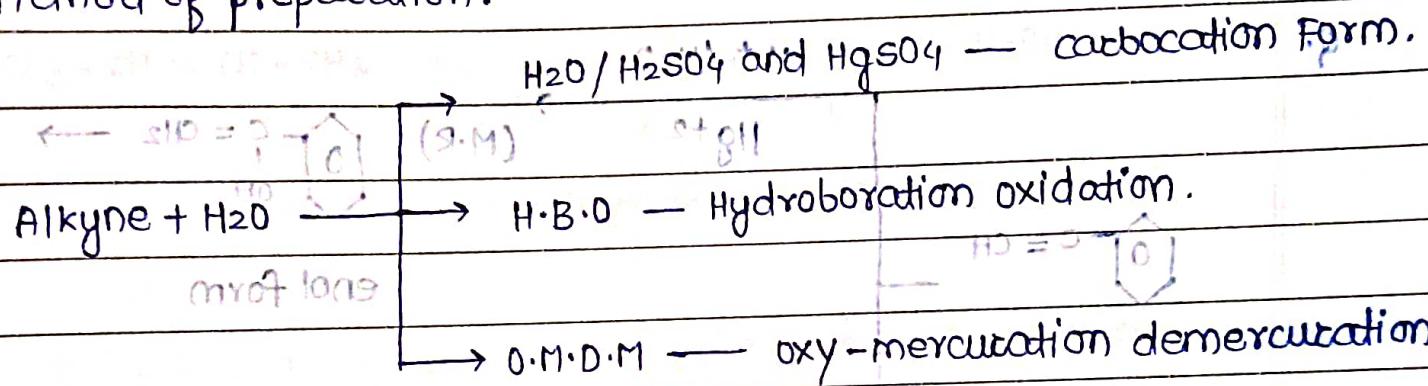


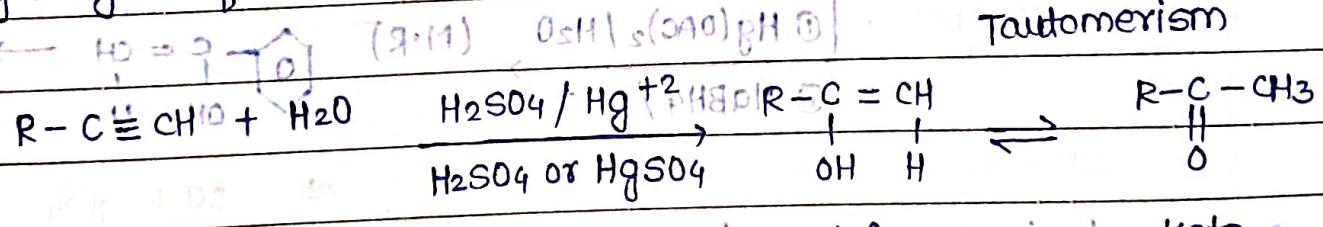
Aldehyde and Ketone.

- ## • Method of preparation:



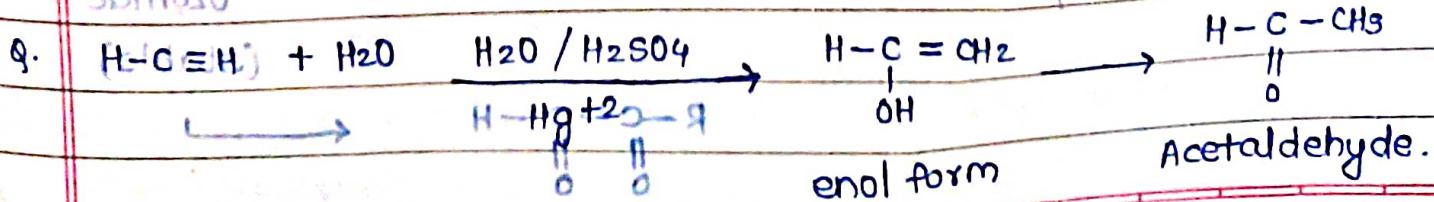
(i) Addition of water in Alkyne: $\text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CH}_2\text{OH}$

a) Hydrolysis of Alkyne in presence of H_2SO_4 and $HgSO_4$

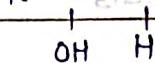
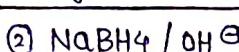
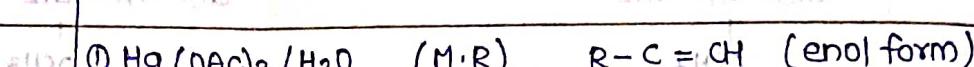
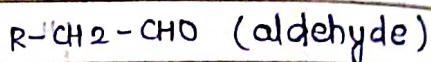
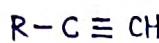
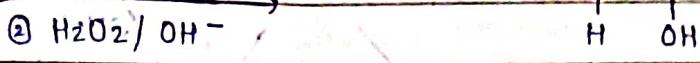


- Note: No rearrangement (unstable)

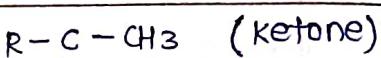
Note: No rearrangement occurs — Aliphatic enol form is unstable and convert into ald/keto form.



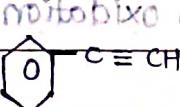
(6) H·B·O and O·M·D·M



Aldehydes and Ketones



ketone in hood

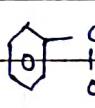
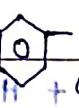
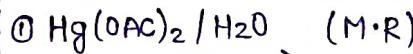


enol form

(ketone)



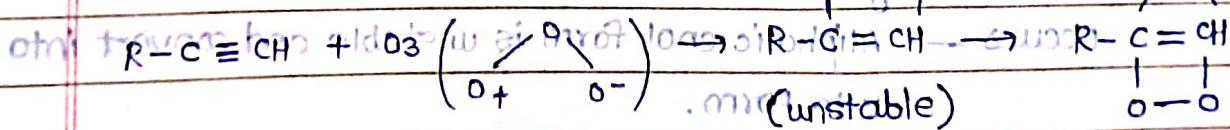
(aldehyde)



(ketone)

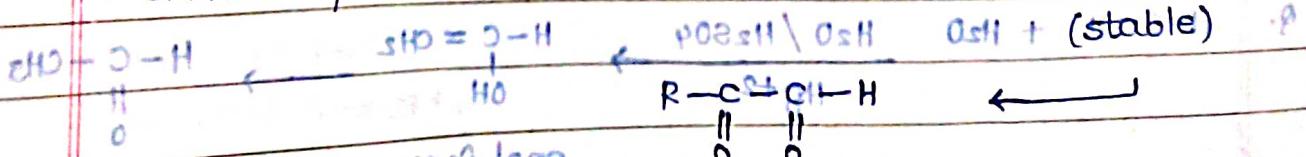
• ozonolysis of Alkyne and Alkene:

(aldehyde)



• oxidation process

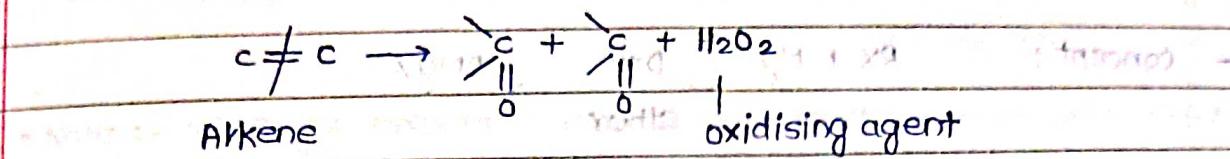
Ozonide



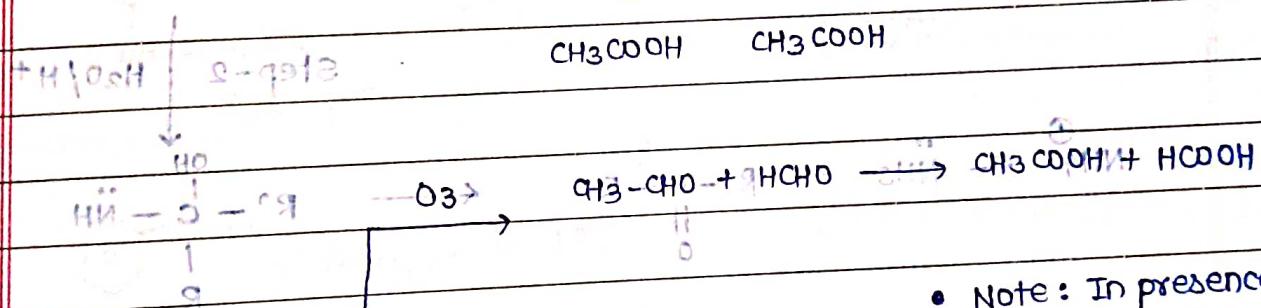
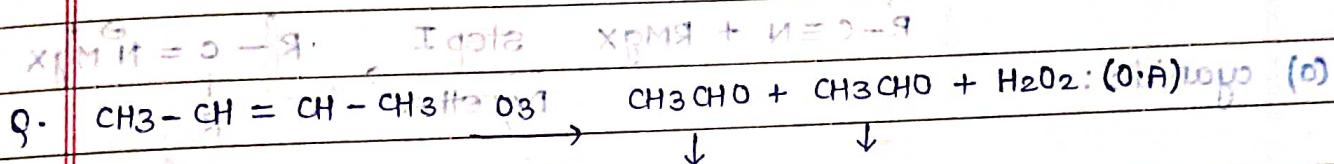
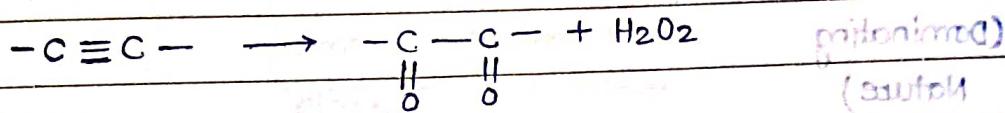
Acetone

metol

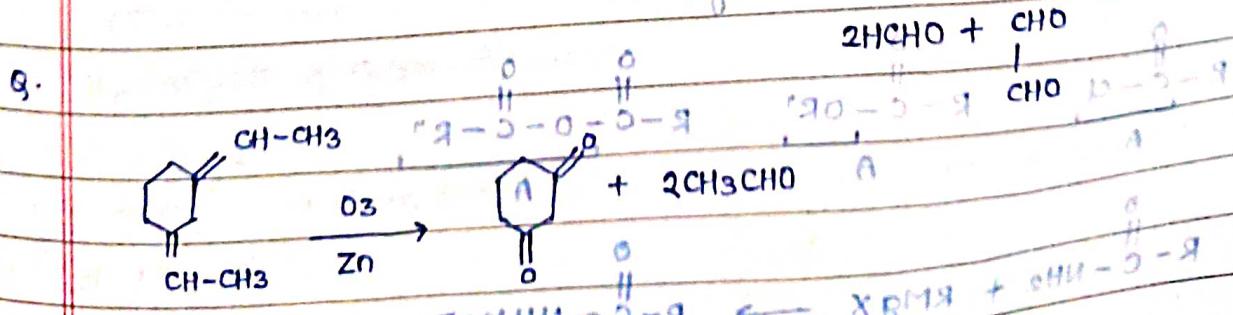
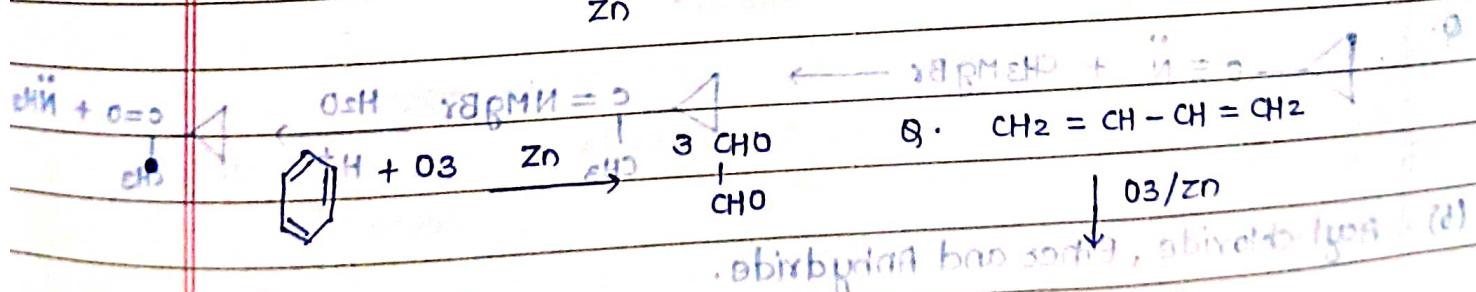
- Note - ozonolysis — 2 bond break hate hain



Note - ketone does not oxidise by H_2O_2 .

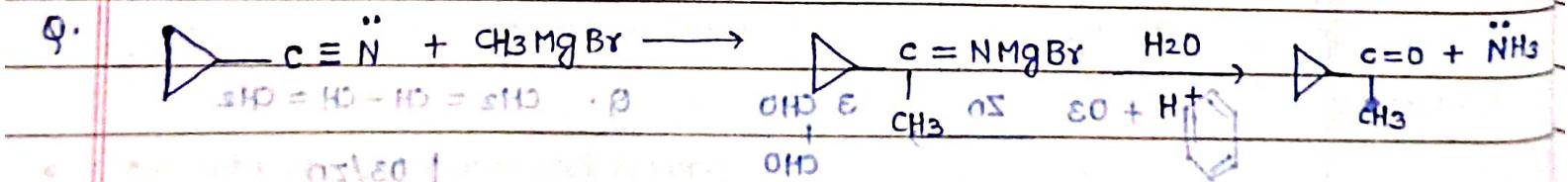
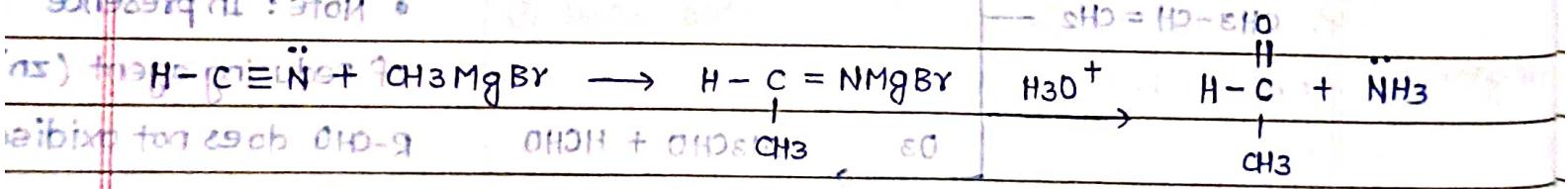
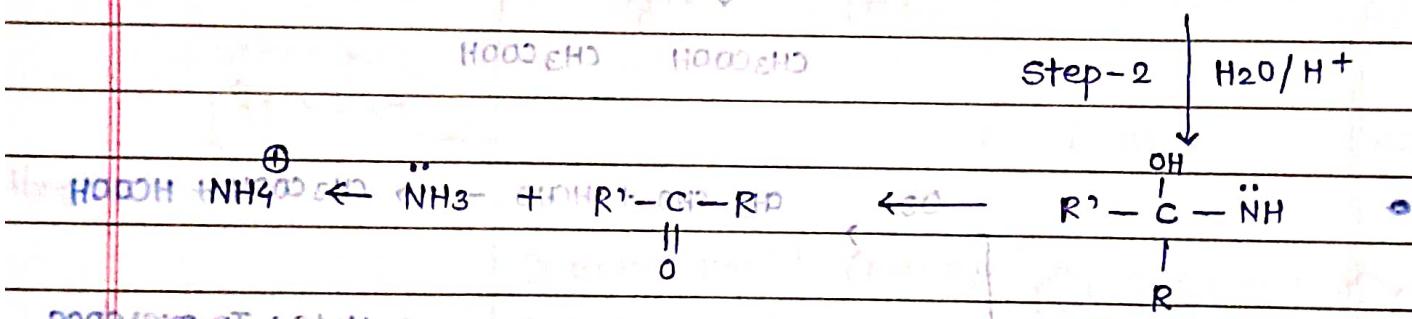
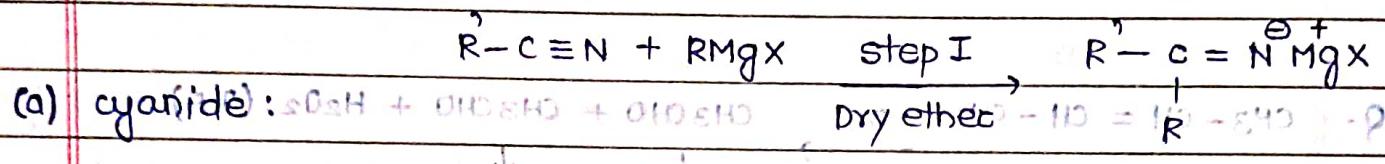
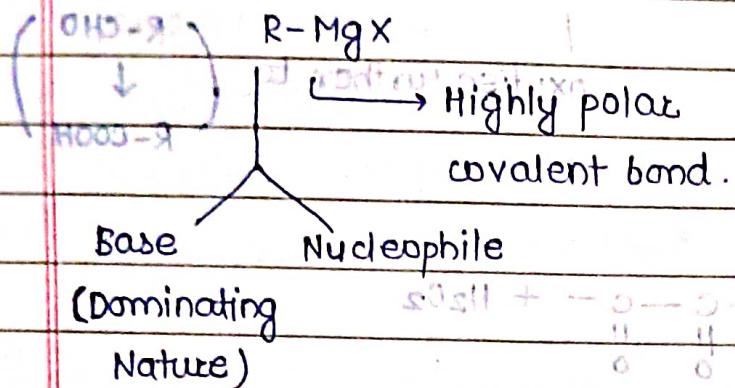


- Note : In presence
of Reducing agent (Zn)
 R-CHO does not oxidise
further.

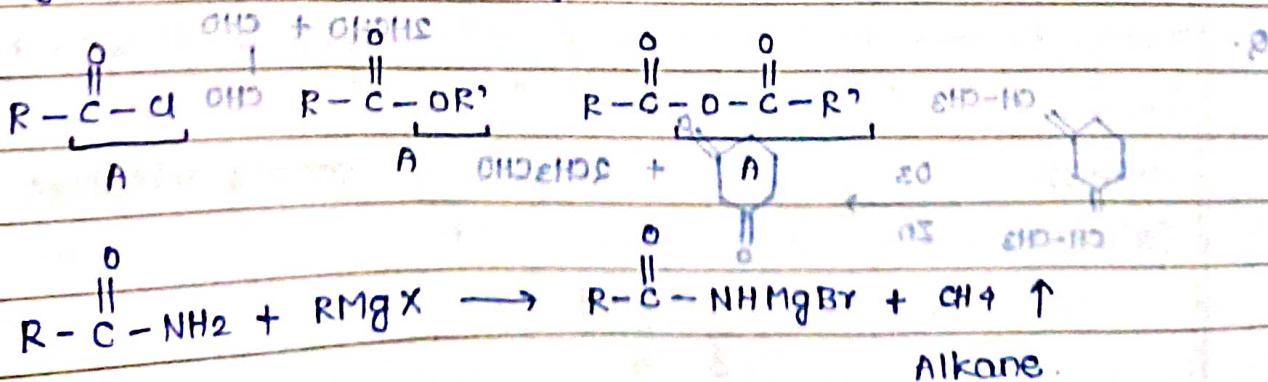


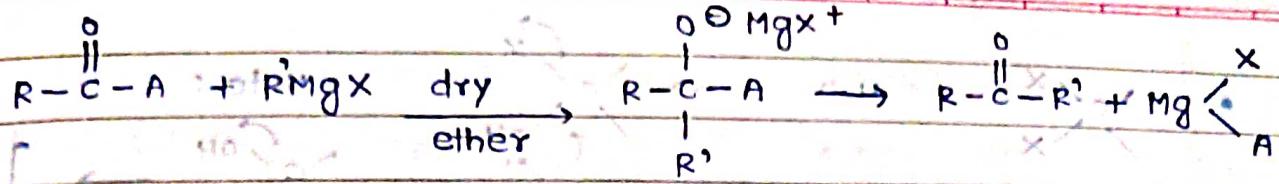
- By Grignard Reagent: $\text{start from a bond} \rightarrow \text{oxidation} \rightarrow \text{stay}$

- concept: $\text{RX} + \text{Mg}$ ^{soot} ^{dry} $\xrightarrow{\text{ether}}$ RMgX
~~fragen nach ihm~~

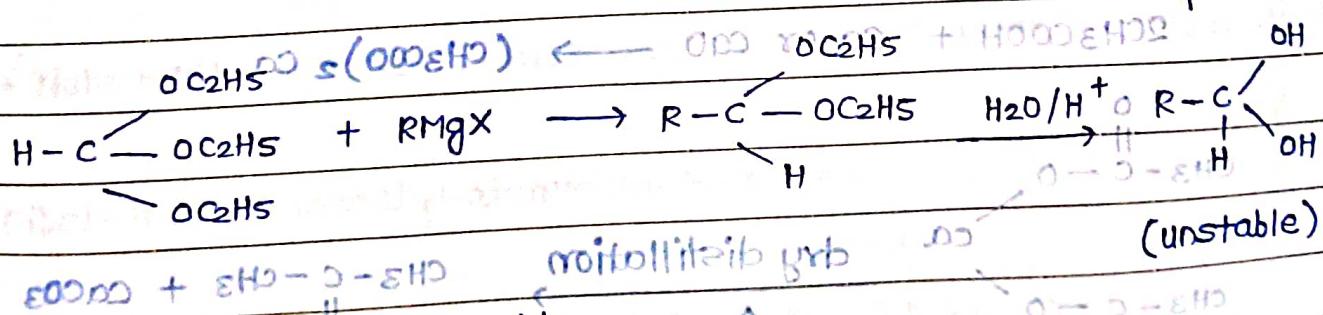
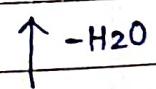
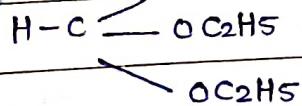
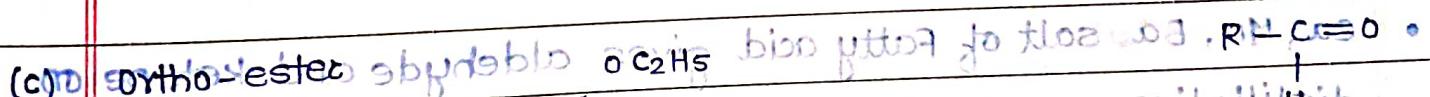
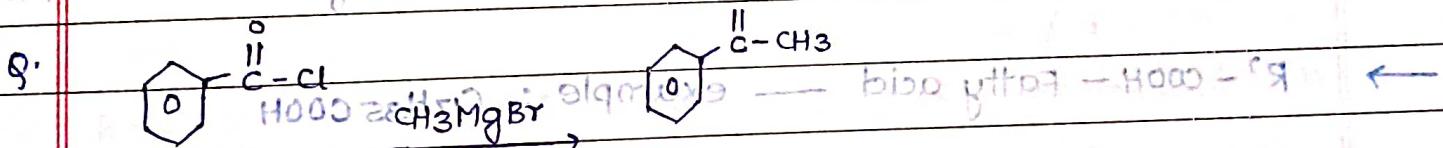
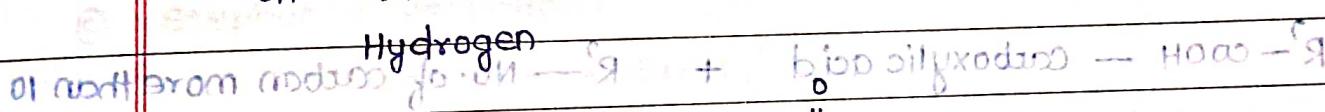
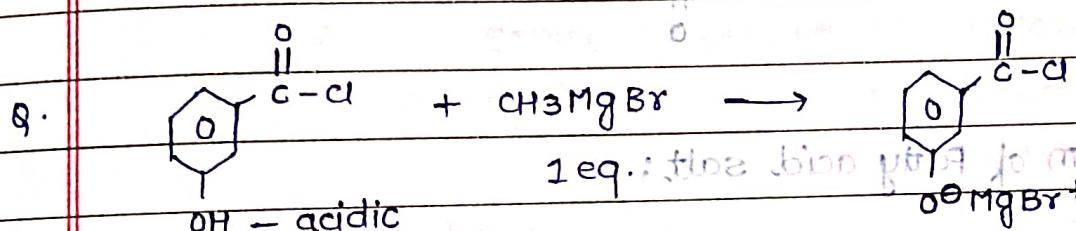
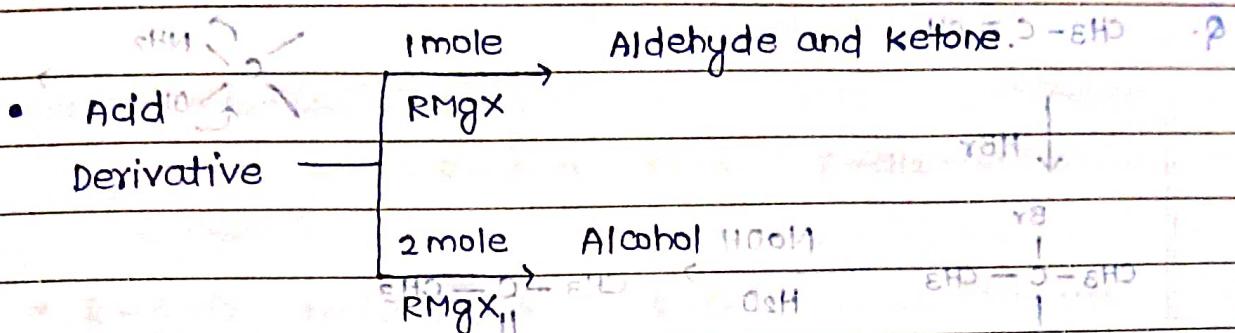


(b) Acyl chloride, Ether and Anhydride.



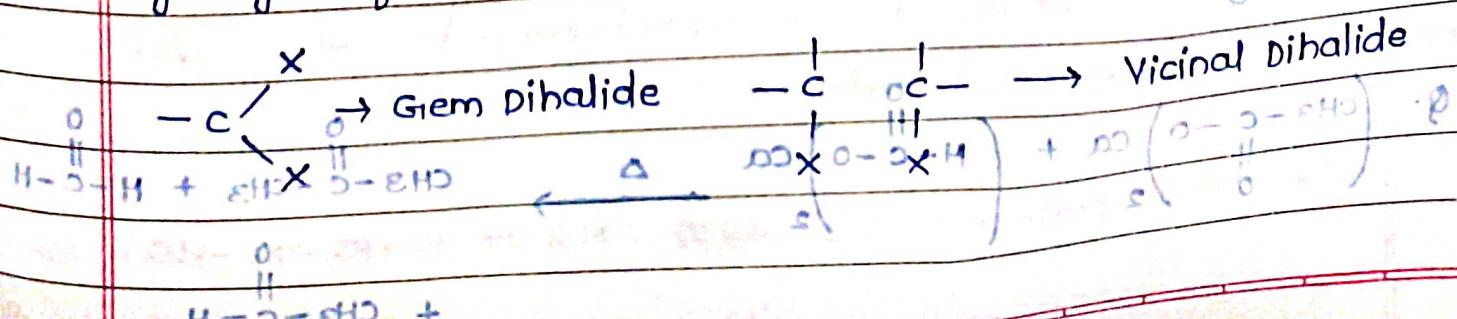


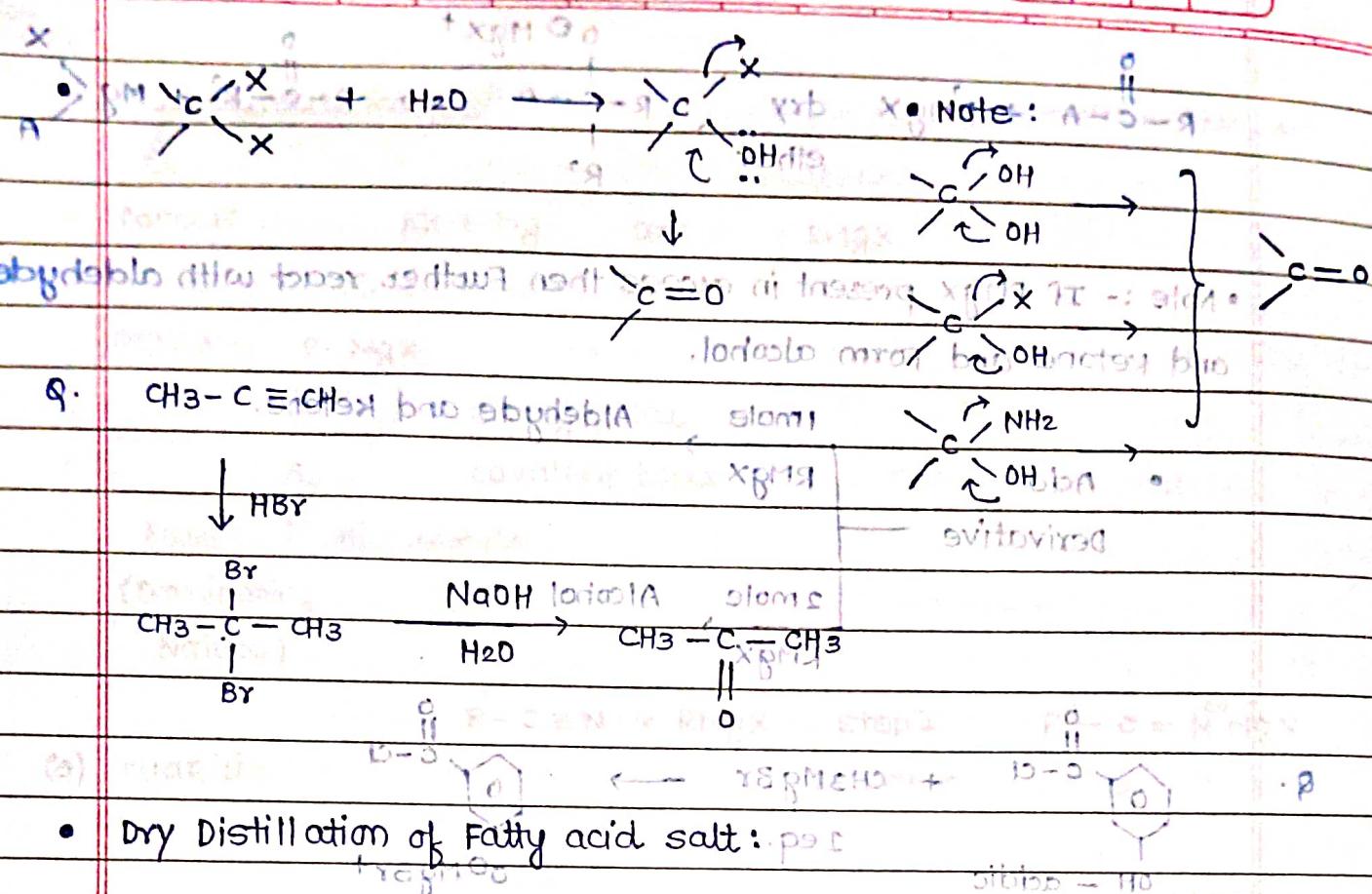
- Note :- If $RMgX$ present in excess then further react with aldehyde and ketone and form alcohol.



(unstable)

- Hydrolysis of Gem-dihalide:

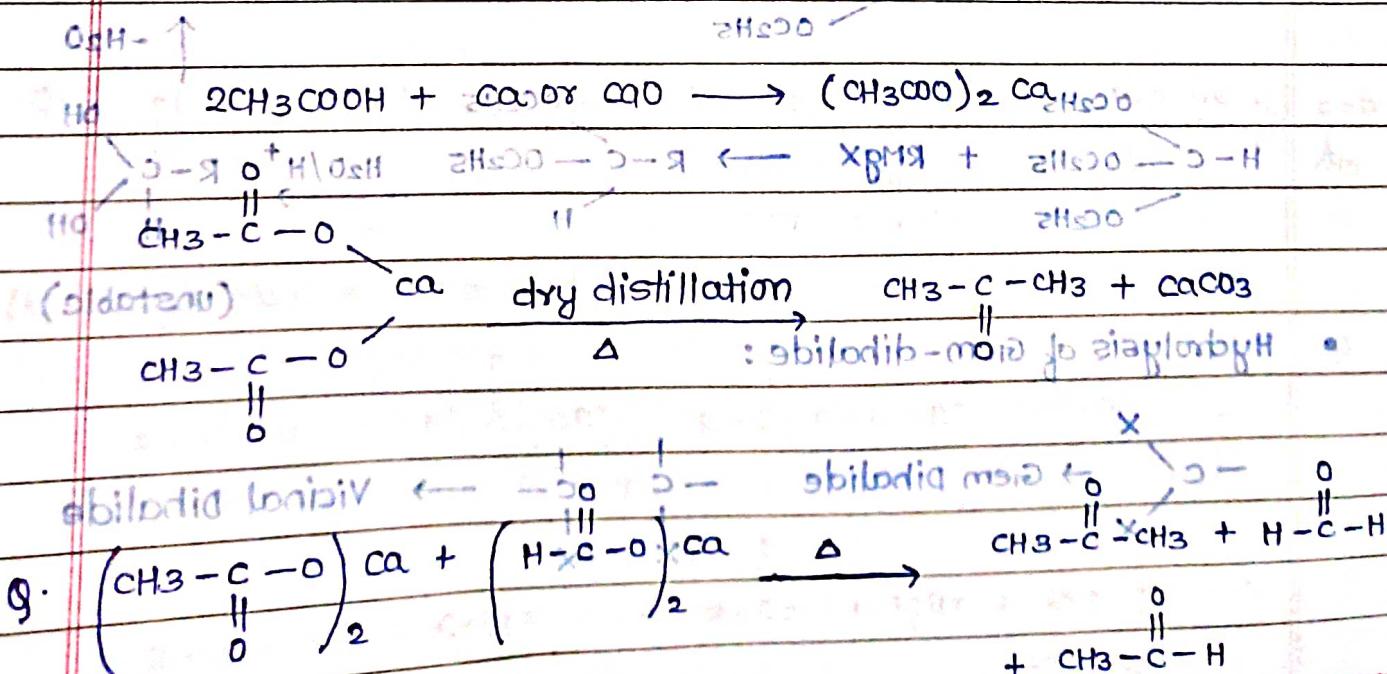




$R'-COOH$ — carboxylic acid + R' — No. of carbon more than 10

→ $R'-COOH$ - Fatty acid — example : $C_{17}H_{35}COOH$

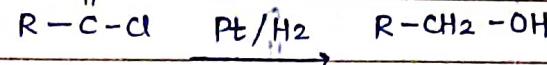
- Ca_2^+, Mn^+ , Ba salt of fatty acid gives aldehyde and ketone on distillation.



- Method of preparation (only aldehyde):
 - $\text{CH}_2 = \text{CH}_2 + \text{CH}_2 - \text{COOH} \xrightarrow{\text{catalytic HgCl}_2}$

- Method of preparation (only aldehyde):

① Rosenmund reduction



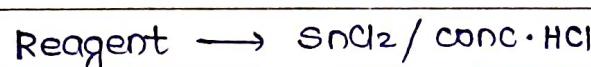
Aldehydes and Ketones

- $\text{R}-\underset{\substack{\parallel \\ \text{O}}}{\text{C}}-\text{Cl} \xrightarrow[\text{Boiling solvent}]{} \text{Pd/BaSO}_4, \text{s} \quad \text{R-CHO.}$ $\xrightarrow{\text{H}_2 \rightarrow \text{decarboxyl}}$
 $\bullet \text{BaSO}_4, \text{Ox, s (high)}$

Boiling mixture solvent = $\text{BaSO}_4 \text{ O}_2 \text{S} \text{ (shimp)}$

anisopropyl xylene (nitrobenzene) - decrease the rate of oxidation

② || Stephen's Reduction:



$$\Theta \mu H + \sigma = \sigma'$$

$$\text{OH} \text{---} \text{H}$$

$$R-C\equiv N + 2H \longrightarrow R-CH=NH \quad HCl \quad \xrightarrow{\text{heat}} \quad R-CH_2-NH_2 \quad HCl$$

④ $\text{H}_2\text{O} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}$

$$\text{④ } \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} \quad \text{↓} -\text{H}_2\text{O} \quad \text{H}_2\text{O} = \text{H}_2 + \text{O}_2$$

$R-C\equiv N$ $\xrightarrow[\text{HCl}]{\text{SnCl}_2}$ $R-CHO$ (это НОР, т.к. $R-CHO$ - кислота)

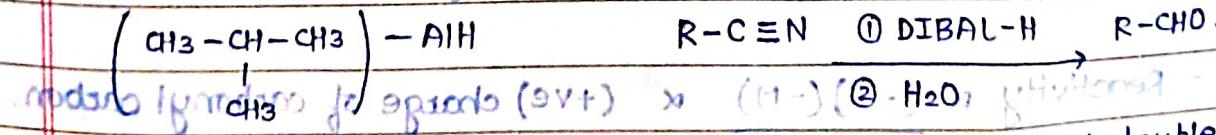
↓ ② $\text{H}_2\text{O} / \text{H}^+$ (negative)

© НИИЭ

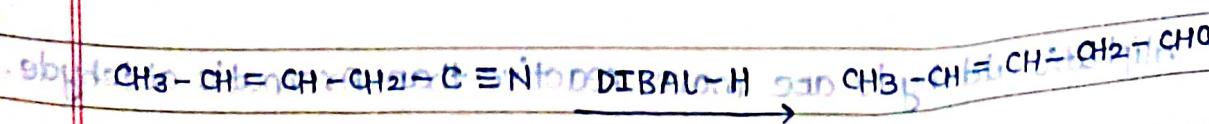
- Note: Dibal-H also reduce -CN group and ester in $-C=O$ (aldehyde)

③ Dibal-H (di-isobutylaluminium hydride):

negative predicate. *negative predicate*



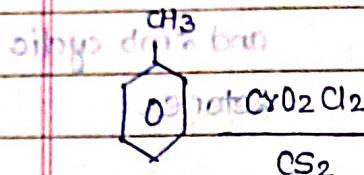
- Note :) Does not effect double bond.



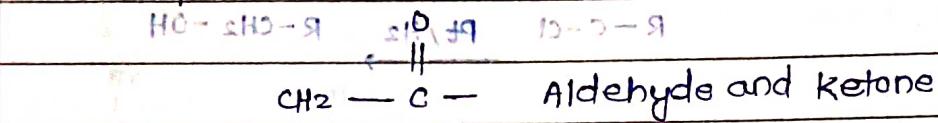
④ Etched reaction:

* only aldehyde form (Aromatic aldehyde)

- Toluene oxidise by CrO_2Cl_2 (chromyl chloride) in presence of CS_2 solvent and form Benzaldehyde.



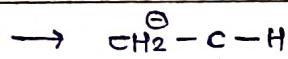
• Chemical properties:



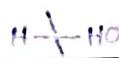
(Very weak α -hydrogen acid) - Nu^- Addition reaction

- Decrease in α -H - Nu^- addition elimination reaction.

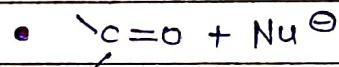
Name reactions



$\text{R}-\text{C}(=\text{O})-\text{Na}^+$ \leftarrow $\text{R}-\text{C}(=\text{O})-\text{Na}^+ + \text{HCl} \rightarrow \text{R}-\text{C}(=\text{O})-\text{H}$



Reduction: ③



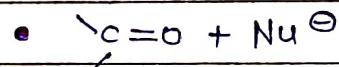
- Nu^- addition reaction: $\text{R}-\text{C}(=\text{O})-\text{H} \rightarrow \text{R}-\text{C}(=\text{O})-\text{Na}^+$

① H_2O] Weak Nu^-

② $\text{R}-\text{OH}$ $\text{O}^\ominus-\text{H}^\oplus$

③ RMgX , RLi , R_{2}CuLi (Gilman's Reagent)

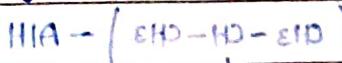
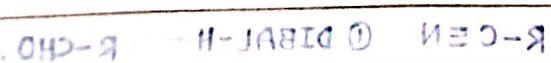
④ NaHSO_3



⑤ NaCN/HCN : $\text{R}-\text{C}(=\text{O})-\text{H} \rightarrow \text{R}-\text{C}(=\text{O})-\text{Na}^+$



- Reactivity \propto steric hindrance. (Variable in alkyl group)

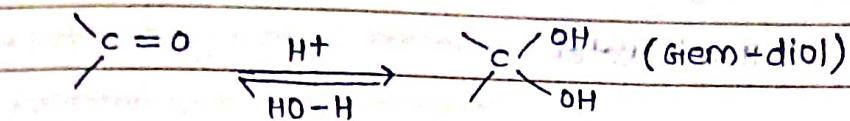


- Reactivity $\propto (-I)(-M) \propto (+ve)$ charge of carbonyl carbon.

Aliphatic aldehydes are more reactive than Aromatic aldehydes.

Aliphatic aldehydes are more reactive than Aromatic aldehydes.

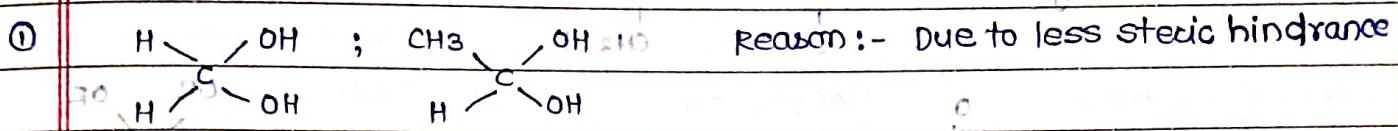
(Notes) Addition of $\text{H}_2\text{O}/\text{H}^+$:



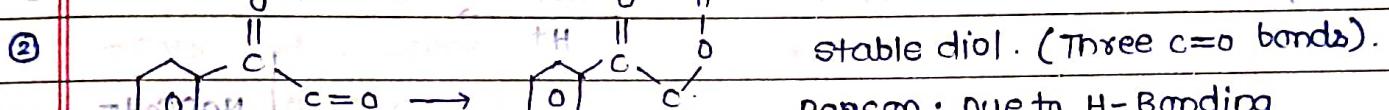
~~and equilibrium of formed isomer is also unstable~~

Note: If equilibrium shifted to forward direction then first step, diol is called stable diol.

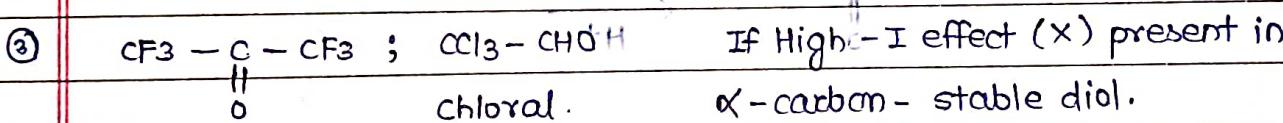
Note: equilibrium is shifted to backward direction.



Reason: Due to less steric hindrance

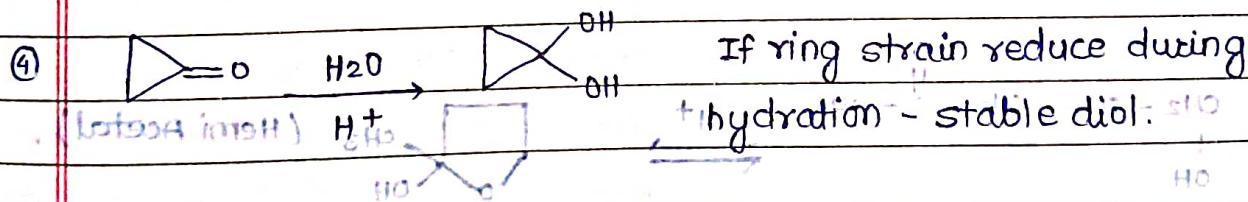


Reason: Due to H-Bonding



If High -I effect (x) present in α -carbon - stable diol.

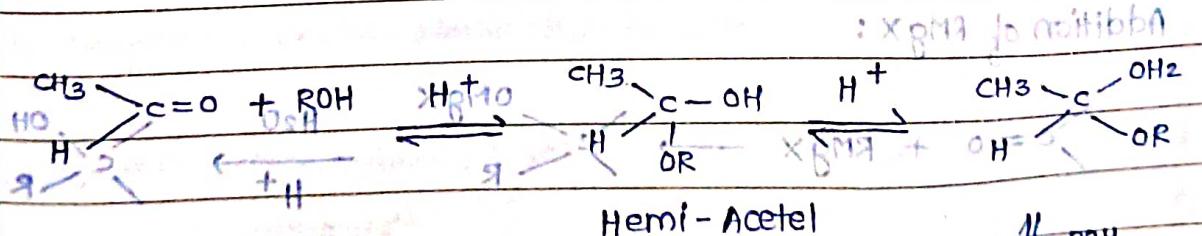
Reason: Due to -I effect



If ring strain reduce during

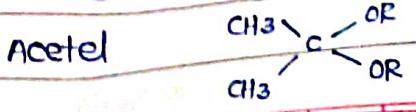
hydration - stable diol.

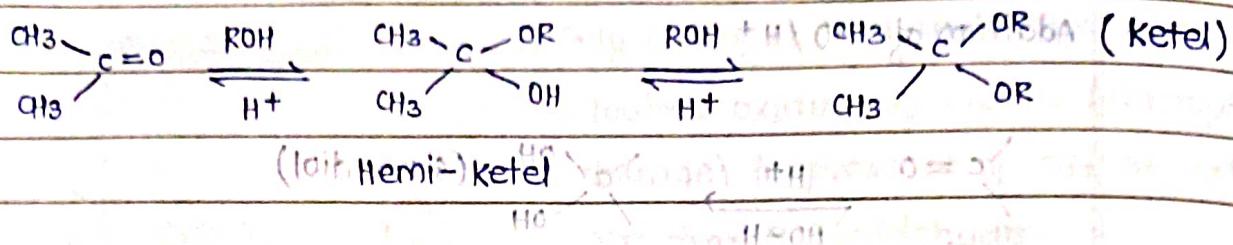
• Reaction with ROH / H^+ :



: XBR₃ to HOBBA

: ROH to HOBBA



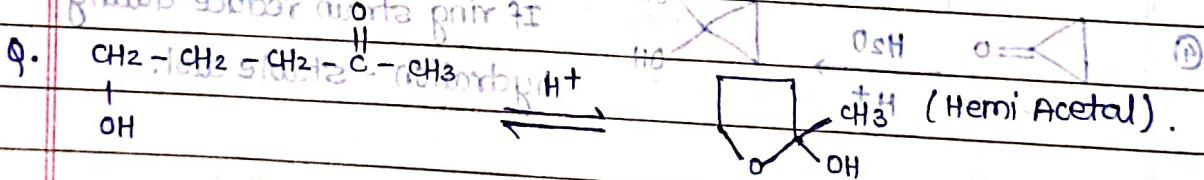
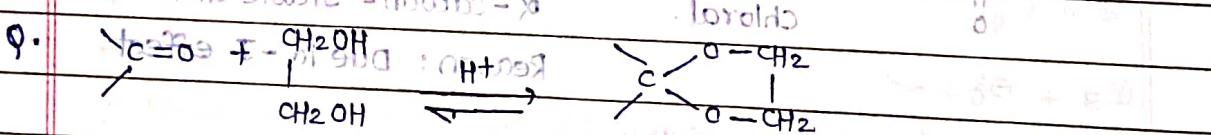
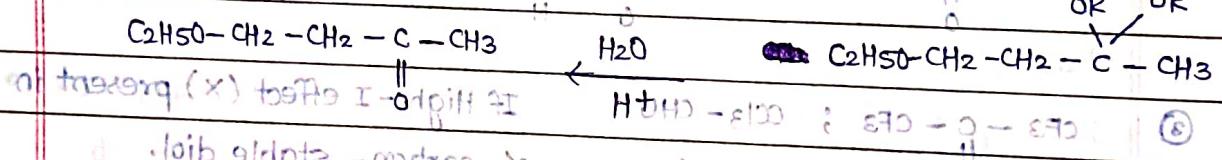
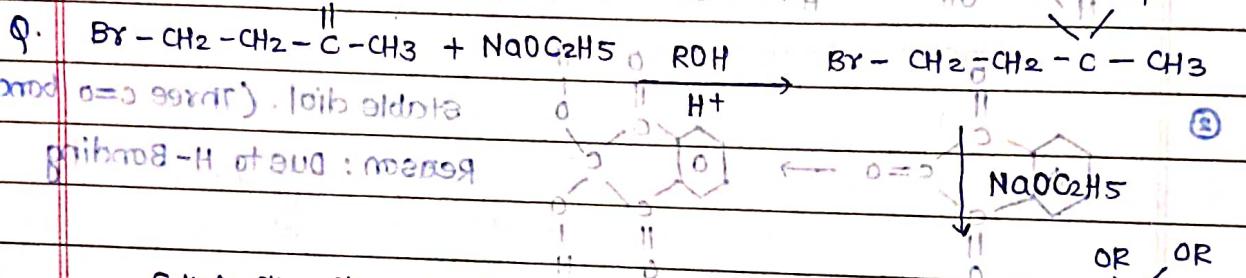


- Note : Acetal and ketel further convert in $\text{C}=\text{O}$ group in

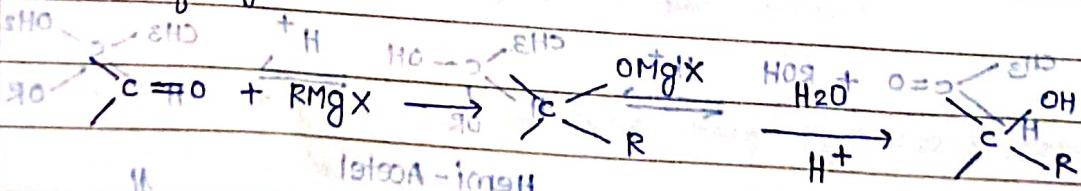
presence of acidic hydrolysis: मुद्रितपा टी ; शोला

(protect group kaha jata hain Alcohol + kondu to formation of Acetal and Ketel.)

Protecting order is $\text{CH}_2\text{SH} > \text{CH}_2\text{OH} > \text{CH}_3\text{OH}$.



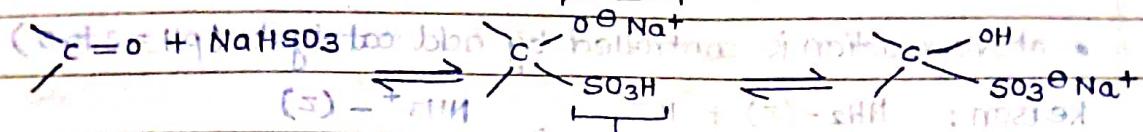
- ## • Addition of RMgX :



- ### • Addition of NaHSO_3 :

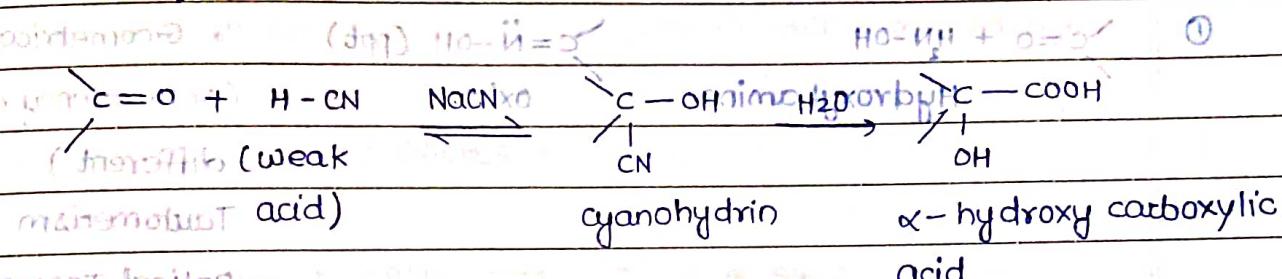
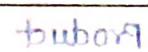
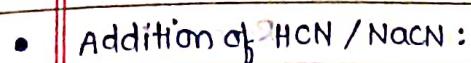


Basic condition

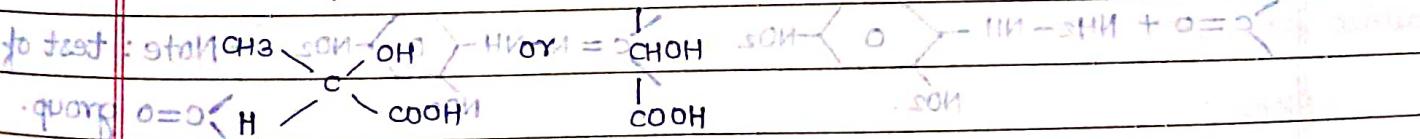
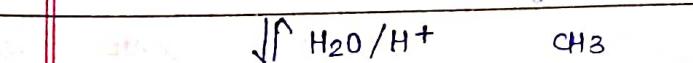
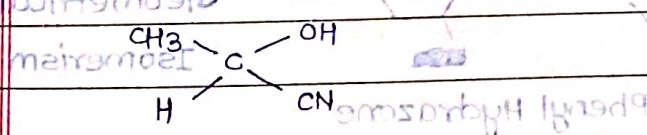
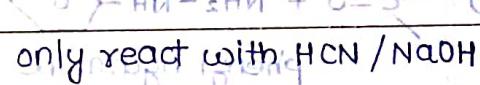
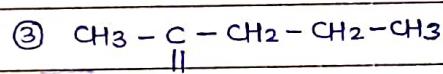
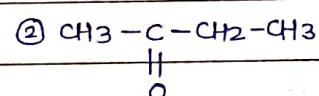
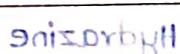


- Note : only methyl ketone. Acidic condition
Reaction with NaHSO_3 , other

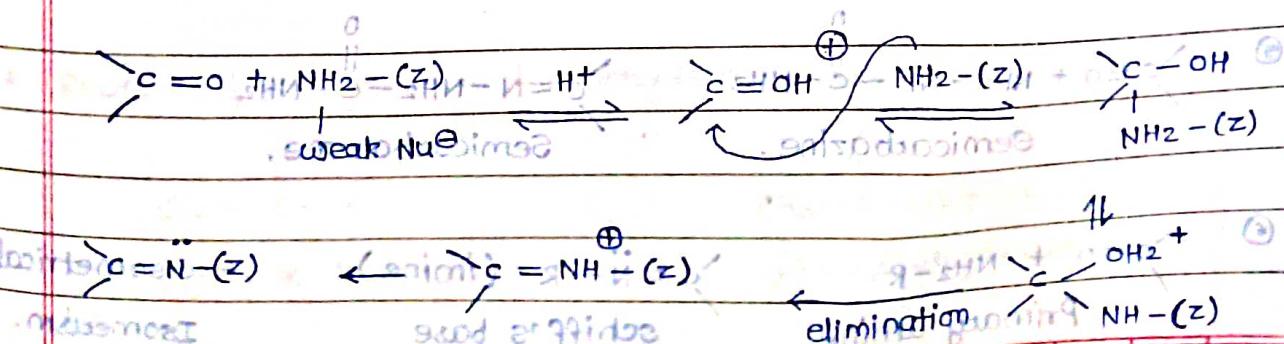
Bulky ketone do not react.



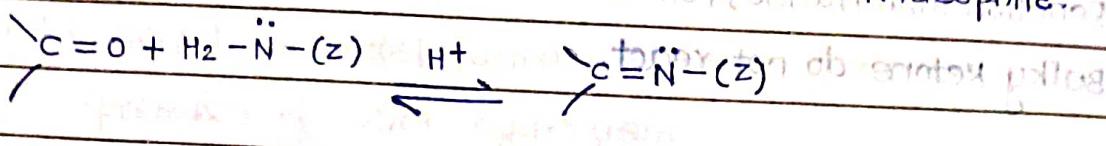
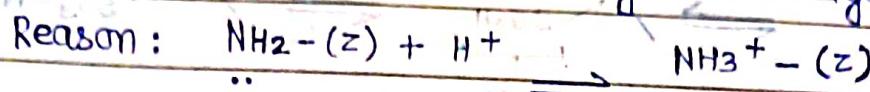
- Note : $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$



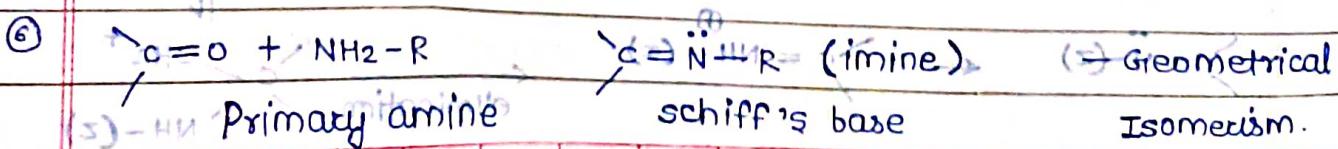
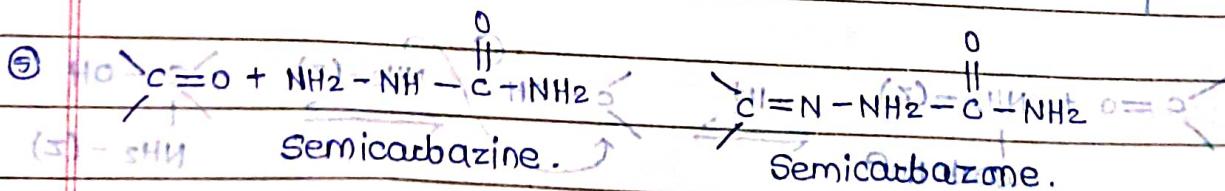
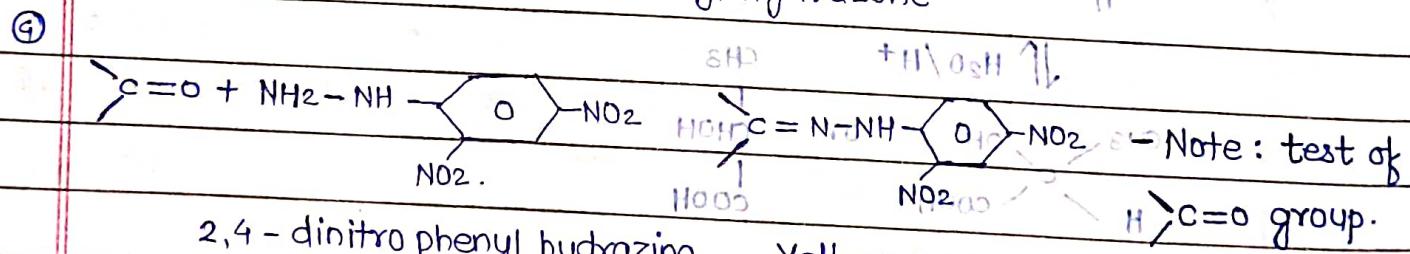
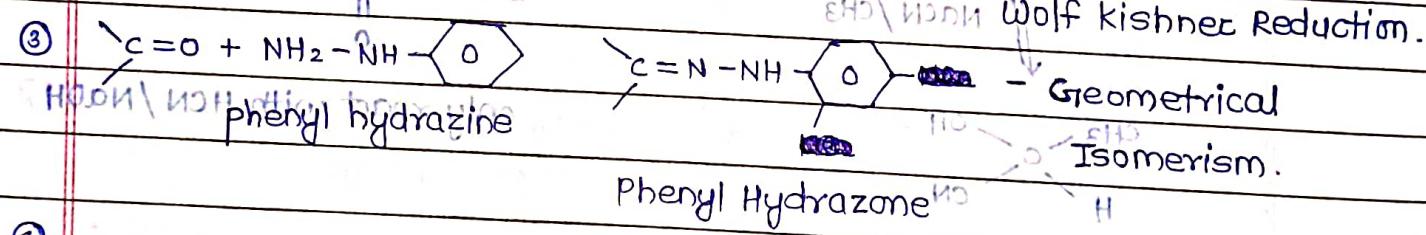
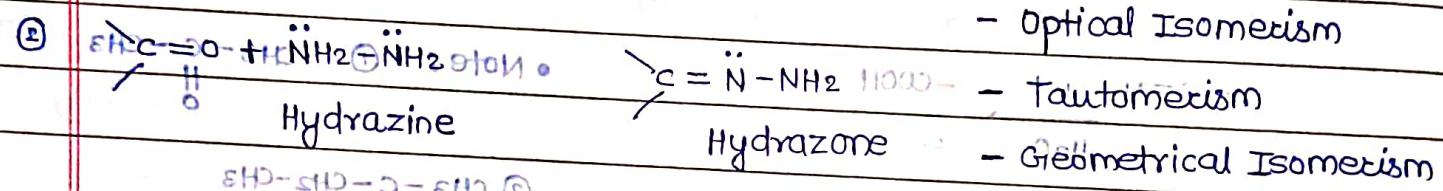
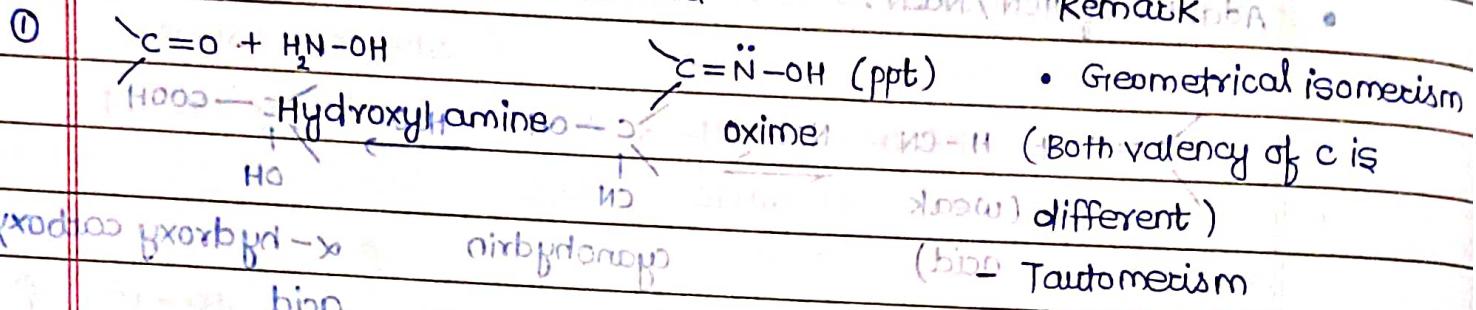
- Nucleophilic Addition-Elimination Reaction : (9th - A.S.)

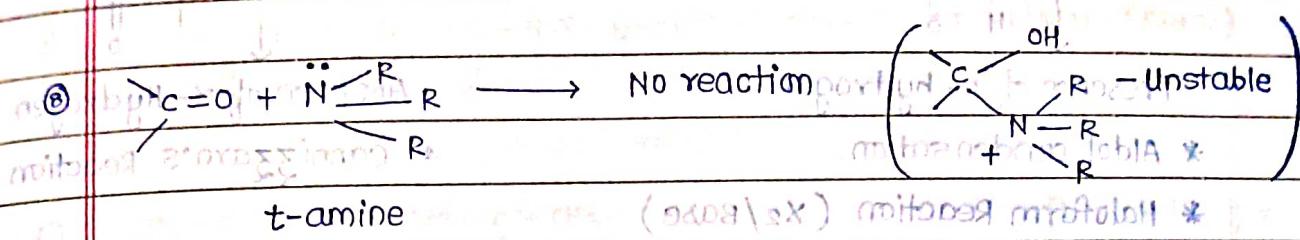
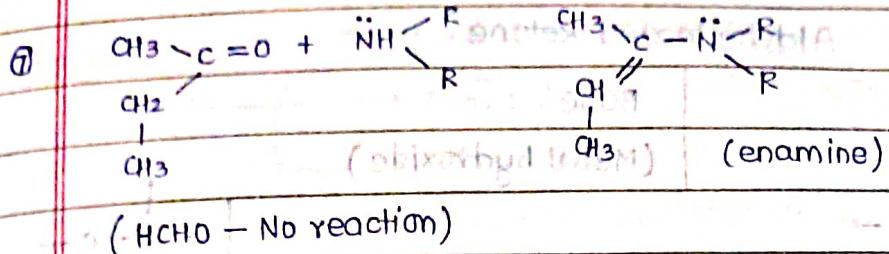


- above reaction is controlled by acid catalyst (pH = 3 to 5)

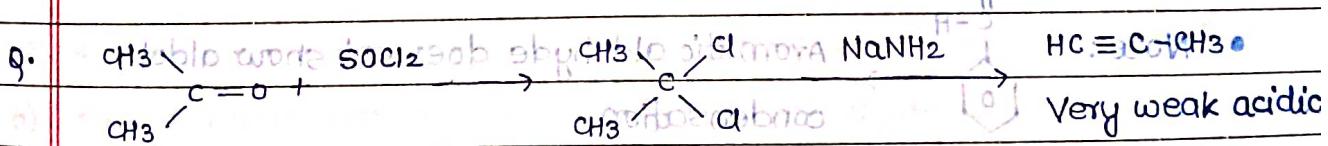
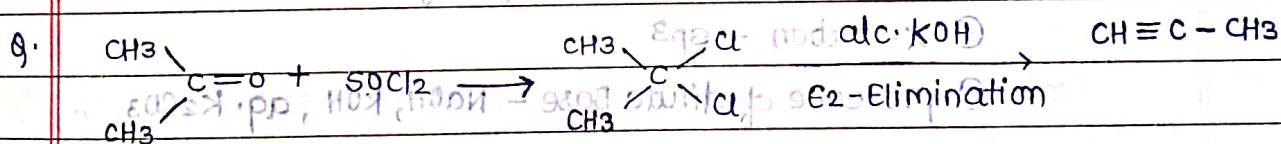
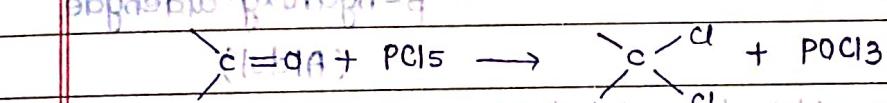
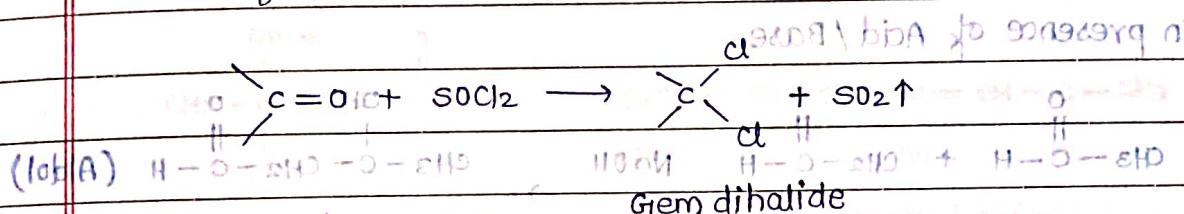


Reagent Product Remark





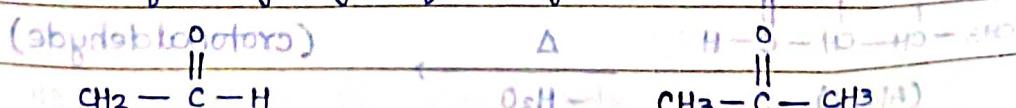
• Addition of PCl_5 and SOCl_2 :



• Note: KOH — push the reaction in Backward Rxn

NaNH₂ — push the reaction in Forward Rxn.

• Reaction of α -hydrogen of aldehyde and ketone:



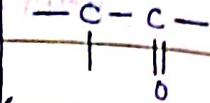
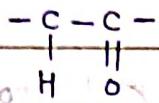
$\text{H} — \alpha\text{-Hydrogen}$ $\text{H} — \alpha\text{-Hydrogen}$.

Condensation

Aldehyde and ketone

Base

(Metal hydroxide)



Presence of α -hydrogen

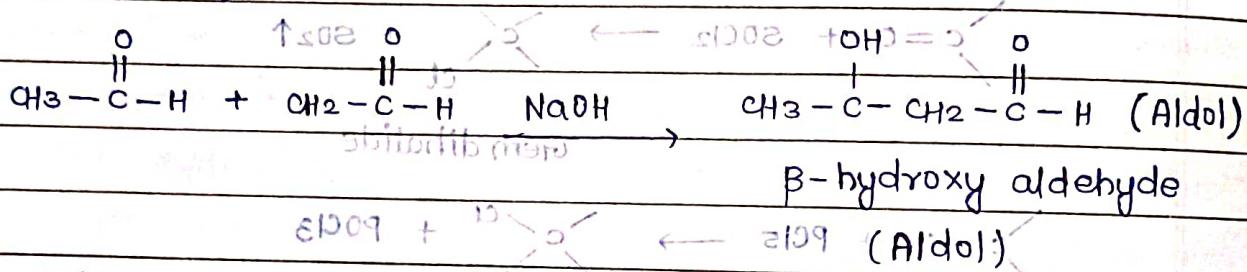
* Aldol condensation.

* Haloform Reaction (X_2/base)

Absence of α -Hydrogen

* Cannizzaro's Reaction

- ① Aldol condensation: two molecules of aldehyde / ketone dimerization occurs in presence of Acid / Base.

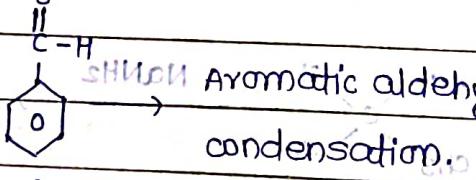


- condition : ① only aldehyde and ketone.
② having at least 1 α -hydrogen.

③ α -carbon $\rightarrow \text{sp}^3$

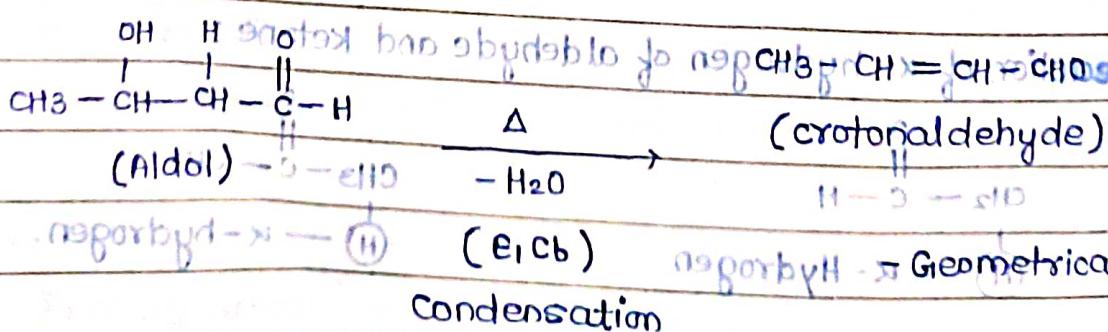
④ presence of dilute base $\leftarrow \text{NaOH}, \text{KOH}, \text{aq. K}_2\text{CO}_3$

• Note: $\text{HC}\equiv\text{C}-\text{CH}_3$



$\text{CH}_3-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{H} \xrightarrow{\text{NaOH}} \text{CH}_3-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{H} \rightarrow \text{X}$ Due to absence of α -hydrogen

- Mech: of aldol condensation :

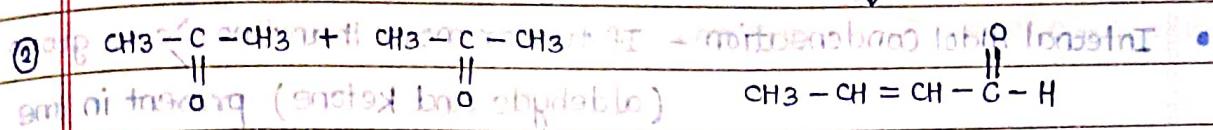
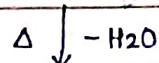
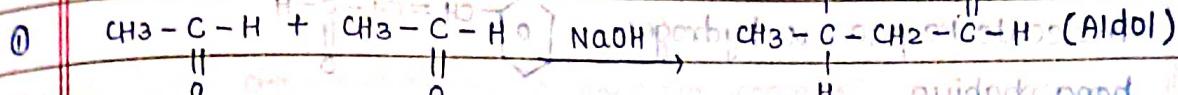


Geometrical Isomerism

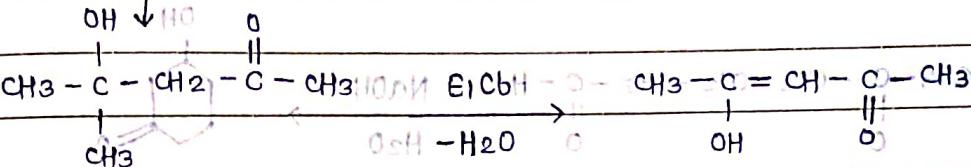
- Condensation - Removal of atom/molecules in presence of Reagent / Δ .

EICb \rightarrow Poor L.G.

NaOH \rightarrow Strong Base



NaOH (crotonaldehyde)



β -Hydroxy-Ketone (Mesityl oxide)

- Note : Aldehyde gives easily aldol condensation reaction in compare to ketone due to less bulkiness.

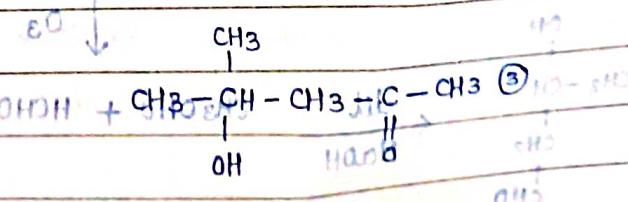
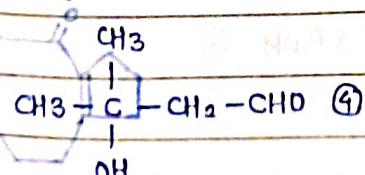
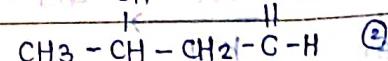
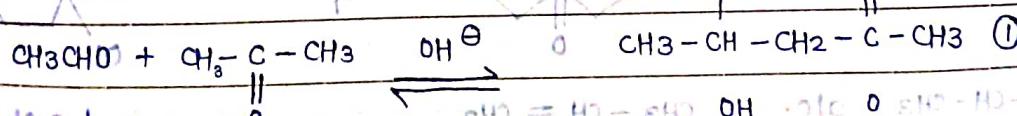
② Gross aldol condensation (claisen schmidt condensation)

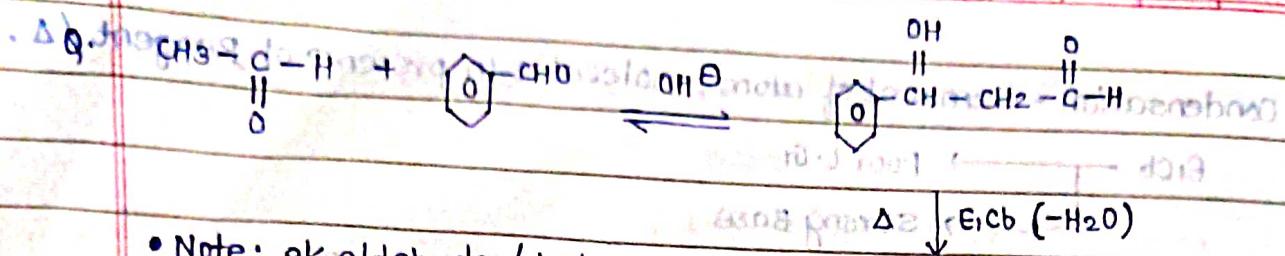
a) two different aldehyd'e.

Note : Form mixture of β -hydroxy aldehyde and ketone.

b) two different ketone

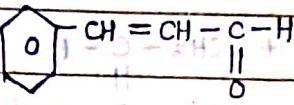
c) one aldehyde and one ketone



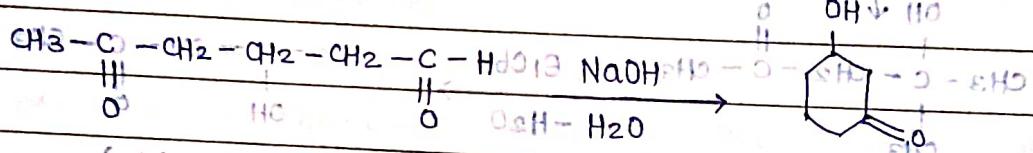


- Note: ek aldehyde / ketone

molecule ke paas α -hydrogen hona chahiye.



- Internal Aldol Condensation - If two or more than two C=O group (aldehyde and ketone) present in one molecule.



(abixa (lycine))

- stability order :

ring

ring

ring

ring

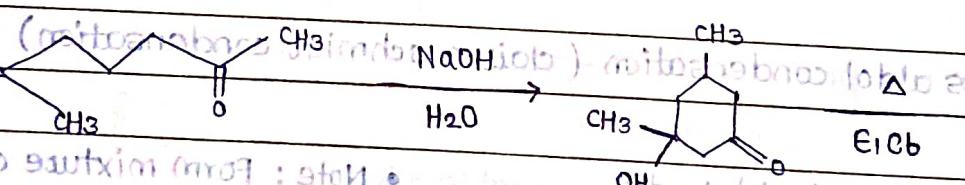
CH₃

CH₃

CH₃

CH₃

Q.



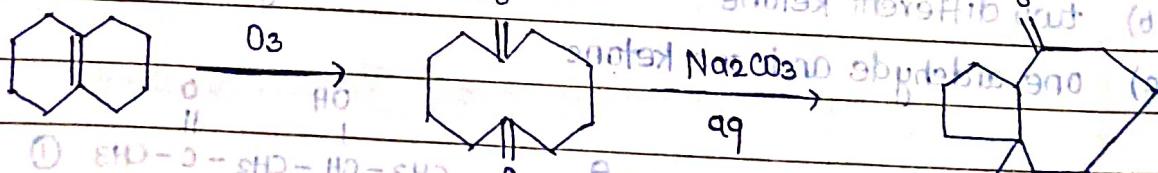
CH₃

CH₃

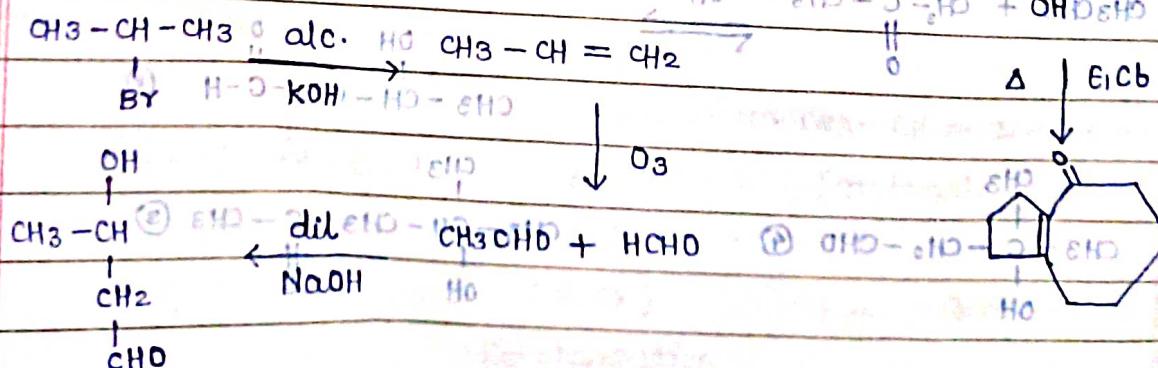
CH₃

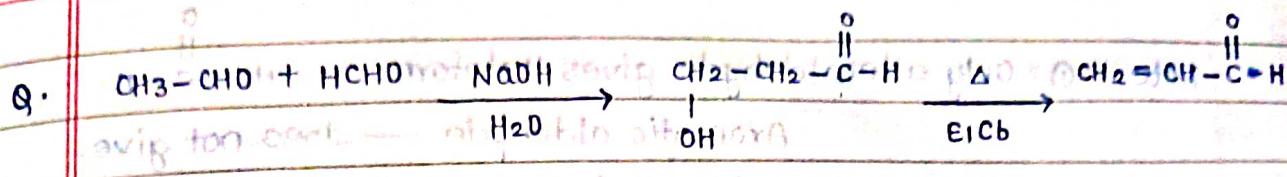
CH₃

Q.

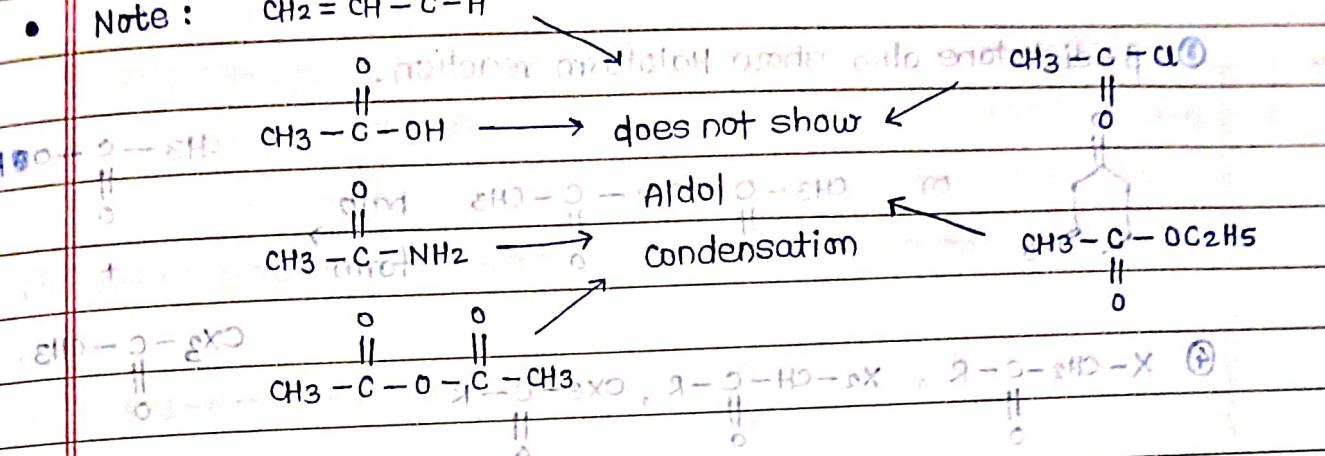


Q.



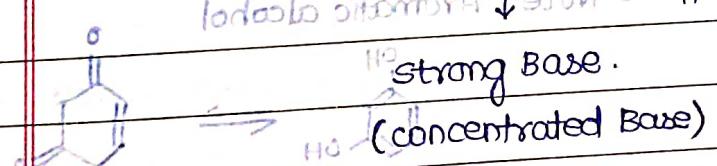
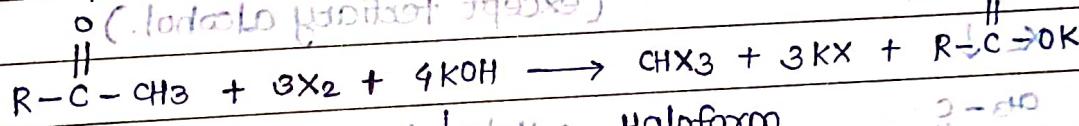


Note : $\text{CH}_2=\text{CH}-\text{C}(=\text{O})-\text{H}$



Haloform Reaction : (V) (V) (V)

- Example of α -hydrogen of Aldehyde and Ketone : $\text{CH}_3\text{-CHO}$ (V)



- ① CHCl_3 - chloroform (gas)
- ② CHBr_3 - Bromoform (liquid)
- ③ CHI_3 - Iodoform (yellow crystalline solid)

- only those aldehyde and

Ketones show haloform rxn (iodoform test colourless)

which have $\text{CH}_3-\text{C}(=\text{O})-$ group (Acetyl test colourless)

group

(-H₂O-EtOH) good solvents for haloform test $\text{H}_2\text{O} \rightarrow$ Iodoform (V)

total no. of mole of base used in haloform rxn = 4 mole.

X₂ used in rxn \rightarrow 3 mole/litre for acet - Iodoform (V)

Reagents - ① $\text{X}_2/\text{KOH} \rightarrow \text{X}_2 + \text{OH}^- \rightarrow \text{X}^\ominus + \text{XO}_3^\ominus$

② $\text{NaOX}/\text{Cl}_2 + \text{NaOH} \rightarrow \text{NaCl} + \text{NaOCl} + \text{H}_2\text{O}$ (V)

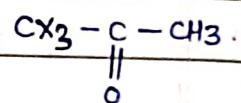
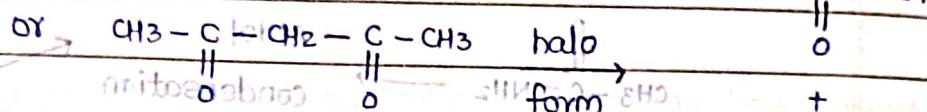
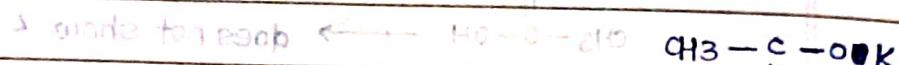
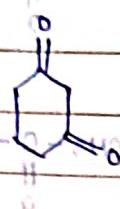
③ $\text{KI}/\text{KIO}_3 \rightarrow \text{X}^\ominus$ (V)

H • Note: ① Only acetaldehyde gives Haloform. $\text{CH}_3-\text{C}-\text{H}$

Aromatic aldehyde — does not give.

② All methyl ketone gives Haloform reaction. $\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}$

③ β -di ketone also show Haloform reaction.



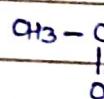
④ $\text{X}-\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}$, $\text{X}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{C}-\text{R}$, $\text{CX}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}$

(v)

(v)

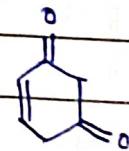
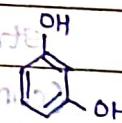
(v) : mild strong mataloff

⑤ $\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{OH}$ (2° alcohol) gives haloform reaction. (except tertiary alcohol.)



mataloff

• Note: Aromatic alcohol



(also) mataloff - ① $\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{OH}$

(biwpil) mataloff - ② $\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{OH}$

Resacetophenone -

③ 1' alcohol — only ethyl alcohol gives haloform reaction. (also it is a test for ethyl alcohol)

(quip)

⑦ 2' alcohol — all secondary alcohol which have $\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-$ condition.

• Note: = rxn mataloff in base of base of oxo for oxo H₂O

⑧ 1' alcohol - does not show haloform reaction in base sX

$\text{XO} + \text{RX} \longrightarrow \text{HO} + \text{R}_2\text{X}$ $\xleftarrow{\text{H}_2\text{O}/\text{HCl}}$ ① $\text{R}_2\text{X} \rightarrow \text{R}_2\text{C}-\text{O}-\text{X}$

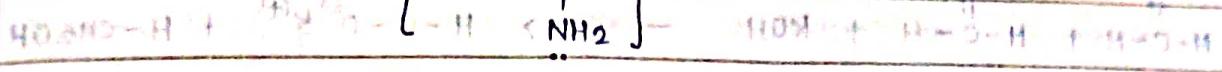
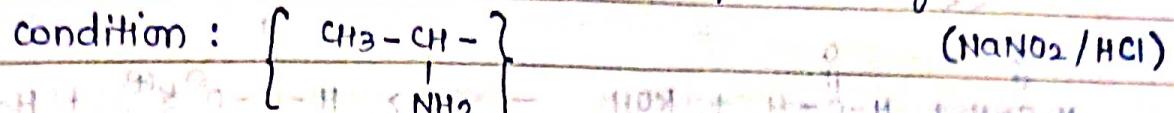
⑨ $\text{H}_2\text{O} + \text{R}_2\text{C}-\text{O}-\text{X} \xrightarrow{\text{KOH/KHCO}_3} \text{R}_2\text{C}-\text{O}-\text{H} + \text{H}_2\text{O} + \text{CO}_2$ ② $\text{R}_2\text{C}-\text{O}-\text{H} \rightarrow \text{R}_2\text{C}-\text{OH}$

(v)

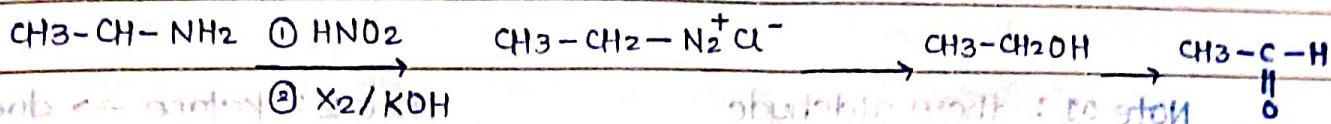
(v)

(v)

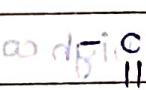
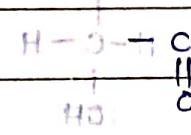
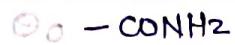
⑩ Amine: Amine shows haloform reaction in presence of HNO_2 and NaNO_2/HCl



(+) or (-) isomers of $\text{CH}_3-\text{CH}_2-\text{NH}_2$ gives same product (A)

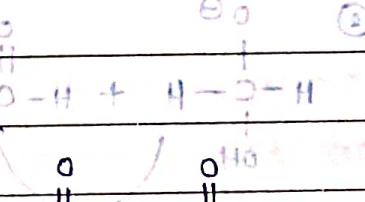
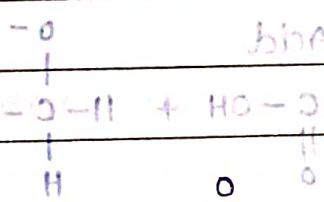


⑪ Note : (-ve haloform test)



-ve haloform test

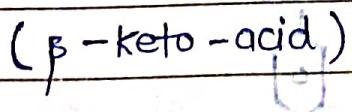
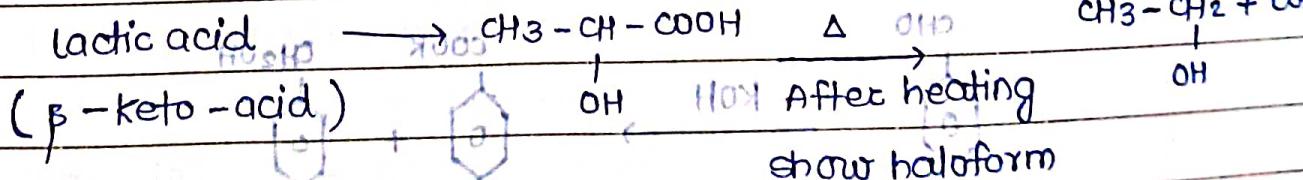
- good leaving group



Note : $\text{CH}_3-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{OR} \xrightarrow[2]{\text{X}_2} \text{CH}_3-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{R} + \text{ROH}$

(exception : ethyl ester only gives haloform test)

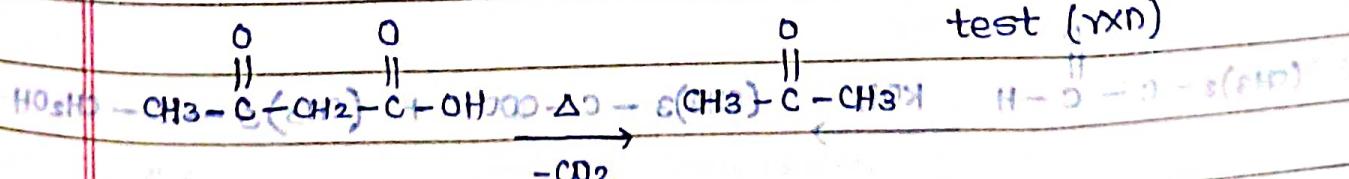
Note :



After heating

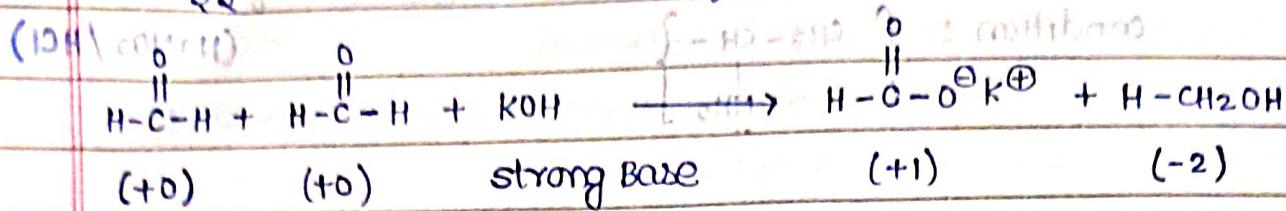
show haloform

test (rxn)



Nahit dega but after heating dega Haloform Rxn (Iodoform test)

Cannizzaro's Reaction (absence of α -hydrogen) ⑩



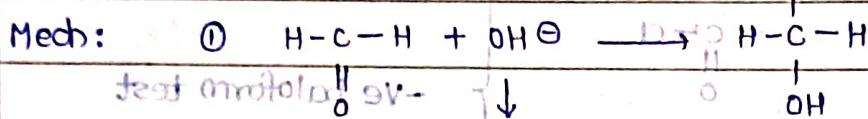
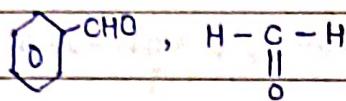
Note 01: these aldehyde

gives Cannizzaro's rxn - absence
of α -hydrogen ho.

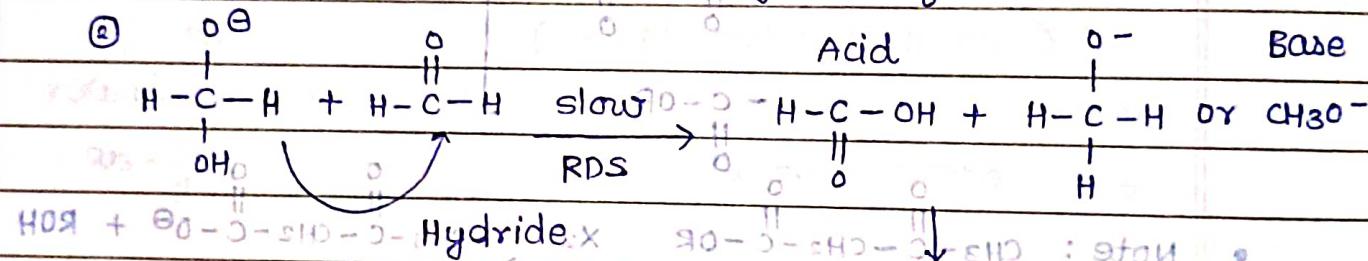
Note 2: ketone \rightarrow does not

show Cannizzaro's Rxn.

Note: (-ve potential step) ⑪

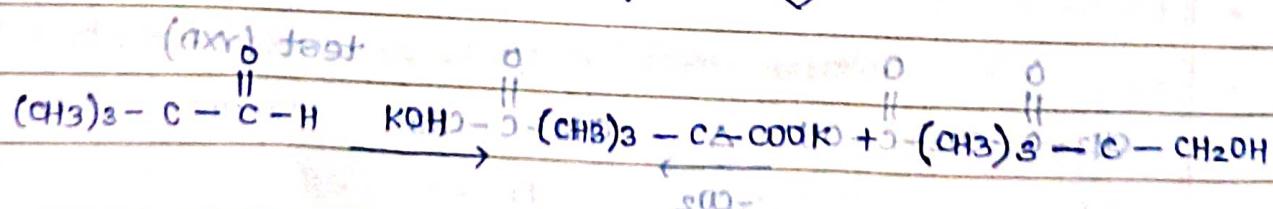
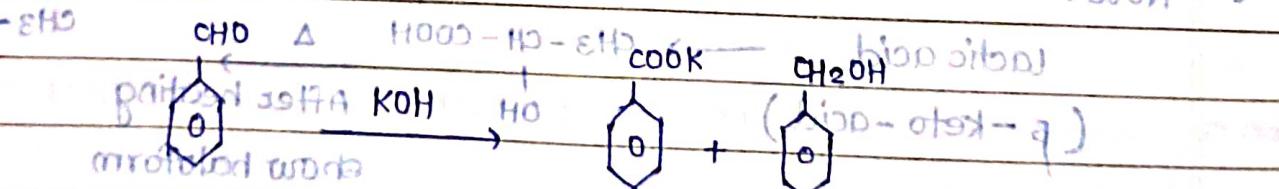


\downarrow $\text{-}\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}^-$ - good leaving group - (Nu^-) = 1 mole high conc. of Base.

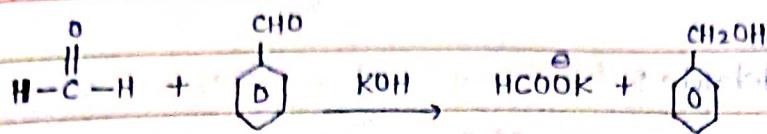


1) Redox reaction. transfer step 2) Disproportionation reaction (also see above) (except for CH_3O^-)

3) Oxidation no. change $\left[\begin{matrix} \text{O} \rightarrow +1 \\ \text{O} \rightarrow -2 \end{matrix} \right]$



Cross Cannizzaro's Reaction: (Using two different aldehydes)
(test enrofloxacin)

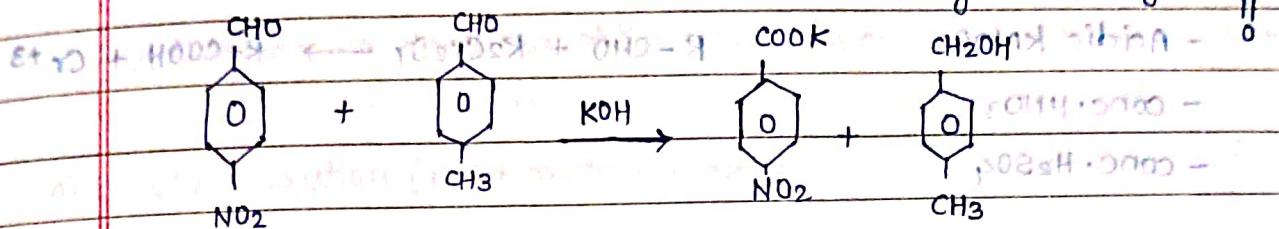


Note-01: Jis pr OH attack hoga
which acid mein convert hoga.

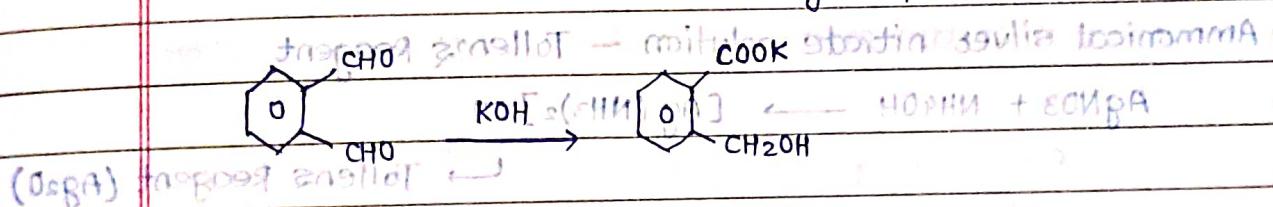
Note-02: OH will attack on (D)

① less hindrance side.

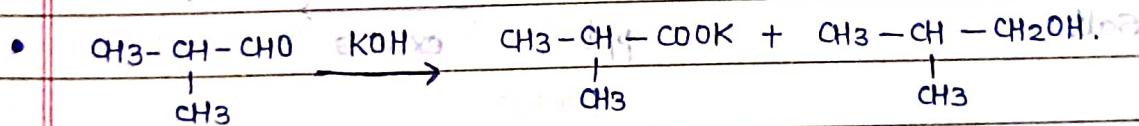
② High +ve charge in c= carbonyl group.



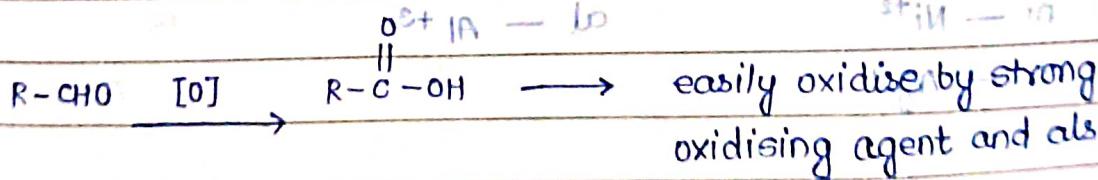
- Internal Cannizzaro's Reaction: If two aldehydes or more than two aldehydes present in one molecule.



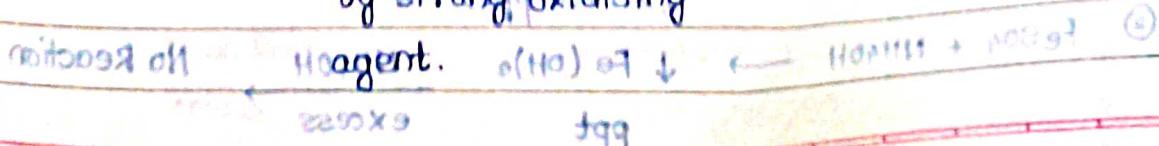
Note: 1) $\text{CH}_3\text{C}(=\text{O})_2\text{H}$ in ph3C(=O)H does not show Cannizzaro's reaction due to good L.G nature of $\text{C}^{\ominus}\text{X}_3$ and $\text{C}^{\ominus}\text{Ph}_3$.



- Oxidation of Aldehyde and ketone:

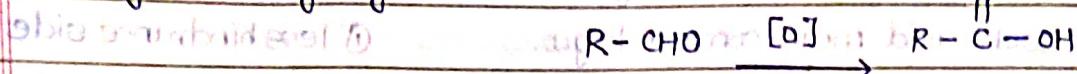


$\text{R}-\overset{\text{O}^{\oplus}}{\underset{\parallel}{\text{C}}}-\text{OH}$ hardly does not oxidise, only oxidise by strong oxidising agent.

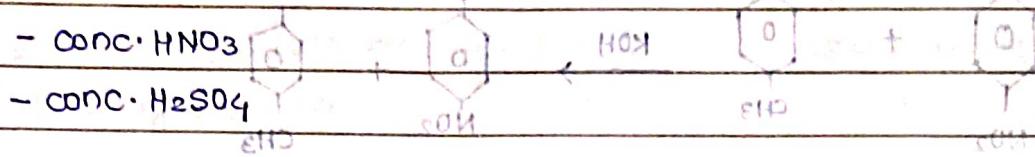
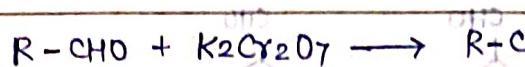
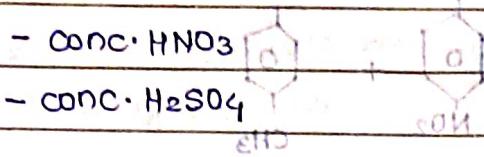
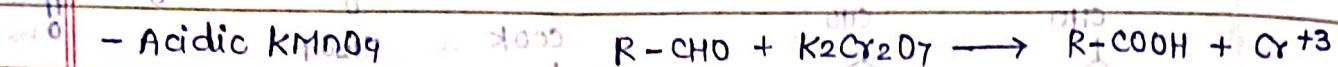


• Oxidation of Aldehyde:

a) Strong oxidising agent:



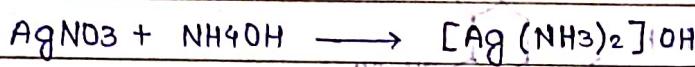
Acidic - $\text{K}_2\text{Cr}_2\text{O}_7$



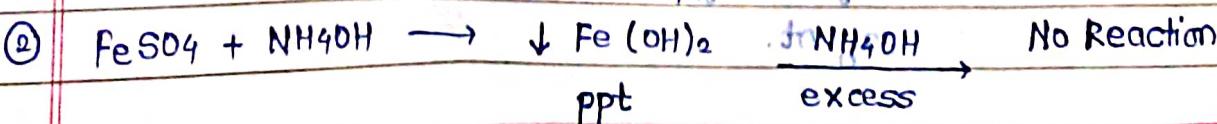
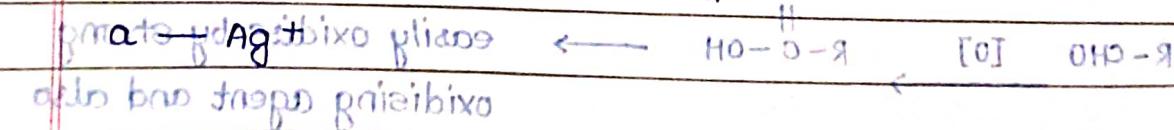
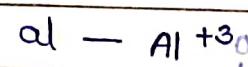
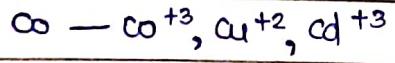
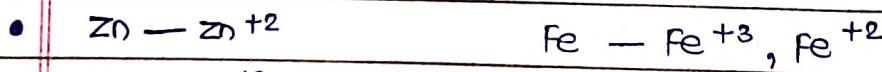
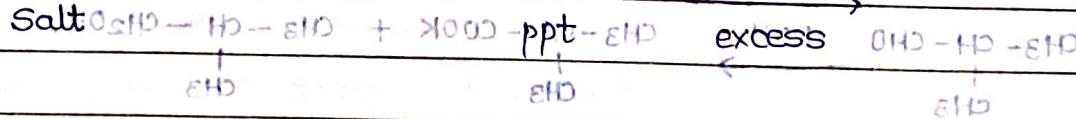
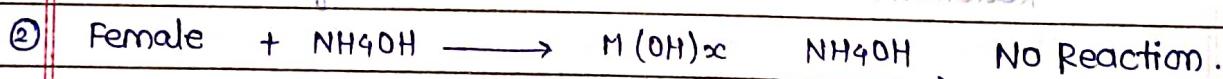
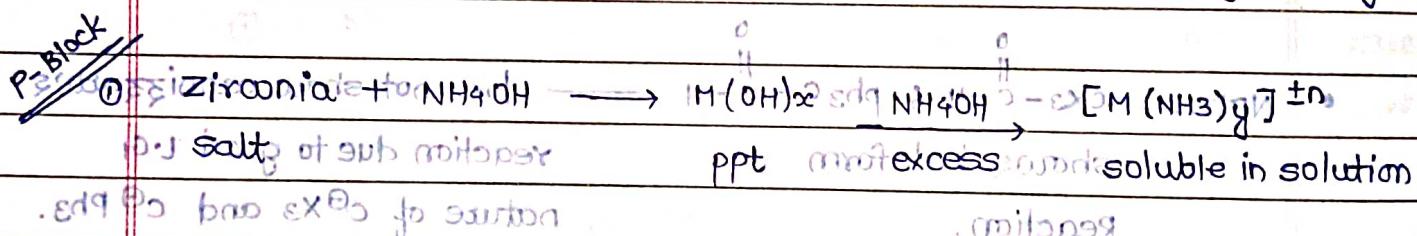
b) Tollen's Reagent (mild oxidising agent)

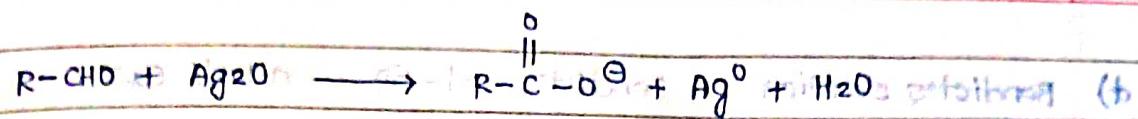
silver nitrate in aqueous solution

Ammonical silver nitrate solution - Tollen's Reagent



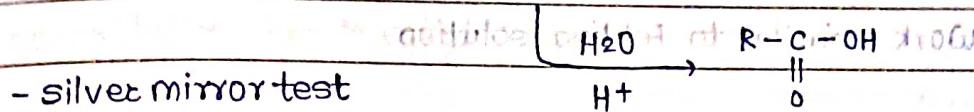
\hookrightarrow Tollen's Reagent (Ag_2O)





silver nitrate Tollen's — (+) Acid salt (mirror)

Reagent salt



- silver mirror test

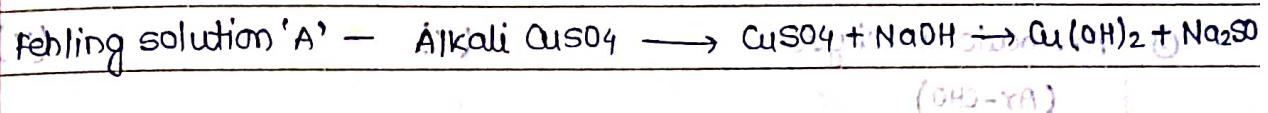
H^+

ketone — does not show silver mirror test (Tollen's Reagent)

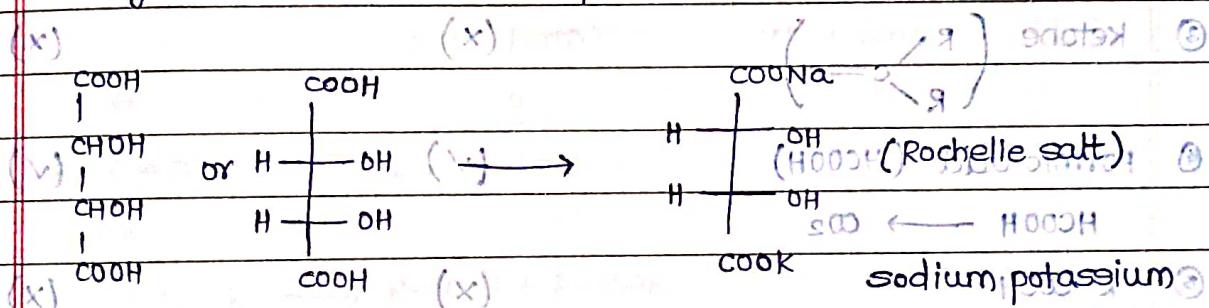
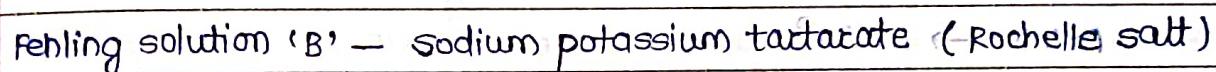
(v) acidic reagent (v)

absorbable solvents (1)

c) Fehling solution (mild oxidising agent)



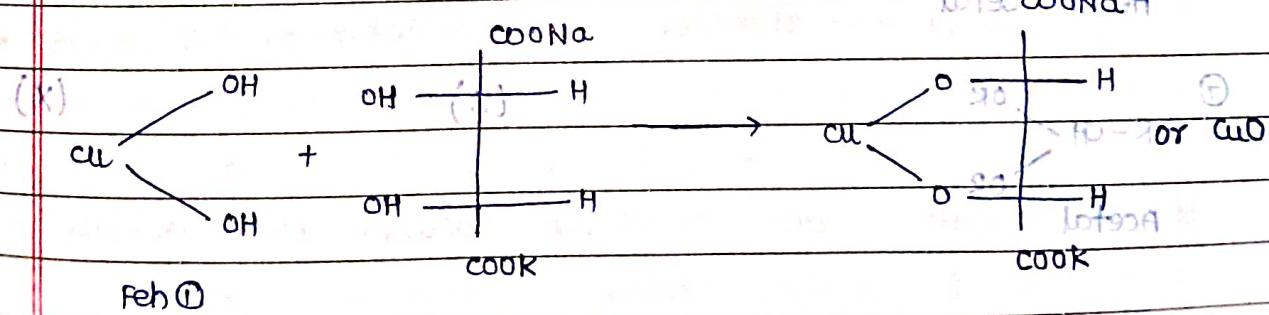
(CH₂-OH)



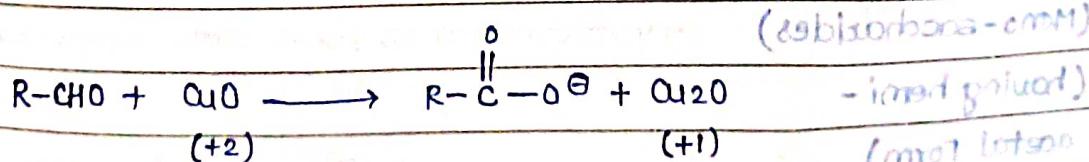
Tartaric acid

tartarate
 H_2O

equal amount — Feh (1) + Feh (2)



(v) Feh (2) Deep-Blue Solution



Deep Blue colour

Reddish Brown colour.

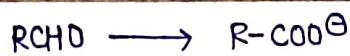
d) Benedict's solution $\xrightarrow{\text{heat}}$ Benedict's sol - ① — alkali ausoq
 (remain) Benedict's sol - ② — sodium potassium citrate

Work + similar to Fehling solution

(tollen's reagent) Molecules reomim sovia w Tollen's Reagent \rightarrow Fehling Solution

① Aliphatic aldehyde (v) (v)

(R-CHO) (togo baizibixa blim) molecules gaiket (v)



② Aromatic aldehyde (v) \leftarrow (v) — 'A' molecules gaiket (x)
 (Ar-CHO)

(tolls ARCHO) \rightarrow ArCOO $^\ominus$ but majeentoq mwiboa \leftarrow 'A' molecules gaiket

③ Ketone (R-C(=O)R) (x) (x)

④ Formic acid (HCOOH) (v) (v)



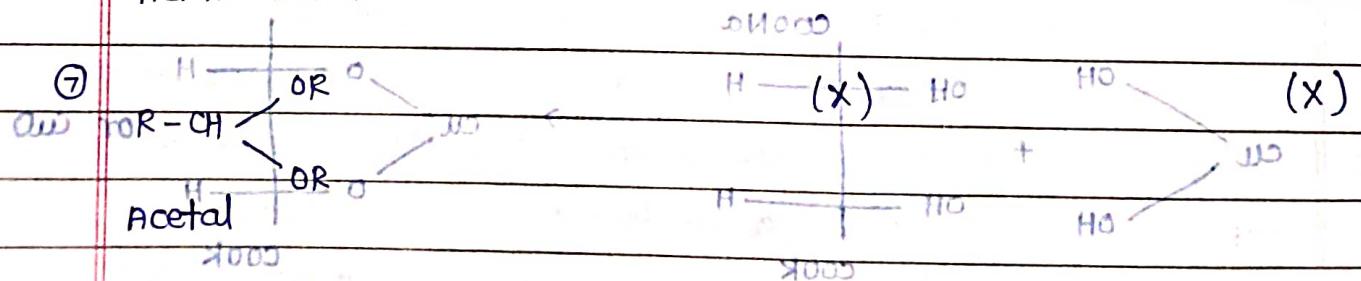
⑤ $\text{R}-\text{COOH}$ molecules (x) (x)

esters

formic acid

⑥ R-CH $\begin{cases} \longrightarrow \text{RCOOH} \\ \text{OR} \end{cases}$ (v) (v)

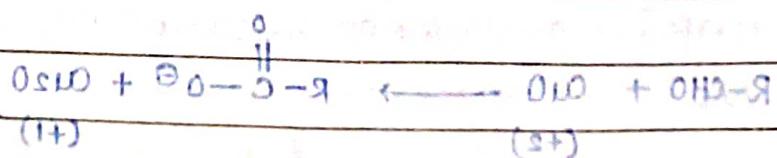
Hemi-acetal



⑧ Carbohydrates (v) (v)

(Mono-saccharides)

(having hemi-acetal form) (+) (+)



- Oxidation of Ketones:

- Ketone does not oxidise easily by mild oxidising agents + ketone → no oxidation due to alkyl group.

- Ketone only oxidises by strong oxidising agent.

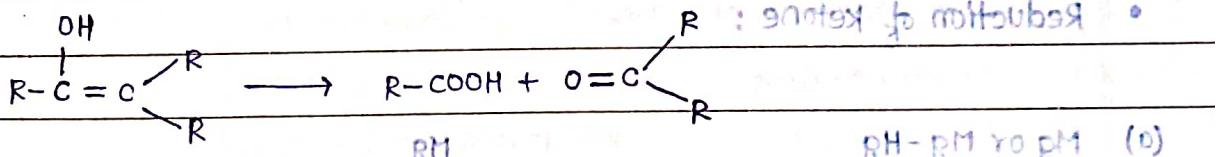
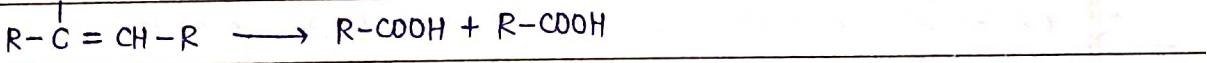
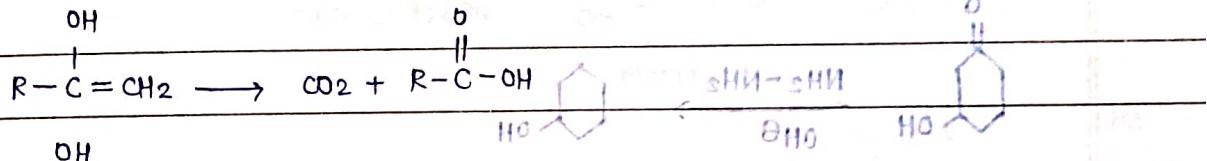
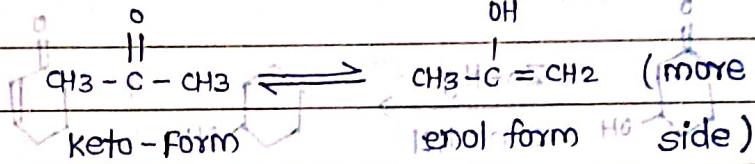
① Acidic KMnO₄

② Acidic K₂Cr₂O₇

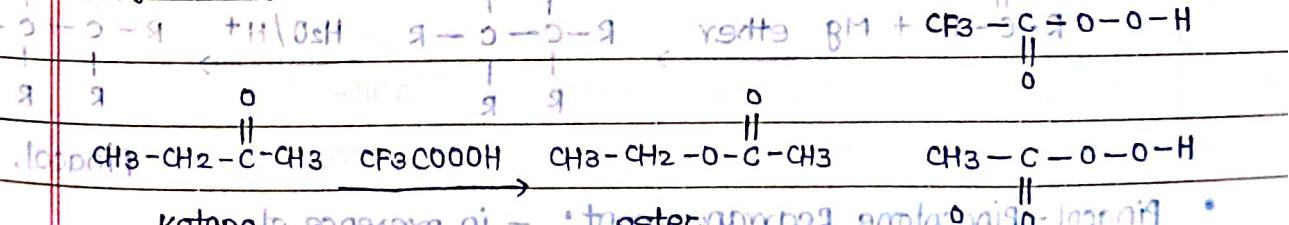
③ Conc. HNO₃.

④ Conc. H₂SO₄.

• Popoff's Rule:



• Baeyer Villiger Oxidation → peroxide — H₂SOf



• bis(oxo acid)

• who : oxygen atom insertion more hindrance in ester side.

• pH : only ketone oxidised

• No Aldehyde oxidation except: H-C=H CF₃COOOH → H-C-OH.

Reduction of Aldehyde and Ketone :

C=O (carbonyl group) \rightarrow CH_2 (Methylene group)

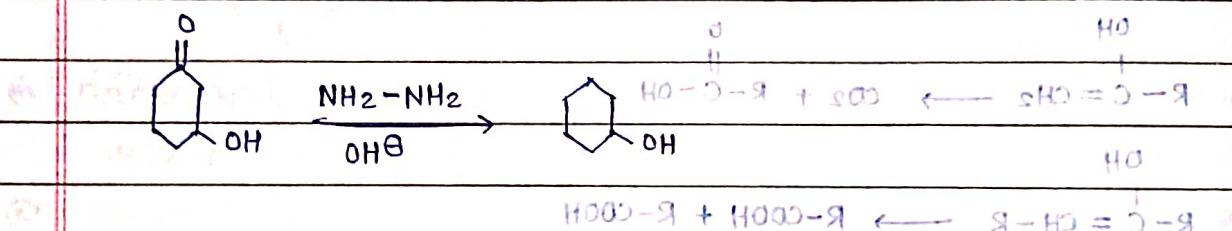
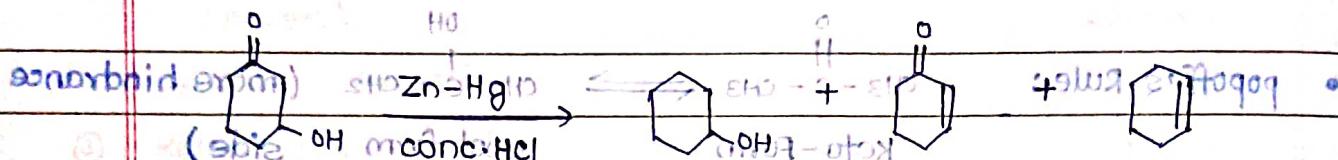
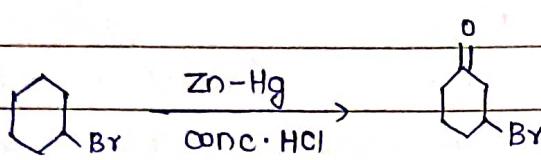
① $\text{H}_2 / \text{Red P} - 150^\circ\text{C}$

② Zn/Hg - conc. HCl — Clemmensen Reduction

③ $\text{NH}_2-\text{NH}_2 / \text{OH}^-$ — Wolf's Kishner Reduction

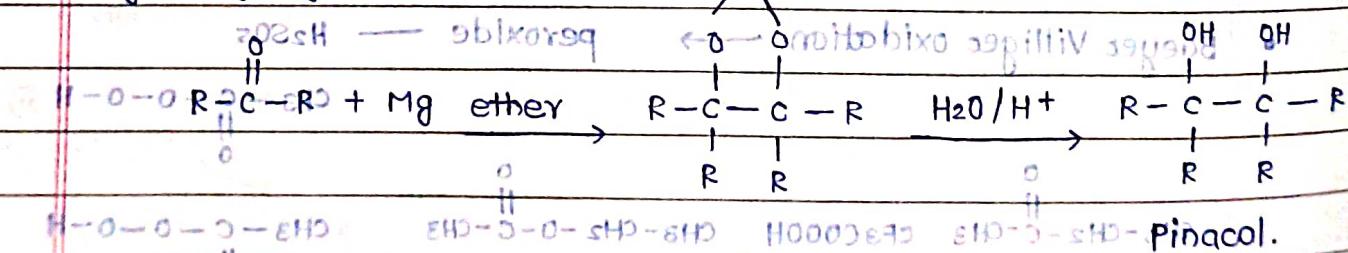
Note:
 o-atom
 Alcohol
 Ether

x
 Good LG

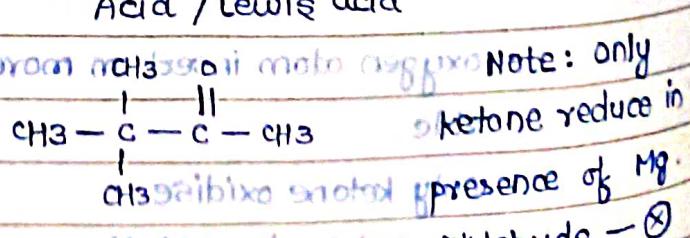
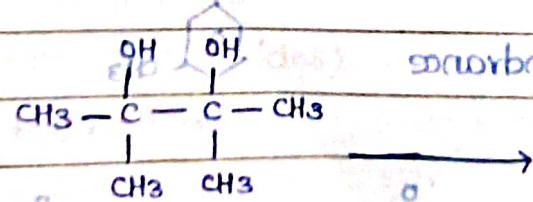


Reduction of ketone :

(a) Mg or Mg-Hg

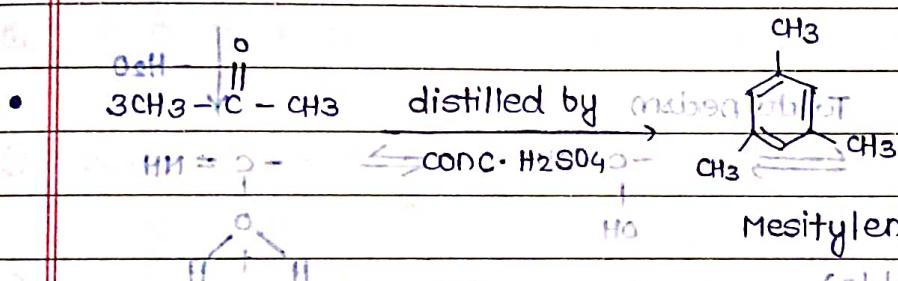
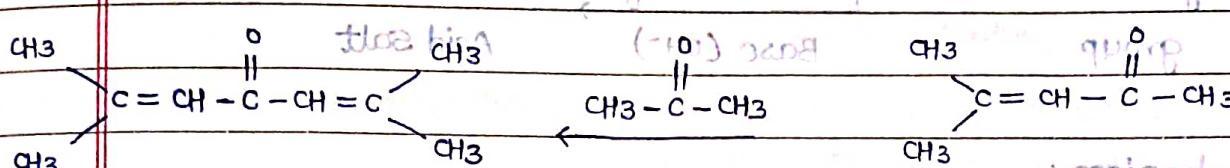
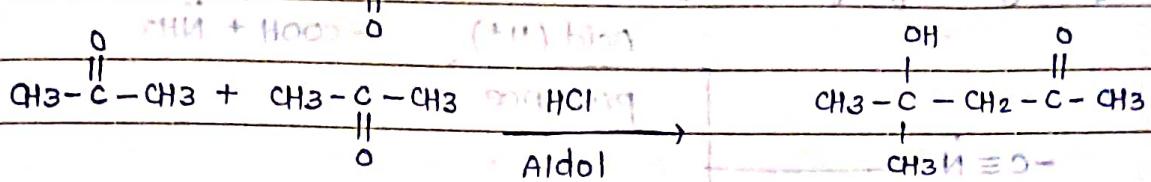


Pinacol $\xrightarrow{\text{ketone reduction}}$ Pinacolone Rearrangement : — in presence of Acid / Lewis acid

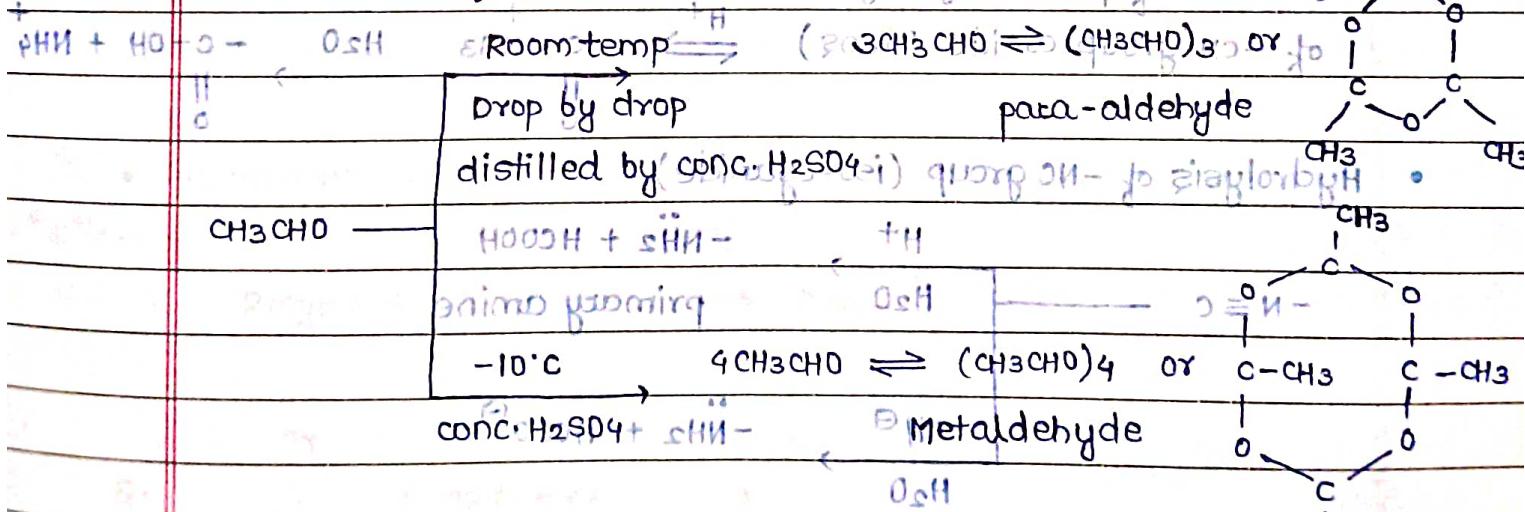


- Condensation: ~~removing data from cloud~~ ~~reducing dimensions in bottom~~

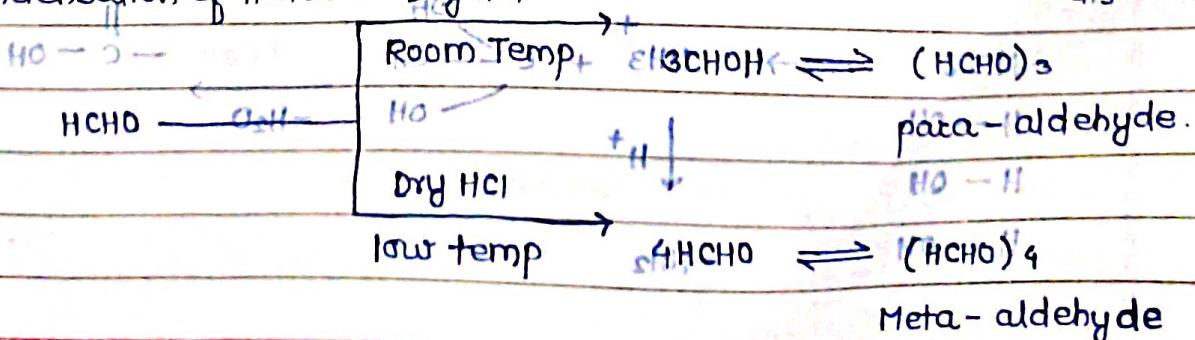
- Condensation of $\text{CH}_3 - \underset{\text{H}}{\text{C}} - \text{CH}_3$ (Acetone) using ZnCl_2 as catalyst. ①



- condensation of CH_3CHO .



- condensation of HCHO: Dry HCl

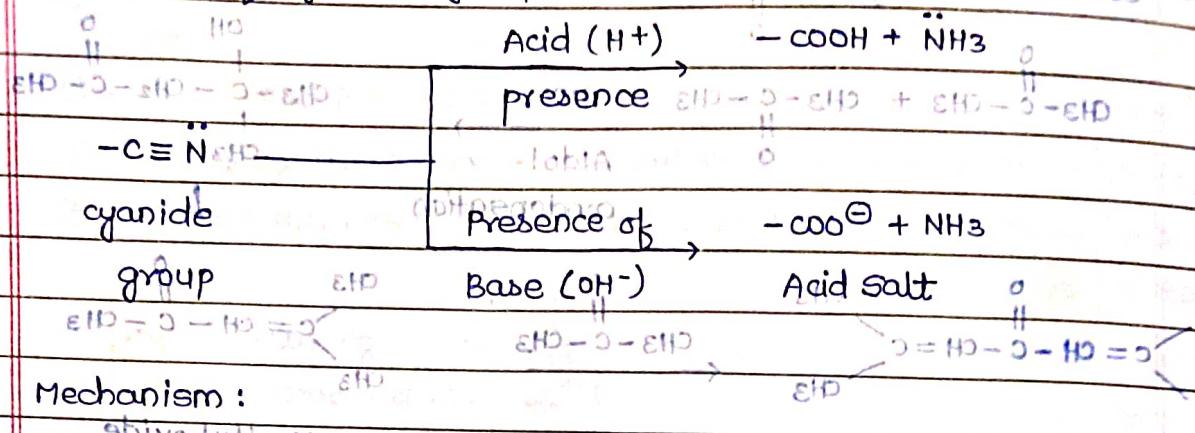


Carboxylic acid

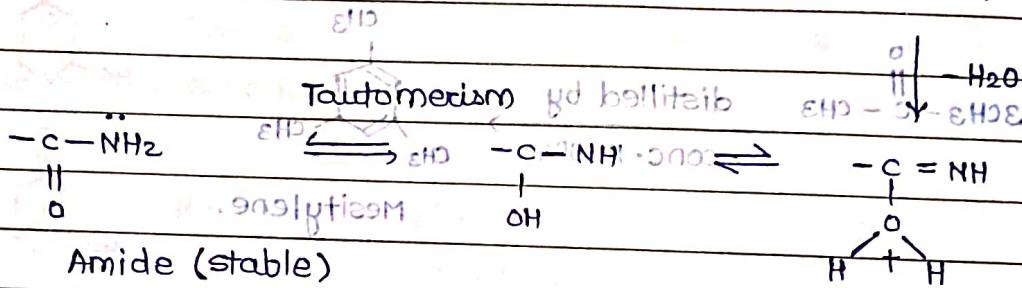
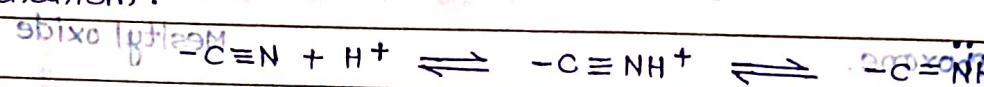
Page No.	
Date	

- Method of Preparation:

- Hydrolysis of cyanide group



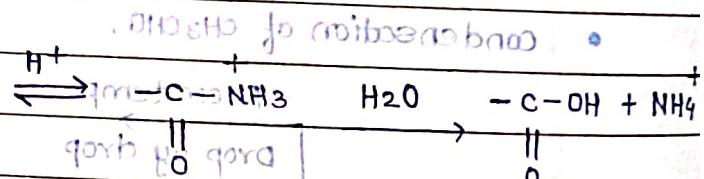
- Mechanism:



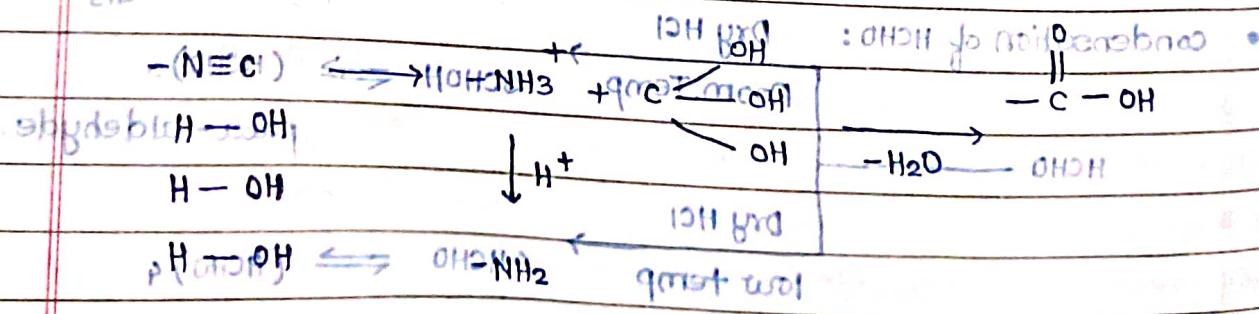
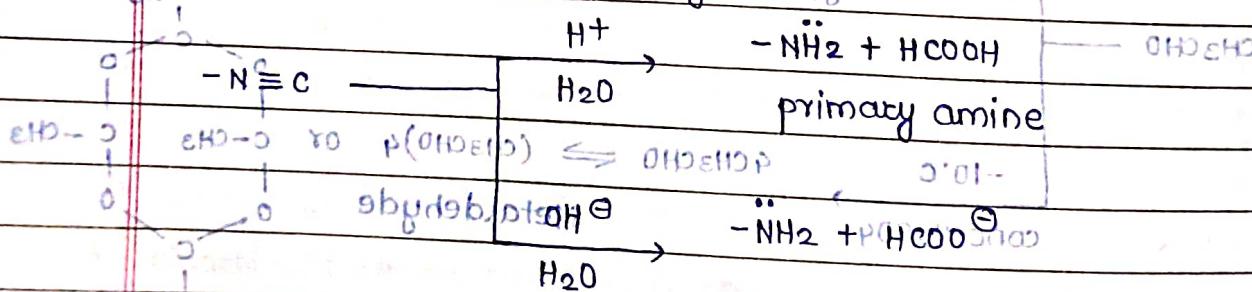
(in case of partial hydrolysis

of RCN group amide forms)

but -CN group

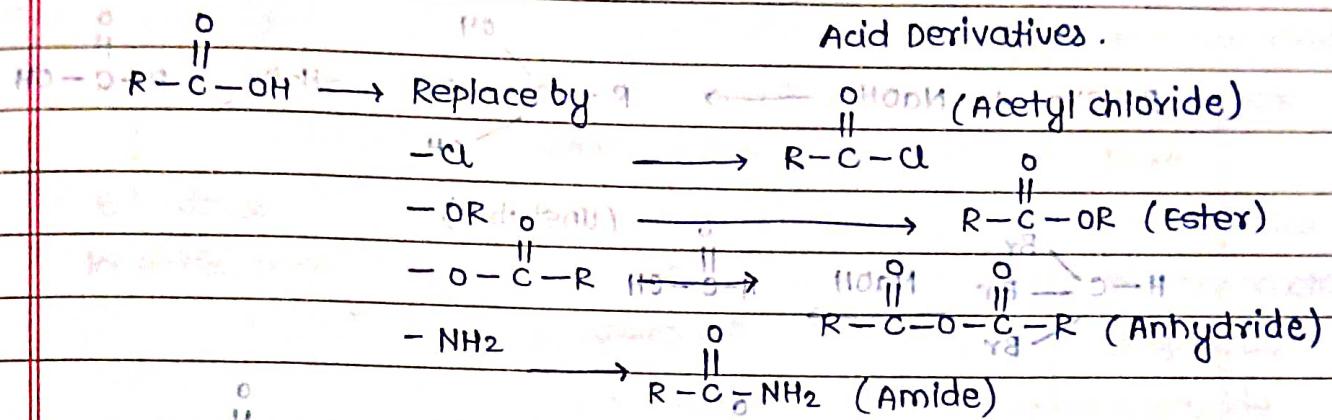


- Hydrolysis of $-\text{NC}$ group (iso-cyanide)

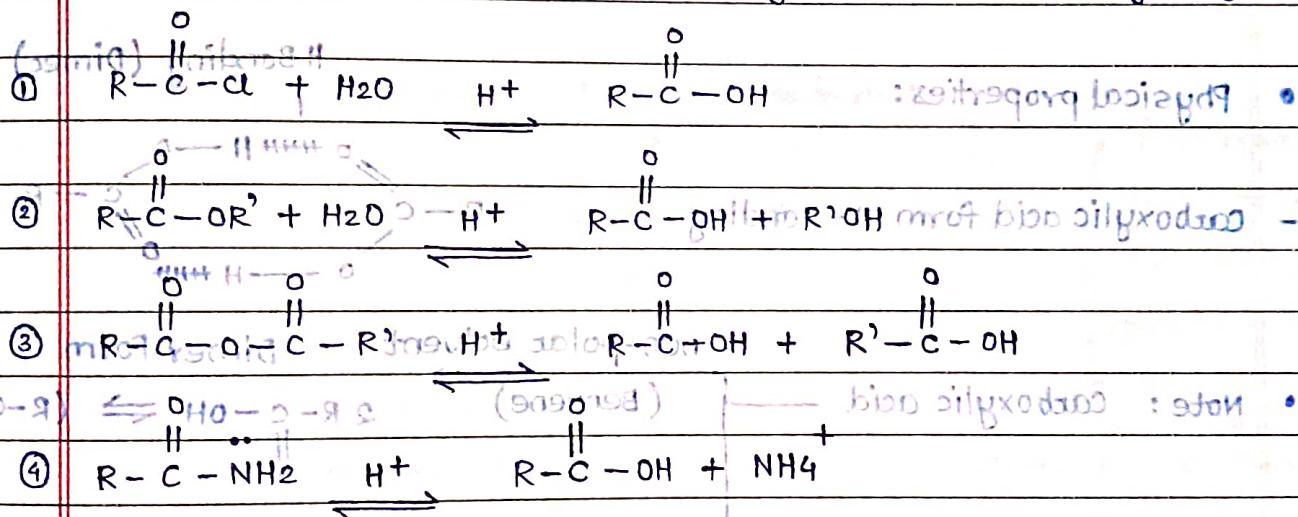


Water-soluble

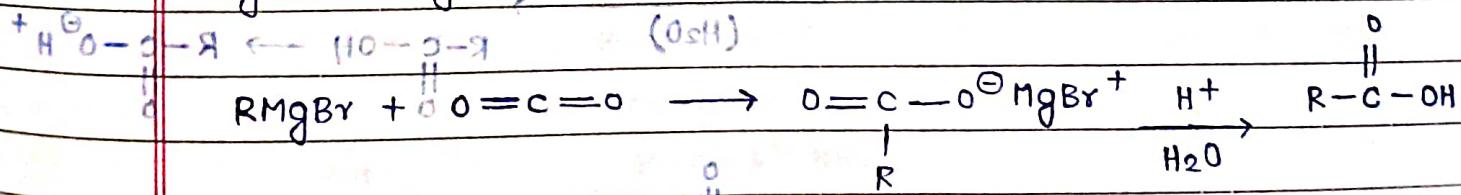
(c) Hydrolysis of Acid derivative:



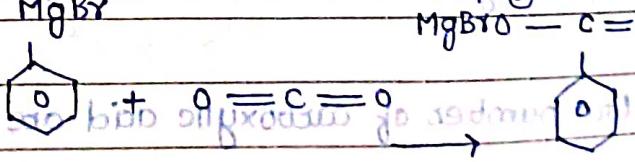
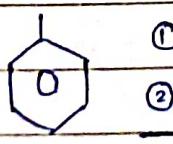
Acid Derivatives — those components which gives carboxylic acid in direct hydrolysis.



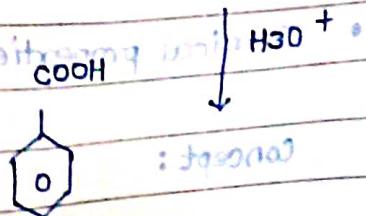
• Grignard Reagent:



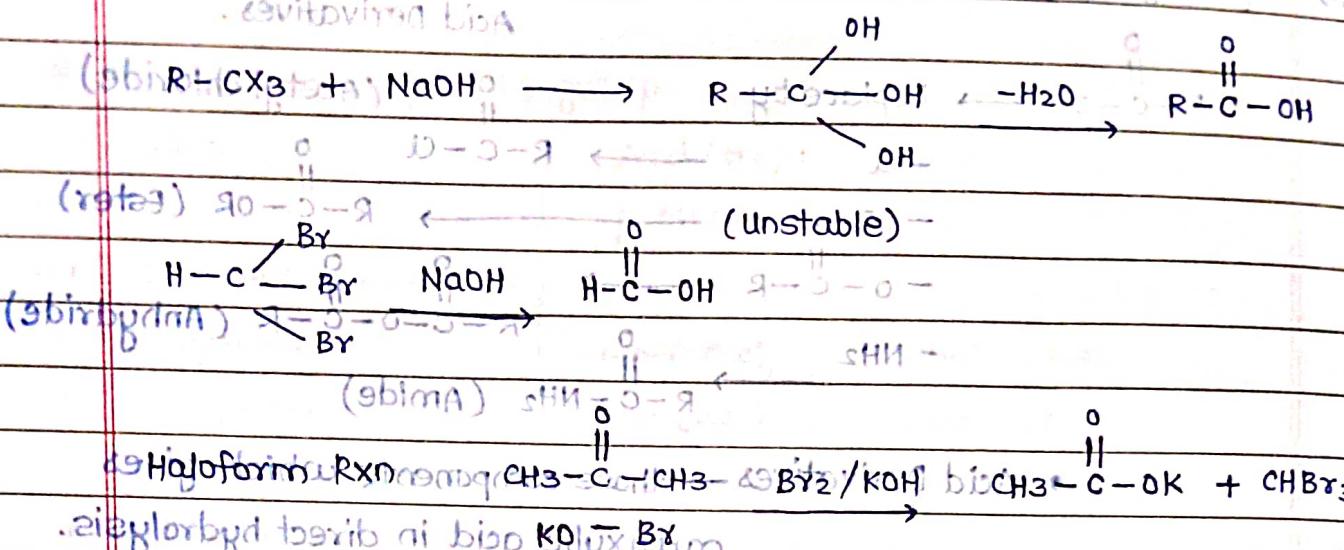
Q.



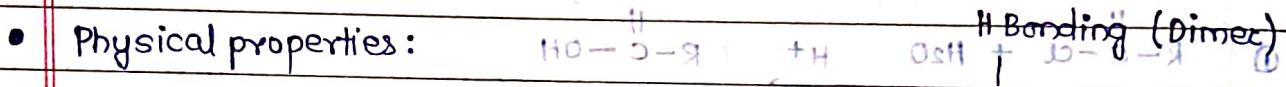
(Benzoic Acid)



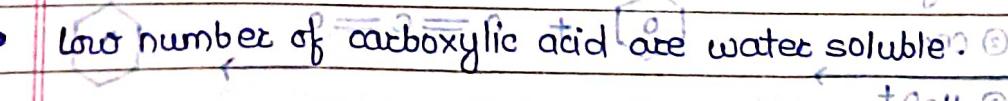
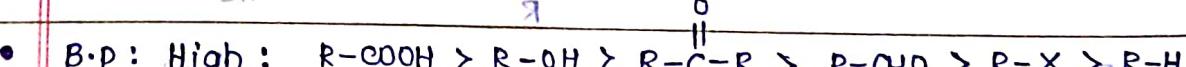
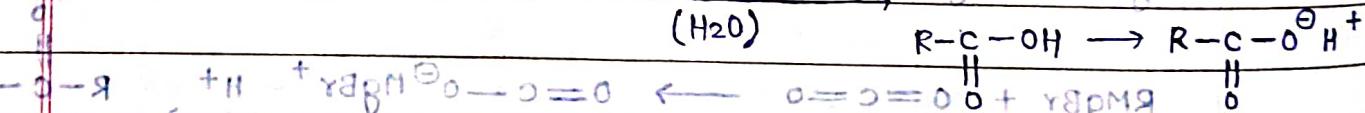
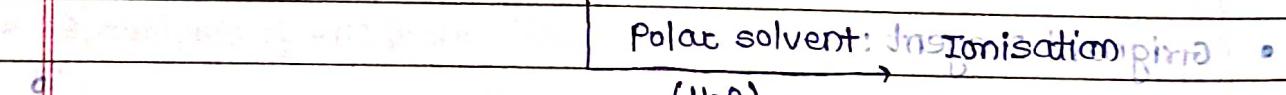
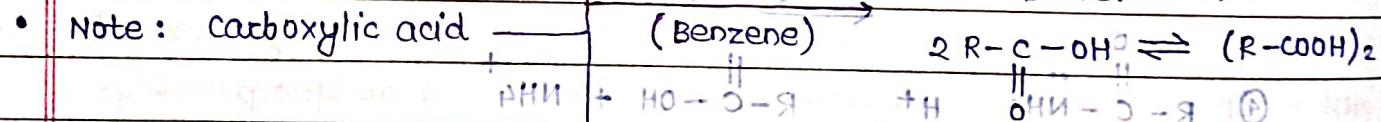
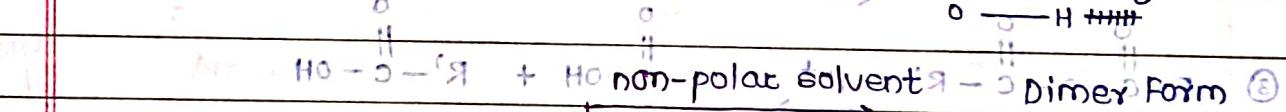
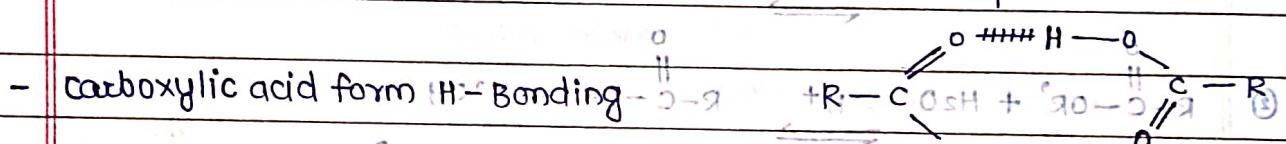
- trihalide Alkane ($R-CX_3$)



- Physical properties:



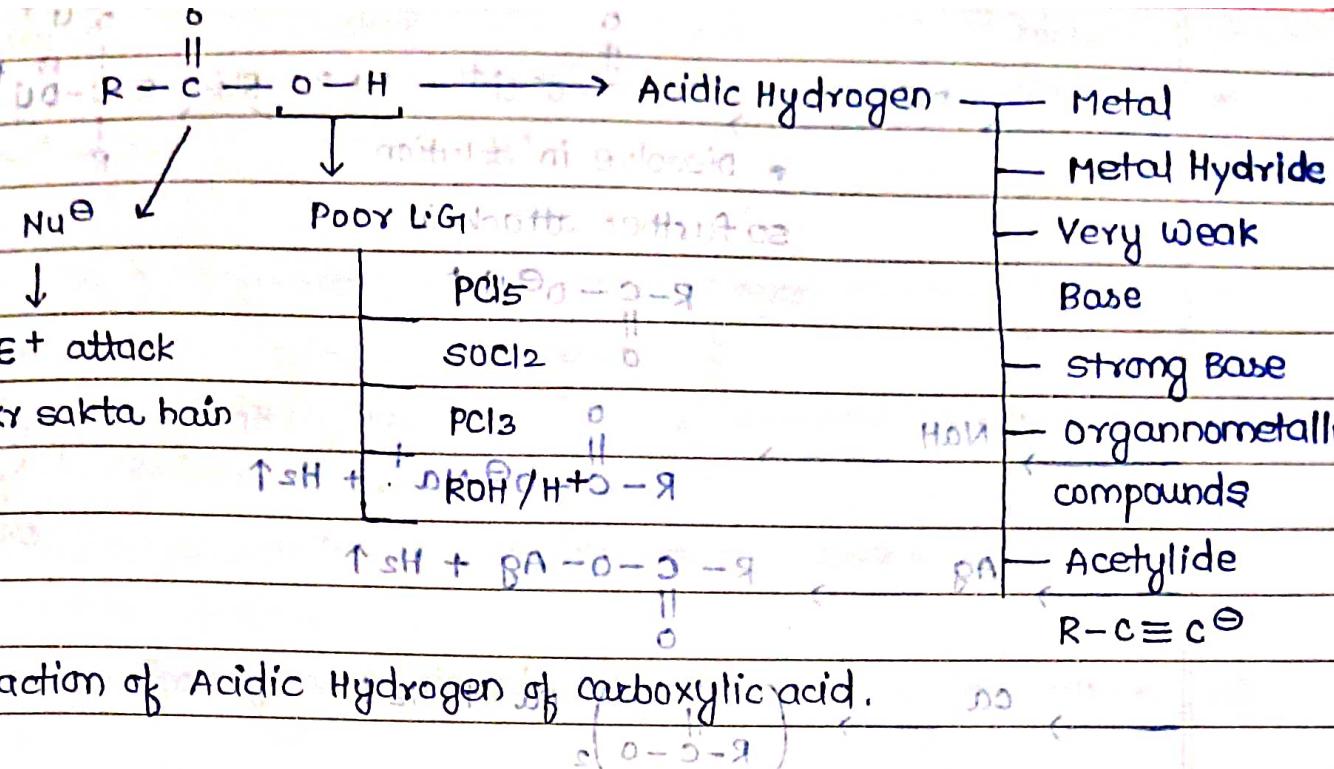
- carboxylic acid form (H \ddot{O} - Bonding)



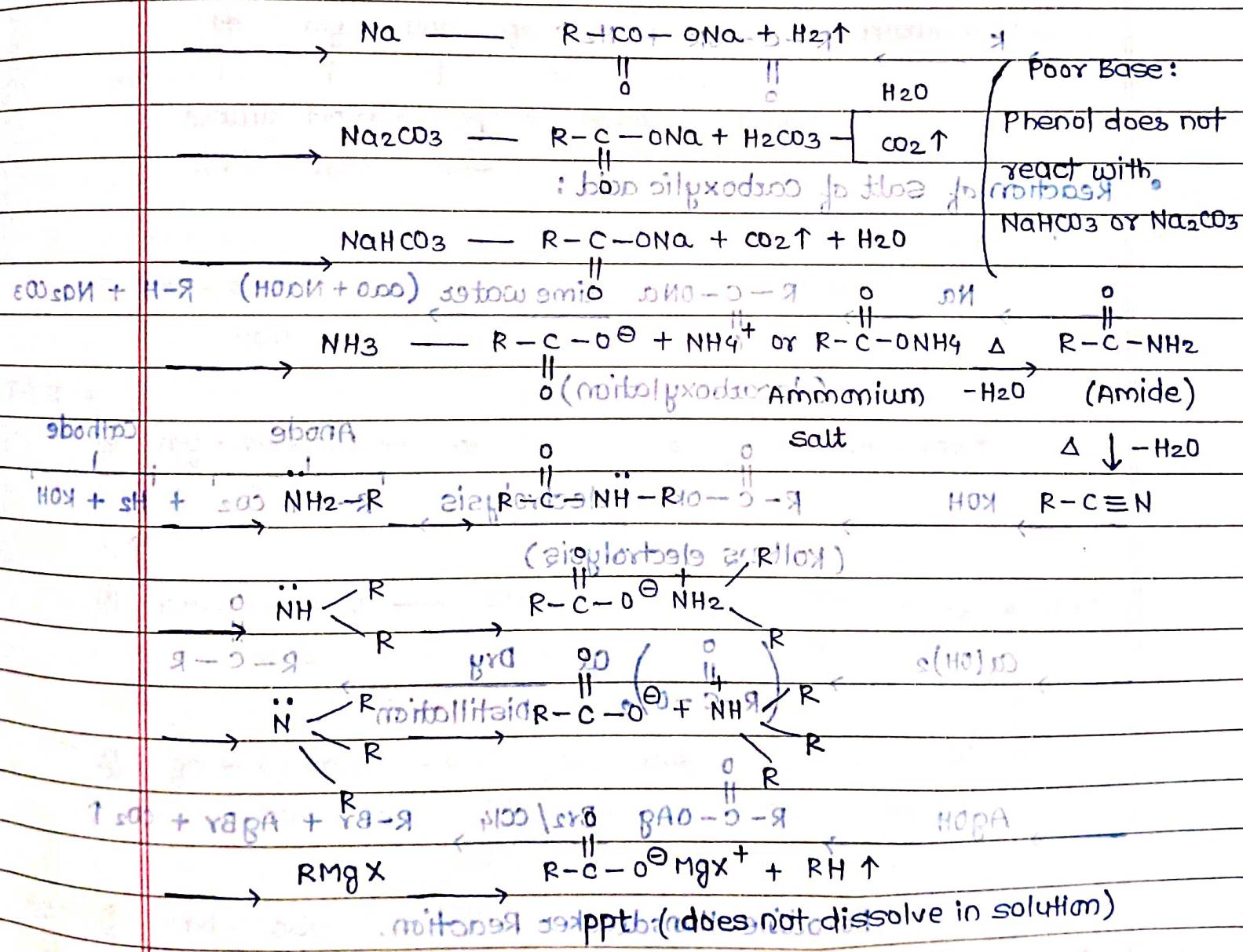
- Chemical properties:

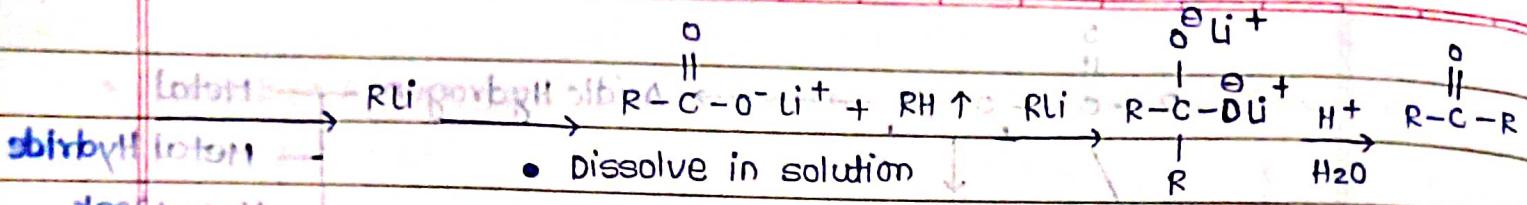
Concept:

(Basic nature)

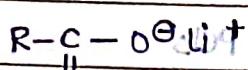


- Reaction of Acidic Hydrogen of carboxylic acid.

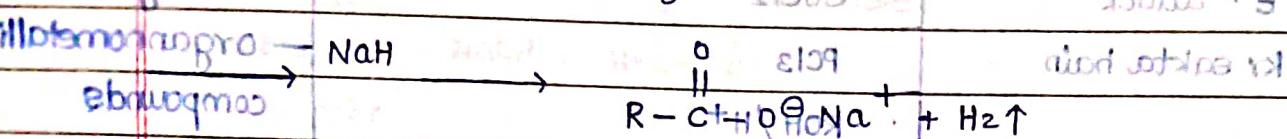




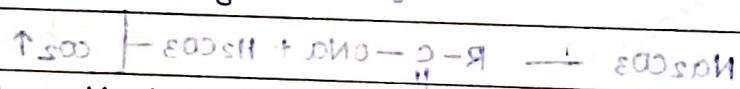
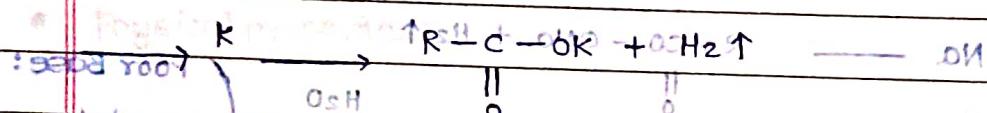
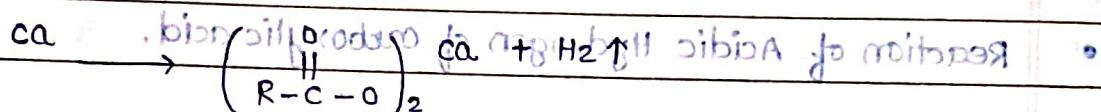
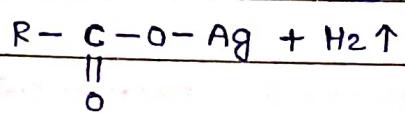
Bases



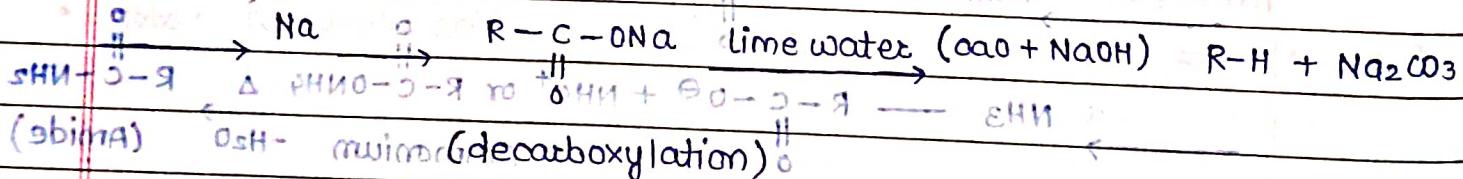
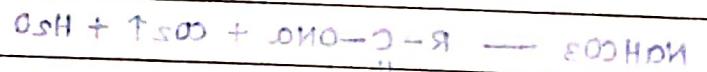
so attack



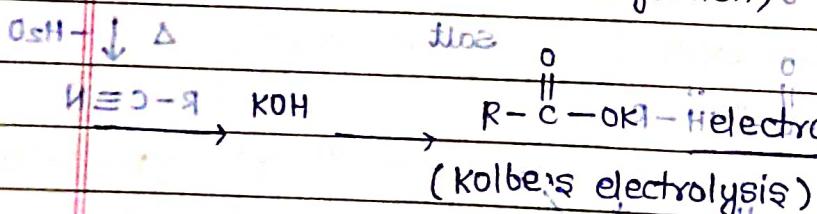
Acetylides



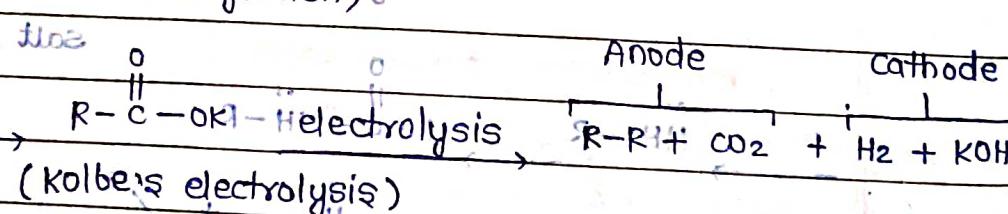
• Reaction of salt of carboxylic acid :



(Amide) (decarboxylation)

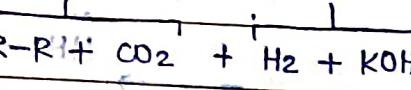


$\downarrow \text{KOH}$



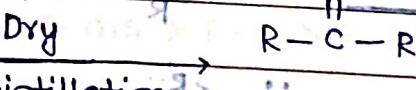
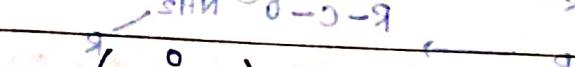
Anode

Cathode

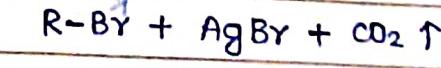
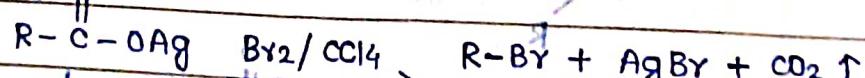


(Kolbe's electrolysis)

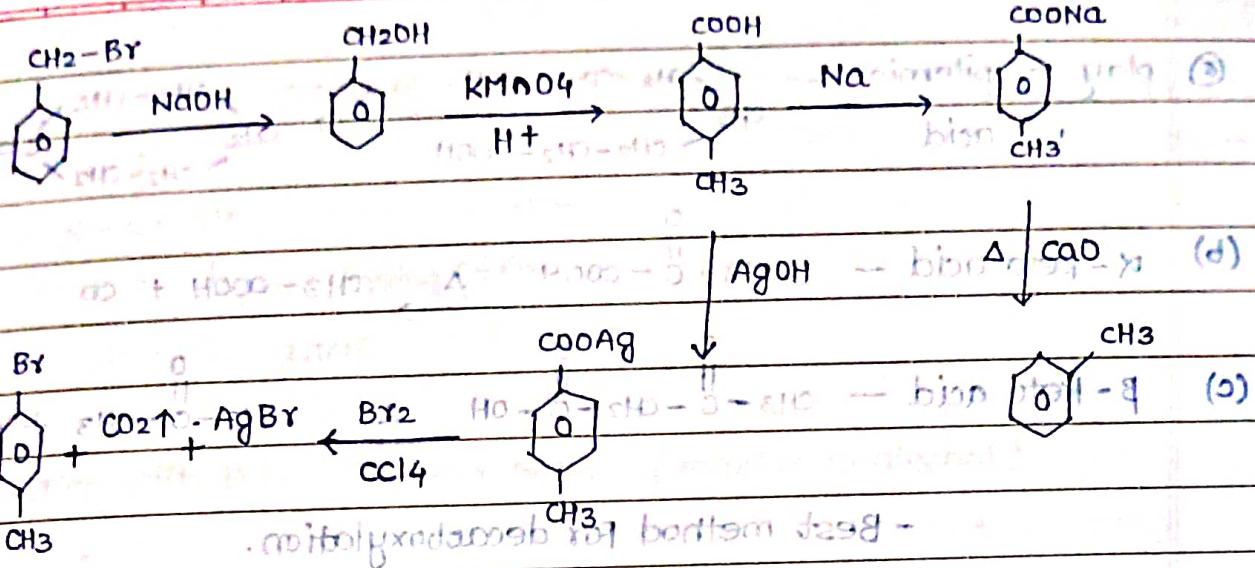
$\downarrow \text{Ca(OH)}_2$



$\downarrow \text{AgOH}$



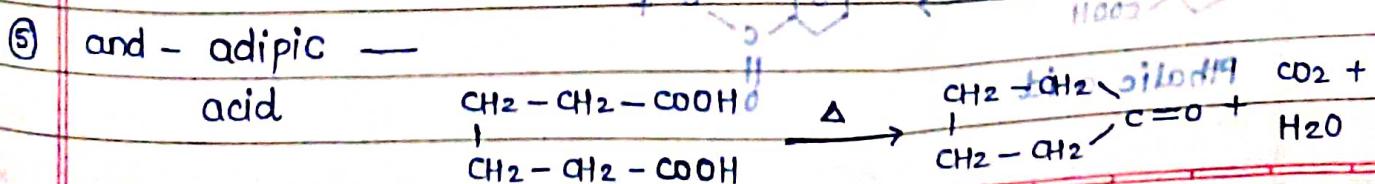
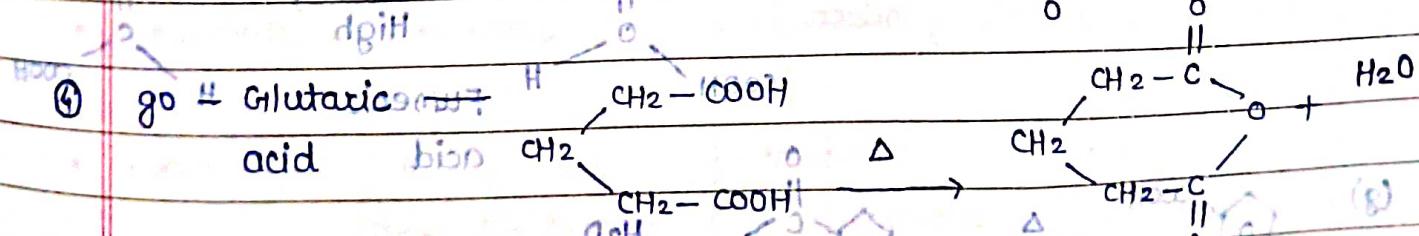
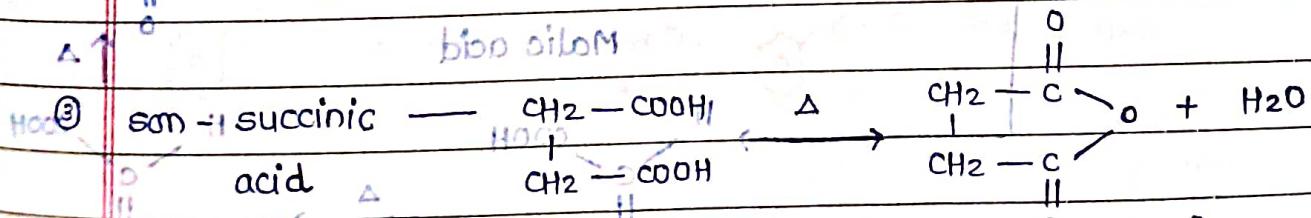
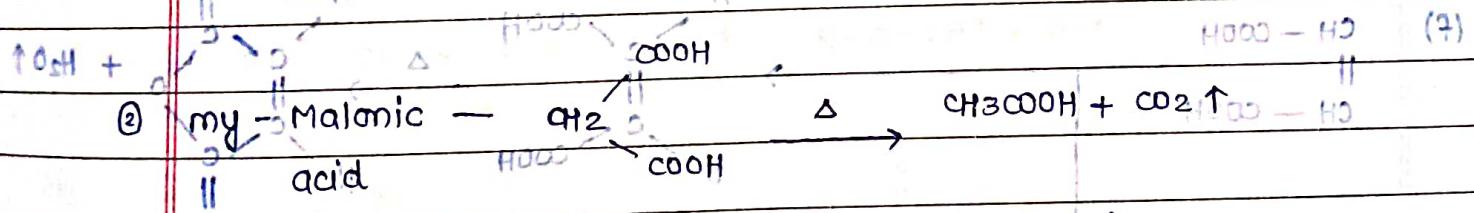
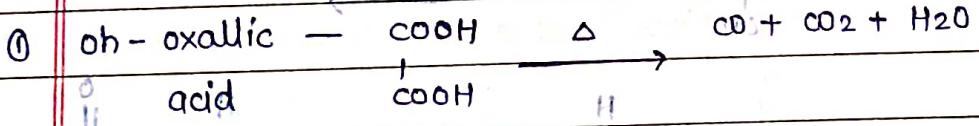
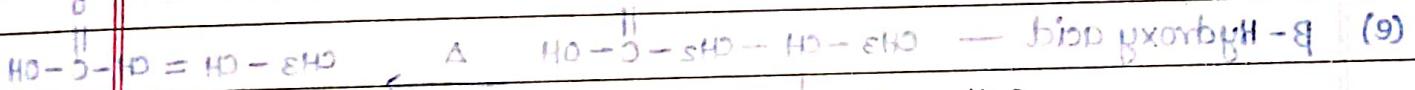
(Formation of Hunsdorff Reaction.)

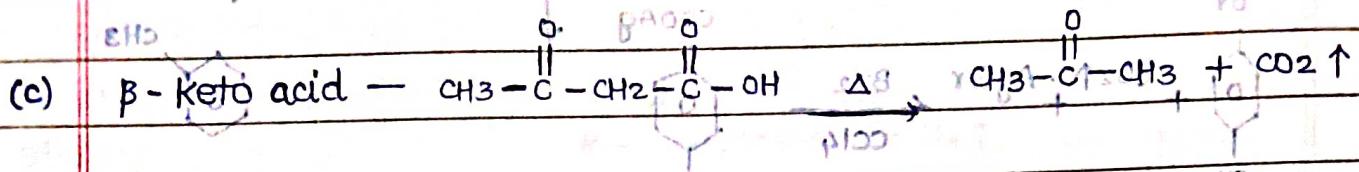
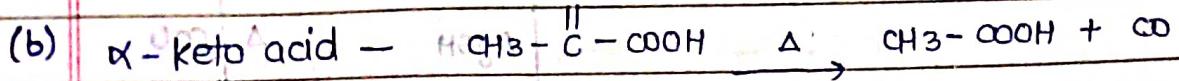
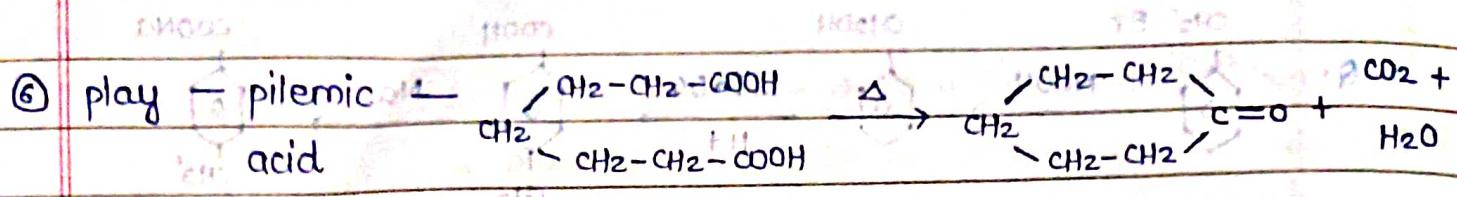


• Heating effect of carboxylic acid: $\text{HO}-\text{CH}_2 \rightarrow \text{biacetyl}$ (b)

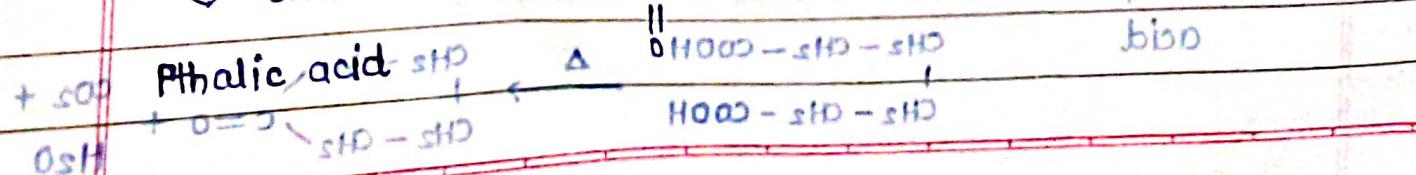
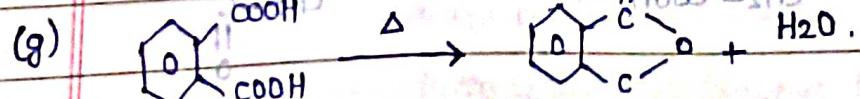
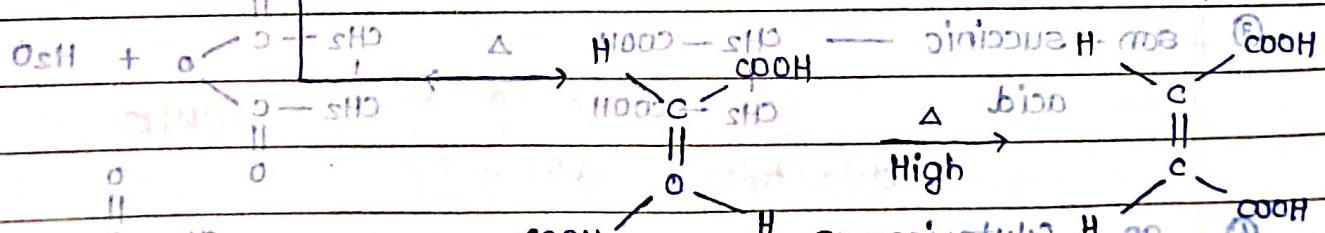
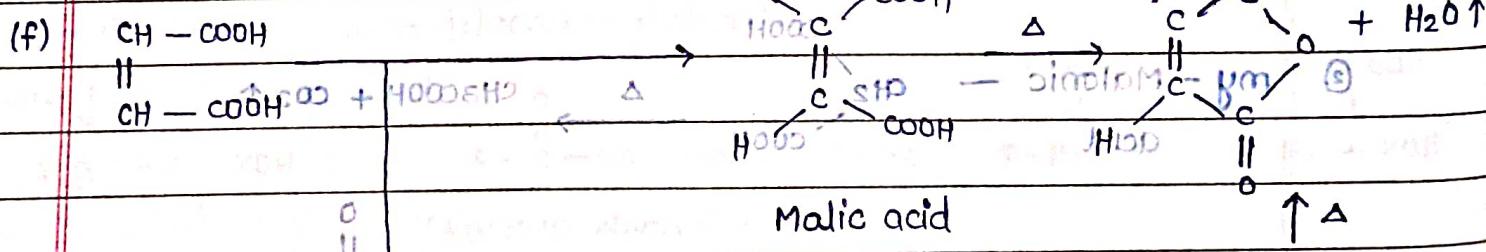
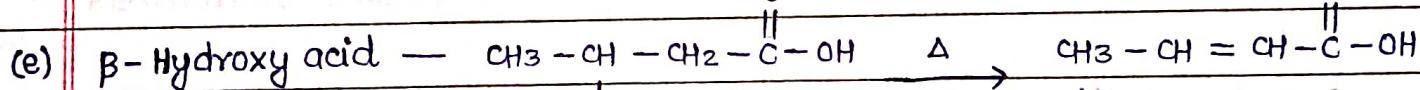
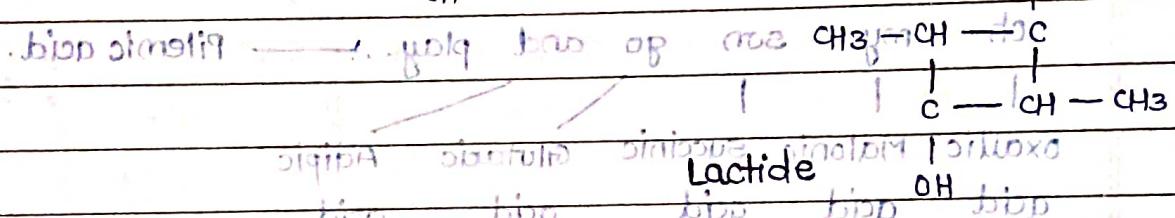
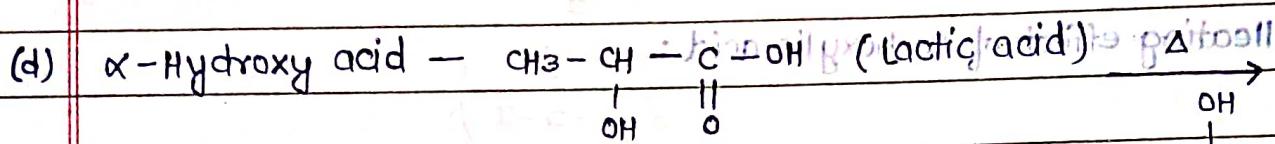
$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH} \rightarrow \text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_3$ (b)
 Pilemic acid.

oxalic Malonic succinic Glutamic Adipic
 acid acid acid acid

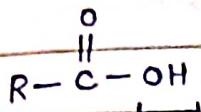




- Best method for decarboxylation.

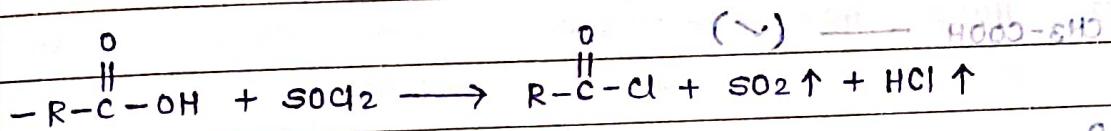
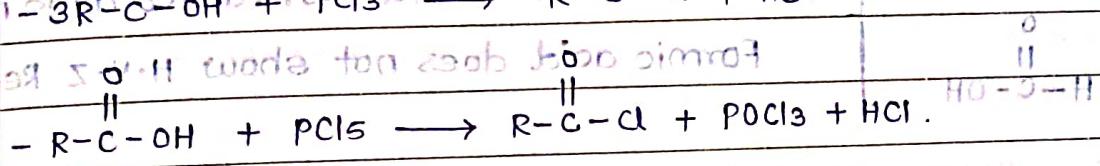
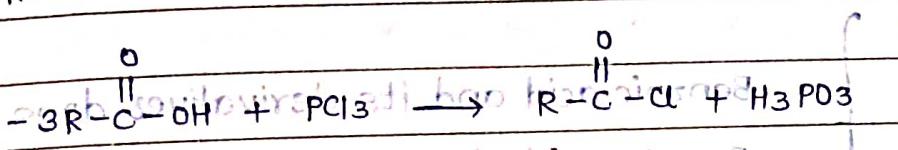


Reaction of OH group of carboxylic Acid:



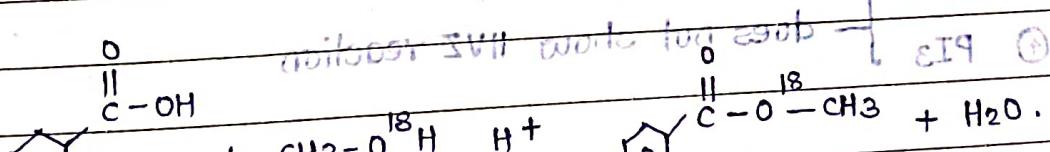
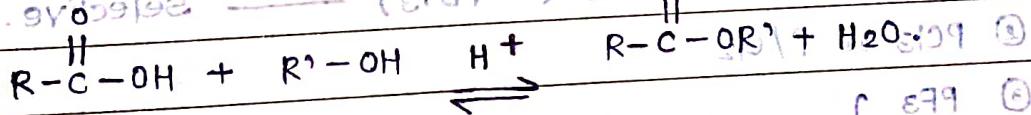
poor leaving group.

(a) Reaction with PCl_3 , PCl_5 , and SOCl_2 (similar to alcohol)



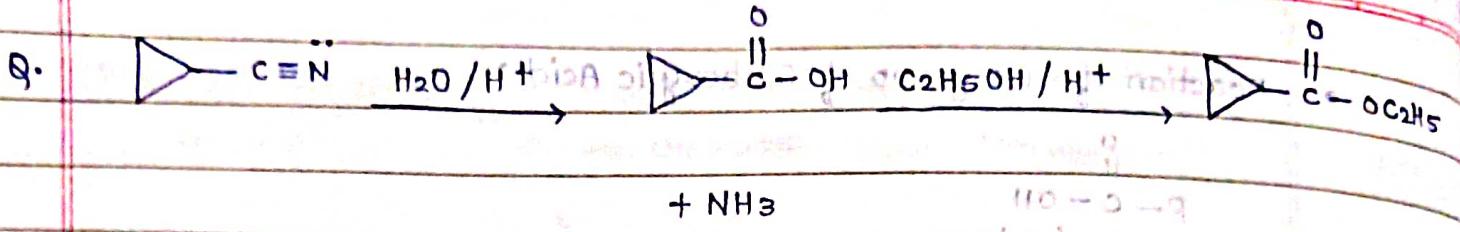
(Note: Best method for preparation of Acetyl chloride)

(b) Reaction with R'-OH (Esterification)

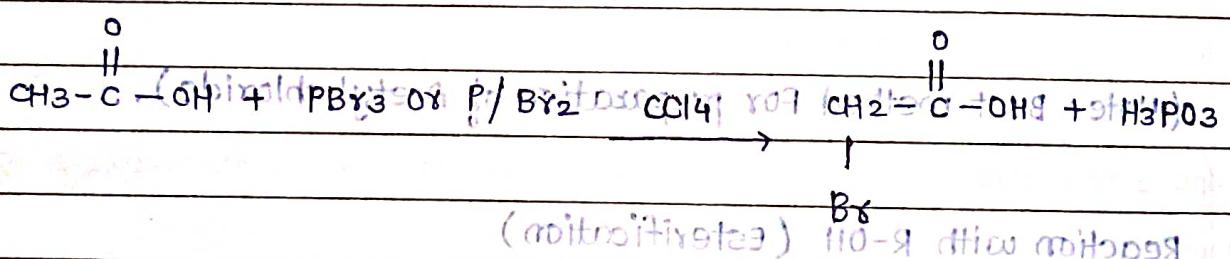
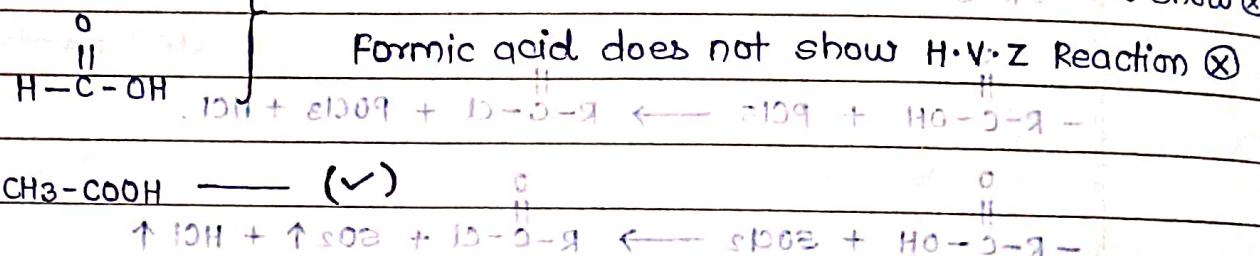
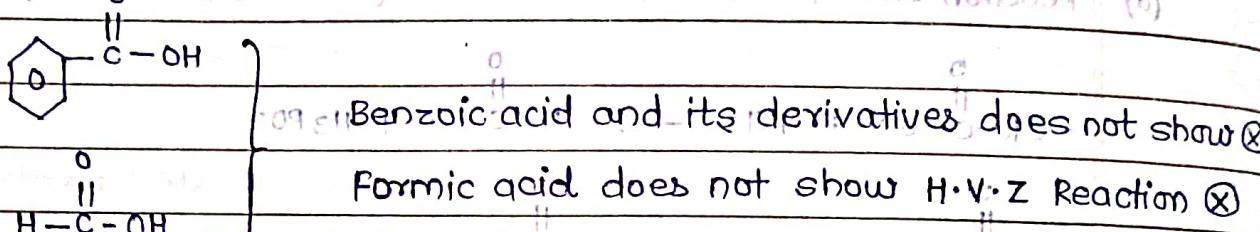


Reactivity \propto positive charge-density of carbonyl carbon - $\left\{ \begin{array}{l} \text{variable } \text{+I-effect} \\ \text{-M-effect} \end{array} \right\}$

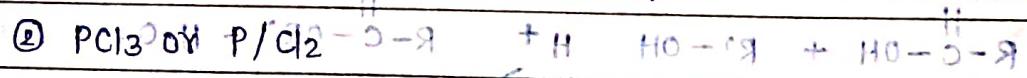
Reactivity \propto $\text{H}-\text{O}-\text{H}$ $\left\{ \begin{array}{l} \text{variable } \text{-SIP} \\ \text{steric hindrance} \end{array} \right\} + \text{H}-\text{O}-\text{H}$ $\left\{ \begin{array}{l} \text{-alkyl group} \end{array} \right\}$



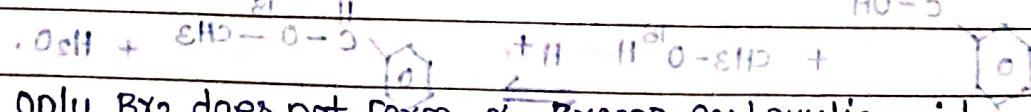
- Hell-Volhard-Zelinsky Reaction (HVZ) Reaction:
- carboxylic acid — condition — having at least one α -hydrogen



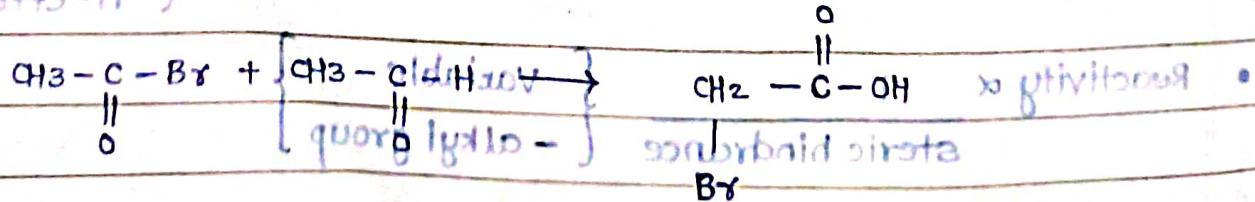
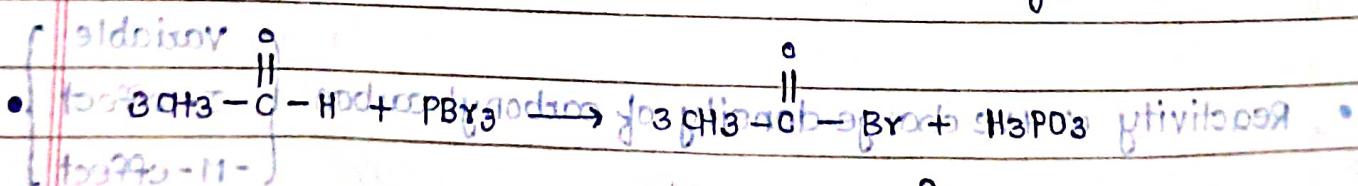
Mech: ① PBr_3 or ($Red\ P\ +\ Br_2 \rightleftharpoons PBrs$) — selective.

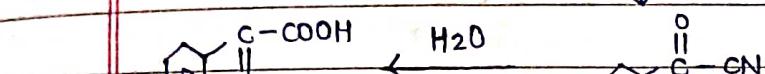
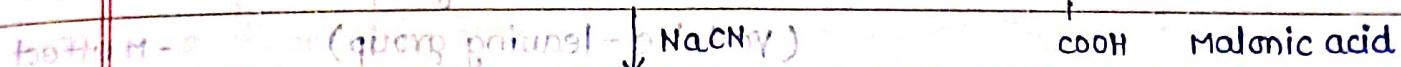
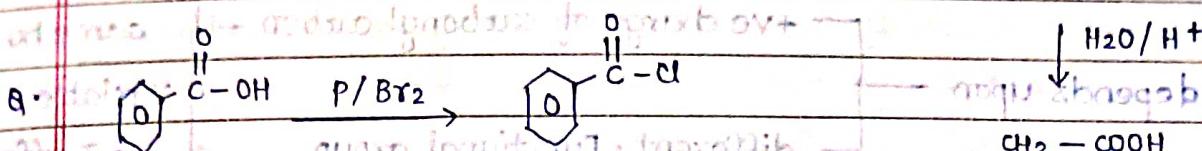
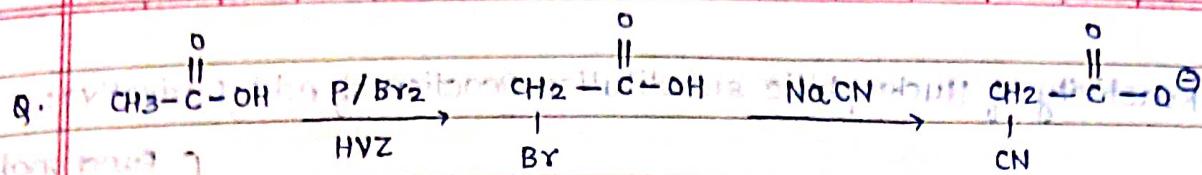


④ PI_3 } does not show HVZ reaction

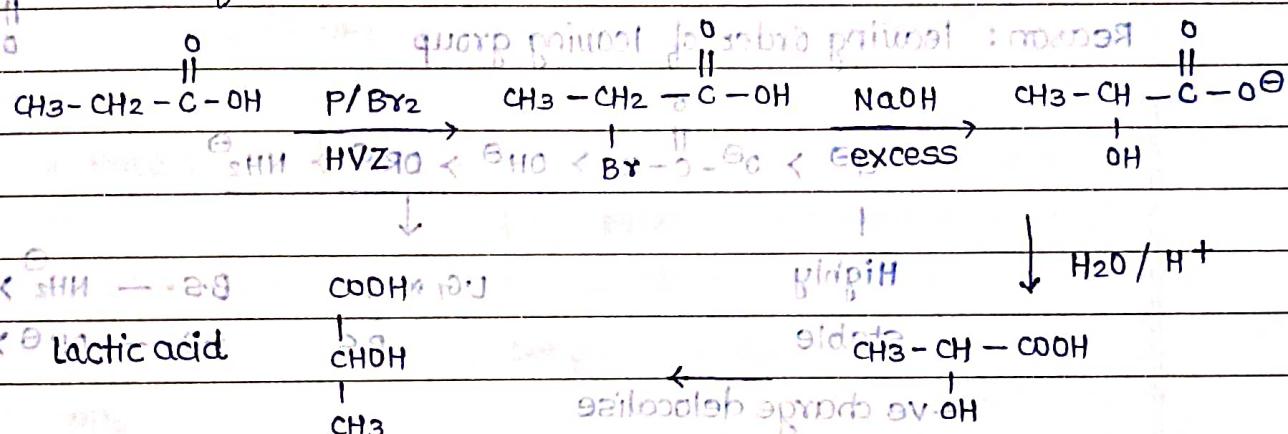


Note: only Br_2 does not form α -Bromo carboxylic acid

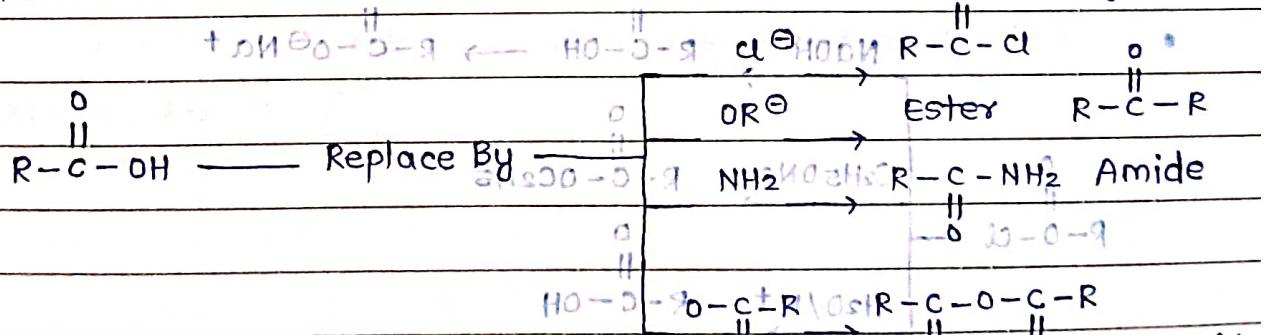




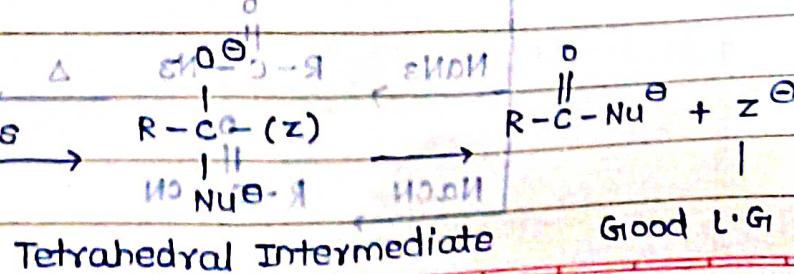
Formation of lactic acid :



• Acid Derivative :



- All acid derivatives show nucleophilic substitution reaction in carbonyl group.



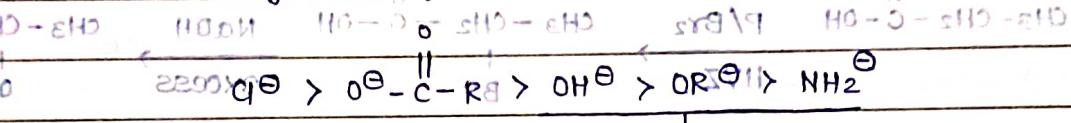
• Reactivity of Nucleophilic substitution Reaction of Acet Derivative:

+ H₂O(l) | +ve charge of carbonyl carbon | Functional group same ho.
depends upon | different functional group. | Variable A
HOCH₂COOH | - I effect
+ HO⁻ | - M effect

bisubstituted molecule → easier (variable-leaving group)

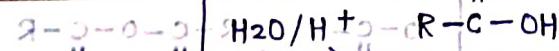
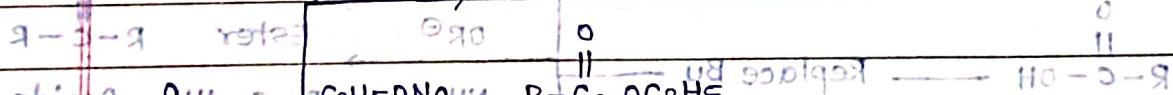
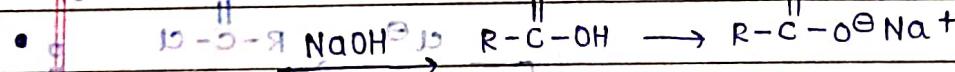
• Reactivity order: R-C-Cl > R-C-O-C-R > R-C-OH > R-C-OR

Reason: leaving order of leaving group

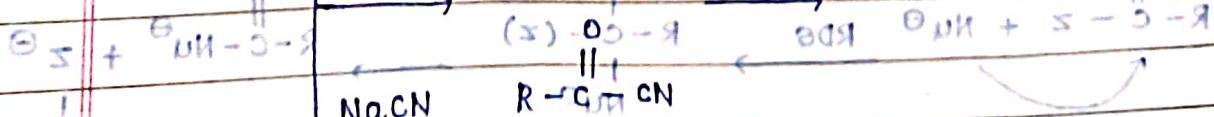
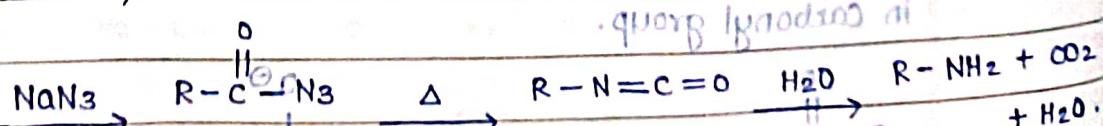


+ H₂O(l) | Highly stable | B.S. — NH₂ > OR[⊖] > OH[⊖]
stable | He-charge delocalise | B.S. — OH[⊖] > OR[⊖] > NH₂
in vacant d-orbital. | OH[⊖] < SH[⊖] < F[⊖] < Cl[⊖] < Br[⊖] < I[⊖]

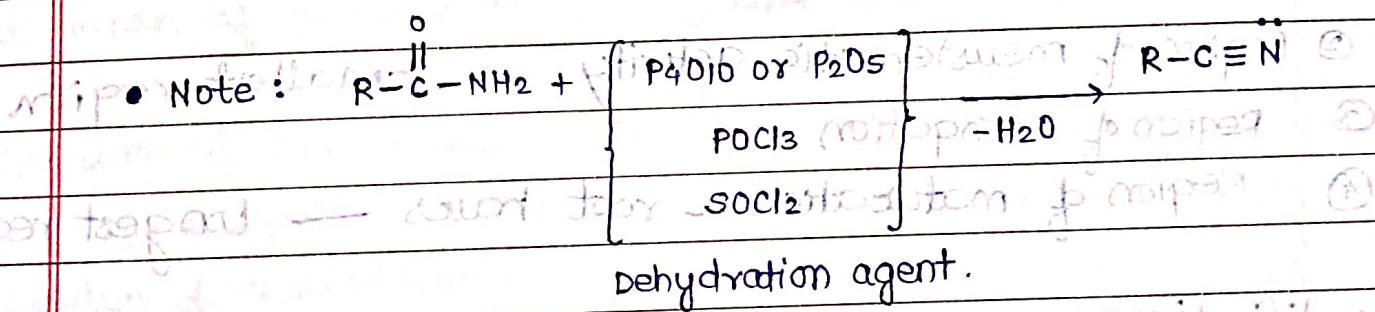
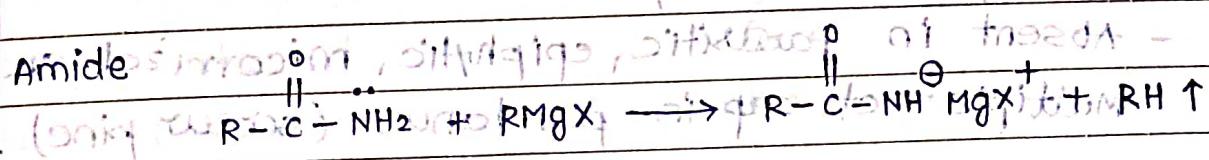
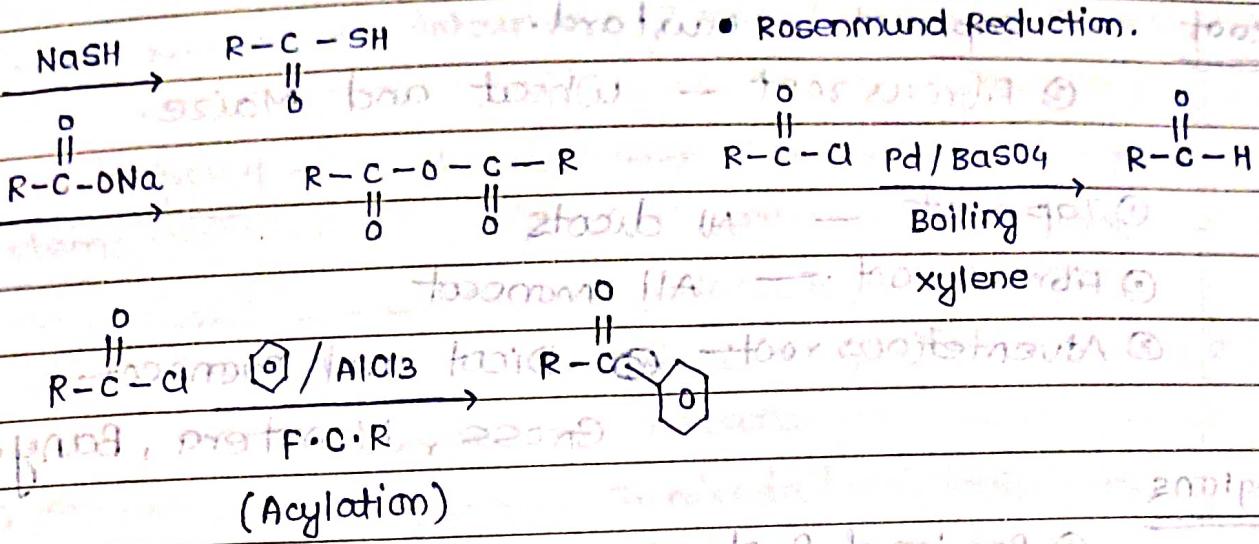
• : suitable bisubstituted molecule



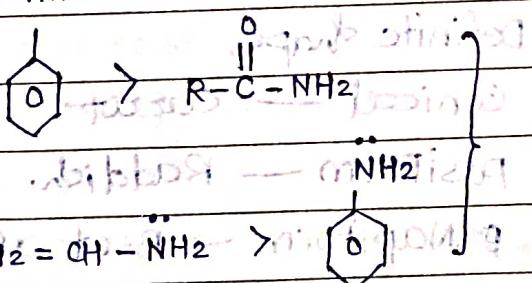
• work as suitable bisubstituted molecule
 $\text{R}-\text{C}-\text{NH}_2 \xrightarrow{\text{NaNH}_2} \text{R}-\text{C}-\text{NH}_2$



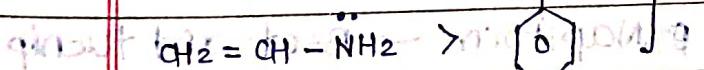
• good leaving group



NH₂



Basic strength \rightarrow more $\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{NH}_2$ due to high E·N than C-atom.



trityl carbonyl — trityl — expand effect about carb and (Tilberini)

Protonicity \rightarrow esterification \rightarrow no nitrogen \rightarrow

ketone bases \rightarrow amide bases \rightarrow stronger base \rightarrow with methyl

nitro group \rightarrow amide bases

strong base

carboxylic acid \rightarrow keto NH \rightarrow less basic \rightarrow stronger

• $\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{NH}_2$ (strongest)