Alcohol Phenol Ether

Alcohol → Hydrogen atom is replaced by –OH group in aliphatic Hydrocarbon

Phenol → H atom is replaced by OH group in aromatic Hydrocarbon

Ether → H atom is replaced by alkoxy ($O-CH_3$) or aryloxy ($O-ph$) in aliphatic/aromatic Hydrocarbon.

Classification

~~Aliphatic Alcohol~~

- OH attached to sp^3 Carbon
  - normal alcohol
  - Allylic alcohol
  - Benzylic alcohol

~~Aromatic Alcohol~~

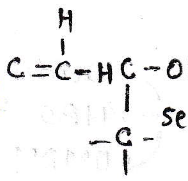
- OH attached to sp^2 Carbon of Benzene.
  - Vinylic alcohol
  - Phenol

→ 1° alcohol Primary $-CH_2-OH$

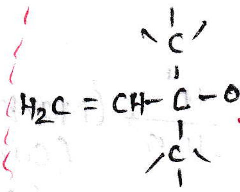
→ 2° alcohol Secondary $>CH-OH$

→ 3° alcohol Tertiary $\geq C-OH$

$H_2C=CH-H_2C-OH$ Primary allylic alcohol

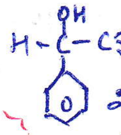


$C=\overset{H}{C}-HC-OH$; $-\underset{|}{\overset{|}{C}}-$ secondry allylic alcohol

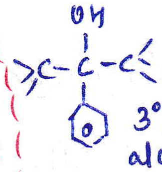


$H_2C=CH-\underset{C}{\overset{C}{C}}-OH$ Tertiary allylic alcohol.

1° Benzylic alcohol

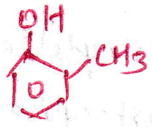


2° Benzylic alcohol



3° Benzylic alcohol

$H_2C=HC-OH$

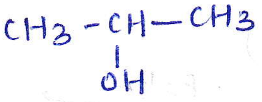


Ether → Symmetrical ether (simple ether) eg. $C_2H_5-O-C_2H_5$ / CH_3-O-CH_3

Ether → Unsymmetrical ether (mixed ether) eg. $C_2H_5-O-CH_3$ / $C_2H_5-O-C_6H_5$

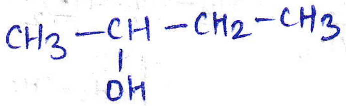
Common Naming of alcohol, phenol, ether

$CH_3-CH_2-CH_2-OH$ n propyl alcohol

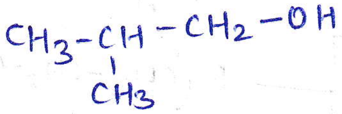


$CH_3-\underset{OH}{CH}-CH_3$ Isopropyl alcohol

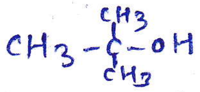
$CH_3-CH_2-CH_2-CH_2-OH$ n butyl alcohol



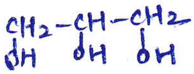
$CH_3-\underset{OH}{CH}-CH_2-CH_3$ Sec butyl alcohol



$CH_3-\underset{CH_3}{CH}-CH_2-OH$ iso butyl alcohol

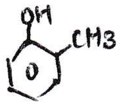


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$ tert butyl alcohol

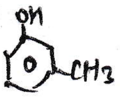


$\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$ Glycerol

phenol

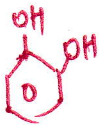


o-cresol

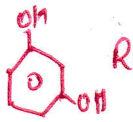


m-cresol

p-cresol



catechol



Resorcinol

quinol or Hydroquin

$CH_3-O-CH_2-CH_3$ ethyl methyl ether

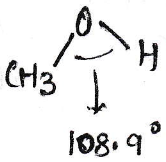
$C_6H_5-O-CH_3$ methyl Phenyl ether (Anisole

$C_6H_5-O-CH_2-CH_3$ ethyl phenyl ether (phenetole)

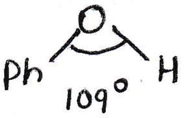
Structure of Functional group

In alcohol → oxygen atom → sp^3 hybridized → (109.5° → Bond angle)
→ 2 lone pair (lonepair–lonepair repulsion)

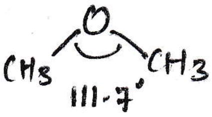
VSEPR



(CH_3) is bulky group
So, bond angle contraction decreases-



(Ph) is more bulky than CH_3



2 bulky group.

General method of Preparation

alkane

alkene
alkyne —X→ ~~एक~~ carbon पर 2OH → aldehyde or ketone forms
alkylhalide

Aldehyde/ketone

Carboxylic acid & derivative

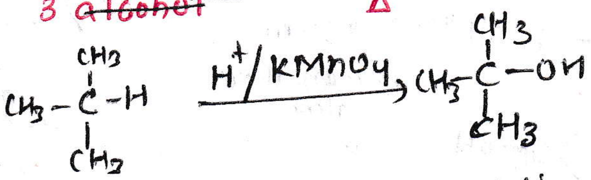
Ester

primary amine

Grignard

① alkane → alcohol

Tertiary ~~alcohol~~ alkane $\xrightarrow[\Delta]{H^+/KMnO_4}$ alcohol
3° ~~alcohol~~ alkane



$$\underset{CH_3}{\overset{CH_3}{CH_3-C-H}} \xrightarrow{H^+/KMnO_4} \underset{CH_3}{\overset{CH_3}{CH_3-C-OH}}$$

② alkene → alcohol
→ acidic Hydration
→ HBO (Hydroboration oxidation)
→ OMDM ~~(OMDM)~~ oxy mercuration demercuration

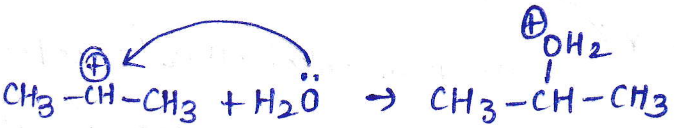
(i) acidic hydration

$$CH_3-CH=CH_2 \xrightarrow[H_2O]{H^+}$$ (Markovnikov Rule)
(carbocation form)
(carbocation Rearrange)

Step 1

$$CH_3-\overset{\oplus}{CH}-CH_3$$

Step 2

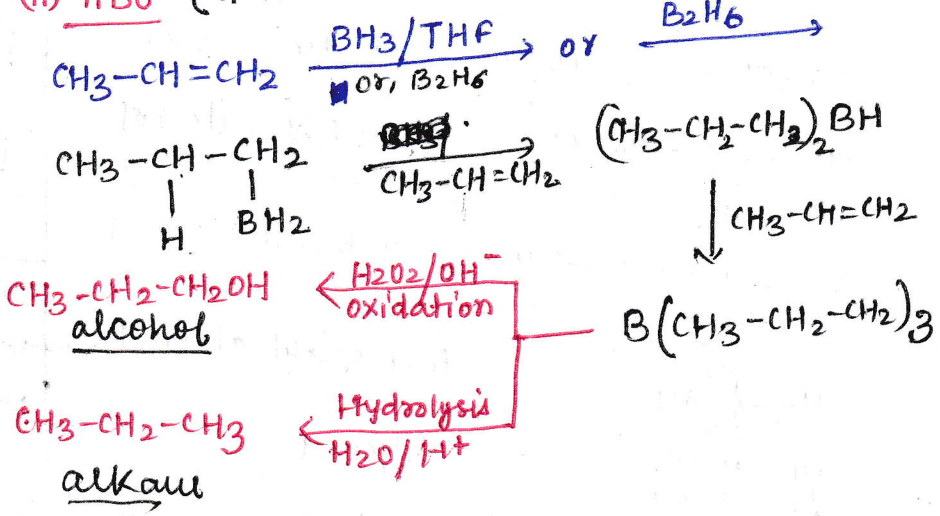


$$CH_3-\overset{\oplus}{CH}-CH_3 + H_2\ddot{O} \rightarrow CH_3-\overset{\overset{\oplus}{O}H_2}{CH}-CH_3$$

Step 3 Remove H^+

$$CH_3-\overset{\overset{\oplus}{O}H_2}{CH}-CH_3 \xrightarrow{-H^+} CH_3-\overset{OH}{CH}-CH_3$$

(ii) HBO (Anti-markovnikov Rule)



$$CH_3-CH=CH_2 \xrightarrow[\text{or, } B_2H_6]{BH_3/THF} \text{ or } \xrightarrow{B_2H_6}$$

$$\underset{H}{CH_3-CH}-\underset{BH_2}{CH_2} \xrightarrow[CH_3-CH=CH_2]{} (CH_3-CH_2-CH_2)_2BH \xrightarrow{CH_3-CH=CH_2} B(CH_3-CH_2-CH_2)_3$$

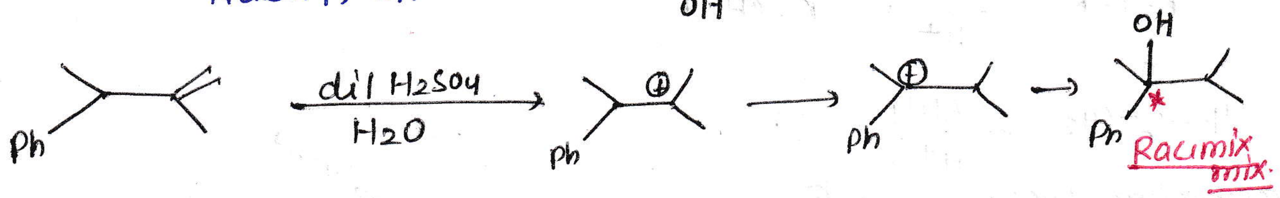
$$B(CH_3-CH_2-CH_2)_3 \xrightarrow[\text{oxidation}]{H_2O_2/OH^-} CH_3-CH_2-CH_2OH$$ alcohol

$$B(CH_3-CH_2-CH_2)_3 \xrightarrow[H_2O/H^+]{\text{Hydrolysis}} CH_3-CH_2-CH_3$$ alkane

(iii) OMDM → markovnikov (without rearrangement)

$$CH_3-CH=CH_2 \xrightarrow[NaBH_4,\ OH^-]{Hg(OAc)_2\ ,H_2O} CH_3-\underset{OH}{CH}-CH_2$$

Question



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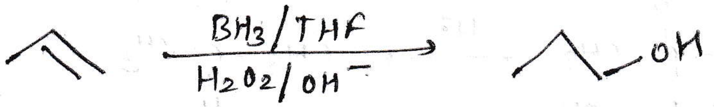

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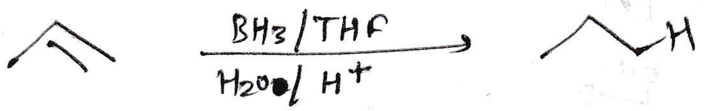

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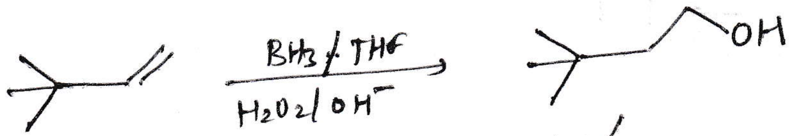

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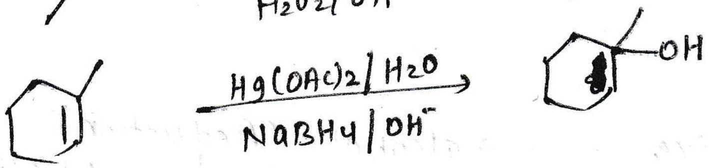

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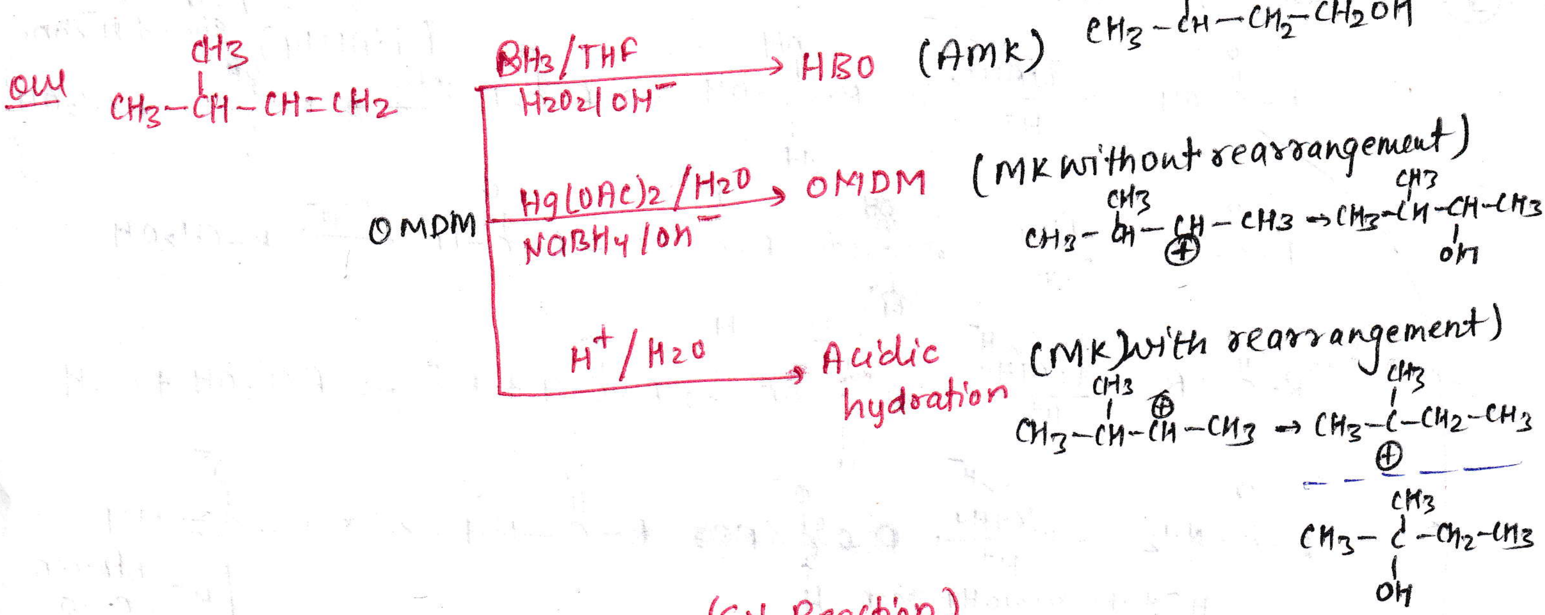
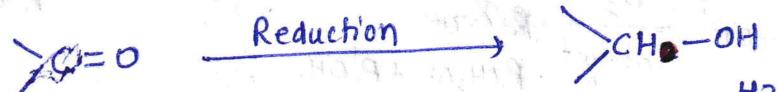


Ⅲ alkylhalide → alcohol → (SN Reaction)

$$CH_3-CH_2-Cl \xrightarrow[\text{or moist } Ag_2O]{aq\ KOH} CH_3-CH_2-OH$$

Ⅳ aldehyde/ketone → alcohol



Reducing agents
(i) Catalytic hydrogenation $\xrightarrow[Ni,Pt,Pd]{H_2}$
(ii) $LiAlH_4$ or $NaBH_4$
not in NCERT { (iii) Na+EtOH or Na in ethanol → [H] provide. (Bouveault Blanc Reduction)
(iv) NaH (Darzen Reduction)

aldehyde → 2[H]
ketone → 2[H] → alcohol.
carboxyllic acid − 4[H]
acid chloride − 4[H]

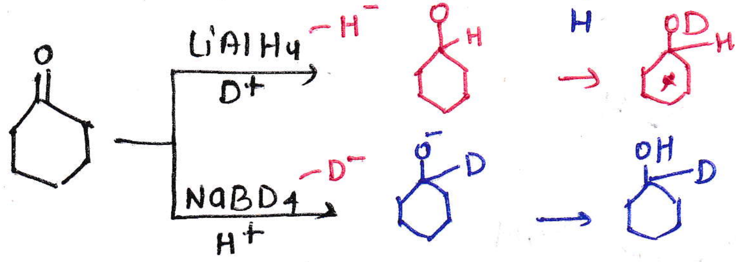
$$R-CHO \xrightarrow[H^+]{LiAlH_4 \; \rightarrow H^-} R-CH_2-OH$$

$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow[H^+]{NaBH_4 \; \rightarrow H^-} R-\overset{OH}{\overset{|}{C}}H-R$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[H^+]{LiAlH_4} ??$$

mechanism $LiAlH_4 \longrightarrow H^{\ominus}$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{H^{\ominus}} CH_3-\underset{H}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-CH_3 \xrightarrow{H^+ \; (Solvent)} CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$$



$$RCHO \xrightarrow[Ni/Pt/Pd]{H_2} RCH_2OH$$

Ⓥ ~~Red~~ Carboxylic acid & derivative ⟶ alcohol. (Reduction)
↓
($LiAlH_4$) → 1 $LiAlH_4$ gives 4 H^- ion.

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[H^+]{LiAlH_4 \; (-H^-)} R-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-OH \rightarrow R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{2^{nd}\,H^-} R-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-H \rightarrow RCH_2OH$$

$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[H^+]{LiAlH_4} R-\underset{H}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-Cl \rightarrow R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{2^{nd}\,H^-} R-CH_2OH$$

$$R-\overset{O}{\overset{\|}{C}}-OR \xrightarrow[H^+]{LiAlH_4 \; (-H^-)} R-\underset{H}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-OR \rightarrow R-\overset{O}{\overset{\|}{C}}-H + RO^- \rightarrow RCH_2OH + ROH$$

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[H^+]{LiAlH_4 \; (-H^-)} R-\overset{O}{\overset{\|}{C}}-NH^{\ominus} \longleftrightarrow R-\overset{O^-}{\overset{|}{C}}=NH$$

H^- take acidic Hydrogen of NH_2

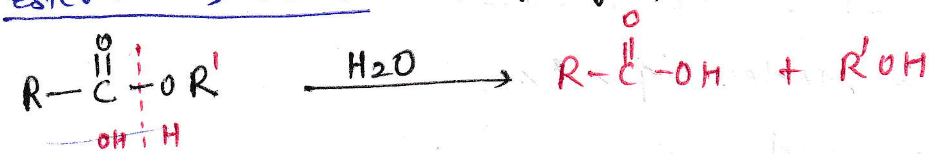
$$R-\overset{O^-}{\overset{|}{C}}=NH \xrightarrow{H^-} R-\overset{H}{\overset{|}{C}}=NH \xrightarrow{H^-} R-CH_2-NH^{\ominus} \xrightarrow{H^+ \text{ from soln}} R-CH_2-NH_2$$

between C–O and C=N C–O is easy to leave

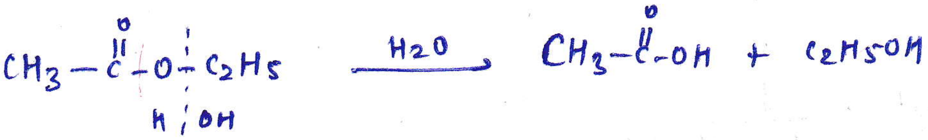
$LiAlH_4$ → Expensive Reducing agent
so, first acid is converted to ester then reduction of ester using catalytic hydrogenation.

$$R-COOH \xrightarrow[H^+]{R'OH} R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow[Catalyst]{H_2} \underline{RCH_2OH} + \underline{R'OH}$$

(VI) Ester ⟶ alcohol (By hydrolysis)

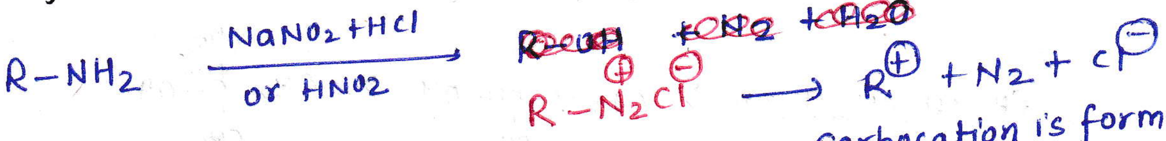


$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow{H_2O} R-\overset{O}{\overset{\|}{C}}-OH + R'OH$$



$$CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \xrightarrow{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-OH + C_2H_5OH$$

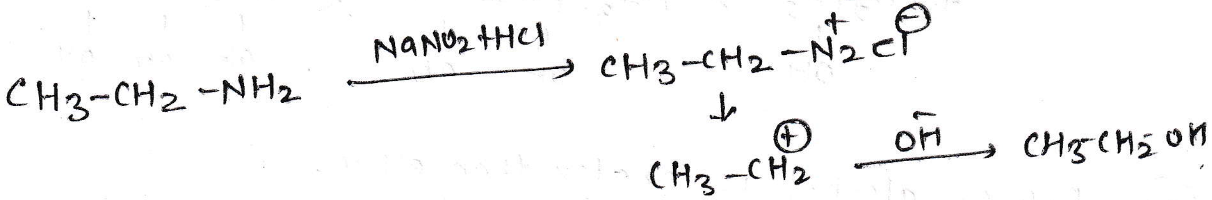
(VII) Primary amine ⟶ alcohol. (using diazonium salt)



$$R-NH_2 \xrightarrow[\text{or } HNO_2]{NaNO_2+HCl} \text{~~R-OH~~ ~~+N_2~~ ~~+H_2O~~} \quad R-\overset{\oplus}{N_2}\overset{\ominus}{Cl} \longrightarrow R^{\oplus} + N_2 + Cl^{\ominus}$$

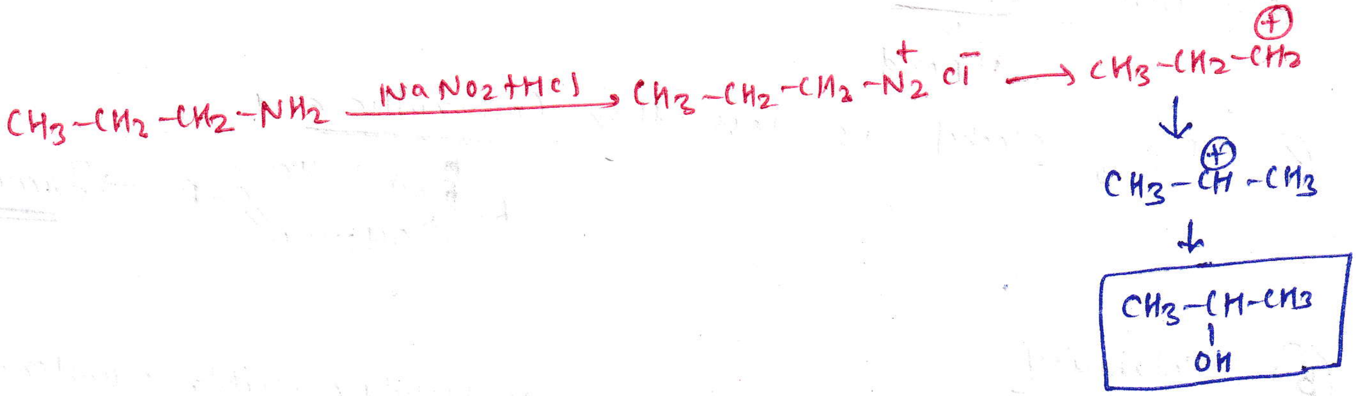
Carbocation is formed and rearrangement occurs.

Que



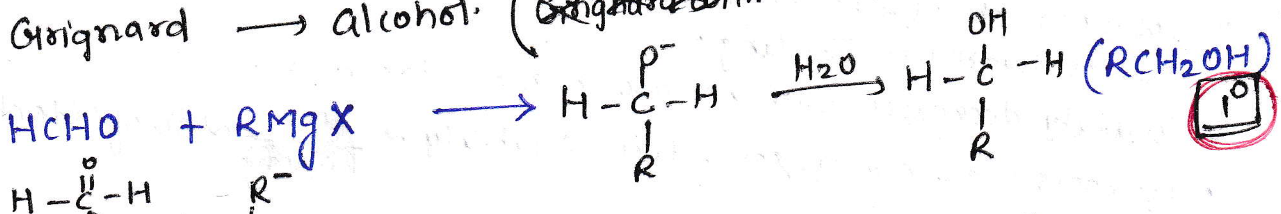
$$CH_3-CH_2-NH_2 \xrightarrow{NaNO_2+HCl} CH_3-CH_2-\overset{+}{N_2}Cl^{\ominus} \downarrow \; CH_3-\overset{\oplus}{CH_2} \xrightarrow{\overline{O}H} CH_3CH_2OH$$

Que



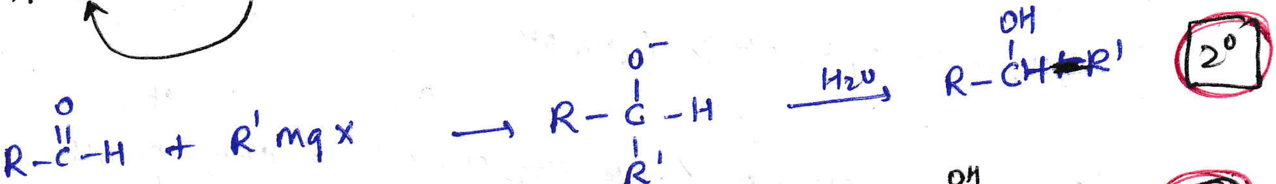
$$CH_3-CH_2-CH_2-NH_2 \xrightarrow{NaNO_2+HCl} CH_3-CH_2-CH_2-\overset{+}{N_2}\,\bar{Cl} \longrightarrow CH_3-CH_2-\overset{\oplus}{CH_2} \downarrow \; CH_3-\overset{\oplus}{CH}-CH_3 \downarrow \; \boxed{CH_3-\underset{OH}{\underset{|}{CH}}-CH_3}$$

(VIII) Grignard ⟶ alcohol. (~~Grignard with~~

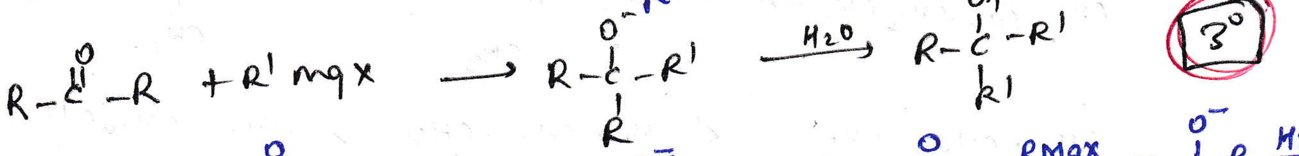


$$HCHO + RMgX \longrightarrow H-\underset{R}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-H \xrightarrow{H_2O} H-\underset{R}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-H \; (RCH_2OH) \; \boxed{1°}$$

$$H-\overset{O}{\overset{\|}{C}}-H \quad R^-$$

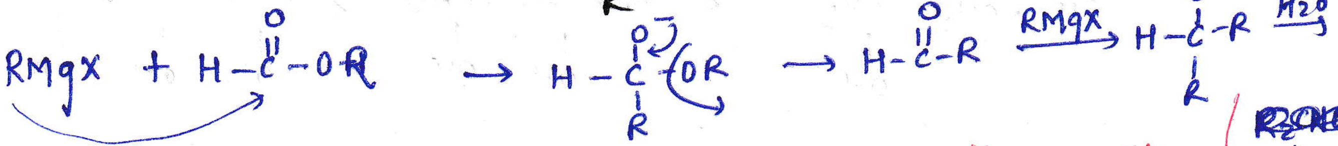


$$R-\overset{O}{\overset{\|}{C}}-H + R'mgx \longrightarrow R-\underset{R'}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-H \xrightarrow{H_2O} R-\overset{OH}{\overset{|}{CH}}\text{~~-R'~~} \; \boxed{2°}$$



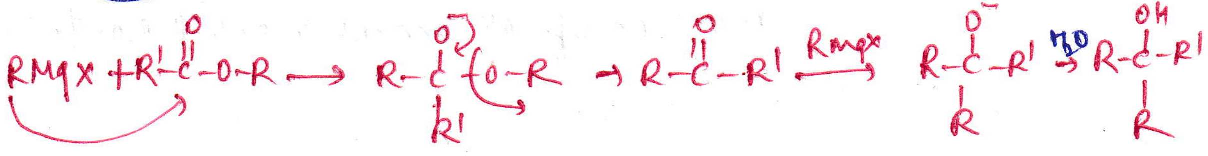
$$R-\overset{O}{\overset{\|}{C}}-R + R'mgx \longrightarrow R-\underset{R}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-R' \xrightarrow{H_2O} R-\underset{R'}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-R' \; \boxed{3°}$$

Que

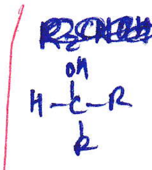


$$RMgx + H-\overset{O}{\overset{\|}{C}}-OR \longrightarrow H-\underset{R}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-OR \longrightarrow H-\overset{O}{\overset{\|}{C}}-R \xrightarrow{RMgx} H-\underset{R}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-R \xrightarrow{H_2O}$$

Que



$$RMgx + R'-\overset{O}{\overset{\|}{C}}-O-R \longrightarrow R-\underset{R'}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-O-R \rightarrow R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{Rmgx} R-\underset{R}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-R' \xrightarrow{H_2O} R-\underset{R}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-R'$$



~~R2CHOH~~

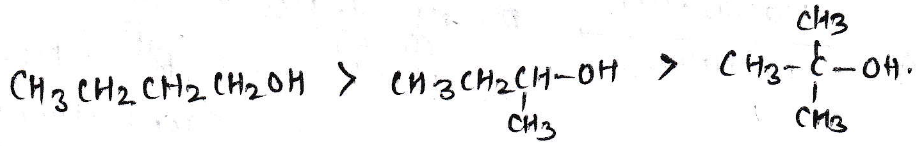
$$H-\underset{R}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-R$$

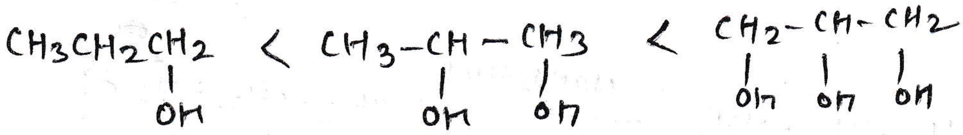
physical property

① • $C_1 - C_{11}$ → colorless Liq *
• C_{12} $\xrightarrow{\text{greater}}$ → solid

② $B.P \propto mol.wt \propto \frac{1}{branching}$

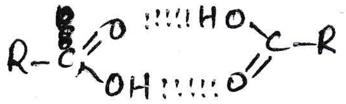
$CH_4H_9OH < C_5H_{11}OH < C_6H_{13}OH$


$CH_3CH_2CH_2CH_2OH > CH_3CH_2\underset{CH_3}{\underset{|}{CH}}-OH > CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH.$


$\underset{OH}{\underset{|}{CH_3CH_2CH_2}} < CH_3-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_3}} < \underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$

③ B.P of alcohol is grater than ether
↓
H·Bond

④ B.P of alcohol is less than Carboxyllic acid

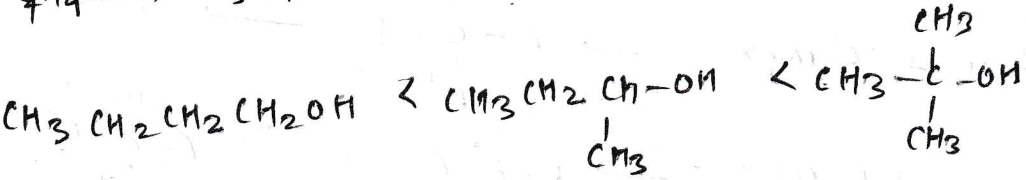


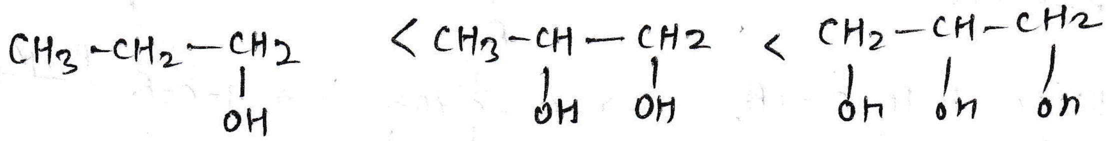
→ Dimer

⑤ Solubility

- Lower alcohol (first 3member) are completely miscible in water. due to Hydrogen Bonding.
- Solubility decreases with increase in molecular mass.
- if molecular mass is same then solubility ∝ ~~branching~~ ∝ no of side chain

$C_4H_9OH > C_5H_{11}OH > C_6H_{13}OH$


$CH_3CH_2CH_2CH_2OH < CH_3CH_2\underset{CH_3}{\underset{|}{CH}}-OH < CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH$


$CH_3-CH_2-\underset{OH}{\underset{|}{CH_2}} < CH_3-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}} < \underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$

more no of OH means more H Bond.

$R-O-H$

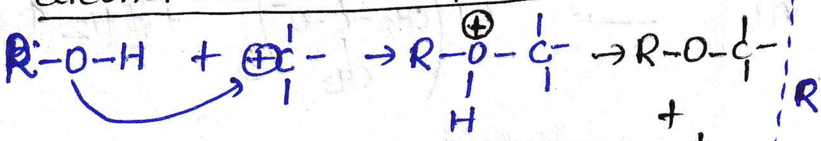
Chemical reaction of Alcohol

$R-O-H$

1)

Breaking of O—H bond

alcohol acts as nucleophile



$$R\ddot{}-O-H + \overset{\oplus}{C} \rightarrow R-\overset{\oplus}{\underset{H}{O}}-C \rightarrow R-O-C + H^+$$

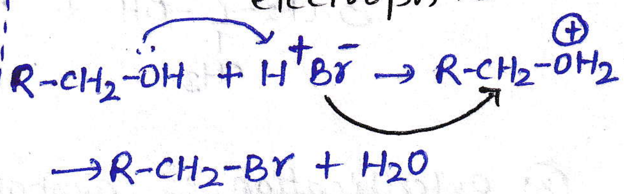
unstable oxonium ion

- Acidic nature of alcohol
- rxn with metal
- Esterification — alkylation
  - Benzoylation
  - acetylation

Extras
- Rxn with aldehyde/ketone
- Rxn with Grignard

Breaking of C—O bond

protonated alcohol acts as electrophile



$$R-CH_2-\ddot{O}H + H^+Br^- \rightarrow R-CH_2-\overset{\oplus}{O}H_2 \rightarrow R-CH_2-Br + H_2O$$

- Rxn with Hydrogen Halide (HX)
- ~~Rxn with Inorganic acid~~ — HNO_3, H_2SO_4
- Rxn with $SOCl_2$ (darzen Rxn)
- Rxn with PCl_5, PCl_3
- Rxn with $SOCl_2$
- Dehydration of alcohol

oxidation ~~$H^+/KMnO_4$~~ ~~$H^+/K_2Cr_2O_7$~~

- normal oxidation
- oxidation with Cu/300°C
- oxidation with HIO_4

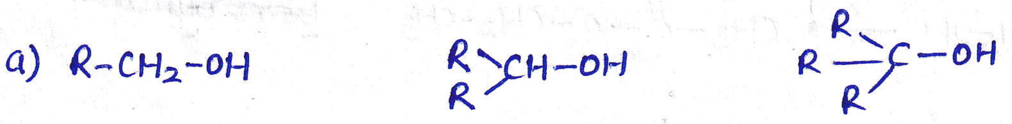
Pinacole Pinnacolone Rearrangement

Test of alcohol

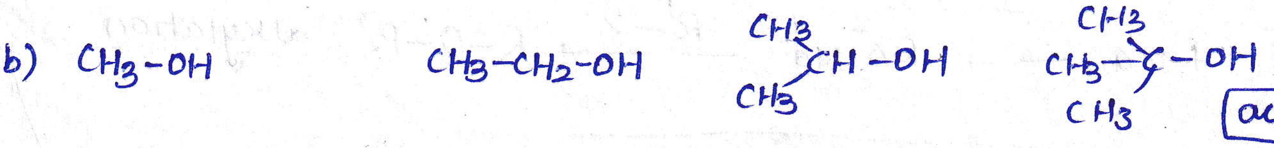
methanol & ethanol

acidic nature of alcohol

- due to polar nature of OH bond (Remove H^+ & make anion)
- acidic nature $\propto -M, -I \propto \frac{1}{+M, +I, +H}$



a) $R-CH_2-OH$ R_2CH-OH R_3C-OH $\boxed{acid \rightarrow a>b>c}$



b) CH_3-OH CH_3-CH_2-OH $(CH_3)_2CH-OH$ $(CH_3)_3C-OH$ $\boxed{acid \rightarrow a>b>c>d}$

- alcohol is less acidic than water (because H_2O is a good proton donor than alcohol)
- alcohol acts as Bronsted acid & Bronsted base.

Bronsted acid → because it is H^+ donor.

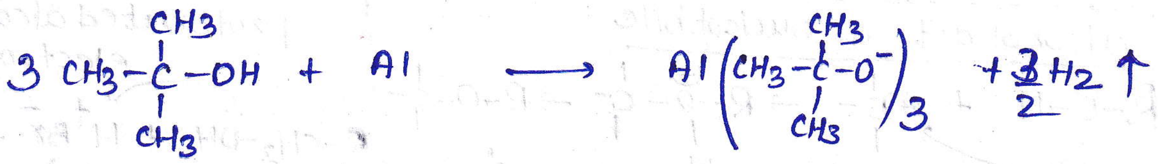
Bronsted base → also accepts H^+

$R-O-H + B^- \rightarrow R-O^- + \cancel{B}HB$

$R-O-H + H^+ \longrightarrow R-\overset{\oplus}{O}H_2$

② **Rxn with metal** alcohol + active metal → alkoxide ion + H_2 gas
(Na, K, Al)

$$R-O-H + Na/K/Al \longrightarrow R-\overset{-}{O}\overset{+}{Na} + \frac{1}{2}H_2$$



$$3\,CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + Al \longrightarrow Al\left(CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^-\right)_3 + \frac{3}{2}H_2\uparrow$$

③ **Esterification** : alcohol → Carboxylic acid / acid chloride / acid anhydride → Ester

$$R'-OH + R-\overset{O}{\overset{||}{C}}-OH \xrightarrow{conc\ H_2SO_4} \underbrace{R-\overset{O}{\overset{||}{C}}}_{acid}-\underbrace{O-R'}_{alcohol} + H_2O$$

$$R-OH + R'-\overset{O}{\overset{||}{C}}\vdots O-\overset{O}{\overset{||}{C}}-R' \xrightarrow{Conc\ H_2SO_4} \underbrace{R'-\overset{O}{\overset{||}{C}}}_{\cancel{\text{acid}}\ \text{anhydride}}-\underbrace{O-R}_{alcohol} + R'-\overset{O}{\overset{||}{C}}-OH$$

$$R-OH + R'-\overset{O}{\overset{||}{C}}-Cl \xrightarrow{pyridine} \underbrace{R'-\overset{O}{\overset{||}{C}}}_{\text{acid chloride}}-\underbrace{O-R}_{alcohol} + HCl$$

pyridine reacts with HCl and forms stable product and inc yield of reaction.

Que $CH_3-\overset{O}{\overset{||}{C}}-OH + C_2H_5OH \xrightarrow{conc\ H_2SO_4} CH_3-\overset{O}{\overset{||}{C}}-O-C_2H_5$

Que $Ph-\overset{O}{\overset{||}{C}}-OH + C_2H_5\overset{18}{O}H \xrightarrow{''} Ph-\overset{O}{\overset{||}{C}}-\overset{18}{O}-C_2H_5$

- acetylation: Introduction of $(CH_3-\overset{O}{\overset{||}{C}}-)$ group in alcohol is acetylation.
- alkylation: ——— $(-R)$ ″ ″ ——— ———
- Benzoylation: $-(OPh)$ ———

$CH_3-\overset{O}{\overset{||}{C}}-OH + CH_3OH \longrightarrow CH_3-\overset{O}{\overset{||}{C}}-O-CH_3$ acetylation

$CH_3-\overset{O}{\overset{||}{C}}-Cl + C_2H_5OH \longrightarrow CH_3-\overset{O}{\overset{||}{C}}-O-CH_2-CH_3$ acetylation ~~Benzoylation~~

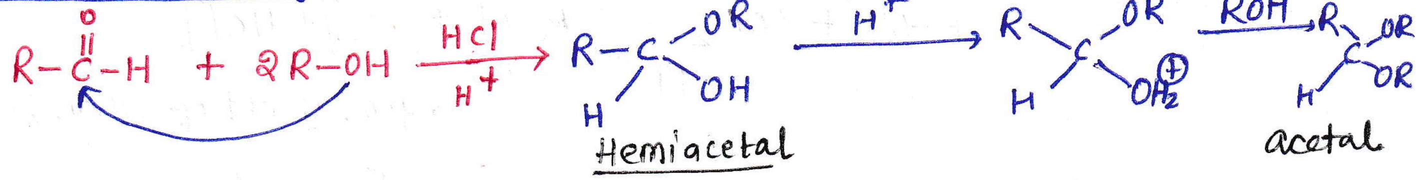
$R-OH + Na \longrightarrow R\overset{-}{O}\overset{+}{Na} \xrightarrow{R'-X} R-O-R'$ alkylation

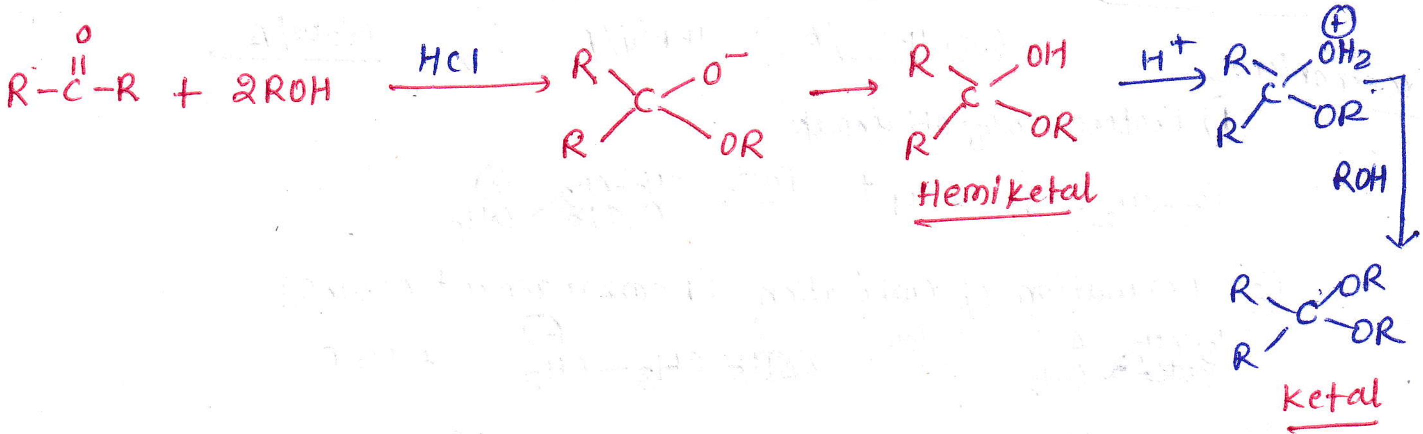
$Ph-\overset{O}{\overset{||}{C}}-Cl + C_2H_5OH \longrightarrow Ph-\overset{O}{\overset{||}{C}}-O-CH_2-CH_3$ Benzoylation

(schotten Baumann Reaction)

Reaction with aldehyde/ketone

aldehyde + alcohol → Hemiacetal → acetal
ketone + " → Hemiketal → ketal





Reaction with Grignard

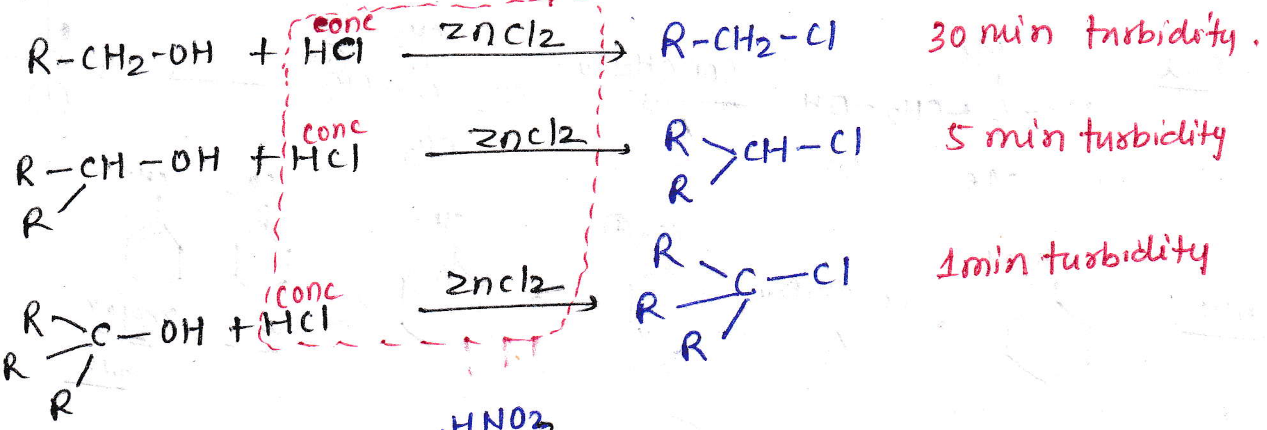
$$\underset{R^-}{R-Mg-X} + \underset{H^+}{R-OH} \longrightarrow R-H + R\bar{O}\overset{+}{Mg}X$$

Reaction involving breaking of Carbon oxygen bond

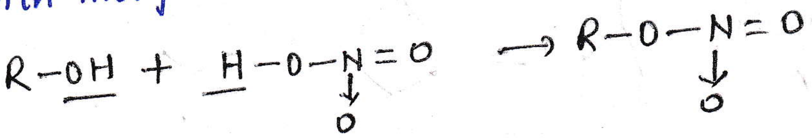
① **Reaction with Hydrogen Halide (HX)**

$$\underset{-H_2O}{ROH + HX} \xrightarrow{ZnX_2} R-X + H_2O$$

→ Lucas Reagent



② **Reaction with Inorganic acid** < HNO_3, H_2SO_4



$$R-\underline{OH} + \underline{H}-O-\underset{\downarrow O}{N}=O \longrightarrow R-O-\underset{\downarrow O}{N}=O$$

$$R-\underline{OH} + \underline{H}-HSO_4 \longrightarrow R-HSO_4$$

③ **Rxⁿ with PCl_5 and PCl_3**

$$R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$$

$$R-OH + PCl_3 \longrightarrow R-Cl + H_3PO_3$$

Reaction with $SOCl_2$ (darzen Reaction)

$$R-OH + SOCl_2 \xrightarrow[\text{pyridine}]{} R-Cl + SO_2\uparrow + HCl\uparrow$$

↳ good yield of alkyl halide.

Dehydration (Removal of H_2O → alkene formation) → E^1 mechanism

$\xrightarrow{\text{conc } H_2SO_4/\Delta}$ $\xrightarrow{H_3PO_4/\Delta}$ $\xrightarrow{Al_2O_3/\Delta}$

mechanism

① Protonation of OH group

$$CH_3-CH_2-OH + H^+ \underset{}{\overset{\text{fast}}{\rightleftharpoons}} CH_3-CH_2-\overset{\oplus}{O}H_2$$

~~C_2H_5~~

② Formation of Carbocation (Rearrangement occurs)

$$CH_3-CH_2-\overset{\oplus}{O}H_2 \overset{\text{slow}}{\rightleftharpoons} CH_3-\overset{\oplus}{C}H_2 + H_2O$$

③ Formation of alkene (elimination of H^+)

$$CH_3-\overset{\oplus}{C}H_2 \rightleftharpoons H_2C=CH_2 + H^+$$

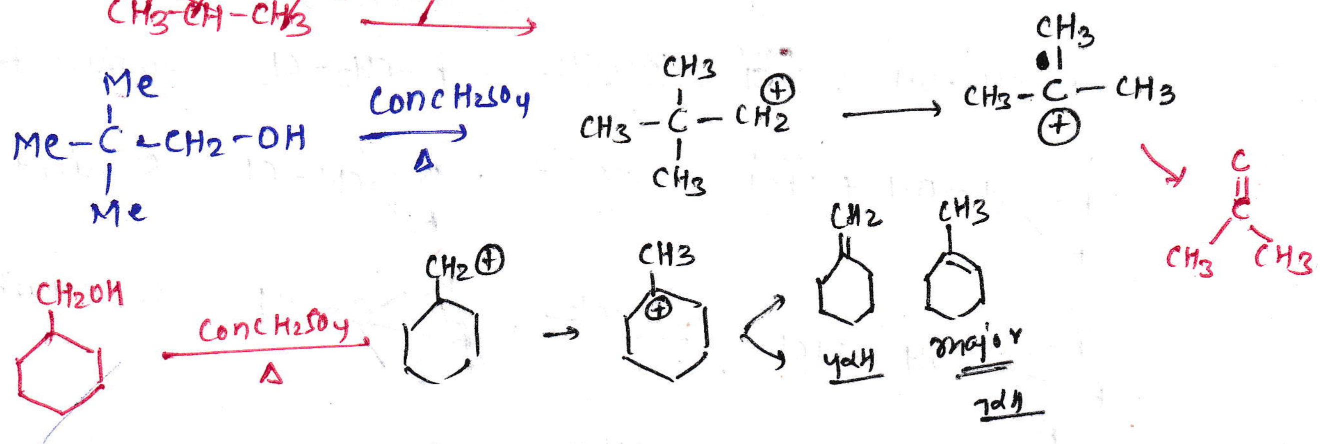
- Carbocation formation
- Reactivity : 3° alcohol > 2° alcohol > 1° alcohol.

~~$CH_3-CH_2-OH \xrightarrow[443K]{H_2SO_4} CH_2=CH_2 + H_2O$~~

~~$CH_3-\underset{}{\overset{OH}{CH}}-CH_3 \longrightarrow$~~

Que

Que



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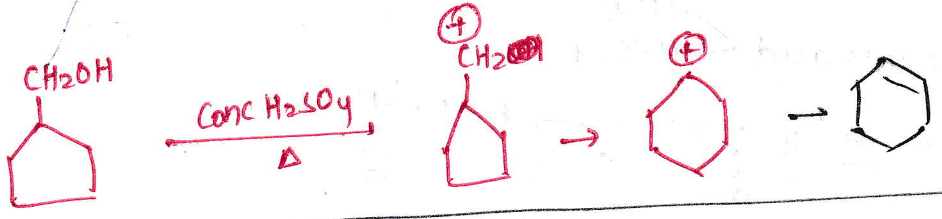


$$C_2H_5OH + \text{conc } H_2SO_4$$

$\xrightarrow{100°C}$ $C_2H_5-HSO_4$

$\xrightarrow{140°C}$ $C_2H_5-O-C_2H_5$ (williamson synthesis)

$\xrightarrow{170°C}$ $CH_2=CH_2$ (Elemination)

oxidation

$$R-CH_2-OH \xrightarrow[\text{or } H^+/K_2Cr_2O_7]{H^+/KMnO_4 \;\; \cancel{\text{oxidation}}} RCHO \longrightarrow RCOOH$$

↳ Strong oxidizing agent.

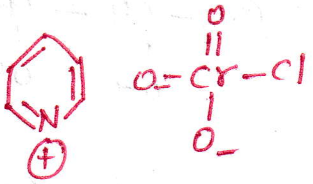
if we want aldehyde.

$$R-CH_2-OH \xrightarrow{CrO_3} RCHO$$

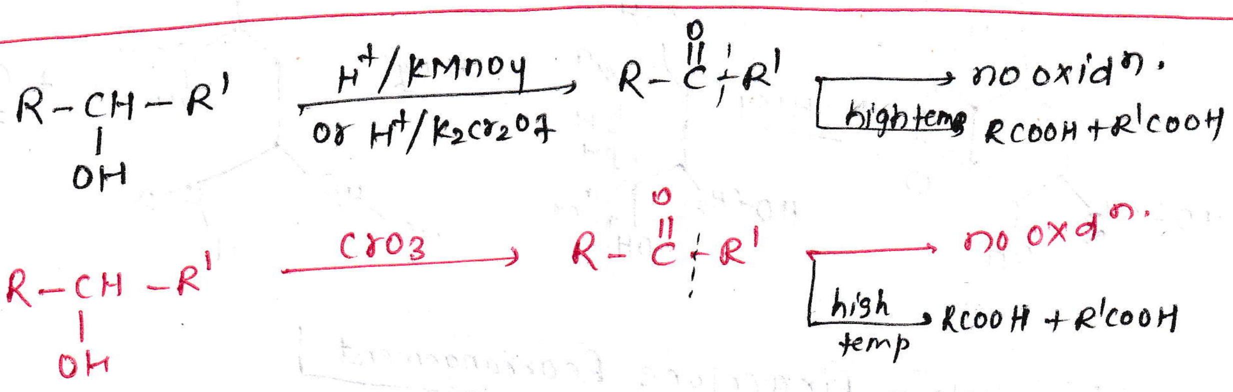
if we want aldehyde in good yield.

$$R-CH_2-OH \xrightarrow{PCC}$$

↳ Pyridinium chloro chromate.



$$R-CH_2-OH \xrightarrow{PCC} R-CHO$$

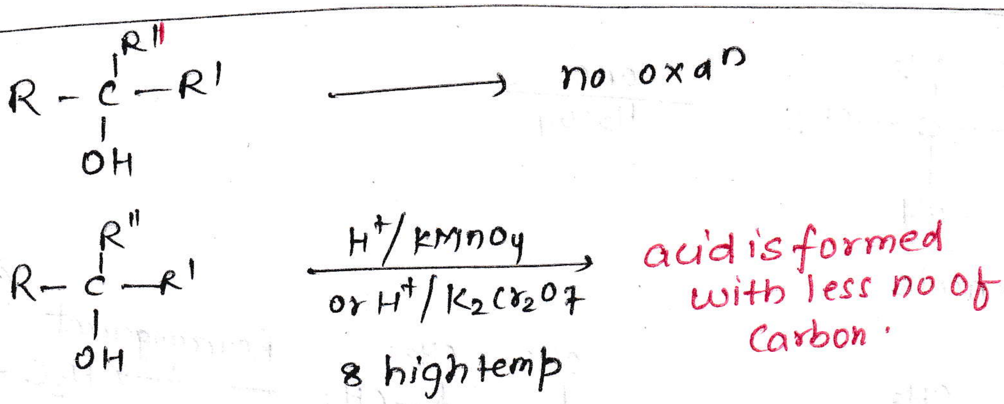


$$R-\underset{\underset{OH}{|}}{CH}-R' \xrightarrow[\text{or } H^+/K_2Cr_2O_7]{H^+/KMnO_4} R-\overset{\overset{O}{\|}}{C}-R' \xrightarrow{} \text{no oxid}^n.$$

high temp → $RCOOH + R'COOH$

$$R-\underset{\underset{OH}{|}}{CH}-R' \xrightarrow{CrO_3} R-\overset{\overset{O}{\|}}{C}-R' \xrightarrow{} \text{no oxd}^n.$$

high temp → $RCOOH + R'COOH$



$$R-\underset{\underset{OH}{|}}{\overset{\overset{R''}{|}}{C}}-R' \longrightarrow \text{no oxa}^n$$

$$R-\underset{\underset{OH}{|}}{\overset{\overset{R''}{|}}{C}}-R' \xrightarrow[\text{or } H^+/K_2Cr_2O_7]{H^+/KMnO_4}$$

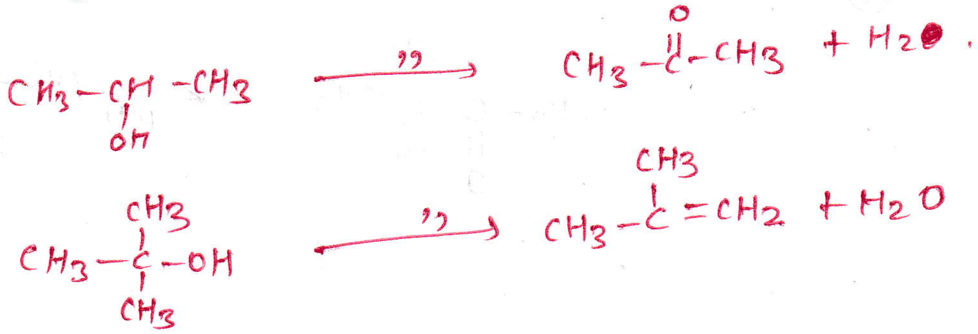
& high temp

acid is formed with less no of Carbon.

---

oxidation with Cu/300°c.

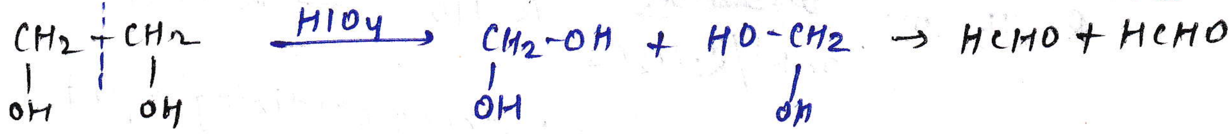
$$CH_3CH_2-OH \xrightarrow[300^\circ c]{Cu} CH_3CHO + H_2$$

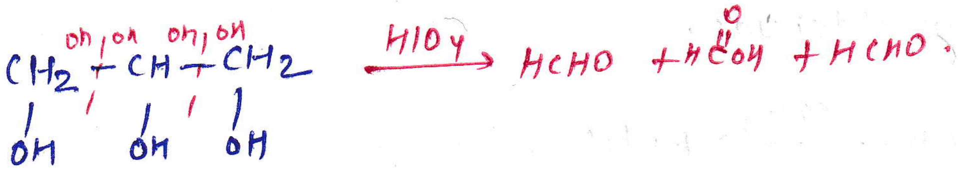


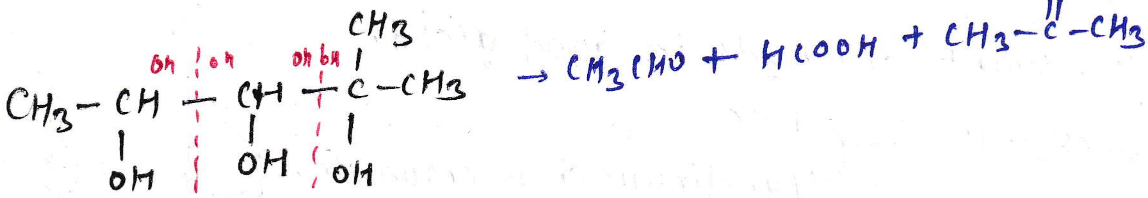
$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{\text{,,}} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H_2.$$

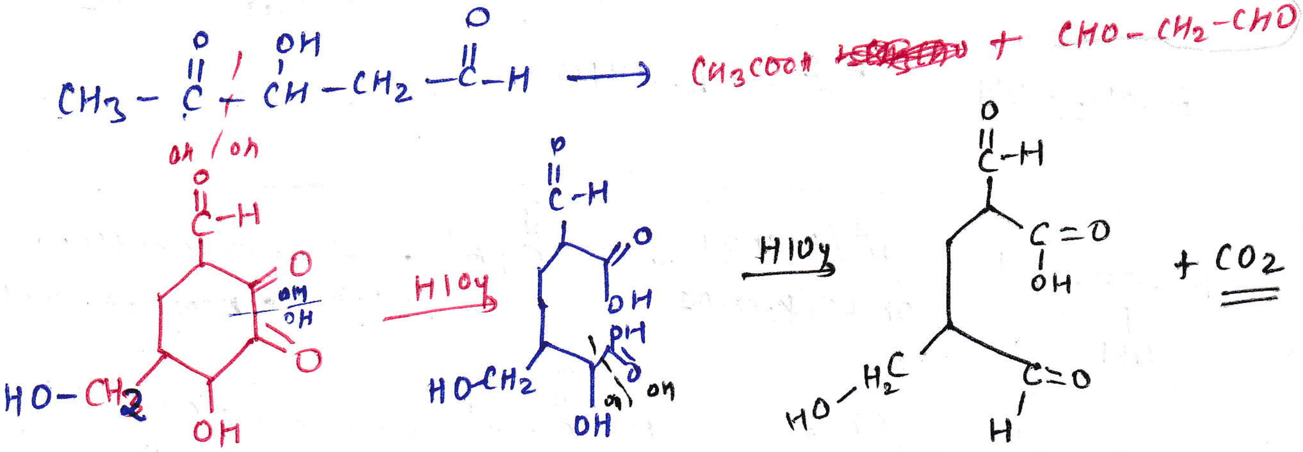
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow{\text{,,}} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 + H_2O$$

oxidation with HIO_4 : [~~2OH~~ 2 vicinal OH, 2 vicinal C=O, 1 OH & 1 C=O vicinal]

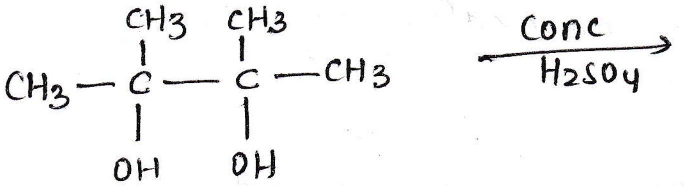




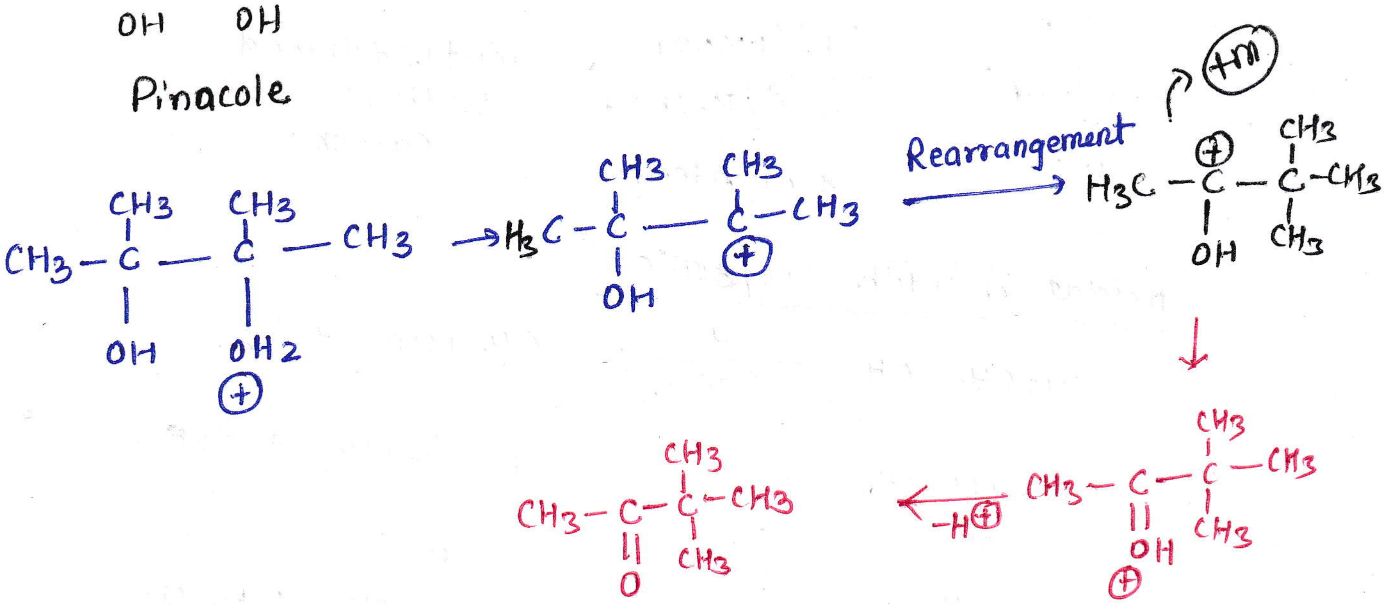




~~Pinnaco~~ Pinacole - Pinacolone Rearrangement



Pinacole



Test of alcohol

Distinguish b/w 1°, 2°, 3° alcohol

① Lucas test → conc HCl + anhydrous $ZnCl_2$

1° alcohol → 30 min turbidity } → on heating

2° " → 5 min turbidity }

3° " → 1 min turbidity } → room temp

↓

alkylhalide.

② Victormayer test → Color test of alcohol

1° alcohol → Red color

2° " → Blue color

3° " → NO Color

$$R-CH_2-OH \xrightarrow{P+I_2} R-CH_2-I \xrightarrow{AgNO_2} R-CH_2-NO_2 \xrightarrow{HNO_2} \text{Red color}$$

$$R_2CH-OH \xrightarrow{''} R_2CHI \xrightarrow{''} R_2CHNO_2 \xrightarrow{HNO_2} \text{Blue Color}$$

$$R_3COH \xrightarrow{''} R_3CI \xrightarrow{''} R_3CNO_2 \xrightarrow{HNO_2} \text{colorless.}$$

③ Dichromate Test

$$1° \xrightarrow[\text{orange}]{H^+/K_2Cr_2O_7} \text{Acid} + Cr^{+3} \text{ (green)}$$

$$2° \xrightarrow[\text{orange}]{''} \text{ketone} + Cr^{+3} \text{ (green)}$$

$$3° \longrightarrow \text{No oxidation (no green color)}$$

④ Test of alcoholic group

$$R-OH \xrightarrow{Na} RONa + \tfrac{1}{2}H_2\uparrow$$

$$R-OH \xrightarrow{PCl_5} R-Cl + POCl_3 + \underline{HCl} \xrightarrow[\text{gas}]{NH_3} NH_4Cl$$

{white fumes}

Methanol & Ethanol

methanol

- wood spirit (destructive distillation of wood) → old method of ppr^n
- modern method. $CO + 2H_2 \xrightarrow[200-300\,atm]{ZnO-Cr_2O_3} CH_3OH$

  573 – 673 K

  ↳ Catalytic hydrogenation of CO.

- colorless liq & highly poisonous.

ethanol

- Commercialy prepared by fermentation.
- Sugar from molasses, sugarcane, fruits (grapes) is converted to glucose & fructos (invertase enzyme.)

$$\underset{\text{Sugar}}{C_{12}H_{12}O_{11}} + H_2O \xrightarrow{\text{invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

glucose/fructose undergo fermentation in presence of enzyme zymase (found in yeast)

$$\underset{\text{glucose/fructose}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} 2C_2H_5OH + 2CO_2$$

Wine-making → Grapes → ripen → when grapes are crushed

Grapes ↓ sugar & yeast

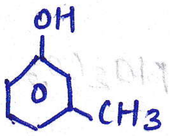
ripen: sugar↑ yeast↑

crushed ↓ Sugar meets enzyme & fermentation starts. } fermentation takes place in absence of air.

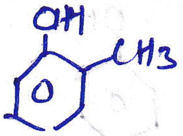
C_2H_5OH is made unfit for drinking by mixing Copper sulphate (to give color) & pyridine (foul smelling liq). It is k/a denaturation of alcohol.

Phenol

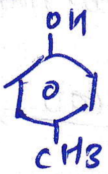
phenol



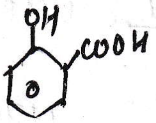
m Cresol



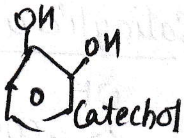
o cresol



p cresol



Salicyclicacid



Catechol

resorcinol

quinol.

- All phenolic Compounds give characteristic color with neutral $FeCl_3$.

$Ph-OH \xrightarrow[FeCl_3]{neutral}$ Voilet color

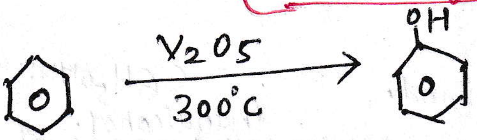
$R-OH \xrightarrow[FeCl_3]{neutral}$ no Color

- also k/a Carbolic acid / Benzonol / hydroxyBenzene.

Methods of Preparation

① Benzene

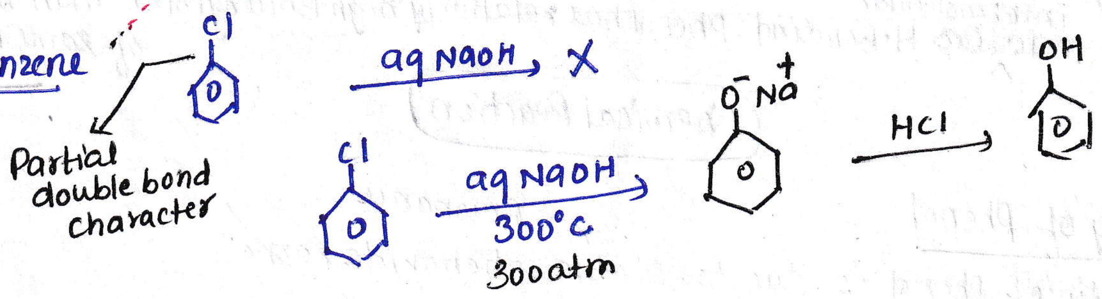
oxidation V_2O_5



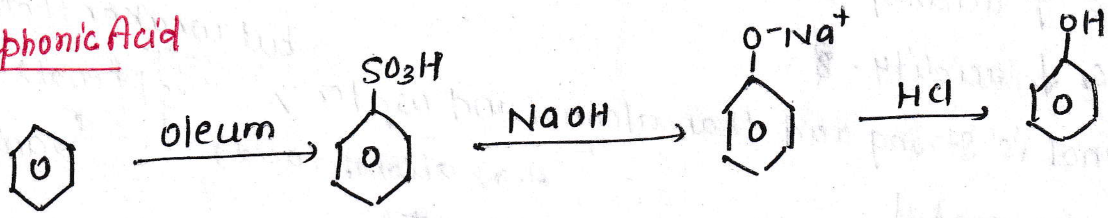
→ oxidation reaction

$R-Cl \xrightarrow{aq\ NaOH} R-OH$ (SN rxn)

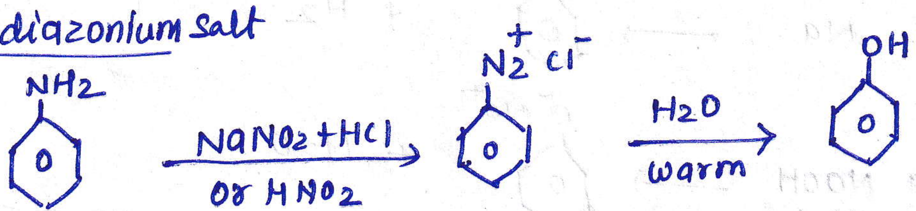
② Chloro Benzene



③ Benzene Sulphonic Acid



④ Benzene diazonium salt



$+ N_2 + HCl$

Aniline (aromatic primary amine)

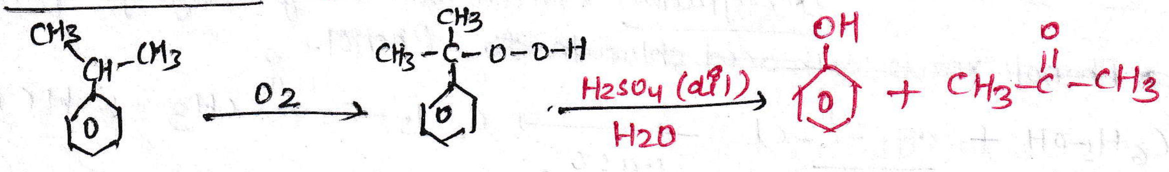
Benzene diazonium chloride

Hydrolysis & warming

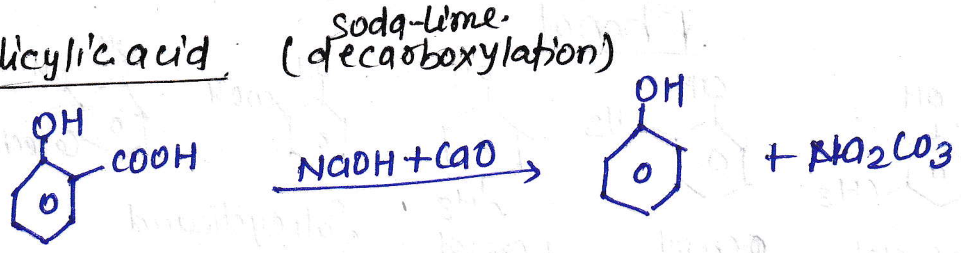
phenol

⑤ From cummene

Cummene + air(O_2) $\xrightarrow{oxidize}$ cummene hydroperoxide $\xrightarrow[Acid]{dil}$ Phenol + acetone



(6) Salicylic acid

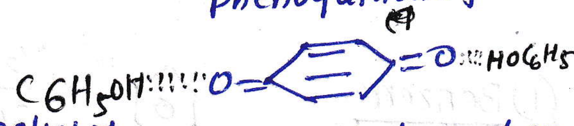


(7) Grignard

$$C_6H_5MgBr \xrightarrow{[O]} C_6H_5OMgBr \xrightarrow{H_2O} C_6H_5OH + Mg\genfrac{}{}{0pt}{}{-Br}{-OH}$$

Physical properties

- it attains pink color on exposure to air & light. (slow oxid^n occurs) ↓ Phenoquinone forms



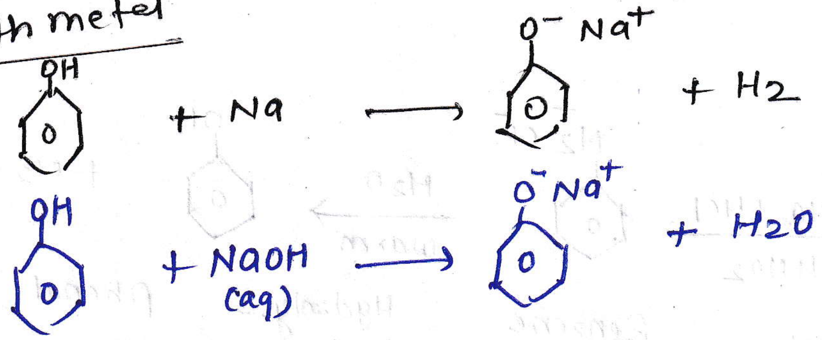
- Solubility of Phenol in water is due to H-Bond.
- Solubility of Phenol in water is much lower than alcohol, because of large Hydrocarbon part.
- Due to ~~[illegible]~~ intermolecular H-Bonding, Phenol has relatively high Boiling Point than other molecule of same molecular mass.

Chemical Reaction

① Acidity of Phenol

- acidity of Phenol is due to stable phenoxide ion. → Resonance
- EWG ↑ acidity
- ERG ↓ acidity.
- Phenol is strong acid than alcohol and water but weaker than Carboxylic acid
  - $H_2O >$ alcohol (acid)
  - ∴ {phenol > H_2O > alcohol} ↳ acidic strength.

② Rx^n with metal



③ Esterification

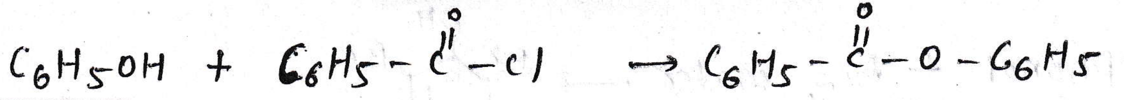
→ alkylation

→ acetylation ($CH_3-\overset{O}{\overset{\|}{C}}-$)

acetylation → introduction of acetyl group in ~~Reactions Phenol reacts with acid chloride to~~ Phenol.

$$C_6H_5OH + CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\substack{\text{Base} \\ \text{(pyridine)} \\ \text{(NaOH)}}]{} C_6H_5-O-\overset{O}{\overset{\|}{C}}-CH_3 + HCl$$

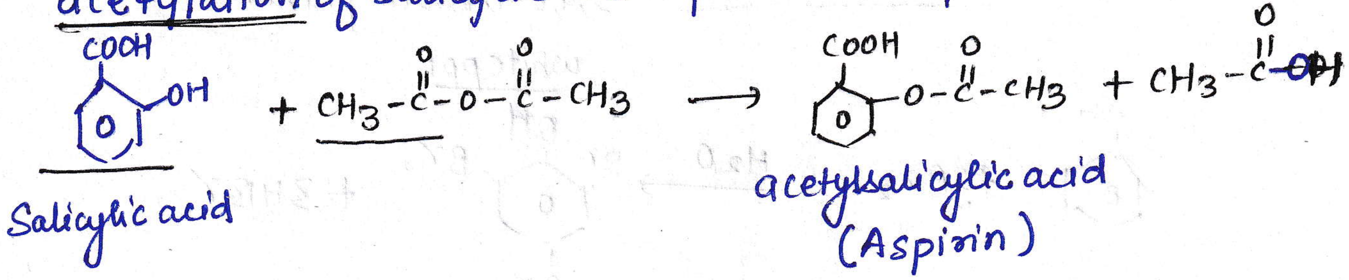
②



$C_6H_5OH + C_6H_5-\overset{O}{\overset{\|}{C}}-Cl \rightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-O-C_6H_5$ Benzoylation

~~Alkylation~~ → ~~ether form~~

acetylation of Salicylic acid produces aspirin.



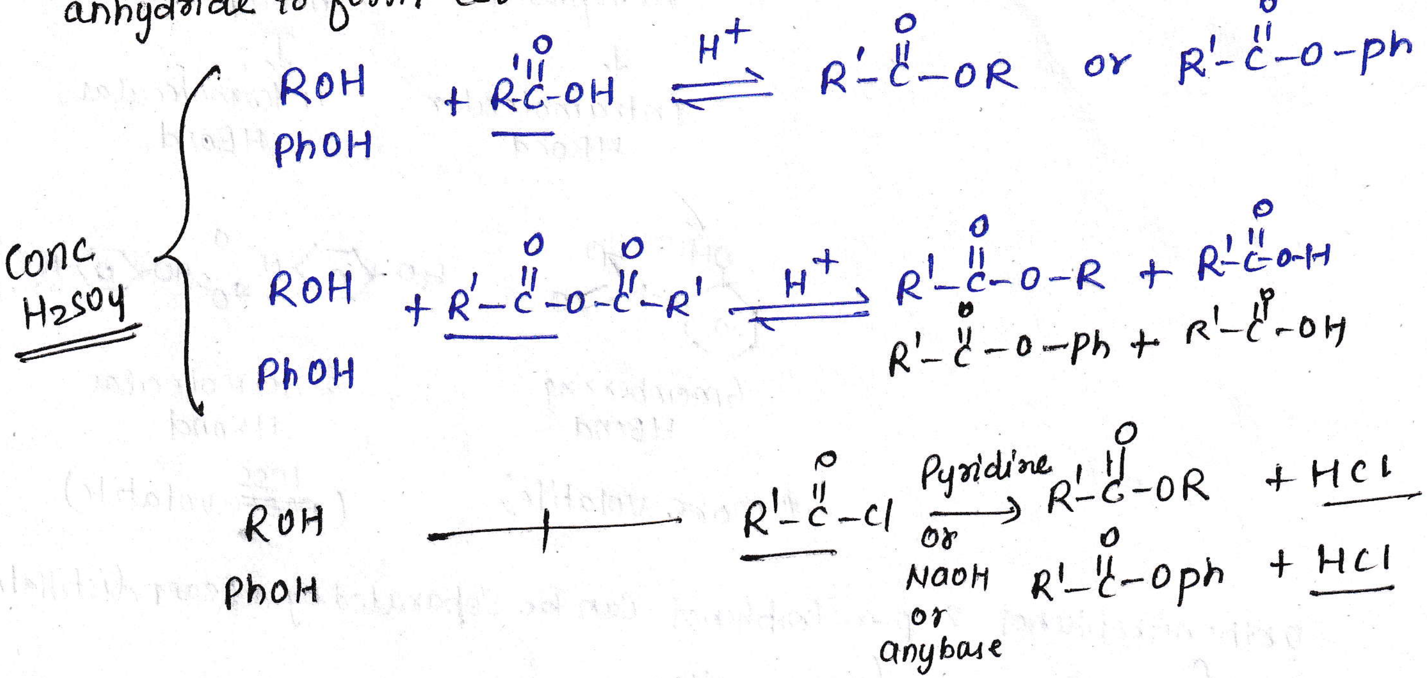
$+ CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow$ $-O-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\overset{O}{\overset{\|}{C}}-\cancel{OH}$

\# alkylation (etherformation) (williamson's Synthesis)

$C_6H_5OH + NaOH \longrightarrow C_6H_5O^-Na^+ \xrightarrow{R-X} C_6H_5OR$

---

alcohol & phenol react with Carboxylic acid, acid chlorides acid anhydride to form ester.



$ROH,\ PhOH + R'\overset{O}{\overset{\|}{C}}-OH \overset{H^+}{\rightleftharpoons} R'-\overset{O}{\overset{\|}{C}}-OR$ or $R'-\overset{O}{\overset{\|}{C}}-O-Ph$

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

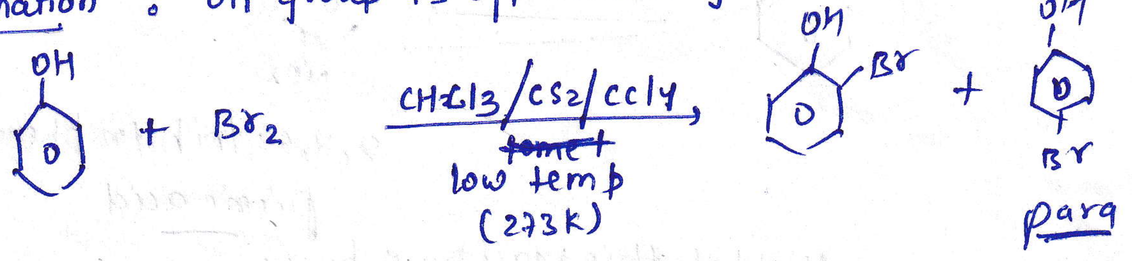
$R'-\overset{O}{\overset{\|}{C}}-O-Ph + R'-\overset{O}{\overset{\|}{C}}-OH$

$ROH,\ PhOH \longrightarrow R'-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{\text{Pyridine}} R'-\overset{O}{\overset{\|}{C}}-OR + HCl$

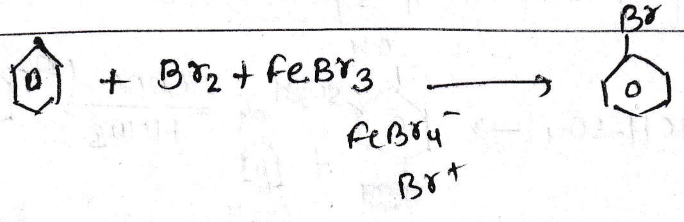
or NaOH or anybase $R'-\overset{O}{\overset{\|}{C}}-Oph + HCl$

Reaction of Phenol due to Benzene ring → electrophilic Substion.
↳ due to OH group (+M)

(i) Halogenation : OH group is o/p directing.

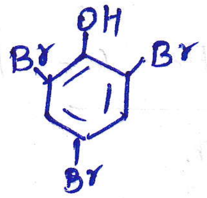


Halogenation of Benzene



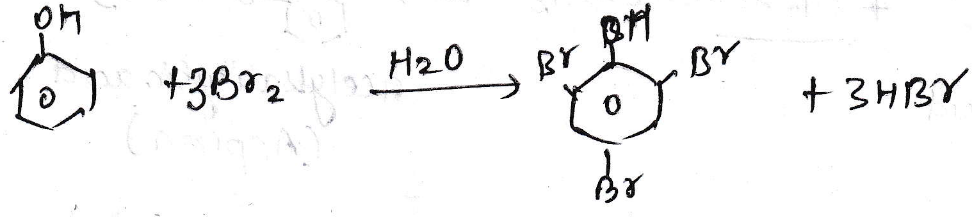
(But in phenol we donot req Lewis acid due to activating nature of OH.)

(ii) Phenol + Br_2 water →



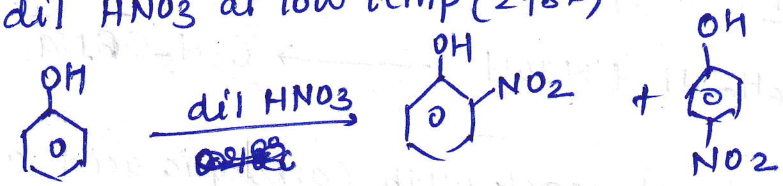
2,4,6-tribromophenol

white ppt



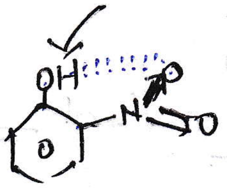
② Nitration

dil HNO_3 at low temp (298K)



ortho nitrophenol
↓
intramolecular HBond

para nitrophenol.
↓
intermolecular HBond



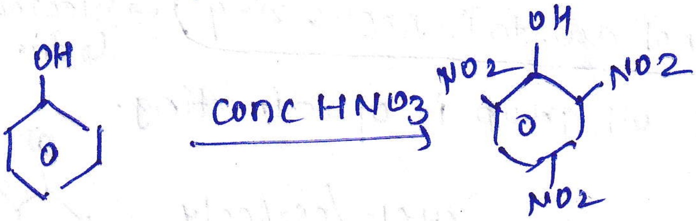
6member ring HBond

(more volatile)

intermolecular HBond

(~~more~~ less volatile)

orthonitrophenol & p-nitrophenol can be separated by steam distillation
↓ more volatile
↓ less volatile.

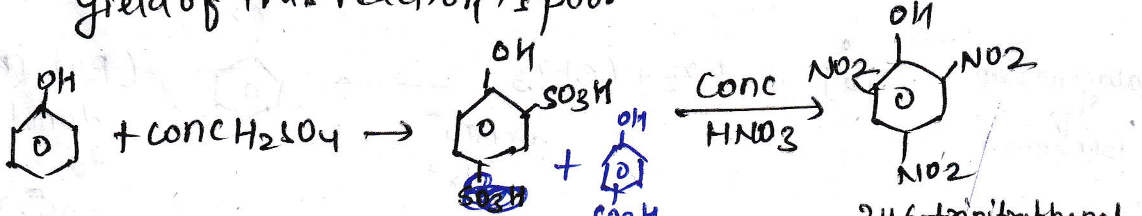


2,4,6-trinitrophenol

Picric acid

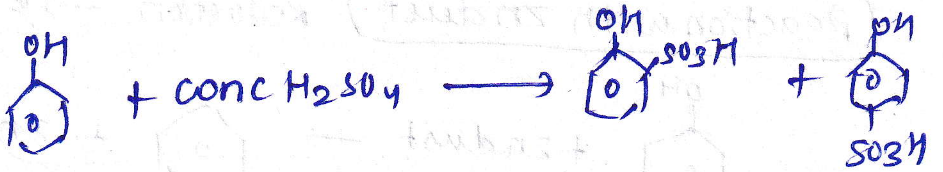
yield of this reaction is poor.

nowadays

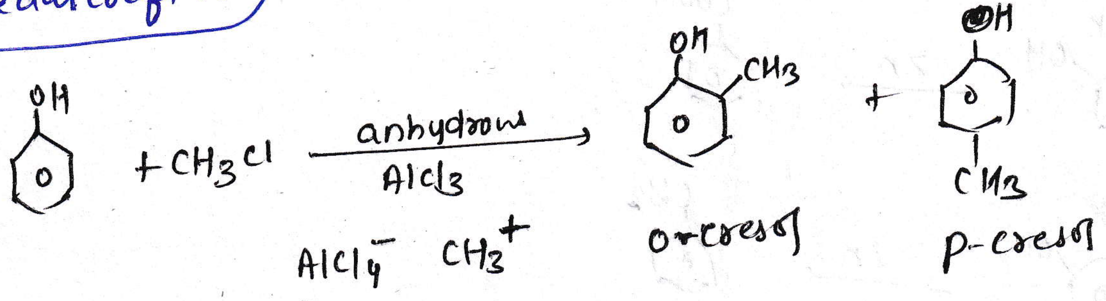


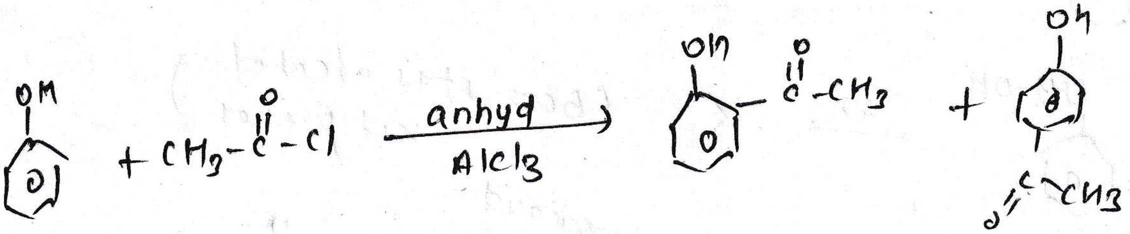
2,4,6-trinitrophenol

Sulphonation



Friedal craft rxn

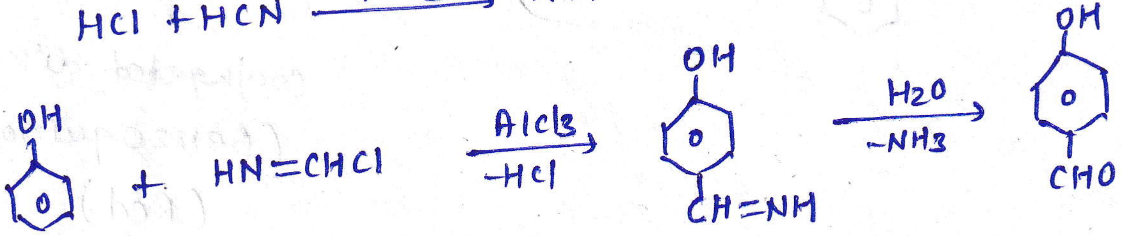




Gattermann Aldehyde

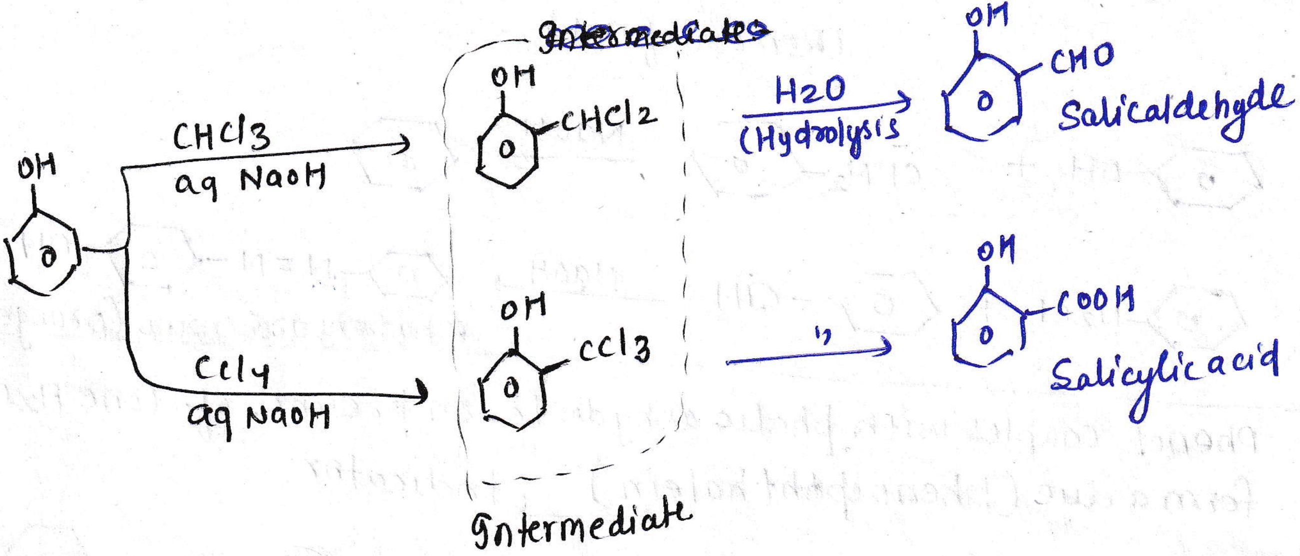
phenol + liq HCN & HCl $\xrightarrow[\text{AlCl}_3]{\text{anhydrous}}$ P hydroxy Benzaldehyde

$HCl + HCN \xrightarrow{AlCl_3} HN=CHCl$



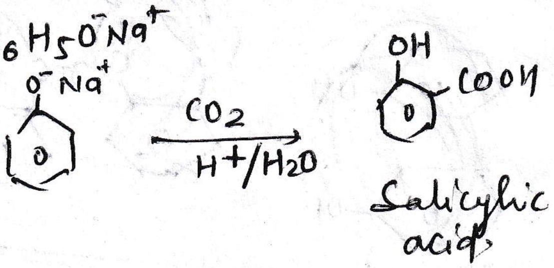
Riemer-Tiemann Rxn

phenol + chloroform $\xrightarrow{NaOH}$ aldehyde group at ortho position of phenol (salicaldehyde)



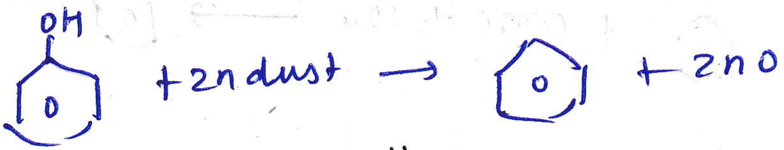
Kolbe-Shmidt Reaction
Kolbe Reaction

$C_6H_5OH + NaOH \rightarrow C_6H_5O^-Na^+$



Reaction with Zn dust

Reduction → Benzene



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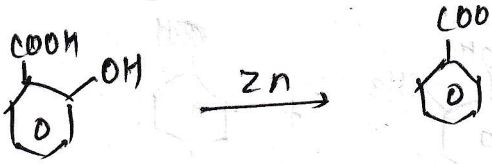

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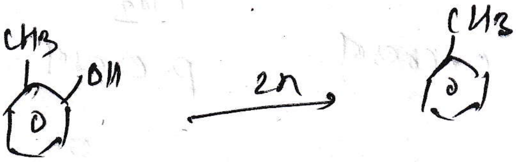

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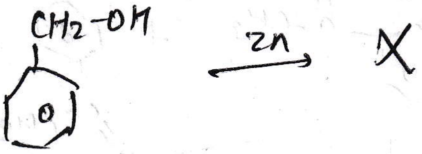
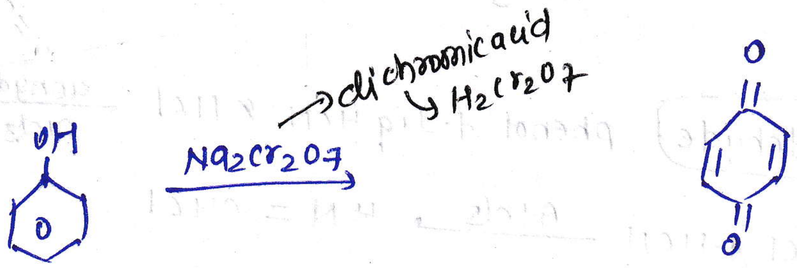


(bcoz it's alcohol not phenol)

Oxidation



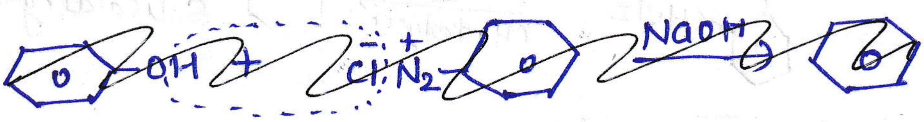
conjugated diketone
(Benzoquinone)
(Red)

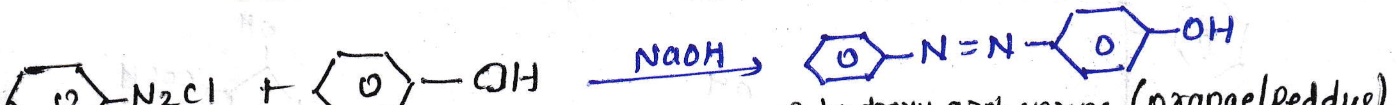
Coupling Reaction

Phenol + Benzenediazonium chloride $\xrightarrow[\text{medium}]{\text{Basic}}$ dye formation.

p-Hydroxyazobenzene.

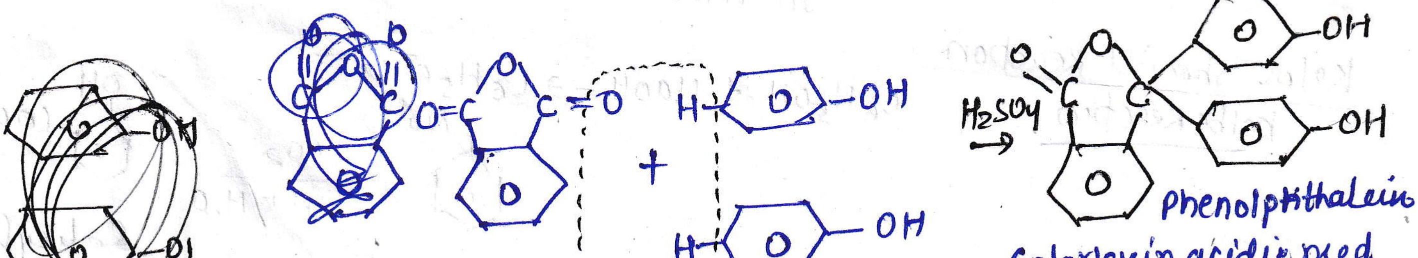
(Removal of HCl)





p-hydroxy azobenzene (orange/Red dye).

Phenol couples with phalic anhydride in presence of conc H_2SO_4 to form a dye (phenolphthalein), indicator



Colorless in acidic med
& Pink in basic med.

Ether

Methods of Preparation

alkyl halide → williamson Synthesis { Symmetrical ether / unsymmetrical ether

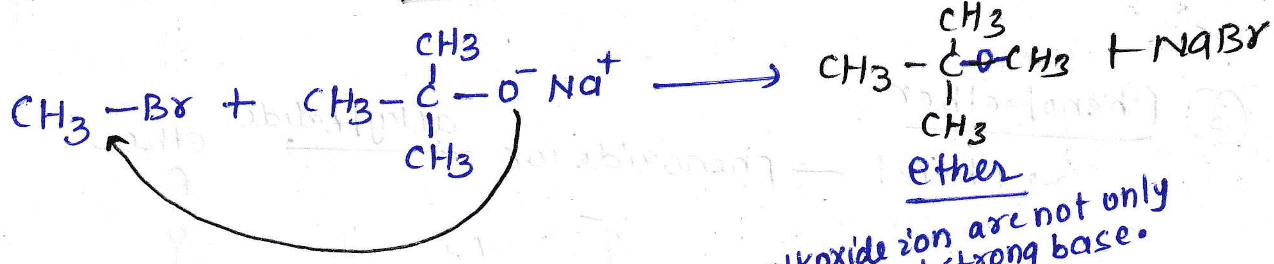
alcohol → dehydration of alcohol

phenol → ether | using other alkyl halide

Willamson Synthesis

alkyl halide + Sodium alkoxide → ether {S_N2 reaction}
↓
RO^- attack on primary alkyl halide

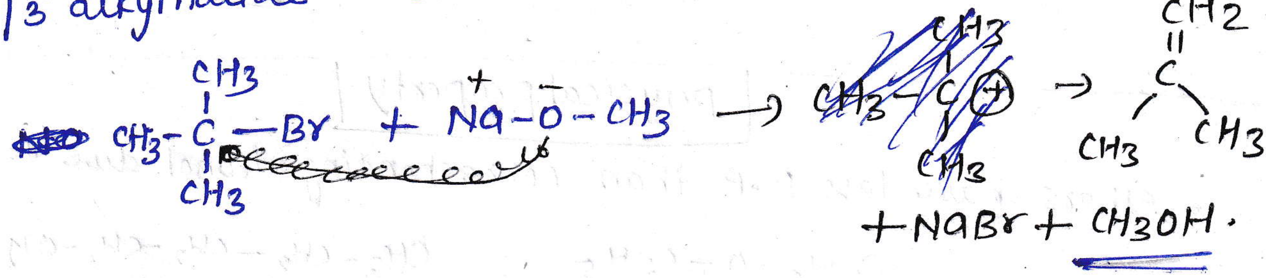
$$R{-}X + \overset{+}{Na}{-}\underline{\bar{O}{-}R'} \longrightarrow R'{-}O{-}R + NaX \quad \{S_N2\}$$



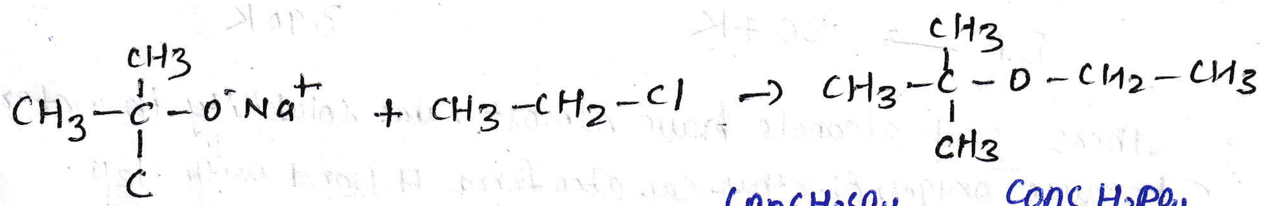
$$CH_3{-}Br + CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}O^-Na^+ \longrightarrow \underbrace{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}O{-}CH_3}_{\text{ether}} + NaBr$$

1° alkyl halide → ether

2° | 3° alkyl halide → elemination (alkene product) → because alkoxide ion are not only nucleophile but strong base.



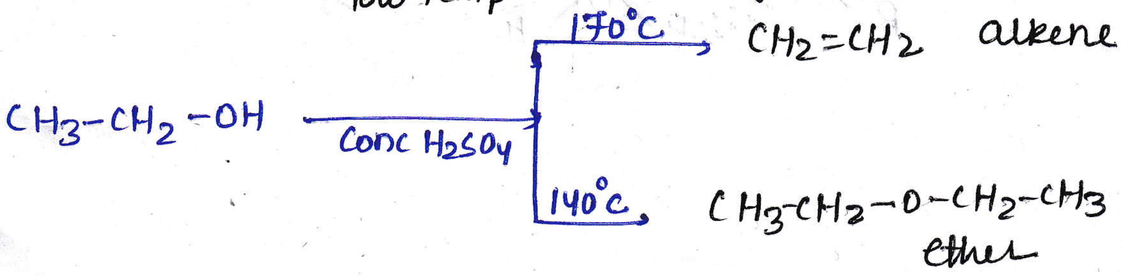
$$CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}Br + \overset{+}{Na}{-}\bar{O}{-}CH_3 \longrightarrow \cancel{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}\oplus} \rightarrow \overset{CH_2}{\underset{CH_3\quad CH_3}{\overset{\|}{C}}} + NaBr + \underline{CH_3OH}.$$



$$CH_3{-}\underset{C}{\overset{CH_3}{C}}{-}O^-Na^+ + CH_3{-}CH_2{-}Cl \rightarrow CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}O{-}CH_2{-}CH_3$$

From alcohol → dehydration of alcohol $\xrightarrow[\Delta]{Conc\,H_2SO_4}$ $\xrightarrow[\Delta]{Conc\,H_3PO_4}$

↳ ether as well as alkene is formed
low temp. — high temp



$$CH_3{-}CH_2{-}OH \xrightarrow{Conc\,H_2SO_4} \begin{cases} \xrightarrow{170°C} CH_2{=}CH_2 \quad \text{alkene} \\ \xrightarrow{140°C} CH_3{-}CH_2{-}O{-}CH_2{-}CH_3 \quad \text{ether} \end{cases}$$

ether formation is done by S_N2 mechanism.

mechanism

(i) $CH_3-CH_2-OH + H^+ \rightarrow CH_3-CH_2-\overset{\oplus}{O}H_2$

(ii) $CH_3-CH_2-\ddot{O}H + CH_3-CH_2-\overset{\oplus}{O}H_2 \rightarrow CH_3-CH_2-\overset{\oplus}{\underset{H}{O}}-CH_2-CH_3$

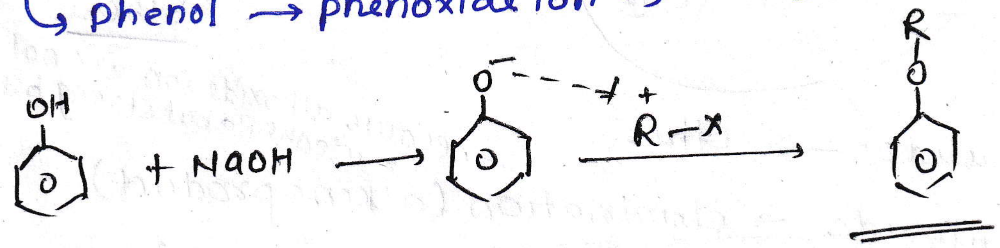
$$\downarrow \text{Remove } H^+$$

$CH_3-CH_2-O-CH_2-CH_3$

- alcohol (primary) → ether → S_N2
- alcohol (secondary) (Tertiary) → S_N1 → alkene forme

③ Phenol→ether

↳ phenol → phenoxide ion $\xrightarrow{\text{alkyl halide}}$ ether



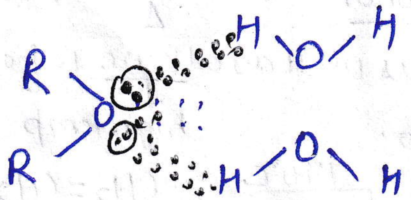
physical property

- ethers have less B.P than corresponding alcohol due to H-Bond in alcohol.

$C_2H_5-O-C_2H_5$ $\quad$ $CH_3-CH_2-CH_2-CH_2-OH$

B.P → 307K $\quad$ 390K

- ethers and alcohols have almost same solubility in waters because oxygen of ether can also form H Bond with H_2O.



Ether

① clevage of C—O bond in ether

② Electrophillic Substitution

Cleavage of C—O bond is done with the help of excess of HX.

(I) $R-O-R + HX \longrightarrow RX + ROH$

$R-O-H + HX \longrightarrow RX + H_2O$

(II) $R \vdots O-Ar + HX \rightarrow RX + Ar-OH$ (Phenol)

bcoz $Ar-O^-$ is phenoxide (Resonance stabilized)

(III) $R-O-R' + HX \longrightarrow RX + R'OH$

- If oxonium ion gives more stable carbocation → [$PhCH_2^{\oplus}$, $CH_2=CH-\overset{\oplus}{C}H_2$, $(CH_3)_3C^{\oplus}$ → SN¹
- less stable carbocation → [Ph^+, $CH_2=CH_2^+$, $CH_3-CH_2^+$ → SN 2

~~when 1°/2° alkyl group present → lowest alkyl group forms alkyl halide.~~ {SN2}

~~in 3° alkyl group → halide formed is tertiary halide.~~ {SN¹}

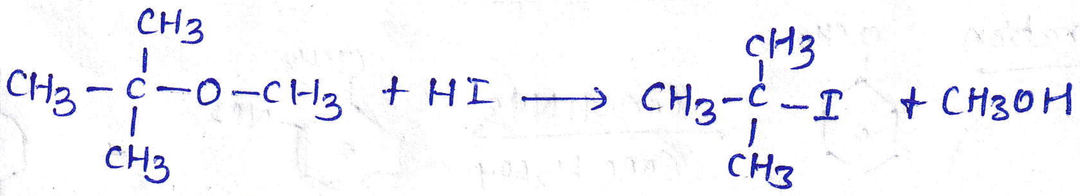
less hindered Carbon attack.

Que $CH_3-O-CH_2CH_3 + HI \rightarrow CH_3I + CH_3CH_2OH$

if HI is in excess

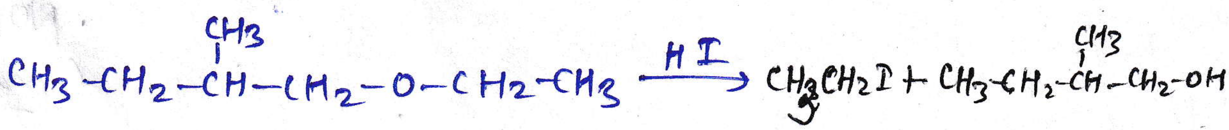
$C_2H_5OH + HI \rightarrow C_2H_5I$

Que



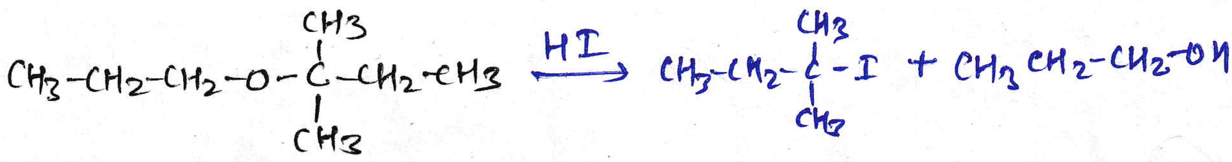
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3 + HI \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I + CH_3OH$$

Que



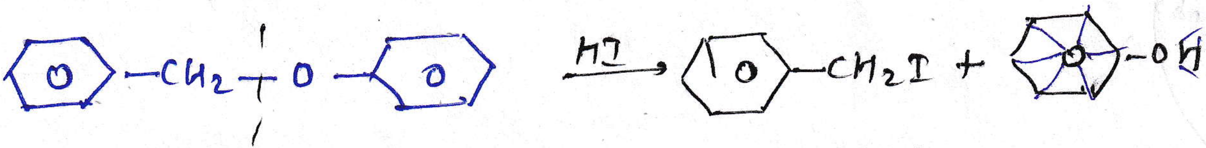
$$CH_3-CH_2-\overset{CH_3}{CH}-CH_2-O-CH_2-CH_3 \xrightarrow{HI} CH_3CH_2I + CH_3-CH_2-\overset{CH_3}{CH}-CH_2-OH$$

Que



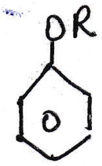
$$CH_3-CH_2-CH_2-O-\underset{CH_3}{C}-CH_2-CH_3 \xrightarrow{HI} CH_3-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-I + CH_3CH_2-CH_2-OH$$

Que



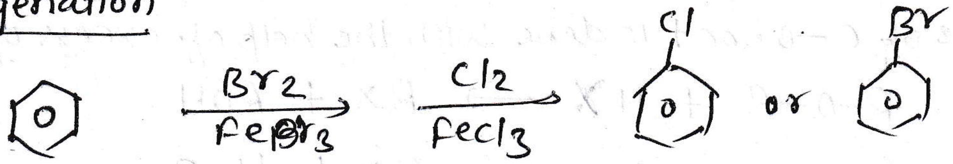
Que

Electrophillic Substn

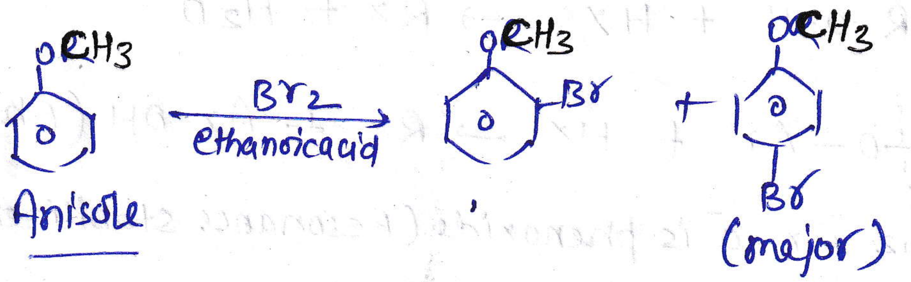


→ OR is o/p directing.

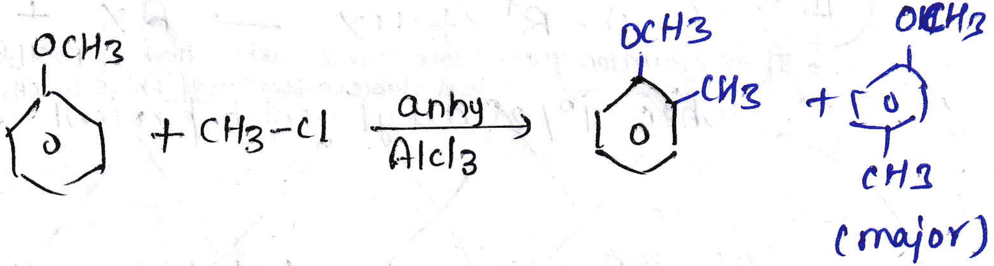
(i) Halogenation

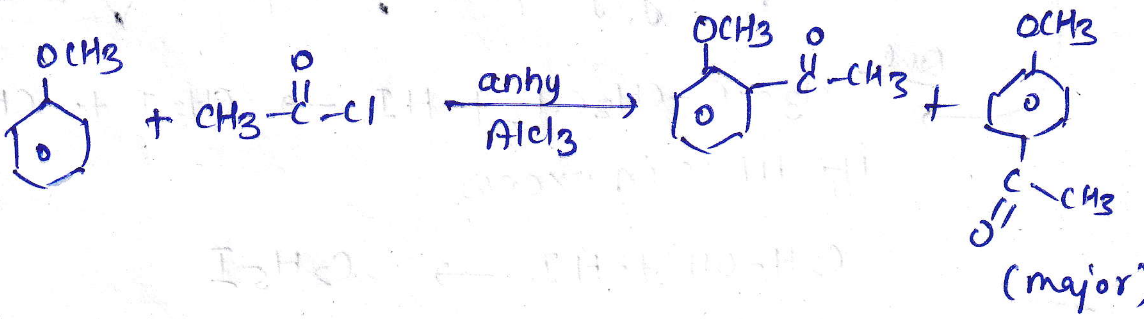


due to OR ring is activated so, lewis acid is not needed

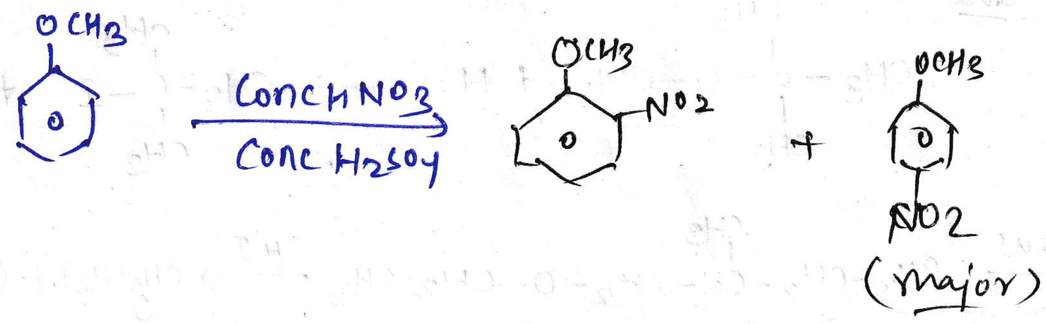


(ii) Friedal craft





(iii) nitration



Testseries