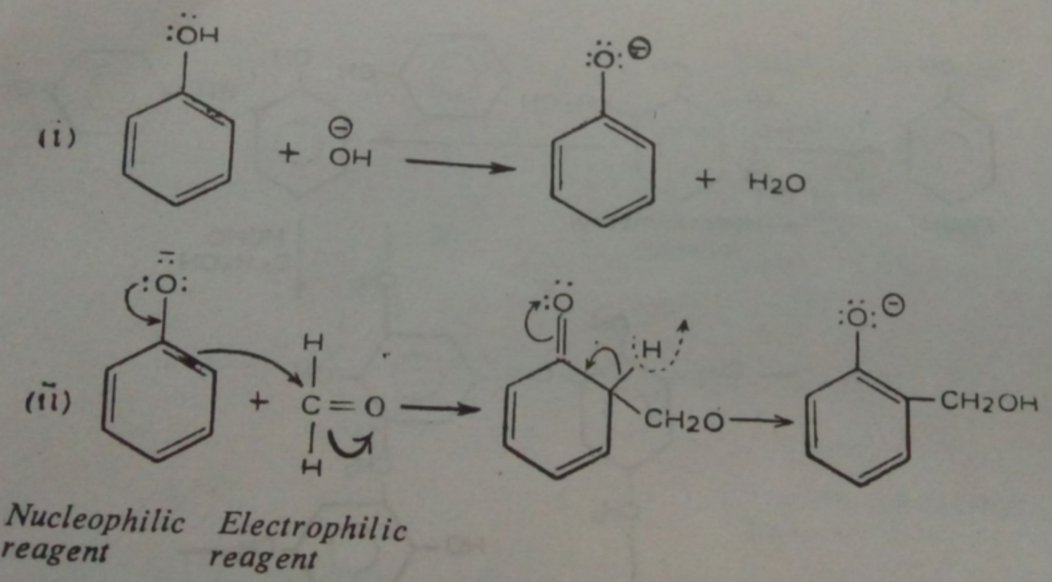
$$H-\overset{H}{C}=O + H^+ \rightleftharpoons \left[H-\overset{H}{C}=\overset{\oplus}{O}H \longleftrightarrow H-\overset{H}{\underset{\oplus}{C}}-OH \right]$$

Protonated formaldehyde

(*ii*)



Base catalysed reaction :

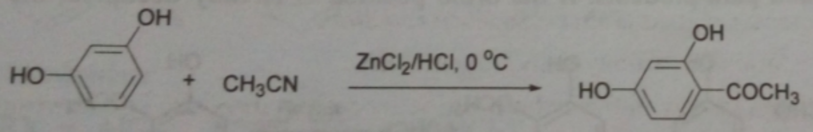


This reaction is also known as **Leaderer-Manase reaction.**

Houben-Hoesch reaction

Friedel-Crafts acylation with nitriles and HCl is called the *Houben-Hoesch reaction*. In most cases, a Lewis acid, zinc chloride is generally used.

$$ArH + RCN \xrightarrow[ZnCl_2]{HCl} ArCOR$$



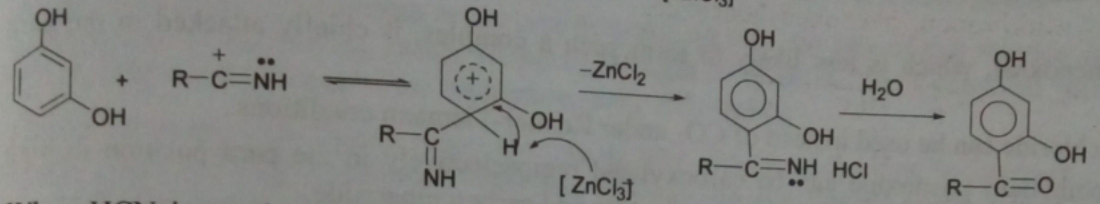
The reaction is useful only for phenols, phenolic esters and some heterocyclic compounds (e.g., pyrrole).

Mechanism

The first stage involves an attack on the substrate by a species containing the nitrile and HCl to give an imine salt.

In the second stage, the salt is hydrolysed to the products.

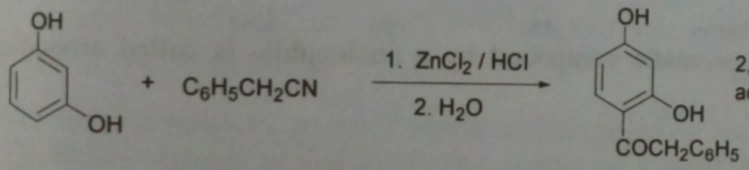
$$R-C\equiv N \;+\; 2HCl \;+\; ZnCl_2 \longrightarrow R-\overset{+}{C}=NH.HCl \;+\; [ZnCl_3]^-$$



When HCN is employed in place of RCN, aromatic aldehydes are obtained. This modification is called the *Gattermann synthesis*.

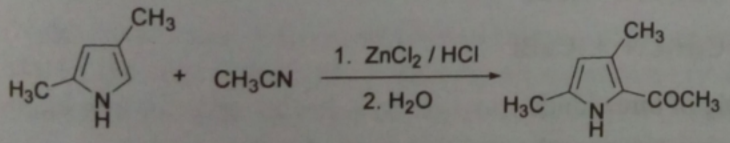
Some other examples of Houben-Hoesch reaction are:

1) Preparation of ω-substituted acetophenone



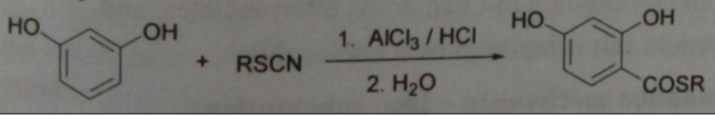
2,4-dihydroxy-ω-phenyl acetophenone

2) Preparation of heterocyclic ketones



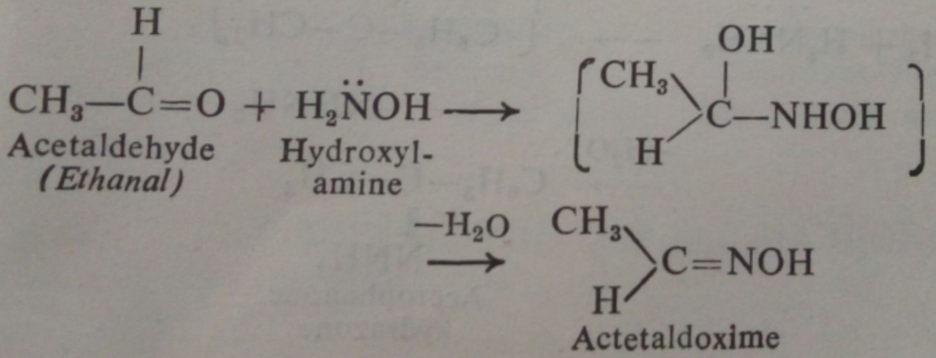
2,4-dimethyl-5-acetylpyrrole

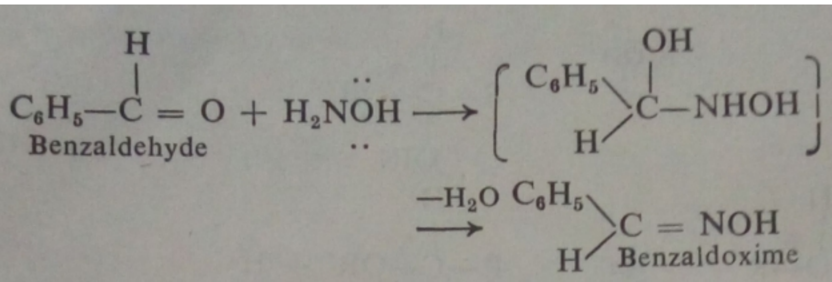
3) Preparation of thioesters



Thioester

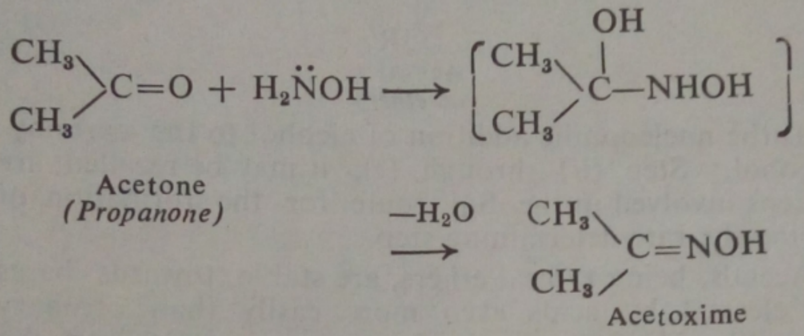
(*a*) **Reaction with hydroxylamine.** They form **oximes**, as illustrated below :





$$C_6H_5-\overset{H}{\overset{|}{C}}=O + H_2\ddot{N}OH \longrightarrow \left[\begin{matrix}C_6H_5\\H\end{matrix}\!\!>\!\overset{OH}{\overset{|}{C}}-NHOH\right] \xrightarrow{-H_2O} \begin{matrix}C_6H_5\\H\end{matrix}\!\!>\!C=NOH$$

Benzaldehyde — Benzaldoxime



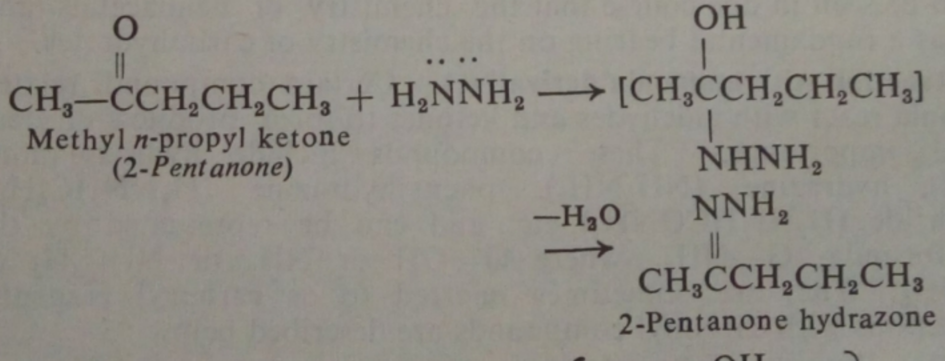
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=O + H_2\ddot{N}OH \longrightarrow \left[\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!\overset{OH}{\overset{|}{C}}-NHOH\right] \xrightarrow{-H_2O} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=NOH$$

Acetone (*Propanone*) — Acetoxime

(*b*) **Reaction with hydrazine**. They from **hydrazones**, as illustrated below :

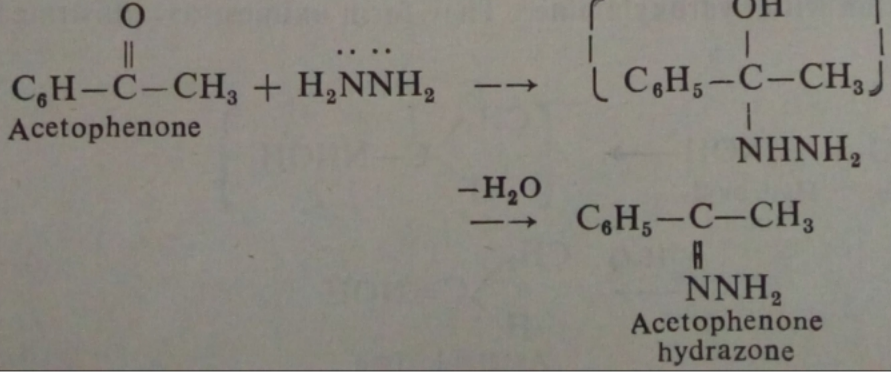
$$C_2H_5CHO + H_2\ddot{N}\ddot{N}H_2 \longrightarrow [C_2H_5CH(OH)NHNH_2] \xrightarrow{-H_2O} C_2H_5CH=NNH_2$$

Propional-dehyde (*Propanal*) — Hydrazine — Propionaldehyde hydrazone



$$CH_3-\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 + H_2\ddot{N}\ddot{N}H_2 \longrightarrow [CH_3\underset{NHNH_2}{\underset{|}{\overset{OH}{\overset{|}{C}}}}CH_2CH_2CH_3] \xrightarrow{-H_2O} CH_3\overset{NNH_2}{\overset{\|}{C}}CH_2CH_2CH_3$$

Methyl *n*-propyl ketone (2-*Pentanone*) — 2-Pentanone hydrazone



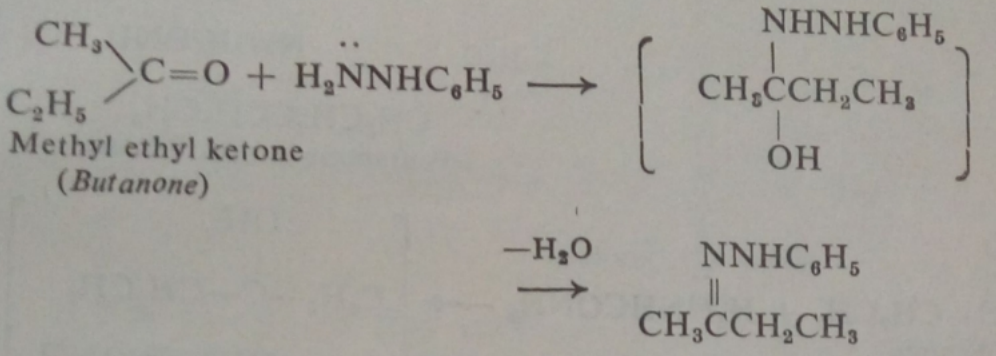
$$C_6H-\overset{O}{\overset{\|}{C}}-CH_3 + H_2\ddot{N}\ddot{N}H_2 \longrightarrow \left[C_6H_5-\underset{NHNH_2}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3\right] \xrightarrow{-H_2O} C_6H_5-\underset{NNH_2}{\underset{\|}{C}}-CH_3$$

Acetophenone — Acetophenone hydrazone

(*c*) **Reaction with phenylhydrazine.** They give rise to **phenylhydrazones,** as examplified below :

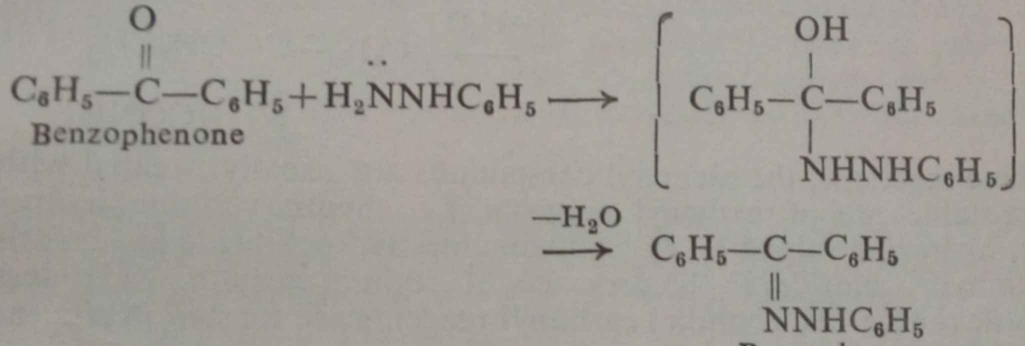
$$n\text{-}C_3H_7CHO + H_2\ddot{N}NHC_6H_5 \longrightarrow [n\text{-}C_3H_7CH(OH)NHNHC_6H_5] \xrightarrow{-H_2O} n\text{-}C_3H_7CH{=}NNHC_6H_5$$

n-Butyraldehyde (*Butanal*) Phenylhydroxylamine *n*-Butyraldehyde phenylhydrazone



Methyl ethyl ketone (*Butanone*)

2-Butanone phenylhydrazone

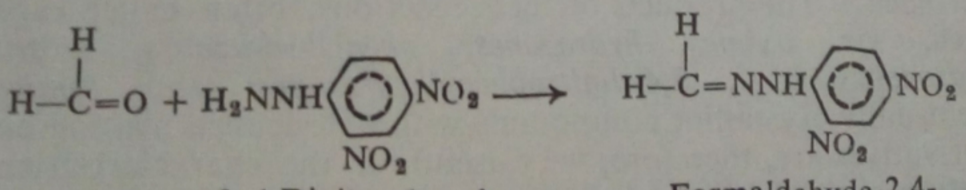


$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 + H_2\ddot{N}NHC_6H_5 \longrightarrow \left[C_6H_5-\underset{\underset{\displaystyle NHNHC_6H_5}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-C_6H_5 \right] \xrightarrow{-H_2O} C_6H_5-\underset{\underset{\displaystyle NNHC_6H_5}{\|}}{C}-C_6H_5$$

Benzophenone

Benzophenone phenylhydrazone

Substituted phenylhydrazines like *p*-nitrophenylhydrazine, 2, 4-dinitrophenylhydrazine, etc., have also been used in place of phenyl hydrazine. The products then are the corresponding substituted phenyl-hydrazones. For example,

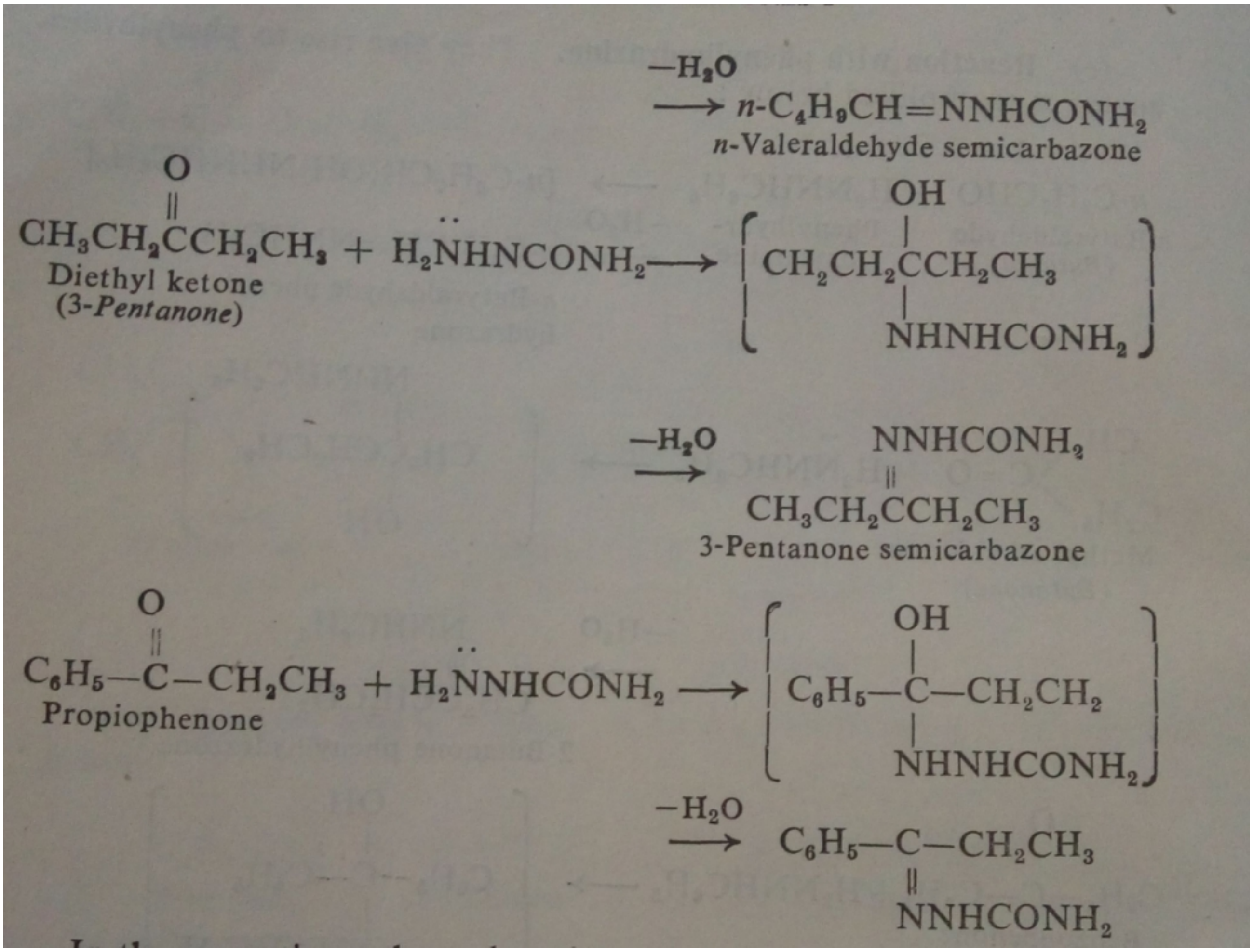


Formaldehyde (*Methanal*) 2, 4-Dinitrophenyl hydrazine Formaldehyde-2,4-dinitrophenylhydrazone

(*d*) **Reaction with semicarbazide.** They yield **semicarbazones,** as illustrated below :

$$n\text{-}C_4H_9CHO + H_2\ddot{N}NHCONH_2 \longrightarrow [n\text{-}C_4H_9CH(OH)NHNHCONH_2]$$

n-Valeraldehyde (*Pentanal*) Semicarbazide



$$\xrightarrow{-H_2O} n\text{-}C_4H_9CH{=}NNHCONH_2$$

n-Valeraldehyde semicarbazone

$$\underset{\substack{\text{Diethyl ketone}\\ \text{(3-}\textit{Pentanone}\text{)}}}{CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3} + H_2\ddot{N}NHCONH_2 \longrightarrow \left[\begin{array}{c} OH \\ | \\ CH_2CH_2CCH_2CH_3 \\ | \\ NHNHCONH_2 \end{array}\right]$$

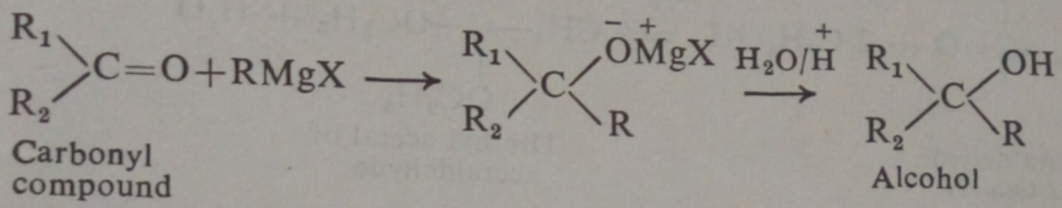
$$\xrightarrow{-H_2O} \begin{array}{c} NNHCONH_2 \\ \| \\ CH_3CH_2CCH_2CH_3 \end{array}$$

3-Pentanone semicarbazone

$$\underset{\text{Propiophenone}}{C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}CH_2CH_3} + H_2\ddot{N}NHCONH_2 \longrightarrow \left[\begin{array}{c} OH \\ | \\ C_6H_5{-}C{-}CH_2CH_2 \\ | \\ NHNHCONH_2 \end{array}\right]$$

$$\xrightarrow{-H_2O} \begin{array}{c} C_6H_5{-}C{-}CH_2CH_3 \\ \| \\ NNHCONH_2 \end{array}$$

3. **Addition of Grignard reagents.** Grignard reagents add to the carbonyl group of aldehydes and ketones to form **alcohols.**



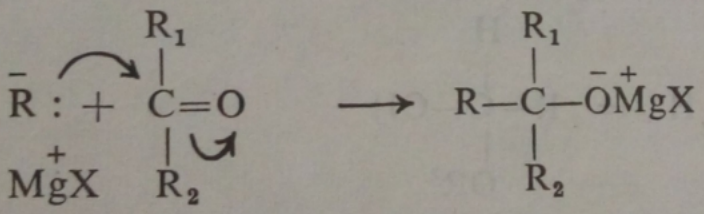
[R_1 and R_2 may be identical or different, and they may be H or/and alkyl/aryl groups ; R may be an alkyl/aryl group]

Mechanism. It involves the nucleophilic addition of the Grignard reagent to the carbonyl group as shown below :

(*i*) $R-\vdots\, MgX \longrightarrow \overset{-}{R}: + \overset{+}{Mg}X$

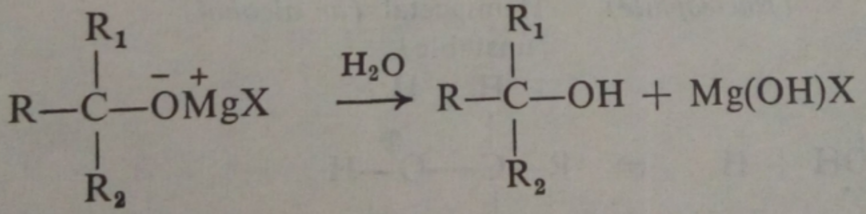
(Nucleophile)

(*ii*)



$$\overset{-}{R}: + \underset{R_2}{\overset{R_1}{C}}=O \qquad \overset{+}{Mg}X \longrightarrow R-\underset{R_2}{\overset{R_1}{C}}-\overset{-}{O}\overset{+}{Mg}X$$

(*iii*)



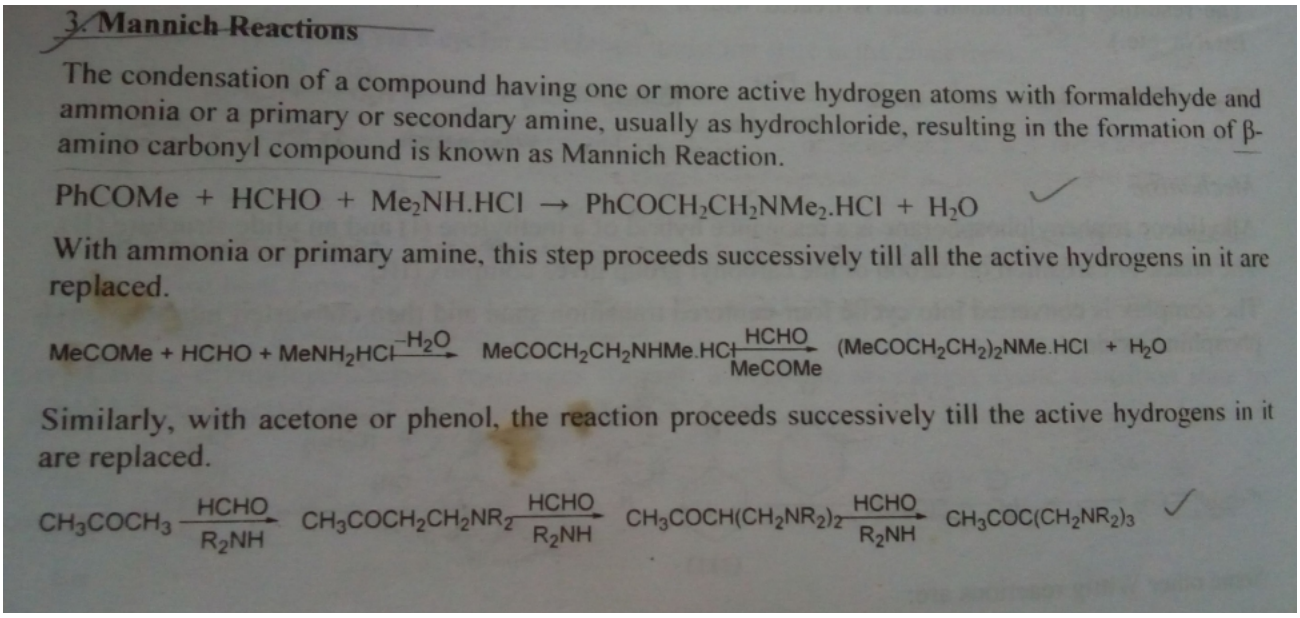
$$R-\underset{R_2}{\overset{R_1}{C}}-\overset{-}{O}\overset{+}{Mg}X \xrightarrow{H_2O} R-\underset{R_2}{\overset{R_1}{C}}-OH + Mg(OH)X$$

(*iv*) $Mg(OH)X + \overset{+}{H} \longrightarrow \overset{++}{Mg} + \overset{-}{X} + H_2O$

The step (*i*) generates the alkyl/aryl carbanion (nculeophile) which then attacks the electron-deficient carbonyl carbon in the usual manner.

Although the magnesium salt of the weakly acidic alcohol formed in step (*ii*) can be decomposed even by water (water is a stronger acid than alcohol, the Mg(OH)X formed in step (*iii*) is gelatinous and is better handled if some mineral acid (say, HCl) is used to convert Mg(OH)X into water soluble magnesium salts.

the formation of



3. Mannich Reactions

The condensation of a compound having one or more active hydrogen atoms with formaldehyde and ammonia or a primary or secondary amine, usually as hydrochloride, resulting in the formation of β-amino carbonyl compound is known as Mannich Reaction.

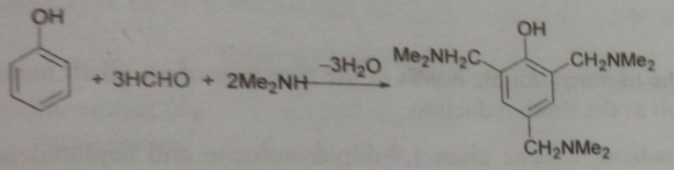
$$PhCOMe + HCHO + Me_2NH.HCl \rightarrow PhCOCH_2CH_2NMe_2.HCl + H_2O$$ ✓

With ammonia or primary amine, this step proceeds successively till all the active hydrogens in it are replaced.

$$MeCOMe + HCHO + MeNH_2HCl \xrightarrow{-H_2O} MeCOCH_2CH_2NHMe.HCl \xrightarrow[MeCOMe]{HCHO} (MeCOCH_2CH_2)_2NMe.HCl + H_2O$$

Similarly, with acetone or phenol, the reaction proceeds successively till the active hydrogens in it are replaced.

$$CH_3COCH_3 \xrightarrow[R_2NH]{HCHO} CH_3COCH_2CH_2NR_2 \xrightarrow[R_2NH]{HCHO} CH_3COCH(CH_2NR_2)_2 \xrightarrow[R_2NH]{HCHO} CH_3COC(CH_2NR_2)_3$$ ✓

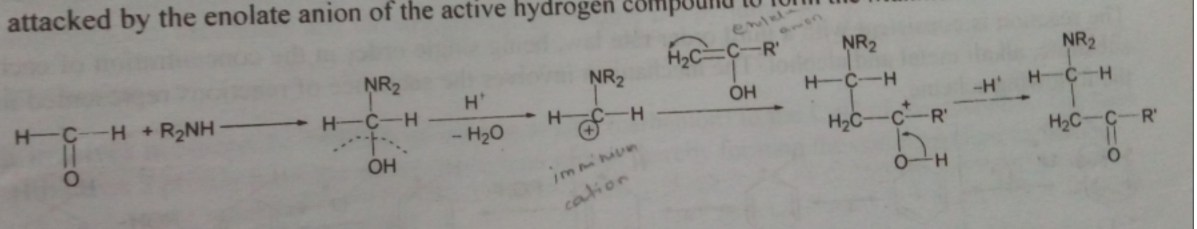


Mechanism

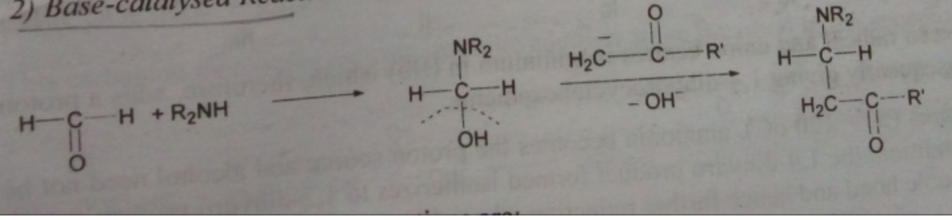
There are two types of mechanism for Mannich reactions.

1) Acid-catalysed reactions:

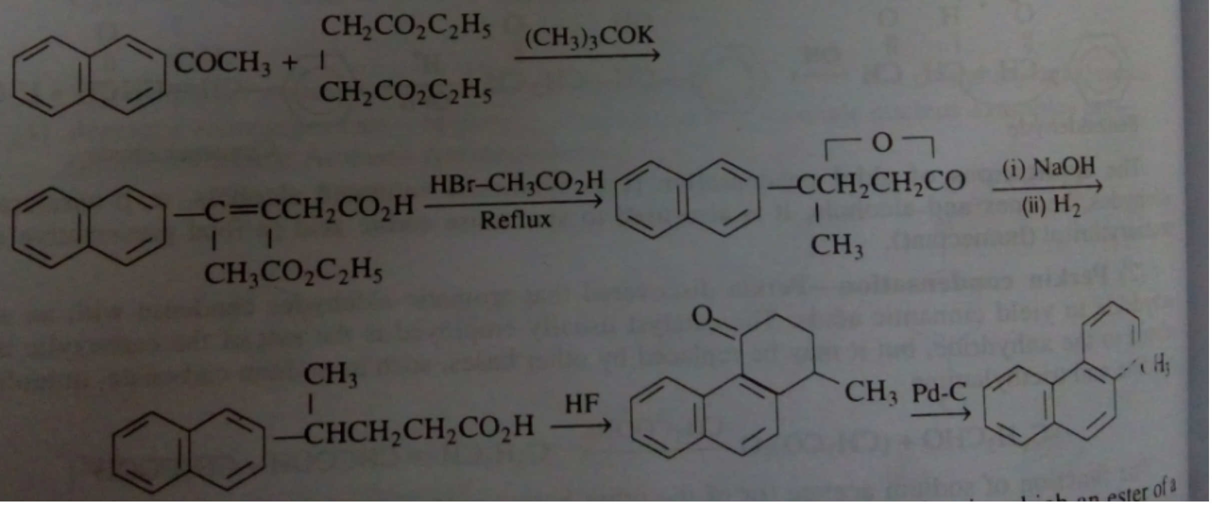
The amine and HCHO in the presence of H^+ condense to form imminium cation, which is then attacked by the enolate anion of the active hydrogen compound to form the Mannich base.

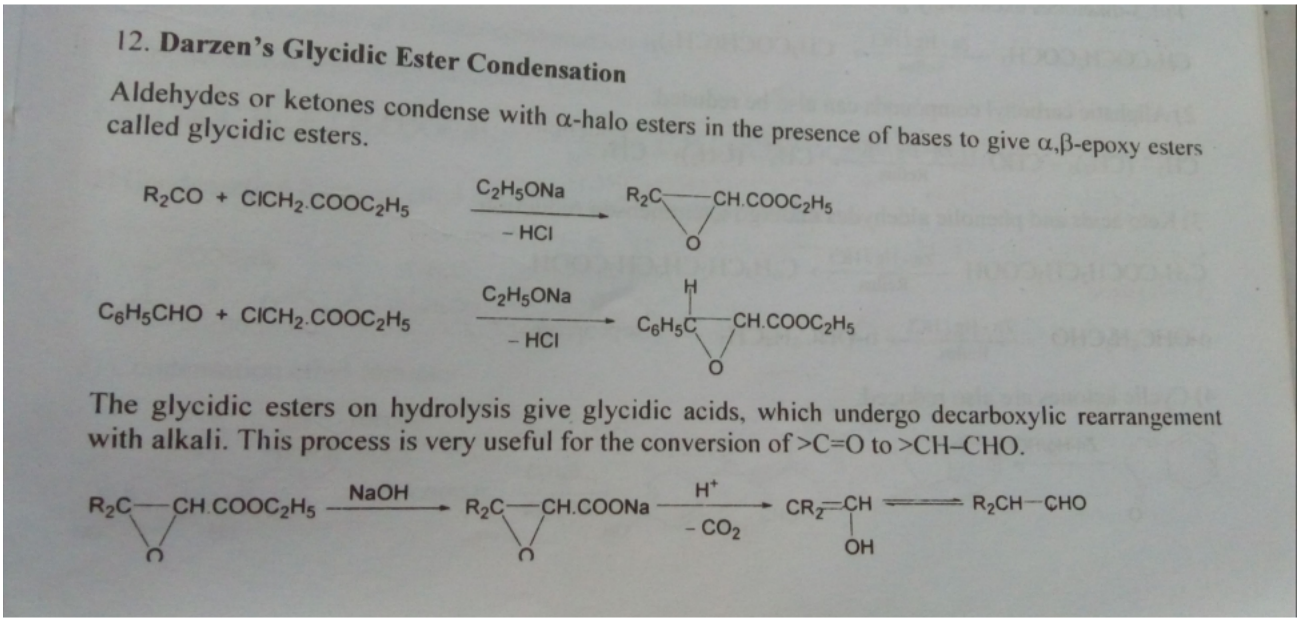


2) Base-catalysed Reaction



(3) **Stobbe condensation**—This addition involves carbanions from a wide variety of CH_2XY types but particularly where X and/or Y are CO_2R groups, *e.g.*, $CH_2(CO_2Et)_2$; organic bases are often used as catalysts. In most cases the intermediate aldol is dehydrated to the αβ-unsaturated product (ester). An example is with carbanions derived from esters of 1, 4-butandioic (succinic) acid, *e.g.*, $(CH_2CO_2Et)_2$ and aldehydes or ketones, employing alkoxide ions as base catalysts in the stobbe condensation. Stobbe condensation is also used to prepare phenanthrene derivatives.





12. Darzen's Glycidic Ester Condensation

Aldehydes or ketones condense with α-halo esters in the presence of bases to give α,β-epoxy esters called glycidic esters.

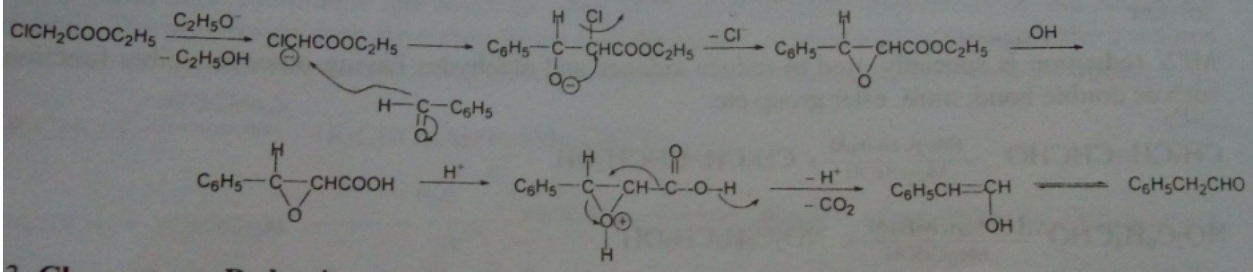
$$R_2CO + ClCH_2.COOC_2H_5 \xrightarrow[-\,HCl]{C_2H_5ONa} R_2C\underset{O}{\diagdown\!\diagup}CH.COOC_2H_5$$

$$C_6H_5CHO + ClCH_2.COOC_2H_5 \xrightarrow[-\,HCl]{C_2H_5ONa} C_6H_5\overset{H}{C}\underset{O}{\diagdown\!\diagup}CH.COOC_2H_5$$

The glycidic esters on hydrolysis give glycidic acids, which undergo decarboxylic rearrangement with alkali. This process is very useful for the conversion of >C=O to >CH–CHO.

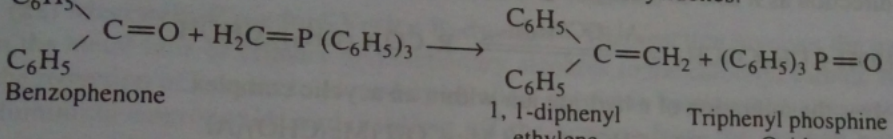
$$R_2C\underset{O}{\diagdown\!\diagup}CH.COOC_2H_5 \xrightarrow{NaOH} R_2C\underset{O}{\diagdown\!\diagup}CH.COONa \xrightarrow[-\,CO_2]{H^+} CR_2{=}\underset{OH}{CH} \rightleftharpoons R_2CH\text{—}CHO$$

Mechanism


ClCH2COOC2H5
C2H5O⁻
– C2H5OH
ClCHCOOC2H5
H—C—C6H5
O
C6H5—C—CHCOOC2H5
H
Cl
O
– Cl⁻
C6H5—C—CHCOOC2H5
H
O
OH
C6H5—C—CHCOOH
H
O
H⁺
C6H5—C—CH—C—O—H
H
O
O
H
– H⁺
– CO2
C6H5CH═CH
OH
C6H5CH2CHO

introduction of

(17) **Wittig reaction**—It involves the preparation of olefins by the interaction of aldehydes or ketones (aliphatic or aromatic) with triphenylphosphine alkylidenes.

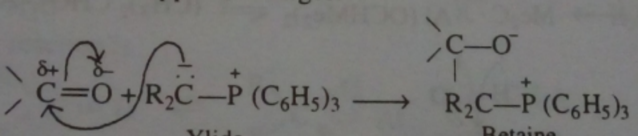


$$(C_6H_5)_2C{=}O + H_2C{=}P(C_6H_5)_3 \longrightarrow (C_6H_5)_2C{=}CH_2 + (C_6H_5)_3P{=}O$$

Benzophenone   1, 1-diphenyl ethylene   Triphenyl phosphine Oxide

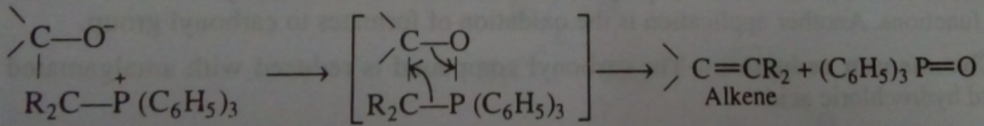
In this reaction two steps are involved.

Step 1 : The negative carbon of the ylide attacks the carbonyl carbon to form a betaine. A betaine is a molecule having non adjacent opposite charges.



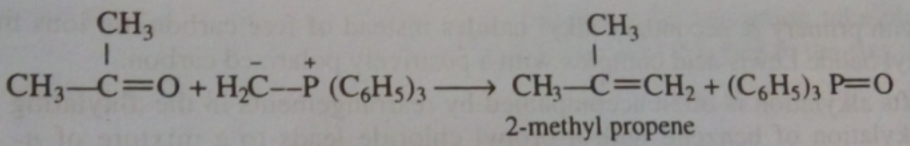
Ylide   Betaine

Step 2 : The betaine undergoes elimination of triphenylphosphine oxide to give the alkene.



Betaine   Alkene

The Wittig reaction is an excellent method of making alkenes from aldehydes and ketones. For example

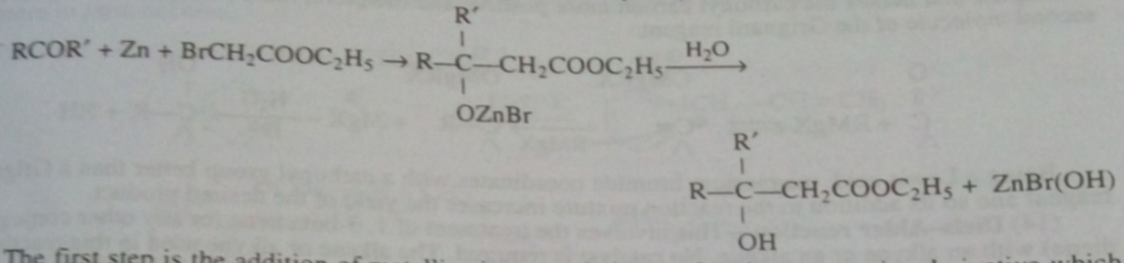


$$CH_3-\overset{CH_3}{\overset{|}{C}}=O + H_2\overset{-}{C}-\overset{+}{P}(C_6H_5)_3 \longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 + (C_6H_5)_3P=O$$

2-methyl propene

This reaction is also used for the preparation of carbodi-imides (reagent), stepping up aldehydes and in synthesis of natural products (*e.g.* β-carotene, esters, vitamin A_1, corticoids etc.).

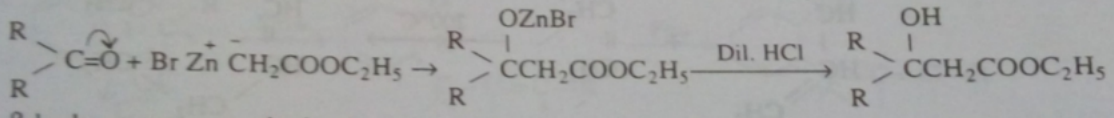
(12) **Reformatsky reaction**—It involves the reaction of carbonyl compounds (aldehydes or ketones) with Zinc metal and an α-bromoester to give after hydrolysis is β-hydroxyesters.



$$RCOR' + Zn + BrCH_2COOC_2H_5 \rightarrow R\!-\!\underset{OZnBr}{\overset{R'}{C}}\!-\!CH_2COOC_2H_5 \xrightarrow{H_2O} R\!-\!\underset{OH}{\overset{R'}{C}}\!-\!CH_2COOC_2H_5 + ZnBr(OH)$$

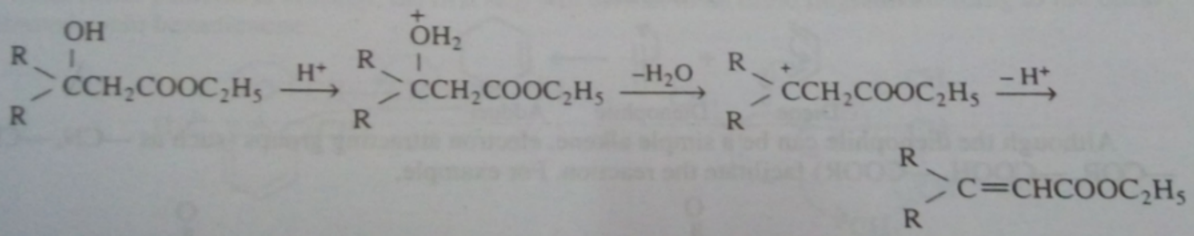
The first step is the addition of metallic zinc on α-haloester forming organozinc derivative which then adds to the carbonyl group of the aldehyde or ketone. Organozinc compounds are less reactive than Grignard reagents and hence they do not react with the ester function.

$$BrCH_2COOC_2H_5 + Zn \rightleftharpoons Br\overset{+}{Z}\overset{-}{n}\,CH_2COOC_2H_5$$



$$\begin{matrix}R\\R\end{matrix}\!\!>C=O + Br\overset{+}{Z}\overset{-}{n}\,CH_2COOC_2H_5 \rightarrow \begin{matrix}R\\R\end{matrix}\!\!>\overset{OZnBr}{C}CH_2COOC_2H_5 \xrightarrow{\text{Dil. HCl}} \begin{matrix}R\\R\end{matrix}\!\!>\overset{OH}{C}CH_2COOC_2H_5$$

The β-hydroxy esters so obtained, readily undergo acid catalysed dehydration to α, β-unsaturated esters.



$$\begin{matrix}R\\R\end{matrix}\!\!>\overset{OH}{C}CH_2COOC_2H_5 \xrightarrow{H^+} \begin{matrix}R\\R\end{matrix}\!\!>\overset{\overset{+}{O}H_2}{C}CH_2COOC_2H_5 \xrightarrow{-H_2O} \begin{matrix}R\\R\end{matrix}\!\!>\overset{+}{C}CH_2COOC_2H_5 \xrightarrow{-H^+} \begin{matrix}R\\R\end{matrix}\!\!>C=CHCOOC_2H_5$$

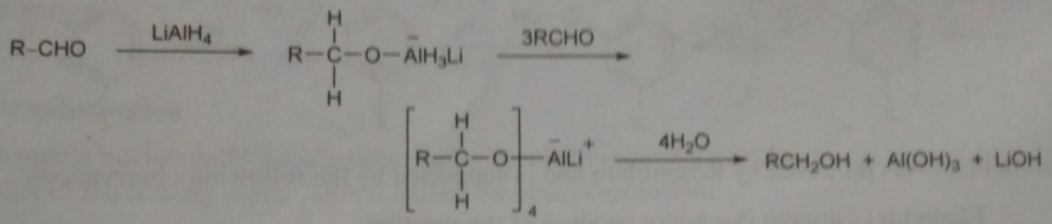
A drawback of this reaction is the formation of β-ketoesters as a side product by the self condensation of the α-bromo esters.

Reformatsky reaction is used for the synthesis of β-hydroxyesters, β-hydroxy-acids, unsaturated esters unsaturated and saturated carboxylic acids and natural products (*e.g.*, camphoronic acid, Vitamin A, oestrone etc.).

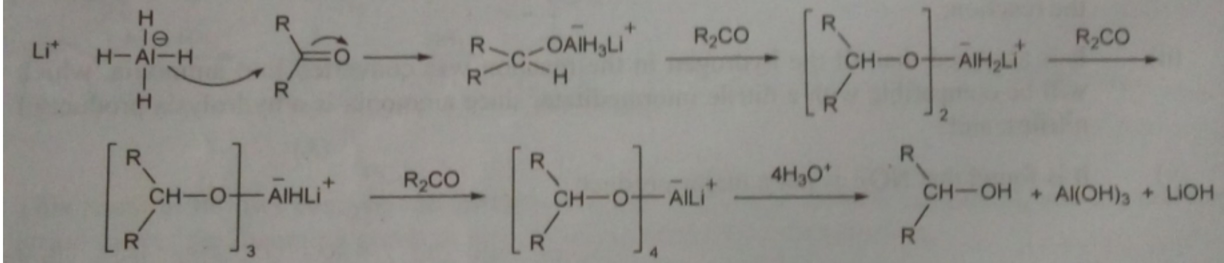
1. Lithium Aluminium Hydride $LiAlH_4$

Lithium aluminium hydride, a more useful reagent in organic chemistry, can reduce a large variety of compounds such as aldehydes, ketones, acids, and its derivatives like esters, amides, etc.

$LiAlH_4$ reduces carbonyl compounds to alcohols. In these reactions, the initial product is the aluminium salt of alcohol (aluminium alkoxide) which on treatment with aqueous acid yields the free alcohol. One mole of $LiAlH_4$ can reduce four moles of a carbonyl compound, as illustrated below:



Mechanism



Examples:

Aldehydes are reduced to primary alcohols

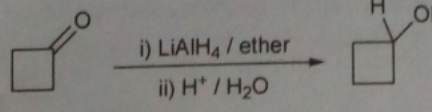
i) $CH_3CHO \xrightarrow{LiAlH_4} CH_3CH_2OH$

ii) $CH_3(CH_2)_5CHO \xrightarrow{LiAlH_4} CH_3(CH_2)_5CH_2OH$

Ketones are reduced to secondary alcohols

i) $CH_3CH_2COCH_3 \xrightarrow{LiAlH_4} CH_3CH_2CHOHCH_3$

ii)



Carboxylic acids are reduced to primary alcohols

iii) $RCH(NH_2)COOH \xrightarrow{LiAlH_4} RCH(NH_2)CH_2OH$

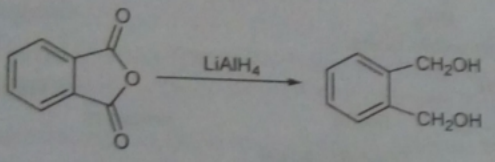
iv) $PhCH{=}CHCOOH \xrightarrow{LiAlH_4} PhCH{=}CHCH_2OH$

Esters are reduced to primary alcohols

i) $C_6H_5COOC_2H_5 \xrightarrow{LiAlH_4} C_6H_5CH_2OH$

ii) $CH_3CH{=}CHCOOC_2H_5 \xrightarrow{LiAlH_4} CH_3CH{=}CHCH_2OH$

Anhydrides are reduced to diols



2. Sodium Borohydride $NaBH_4$

Sodium borohydride is mainly used as a reducing agent in ethanol or isopropanol. Its advantages over $LiAlH_4$ are:

a) more selective as it reduces only the ketones and aldehydes to the corresponding alcohols

i) $CH_3COCH_2COCH_3 \xrightarrow{NaBH_4} CH_3CH(OH)CH_2CH(OH)CH_3$

Acetylacetone → Pentane-2,4-diol

ii) $CH_3CH{=}CHCHO \xrightarrow{NaBH_4} CH_3CH{=}CHCH_2OH$

Crotonaldehyde (but-2-enal) → Crotyl alcohol (but-2-en-1-ol)

iii) $CH_2OH(CHOH)_4CHO \xrightarrow{NaBH_4} CH_2OH(CHOH)_4CH_2OH$

Glucose → Sorbitol

b) much milder reducing agent as it reduces only the ketones and aldeydes without attacking other reducible groups viz., esters, epoxides, carboxylic acids, nitriles, nitro, etc.

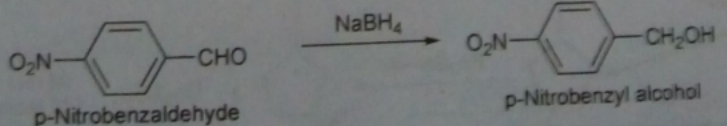
i) $CNCH_2CH_2CHO \xrightarrow{NaBH_4} CNCH_2CH_2CH_2OH$

3-Cyanopropionaldehyde → 4-Hydroxybutyronitrile

ii) $C_6H_5COCH_2CH_2COOH \xrightarrow{NaBH_4} C_6H_5CH(OH)CH_2CH_2COOH$

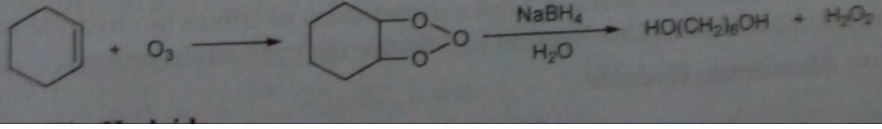
β-Benzoylpropionic acid → γ-Hydroxyphenyl butyric acid

iii)



p-Nitrobenzaldehyde p-Nitrobenzyl alcohol

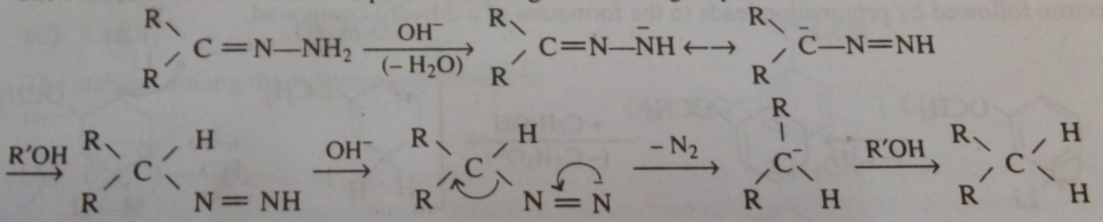
c) reduces also lactones and ozonides to alcohols.



(21) **Wolf-Kishner reduction**—Reduction of hydrazones, semicarbazones or azines of aldehydes and ketones to hydrocarbons in vigorously basic conditions (C_2H_5ONa or NaOH) with the evolution of nitrogen is known as Wolf-Kishner reduction.

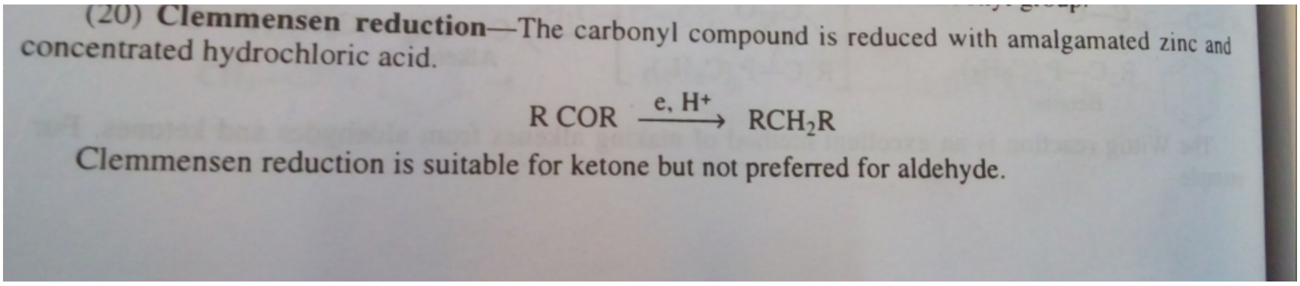
$$\underset{\text{Ketone}}{R_2C{=}O} + H_2N\,.\,NH_2 \longrightarrow \underset{\text{Hydrazone}}{R_2C{=}N\,.\,NH_2} \xrightarrow{C_2H_5ONa \text{ or } NaOH} N_2 + R_2CH_2$$

The reaction is believed to take place according to following steps—



During the reduction of semicarbazones or azines the derivatives are first converted to hydrazones.

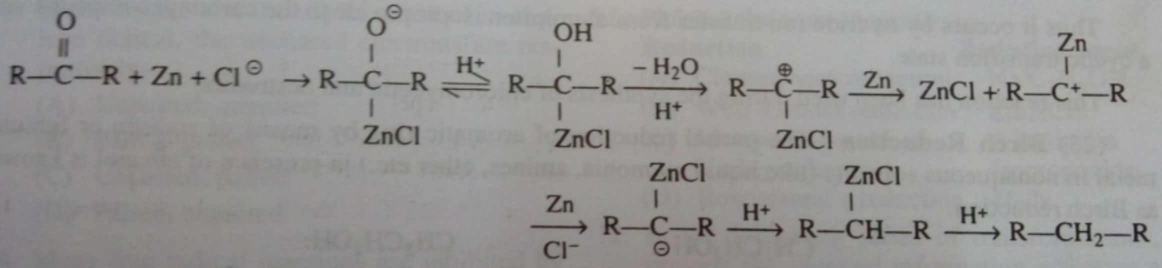
Wolf-Kishner reduction has been used for the reduction of carbonyl group to methylene group during the synthesis of a large variety of products for *e.g.* in reduction of camphor to camphane, in synthesis of pyrroles, in elucidating the structure of oestrone.



(20) **Clemmensen reduction**—The carbonyl compound is reduced with amalgamated zinc and concentrated hydrochloric acid.

$$\text{R COR} \xrightarrow{\text{e, H}^+} \text{RCH}_2\text{R}$$

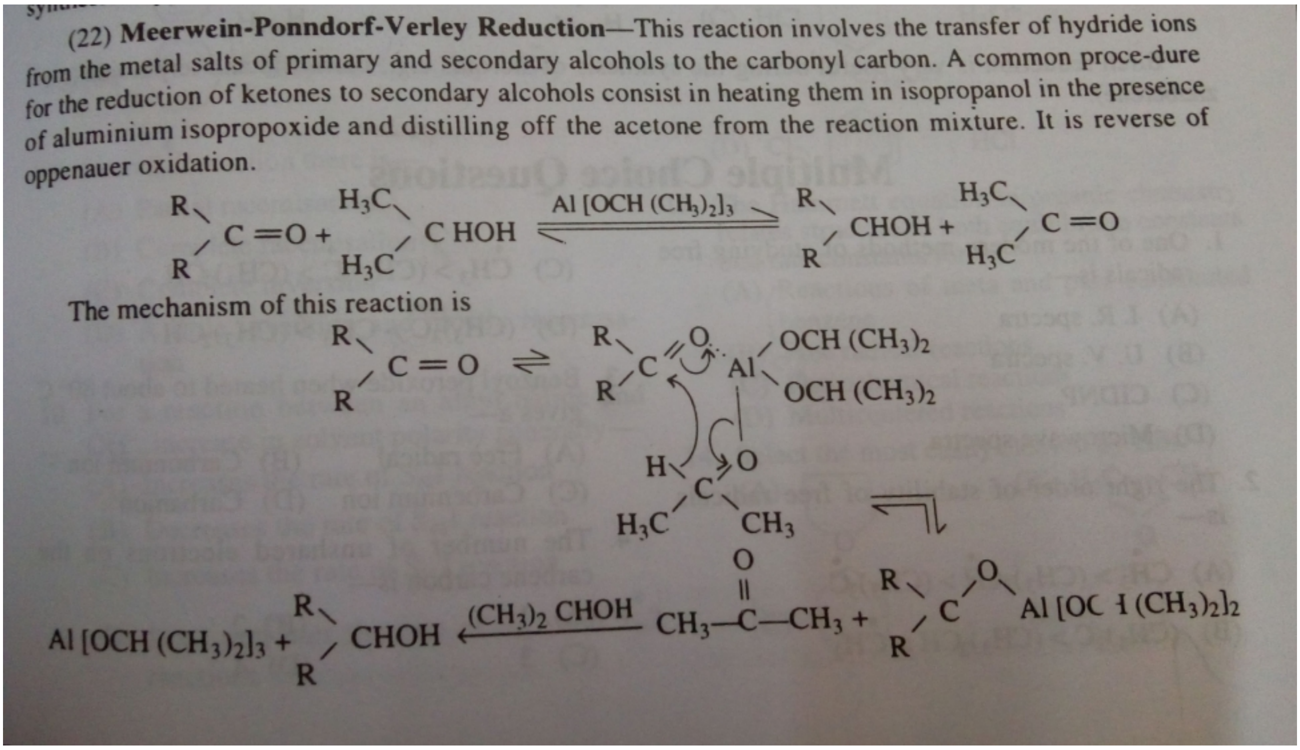
Clemmensen reduction is suitable for ketone but not preferred for aldehyde.



$$R-\overset{O}{\overset{\|}{C}}-R + Zn + Cl^{\ominus} \rightarrow R-\underset{ZnCl}{\overset{O^{\ominus}}{C}}-R \xrightleftharpoons{H^+} R-\underset{ZnCl}{\overset{OH}{C}}-R \xrightarrow[H^+]{-H_2O} R-\underset{ZnCl}{\overset{\oplus}{C}}-R \xrightarrow{Zn} ZnCl + R-\overset{Zn}{C^+}-R$$

$$\xrightarrow[Cl^-]{Zn} R-\underset{\ominus}{\overset{ZnCl}{C}}-R \xrightarrow{H^+} R-\overset{ZnCl}{CH}-R \xrightarrow{H^+} R-CH_2-R$$

Clemmensen reduction is easy to perform but it fails with some substrate which are sensitive to acids and possess high molecular weight, for such cases a modified Clemmensen reduction is used in which activated zinc and gaseous HCl in an organic solvent such as ether or acetic anhydride is used.



(22) **Meerwein-Ponndorf-Verley Reduction**—This reaction involves the transfer of hydride ions from the metal salts of primary and secondary alcohols to the carbonyl carbon. A common proce-dure for the reduction of ketones to secondary alcohols consist in heating them in isopropanol in the presence of aluminium isopropoxide and distilling off the acetone from the reaction mixture. It is reverse of oppenauer oxidation.

$$R_2C{=}O + (H_3C)_2CHOH \underset{}{\overset{Al[OCH(CH_3)_2]_3}{\rightleftharpoons}} R_2CHOH + (H_3C)_2C{=}O$$

The mechanism of this reaction is

$$R_2C{=}O \rightleftharpoons R_2C{=}\ddot{O}{\cdot\cdot}Al(OCH(CH_3)_2)_2\text{—}O\text{—}CH(CH_3)_2 \rightleftharpoons CH_3\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_3 + R_2C\text{—}O\text{—}Al[OCH(CH_3)_2]_2$$

$$\xleftarrow{(CH_3)_2\,CHOH} Al[OCH(CH_3)_2]_3 + R_2CHOH$$