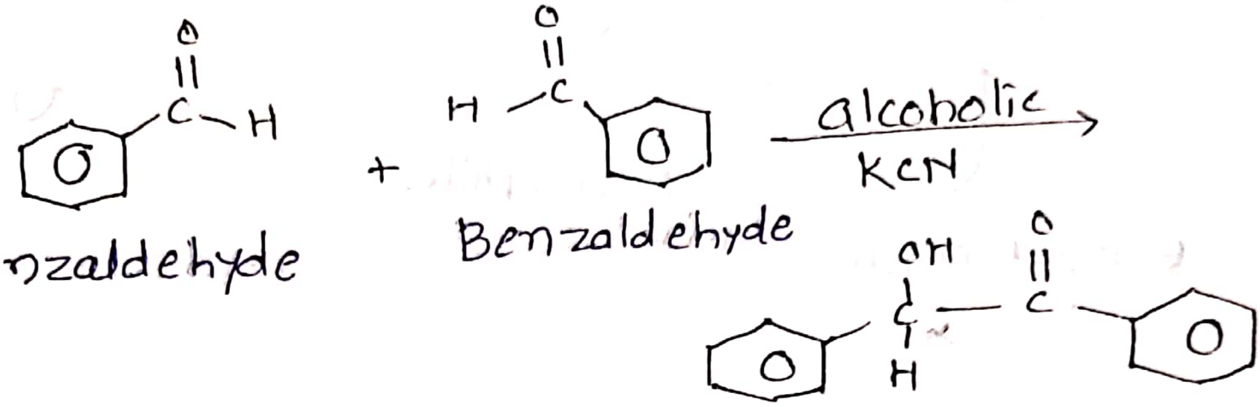
(NAME REACTION)

① Benzoin Condensation

The condensation of aromatic aldehydes (with no α-hydrogen atom) in presence of cyanide ion as a catalyst to give α-hydroxy ketone (Benzoin) called benzoin condensation.



α-hydroxy Ketone
(Benzoin)

References:-

i) If α-hydrogen present on aldehyde Aldol condensation take place.

ii) Direct formation of carbanion is not possible as there is no α-hydrogen atom.

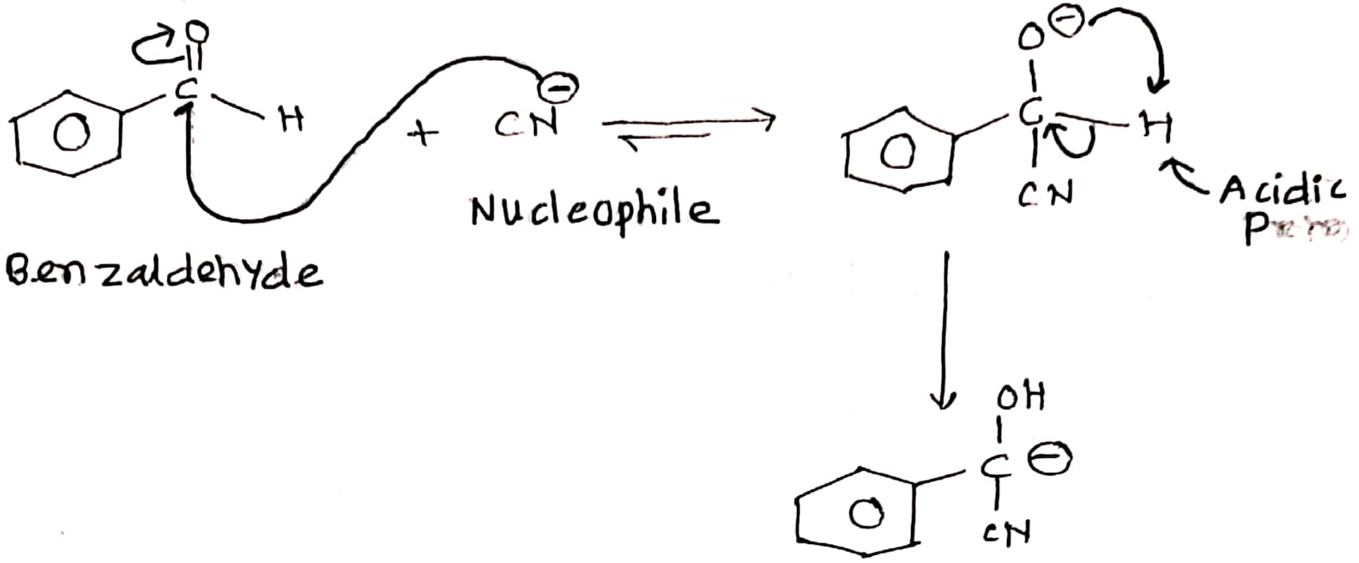
iii) Carbanion formation take place by involving attachment of CN^- to the carbonyl group.

Mechanism:-

Step-I :- Ionisation of KCN take place as

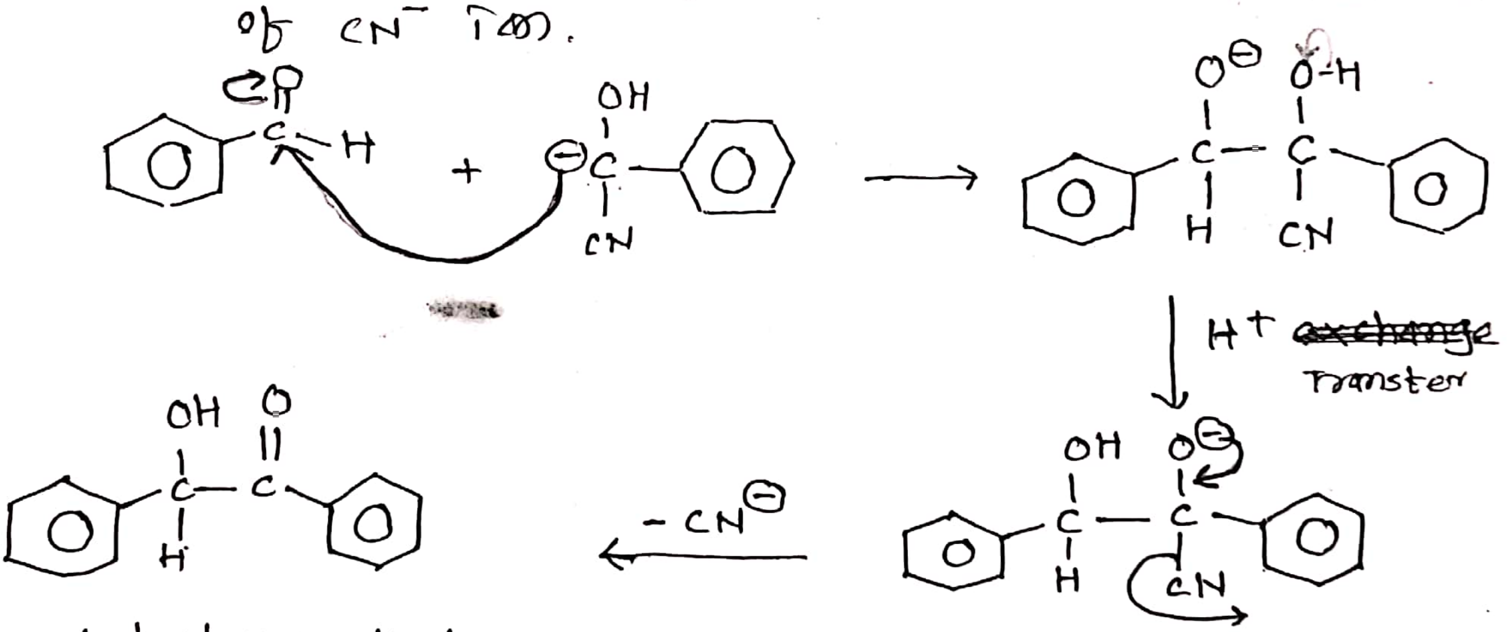
$$KCN \rightleftharpoons K^+ + CN^-$$

Step-II :- formation of carbanion by attack of CN^- ion on carbonyl group



Carbanion (A)

Step-III :- The Attack of carbanion (A) on another benzaldehyde to ~~[illegible]~~ give benzoin ~~[illegible]~~ by Proton exchange followed by elimination of CN^- ion.



α-hydroxy Ketone
(Benzoin)

(As CN^- is good leaving group)

② Knoevengel Reaction

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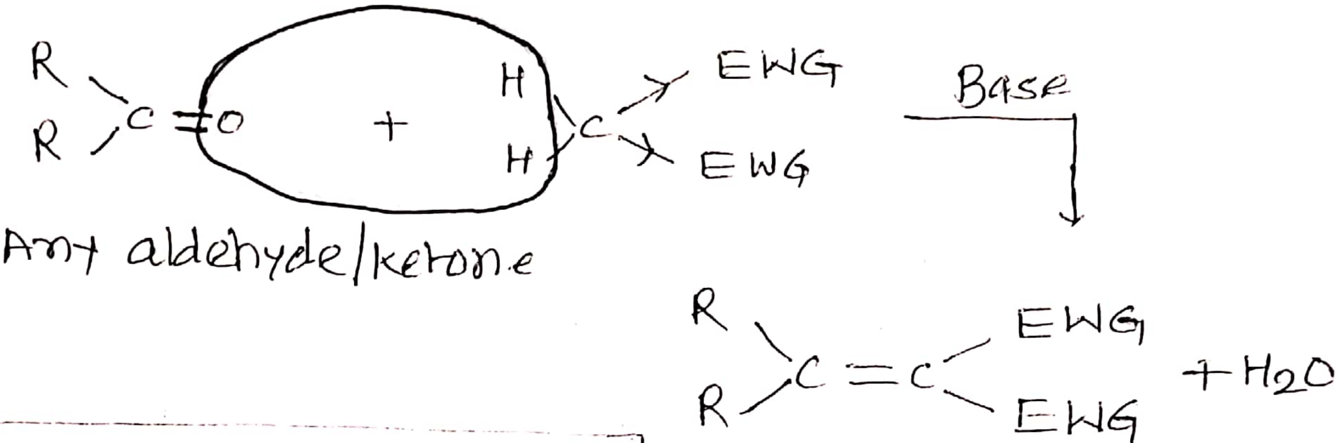
The condensation of aldehyde or ketone with active methylene compounds in the presence of weak base to give α-β unsaturated compounds called knoevengel reaction.

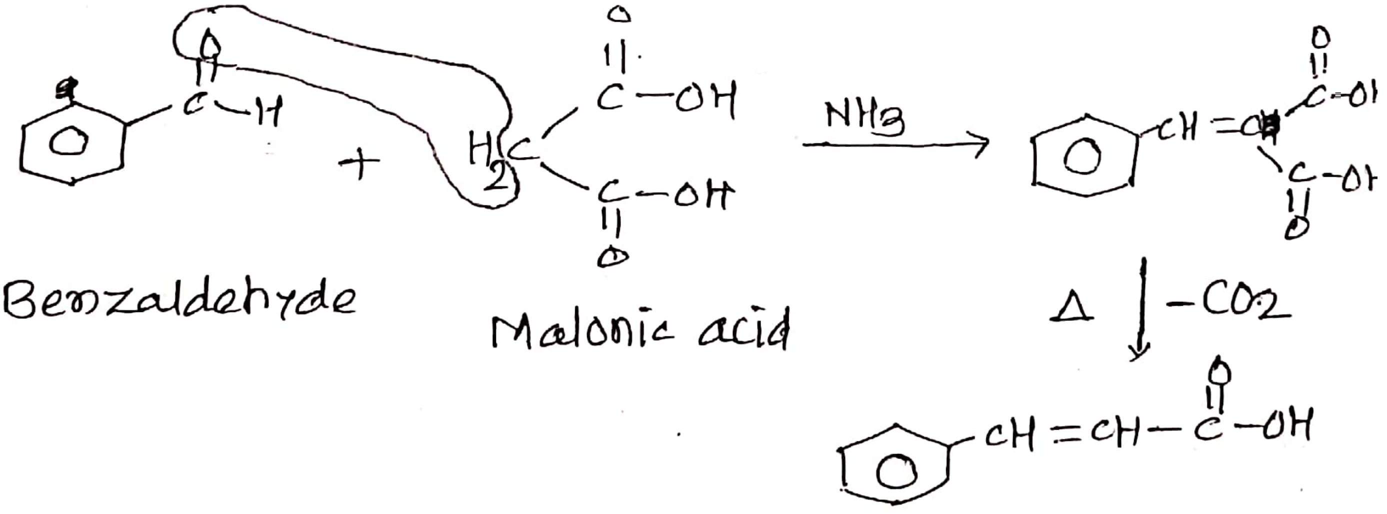


Any aldehyde/ketone

α-β unsaturated compounds.

EWG = Electron withdrawing group

Ex:- 1. When benzaldehyde reacts with malonic acid in presence of ammonia it gives α-β unsaturated compounds.



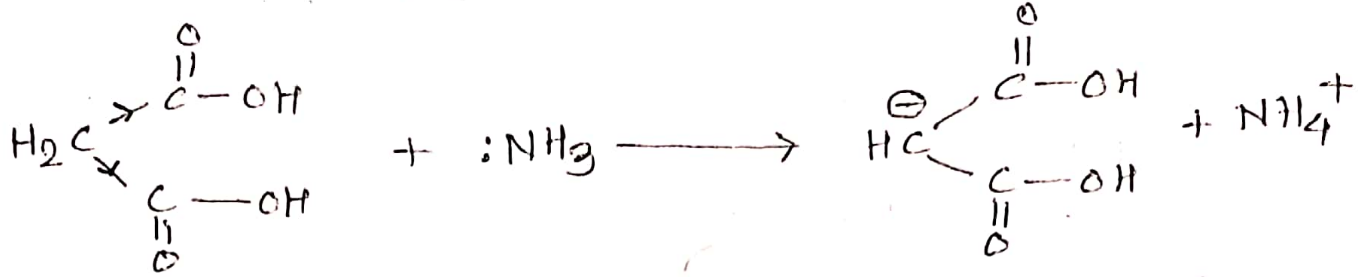
Benzaldehyde

Malonic acid

cinnamic acid.

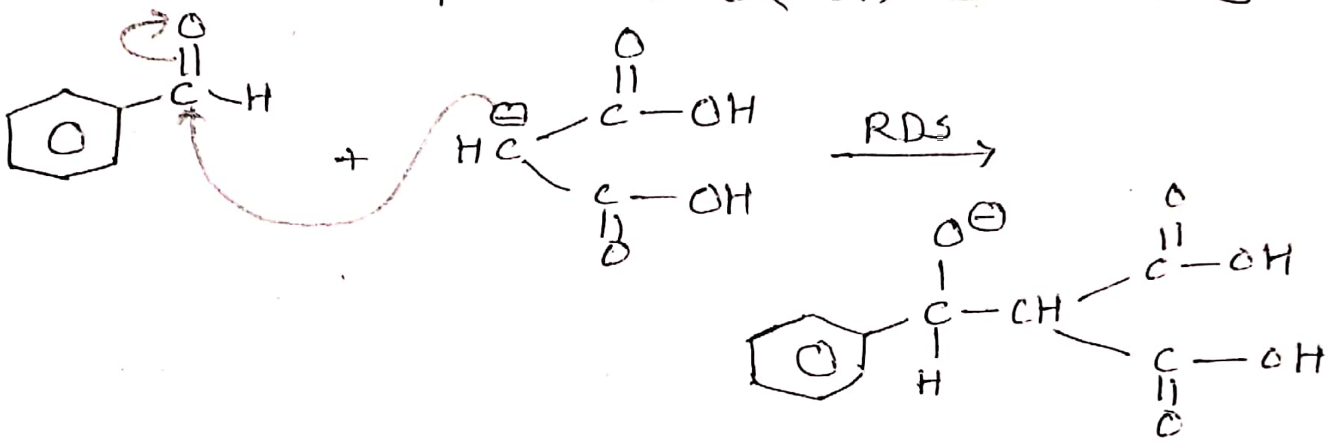
Mechanism

Step-I : Base abstract proton from active methylene compound and forms carbanion (Nucleophile)



(Nucleophile)

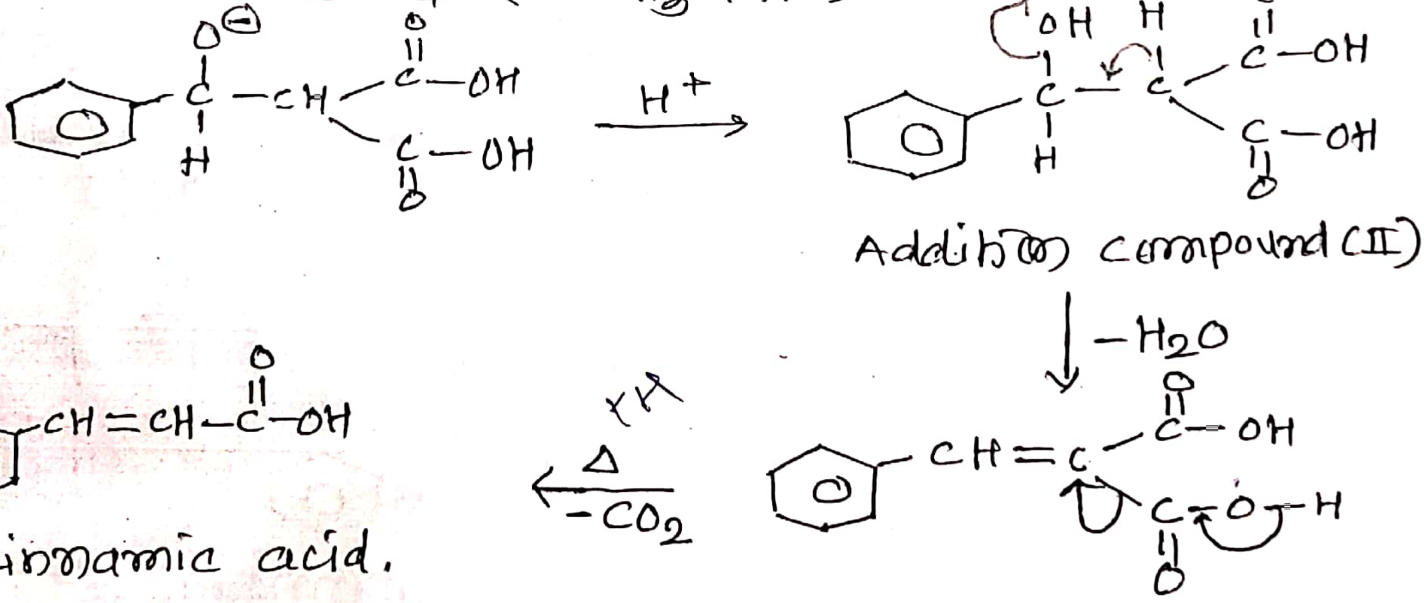
Step-II : formation of addition compound (I) by nucleophilic attack on carbonyl group.



Addition compound (I)

Step-III : Protonation of addition compound (I)

$(NH_4^+ \rightleftharpoons NH_3 + H^+)$

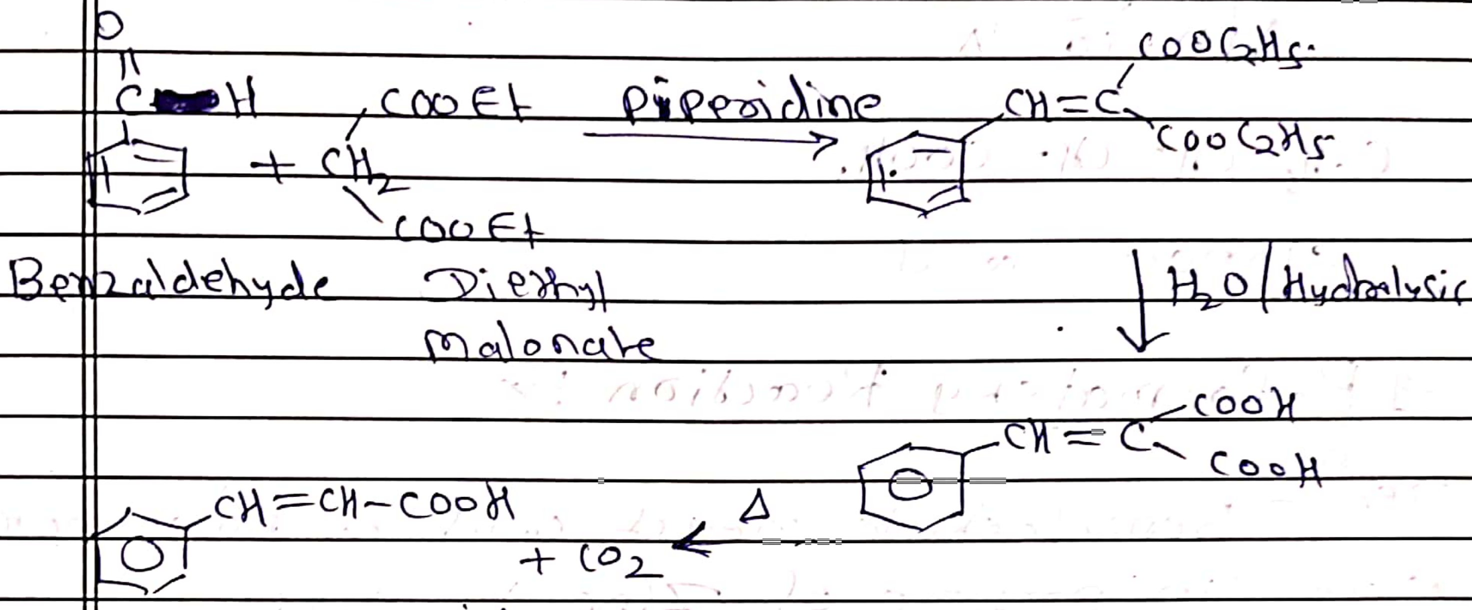


Addition compound (II)

cinnamic acid.

2] Knoevenagel condensation

Benzaldehyde undergo condensation with compound containing active methylene groups such as diethyl malonate, ethyl acetoacetate ethyl cyanoacetate etc. in presence of organi base (piperidine, pyridine) to form α, β - unsaturated esters which on hydrolysis & heating give respective α, β - unsaturated acids.



Benzaldehyde

Diethyl malonate

Cinnamic acid

(α, β- unsaturated acid)

Mechanism :-

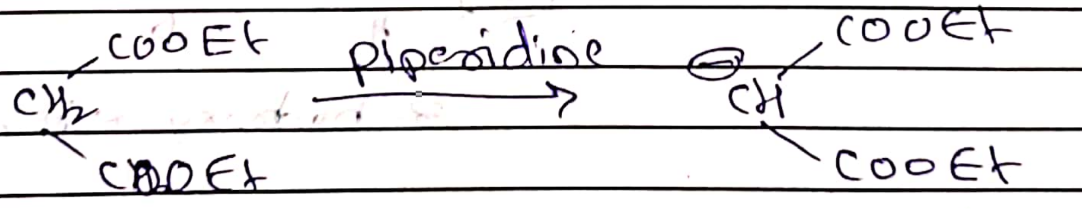
Step 1 : proton abstraction by base (B)

2] Nucleophilic addition at carbonyl carbon

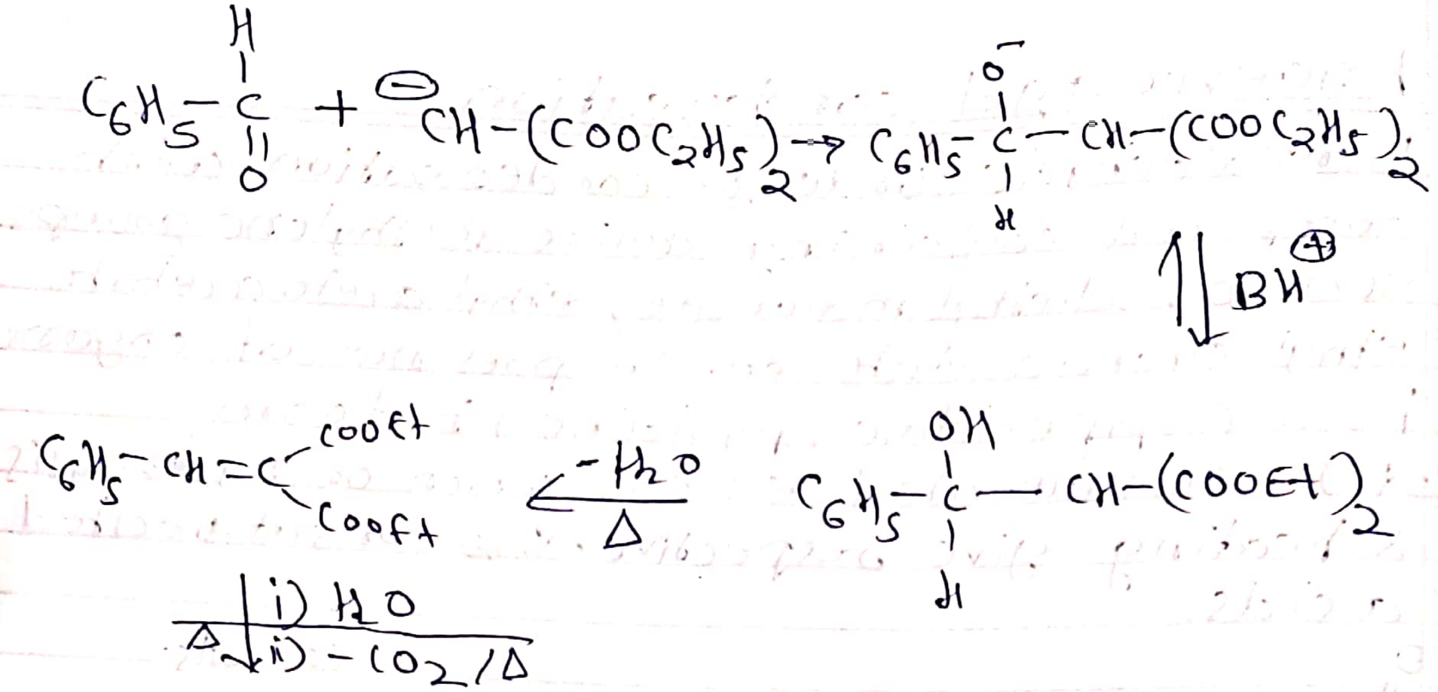
3] Elimination of water

4] Hydrolysis & decarboxylation

Step I



carbanion

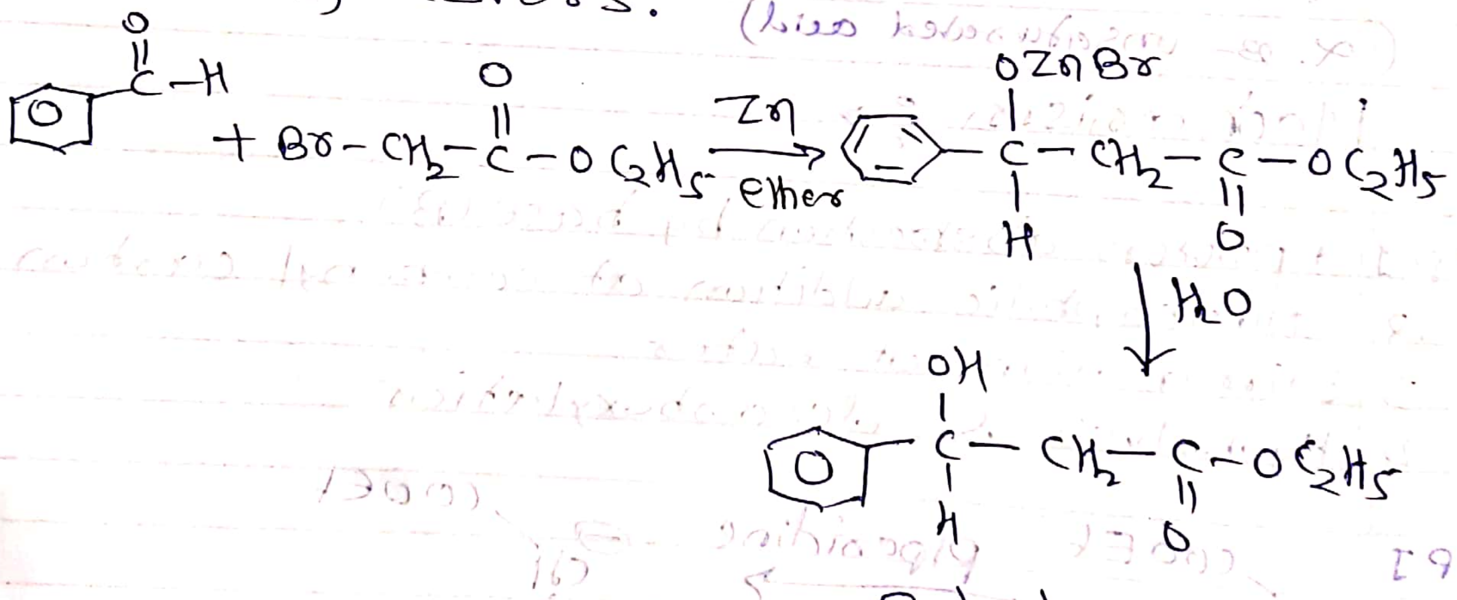


$C_6H_5-CH=CH-COOH.$

cinnamic acid

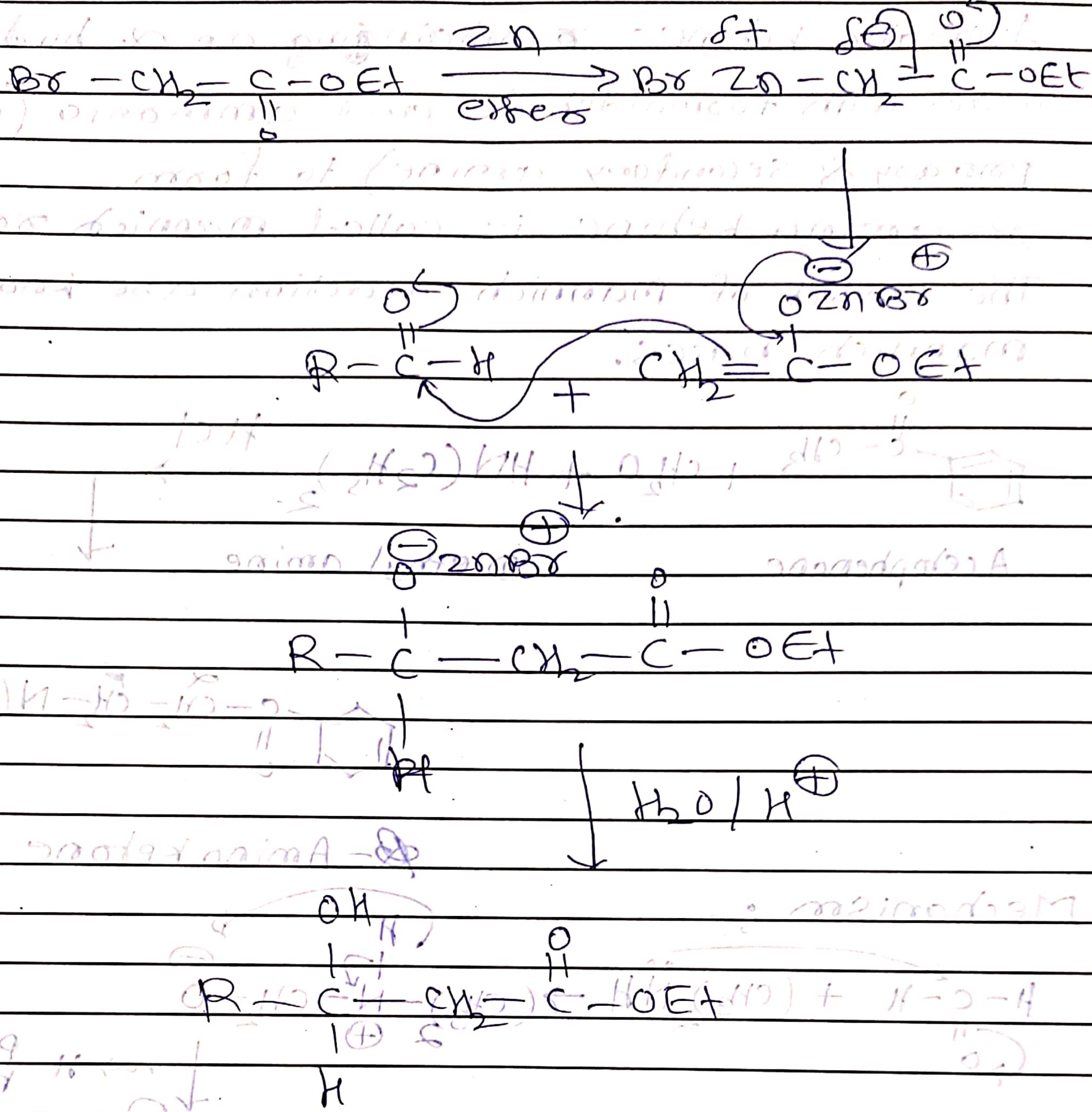
3 Reformatsky Reaction :→

Def^n :- Benzaldehyde react with α-halogenated ester in presence of Zinc to give β-hydroxy esters.



β-hydroxy ester

Mechanism



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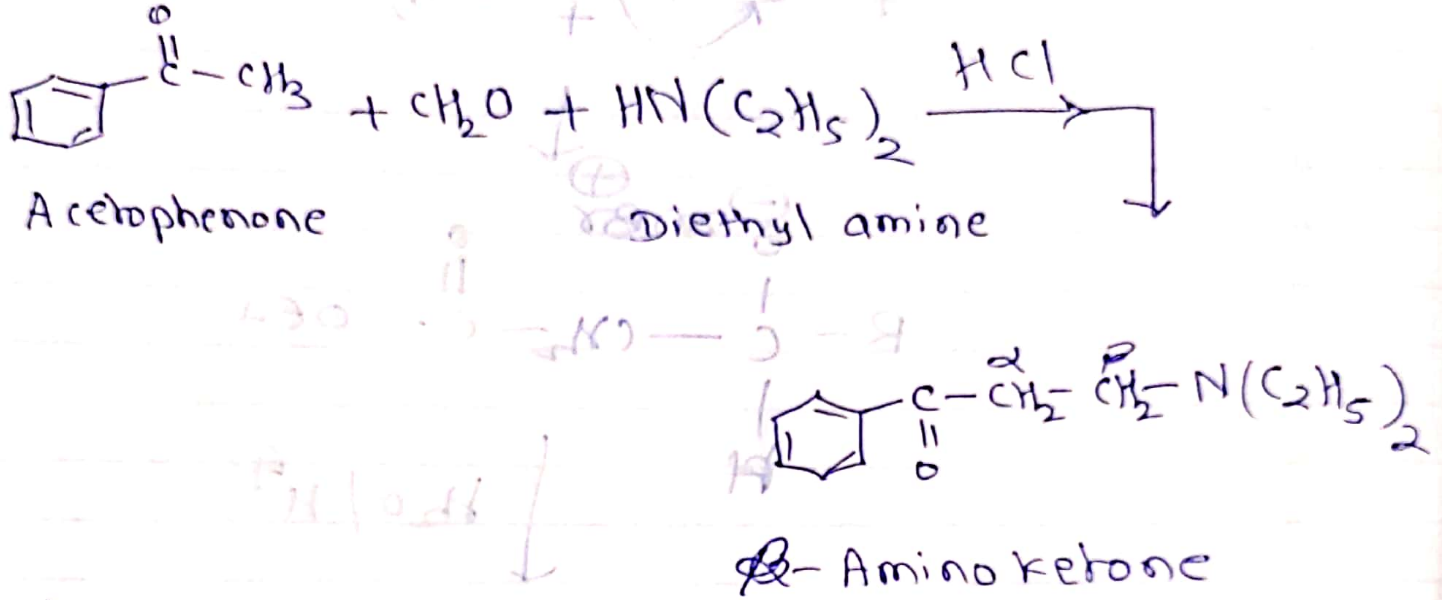
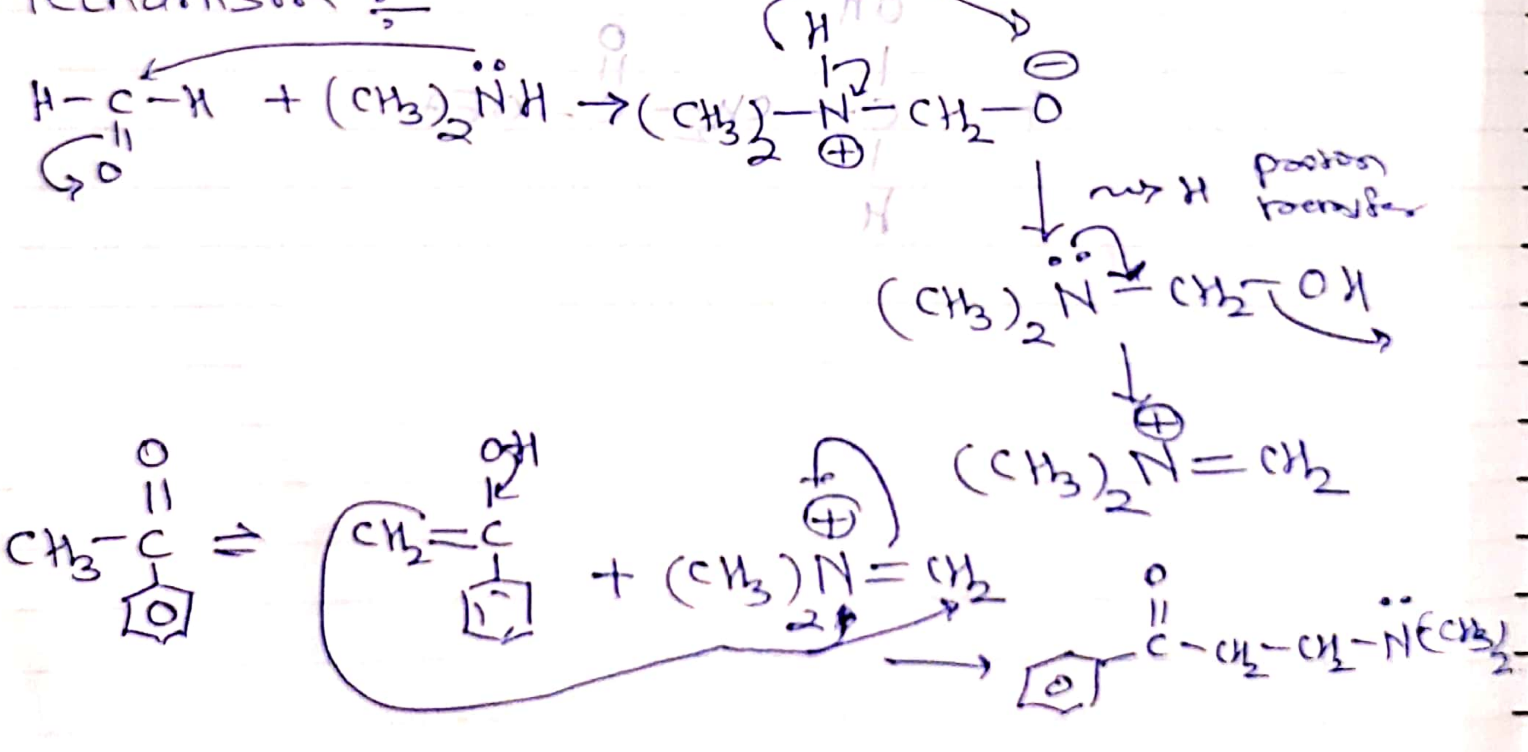
3] Mannich Reaction :→

Aromatic ketones containing an α-hydrogen react with formaldehyde and ammonia (or primary & secondary amine) to form β-amino ketone is called mannich reaction. The product of mannich reaction are known as mannich bases.



Mechanism :-



4] Perkins Reactions :→

condensation of aromatic aldehydes and aliphatic unhydrides in presence of sodium or potassium salt of acid to form α-β unsaturated aromatic acids.

The acid unhydride should have at least two α-hydrogens.

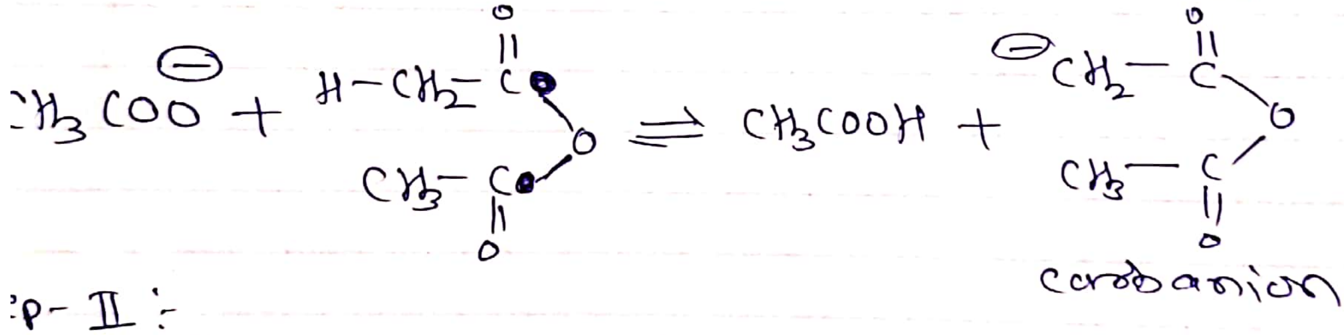
$$C_6H_5-CHO + (CH_3-CO)_2O \xrightarrow[170-180^\circ C,\ 5h]{CH_3CO\bar{O}\overset{+}{Na}} C_6H_5-CH=CH-COOH + CH_3COOH$$

Benzaldehyde Acetic unhydride α,β-unsaturated acid A.A.

echanism :→

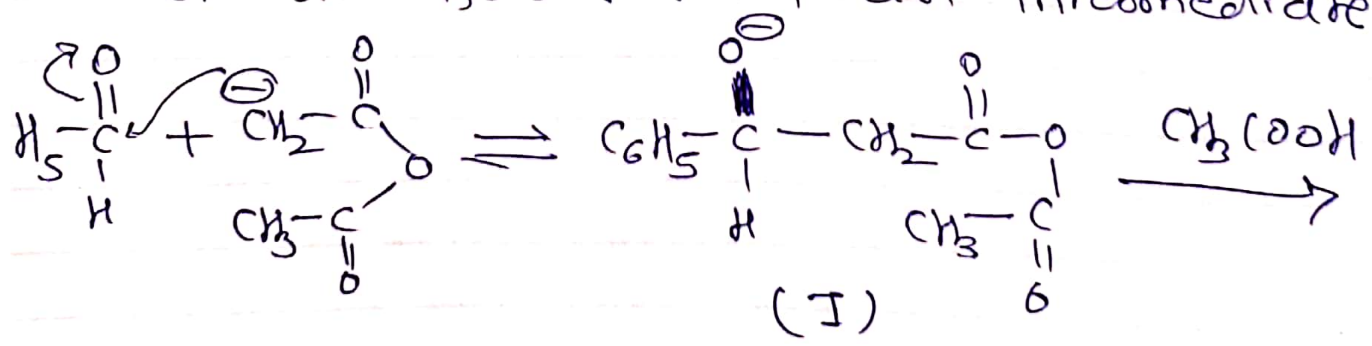
$$CH_3CO\bar{O}\overset{+}{Na} \rightleftharpoons CH_3COO^{\ominus} + Na^{\oplus}$$

tep-I: Acetate ion abstract proton from α-carbon of unhydride to form carbanion.

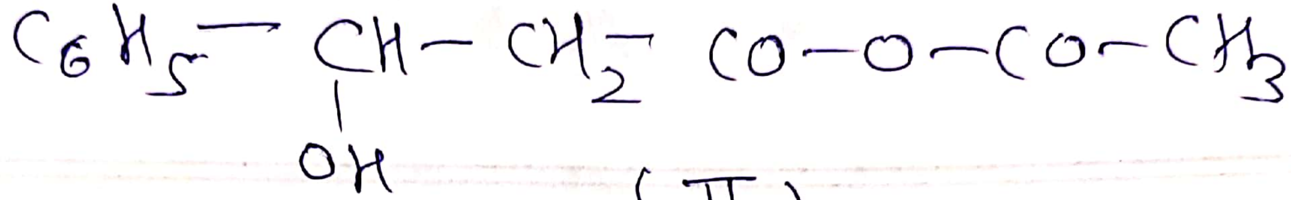


p- II :-

The carbanion attack on carbonyl carbon of aldehyde to form an intermediate (I)



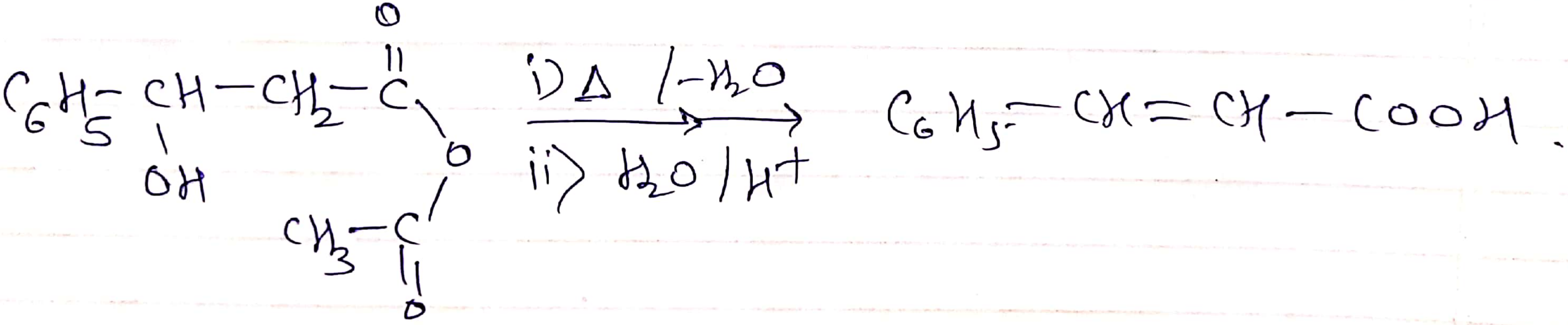
~~Step (III)~~: $\longrightarrow$



$C_6H_5-\underset{OH}{\underset{|}{CH}}-CH_2-CO-O-CO-CH_3$

(II)

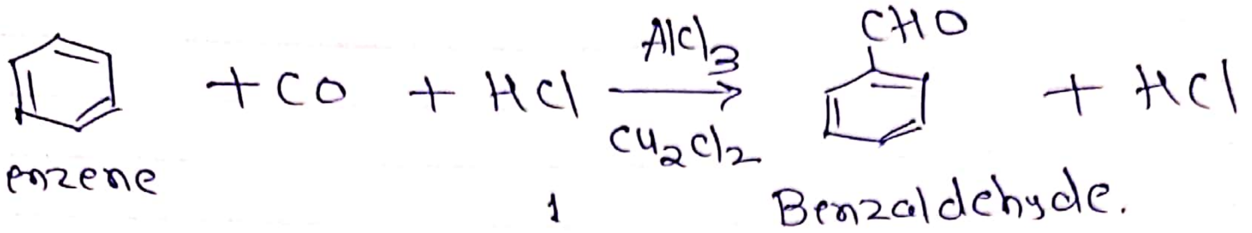
Step-III Intermediate (II) on dehydration on heating ~~to form~~ & hydrolysis to form α-~~β~~ unsaturated acid.



$C_6H_5-\underset{OH}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{||}{C}}-O-\underset{O}{\underset{||}{C}}-CH_3 \xrightarrow[ii)\ H_2O/H^+]{i)\ \Delta\ /-H_2O} C_6H_5-CH=CH-COOH.$

6] Gatterman Koch reaction :→

The treatment of benzene with CO_2 & HCl in presence of unhydrous $AlCl_3$ catalyst is called Gatterman Koch synthesis.



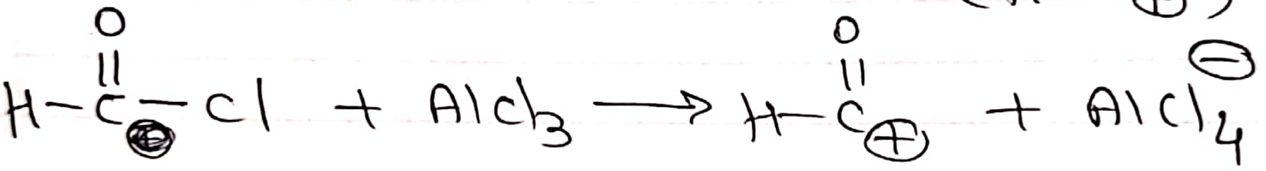
Mechanism :-

step 1 :- CO_2 & HCl react ~~with~~ to form unstable formyl chloride.

$$CO + HCl \longrightarrow H-\overset{O}{\overset{\|}{C}}-Cl$$

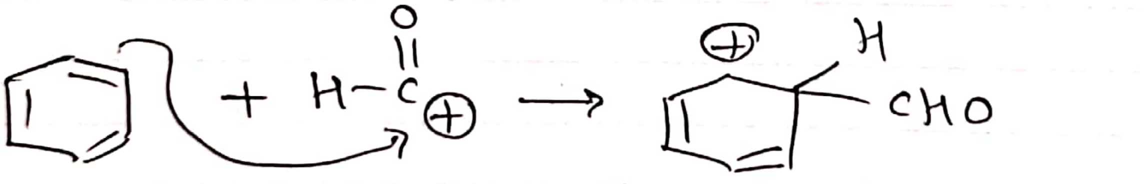
Formyl chloride

tep·2 :→ Formation of electrophile ($H-\overset{O}{\overset{\|}{C}}^{\oplus}$)



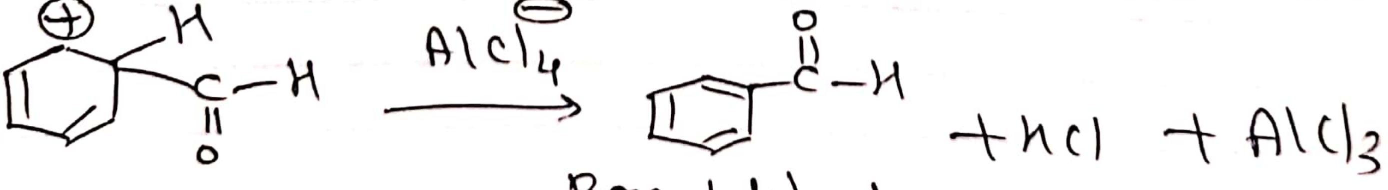
$$H-\overset{O}{\overset{\|}{C}}-Cl + AlCl_3 \longrightarrow H-\overset{O}{\overset{\|}{C}}^{\oplus} + AlCl_4^{\ominus}$$

ep 3 :→ Attack of electrophile on benzene ring to give carbonium ion.



(carbonium ion)
Resonance stabilized.

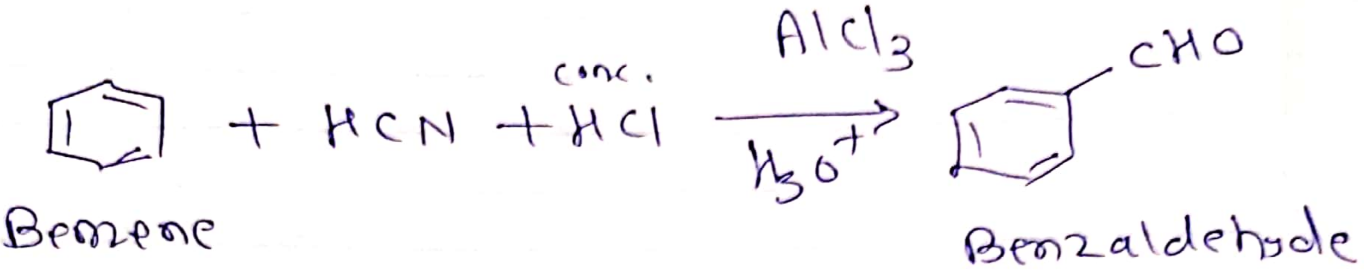
ep 4 :- Removel of proton gives benzaldehyde



Benzaldehyde.

7] Gatterman synthesis :→ (Gatterman Formylation)

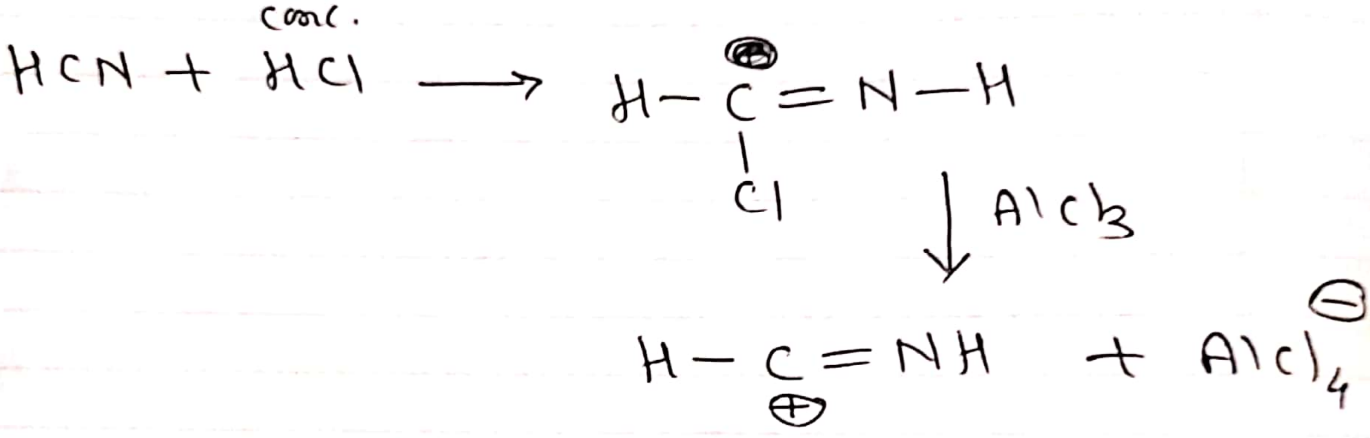
The aromatic compounds are formylated by a mixture of hydrogen cyanide (HCN) & HCl in presence of $AlCl_3$ is called gatterman synthesis.



$C_6H_6 + HCN + \text{conc. } HCl \xrightarrow[H_3O^+]{AlCl_3} C_6H_5CHO$

Mechanism :→

Step I :→ Formation of electrophile

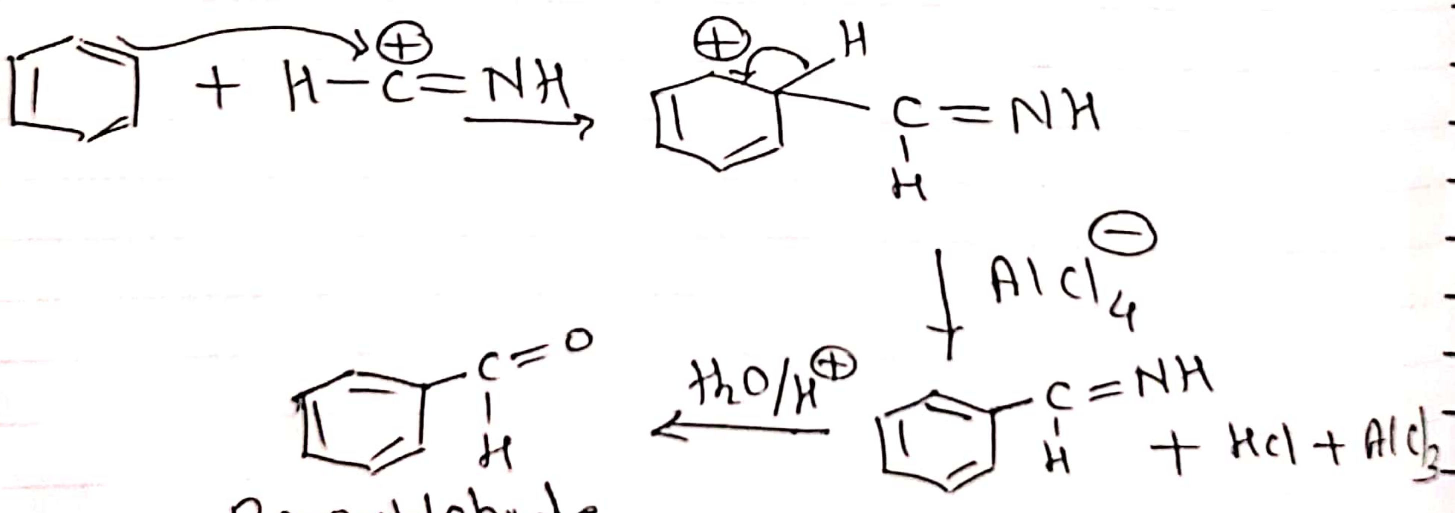


$$HCN + \overset{\text{conc.}}{HCl} \longrightarrow H-\overset{\oplus}{\underset{Cl}{\underset{|}{C}}}=N-H$$

$$\downarrow AlCl_3$$

$$H-\underset{\oplus}{C}=NH + AlCl_4^{\ominus}$$

Step II : Attack of electrophilic on aromatic compounds.



Benzaldehyde.

1 Clemmensen Reduction Reaction :→

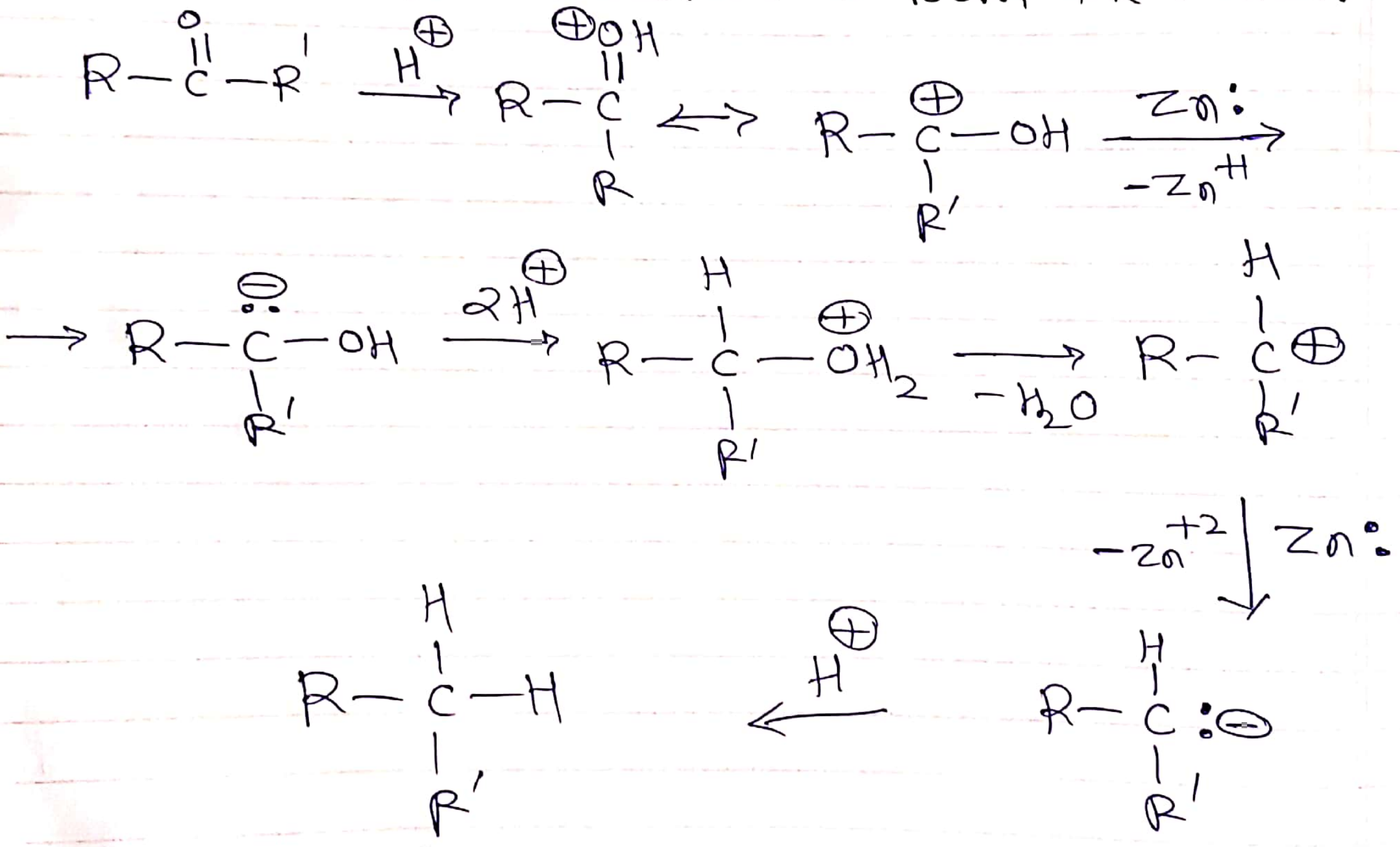
The reduction of carbonyl groups of aldehydes and ketones to methylene groups in presence of Zn-Hg & conc. HCl is known as clemmensen reduction.

$$C_6H_5-COCH_3 \xrightarrow[\text{Conc. HCl}]{Zn-Hg} C_6H_5-CH_2-CH_3$$

Acetophenone Reflux Ethyl benzene

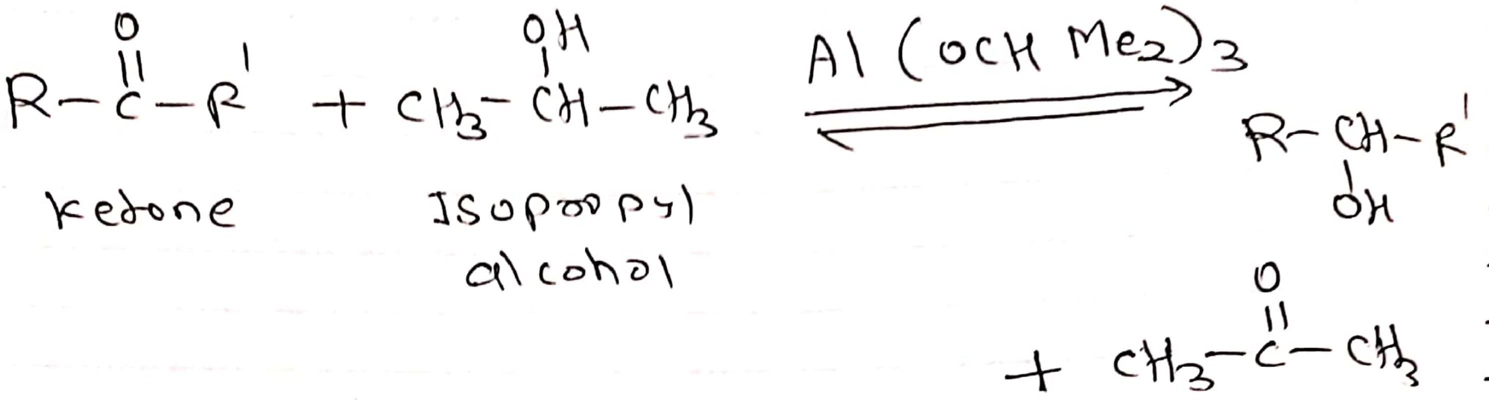
Mechanism :→

Reduction under acid condition involves protonated carbonyl group to which electrons are transferred from the metal.



2] Meervin - Pondorrof verly Reaction :-
(M. P. V. reduction)

The reaction involves reduction of ~~alde~~ aldehydes or ketones to alcohols by treatment with aluminium isopropoxide in excess of Isopropyl alcohol.



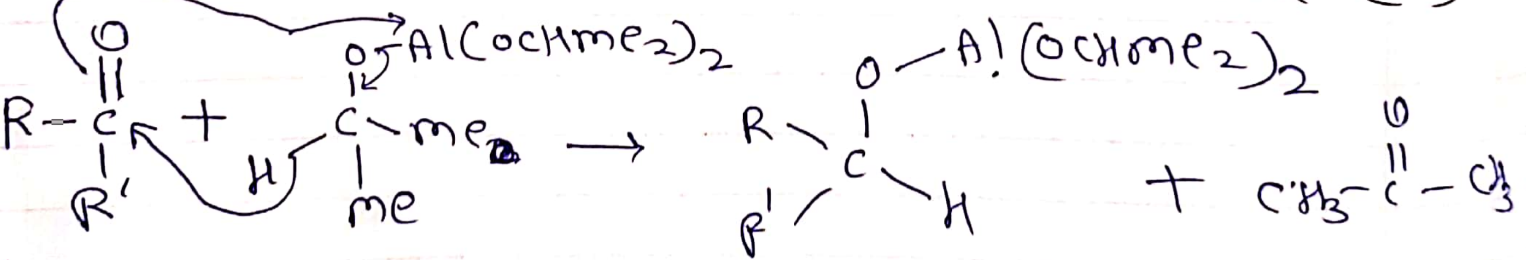
$$R-\overset{O}{\overset{\|}{C}}-R' + CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 \xrightleftharpoons{Al(OCH\,Me_2)_3} R-\underset{OH}{\underset{|}{CH}}-R' + CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

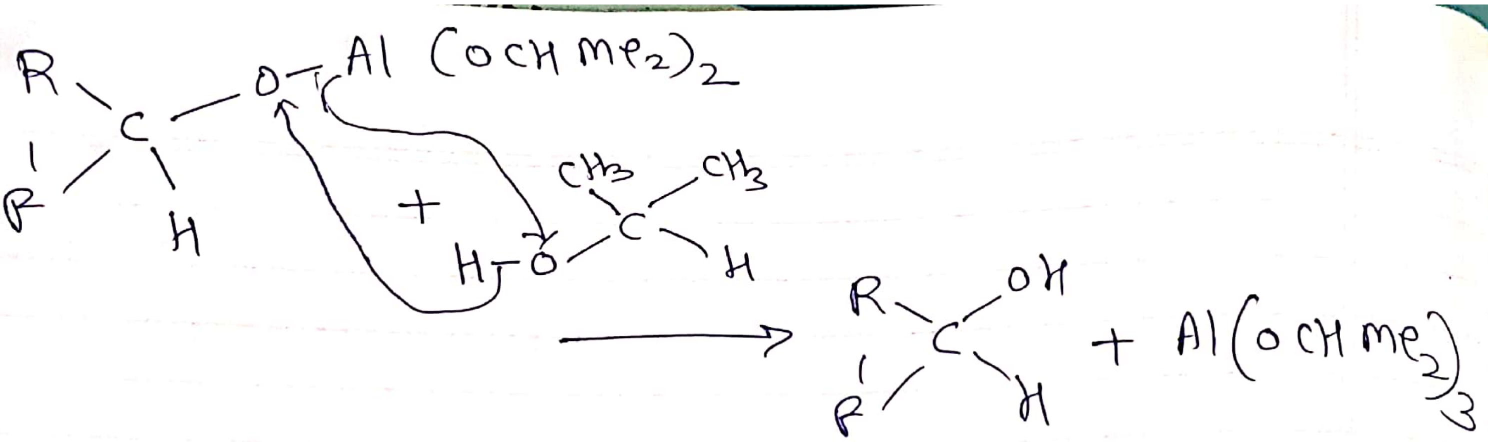
- The reaction is reversible.
- The reverse reaction, called Oppenauer oxidation is employed for oxidⁿ of alcohols, using aluminium t-butoxide as catalyst in presence of excess acetone.

Mechanism :-

The mechanism involves

i) in which Hydrogen ion from the α-CH bond of alkoxide migrates to carbonyl carbon to ketone to yield mixed alkoxide (II)

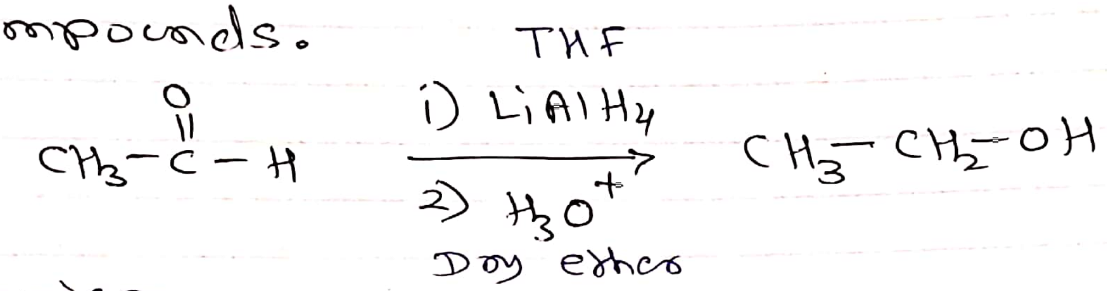




3 Reduction with LiAlH₄ :→

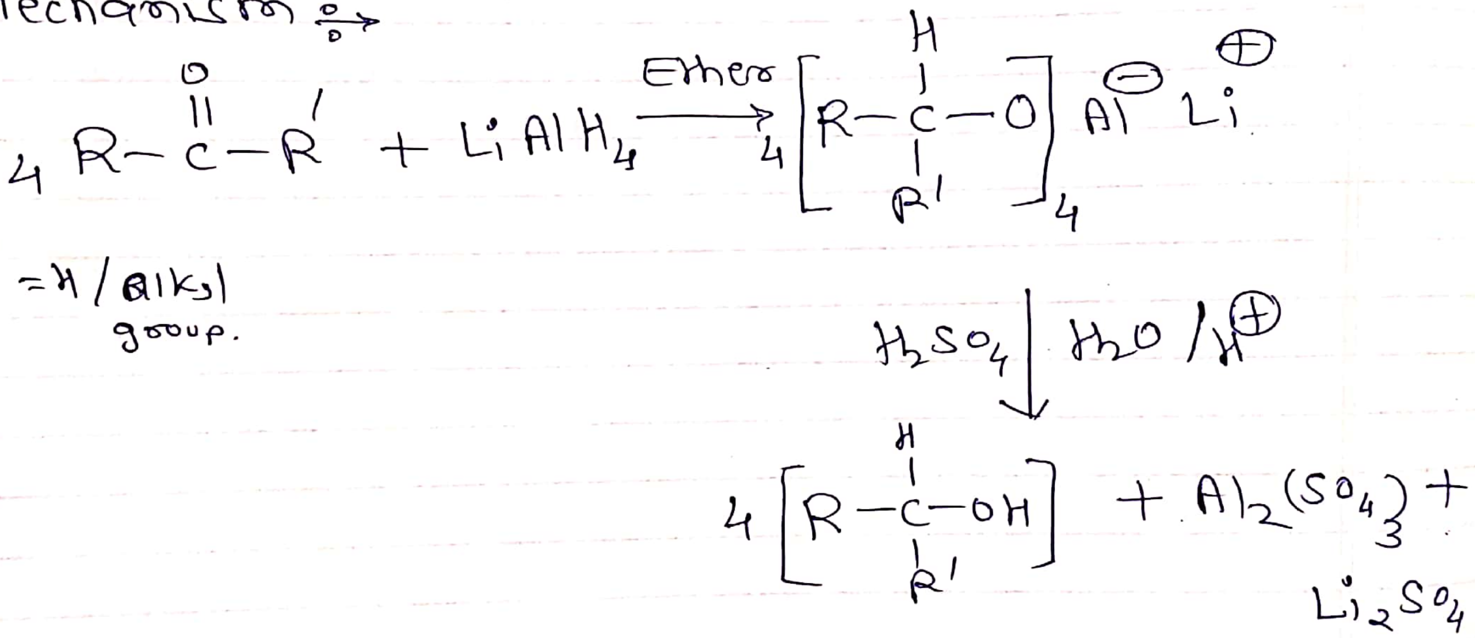
- Lithium aluminium hydride ($LiAlH_4$) is one of reagent used for reduction of carbonyl compounds.

Ex:→



$$CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\substack{2)\ H_3O^+ \\ \text{Dry ether}}]{\substack{\text{THF} \\ i)\ LiAlH_4}} CH_3-CH_2-OH$$

Mechanism :→



$$4\,R-\overset{O}{\overset{\|}{C}}-R' + LiAlH_4 \xrightarrow{\text{Ether}} 4\left[R-\overset{H}{\underset{R'}{C}}-O\right]_4 Al^{\ominus}\,Li^{\oplus}$$

$$\Big\downarrow H_2SO_4 \,|\, H_2O/H^{\oplus}$$

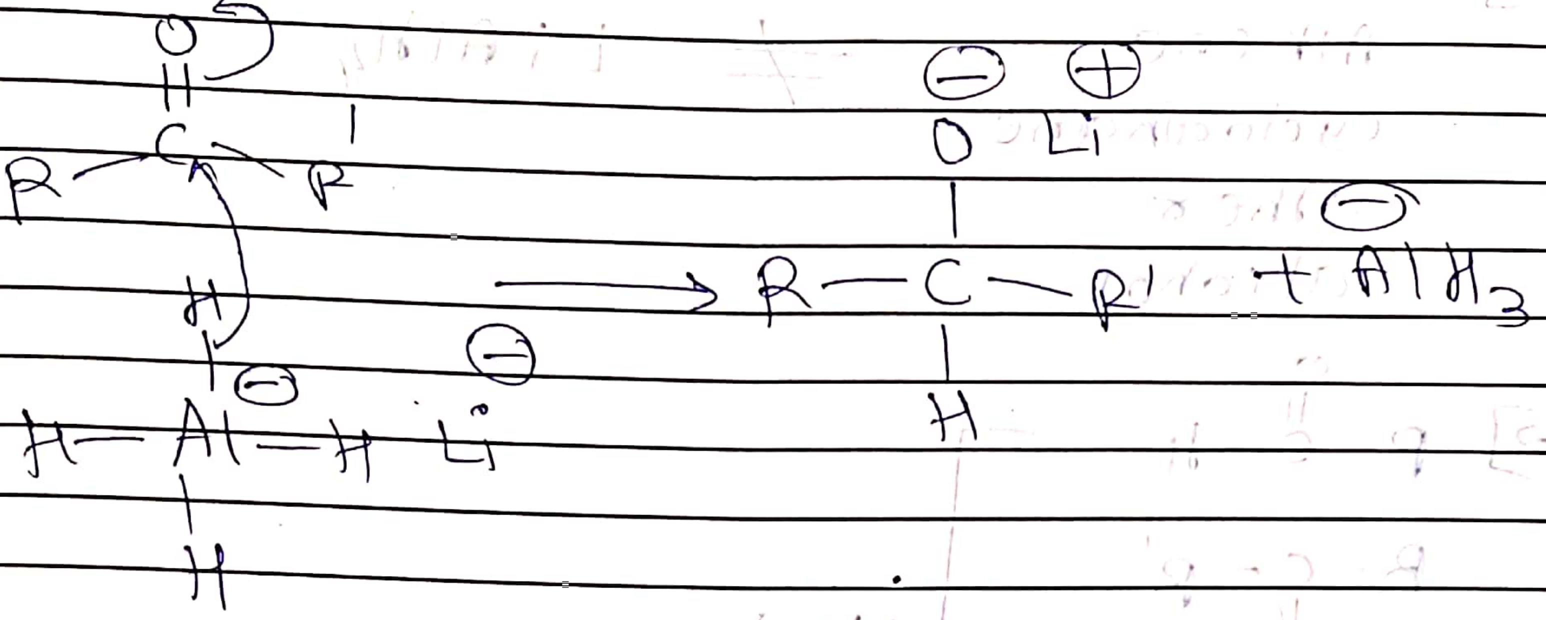
$$4\left[R-\overset{H}{\underset{R'}{C}}-OH\right] + Al_2(SO_4)_3 + Li_2SO_4$$

R' = H / alkyl group.

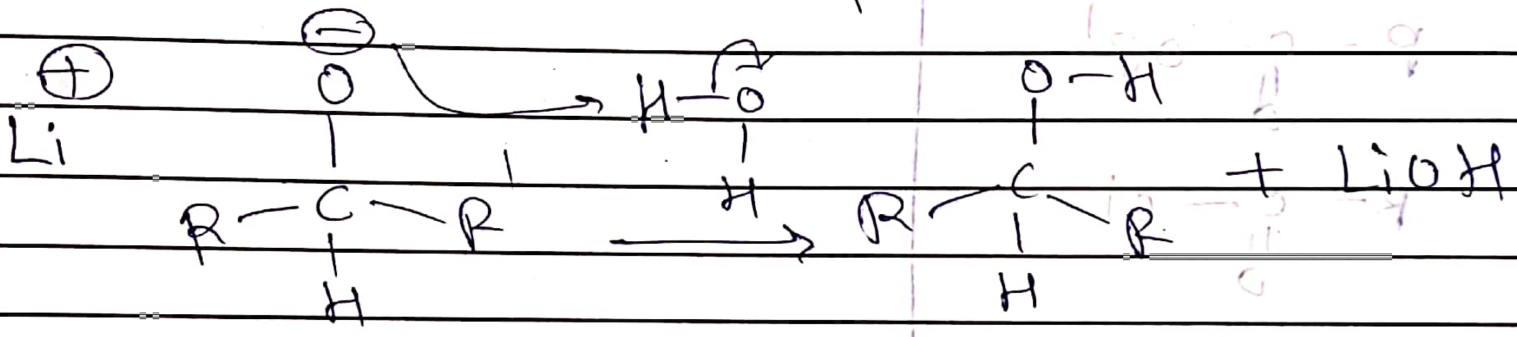
Step of mechanism

~~Attack~~

Nucleophilic attack by hydride anions



The alkoxide is protonated



preparation :

$$4\,LiH + AlCl_3 \xrightarrow{\text{Dry ether}} LiAlH_4 + 3\,LiCl$$

Examples ⇒

Functional Group — product

1] Alkane
Alkene
cycloalkane
ether
alcohol

not react with. $\neq$ $LiAlH_4$

2] $R-\overset{O}{\overset{\|}{C}}-H$

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

$R-COOH$

$R-\underset{\underset{O}{\|}}{C}-OR'$

$R-\underset{\underset{O}{\|}}{C}-Cl$

$(R-\underset{\underset{O}{\|}}{C})_2O$

Lactone.

$\xrightarrow{LiAlH_4}$ Alcohol.

- $R-\underset{\underset{O}{\|}}{C}-NH_2$

Imine

- $>C=NH$
- $-CN$
- $-NO_2$

$\xrightarrow{LiAlH_4}$ Amines.

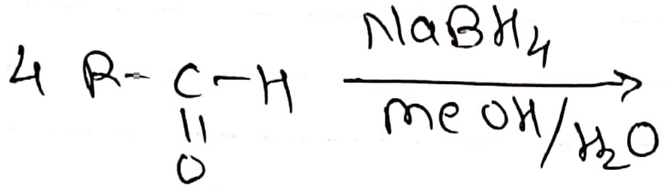
4] Sodium Borohydride ($NaBH_4$)

Preparation ⇒ It is reducing agent.

$$4\,NaH + B(OCH_3)_3 \xrightarrow{250^{\circ}C} NaBH_4 + 3\,CH_3ONa$$

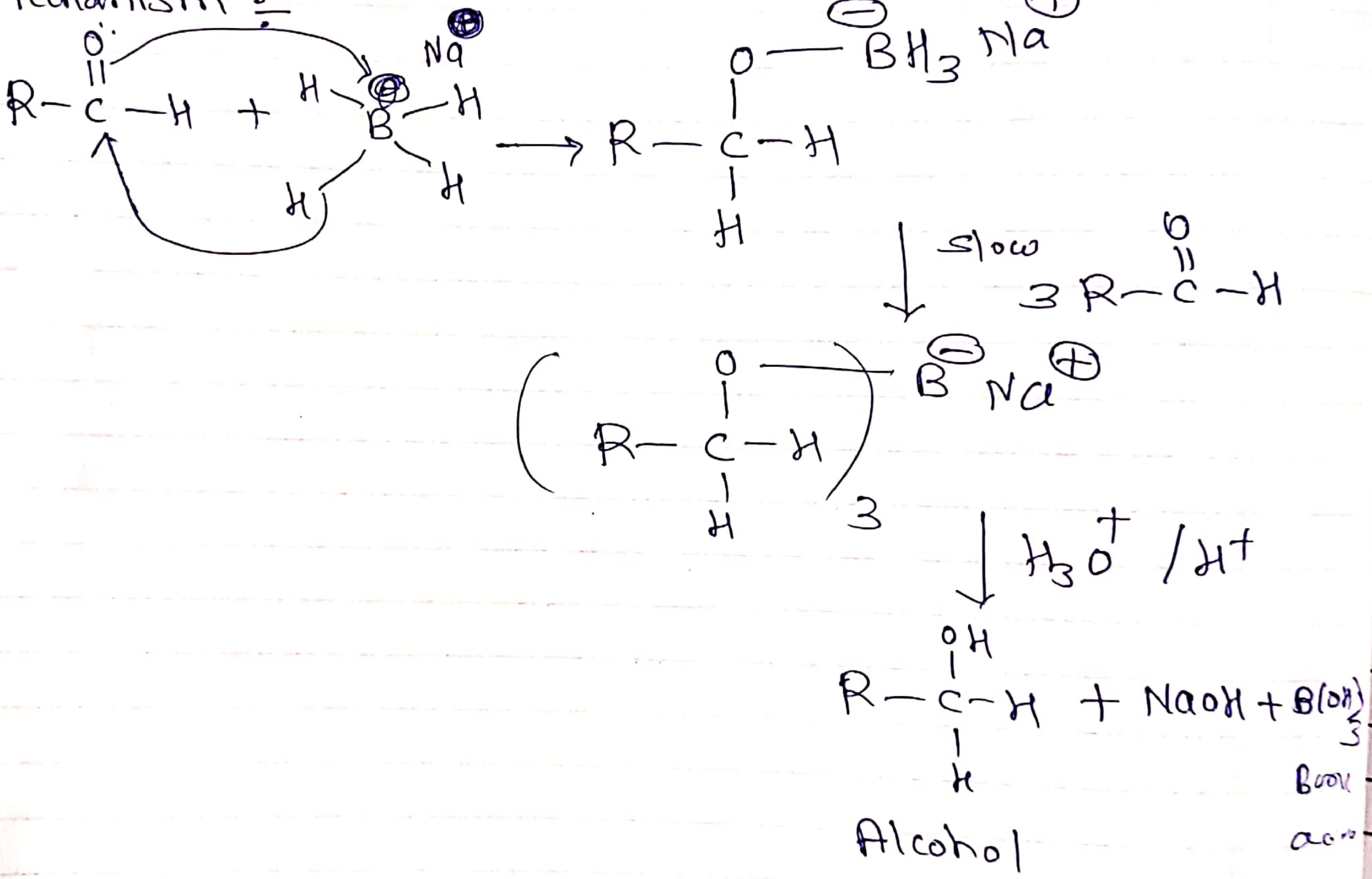
Example :-

- It is chemo selective reagent



$$4\,R-\overset{}{\underset{\underset{O}{\|}}{C}}-H \xrightarrow[MeOH/H_2O]{NaBH_4} R-CH_2-OH$$

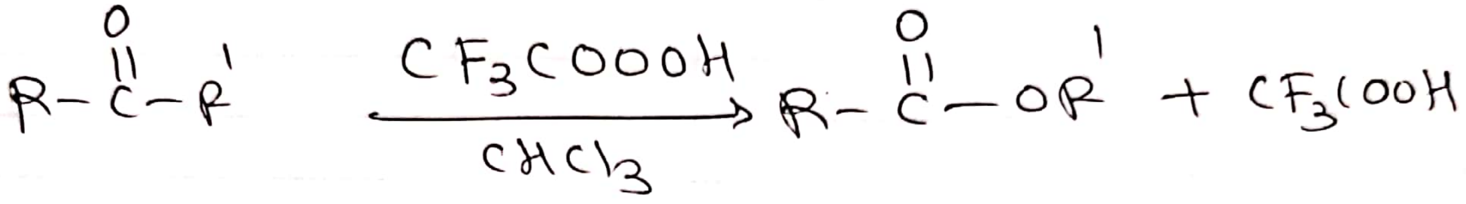
Mechanism :-



* Baeyer-villiger Rearrangement

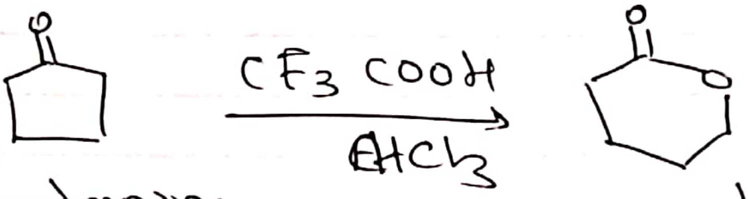
It is example of migration of group from carbon to electron deficient oxygen.

Defⁿ :- oxidation of ketones to esters by the treatment with peracids such as peracetic acid, per benzoic acid pertrifluoroacetic acid etc.



$$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow[CHCl_3]{CF_3COOOH} R-\overset{O}{\overset{\|}{C}}-OR' + CF_3COOH$$

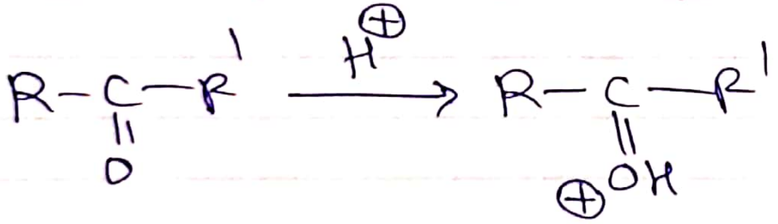
— cyclic ketone to Lactones.



cyclopentanone Lactone

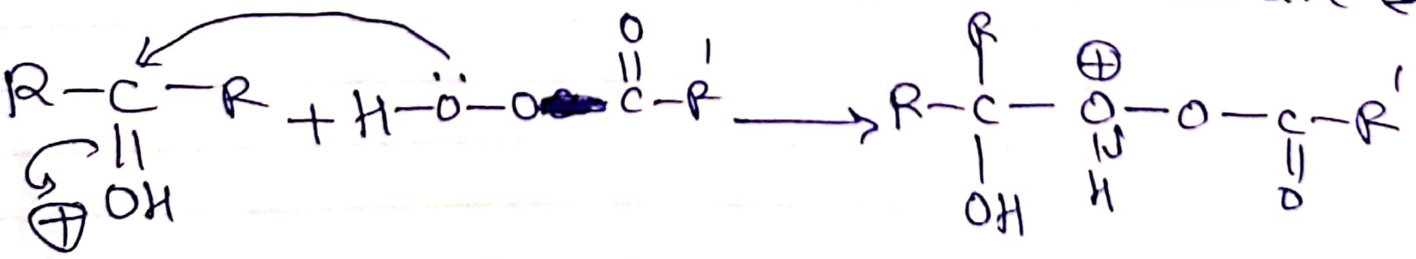
Mechanism :-

Step. I protonation of ketone



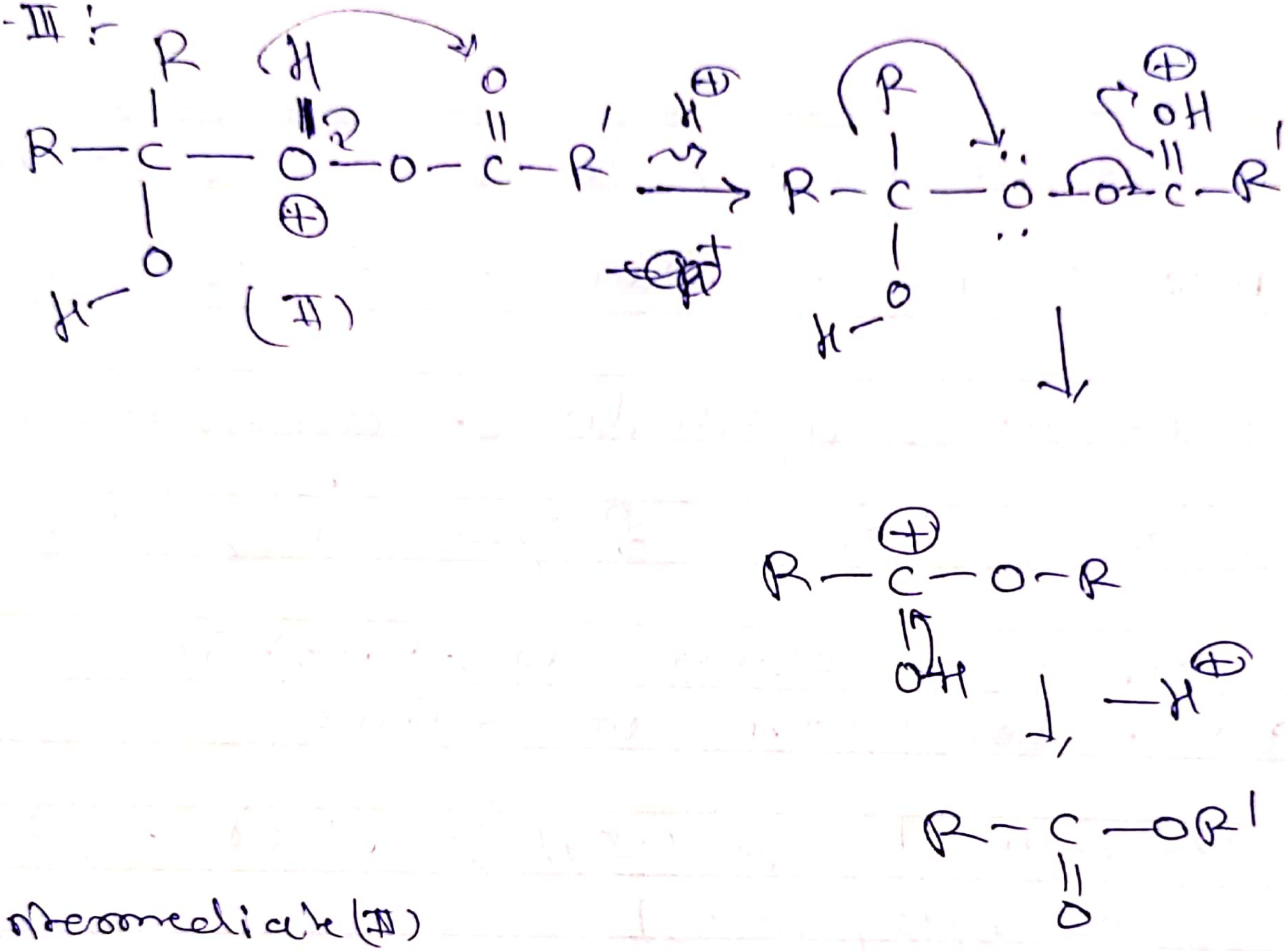
$$R-\underset{\overset{\|}{O}}{C}-R' \xrightarrow{H^{\oplus}} R-\underset{\overset{\|}{\overset{\oplus}{O}H}}{C}-R'$$

Step II :- Nucleophilic attack of peracid on protonated ketone give intermediate (I)



$$R-\underset{\overset{\|}{\overset{\oplus}{O}H}}{C}-R + H-\ddot{O}-O-\overset{O}{\overset{\|}{C}}-R' \longrightarrow R-\underset{OH}{\overset{R}{C}}-\underset{H}{\overset{\oplus}{O}}-O-\underset{\overset{\|}{O}}{C}-R'$$

Step-III :-



Intermediate (II)

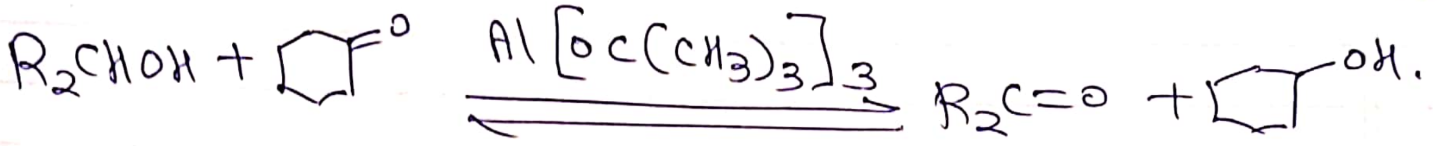
- ~~peroxide ion~~ lose - carboxylate anion & migration of group from carbon to electron deficient oxygen to yield protonated ester by loss of proton.

* Oppenauer Oxid^n Rea^n :→

The rea^n is revers of Meerwin Pondorf verley reduction. The reaction involves oxidation of Secondary alcohol to ketone. ~~& base~~

- When a secondary alcohol in acetone or cyclohexanone is refluxed with aluminium ter. Butoxide in benzene or toluene solution, the secondary alcohol is dehydrogenated to ketone & hydrogen are transferred to acetone or cyclohexanone converting them to alcohols.

$$R_2CHOH + (CH_3)_2C{=}O \overset{Al[OC(CH_3)_3]_3}{\rightleftharpoons} R_2C{=}O + (CH_3)_2CH{-}OH$$



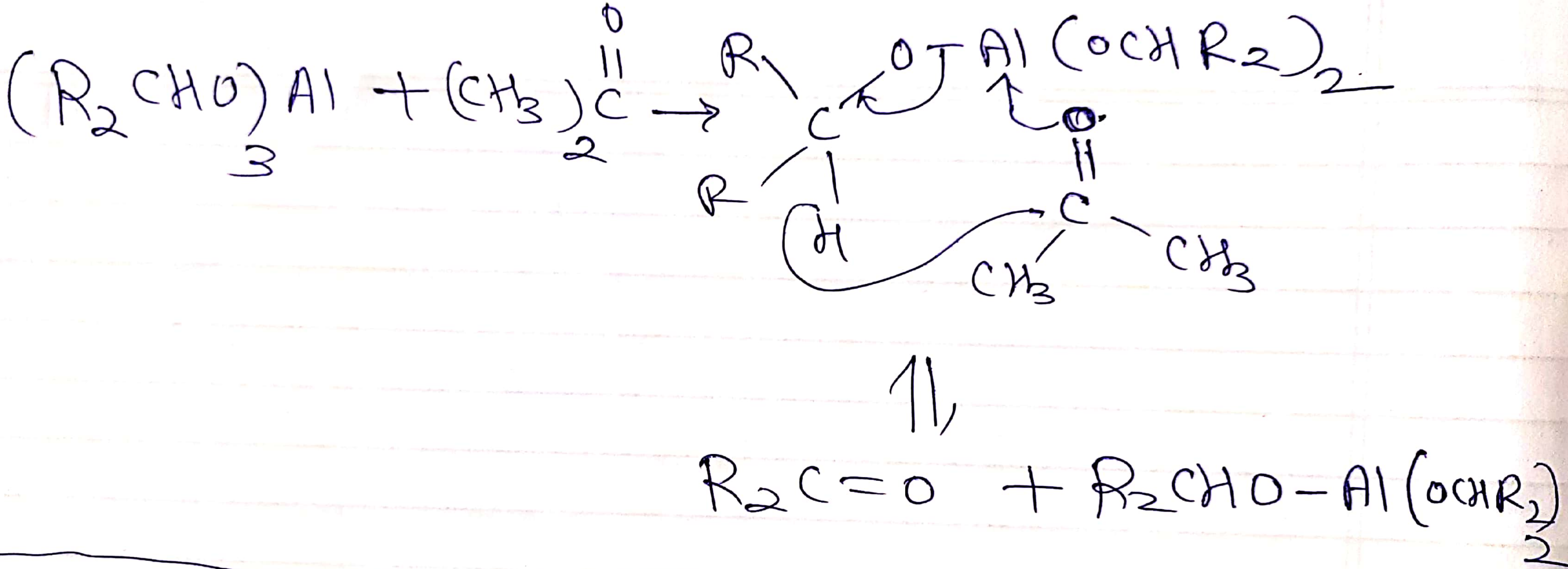
Mechanism :→

Step

I : Alcohol & aluminium ter. butoxide react to form aluminium derivative of secondary alcohol.

$$3\ R_2CHOH + Al[OC(CH_3)_3]_3 \rightleftharpoons (R_2CHO)_3Al + 3(CH_3)_3C{-}OH$$

II : Aluminium derivatives forms with acetone a cyclic transition state which undergoes internal hydride ion transfer resulting in oxidation of alcohol to ketone.


$(R_2CHO)_3Al + (CH_3)_2C=O \rightarrow$
R
R
C
O
Al$(OCHR_2)_2$
H
O
C
CH_3
CH_3
$\rightleftharpoons$
$R_2C=O + R_2CHO-Al(OCHR_2)_2$