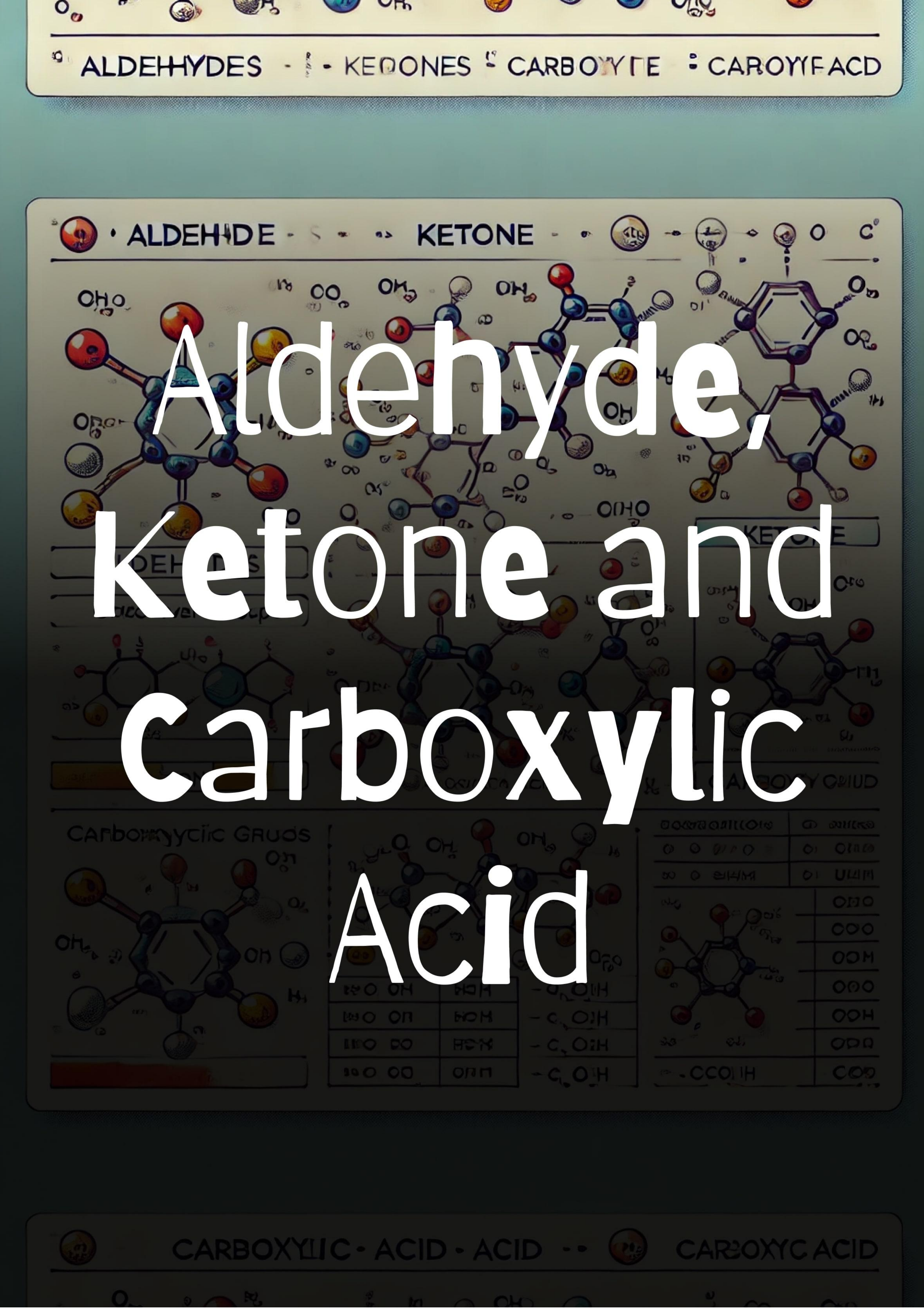


Aldehyde, Ketone and Carboxylic Acid

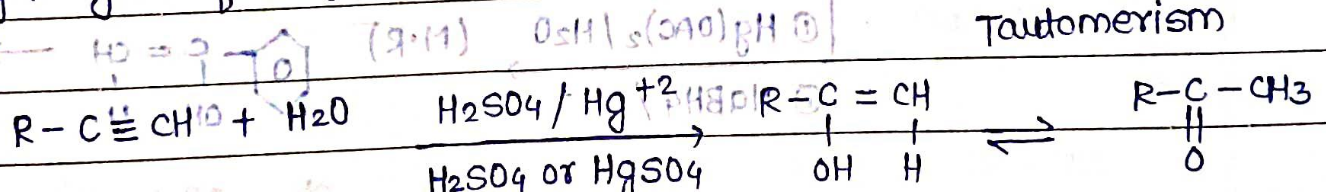
Aldehyde and Ketone.

- Method of preparation:

Alkyne + H_2O →
- → H_2O / H_2SO_4 and $HgSO_4$ — carbocation Form.
- → H·B·O — Hydroboration oxidation.
- → O·M·D·M — oxy-mercuration demercuration

(1) Addition of water in Alkyne:

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



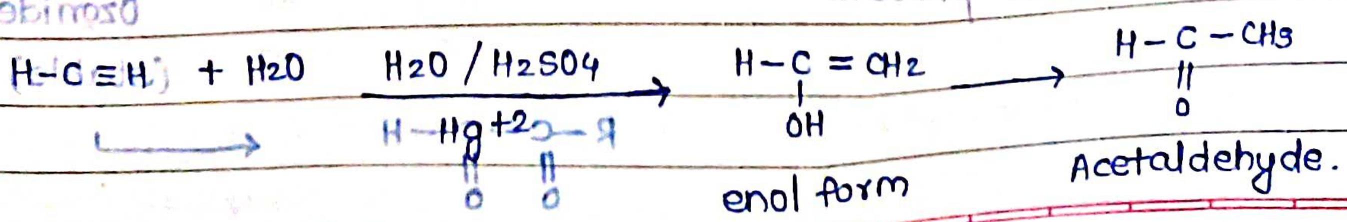
$$R-C\equiv CH + H_2O \xrightarrow[H_2SO_4 \text{ or } HgSO_4]{H_2SO_4 / Hg^{+2}} \underset{\text{enol form}}{R-\underset{OH}{C}=\underset{H}{CH}} \underset{\text{Tautomerism}}{\rightleftharpoons} \underset{\text{Keto.}}{R-\overset{}{\underset{O}{\overset{\|}{C}}}-CH_3}$$

Tautomerism

enol form Keto.

(unstable)

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

Q. 

$$H-C\equiv H + H_2O \xrightarrow[Hg^{+2}]{H_2O / H_2SO_4} \underset{OH}{H-\underset{|}{C}}=CH_2 \longrightarrow H-\underset{O}{\overset{}{\underset{\|}{C}}}-CH_3$$

enol form

Acetaldehyde.

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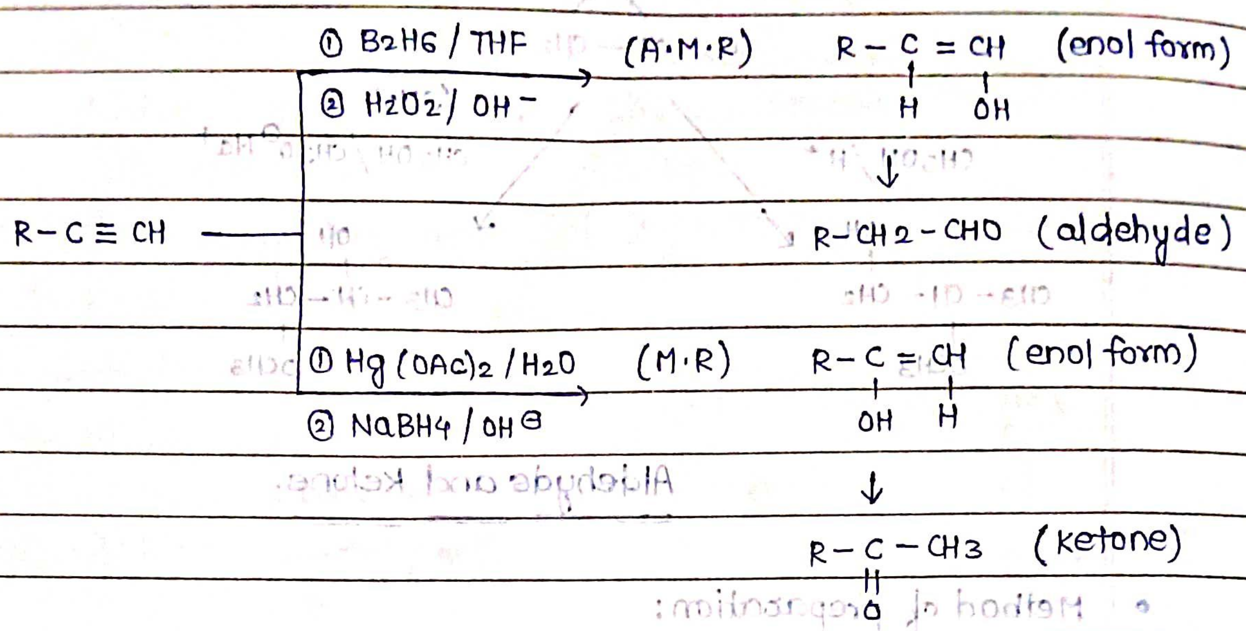
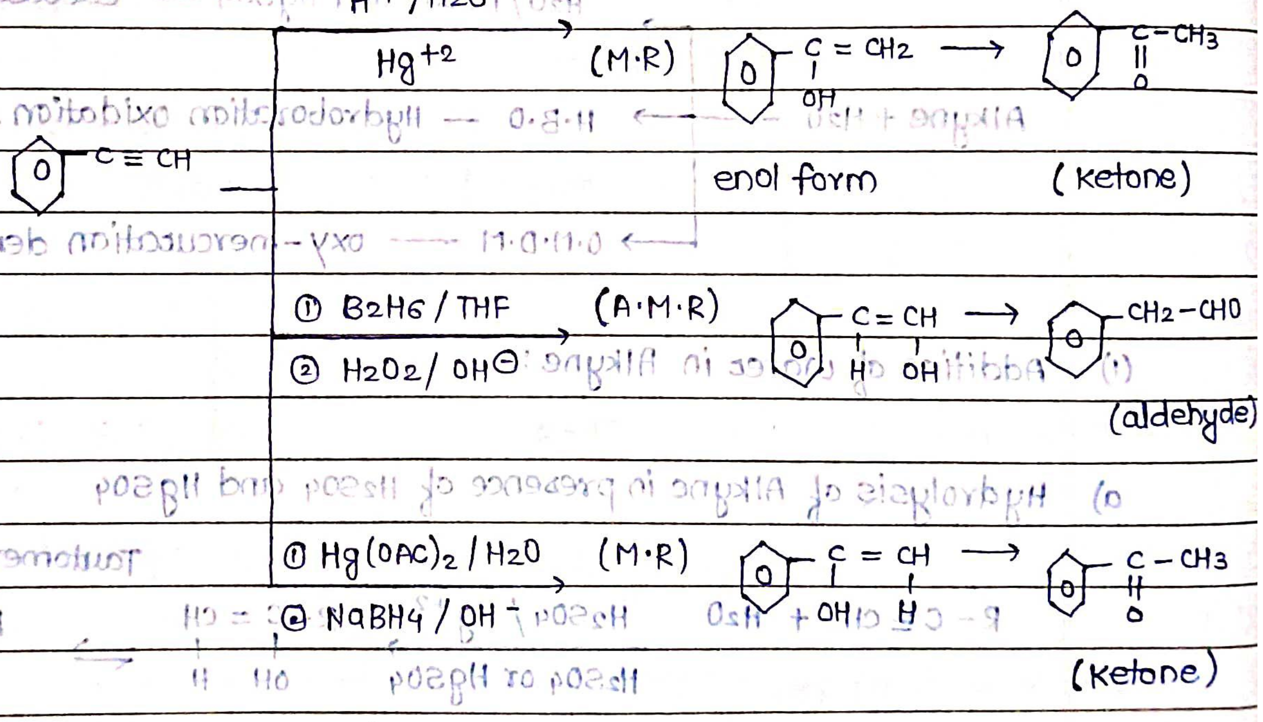
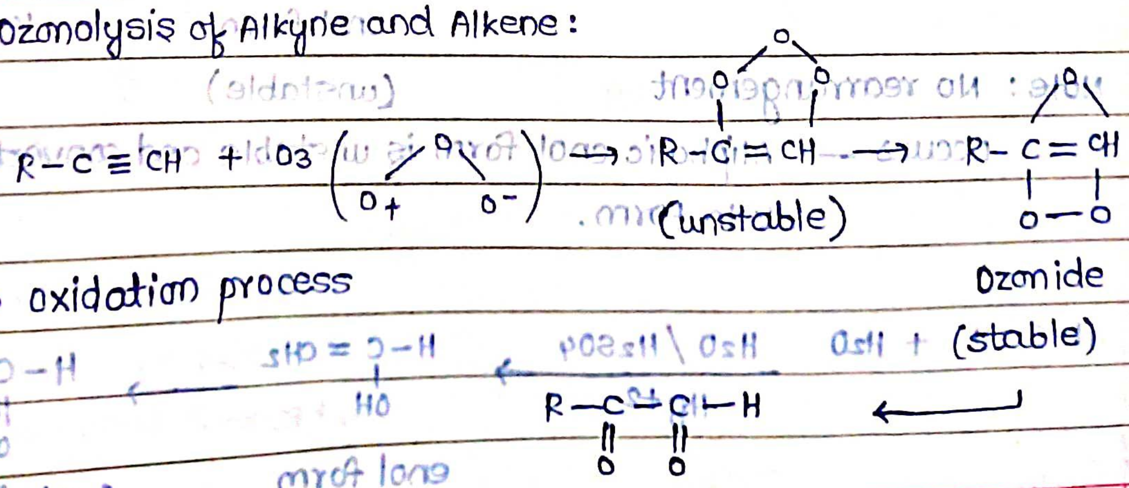
Date

(6) H·B·O and O·M·D·M



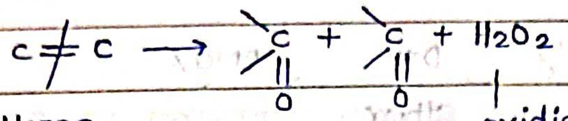


- Ozonolysis of Alkyne and Alkene :



- oxidation process

- Note - ozonolysis — 2 bond break hote hain



oxidising agent
|
oxidise further to (R-CHO ↓ R-COOH)

Note - ketone does not oxidise by H_2O_2.

$$-C\equiv C- \longrightarrow -\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}- + H_2O_2$$

Q. $CH_3-CH=CH-CH_3 \xrightarrow{O_3} CH_3CHO + CH_3CHO + H_2O_2 : (O\cdot A)$

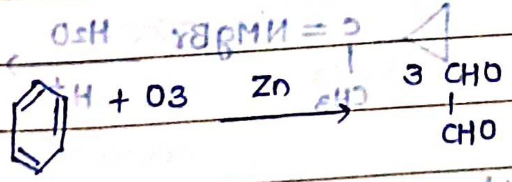
$\downarrow \quad \downarrow$

$CH_3COOH \quad CH_3COOH$

- $CH_3-CH=CH_2 \xrightarrow{O_3} CH_3-\underset{\underset{O}{\|}}{C}HO + HCHO \longrightarrow CH_3COOH + HCOOH$

$CH_3-CH=CH_2 \xrightarrow[Zn]{O_3} CH_3CHO + HCHO$

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

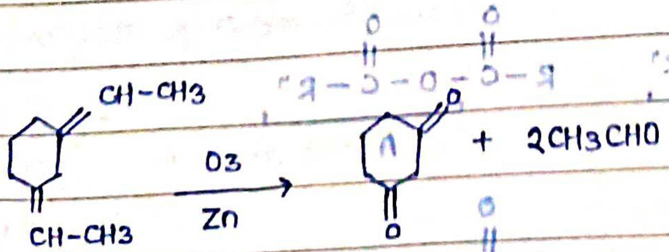


Q. $CH_2=CH-CH=CH_2$

$\downarrow O_3/Zn$

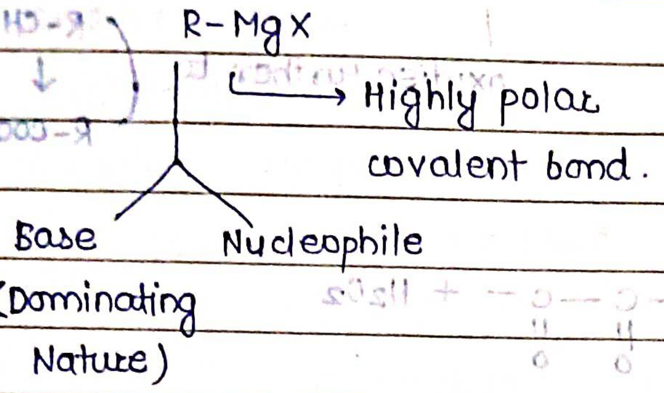
$2HCHO + \underset{CHO}{\overset{CHO}{|}}$

Q.



- **By Grignard Reagent :**

- Concept : $RX + Mg \xrightarrow[\text{ether}]{\text{Dry}} RMgX$



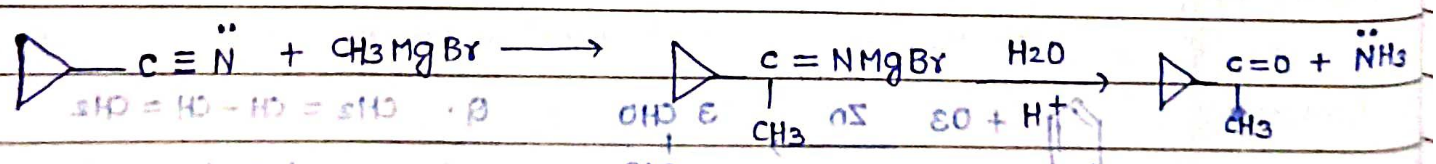
(a) cyanide : $R'-C\equiv N + RMgX \xrightarrow[\text{Dry ether}]{\text{step I}} R'-\underset{R}{\underset{|}{C}}=\overset{\ominus}{N}\overset{+}{Mg}X$

Step-2 H_2O/H^+

$\overset{\oplus}{N}H_4 \leftarrow \ddot{N}H_3 + R'-\underset{O}{\underset{||}{C}}-R \longleftarrow R'-\underset{R}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\ddot{N}H$

$H-C\equiv\ddot{N} + CH_3MgBr \longrightarrow H-\underset{CH_3}{\underset{|}{C}}=NMgBr \xrightarrow{H_3O^+} H-\underset{CH_3}{\underset{|}{\overset{O}{\overset{||}{C}}}} + \ddot{N}H_3$

Q.

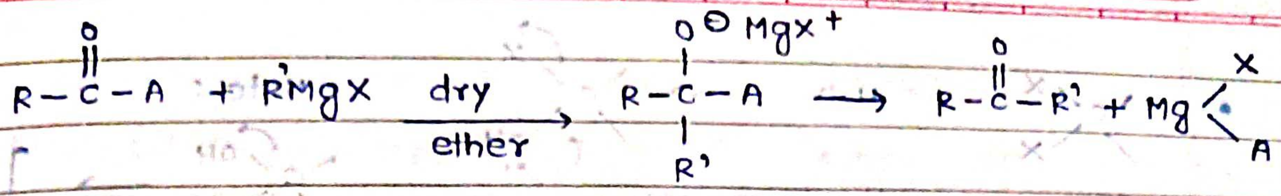


(b) Acyl chloride, Ether and Anhydride.

$\underbrace{R-\overset{O}{\overset{||}{C}}-Cl}_{A}$ $\quad R-\underbrace{\overset{O}{\overset{||}{C}}-OR'}_{A}$ $\quad R-\overset{O}{\overset{||}{C}}-\underbrace{O-\overset{O}{\overset{||}{C}}-R'}_{A}$

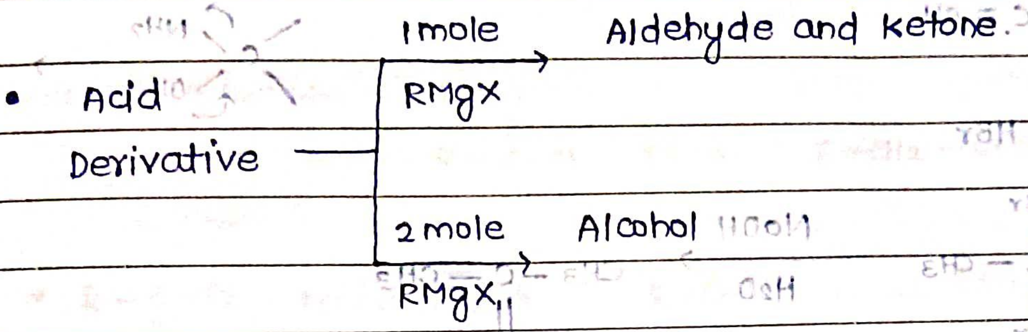
$R-\overset{O}{\overset{||}{C}}-NH_2 + RMgX \longrightarrow R-\overset{O}{\overset{||}{C}}-NHMgBr + CH_4\uparrow$

Alkane.

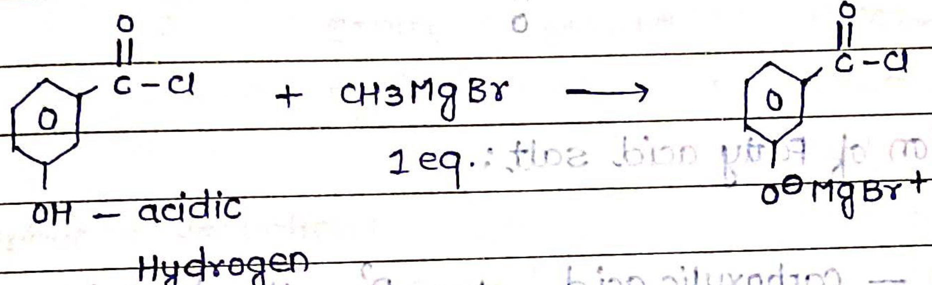


$$R-\overset{O}{\overset{\|}{C}}-A + R'MgX \xrightarrow[\text{ether}]{\text{dry}} R-\underset{R'}{\underset{|}{\overset{O^{\ominus}MgX^{+}}{\overset{|}{C}}}}-A \longrightarrow R-\overset{O}{\overset{\|}{C}}-R' + Mg\langle^{X}_{A}$$

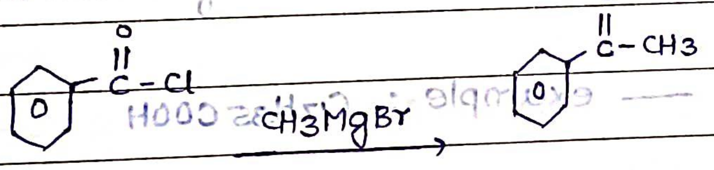
- Note :- If RMgX present in excess then Further react with aldehyde and ketone and Form alcohol.



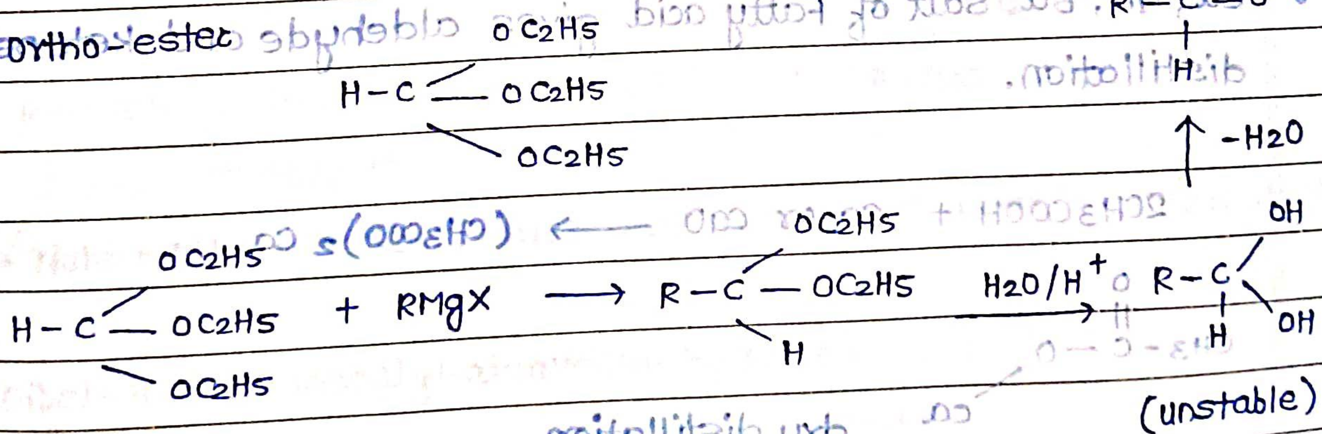
Q.



Q.

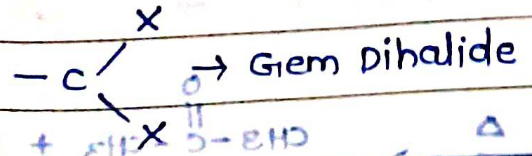


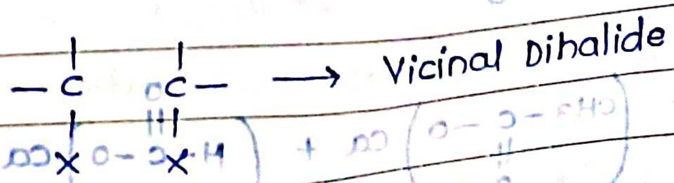
(c) Ortho-ester

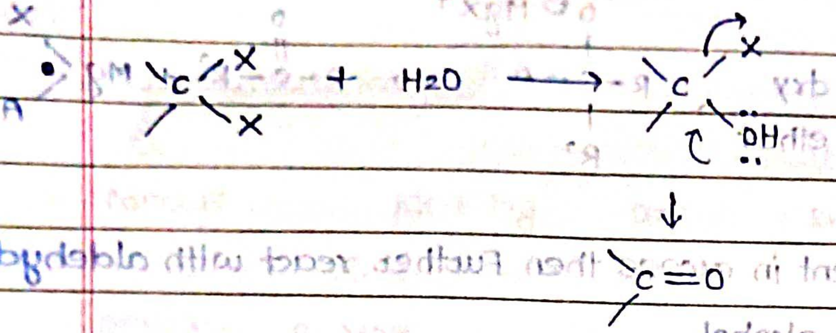


$$H-C\begin{matrix}OC_2H_5\\ OC_2H_5\\ OC_2H_5\end{matrix} + RMgX \longrightarrow R-C\begin{matrix}OC_2H_5\\ H\end{matrix}\xrightarrow{H_2O/H^+} R-\underset{H}{\underset{|}{C}}\begin{matrix}OH\\ OH\end{matrix}\ (\text{unstable}) \xrightarrow{-H_2O} R-\underset{H}{\underset{|}{C}}=O$$

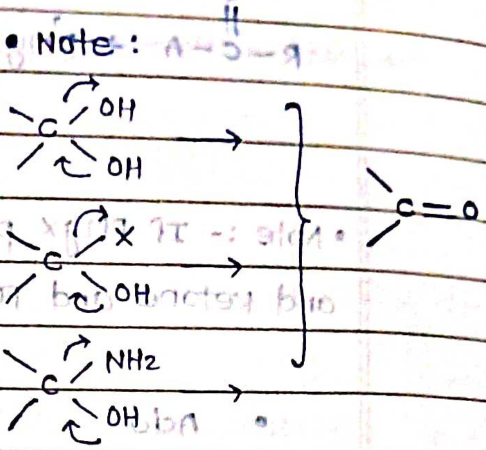
- Hydrolysis of Gem-dihalide :



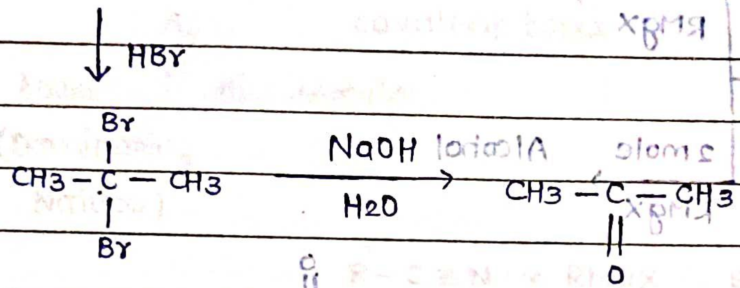




- Note :



Q. $CH_3-C\equiv CH$



$$CH_3-C\equiv CH \xrightarrow{HBr} CH_3-CBr_2-CH_3 \xrightarrow[H_2O]{NaOH} CH_3-\overset{\overset{\large O}{\|}}{C}-CH_3$$

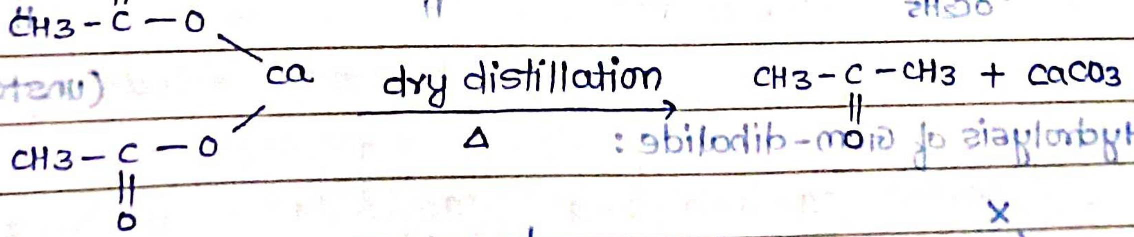
- Dry Distillation of Fatty acid salt :

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

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

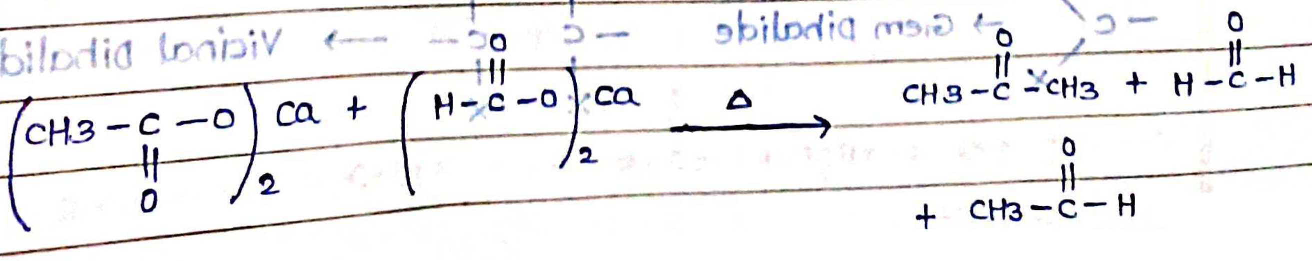
- Ca, Mn, Ba salt of Fatty acid gives aldehyde and ketone (on) distillation.

$$2CH_3COOH + Ca \text{ or } CaO \longrightarrow (CH_3COO)_2Ca$$

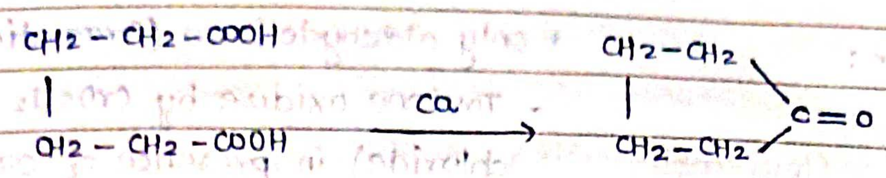


$$(CH_3COO)_2Ca \xrightarrow[\Delta]{\text{dry distillation}} CH_3-\overset{\overset{\large O}{\|}}{C}-CH_3 + CaCO_3$$

Q.



$$(CH_3COO)_2Ca + (HCOO)_2Ca \xrightarrow{\Delta} CH_3COCH_3 + HCHO + CH_3CHO$$

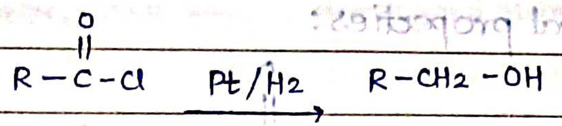
Q. 

$CH_2-CH_2-COOH \,|\, CH_2-CH_2-COOH \xrightarrow{Ca}$ $CH_2-CH_2 \,|\, CH_2-CH_2 > C=O$

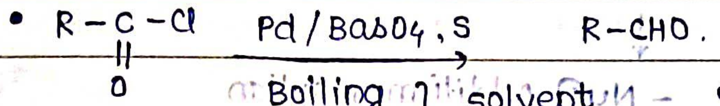
- Note : 1 mole add → 4 mb, 5 mb, and 6 mb cyclic Ketone.

- Method of preparation (only aldehyde) :

① Rosenmund reduction :



$R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{Pt/H_2} R-CH_2-OH$



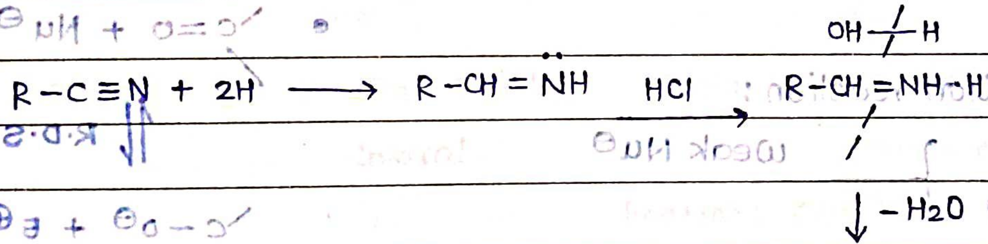
- $R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow{Pd/BaSO_4,\ S} R-CHO.$

Boiling } solvent
xylene

- $BaSO_4$ or S : Decrease the rate of oxidation.

② Stephen's Reduction :

Reagent ⟶ $SnCl_2$ / conc·HCl

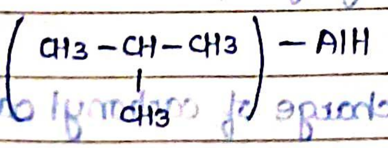


$R-C\equiv N + 2H \longrightarrow R-CH=\ddot{N}H \xrightarrow{HCl} R-CH=NH\cdot HCl \xrightarrow{-H_2O}$ (OH ⁄ H)

$R-C\equiv N \xrightarrow[\text{② } H_2O/H^+]{\text{① } SnCl_2/HCl} R-CHO$

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

③ Dibal-H (Di-isobutyl aluminium hydride)



$\left(CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3\right)-AlH$

$R-C\equiv N \xrightarrow[\text{② } H_2O]{\text{① DIBAL-H}} R-CHO.$

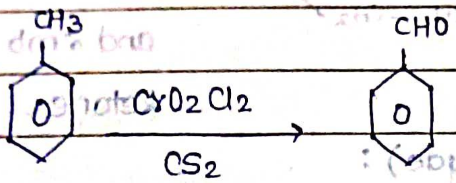
- Note : Does not effect double bond.

$CH_3-CH=CH-CH_2-C\equiv N \xrightarrow{DIBAL-H} CH_3-CH=CH-CH_2-CHO$

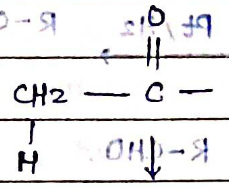
④ Etard Reaction :

* only aldehyde form (Aromatic aldehyde)

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



- Chemical properties :

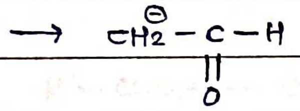


$CH_2 - \overset{O}{\overset{\|}{C}} -$ Aldehyde and Ketone

(very weak ← H
acid) α-hydrogen

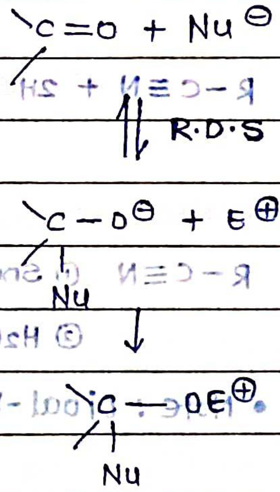
- Nu⊖ Addition reaction
- Nu⊖ addition elimination reaction.

Name reaction



$\rightarrow \overset{\ominus}{C}H_2 - \underset{O}{\underset{\|}{C}} - H$

- Nu⊖ addition reaction :



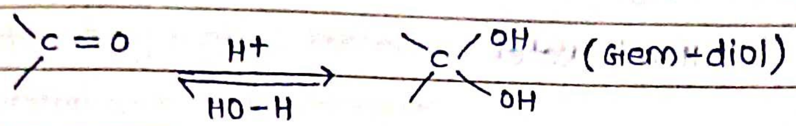
① H_2O } Weak Nu⊖
② R−OH
③ RMgX, RLi, RCuCl, R_2CuLi (Gilmann Reagent)
④ $NaHSO_3$
⑤ NaCN / HCN

- Reactivity ∝ $\frac{1}{\text{steric hindrance}}$. (Variable alkyl group)

- Reactivity ∝ $\frac{(-I)(-M)}{(+I)(+M)}$ ∝ (+ve) charge of carbonyl carbon.

Aliphatic aldehyde are more reactive than Aromatic aldehyde.

Addition of H_2O / H^+ :

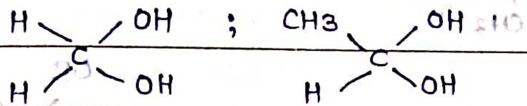


↳ unstable.

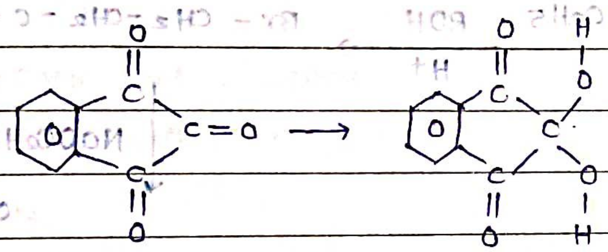
Note : If Equilibrium shifted forward direction then diol is called stable diol.

Note : Equilibrium is shifted to Backward direction.

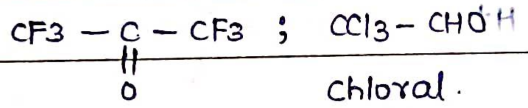
Stable Diol

① 

Reason :- Due to less steric hindrance

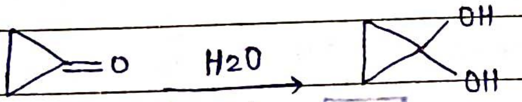
② 

stable diol. (Three C=O bonds).
Reason : Due to H-Bonding

③ 
$CF_3-\underset{\underset{O}{||}}{C}-CF_3$; CCl_3-CHO

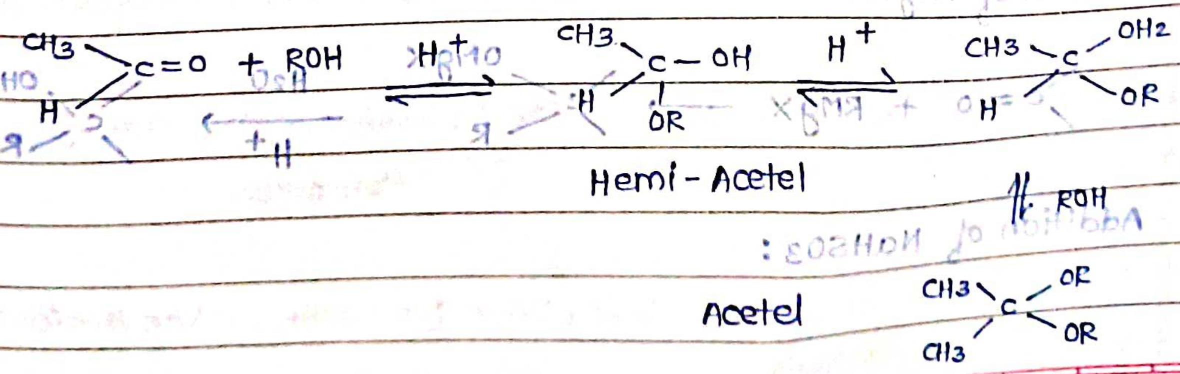
Chloral.

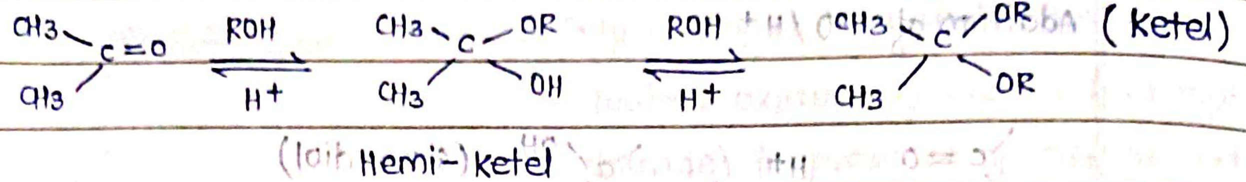
If High -I effect (X) present in α-carbon - stable diol.
Reason : Due to -I effect

④ 

If ring strain reduce during hydration - stable diol.

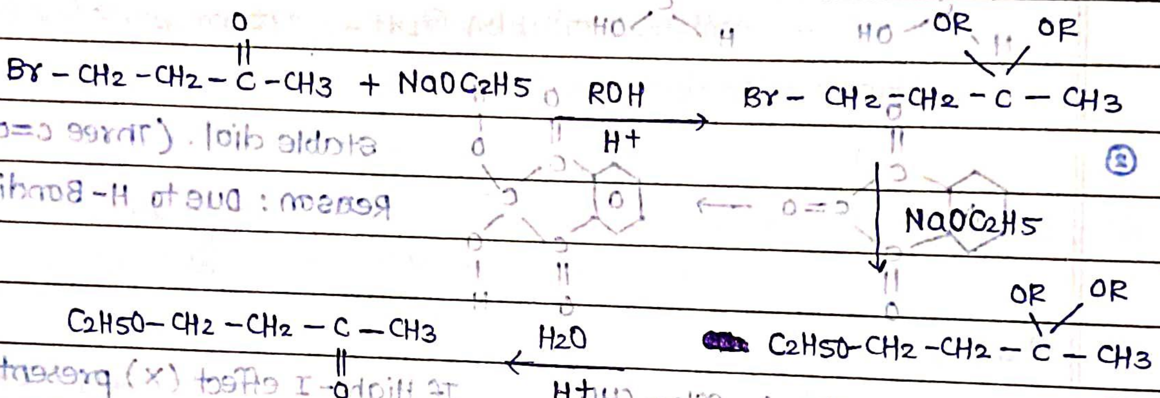
- Reaction with ROH / H^+ :

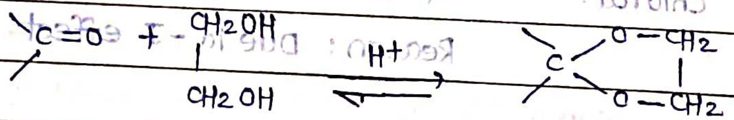


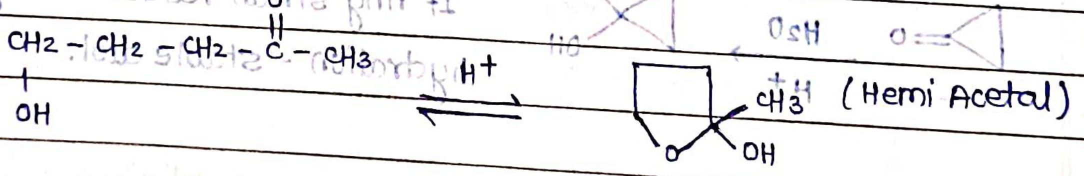


- Note: Acetal and ketel further convert in >C=O group in presence of acidic hydrolysis.
(protect group kaha jata hain Alcohol ko due to formation of Acetal and ketel.)

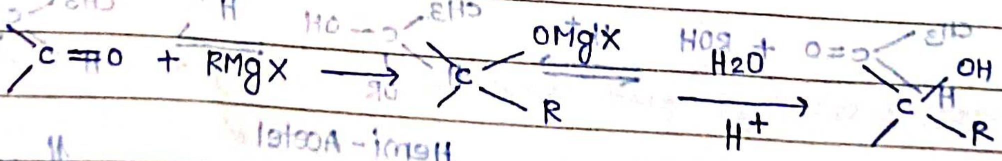
Protecting order : $\underset{CH_2SH}{\overset{CH_2SH}{|}}$ > $\underset{CH_2OH}{\overset{CH_2OH}{|}}$ > CH_3OH.

Q. 

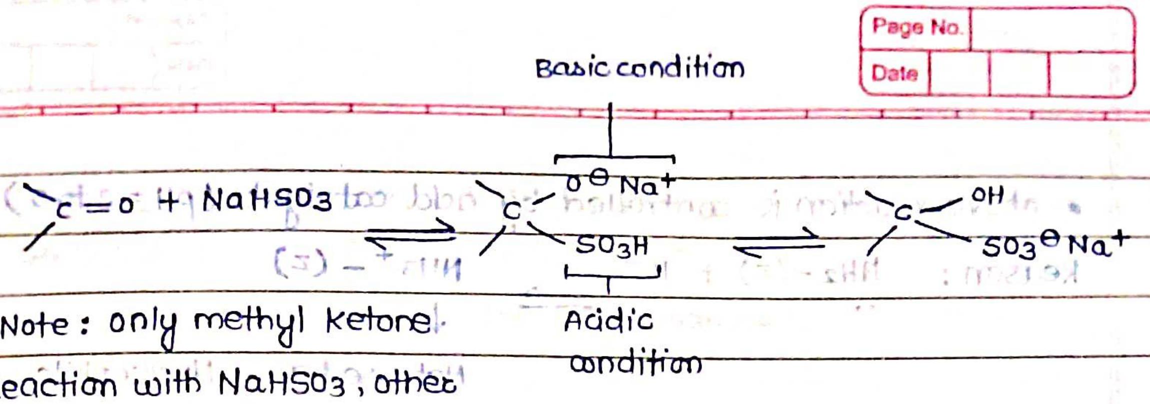
Q. 

Q. 

- Addition of RMgX :



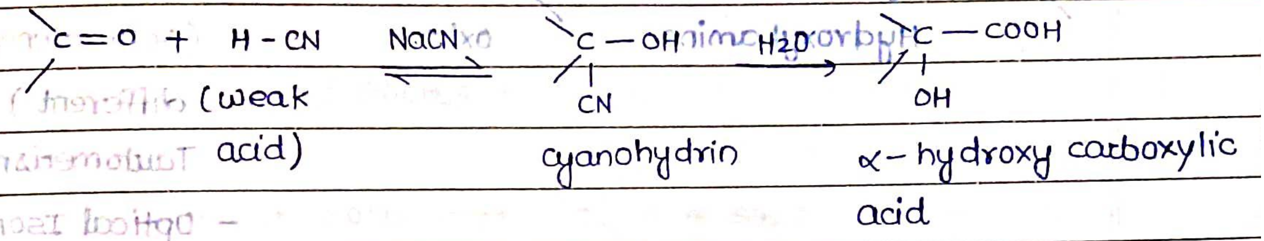
- Addition of NaHSO3 :



$>C=O + NaHSO_3 \rightleftharpoons >C(O^{\ominus}Na^{+})(SO_3H) \rightleftharpoons >C(OH)(SO_3^{\ominus}Na^{+})$

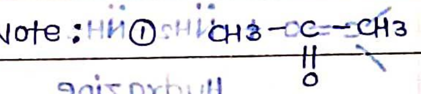
- Note : only methyl Ketone Reaction with $NaHSO_3$, other Bulky Ketone do not react.

- Addition of HCN / NaCN :

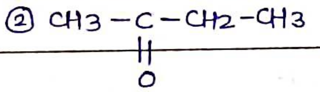


$>C=O + H-CN \underset{}{\overset{NaCN}{\rightleftharpoons}} >C(OH)(CN) \xrightarrow{H_2O} >C(OH)-COOH$

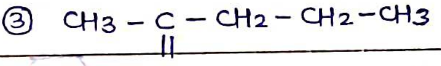
$-C\equiv N \xrightarrow[H_2O]{H^+} -COOH$

- Note : ① 

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

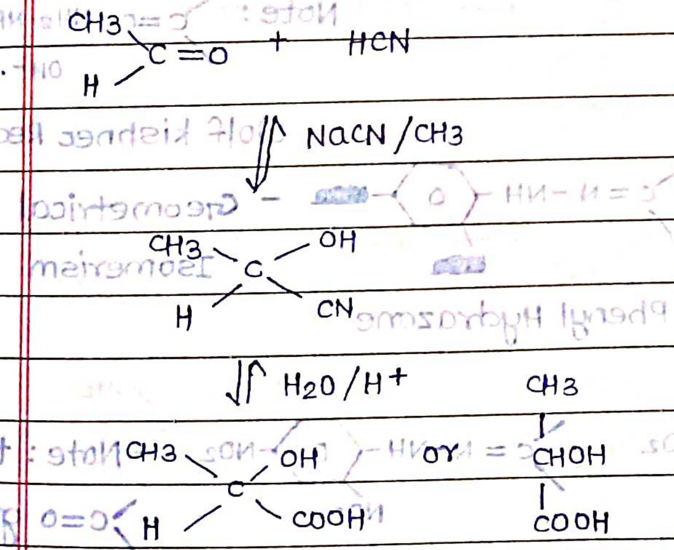
② 

$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$

③ 

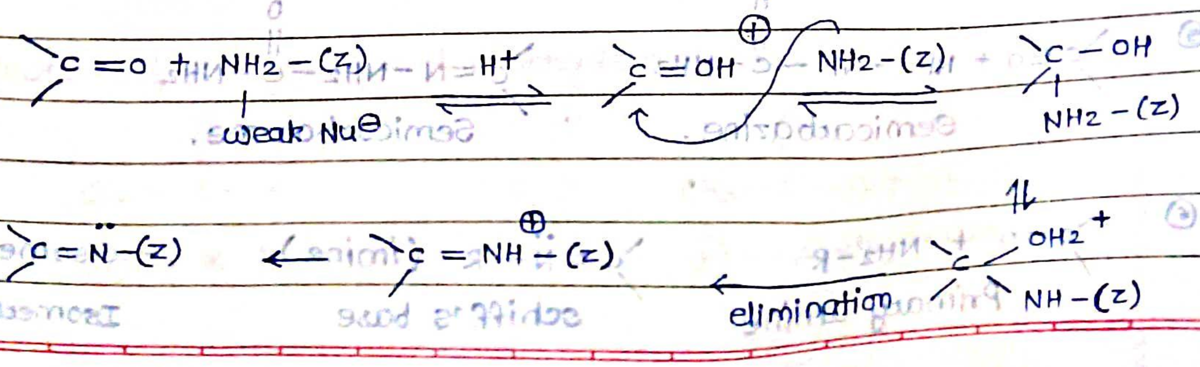
$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_3$

only react with HCN / NaOH

Q. 

$CH_3(H)C=O + HCN \xrightarrow{NaCN} CH_3(H)C(OH)(CN) \xrightarrow{H_2O/H^+} CH_3(H)C(OH)(COOH) = CH_3-CHOH-COOH$

- Nucleophilic addition - Elimination Reaction :



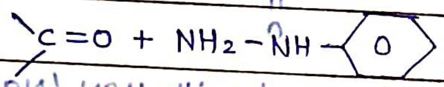
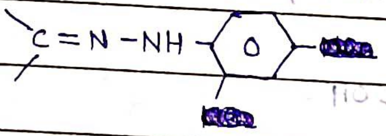
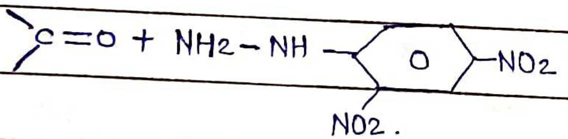
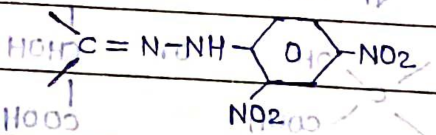
- above reaction is controlled by acid catalyst (pH = 3 to 5)

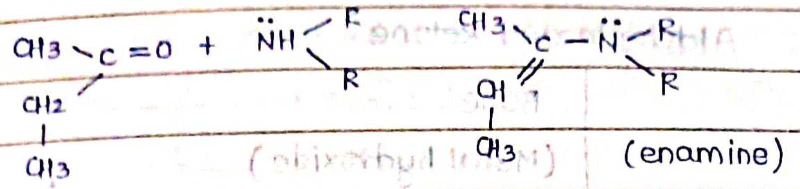
Reason : $\ddot{N}H_2-(Z) + H^+ \rightleftharpoons NH_3^+-(Z)$

↓

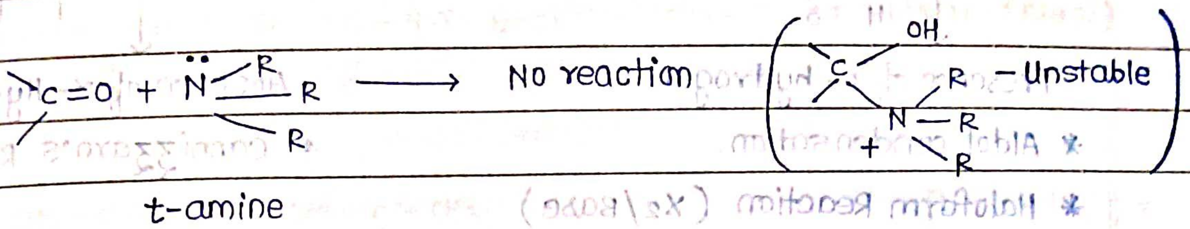
Not used as a Nucleophile.

$$>C=O + H_2-\ddot{N}-(Z) \xrightleftharpoons{H^+} >C=\ddot{N}-(Z)$$

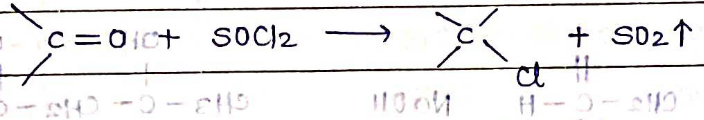
	Reagent	Product	Remark
①	$>C=O + H_2N-OH$ Hydroxylamine	$>C=\ddot{N}-OH$ (ppt) oxime	• Geometrical isomerism (Both valency of c is different) – Tautomerism – Optical Isomerism
②	$>C=O + \ddot{N}H_2-\ddot{N}H_2$ Hydrazine	$>C=\ddot{N}-NH_2$ Hydrazone	– Tautomerism – Geometrical Isomerism Note : $>C=O \xrightarrow[OH^-,\ \Delta]{NH_2-NH_2} >CH_2$ Wolf kishner Reduction.
③	 $>C=O + NH_2-NH-C_6H_5$ phenyl hydrazine	 $>C=N-NH-C_6H_5$ Phenyl Hydrazone	– Geometrical Isomerism.
④	 $>C=O + NH_2-NH-C_6H_3(NO_2)_2$ 2,4 – dinitro phenyl hydrazine (2,4 – DNP)	 $>C=N-NH-C_6H_3(NO_2)_2$ Yellow orange coloured crystal.	– Note : test of $>C=O$ group.
⑤	$>C=O + NH_2-NH-\overset{O}{\overset{\|}{C}}-NH_2$ Semicarbazine.	$>C=N-NH-\overset{O}{\overset{\|}{C}}-NH_2$ Semicarbazone.	
⑥	$>C=O + NH_2-R$ Primary amine	$>C=\ddot{N}-R$ (imine) schiff's base	(→) Geometrical Isomerism.

⑦ 

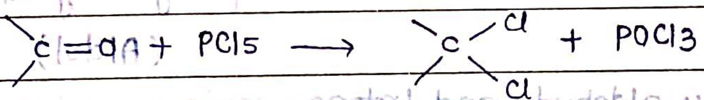
(HCHO – No reaction)

⑧ 

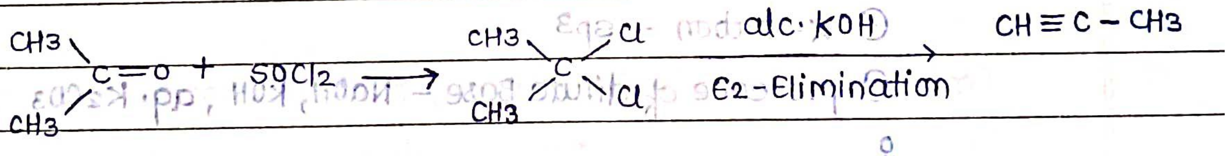
- **Addition of PCl_5 and $SOCl_2$:**

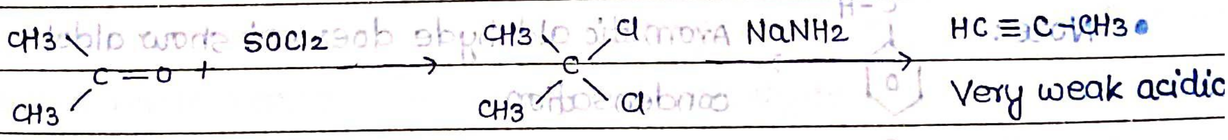


Gem dihalide



Gem dihalide

Q. 

Q. 

$\downarrow NaNH_2$

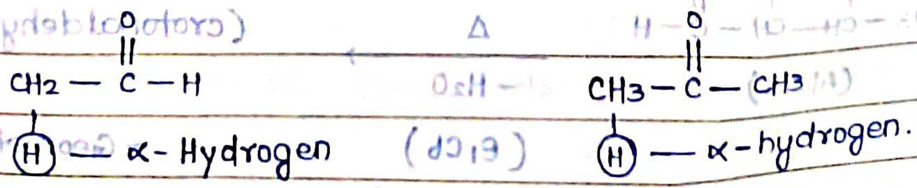
$Na^+\bar{C}\equiv C-CH_3$

Acetilyde

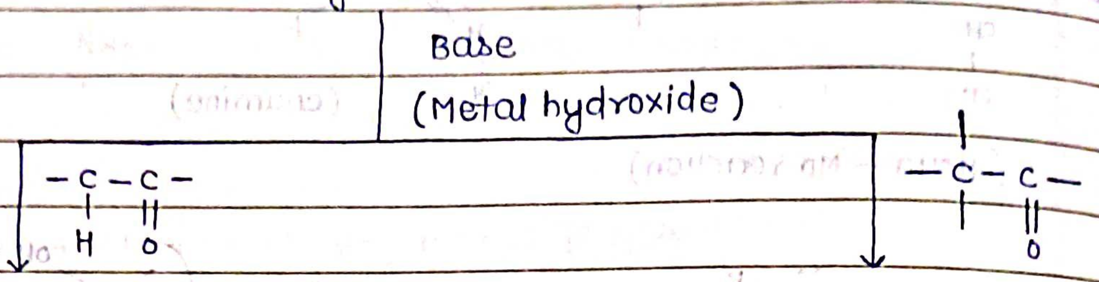
- Note : KOH — push the reaction in Backward Rxn

NaNH2 — push the reaction in Forward Rxn.

- **Reaction of α-H hydrogen of aldehyde and Ketone :**

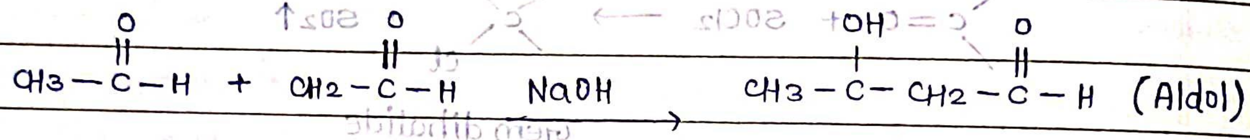


Aldehyde and ketone



Presence of α-hydrogen	Absence of α-Hydrogen
* Aldol condensation.	* Cannizzaro's Reaction
* Haloform Reaction (X_2/Base)	

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



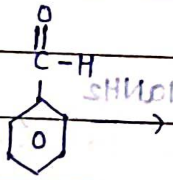
$$CH_3-\overset{O}{\overset{\|}{C}}-H + CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaOH} CH_3-\overset{OH}{\overset{|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H \text{ (Aldol)}$$

β-hydroxy aldehyde

(Aldol)

- Condition : ① only aldehyde and ketone.
  - ② having at least 1 α-hydrogen.
  - ③ α-carbon – sp^3
  - ④ presence of dilute Base – NaOH, KOH, aq. K_2CO_3

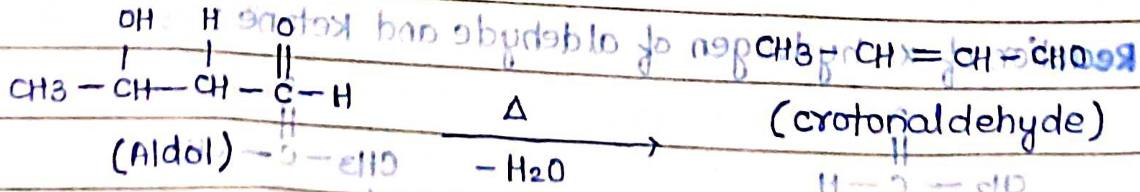
- Note:



→ Aromatic aldehyde does not show aldol condensation.

$$H-\overset{O}{\overset{\|}{C}}-H \longrightarrow ⊗$$ Due to absence of α-hydrogen

- Mech: of aldol condensation :



$$\underset{\text{(Aldol)}}{CH_3-\overset{OH}{\overset{|}{CH}}-\overset{H}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-H} \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$$

(crotonaldehyde)

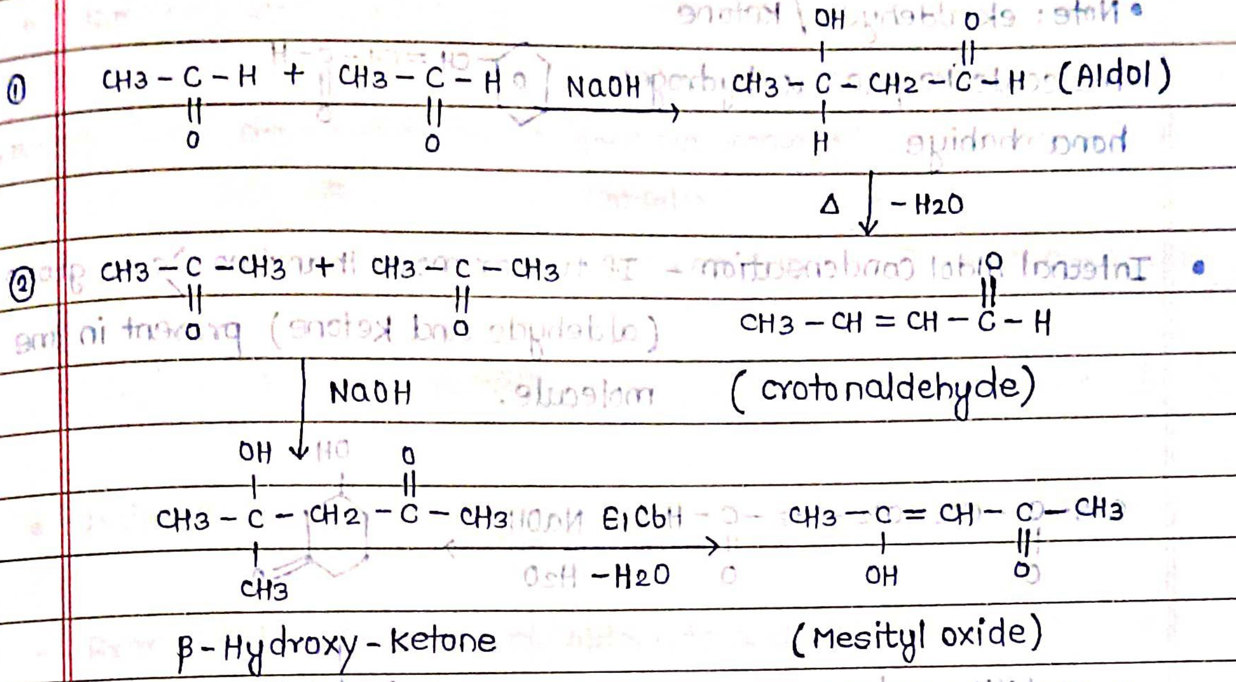
(E_1Cb)

Condensation

π Geometrical Isomerism

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

E1Cb → Poor L.G; → Strong Base



① $CH_3-\overset{O}{\underset{}{C}}-H + CH_3-\overset{O}{C}-H \xrightarrow{NaOH} CH_3-\underset{H}{\overset{OH}{C}}-CH_2-\overset{O}{C}-H$ (Aldol)

$\xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-\overset{O}{C}-H$ (crotonaldehyde)

② $CH_3-\overset{O}{C}-CH_3 + CH_3-\overset{O}{C}-CH_3 \xrightarrow{NaOH} CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2-\overset{O}{C}-CH_3$ (β-Hydroxy-Ketone)

$\xrightarrow[-H_2O]{E_1Cb} CH_3-\underset{OH}{C}=CH-\underset{O}{C}-CH_3$ (Mesityl oxide)

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

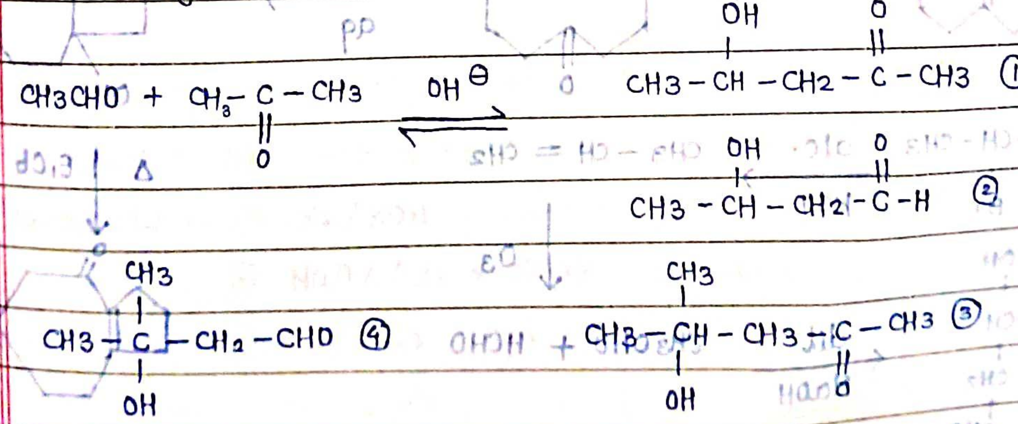
② Cross aldol condensation (claisen schmidt condensation)

a) two different aldehyde.

b) two different ketone

c) one aldehyde and one ketone

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



$CH_3CHO + CH_3-\underset{O}{C}-CH_3 \underset{}{\overset{OH^\ominus}{\rightleftharpoons}} CH_3-\overset{OH}{CH}-CH_2-\overset{O}{C}-CH_3$ ①

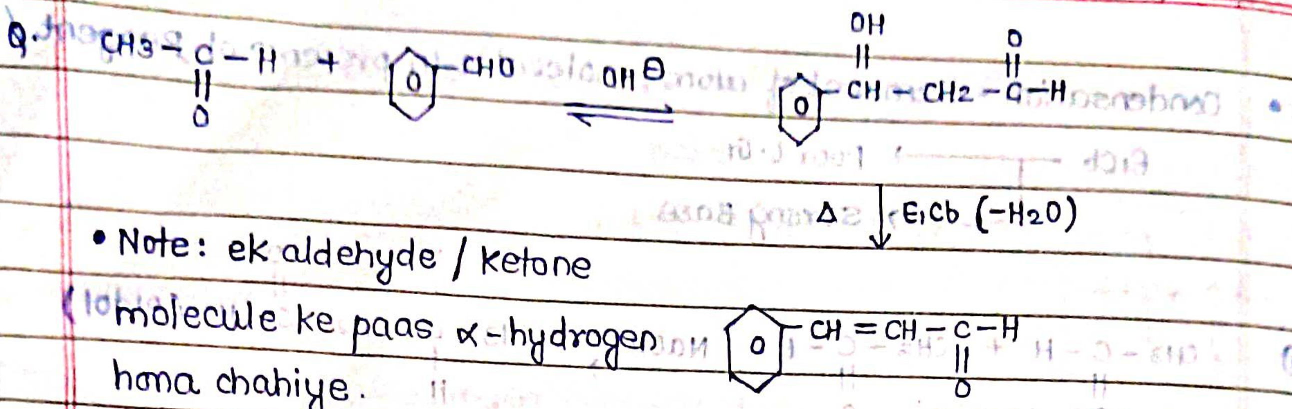
$CH_3-\overset{OH}{CH}-CH_2-\overset{O}{C}-H$ ②

$CH_3-\underset{OH}{\overset{CH_3}{CH}}-CH_3-\underset{O}{C}-CH_3$ ③

$\downarrow \Delta$

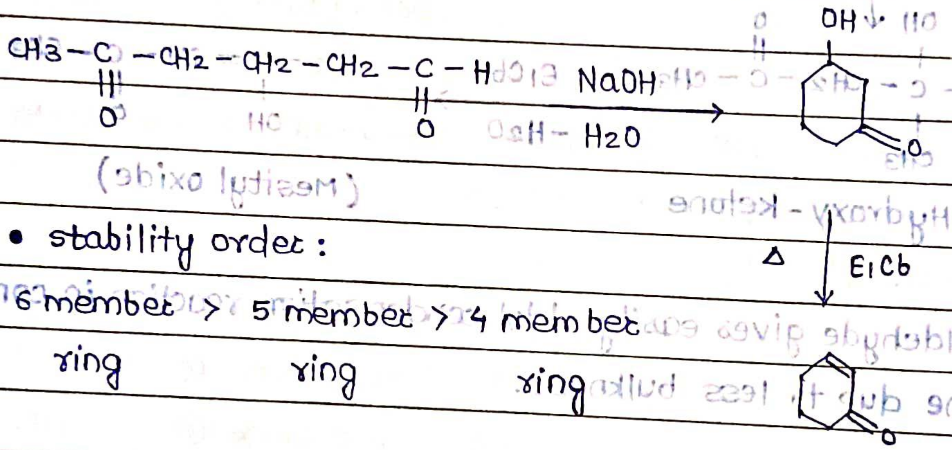
$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2-CHO$ ④

Δ Q.



- Note: ek aldehyde / ketone molecule ke paas α-hydrogen hona chahiye.

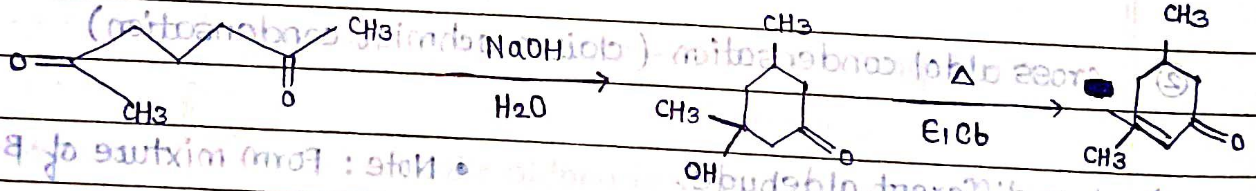
- Internal Aldol Condensation – If two or more than two >C=O group (aldehyde and ketone) present in one molecule.



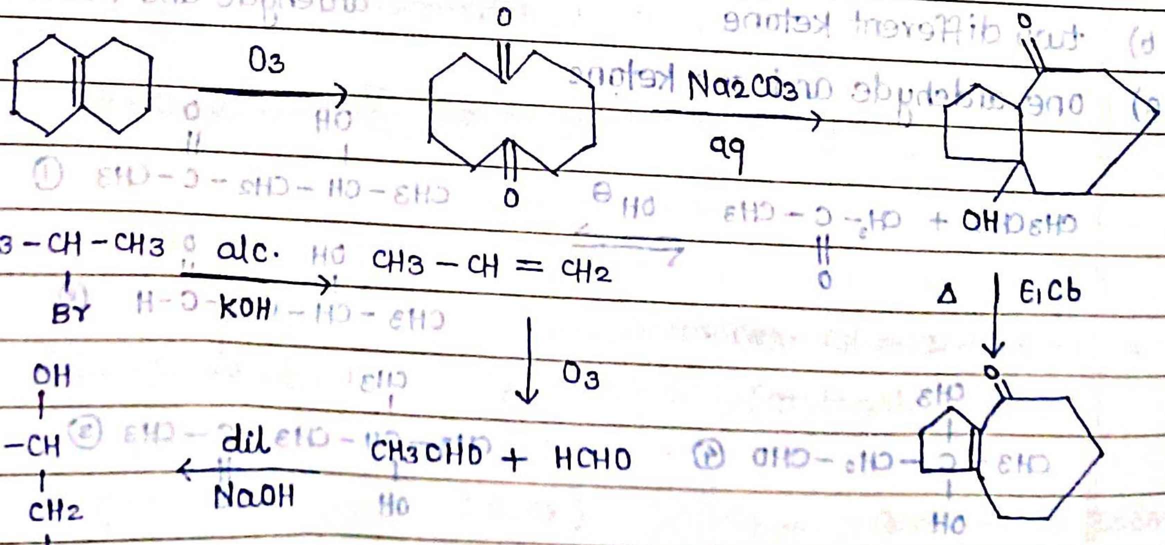
- stability order :

6 member ring > 5 member ring > 4 member ring

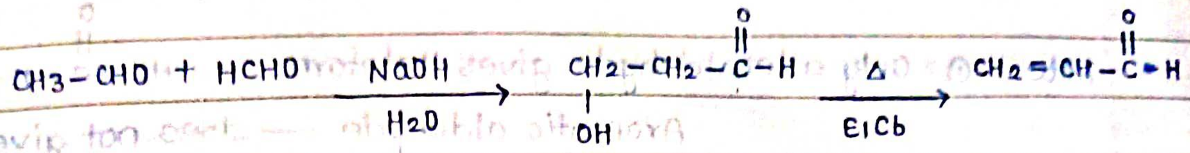
Q.



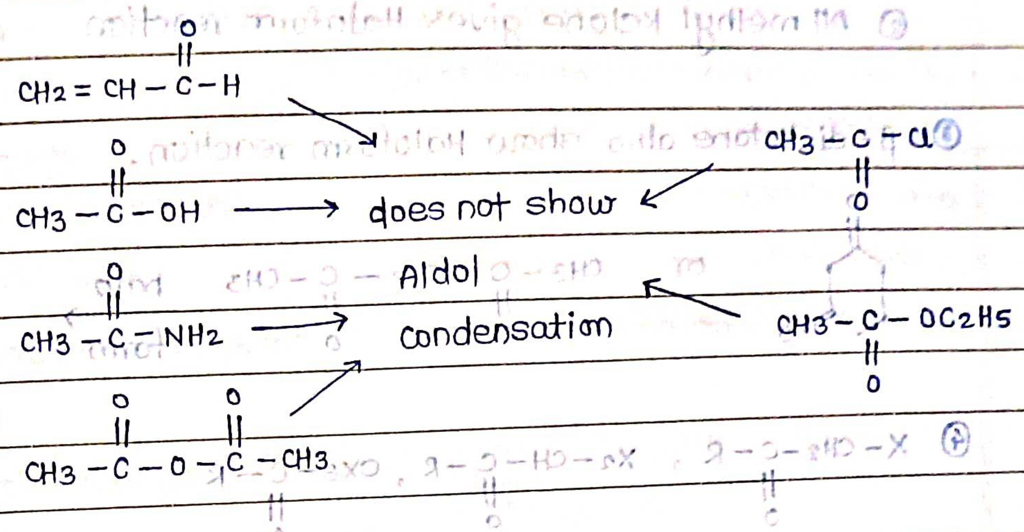
Q.



Q. $CH_3-\underset{Br}{CH}-CH_3 \xrightarrow[KOH]{alc.} CH_3-CH=CH_2 \xrightarrow{O_3} CH_3CHO + HCHO \xrightarrow[NaOH]{dil} CH_3-\overset{OH}{CH}-CH_2-CHO$

Q. 

$$CH_3-CHO + HCHO \xrightarrow[H_2O]{NaOH} \underset{OH}{\underset{|}{CH_2}}-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[E_1Cb]{\Delta} CH_2=CH-\overset{O}{\overset{\|}{C}}-H$$

- Note : 

$CH_2=CH-\overset{O}{\overset{\|}{C}}-H$ → Aldol condensation

$CH_3-\overset{O}{\overset{\|}{C}}-OH \longrightarrow$ does not show

$CH_3-\underset{O}{\underset{\|}{C}}-Cl$ → does not show

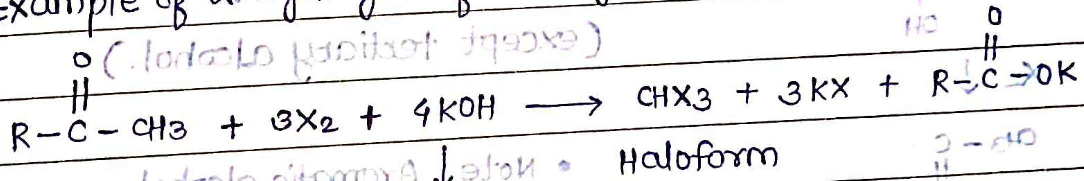
$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \longrightarrow$ Aldol condensation

$CH_3-\underset{O}{\underset{\|}{C}}-OC_2H_5$ → Aldol condensation

$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$ → Aldol condensation

- Haloform Reaction :

- Example of α-hydrogen of Aldehyde and Ketone :



$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3X_2 + 4KOH \longrightarrow CHX_3 + 3KX + R-\overset{O}{\overset{\|}{C}}-OK$$

Haloform

↓ Strong Base.
(concentrated Base)

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

- Only those aldehyde and ketone show haloform rxn which have $CH_3-\underset{O}{\underset{\|}{C}}-$ group (Acetyl group)

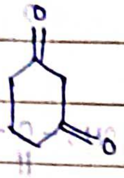
- total no. of mole of Base used in haloform rxn = 4 mole.
- X_2 used in rxn → 3 mole.
- Reagents — ① X_2/KOH ⟶ $X_2 + OH^- \longrightarrow X^{\ominus} + XO_3^{\ominus}$
  ② $NaOX / Cl_2 + NaOH \longrightarrow NaCl + NaClO_3 + H_2O$
  ③ $KI/KIO_3 \longrightarrow$ ∞.

Note: ① Only acetaldehyde gives Haloform. $CH_3-\overset{O}{\overset{\|}{C}}-H$

Aromatic aldehyde — does not give.

② All methyl ketone gives Haloform reaction. $CH_3-\underset{O}{\underset{\|}{C}}-R$

③ β-di ketone also show Haloform reaction.



or $CH_3-\underset{O}{\underset{\|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-CH_3 \xrightarrow[\text{form}]{\text{halo}} CH_3-\underset{O}{\underset{\|}{C}}-OK + CX_3-\underset{O}{\underset{\|}{C}}-CH_3$.

④ $X-CH_2-\underset{O}{\underset{\|}{C}}-R$, $X_2-CH-\underset{O}{\underset{\|}{C}}-R$, $CX_3-\underset{O}{\underset{\|}{C}}-R$

(✓) (✓) (✓)

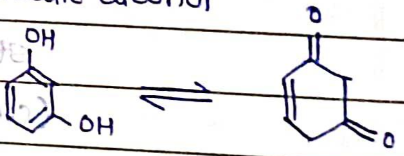
⑤ $CH_3-\underset{OH}{\underset{|}{CH}}$ (2-ol) — gives haloform reaction.

(except tertiary alcohol.)

$\downarrow X_2$

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

- Note: Aromatic alcohol



Resolcinol

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

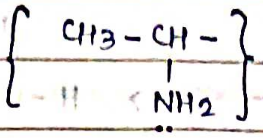
⑦ 2' alcohol – all secondary alcohol which have $\left(CH_3-\underset{OH}{\underset{|}{CH}}-\right)$ condition.

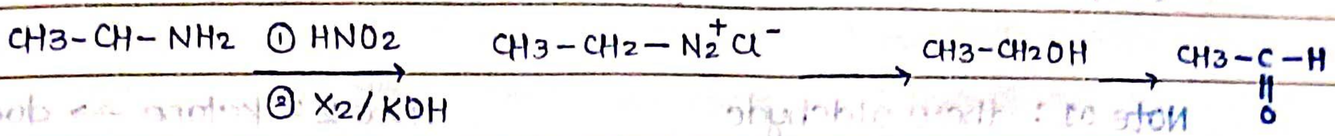
⑧ 1' alcohol - does not show haloform reaction.

⑨ $CH_3-\overset{X}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-$; $CH_3-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}$; $CH_3-\overset{OH}{\overset{|}{\underset{OH}{\underset{|}{C}}}}$

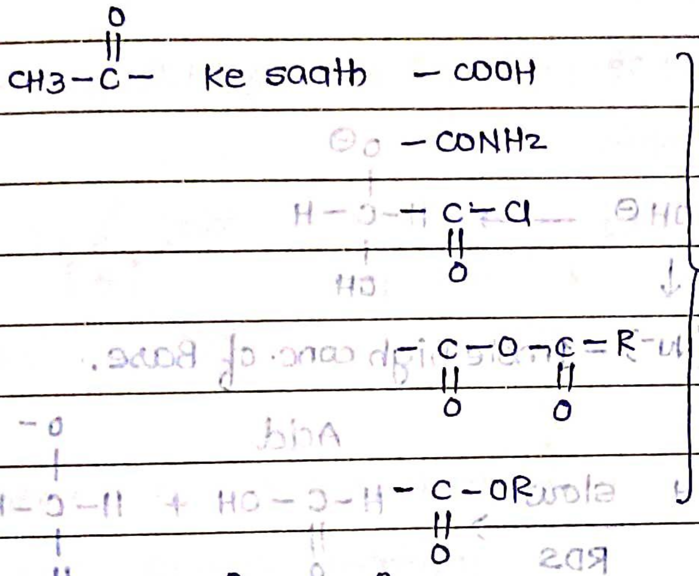
(✓) (✓) (✓)

⑩ **Amine :** Amine show haloform reaction in presence of HNO_2 $(NaNO_2/HCl)$

condition :

$$\left\{\begin{matrix} CH_3-\underset{|}{CH}- \\ -H \quad \ddot{N}H_2 \end{matrix}\right\}$$

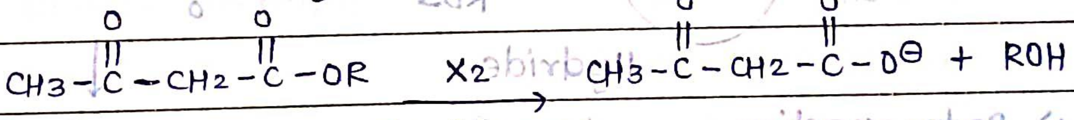

$$CH_3-CH-NH_2 \xrightarrow[\text{② } X_2/KOH]{\text{① } HNO_2} CH_3-CH_2-N_2^+Cl^- \longrightarrow CH_3-CH_2OH \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-H$$

⑪ Note : (-ve haloform test)


$$CH_3-\overset{\overset{O}{\|}}{C}- \text{ ke saath } -COOH$$
$$-CONH_2$$
$$\underset{\underset{O}{\|}}{C}-Cl$$
$$-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}=R$$
$$-\underset{\underset{O}{\|}}{C}-OR$$

-ve haloform test

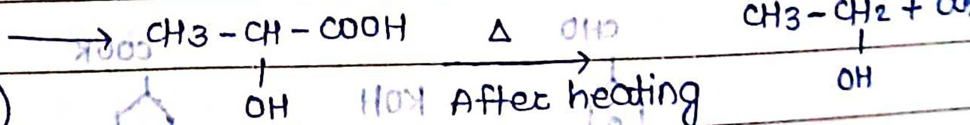
- good leaving group

- Note :

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OR \xrightarrow[OH]{X_2} CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-O^{\ominus} + ROH$$

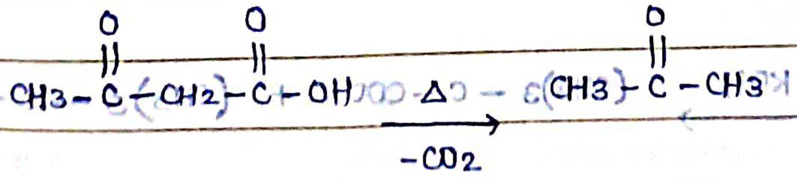
(exception : ethyl ester only gives haloform test)

- Note :

lactic acid
(β-keto-acid)

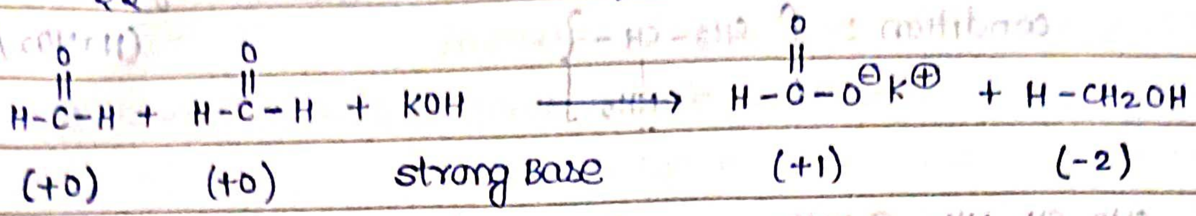

$$\longrightarrow CH_3-\underset{\underset{OH}{|}}{CH}-COOH \xrightarrow[\text{After heating}]{\Delta} CH_3-\underset{\underset{OH}{|}}{CH_2} + CO$$

show haloform test (rxn)


$$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[-CO_2]{\Delta} (CH_3)-\overset{\overset{O}{\|}}{C}-CH_3$$

Nahi dega but after heating dega Haloform RxD
(Iodoform test)

- Cannizzaro's Reaction (absence of α-Hydrogen).

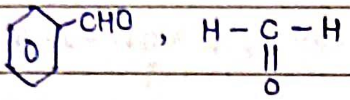


$$H-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H + KOH \longrightarrow H-\overset{O}{\overset{\|}{C}}-O^{\ominus}K^{\oplus} + H-CH_2OH$$

(+0) (+0) strong Base (+1) (-2)

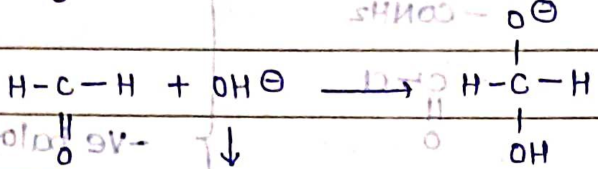
Note 01 : these aldehyde gives cannizzaro's rxn - absence of α-hydrogen ho.

Note 2 : ketone → does not show Cannizzaro's Rxn.



$$H-\underset{O}{\underset{\|}{C}}-H$$

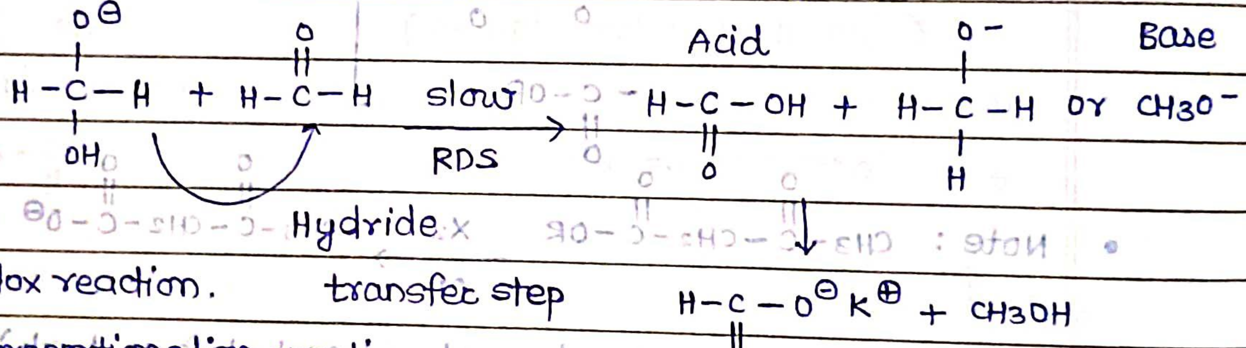
Mech: ①



$$H-\underset{O}{\underset{\|}{C}}-H + OH^{\ominus} \longrightarrow H-\overset{O^{\ominus}}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-H$$

(Nu^-) - 1mole high conc. of Base.

②



$$H-\overset{O^{\ominus}}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-H + H-\overset{O}{\overset{\|}{C}}-H \xrightarrow[RDS]{slow} \overset{Acid}{H-\underset{O}{\underset{\|}{C}}-OH} + \overset{Base}{H-\overset{O^-}{\overset{|}{\underset{H}{\underset{|}{C}}}}-H \text{ or } CH_3O^-}$$

Hydride transfer step

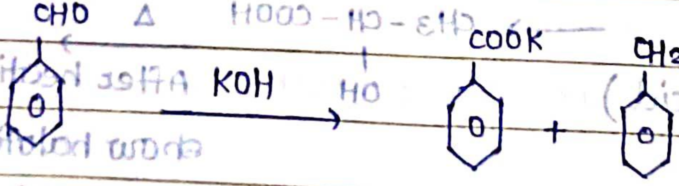
$$\downarrow$$

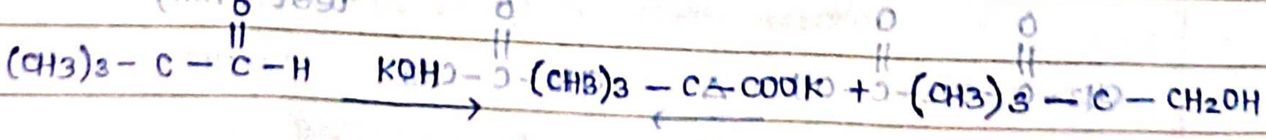
$$H-\underset{O}{\underset{\|}{C}}-O^{\ominus}K^{\oplus} + CH_3OH$$

1> Redox reaction.

2> Disproportionation reaction

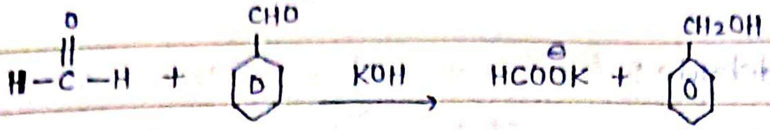
3> Oxidation no. change $\begin{bmatrix} 0 \rightarrow +1 \\ 0 \rightarrow -2 \end{bmatrix}$





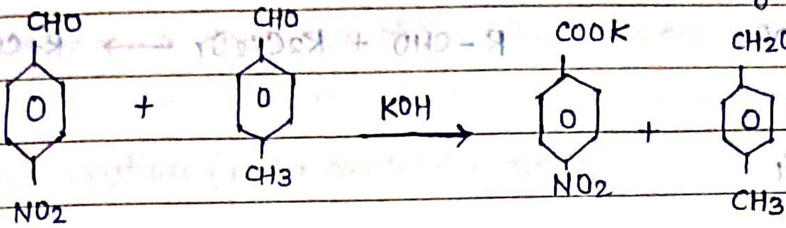
$$(CH_3)_3-C-\overset{O}{\overset{\|}{C}}-H \xrightarrow{KOH} (CH_3)_3-C-COOK + (CH_3)_3-C-CH_2OH$$

- Cross cannizzaro's Reaction (Using two different aldehydes)

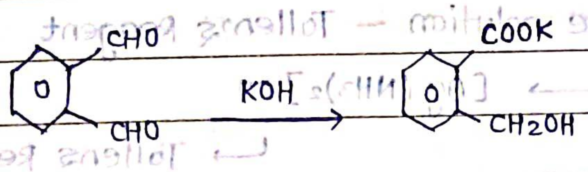


Note-01: Jis pr OH attack hoga woh acid mein convert hoga.

Note 02: OH will attack on
① less hindrance side
② High +ve charge in $-\overset{O}{\overset{\|}{C}}-$ carb



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



- Note : 1) $CX_3-\overset{O}{\overset{\|}{C}}-H$; $Ph_3C-\overset{O}{\overset{\|}{C}}-H$ ←—— does not show cannizzaro's reaction due to good L.G nature of $C^{\ominus}X_3$ and $C^{\ominus}Ph_3$.

shows haloform Reaction.

- $$CH_3-\underset{CH_3}{\underset{|}{CH}}-CHO \xrightarrow{KOH} CH_3-\underset{CH_3}{\underset{|}{CH}}-COOK + CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2OH.$$

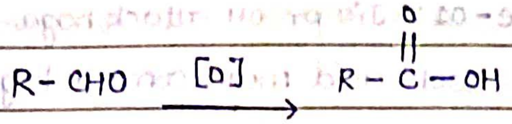
- Oxidation of Aldehyde and ketone :

$R-CHO \xrightarrow{[O]} R-\overset{O}{\overset{\|}{C}}-OH$ ⟶ easily oxidise by strong oxidising agent and also ←— mild oxidising agent.

$\begin{matrix}R \\ R\end{matrix}\!\!>C=O \xrightarrow{[O]}$ easily does not oxidise, only oxidise by strong oxidising agent.

- Oxidation of Aldehyde :

a) Strong oxidising agent :


$R-CHO \xrightarrow{[O]} R-\overset{O}{\overset{\|}{C}}-OH$

- acidic $K_2Cr_2O_7$
- Acidic $KMnO_4$ $R-CHO + K_2Cr_2O_7 \longrightarrow R-COOH + Cr^{+3}$
- conc. HNO_3
- conc. H_2SO_4

b) Tollen's Reagent (mild oxidising agent)

Ammonical silver nitrate solution — Tollen's Reagent

$AgNO_3 + NH_4OH \longrightarrow [Ag(NH_3)_2]OH$

↳ Tollens Reagent (Ag_2O)

P-Block

① Zinconia + $NH_4OH \longrightarrow M(OH)_x \xrightarrow[\text{excess}]{NH_4OH} [M(NH_3)_y]^{\pm n}$

salt ppt soluble in solution

② Female + $NH_4OH \longrightarrow M(OH)_x \xrightarrow[\text{excess}]{NH_4OH}$ No Reaction.

Salt ppt

- Zn — Zn^{+2} Fe — Fe^{+3}, Fe^{+2}

Co — Co^{+3}, Cu^{+2}, Cd^{+3} Mn : Mn^{+2}

Ni — Ni^{+2} Al — Al^{+3}

a — Ag^+

① $ZnSO_4 + NH_4OH \longrightarrow Zn(OH)_2 \xrightarrow[\text{excess}]{NH_4OH} [Zn(NH_3)_4]SO_4$

ppt Soluble.

(white ppt)

② $FeSO_4 + NH_4OH \longrightarrow \downarrow Fe(OH)_2 \xrightarrow[\text{excess}]{NH_4OH}$ No Reaction

ppt

- $R-CHO + Ag_2O \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^{\ominus} + Ag^0 + H_2O$

Tollen's Reagent — Acid Salt — (mirror)

$\xrightarrow[H^+]{H_2O} R-\underset{O}{\underset{\|}{C}}-OH$

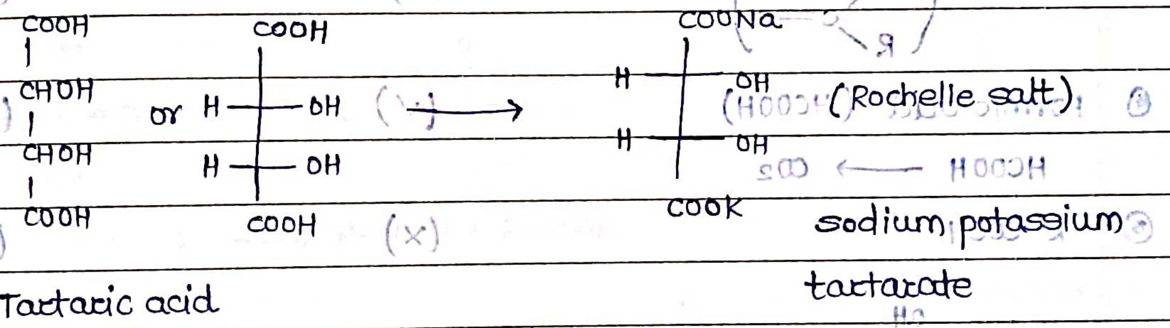
- silver mirror test

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

c) Fehling solution (mild oxidising agent)

Fehling solution 'A' — Alkali $CuSO_4$ → $CuSO_4 + NaOH \rightarrow Cu(OH)_2 + Na_2SO$

Fehling solution 'B' — Sodium potassium tartarate (Rochelle salt)

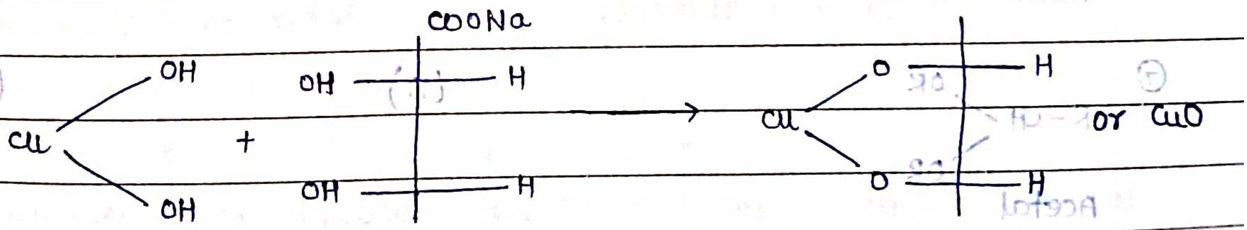


Tartaric acid

(Rochelle salt)

sodium potassium tartarate

equal amount — Feh ① + Feh ②



Feh ①

Feh ②

Deep-Blue solution

$R-CHO + CuO \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^{\ominus} + Cu_2O$

(+2) (+1)

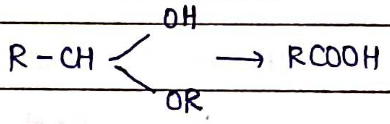
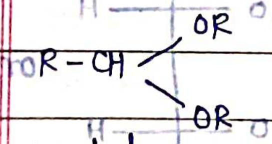
Deep Blue colour — Reddish Brown colour.

d) Bendict's solution

Bendict's sol - ⓪① — alkali $CuSO_4$

Bendict's sol - ⓪② — sodium potassium citrate

Work + similar to Fehling solution

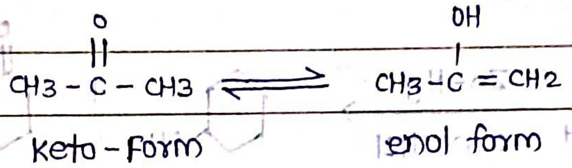
Molecules	Tollen's Reagent	Fehling Solution
① Aliphatic aldehyde (R-CHO) $RCHO \longrightarrow R\text{-}COO^{\ominus}$	(✓)	(✓)
② Aromatic aldehyde (Ar-CHO) $ArCHO \longrightarrow ArCOO^{\ominus}$	(✓)	(×)
③ Ketone 	(×)	(×)
④ Formic acid (HCOOH) $HCOOH \longrightarrow CO_2$	(✓)	(✓)
⑤ R-COOH	(×)	(×)
⑥  Hemi-acetal	(✓)	(✓)
⑦  Acetal	(×)	(×)
⑧ Carbohydrates (Mono-saccharides) (having hemi-acetal form)	(✓)	(✓)

- Oxidation of ketones:

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

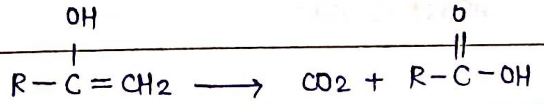
- Ketone only oxidise by strong oxidising agent.
  ① acidic $KMnO_4$
  ② acidic $K_2Cr_2O_7$
  ③ conc. HNO_3.
  ④ conc. H_2SO_4.

- popoff's Rule:

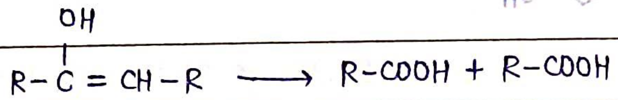


$$\underset{\text{Keto-Form}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} \rightleftharpoons \underset{\text{enol form}}{CH_3-\overset{OH}{\overset{|}{C}}=CH_2}$$

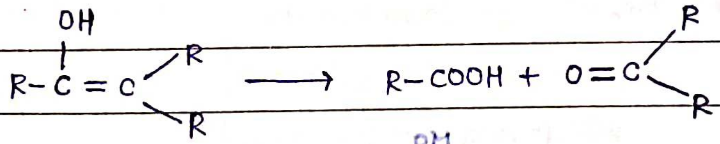
(more hindrance side)



$$R-\overset{OH}{\overset{|}{C}}=CH_2 \longrightarrow CO_2 + R-\overset{O}{\overset{\|}{C}}-OH$$

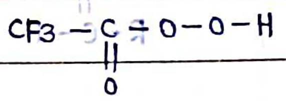


$$R-\overset{OH}{\overset{|}{C}}=CH-R \longrightarrow R-COOH + R-COOH$$

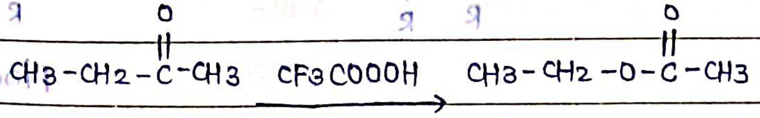


$$R-\overset{OH}{\overset{|}{C}}=C\begin{matrix}R\\R\end{matrix} \longrightarrow R-COOH + O=C\begin{matrix}R\\R\end{matrix}$$

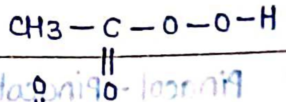
- Baeyer Villiger oxidation ⟶ peroxide — H_2SO_5



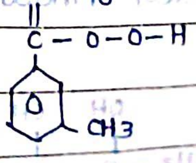
$$CF_3-\underset{O}{\underset{\|}{C}}-O-O-H$$



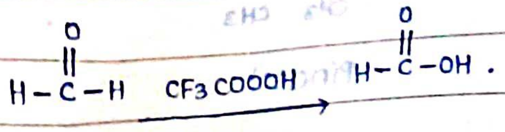
$$\underset{\text{Ketone}}{CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow{CF_3COOOH} \underset{\text{ester}}{CH_3-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3}$$



$$CH_3-\underset{O}{\underset{\|}{C}}-O-O-H$$



- oxygen atom insert on more hindrance side.
- only ketone oxidise.
- No Aldehyde oxidation except:



$$H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{CF_3COOOH} H-\overset{O}{\overset{\|}{C}}-OH.$$

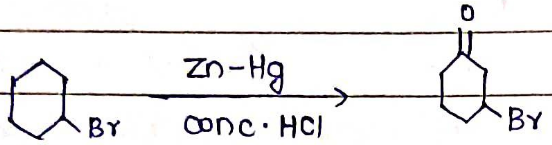
- Reduction of Aldehyde and ketone :

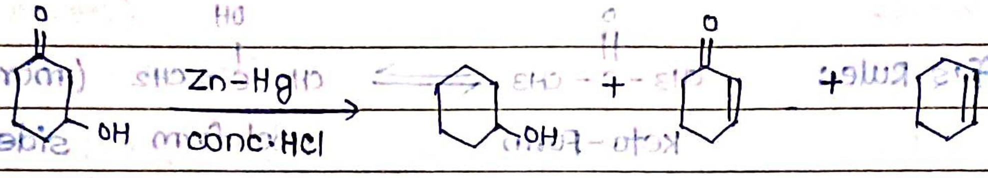
a) $>C=O$ (carbonyl group) ⟶ $>CH_2$ (Methylene group)

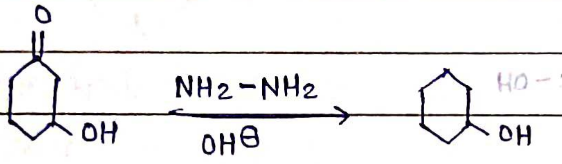
① — H_2 / Red P — 150°C

② — Zn/Hg – conc. HCl — Clemmensen Reduction — { Note: ⊗ O-atom, Alcohol, Ether }

③ — NH_2-NH_2 / $OH^\ominus$ — Wolf's kishner Reduction — { ⊗ −X, − Good L.G }

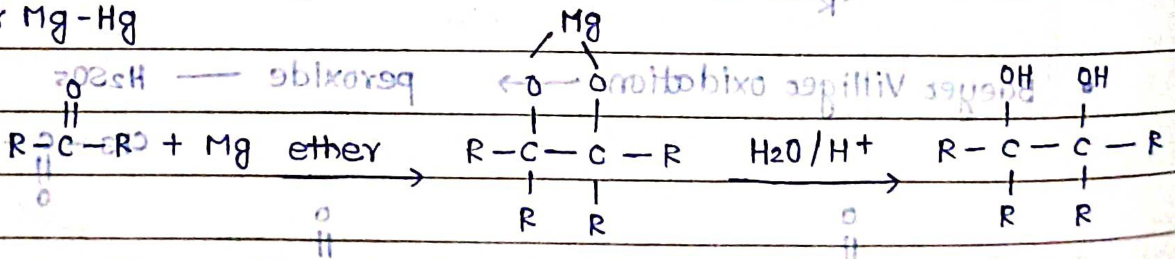






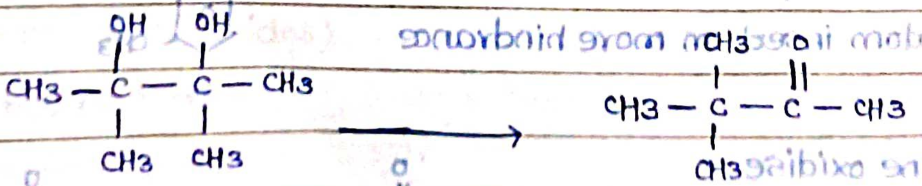
- Reduction of ketone :

(a) Mg or Mg-Hg



Pinacol.

- Pinacol – Pinacolone Rearrangement : – in presence of Acid / Lewis acid

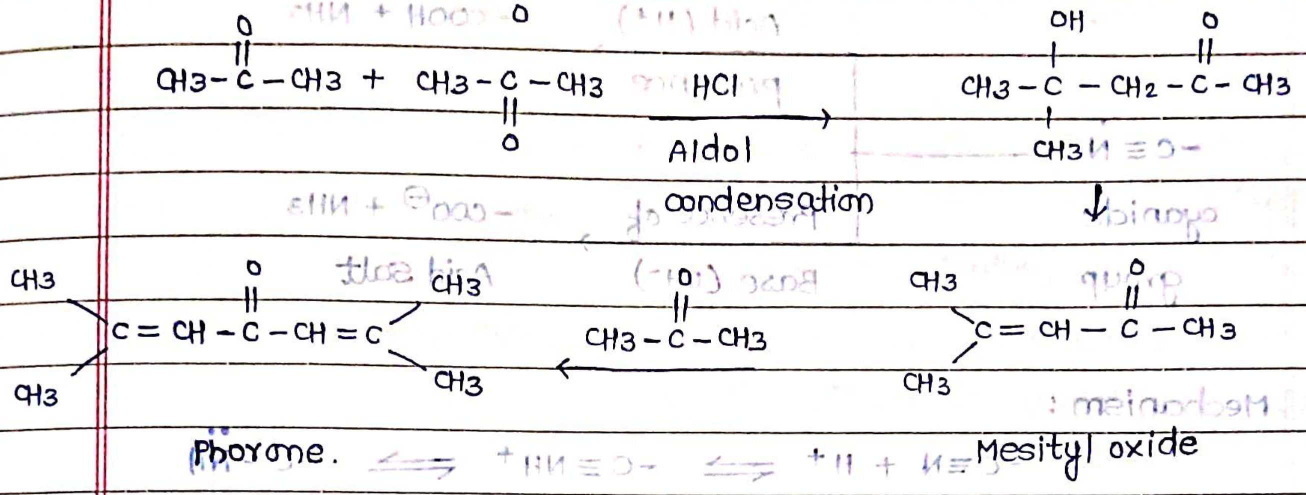


Pinacol   Pinacolone

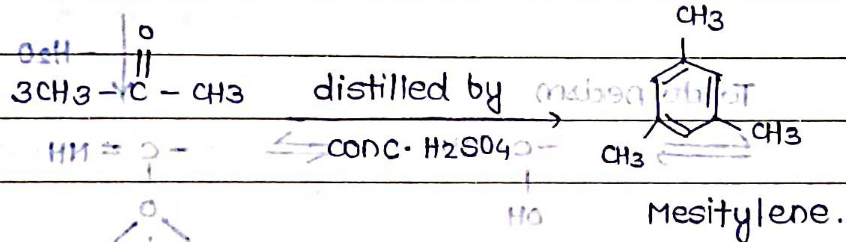
Note: only ketone reduce in presence of Mg. Aldehyde – ⊗

- Condensation :

- Condensation of $CH_3-\underset{\overset{\|}{O}}{C}-CH_3$ (Acetone)

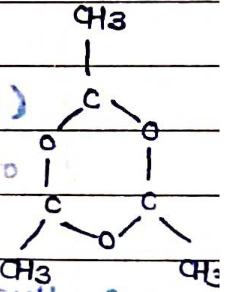


- $3CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ distilled by conc. H_2SO_4



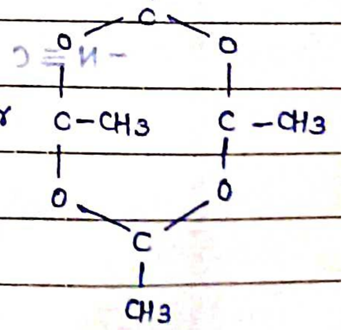
- Condensation of CH_3CHO.

CH_3CHO — Room temp, Drop by drop, distilled by conc. H_2SO_4 → $3CH_3CHO \rightleftharpoons (CH_3CHO)_3$ or



para-aldehyde

CH_3CHO — $-10°C$, conc. H_2SO_4 → $4CH_3CHO \rightleftharpoons (CH_3CHO)_4$ or



Metaldehyde

- Condensation of HCHO :

HCHO — Dry HCl, Room Temp → $3HCHO \rightleftharpoons (HCHO)_3$ para-aldehyde.

HCHO — Dry HCl, low temp → $4HCHO \rightleftharpoons (HCHO)_4$ Meta-aldehyde

Carboxylic acid

- **Method of Preparation :**

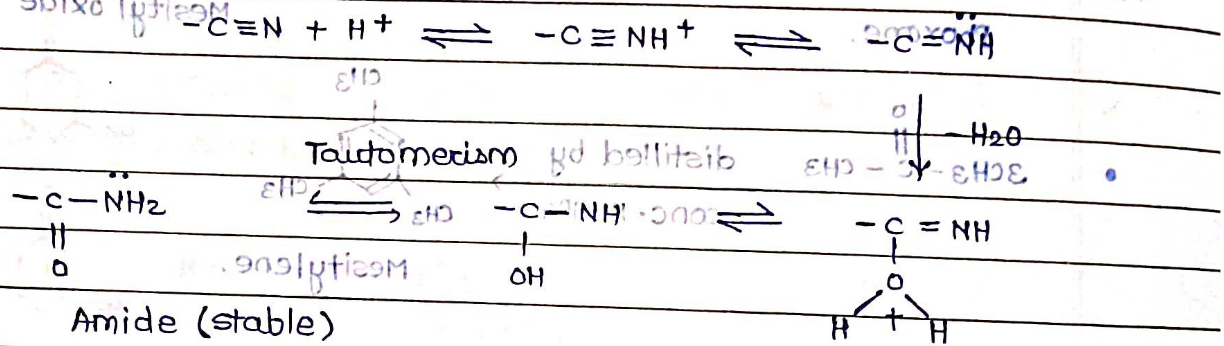
① Hydrolysis of cyanide group :

$-C\equiv \ddot{N}$ (cyanide group)

Acid (H^+) presence: $-C\equiv \ddot{N} \rightarrow -COOH + \ddot{N}H_3$

Presence of Base (OH^-): $-C\equiv \ddot{N} \rightarrow -COO^{\ominus} + NH_3$ (Acid Salt)

- **Mechanism :**



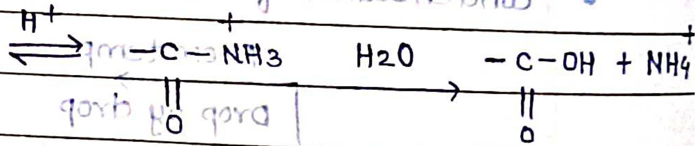
$-C\equiv N + H^+ \rightleftharpoons -C\equiv NH^+ \rightleftharpoons -\overset{+}{C}=\ddot{N}H$

$\downarrow H_2O$

$-C(=NH)-\overset{+}{O}H_2 \rightleftharpoons -C(OH)=NH \underset{\text{Tautomerism}}{\rightleftharpoons} -C(=O)-\ddot{N}H_2$

Amide (stable)

(in case of partial hydrolysis of −CN(group) amide forms)

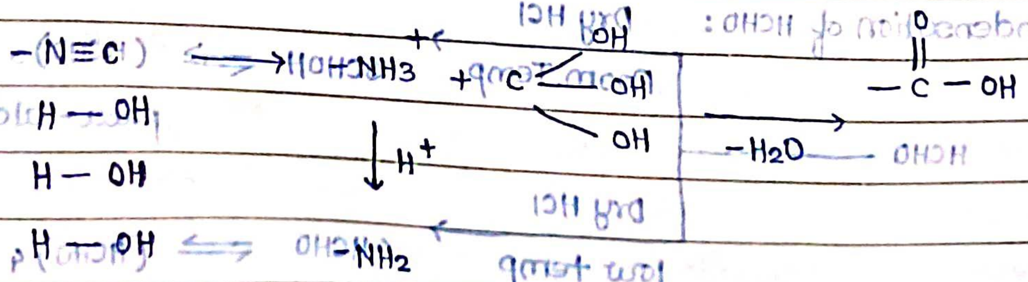


$\xrightarrow{H^+} -C(=O)-\overset{+}{N}H_3 \xrightarrow{H_2O} -C(=O)-OH + NH_4^+$

- **Hydrolysis of −NC group (iso-cyanide)**

$-N\equiv C \xrightarrow[H_2O]{H^+} -\ddot{N}H_2 + HCOOH$ (primary amine)

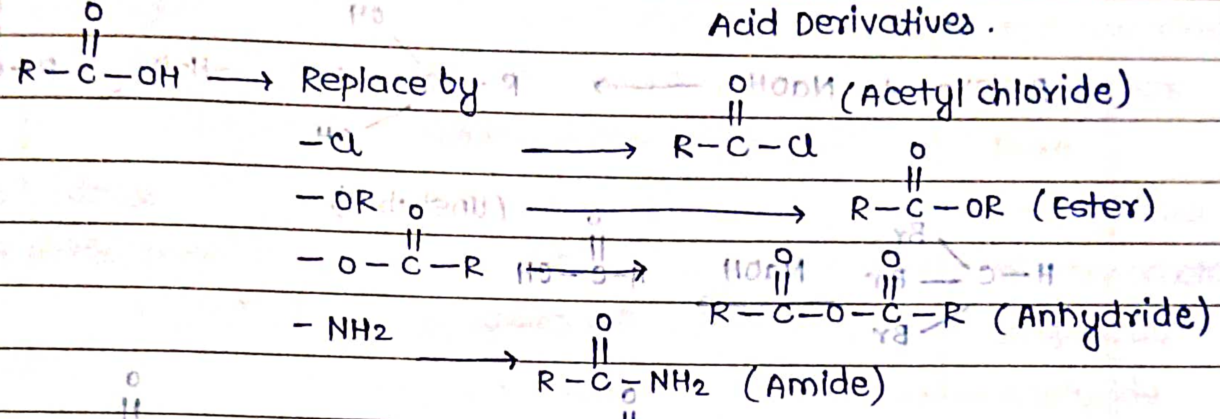
$-N\equiv C \xrightarrow[H_2O]{OH^{\ominus}} -\ddot{N}H_2 + HCOO^{\ominus}$



$-(N\equiv C) \;\; \begin{matrix} H-OH \\ H-OH \end{matrix} \longrightarrow -NH_3^+ + C(OH)_3 \xrightarrow{-H_2O} -C(=O)-OH$

$-NH_3^+ \xrightarrow{H^+} -NH_2$

(c) **Hydrolysis of Acid derivative:**



Acid Derivatives.

$R-\overset{O}{\overset{\|}{C}}-OH \longrightarrow$ Replace by

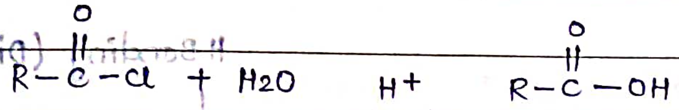
$-Cl \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl$ (Acetyl chloride)

$-OR \longrightarrow R-\overset{O}{\overset{\|}{C}}-OR$ (Ester)

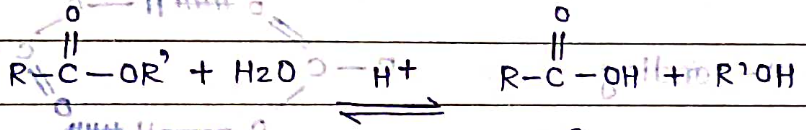
$-O-\overset{O}{\overset{\|}{C}}-R \longrightarrow R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ (Anhydride)

$-NH_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2$ (Amide)

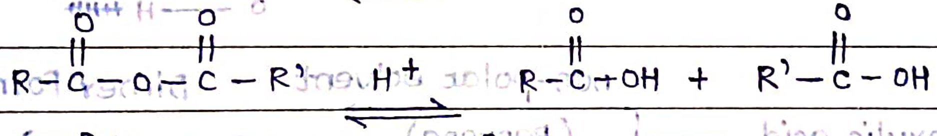
- Acid Derivatives — those components which gives carboxylic acid in direct hydrolysis.

① 

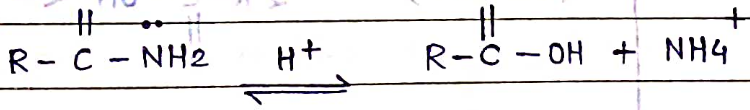
$R-\overset{O}{\overset{\|}{C}}-Cl + H_2O \overset{H^+}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-OH$

② 

$R-\overset{O}{\overset{\|}{C}}-OR' + H_2O \overset{H^+}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-OH + R'OH$

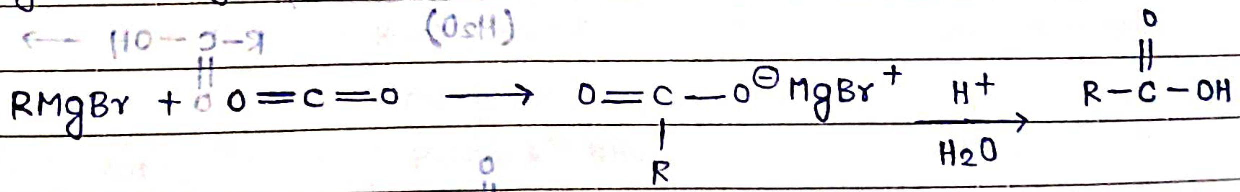
③ 

$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R' \overset{H^+}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-OH + R'-\overset{O}{\overset{\|}{C}}-OH$

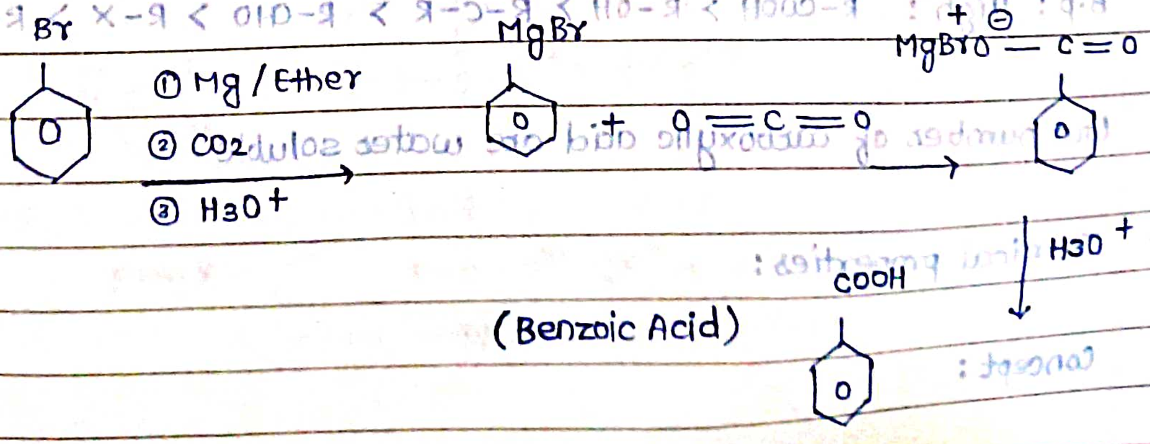
④ 

$R-\overset{O}{\overset{\|}{C}}-NH_2 \overset{H^+}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-OH + NH_4^+$

- **Grignard Reagent:**



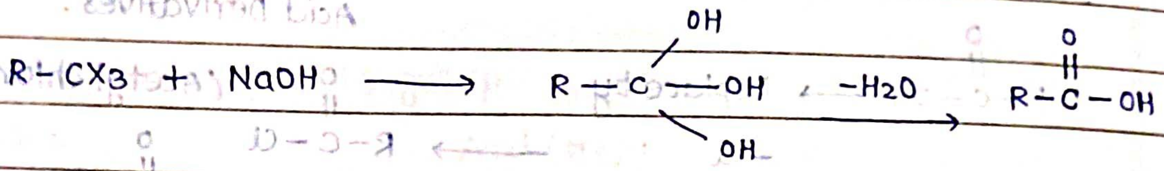
$RMgBr + O=C=O \longrightarrow O=\underset{R}{\underset{|}{C}}-O^{\ominus}MgBr^{+} \xrightarrow[H_2O]{H^+} R-\overset{O}{\overset{\|}{C}}-OH$

Q. 

① Mg / Ether
② CO_2
③ H_3O^+

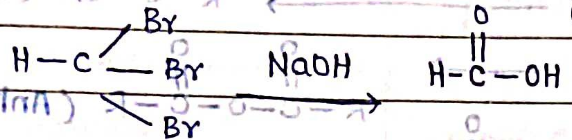
(Benzoic Acid)

- trihalide Alkane (R-CX3)



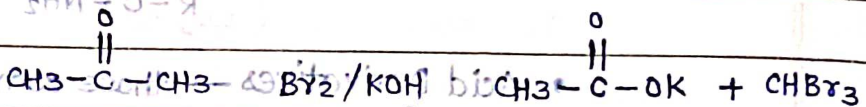
$R-CX_3 + NaOH \longrightarrow R-C(OH)_3 \xrightarrow{-H_2O} R-\overset{O}{\overset{\|}{C}}-OH$

(unstable)



$H-CBr_3 \xrightarrow{NaOH} H-\overset{O}{\overset{\|}{C}}-OH$

Haloform Rxn

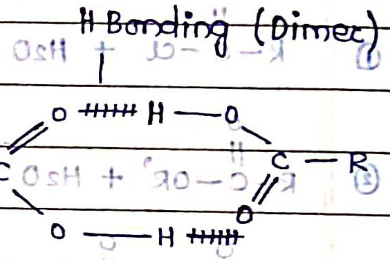


$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[KO-Br]{Br_2/KOH} CH_3-\overset{O}{\overset{\|}{C}}-OK + CHBr_3$

- Physical properties :

- carboxylic acid form H-Bonding

H Bonding (Dimer)



- Note : carboxylic acid

non-polar solvent (Benzene) → Dimer Form

$2\,R-\underset{O}{\underset{\|}{C}}-OH \rightleftharpoons (R-COOH)_2$

Polar solvent: (H2O) → Ionisation

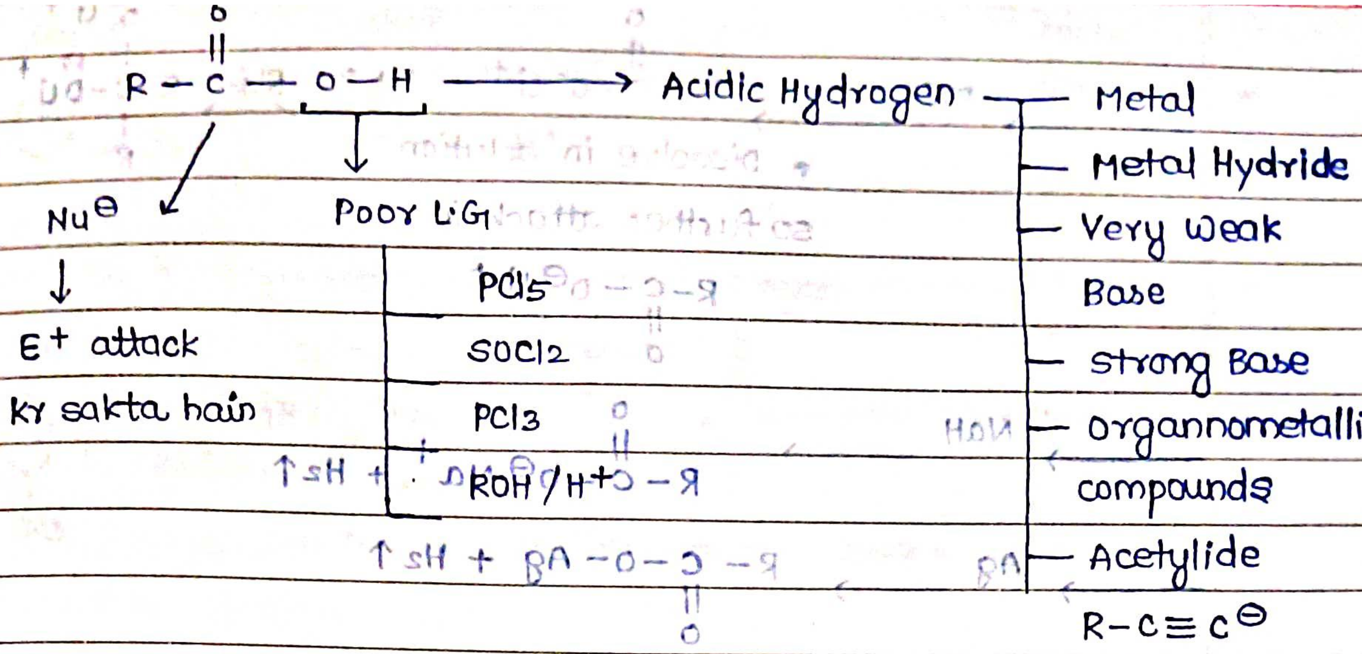
$R-\underset{O}{\underset{\|}{C}}-OH \longrightarrow R-\underset{O}{\underset{\|}{C}}-O^{\ominus}H^{+}$

- B.p : High : $R-COOH > R-OH > R-\overset{O}{\overset{\|}{C}}-R > R-CHO > R-X > R-H$

- Low number of carboxylic acid are water soluble.

- Chemical properties :

Concept :



- Reaction of Acidic Hydrogen of carboxylic acid.

$\longrightarrow$ Na — $R-\underset{\|}{\underset{O}{C}}O-ONa + H_2\uparrow$

$\longrightarrow$ Na_2CO_3 — $R-\underset{\|}{C}-ONa + H_2CO_3$ — H_2O, $CO_2\uparrow$

$\longrightarrow$ $NaHCO_3$ — $R-\underset{\|}{C}-ONa + CO_2\uparrow + H_2O$

Poor Base: Phenol does not react with $NaHCO_3$ or Na_2CO_3

$\longrightarrow$ NH_3 — $R-\underset{\underset{O}{\|}}{C}-O^{\ominus} + NH_4^{+}$ or $R-\overset{O}{\overset{\|}{C}}-ONH_4$ $\xrightarrow[-H_2O]{\Delta}$ $R-\overset{O}{\overset{\|}{C}}-NH_2$

Ammonium salt (Amide)

$\Delta \downarrow -H_2O$

$R-C\equiv N$

$\longrightarrow$ $\ddot{N}H_2-R$ $\longrightarrow$ $R-\overset{O}{\overset{\|}{C}}-\ddot{N}H-R$

$\longrightarrow$ $\ddot{N}HR_2$ $\longrightarrow$ $R-\underset{}{\overset{\|}{C}}-O^{\ominus}\ \overset{+}{N}H_2R_2$

$\longrightarrow$ $\ddot{N}R_3$ $\longrightarrow$ $R-\overset{O}{\overset{\|}{C}}-O^{\ominus} + \overset{+}{N}HR_3$

$\longrightarrow$ RMgX $\longrightarrow$ $R-\overset{\|}{C}-O^{\ominus}MgX^{+} + RH\uparrow$

ppt (does not dissolve in solution)

$\xrightarrow{}$ RLi $\xrightarrow{} R-\overset{O}{\overset{\|}{C}}-O^- Li^+ + RH\uparrow \xrightarrow{RLi} R-\underset{R}{\underset{|}{\overset{O^{\ominus}Li^+}{\overset{|}{C}}}}-O^{\ominus}Li^+ \xrightarrow[H_2O]{H^+} R-\overset{O}{\overset{\|}{C}}-R$

- Dissolve in solution so further attack in $R-\underset{O}{\underset{\|}{C}}-O^{\ominus}Li^+$

$\xrightarrow{}$ NaH $\xrightarrow{} R-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^+ + H_2\uparrow$

$\xrightarrow{}$ Ag $\xrightarrow{} R-\underset{O}{\underset{\|}{C}}-O-Ag + H_2\uparrow$

$\xrightarrow{}$ Ca $\xrightarrow{} \left(R-\overset{O}{\overset{\|}{C}}-O\right)_2 Ca + H_2\uparrow$

$\xrightarrow{}$ K $\xrightarrow{} R-\underset{O}{\underset{\|}{C}}-OK + H_2\uparrow$

- Reaction of salt of carboxylic acid :

$\xrightarrow{}$ Na $\xrightarrow{} R-C-ONa \xrightarrow{\text{lime water } (CaO + NaOH)} R-H + Na_2CO_3$

(decarboxylation)

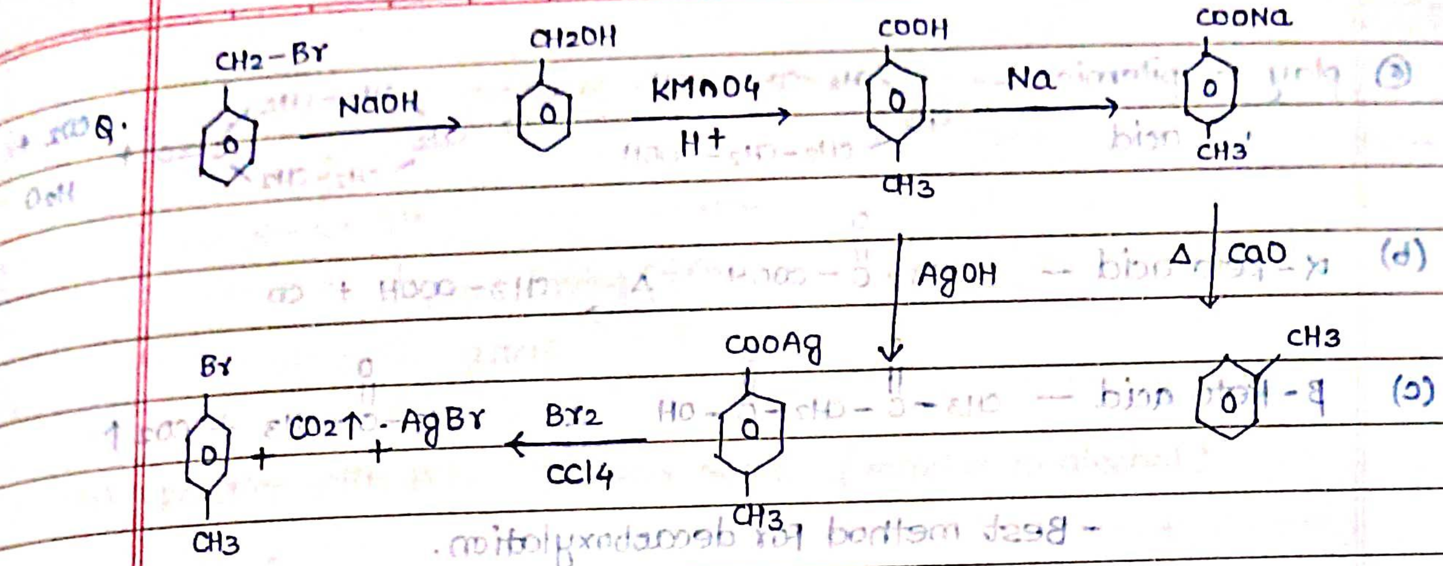
$\xrightarrow{}$ KOH $\xrightarrow{} R-\overset{O}{\overset{\|}{C}}-OK \xrightarrow{\text{electrolysis}} \underbrace{R-R + CO_2}_{\text{Anode}} + \underbrace{H_2 + KOH}_{\text{cathode}}$

(Kolbe's electrolysis)

$\xrightarrow{}$ Ca(OH)$_2$ $\xrightarrow{} \left(R-\overset{O}{\overset{\|}{C}}-O\right)_2 Ca \xrightarrow[\text{Distillation}]{\text{Dry}} R-\overset{O}{\overset{\|}{C}}-R$

$\xrightarrow{}$ AgOH $\xrightarrow{} R-\overset{O}{\overset{\|}{C}}-OAg \xrightarrow{Br_2/CCl_4} R-Br + AgBr + CO_2\uparrow$

Borodine-Hunsdiecker Reaction.



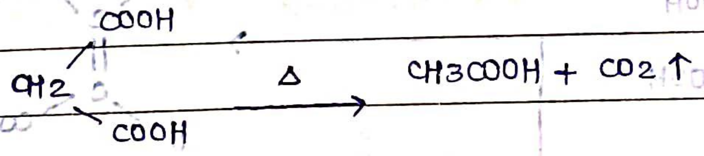
- **Heating effect of carboxylic acid :**

oh my son go and play. —— Pilemic acid.

oxallic acid
Malonic acid
succinic acid
Glutaric acid
Adipic acid

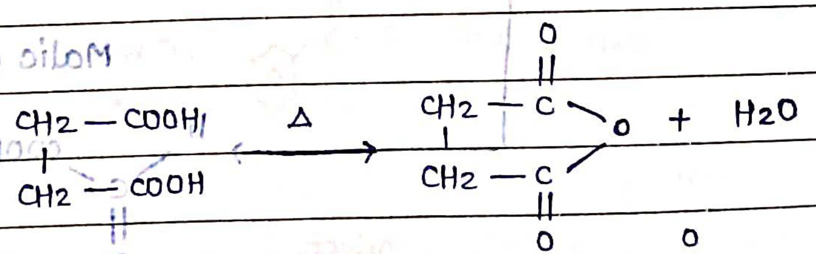
① oh - oxallic acid — $\begin{matrix}COOH\\|\\COOH\end{matrix} \xrightarrow{\Delta} CO + CO_2 + H_2O$

② my - Malonic acid —

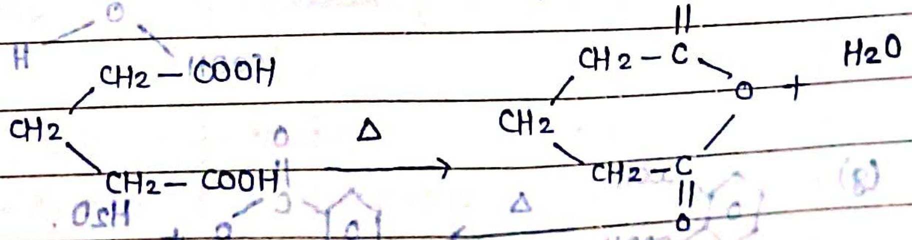


$CH_2(COOH)_2 \xrightarrow{\Delta} CH_3COOH + CO_2\uparrow$

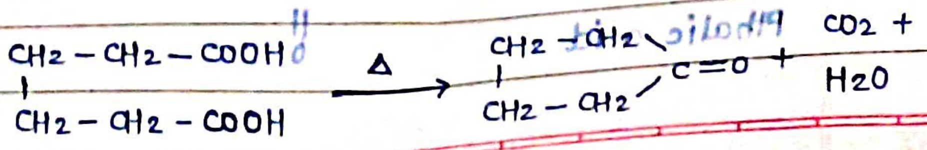
③ son - succinic acid —



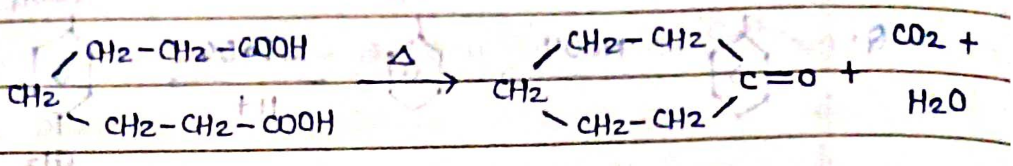
④ go - Glutaric acid



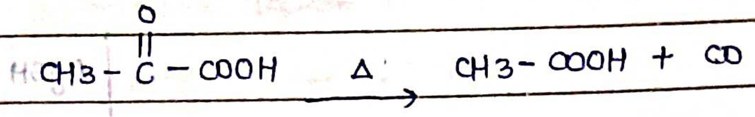
⑤ and - adipic acid —



⑥ play - pilemic acid —

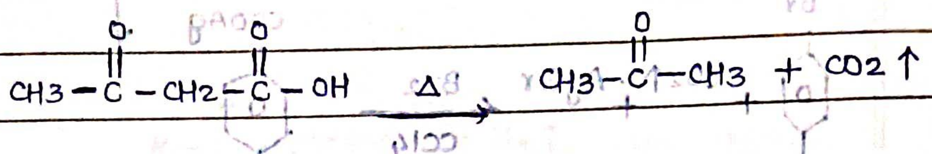


(b) α-Keto acid —



$$CH_3-\overset{O}{\overset{\|}{C}}-COOH \xrightarrow{\Delta} CH_3-COOH + CO$$

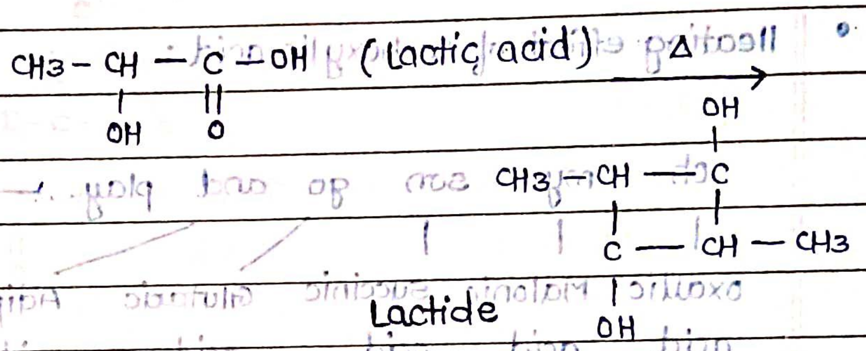
(c) β-Keto acid —



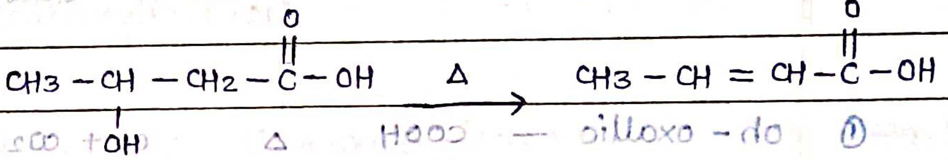
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CO_2\uparrow$$

- Best method for decarboxylation.

(d) α-Hydroxy acid —

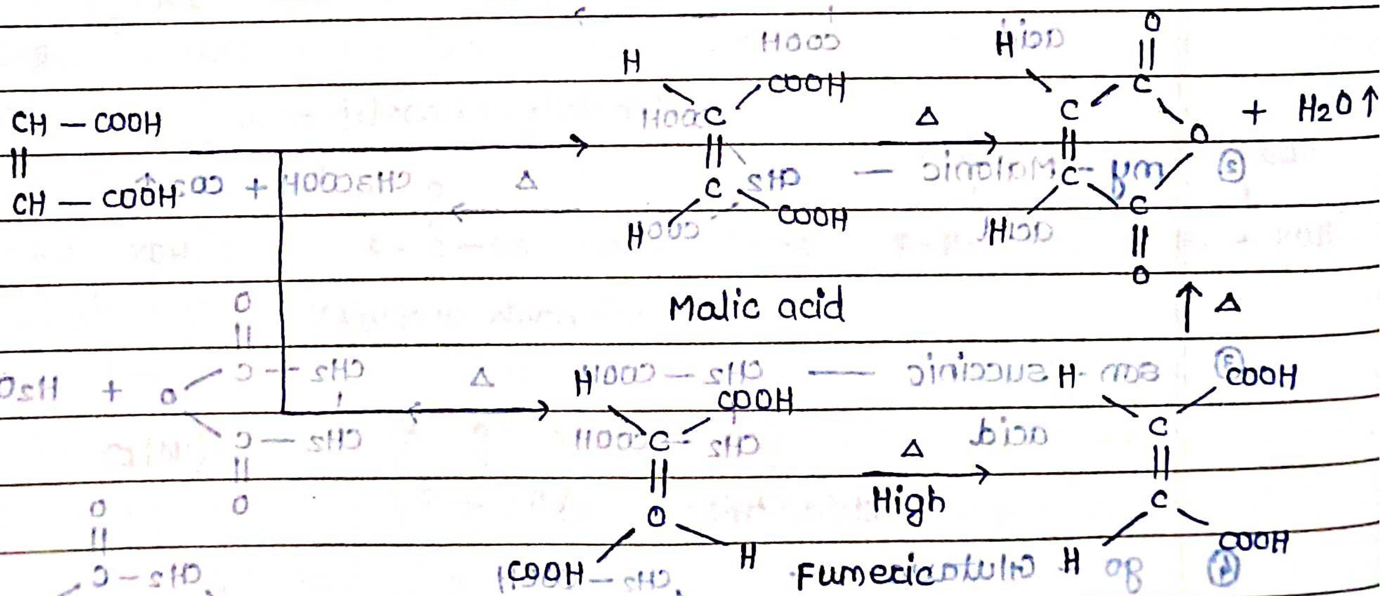


(e) β-Hydroxy acid —

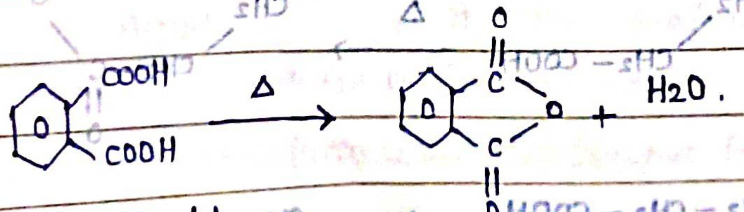


$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\Delta} CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-OH$$

(f)

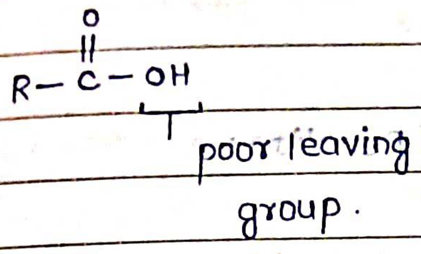


(g)



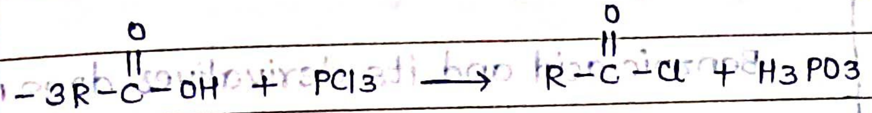
Phthalic acid

- Reaction of –OH group of carboxylic Acid :

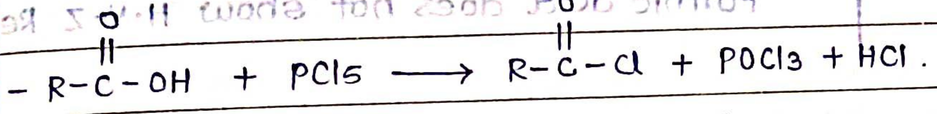


$R-\overset{O}{\overset{\|}{C}}-\underbrace{OH}_{\text{poor leaving group}}$

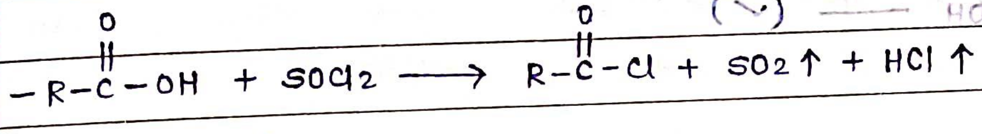
(a) Reaction with PCl_3, PCl_5, and $SOCl_2$ (similar to alcohol)



$- 3R-\overset{O}{\overset{\|}{C}}-OH + PCl_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3$



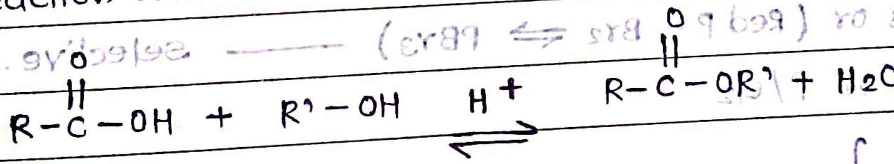
$- R-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + HCl$.



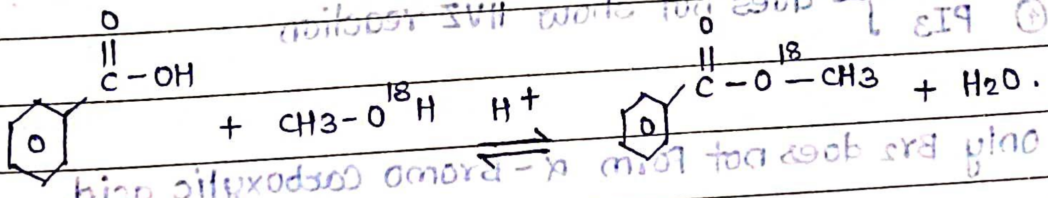
$- R-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl + SO_2\uparrow + HCl\uparrow$

(Note: Best method for preparation of Acetyl chloride).

(b) Reaction with R–OH (Esterification)

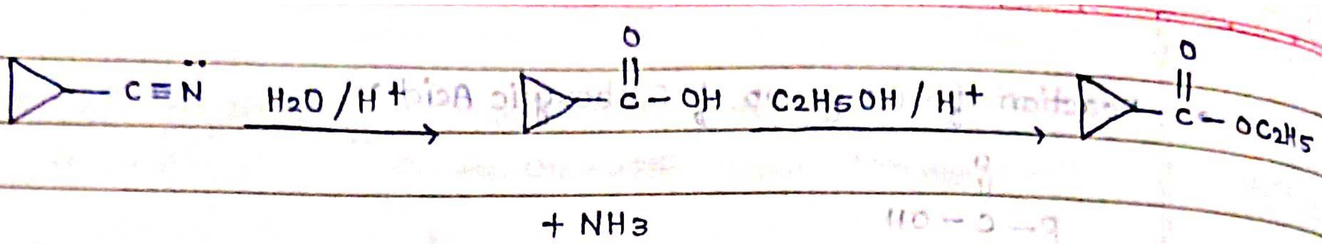


$R-\overset{O}{\overset{\|}{C}}-OH + R'-OH \overset{H^+}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-OR' + H_2O$



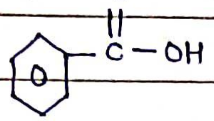
- Reactivity ∝ +ve charge density of carbonyl carbon – { variable
  - –I- effect
  - –M- effect

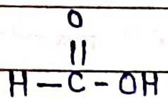
- Reactivity ∝ $\dfrac{\quad}{\text{steric hindrance}}$ { variable
  - – alkyl group

Q. 

- **Hell Volhard zelinsky Reaction (HVZ) Reaction :**

- Carboxylic acid — Condition — having atleast one α-hydrogen

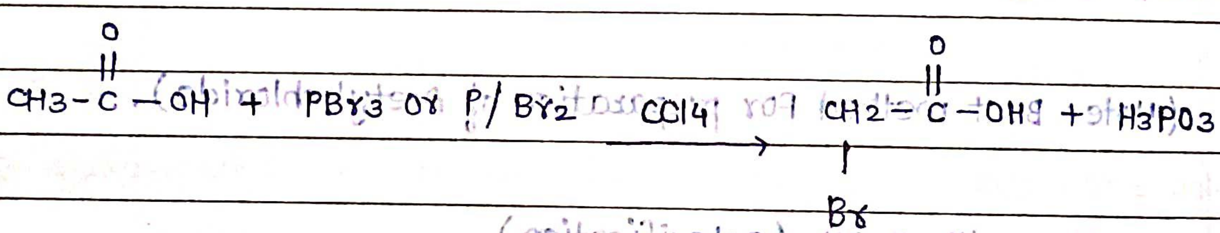



$H-\overset{O}{\overset{\|}{C}}-OH$

Benzoic acid and its derivatives does not show ⊗

Formic acid does not show H·V·Z Reaction ⊗

CH_3-COOH —— (✓)


$CH_3-\overset{O}{\overset{\|}{C}}-OH + PBr_3 \text{ or } P/Br_2 \xrightarrow{CCl_4} \underset{Br}{\underset{|}{CH_2}}-\overset{O}{\overset{\|}{C}}-OH + H_3PO_3$

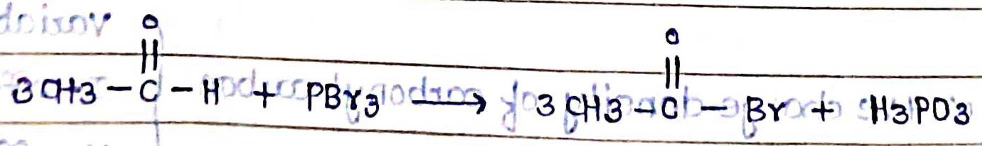
Mech : ① PBr_3 or (Red P + $Br_2 \rightleftharpoons PBr_3$) —— selective.

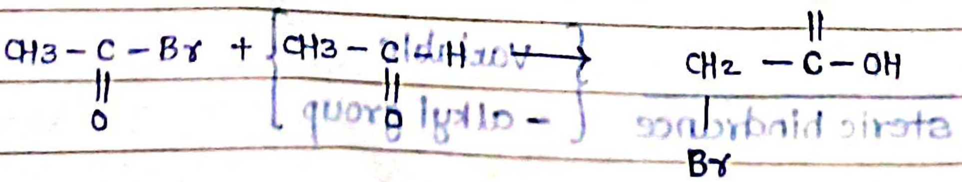
② PCl_3 or P/Cl_2

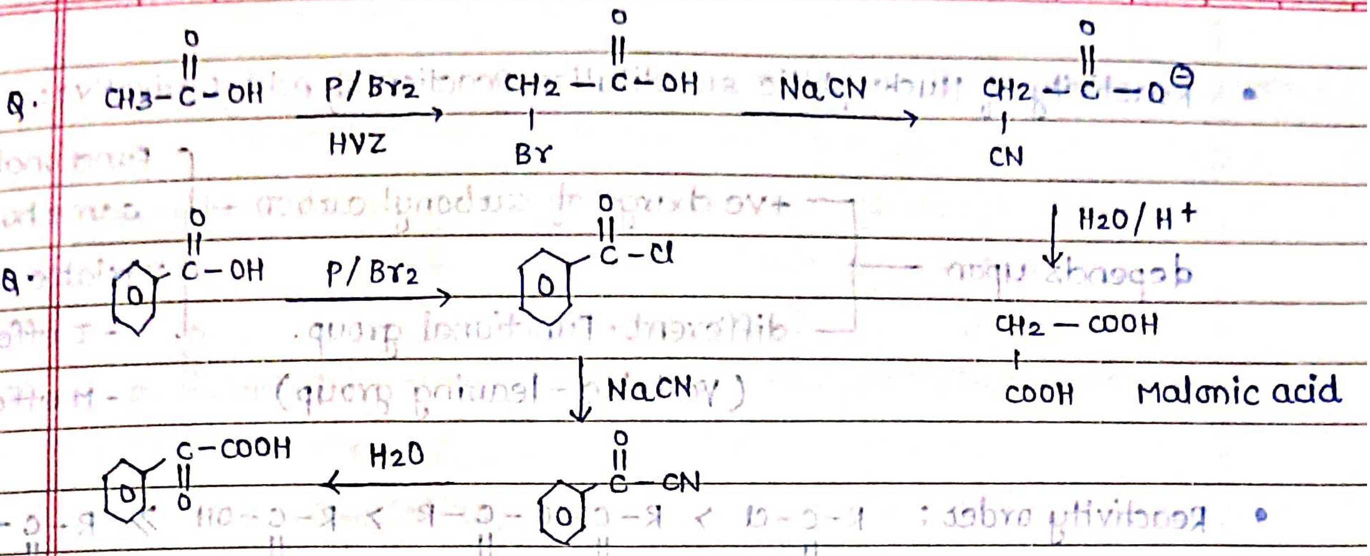
③ PF_3 } ~~does not show HVZ reaction~~

④ PI_3

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

- 
$3CH_3-\overset{O}{\overset{\|}{C}}-H + PBr_3 \longrightarrow 3CH_3-\overset{O}{\overset{\|}{C}}-Br + H_3PO_3$

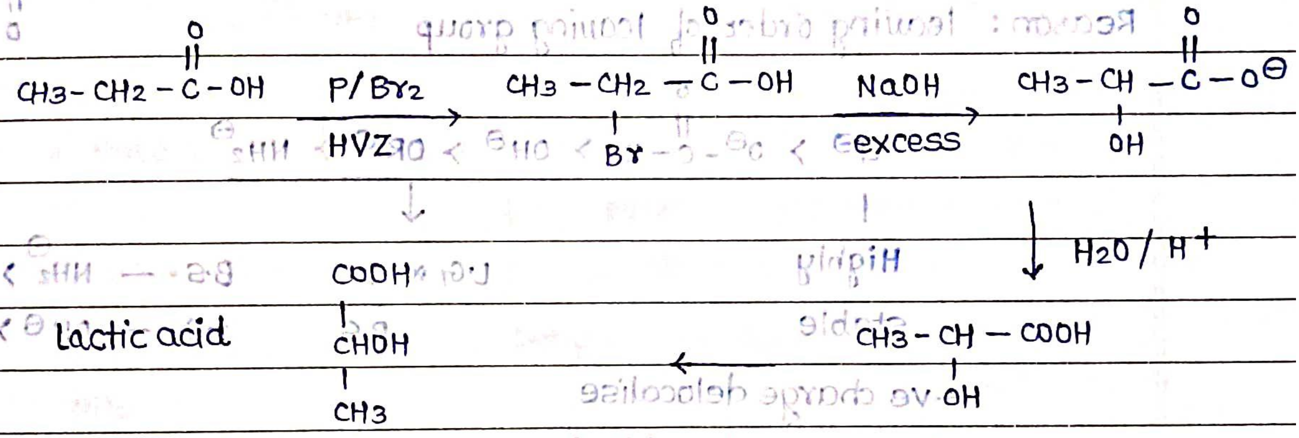

$CH_3-\underset{O}{\underset{\|}{C}}-Br + \left\{CH_3-\underset{O}{\underset{\|}{C}}-OH\right\} \longrightarrow \underset{Br}{\underset{|}{CH_2}}-\overset{O}{\overset{\|}{C}}-OH$



Q. $CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[HVZ]{P/Br_2} \underset{Br}{CH_2}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NaCN} \underset{CN}{CH_2}-\overset{O}{\overset{\|}{C}}-O^{\ominus} \xrightarrow{H_2O/H^+} \underset{COOH}{CH_2}-COOH$ Malonic acid

Q. $C_6H_5-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{P/Br_2} C_6H_5-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{NaCN} C_6H_5-\overset{O}{\overset{\|}{C}}-CN \xrightarrow{H_2O} C_6H_5-\underset{O}{\underset{\|}{C}}-COOH$

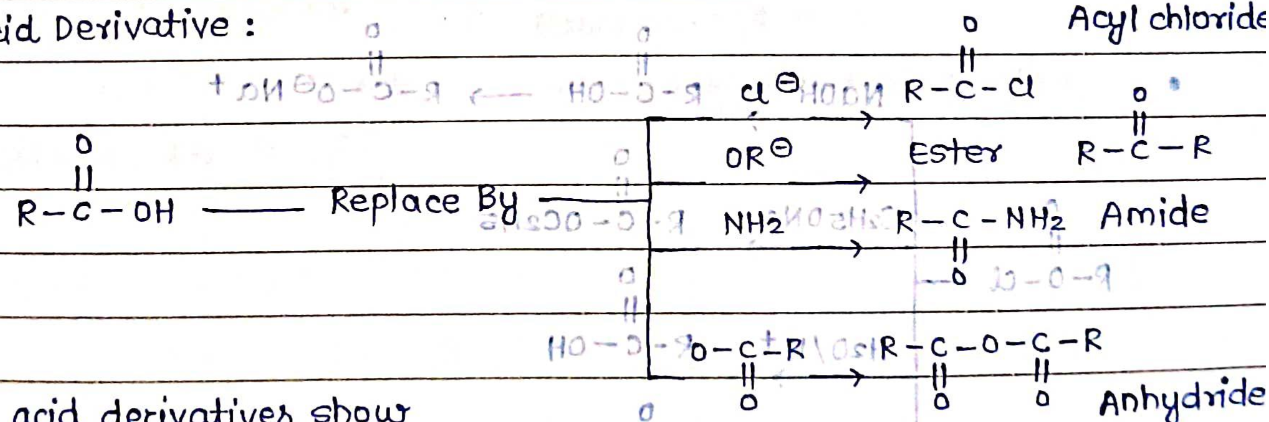
- Formation of lactic acid :



$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[HVZ]{P/Br_2} CH_3-\underset{Br}{CH_2}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[excess]{NaOH} CH_3-\underset{OH}{CH}-\overset{O}{\overset{\|}{C}}-O^{\ominus} \xrightarrow{H_2O/H^+} CH_3-\underset{OH}{CH}-COOH$

Lactic acid $COOH-CHOH-CH_3$

- Acid Derivative :



$R-\overset{O}{\overset{\|}{C}}-OH$ —— Replace By

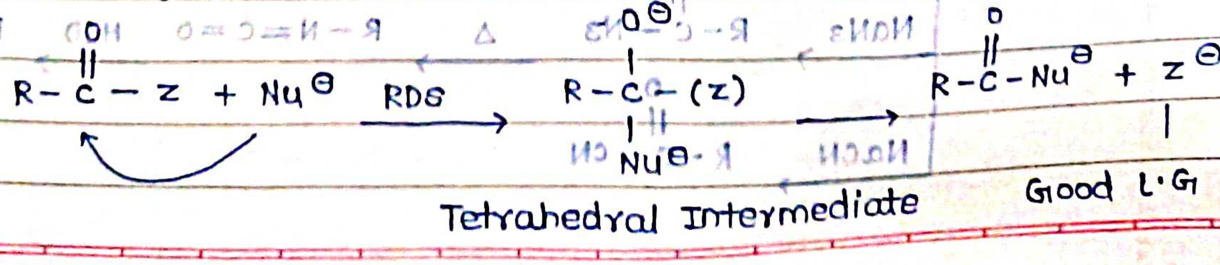
$\xrightarrow{Cl^{\ominus}} R-\overset{O}{\overset{\|}{C}}-Cl$ Acyl chloride

$\xrightarrow{OR^{\ominus}}$ Ester $R-\overset{O}{\overset{\|}{C}}-R$

$\xrightarrow{NH_2} R-\overset{O}{\overset{\|}{C}}-NH_2$ Amide

$\xrightarrow{O-\overset{O}{\overset{\|}{C}}-R} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ Anhydride

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



$R-\overset{O}{\overset{\|}{C}}-Z + Nu^{\ominus} \xrightarrow{RDS} R-\overset{O^{\ominus}}{\underset{Nu}{C}}-(Z) \longrightarrow R-\overset{O}{\overset{\|}{C}}-Nu^{\ominus} + \underset{\text{Good L.G}}{Z^{\ominus}}$

Tetrahedral Intermediate

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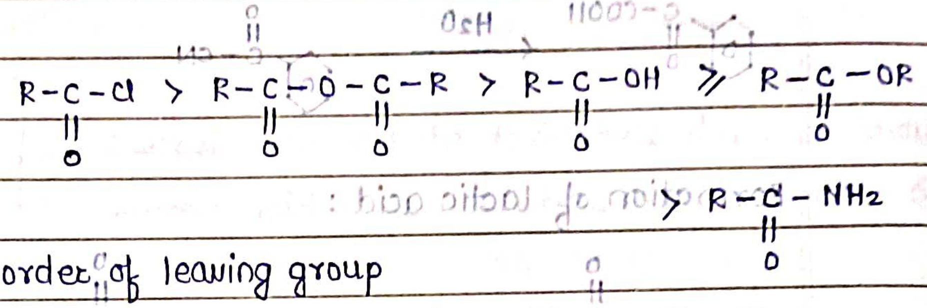
Date

- Reactivity of Nucleophilic substitution Reaction of Acid Derivative:

depends upon — +ve charge of carbonyl carbon — Functional group same no. / Variable — -I effect, -M effect

depends upon — different Functional group. (Variable - leaving group)



- Reactivity order : $R-\underset{\underset{O}{||}}{C}-Cl > R-\underset{\underset{O}{||}}{C}-O-\underset{\underset{O}{||}}{C}-R > R-\underset{\underset{O}{||}}{C}-OH \gg R-\underset{\underset{O}{||}}{C}-OR > R-\underset{\underset{O}{||}}{C}-NH_2$

Reason: leaving order of leaving group

$Cl^{\ominus} > O^{\ominus}-\overset{\overset{O}{||}}{C}-R > OH^{\ominus} > OR^{\ominus} > NH_2^{\ominus}$

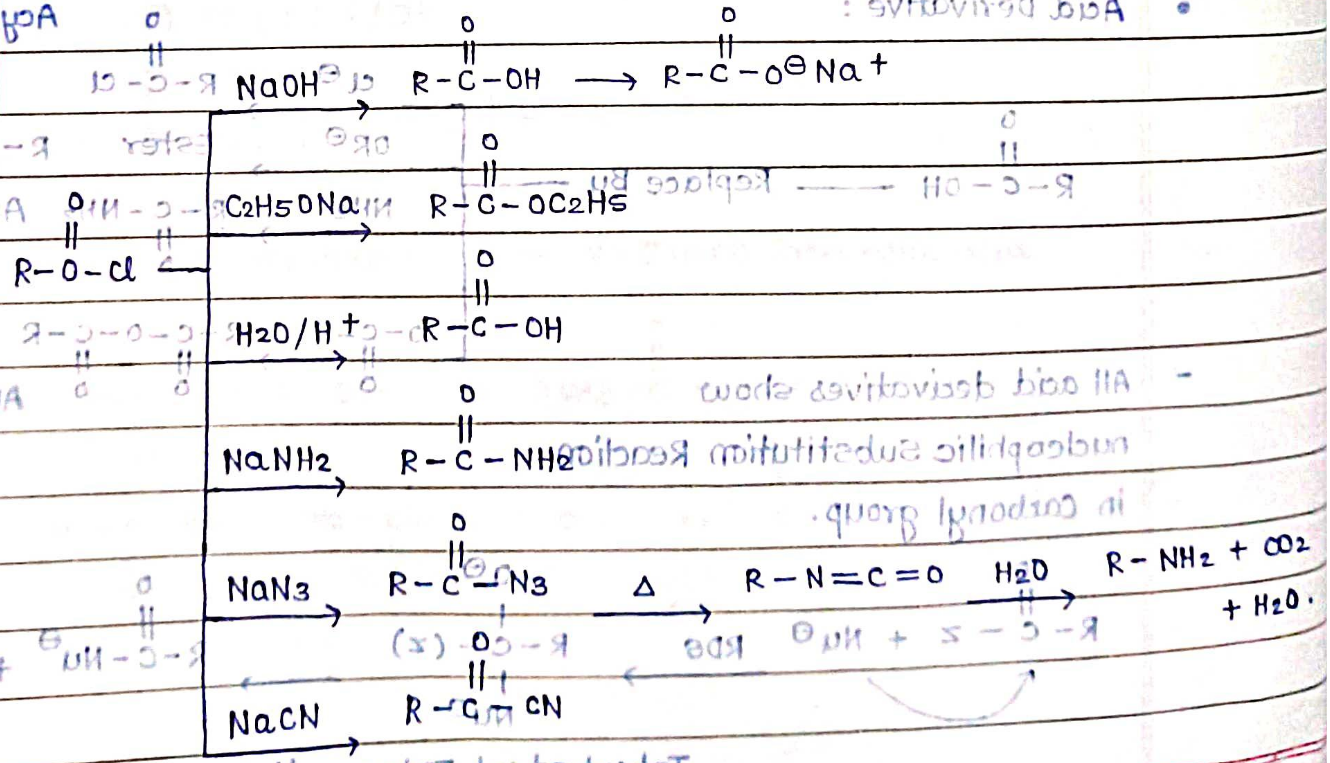
Highly stable
-ve charge delocalise
in vacant d-orbital.

L·G ∝ $\frac{1}{B.S}$

B·S· — $NH_2^{\ominus} > OR^{\ominus} > OH^{\ominus}$

L·G· — $OH^{\ominus} > OR^{\ominus} > NH_2^{\ominus}$

$OH^{\ominus} < SH^{\ominus}$ $F^{\ominus} < Cl^{\ominus} < Br^{\ominus} < I^{\ominus}$



- $R-\overset{\overset{O}{||}}{O}-Cl \xrightarrow{NaOH} R-\overset{\overset{O}{||}}{C}-OH \longrightarrow R-\overset{\overset{O}{||}}{C}-O^{\ominus}Na^{+}$

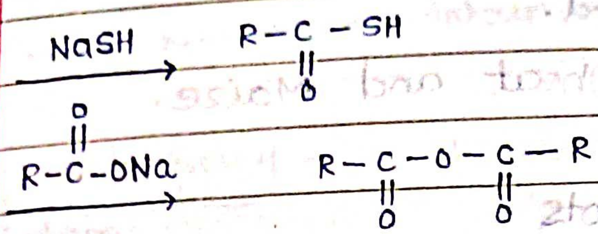
$\xrightarrow{C_2H_5ONa} R-\overset{\overset{O}{||}}{C}-OC_2H_5$

$\xrightarrow{H_2O/H^{+}} R-\overset{\overset{O}{||}}{C}-OH$

$\xrightarrow{NaNH_2} R-\overset{\overset{O}{||}}{C}-NH_2$

$\xrightarrow{NaN_3} R-\overset{\overset{O}{||}}{C}-N_3 \xrightarrow{\Delta} R-N=C=O \xrightarrow{H_2O} R-NH_2 + CO_2 + H_2O.$

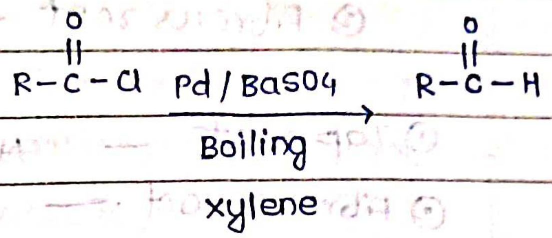
$\xrightarrow{NaCN} R-\overset{\overset{O}{||}}{C}-CN$



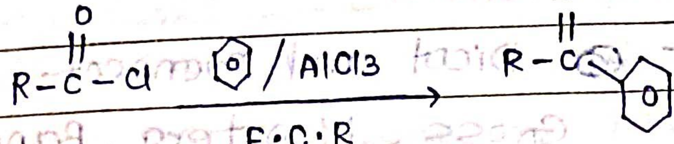
$$\xrightarrow{NaSH} R-\underset{\overset{\|}{O}}{C}-SH$$

$$R-\overset{\overset{O}{\|}}{C}-ONa \longrightarrow R-\underset{\overset{\|}{O}}{C}-O-\underset{\overset{\|}{O}}{C}-R$$

- Rosenmund Reduction.



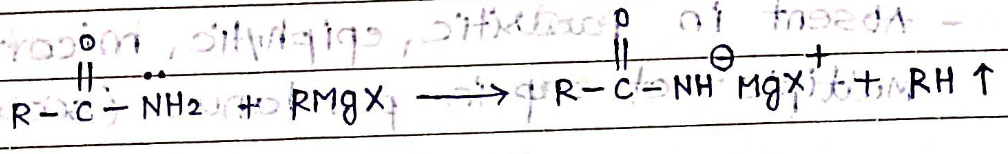
$$R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[\text{Boiling xylene}]{Pd/BaSO_4} R-\overset{\overset{O}{\|}}{C}-H$$



$$R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[F \cdot C \cdot R]{C_6H_6 / AlCl_3} R-\overset{\overset{O}{\|}}{C}-C_6H_5$$

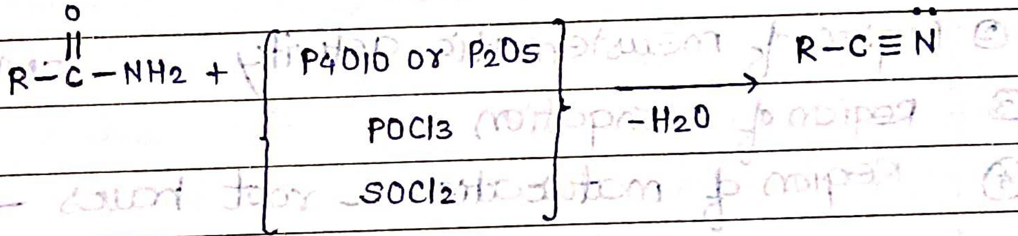
(Acylation)

- Amide



$$R-\overset{\overset{O}{\|}}{C}-\ddot{N}H_2 + RMgX \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{N}H \; \overset{+}{Mg}X + RH \uparrow$$

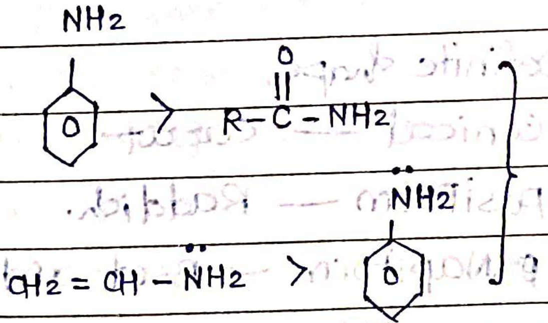
- Note :



$$R-\overset{\overset{O}{\|}}{C}-NH_2 + \left[\begin{array}{c} P_4O_{10} \text{ or } P_2O_5 \\ POCl_3 \\ SOCl_2 \end{array}\right] \xrightarrow{-H_2O} R-C\equiv\ddot{N}$$

Dehydration agent.

-



$$C_6H_5NH_2 > R-\overset{\overset{O}{\|}}{C}-NH_2$$

$$CH_2=CH-\ddot{N}H_2 > C_6H_5\ddot{N}H_2$$

Basic strength

due to high E.N than C-atom.