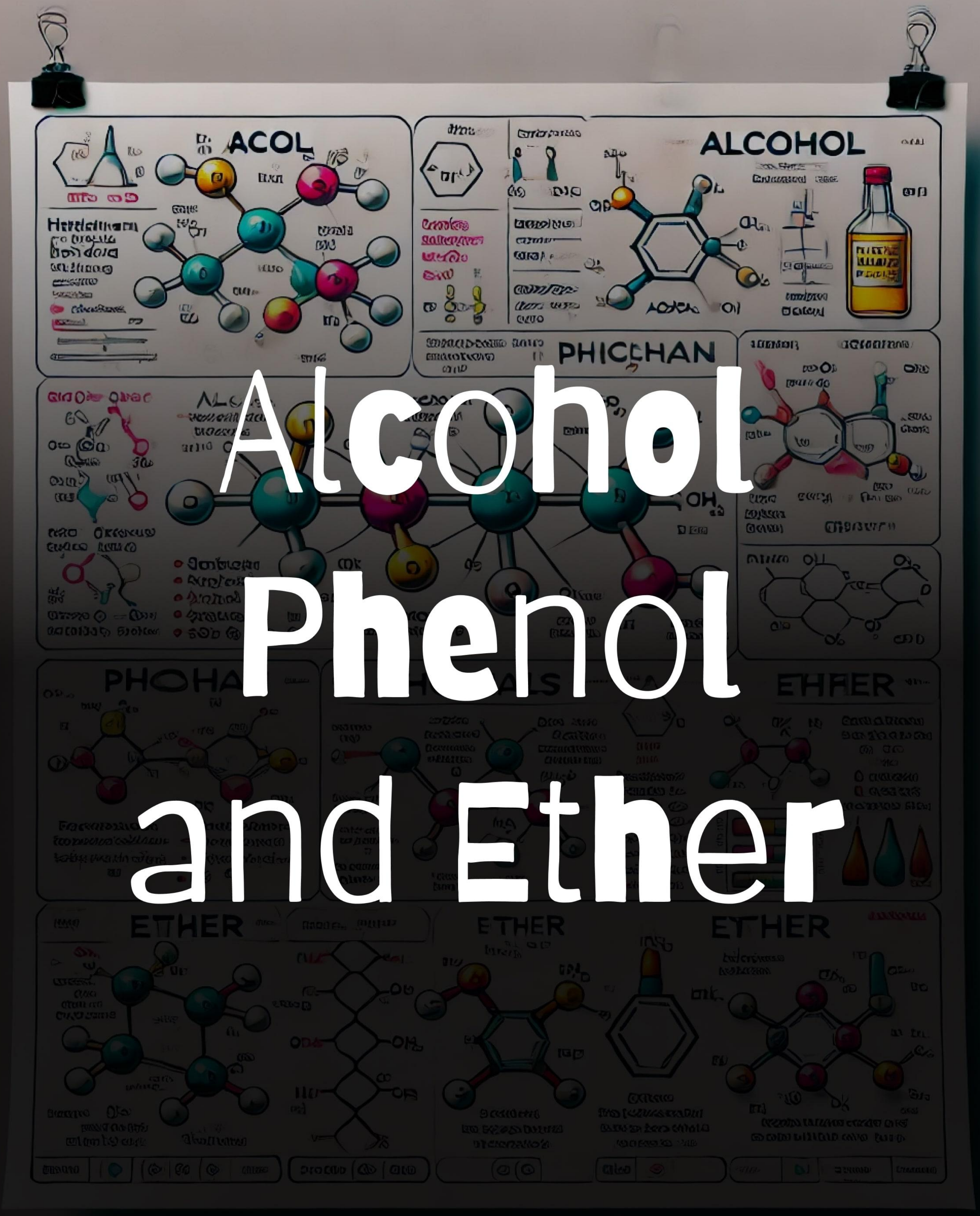
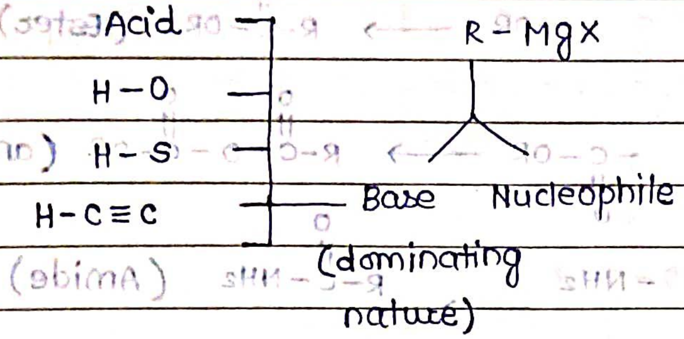
Alcohol Phenol and Ether



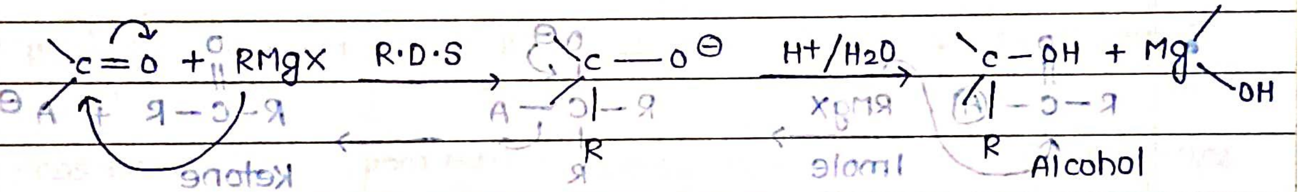
Alcohol Phenol Ether

- Method of preparation:

① Grignard Reagent: $R-X + Mg \xrightarrow{\text{Dry ether}} RMgX$



- From aldehyde and Ketone $\begin{matrix}H\\R\end{matrix}\!>C=O$; $\begin{matrix}R\\R\end{matrix}\!>C=O$

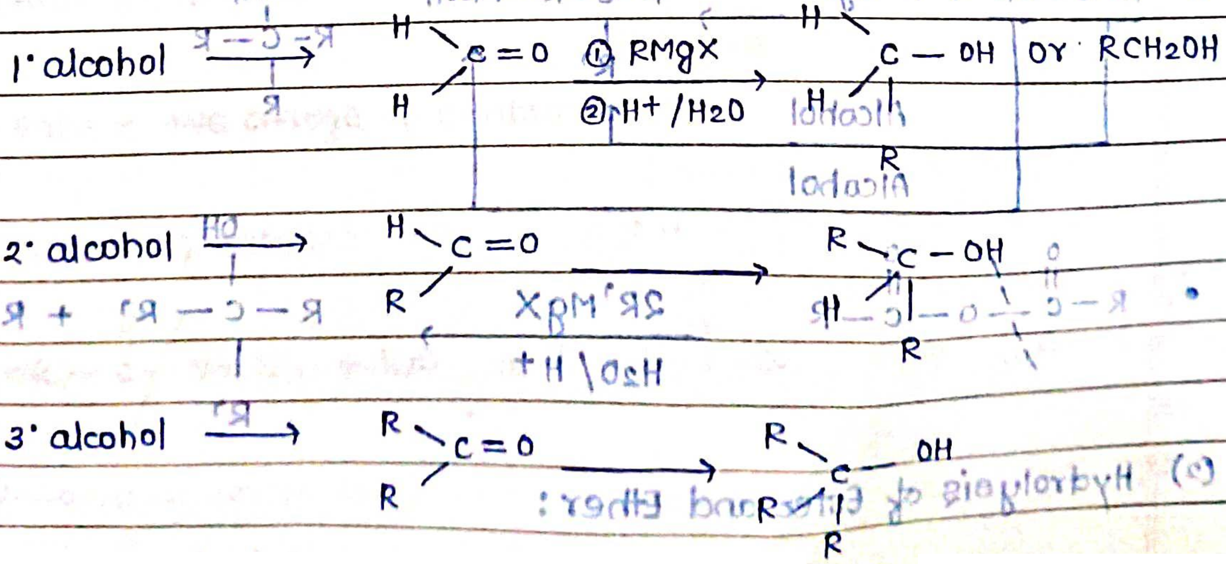


① Rate ∝ +ve charge on C-atom of aldehyde and ketone. ——— Variable

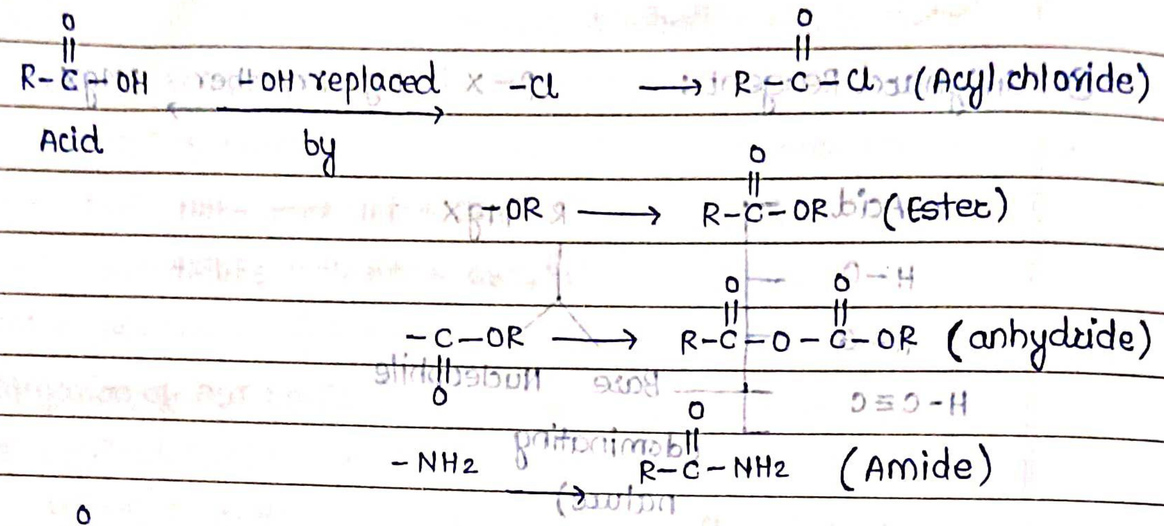
① −I effect group.

② Resonance no. (only alkyl group attach).

② Rate ∝ $\frac{1}{\text{steric hindrance}}$



- From Acid and Acid Derivative :



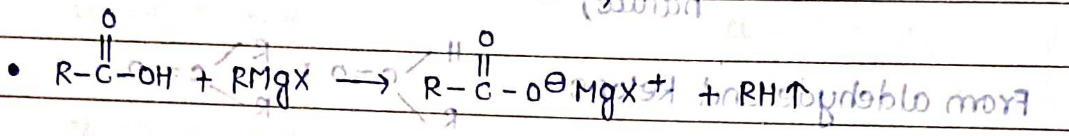
$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{by}]{-OH \text{ replaced}} -Cl \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl \text{ (Acyl chloride)}$$

Acid

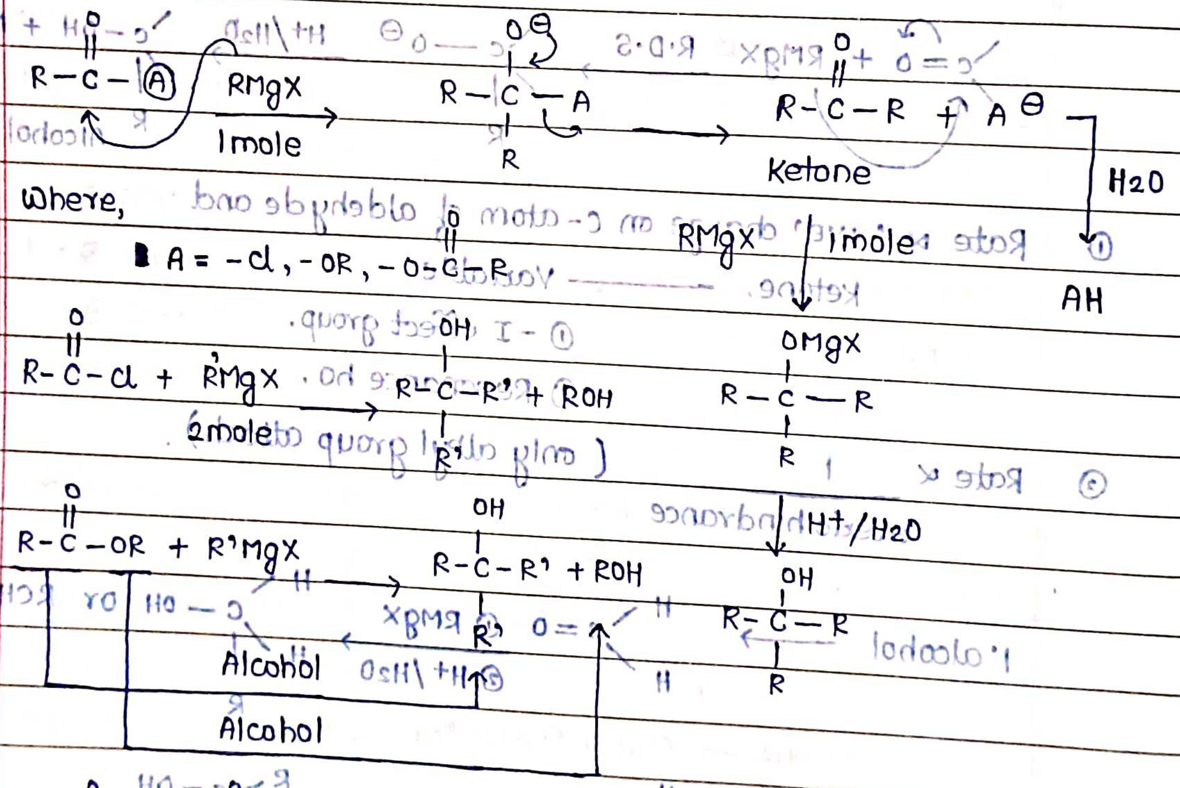
$$-OR \longrightarrow R-\overset{O}{\overset{\|}{C}}-OR \text{ (Ester)}$$

$$-\underset{O}{\underset{\|}{C}}-OR \longrightarrow R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-OR \text{ (anhydride)}$$

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



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



$$R-\overset{O}{\overset{\|}{C}}-Ⓐ \xrightarrow[\text{1mole}]{RMgX} R-\underset{R}{\overset{O^{\ominus}}{C}}-A \longrightarrow \underset{\text{Ketone}}{R-\overset{O}{\overset{\|}{C}}-R} + A^{\ominus} \xrightarrow{H_2O} AH$$

Where,

A = $-Cl, -OR, -O-\overset{O}{\overset{\|}{C}}-R$

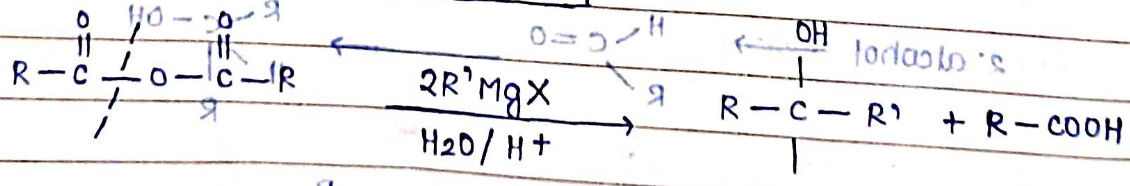
$$\text{Ketone} \xrightarrow{RMgX \text{ 1mole}} R-\underset{R}{\overset{OMgX}{C}}-R \xrightarrow{H^+/H_2O} R-\underset{R}{\overset{OH}{C}}-R$$

$$\bullet\ R-\overset{O}{\overset{\|}{C}}-Cl + R'MgX \xrightarrow{\text{2mole}} R-\underset{R'}{\overset{OH}{C}}-R' + ROH$$

$$\bullet\ R-\overset{O}{\overset{\|}{C}}-OR + R'MgX \longrightarrow R-\underset{R'}{\overset{OH}{C}}-R' + ROH$$

Alcohol

Alcohol



$$\bullet\ R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R \xrightarrow[H_2O/H^+]{2R'MgX} R-\underset{R'}{\overset{OH}{C}}-R' + R-COOH$$

(2) Hydrolysis of Ester and Ether :

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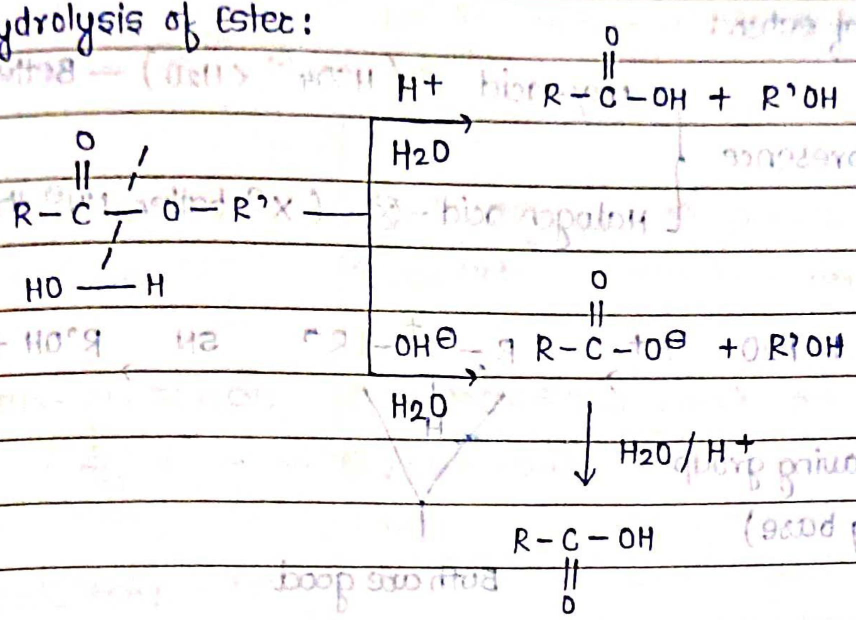
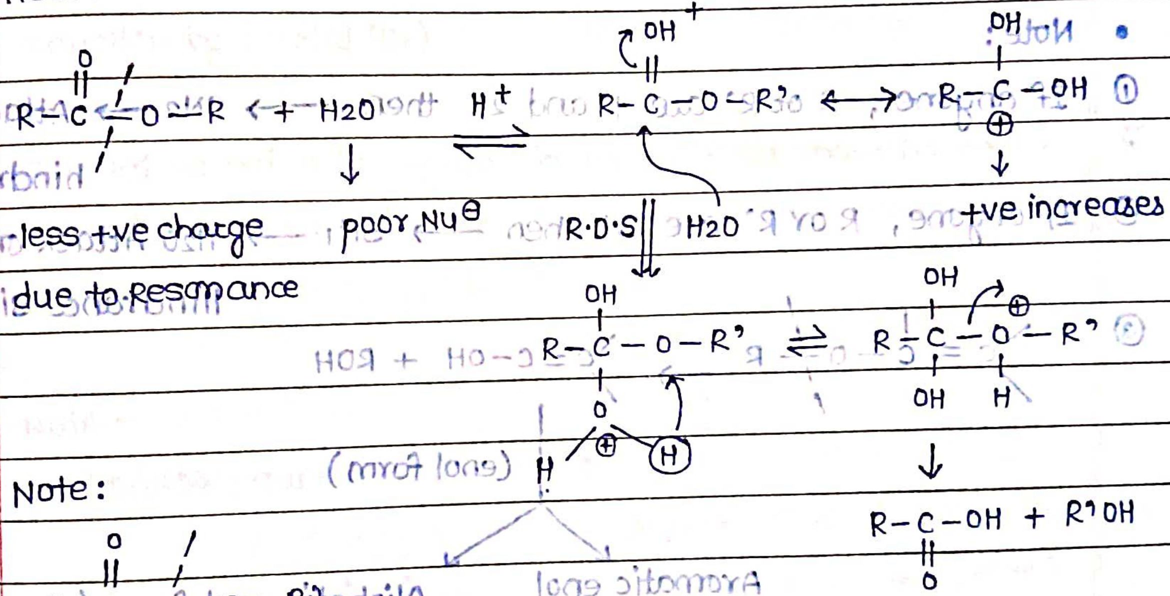
(a) Hydrolysis of Ester:



- Mech:



- Note:

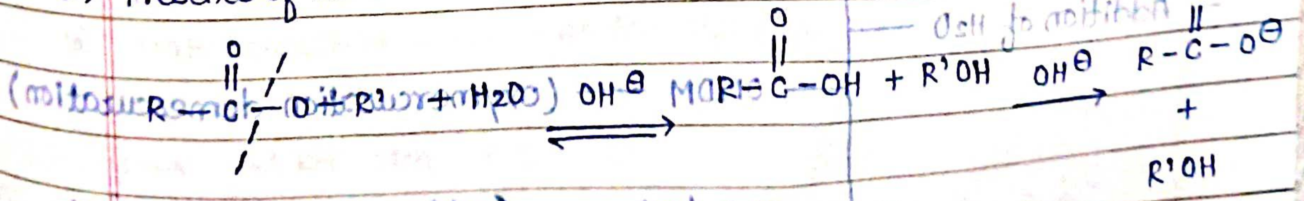
① $R-\overset{O}{\overset{\|}{C}}-O-R'$

Acid | Alcohol

② Rate ∝ $\frac{1}{\text{hindrance}}$.

③ Rate ∝ +ve charge of C-atom.

(b) Presence of Base:



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(c) Hydrolysis of ester :

Acid — presence
- oxy-acid ($HSO_4^\ominus < H_2O$) — Better H_2O Nucleoph
- Halogen acid – ⊗ ($X^\ominus$ better $Nu^\ominus$ than H_2O)

$$R-O-R' + H_2O \xrightarrow{H^+} R-\underset{H}{\overset{+}{O}}-R' \xrightarrow{SN} R'OH + ROH$$

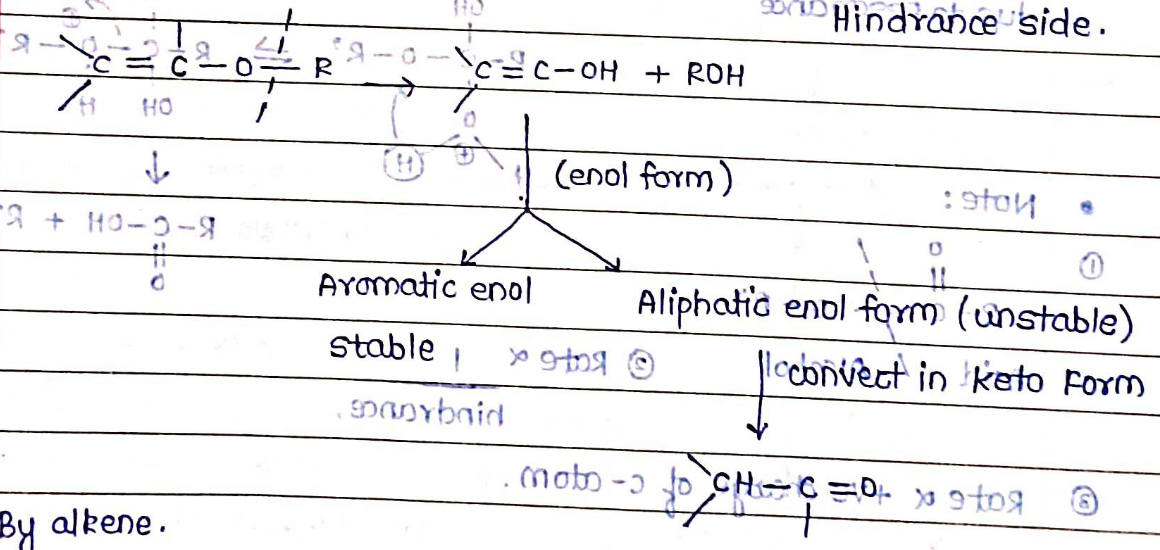
Poor leaving group (strong base)

Both are good leaving group.

- Note :

① If anyone, R or R' are 1° and 2° then ⟶ SN2 ⟶ Attack on less hindrance side (H_2O)

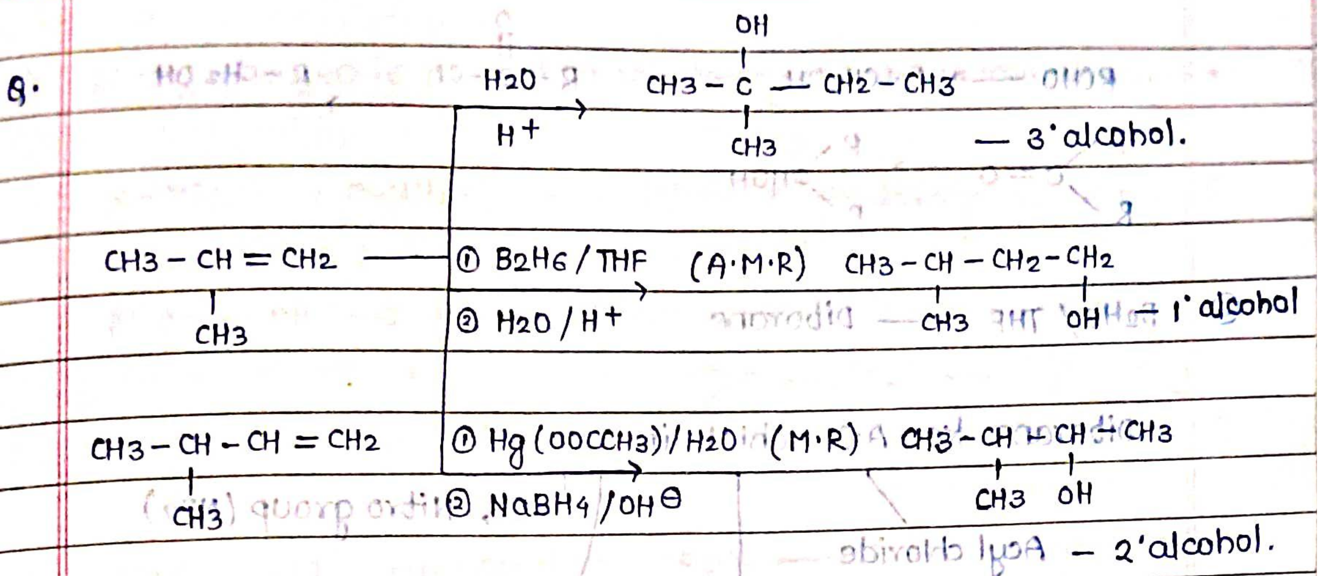
② If anyone, R or R' are 3° then ⟶ SN1 ⟶ H_2O Attack on more Hindrance side.

③ 

(3) By alkene.

- Addition of H_2O
  - H·B·O — (Hydroboration oxidation)
  - OMDM (oxymercuration demercuration)
  - H_2O/H^+ — (add water in presence of oxy acid.)

Q.



$$CH_3-\underset{CH_3}{\underset{|}{CH}}=CH_2 \xrightarrow[H^+]{H_2O} CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-CH_3$$ — 3° alcohol.

$$CH_3-\underset{CH_3}{\underset{|}{CH}}=CH_2 \xrightarrow[\text{② } H_2O/H^+]{\text{① } B_2H_6/THF}\ (A \cdot M \cdot R)\ CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH_2}}$$ — 1° alcohol

$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH=CH_2 \xrightarrow[\text{② } NaBH_4/OH^{\ominus}]{\text{① } Hg(OOCCH_3)_2/H_2O}\ (M \cdot R)\ CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3$$ — 2° alcohol.

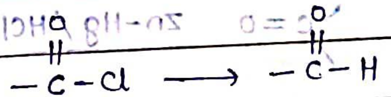
- Reduction :

① Reduction by (Metal / H_2)

" Metal ko hai sabhi pyare, Pr Pd hai kuch khaas humare, Ru-C but Cu-Ba-Cr oxide hi krte hain acid (−COOH) ko alcohol mein convert pyaare."

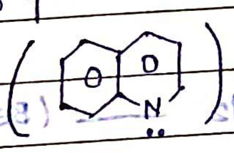
- Note :

① Pd / $BaSO_4$, qunoline solvent :



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

Acyl chloride Aldehyde



(Rosenmund's Reduction)

② Pd / $BaSO_4$, quinoline : Alkyne ⟶ cis ⟶ Alkene.

or

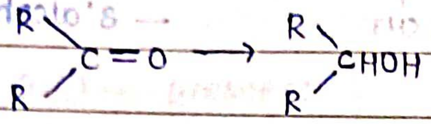
Pd / $CaCO_3$, quinoline (Lindlar's Catalyst)

② $NaBH_4$ / C_2H_5OH — Sodium Boro hydrate

→ Al ka ka AC ko reduce krta hai only.

Aldehyde Ketone Acyl chloride

$RCHO \longrightarrow R-CH_2OH$ $\quad R-\overset{O}{\overset{||}{C}}-Cl \longrightarrow R-CH_2OH$



③ B_2H_6 / THF ⟵ Diborane

Diborane ka A.C. nahi hai ON

- Acyl chloride $\left(-\overset{O}{\overset{||}{C}}-Cl\right)$
- Does not Reduce.
- Nitro group (NO_2)
- Oxime group ($>C=N-OH$)

④ $LiAlH_4$ / Ether or L.A.H ⟶ all Functional group are reduced by L.A.H

- Clemmensen Reduction

$$>C=O \xrightarrow{Zn-Hg\ /\ HCl} >CH_2$$ —— (Best acidic condition)

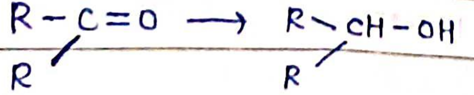
- Wolf-kisner Reduction

$$>C=O \xrightarrow[OH^{\ominus}]{NH_2-NH_2} >CH_2$$ (Best Basic condition)

- Reduction clue :

① C-atom ko atleast one oxygen atom attached ⟶ then it is converted to alcohol.

$R-CHO \longrightarrow RCH_2OH$ $\quad RCOOH \longrightarrow RCH_2OH$



$R-\overset{O}{\overset{||}{C}}-O-\overset{O}{\overset{||}{C}}-R \longrightarrow 2\,RCH_2OH$

$R-\underset{O}{\underset{||}{C}}-Cl \longrightarrow RCH_2OH$ $\quad R-\underset{O}{\underset{||}{C}}-NH_2 \longrightarrow R-CH_2-NH_2$

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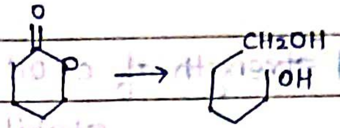
② If any nitrogen is present then directly convert it into NH_2.

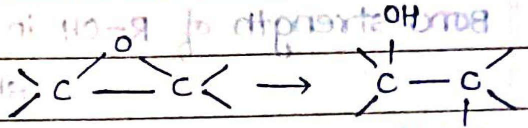
$R-NO_2 \longrightarrow R-NH_2$



Lactone

$R-C\equiv N \longrightarrow R-CH_2-NH_2$

$R-C=N-OH \longrightarrow R-CH_2-NH_2$



epoxide

$-C\equiv C- \longrightarrow CH_3-CH_3$

$R-X \longrightarrow R-H$

- M.O.P By Nitrous acid:

HNO_2 — Nitrous acid → unstable.
↓
using $(NaNO_2+HCl) \longrightarrow HNO_2+NaCl$

$R-\overset{\oplus}{N_2}\overset{\ominus}{Cl} \longrightarrow \overset{\oplus}{R}$

$-\ddot{N}H_2 + HNO_2 \xrightarrow[(NaNO_2+HCl)]{0-05^\circ C} -\overset{\oplus}{N_2}-\overset{\ominus}{Cl}$ Diazonium Salt

→ Aliphatic diazonium salt (unstable)

→ Aromatic Diazonium (stable − 0°−5°C)

- $R-\ddot{N}H_2 \xrightarrow[0-5^\circ C]{NaNO_2+HCl} R-\overset{+}{N_2}Cl \longrightarrow \overset{\oplus}{R} \xrightarrow{H_2O} R-OH$ Alcohol.

↓
Rearrangement
Krta hain.

- Physical properties:

① 1°− 4 number alcohol — highly soluble in water — Due to hydrogen bonding.
② Boiling point ∝ No. of −OH group.
③ Boiling point $\propto \frac{1}{\text{Branch}}$ (M.wt → constant
No. of OH group → same)

- chemical properties :

① Bond strength of C–OH bond —— 1° > 2° > 3° (C–OH)

stability —— 3° > 2° > 1° (C–OH)

② Bond strength of R–OH in alcohol. —— 3° > 2° > 1° (O–H)

stability —— 1° > 2° > 3° (O–H)

③ Acidic strength —— 1° > 2° > 3° alcohol.

- Concept: R —$\boxed{\text{O — H}}$→ Active Hydrogen ① —— Basic condn mein acid-Base Rxn krta hain

② Poor L.G. ③ Nucleophile nature.

H+ or Lewis acid get convected to good L.G and then occurs in SN and E reaction.

$R-\ddot{O}H + H^+ \longrightarrow R-\overset{+}{O}(H)-H \longrightarrow R^+ + H_2O$

Neutral stable molecule

① Reaction of 'H' of alcohol.

$R-O-H \xrightarrow{Na} R-O^-Na^+ + H_2\uparrow$

$\xrightarrow{NaOH} R-ONa + H_2O$

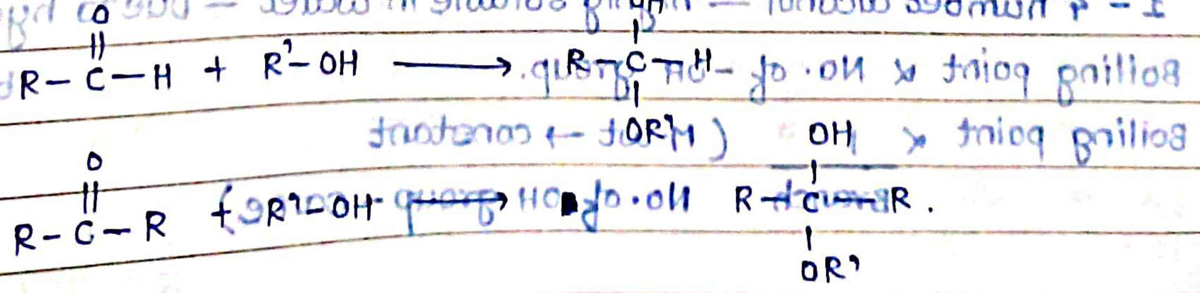
$\xrightarrow{NaH} RONa + H_2\uparrow$

$\xrightarrow{CH_3MgBr} ROMgBr + CH_4$

$\xrightarrow{CH_3C\equiv C^-Na^+} CH_3C\equiv CH + R\bar{O}Na^+$

$\xrightarrow{NaNH_2} NH_3 + RONa.$

② Nucleophilic nature of alcohol (R-OH)



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

$$R-\overset{O}{\overset{\|}{C}}-R + R'-OH \longrightarrow R-\overset{OH}{\underset{OR'}{C}}-R.$$

$R-\overset{O}{\overset{\|}{C}}-Cl + R'-OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-OR'$ (ester)

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

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

⑤ Reaction with Acid

Alcohol ⟶

$\overset{+}{}H_2O$

oxy-acid ⟶ dehydration of ⟶ alkene

$H_2SO_4 \longrightarrow H^+ + HSO_4^\ominus$ Alcohol

$H_3PO_4 \longrightarrow H^+ + H_2PO_4^\ominus$ $\boxed{HSO_4^\ominus}$ ⟶ Behaves as a Bulky Base.

$\overset{+}{}H_2O$

Halogen acid ⟶ substitution ⟶ alkyl halide Reaction

$HX \longrightarrow H^+ + X^\ominus$

(HI > HBr > HCl > HF) Reason – $X^\ominus > H_2O$ – $Nu^\ominus$

Better $Nu^\ominus$ in compare to H_2O.

- $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-OH + H^+ \longrightarrow CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{\oplus}{CH_2} \longrightarrow CH_3-\overset{\oplus}{\underset{CH_3}{\underset{|}{C}}}H-CH_3$

$X^\ominus (Nu^-)$ Subs. RXN ⟶ $CH_3-\overset{|}{\underset{CH_3}{\underset{|}{C}}}-CH_3$

$HSO_4^\ominus$ (Base) ⟶ Elimination: $CH_3-\underset{CH_2}{\underset{\|}{C}}-CH_3$

- Reactivity ∝ stability of carbocation

Rate of dehydration } ∝ stability of carbocation.
Reactivity order with HBr }

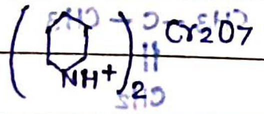
- Note: $-\overset{|}{C}=\overset{|}{C}-OH$ ⟶ Never do dehydration or substitution rxn. Due to partial double bond character.

- Reaction with PCl_3 or Red P/Cl_2, PCl_5 or $SOCl_2$ – Alkyl halide ke MOP me bataya hain.

$$R-O-H + PCl_5 \xrightarrow[Cl]{S_N2} R-Cl + POCl_3$$

- oxidation of alcohol.

	$R-CH_2OH \rightarrow RCOOH$	$R-CH_2OH \rightarrow RCHO$	$R_2CHOH \rightarrow R_2C=$
① Acidic $KMnO_4$ (strong O.A) $MnO_4^{\ominus} \rightarrow Mn^{+2}$ Purple colourless	(✓)	(x)	(✓)
② Acidic $K_2Cr_2O_7$ (strong O.A.) $Cr_2O_7^{-2} \rightarrow Cr^{+3}$ orange green	(✓)	(x) ——	(✓) Note: t-alcohol convert in alkene.
③ Jone's Reagent — Acidic chromic acid soln $CrO_3 + H_2O \rightarrow H_2CrO_4$ or $CrO_3/H_2O/H^+$	(✓)	(x)	(✓)
④ PCC : Pyridinium chloro chromate in CH_2Cl_2 solvent (selective Reagent)	(x)	(✓)	(✓)
⑤ PDC : Pyridinium dichromate	(x)	(✓)	(✓)
⑥ Cu-powder / 300°C (Test of 1°, 2° and 3° Alcohol)	(x)	(✓)	(✓) Note: t-alcohol convert into Alkene.



Sarett's Reagent

Sarett's Reagent in CH_2Cl_2 solvent is known as Collins Reagent

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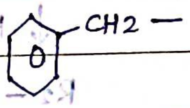
$R-CH_2-OH \xrightarrow[300^\circ C]{Cu} RCHO$ $\quad R_2CH-OH \xrightarrow[300^\circ C]{Cu} R_2C=O$

$R_3C-OH \xrightarrow[300^\circ C]{Cu} R_2C=CH_2$

Note : MnO_2 — oxidising agent

- selective oxidising agent for Allylic and Benzylic position.

$CH=CH-\underset{|}{C}H-$ (Allylic)  (Benzylic) 1° alcohol — $-CHO$

2° alcohol — $>C=O$

- Test of Alcohol :

① Lucas Reagent

$ZnCl_2$ / conc. HCl solution — L.R.

$R-OH + ZnCl_2 \longrightarrow R^{\oplus} \xrightarrow{Cl^{\ominus}} R-Cl$

(L.B) (L.A) carbocation Alkyl halide

(white cloud form hota hain)

1°- Alcohol $\xrightarrow[HCl]{ZnCl_2}$ No rxn at room temperature (Does not form white cloud)

in high temp ⟶ white cloud form.

2°- Alcohol $\xrightarrow[HCl]{ZnCl_2}$ white cloud form after 3-5 minutes.

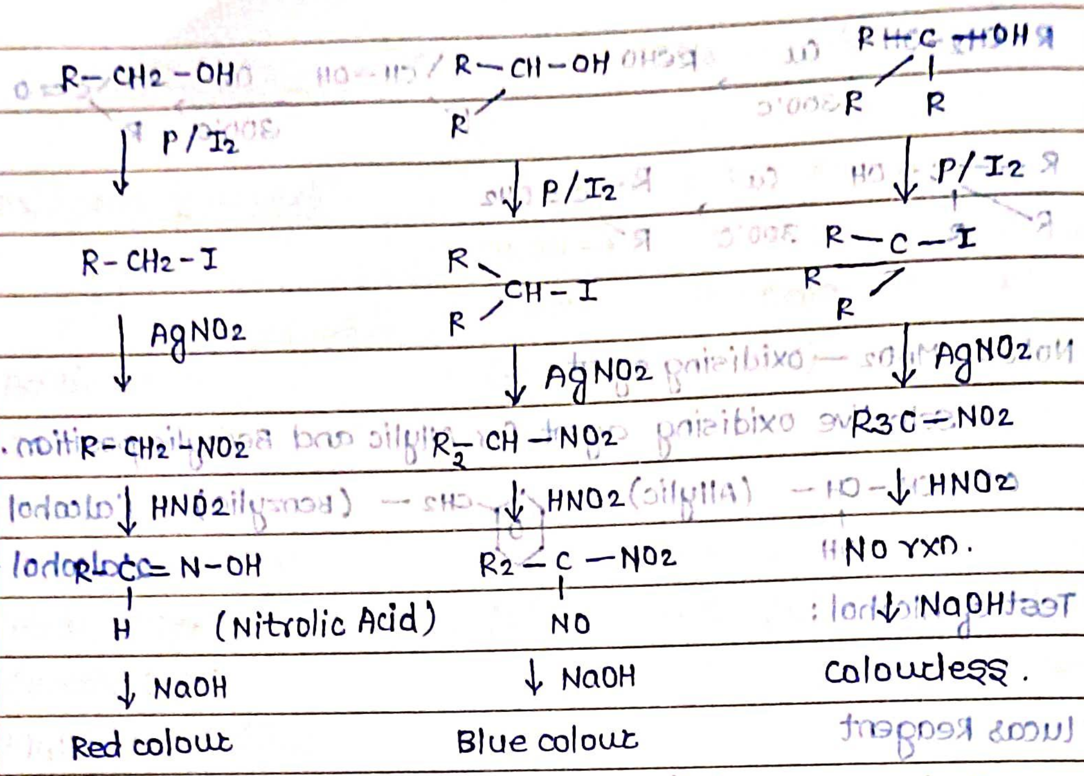
3°- Alcohol $\xrightarrow[HCl]{ZnCl_2}$ white cloud form within 1-2 minutes.

- Reactivity of L.R with alcohol ∝ stability of carbocation.

(Note : $>C=C-OH$ L.R NO rxn)

- Victor-Mayer test : R · B · C

1° 2° 3°



Phenol

- **Method of preparation:**

(① Diazonium salt)

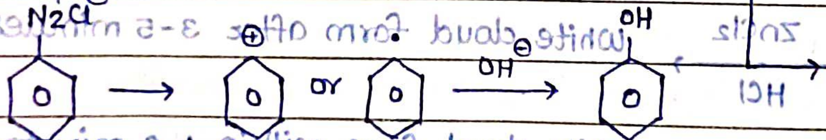
$R-\overset{+}{N_2}\overset{\ominus}{Cl}$ – Unstable.

$-NH_2 + HNO_2 \xrightarrow{0-5°C} \overset{+}{N_2}\overset{\ominus}{Cl}$

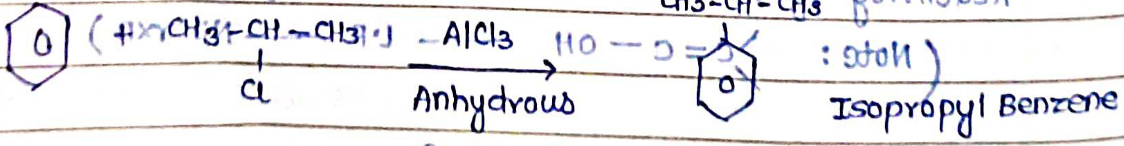
$(NaNO_2 + HCl)$

$Ar-\overset{+}{N_2}\overset{\ominus}{Cl}$ – stable

at 0°C - 5°C



② Air oxidation of cumene further catalysed by Acid.

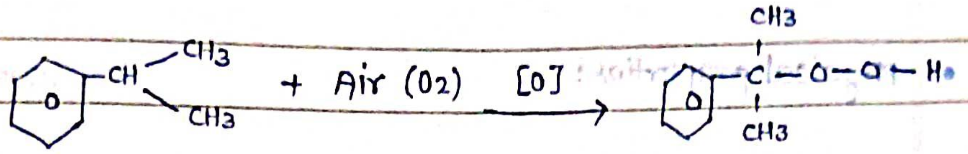


F.C.R.

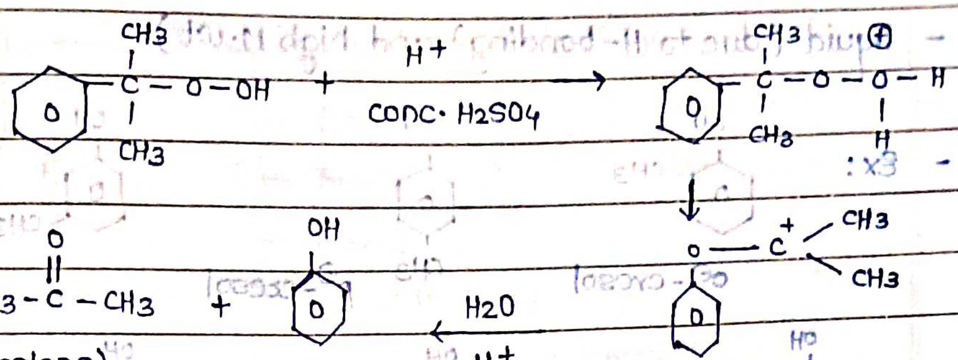
$CH_3-\overset{\oplus}{CH}-CH_3 + \overset{\ominus}{AlCl_4}$

(E^+)

- **Step I :**



- **Step II :**

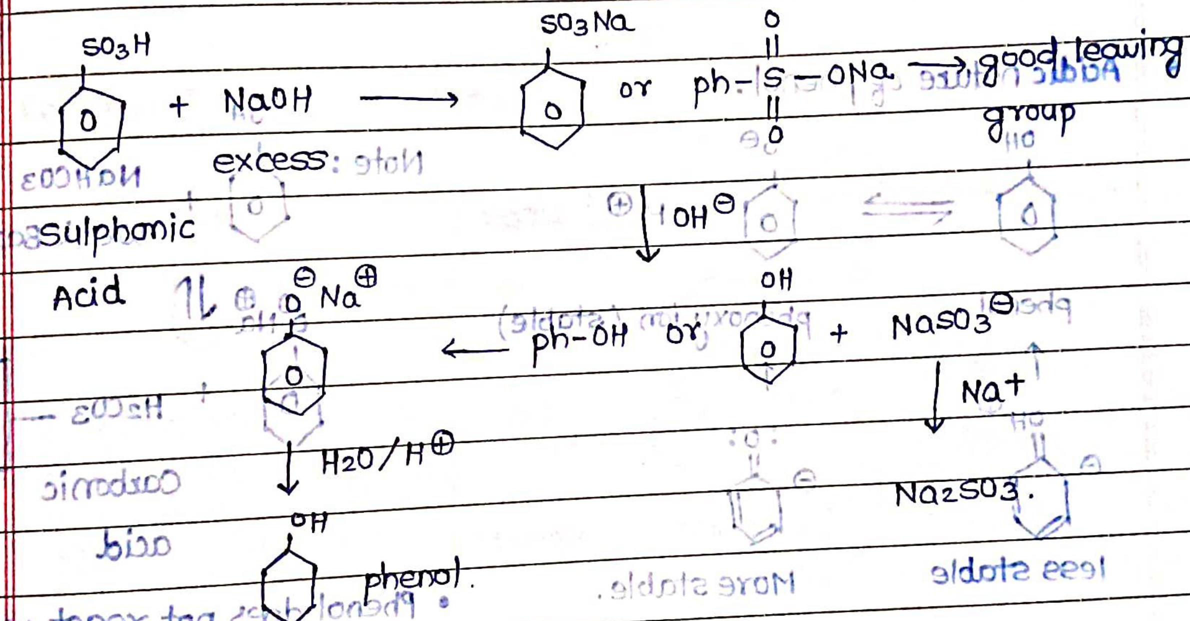


(Acetone) (Phenol)

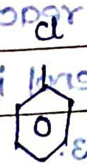
↓

M.O.P of Acetone.

③



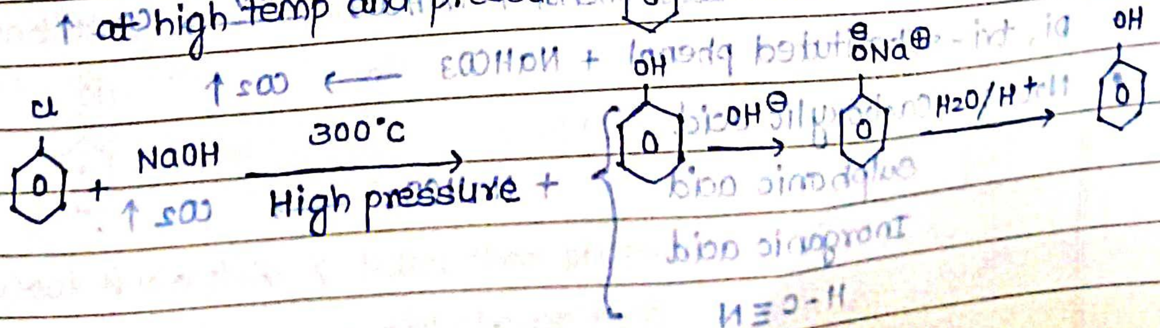
④ Chloro Benzene (Dow's process)



↓ S_N1 and S_N2 ⟶ Nahi dete hain

↓

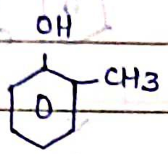
↑ at high temp and pressure  show S_N2 rxn / S_N1 rxn.



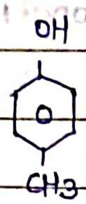
- Physical properties:

- liquid (due to H-bonding) and high M·wt)

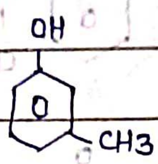
- Ex:



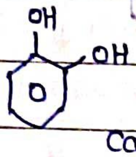
o⊖-cresol



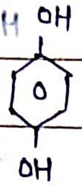
p⊖-cresol



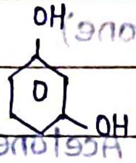
m⊖-cresol



catechol

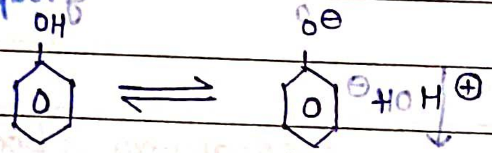


quinol

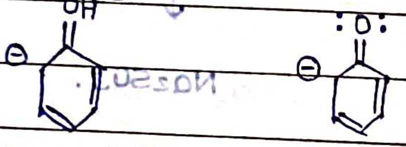


Resol crenol.

- Acidic nature of phenol:

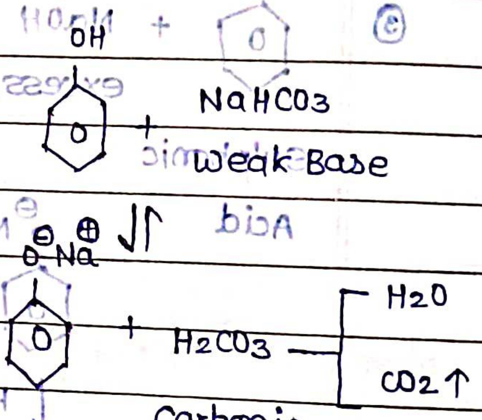


phenol   phenoxy ion (stable)



less stable   More stable.

Note:



Carbonic acid

- Phenol does not react with NaHCO3 bcoz phenol is less acidic than H_2CO_3.

- Acidic stregth of phenol:

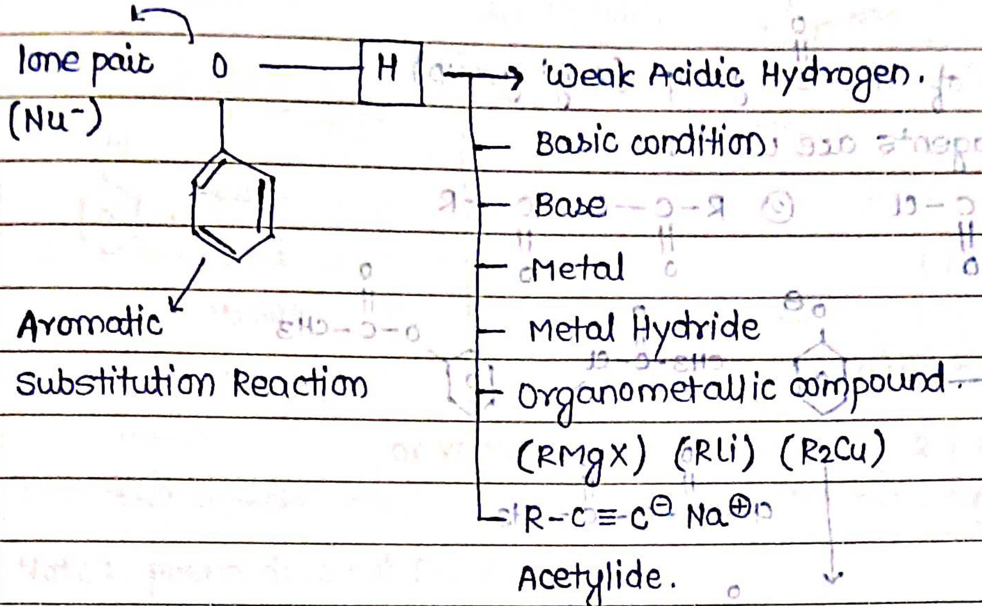
$$A\cdot S \propto \frac{(-I)\ (-M)}{(+I)\ (+M)}$$

- Phenol, mono substituted phenol + $NaHCO_3$ $\xrightarrow{\otimes}$ CO_2 ↑

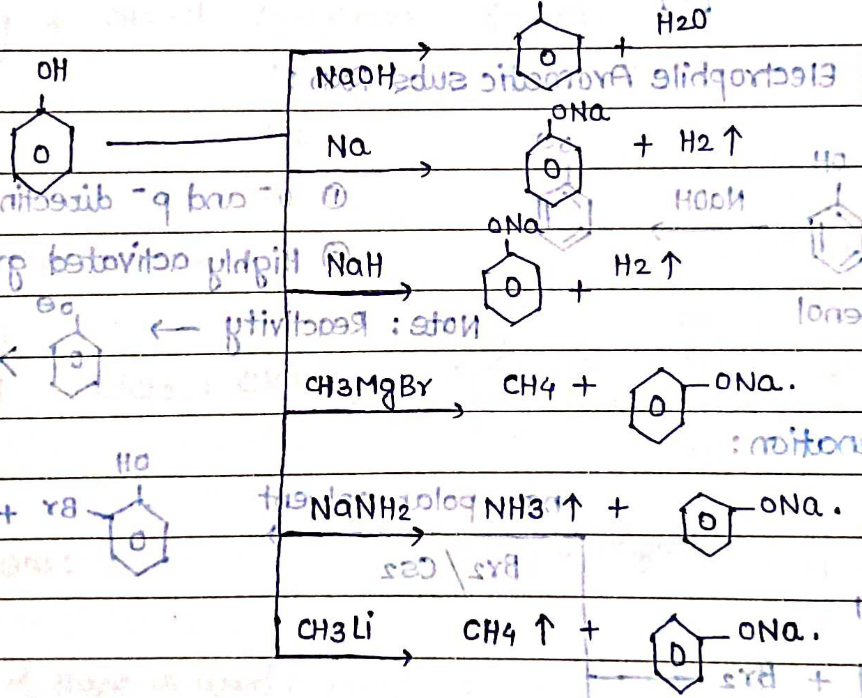
Di, tri-substituted phenol + $NaHCO_3$ ⟶ CO_2 ↑

- Note: Carboxylic acid
Sulphonic acid
Inorganic acid
$H-C\equiv N$
} + $NaHCO_3$ ⟶ CO_2 ↑.

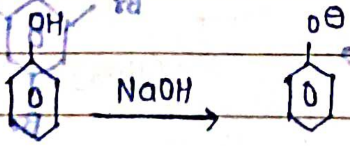
- chemical properties :



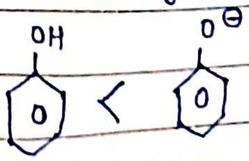
① Reaction of H-atom of phenol.



② Reaction of Nucleophilic nature of phenol



$Nu^{\ominus}$ strength :



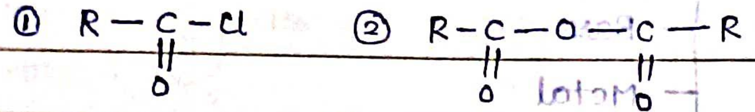
Weak Nucleophile < Better than phenol

- Resonance(I) - -ve charge hain.

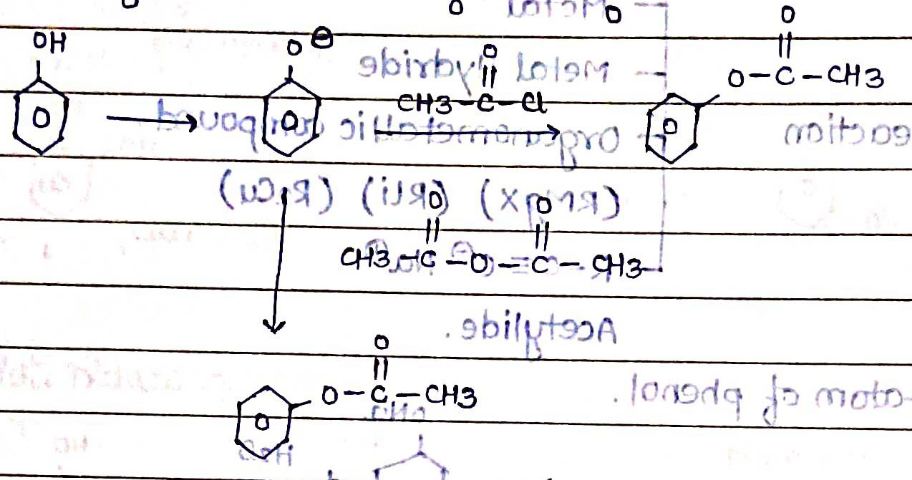
- Bulky

- **Acylation of phenol:**

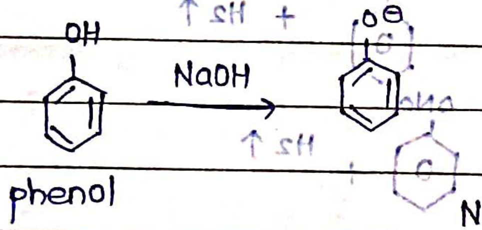
- Addition of $CH_3-\overset{O}{\overset{||}{C}}-$ group (Acyl group)
- Two Reagents are used:



① $R-\underset{O}{\underset{||}{C}}-Cl$ ② $R-\underset{O}{\underset{||}{C}}-O-\underset{O}{\underset{||}{C}}-R$

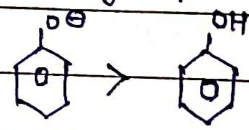


- **Rxn of Electrophile Aromatic subs Rxn:**

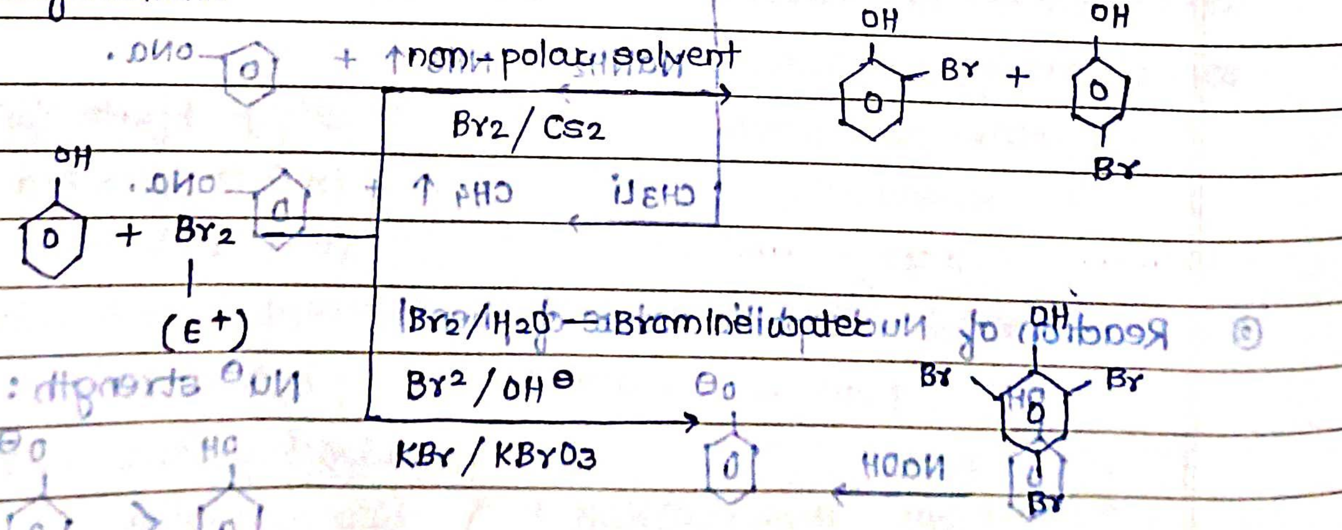


① o⁻ and p⁻ directing.
② Highly activated group.

Note: Reactivity →



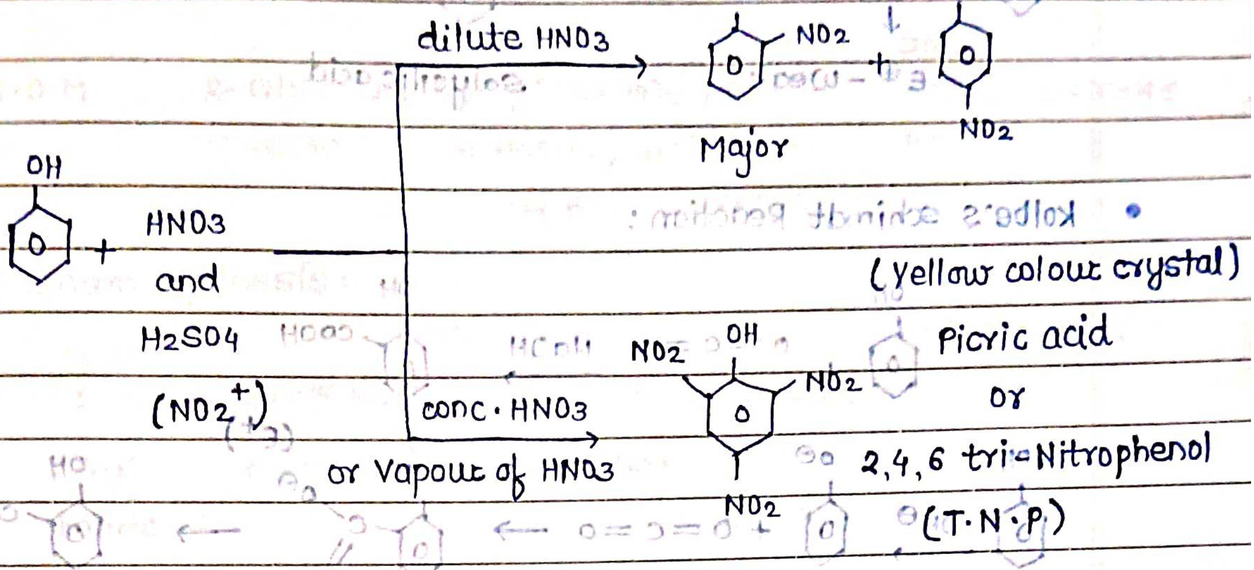
- **Halogenation:**



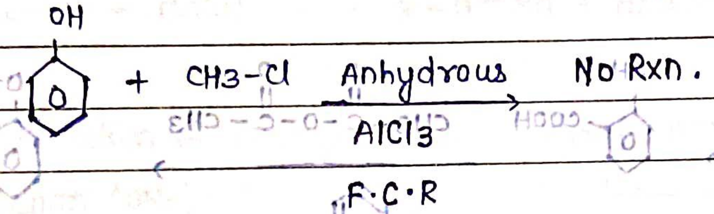
2,4,6-Tri-Bromo-phenol

(White ppt↓)

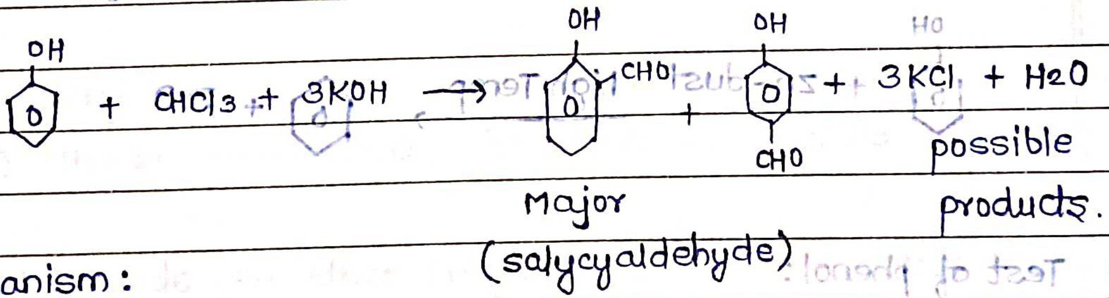
- **Nitration :**



- Note : phenol does not F.C.R



- Riemer - Teimann Reaction :



- Mechanism :

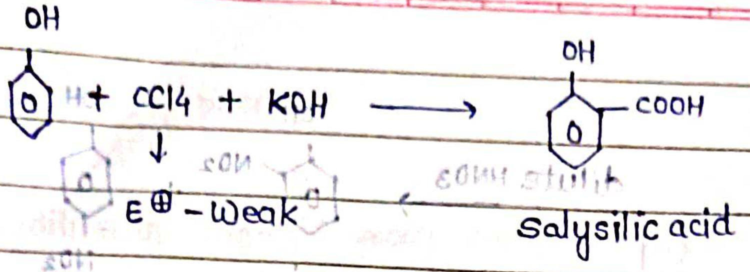
① 3 mole of Base is used

$CHCl_3 + OH^{\ominus} \longrightarrow CCl_3^{\ominus} + H_2O.$
(KOH)

$CCl_3^{\ominus} \longrightarrow CCl_2 + Cl^{\ominus}$

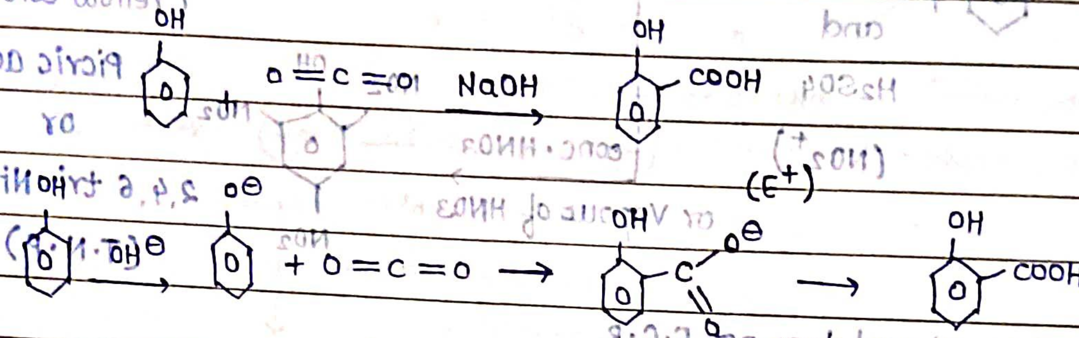
α-elimination → Electroephile (weak - Neutral)
- Dichloro carbene (singlete)

(b)



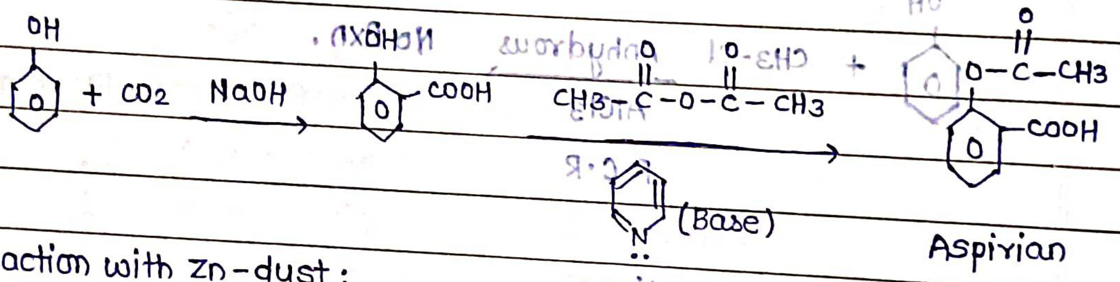
salysilic acid

- **Kolbe's schimdt Reaction :**



Salicylic acid

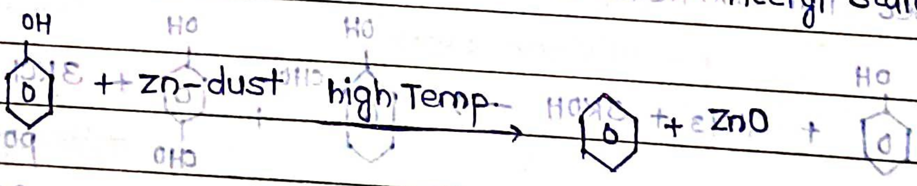
- **Aspirin Formation**



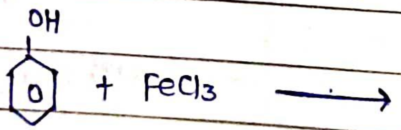
Aspirian

Acetyl Salicylic acid

- **Reaction with Zn-dust :**

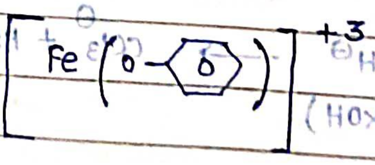


- **Test of phenol :**



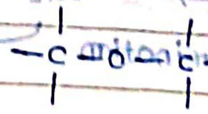
Violet colour complex

Solution



- **Ether :**

$R-O-H \xrightarrow{-H} R-O-R$ (Ether)



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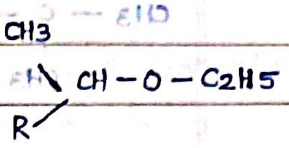
- M·O·P :

① O·M·D·M $R-CH_2=CH_2 \xrightarrow[\text{② } NaBH_4 / OH^{\ominus}]{\text{① } Hg(OOCCH_3)_2 / C_2H_5OH}$



$\underset{R}{\overset{CH_3}{CH}}-O-C_2H_5$

M·R

② Williamson synthesis :

$$\underset{\text{Alkyl halide}}{R-X} + \underset{\text{Alkoxide ion}}{R-O^{\ominus}Na^{\oplus}} \longrightarrow \underset{\text{Ether}}{R-O-R} + NaX$$

- $R-OH + NaOH \longrightarrow R-O^{\ominus}Na + H_2O$

Substitution Reaction (S_N2) ← Strong $Nu^{\ominus}$

Strong Base − Elimination RXN (E2) → steric hindrance

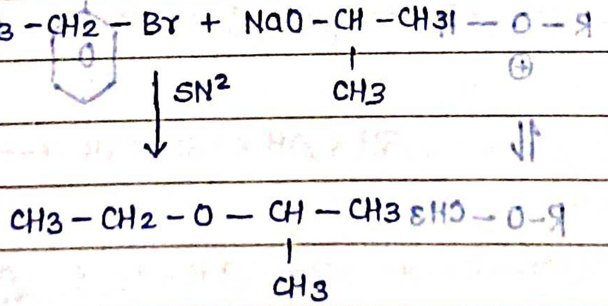
(a) Ether Formation :

Note : Alkyl halide

① CH_3-Br ——— always form ether

$R-O^{\ominus}Na + CH_3Br$
↓
$R-O-CH_3 + NaBr$
(100%)

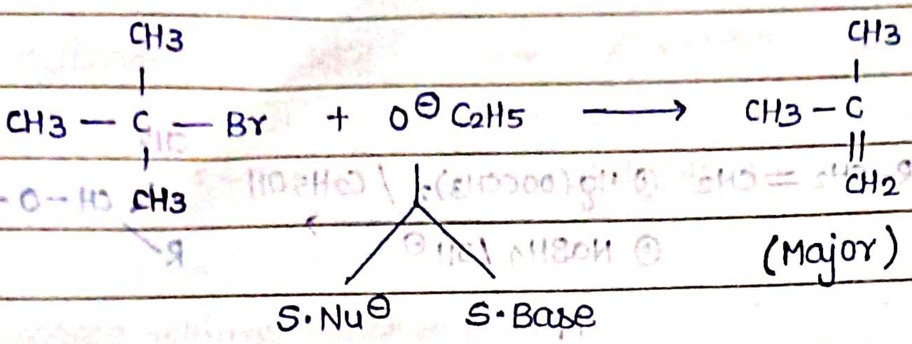
② 1° alkyl halide ⟶ ether (Major)



$$CH_3-CH_2-Br + NaO-\underset{CH_3}{CH}-CH_3 \xrightarrow{S_N2} CH_3-CH_2-O-\underset{CH_3}{CH}-CH_3$$

- No Byproduct
- Best method for formation of Ether By Williamson synthesis

③ 3°− alkyl halide ⟶ Alkene (Major)



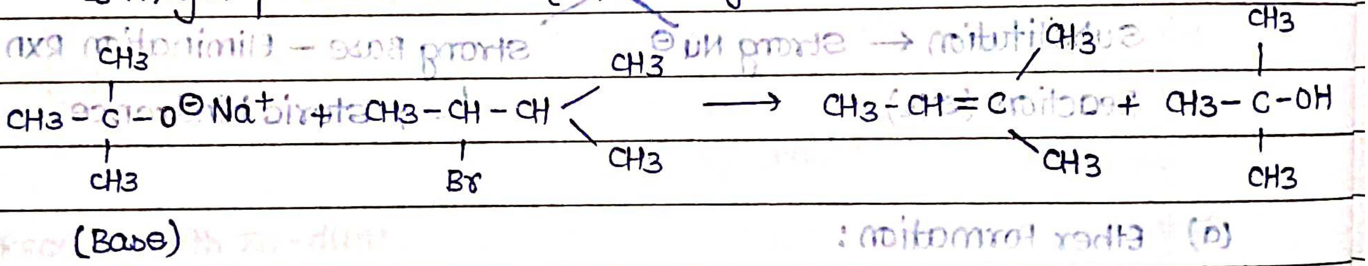
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br + O^{\ominus}C_2H_5 \longrightarrow CH_3-\overset{CH_3}{C}=CH_2$$

⑨ 2' alkyl halide ⟶ Alkene / ether

↳ Normal 2' - alkyl halide pr ether major product hoga.

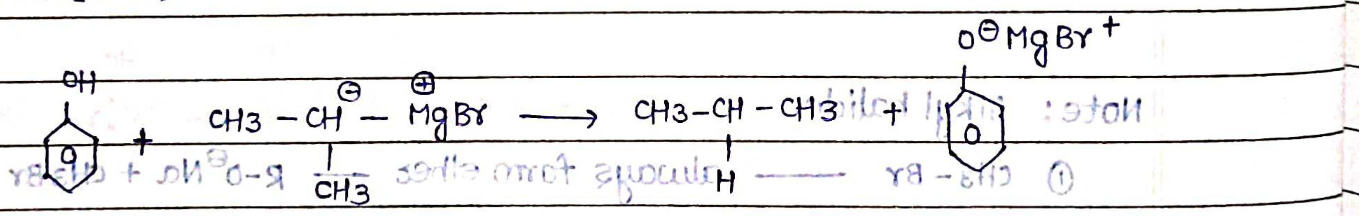
Bulky hone pr alkene major hoga

- Note : In case of Bulky Alkoxide (3' carbon), Alkene form as a major product with (2', 3'-alkyl halide)

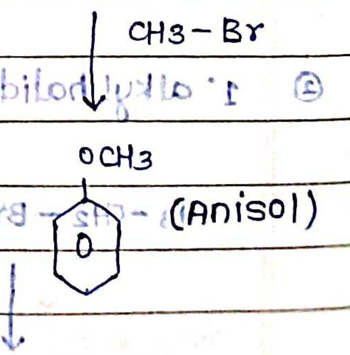


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O^{\ominus}Na^{+} + CH_3-\underset{Br}{CH}-CH(CH_3)_2 \longrightarrow CH_3-CH=C(CH_3)_2 + CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

Q.

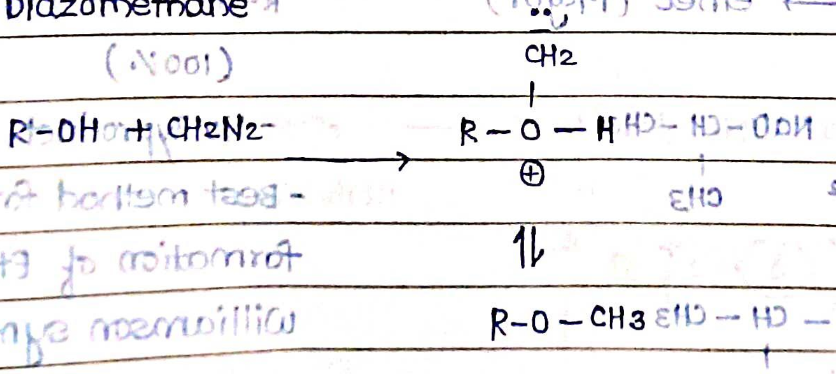


$$C_6H_5OH + CH_3-\underset{CH_3}{\overset{\ominus}{CH}}-\overset{\oplus}{Mg}Br \longrightarrow CH_3-\underset{H}{CH}-CH_3 + C_6H_5O^{\ominus}MgBr^{+}$$



$$\xrightarrow{CH_3-Br} C_6H_5OCH_3$$

③ Diazomethane



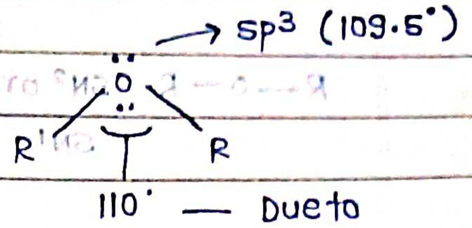
$$R-OH + CH_2N_2 \longrightarrow R-\overset{\ddot{C}H_2}{\underset{\oplus}{O}}-H \rightleftharpoons R-O-CH_3$$

$$\underset{\text{Diazomethane.}}{CH_2N_2} \xrightarrow{\Delta} \underset{\text{Carbene}}{:CH_2} + N_2 \longrightarrow \text{Best L·G}$$

- Physical properties :

R – O – R ⟶ absence of H - bonding

B.p = R-OH > R-O-R



— Due to electronic Repulsion b/w two bulky groups.

I. Chemical properties :

$R-\ddot{O}-R \xrightarrow{H^+} R-\underset{\underset{H}{|}}{\overset{\oplus}{O}}-R$

lone pair (Lewis Base) ; Poor L.G ; ⟶ Good L.G

* Substitution Reaction possible (SN – Rxn)

Acid – Base Reaction

- Acid-Base Reaction :

$R-\ddot{O}-R + HCl \longrightarrow \left[R-\underset{|}{\overset{+}{O}}-R\right] Cl^{\ominus}$

$R-\ddot{O}-R + \underset{\underset{\text{Vacant orbital (L.A)}}{\downarrow}}{B_2H_6} \longrightarrow \underset{R}{R-\overset{\oplus}{O}} \rightarrow \overset{\ominus}{BH_3}$

- Reaction with HX (Halogen acid)

HX ⟶ HI > HBr > HCl > HF

$R-\ddot{O}-R + H-X \longrightarrow R-\underset{\underset{H}{|}}{\overset{\oplus}{O}}-R \overset{X^{\ominus}}{\xrightarrow[S_N2]{}} R-OH + R-X$

Nu⊖ ⟶ $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$

A.S ⟶ HI > HBr > HCl > HF

Note: oxo-acid does not give this type of rxn.

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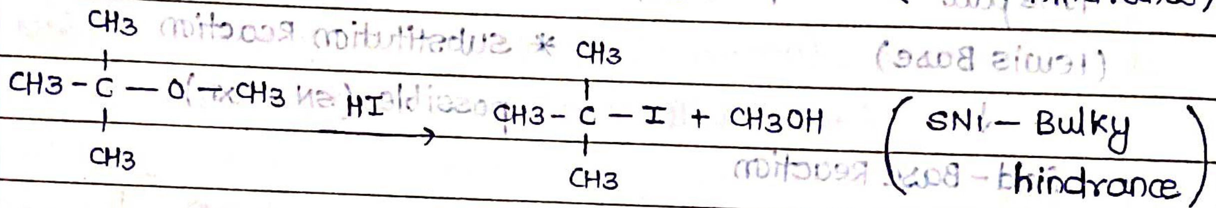
$R—O—R$ $\xrightarrow[\text{or dilute HI}]{\text{Cold HI}}$ $R—O—H + R—I$

SN^2 or SN^1

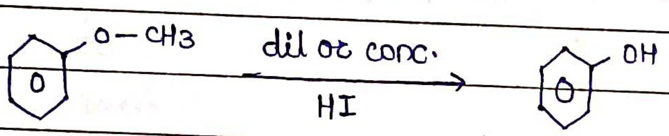
$\xrightarrow[\text{or conc. HI}]{\text{Hot HI}}$ $R\text{-}OH + RI \xrightarrow{HI} R\text{-}I + R\text{-}I$

Q. $CH_3-O-CH_2-CH_3 \xrightarrow{HI} CH_3I + CH_3CH_2OH$ (SN_2 – less hindrance)



Q. $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_3 \xrightarrow{HI} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-I + CH_3OH$ (SN_1 – Bulky hindrance)

Q.



$\xrightarrow[HI]{\text{dil or conc.}}$ + CH_3I

Q. $CH_2=CH-O-CH_3 \xrightarrow[HI]{\text{dil or conc.}} CH_2=CH-OH + CH_3I \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-H + CH_3I$

Aliphatic enol form (unstable)

(Keto form)

- Reaction with H_2O/H^+ :

$$R-O-R' + H^+ \rightleftharpoons R-\overset{\oplus}{\underset{H}{O}}-R' \xrightarrow{H_2O} R-OH + R'-OH$$

Note: All concept are same (HI rxn)

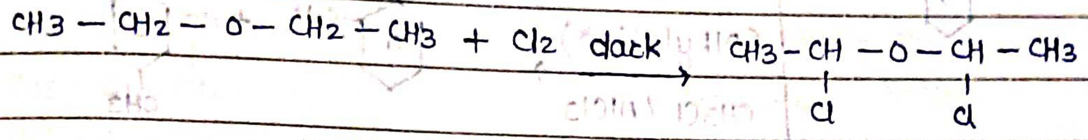
Q. $CH_2=CH-O-CH_3 \xrightarrow{H_2O^{18}/H^+} CH_2=CH-OH + CH_3-O^{18}H$

$\upharpoonleft\downharpoonright$

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

- Halogenation :

(a) In Dark (absence of sunlight or hv energy)



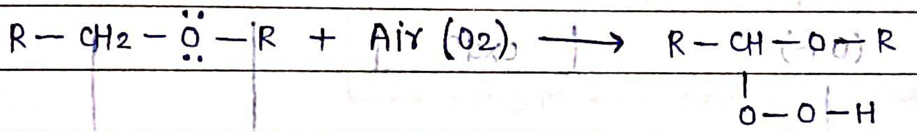
$$CH_3-CH_2-O-CH_2-CH_3 + Cl_2 \xrightarrow{dark} \underset{Cl}{CH_3-CH}-O-\underset{Cl}{CH}-CH_3$$

Mono-halogenation.

(b) In presence of sunlight :

$$CH_3-CH_2-O-CH_2-CH_3 + Cl_2 \xrightarrow{hv} C_2Cl_5-O-C_2Cl_5$$

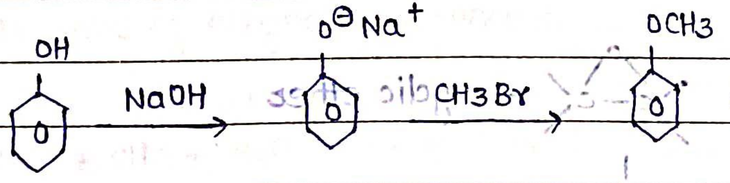
- Oxidation : Ether oxidise by air in very slow rate and form peroxide ether.



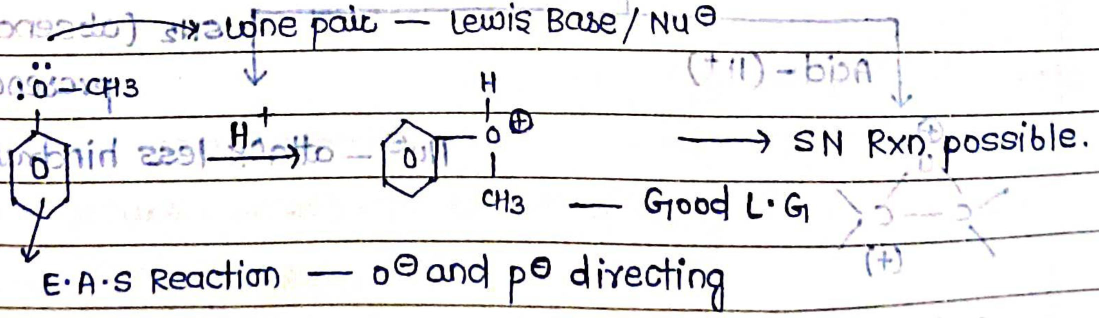
$$R-CH_2-\ddot{O}-R + Air\ (O_2) \longrightarrow R-\underset{O-O-H}{CH}-O-R$$

Ether peroxide ether.

- Aromatic ether :



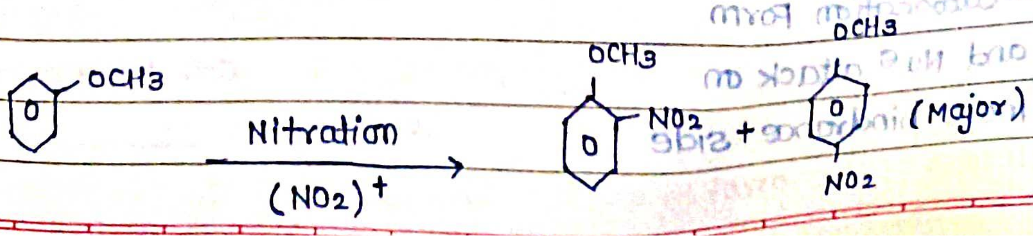
Anisol

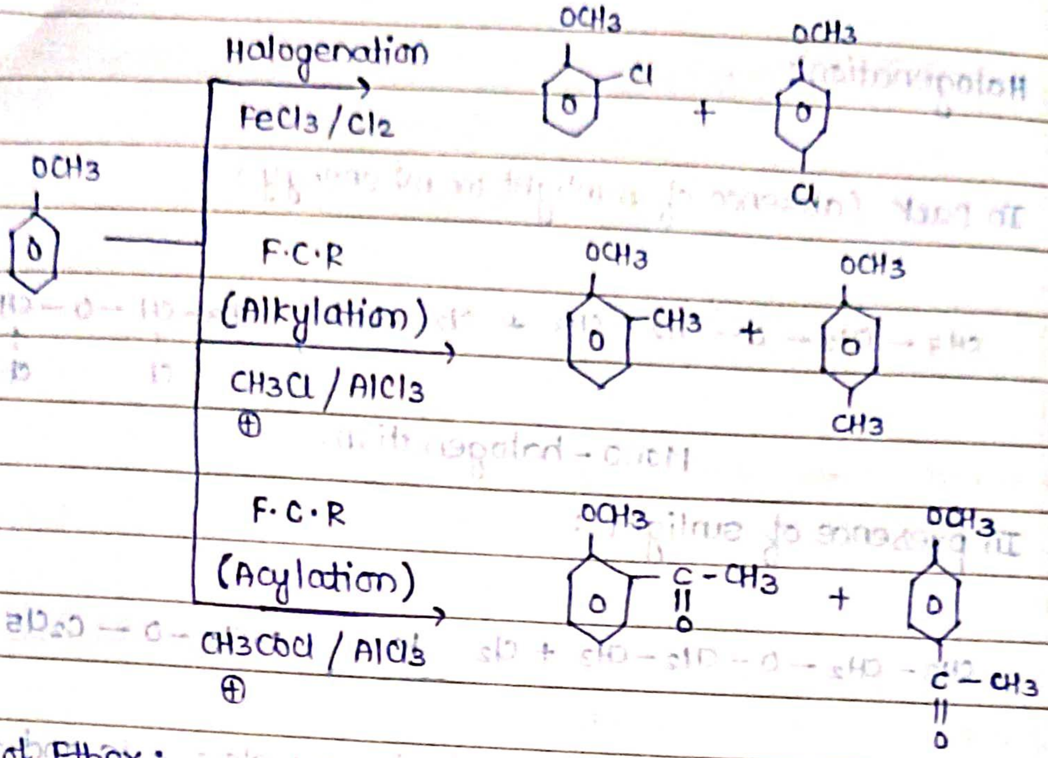


⟶ SN Rxn possible.

— Good L.G

E.A.S Reaction — o⊖ and p⊖ directing





- **Test of Ether :**

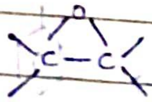
(Purple/pink)

Ether + Ether peroxide + KI ⟶ I_2 + Ether + Alcohol

(O·A) oxdn

Redn

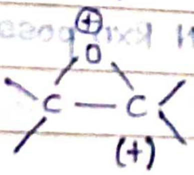
- **Epoxide Ring :**



— cyclic ether

Acid - (H^+)

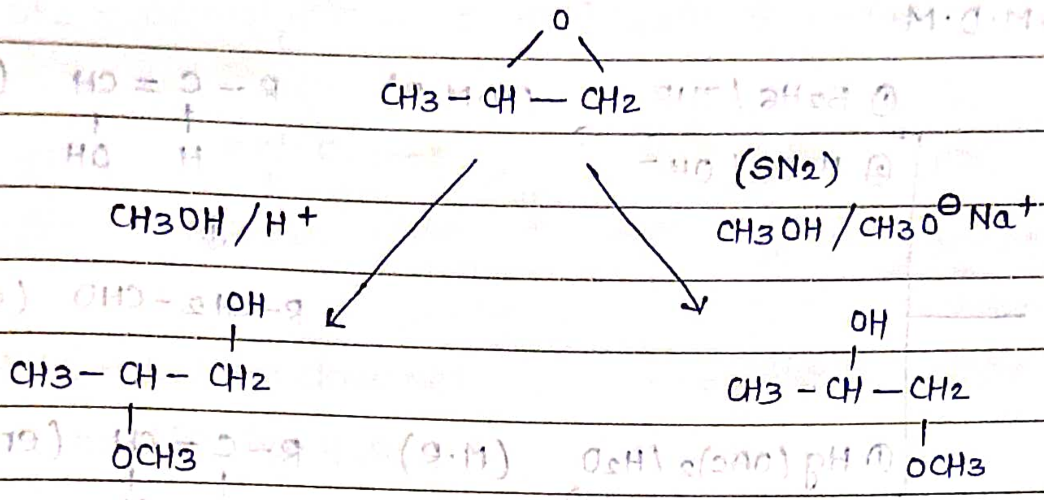
S_N2 (absence of acid or presence of Base)



Nu⊖ - attack less hindrance side

- Carbocation Form and Nu⊖ attack on more hindrance side

•


CH3 – CH — CH2
O
CH3OH / H+
(SN2)
CH3OH / CH3O⊖ Na+
CH3– CH– CH2
OH
OCH3
OH
CH3 – CH — CH2
OCH3