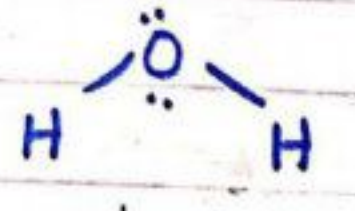
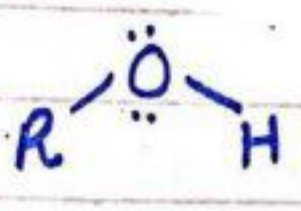
CHAPTER:- 18

ALCOHOLS, PHENOLS & ETHERS

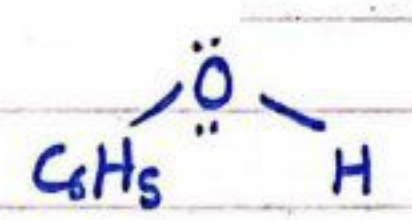
The structure of alcohols, phenols & ethers much resemble with water. Alcohols & Phenols contain hydroxyl group **(OH)** directly attached to alkyl and phenyl groups.



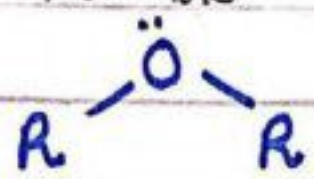
Water



Alcohol



Phenol



Ethers

These compounds are consider as Structural derivative of water

ALCOHOLS

Q:- What are Alcohols? How are they classified?

Alcohols or Alkanol (R-OH):-

When H-atom of alkane is replaced by hydroxyl group **(OH)**, compound form are called Alcohols. They are denoted by **(R-OH)** where **-R** is alkyl group and **(OH)** is hydroxyl group.

Examples:-

① CH_3-OH

Methylalcohol (C.N)

or

Methanol (IUPAC)

② CH_3-CH_2-OH

Ethylalcohol (C·N)

or

Ethanol (IUPAC)

CLASSFICATION OF ALCOHOLS:-

Alcohols are classified into two types:-

1) Monohydric Alcohol
2) Polyhydric Alcohol

MONOHYDRIC ALCOHOLS:-

Alcohols containing only one (OH) group is called monohydric alcohols. It is further classified into three types:-

1) Primary Alcohol (1° Alcohol)
2) Secondary Alcohol (2° Alcohol)
3) Tertiary Alcohol (3° Alcohol)

Primary Alcohol:-

Alcohol in which (OH) group is bonded with primary carbon is called primary alcohol e.g

1) $CH_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2$
   |
   OH

Pri-Propylalcohol (C·N)

or

1-propanol (IUPAC)

4) $\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2$
$\qquad\qquad\qquad\qquad\quad |$
$\qquad\qquad\qquad\qquad\; OH$

Pri-butylalcohol **(C.N)**

or

1-Butanol **(IUPAC)**

Secondary Alcohol:-

Alcohol in which **(OH)** group is bonded with secondary carbon is called secondary Alcohol. e.g

1) $\overset{3}{C}H_3-\overset{2}{C}H-\overset{1}{C}H_3$
$\qquad\quad |$
$\qquad\; OH$

Sec-Propylalcohol OR Isopropylalcohol **(C.N)**

or

2-propanol **(IUPAC)**

2) $\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H-\overset{2}{C}H_2-\overset{1}{C}H_3$
$\qquad\qquad\qquad |$
$\qquad\qquad\quad\; OH$

Sec-Pentylalcohol **(C.N)**

or

3-Pentanol **(IUPAC)**

Tertiary Alcohol:-

Alcohol in which **(OH)** group is bonded with tertiary carbon is called tertiary Alcohol. e.g

$\qquad\quad CH_3$
$\qquad\quad |$
1) $\overset{1}{C}H_3-\overset{2}{C}-\overset{3}{C}H_3$
$\qquad\quad |$
$\qquad\; OH$

Ter-butylalcohol **(C.N)**

or

2-Methyl-2-propanol **(IUPAC)**

2) $CH_3-CH_2-\overset{\overset{OH}{|}}{\underset{CH_3}{|}}C-CH_3$

Tes-pentyl alcohol (C·N)

os

2-Methyl-2-butanol (IUPAC)

POLYHYDRIC ALCOHOLS:-

Alcohols containing more than one (OH) groups is called polyhydric alcohols e.g

1) $CH_2(OH)-CH_2(OH)$

Ethylene glycol (C·N)

os

1,2-Ethanediol (IUPAC)

2) $H_2C(OH)-HC(OH)-CH_3$

Propylene glycol (C·N)

os

1,2-Propanediol (IUPAC)

3) $CH_2(OH)-CH(OH)-CH_2(OH)$

Glycerine OR Glycerol (C·N)

os

1,2,3-Propanetriol (IUPAC)

4) $CH_3-CH(OH)-CH=CH-CH_3$

3-Penten-2-ol

PHYSICAL PROPERTIES:-

1) The first four alcohols are colourless liquids and have sweet smell and burning taste.
2) Alcohols are soluble in water due to H-bonding. But solubility decreases with increase in no. of carbon atoms.
3) Melting and Boiling points of alcohols are higher than that of alkanes due hydrogen bonding

ACIDITY:-

Alcohols are slighty acidic. They are less acidic than water.

Alcohols are - slightly acidic due to more electronegativity of oxygen

$$2R-O-H + 2Na \longrightarrow 2NaOR + H_2$$

$$2H-O-H + 2Na \longrightarrow 2NaOH + H_2$$

METHODS OF PREPARATION:-

1) Hydration of Alkenes:-

1) $CH_2=CH_2 + \overset{+\delta}{H}-\overset{-\delta}{HSO_4} \longrightarrow CH_3-CH_2-O-SO_3H$

$$CH_3-CH_2-\boxed{OSO_3H + H}-OH \xrightarrow{100^\circ C} CH_3-CH_2-OH + H_2SO_4$$

2) Hydrolysis of alkyl sulphate:-

1) $R-X + KOH(aq.) \xrightarrow{H_2O} R-OH + KX$

2) $CH_3-CH_2-Cl + KOH(aq.) \longrightarrow CH_3-CH_2-OH + KCl$

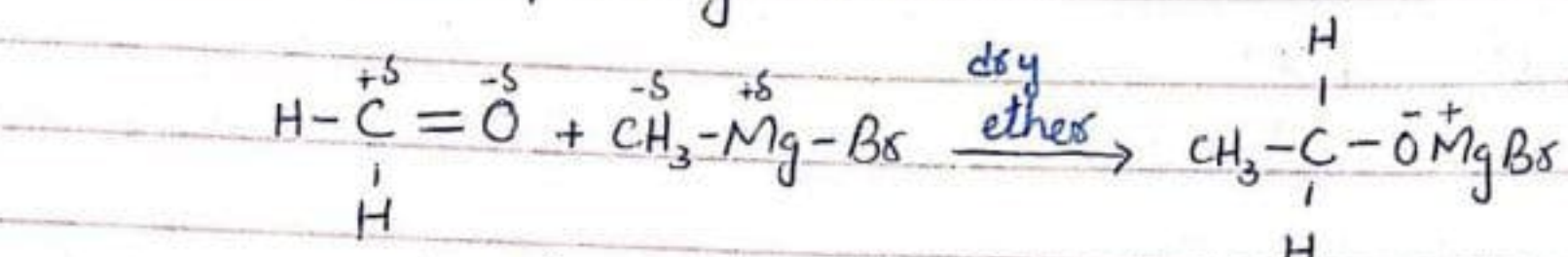
3) Reactions of RLi or RMgX with Aldehydes & Ketones :-

or

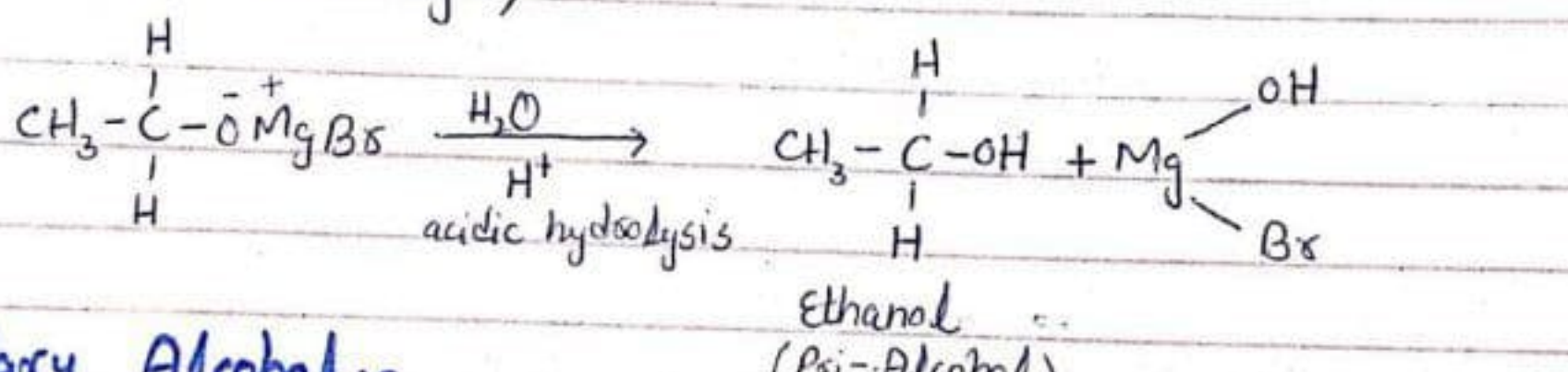
Reaction of Grignard's reagent with carbonyl compounds:-

Primary Alcohol:-

Formaldehyde only reacts with Grignard's reagent and form primary alcohol.



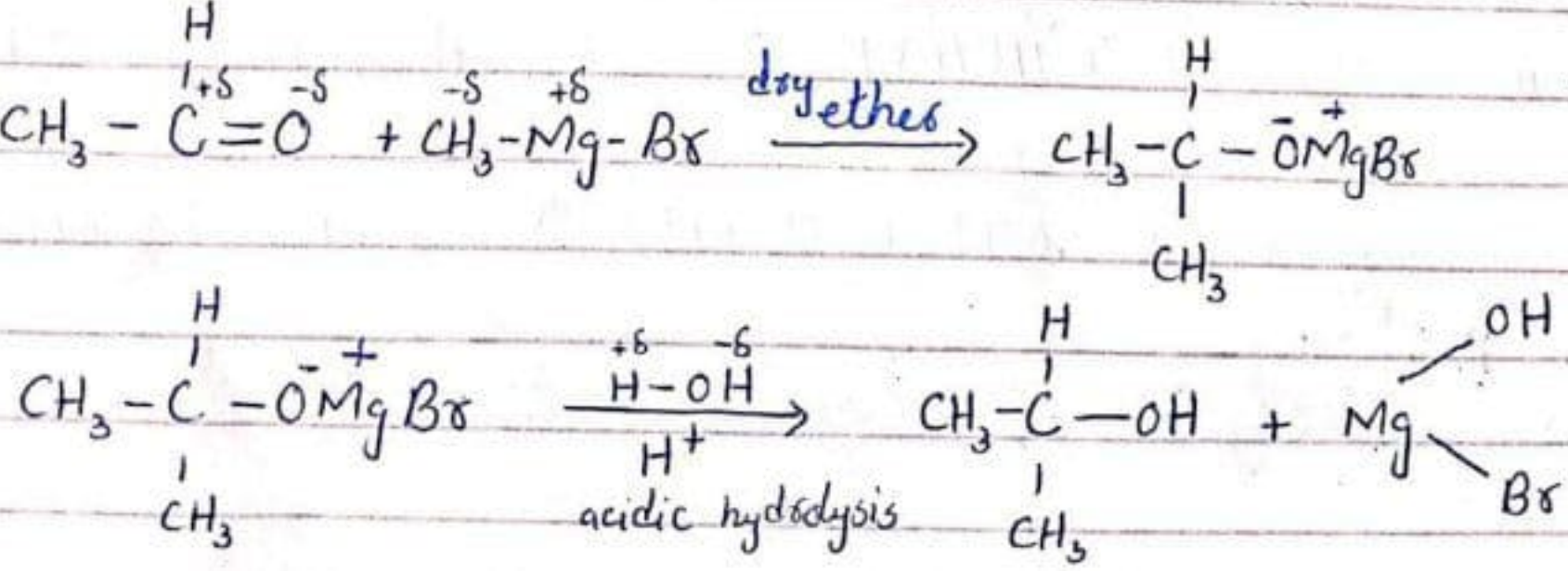
(Formaldehyde)



Ethanol
(Pri-Alcohol)

Secondary Alcohol:-

All other aldehydes except formaldehyde reacts with Grignard's reagent and form secondary alcohols.

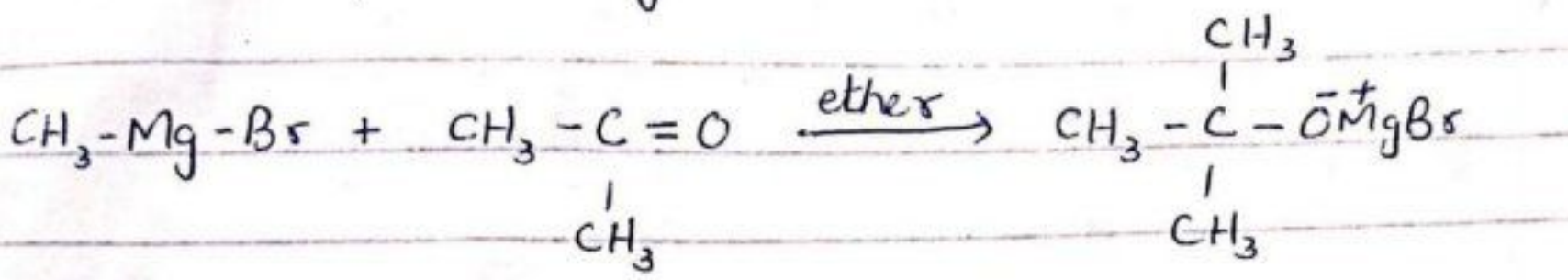


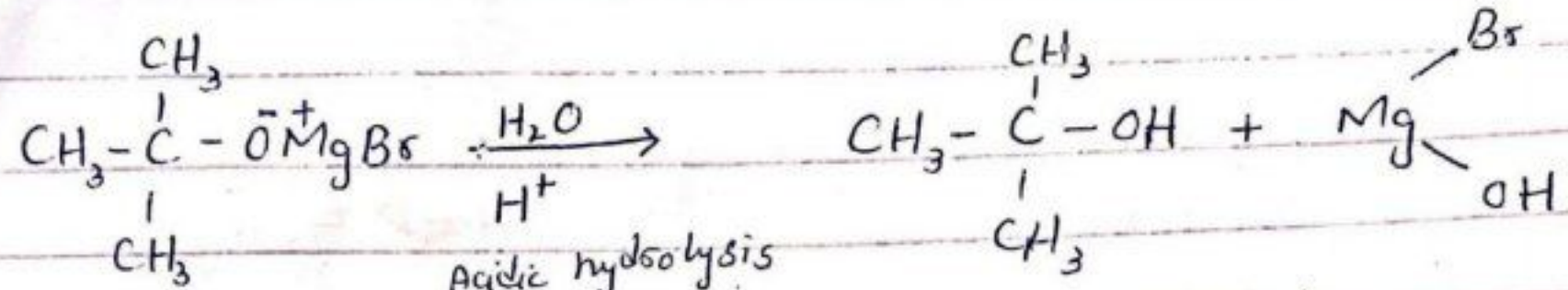
Secondary Alcohol

Tertiary Alcohol:-

All ketones react with Grignard's reagent

and form tertiary Alcohol.



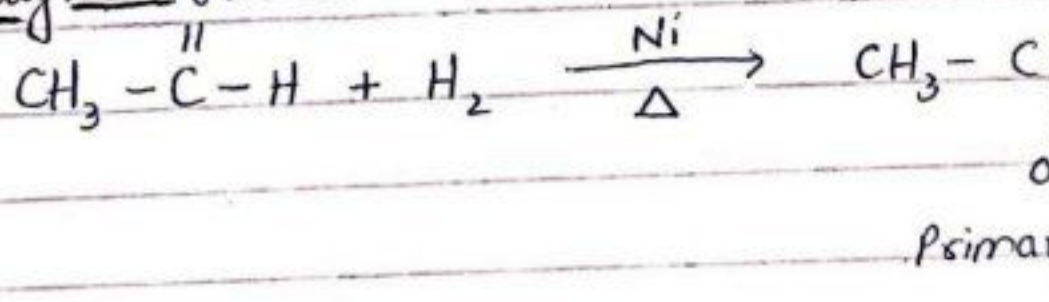


Tertiary Alcohol

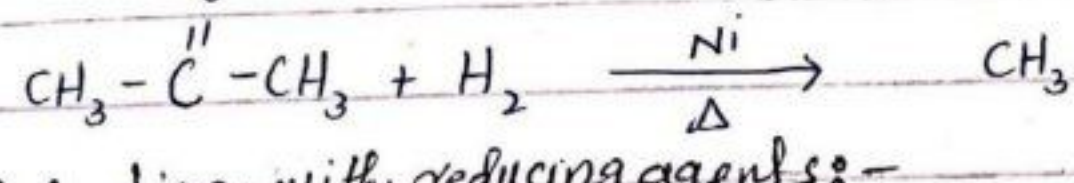
4) Reduction of Aldehydes & Ketones:-

i) Reducing agents are i) H_2/Ni, Pd, Pt
ii) $NaBH_4$, $LiAlH_4$
ii) Aldehyde are reduced into primary (1°) alcohol.
iii) Ketone are reduced into secondary (2°) alcohol.
iv) Carboxylic acid and ester reduced into primary (1°) alcohol.

a) Catalytic reduction:-

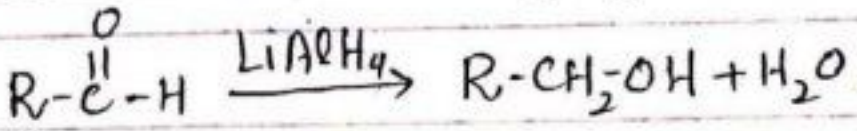


Primary alcohol

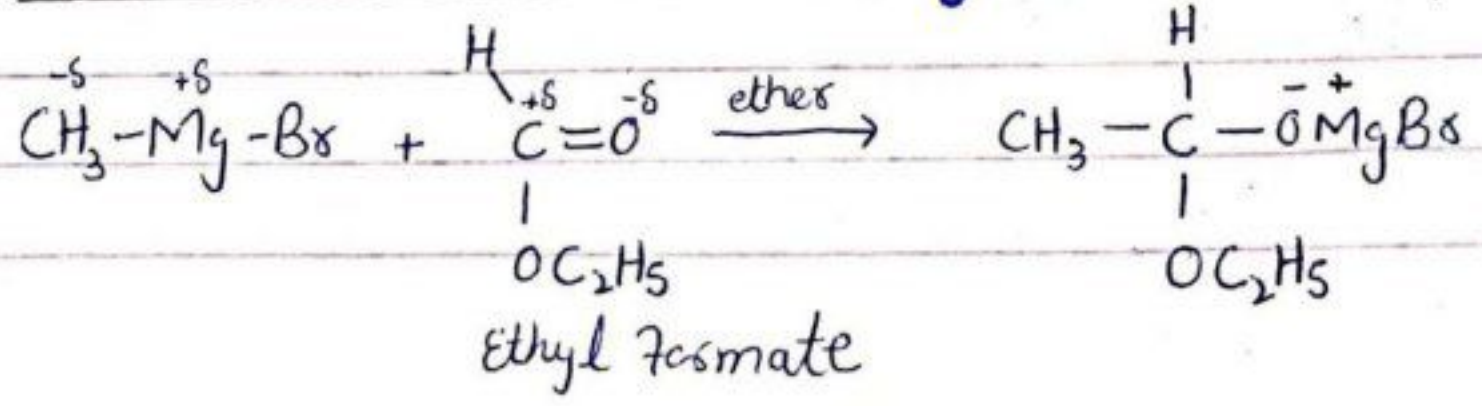


Secondary alcohol

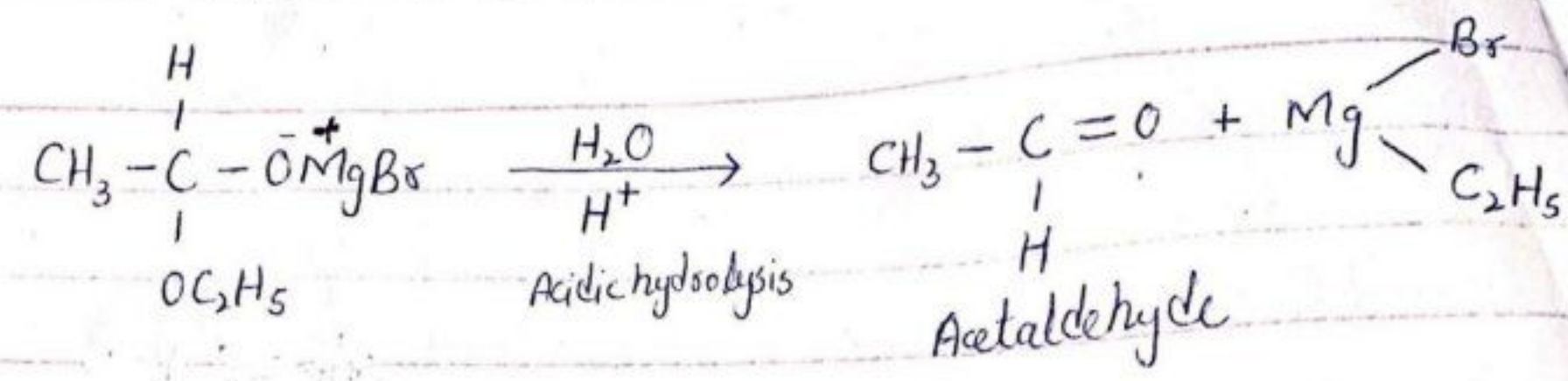
b) Reduction with reducing agents:-



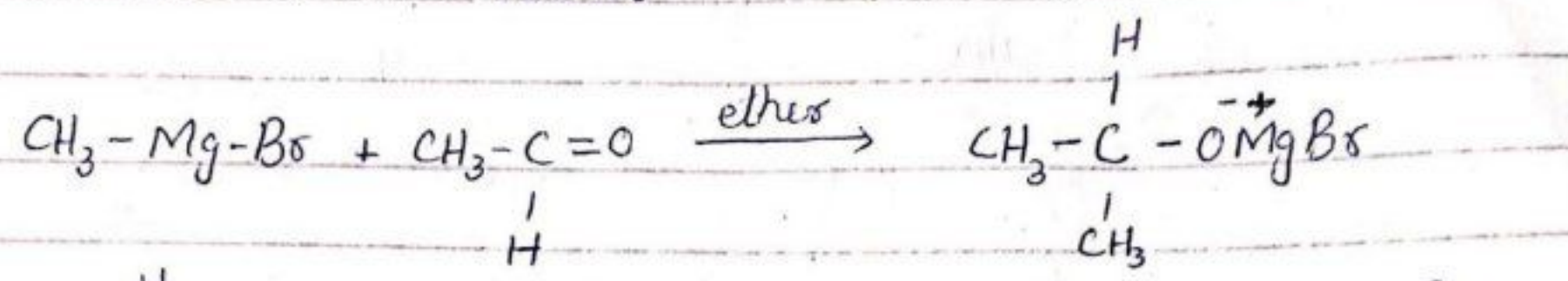
5) Reaction of RLi or RMgX with Esters:-



Ethyl formate

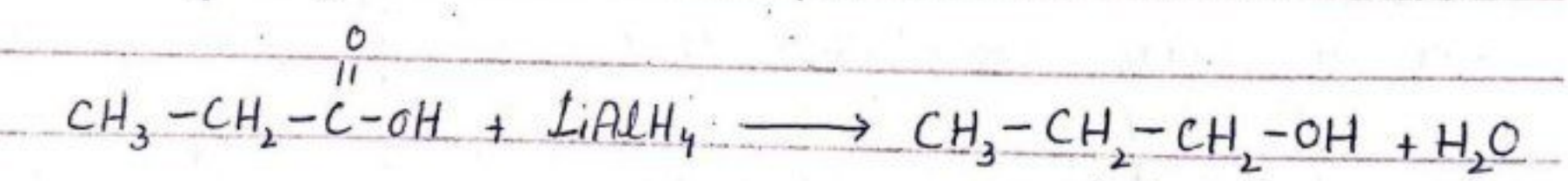


Acetaldehyde again reacts with $CH_3-Mg-Br$ to form alcohol.



6) Reduction of carboxylic acid & Esters:-

Reducing agent is $LiAlH_4$



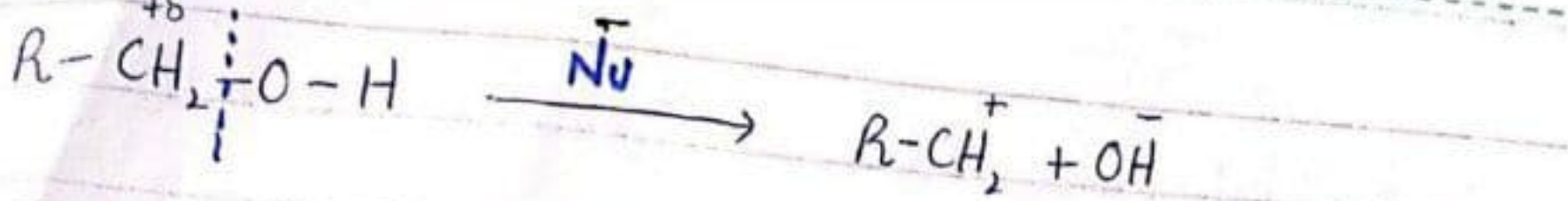
Note:-

Aldehyde and ketone are more reactive than carboxylic acid and ester towards $\bar{N}u$. So carboxylic acid and esters are only reduced by $LiAlH_4$ and **NOT** by less reactive $NaBH_4$

Reactivity:-

Reactivity order of Alcohol depends upon

① Reaction in which C-O bond is broken.

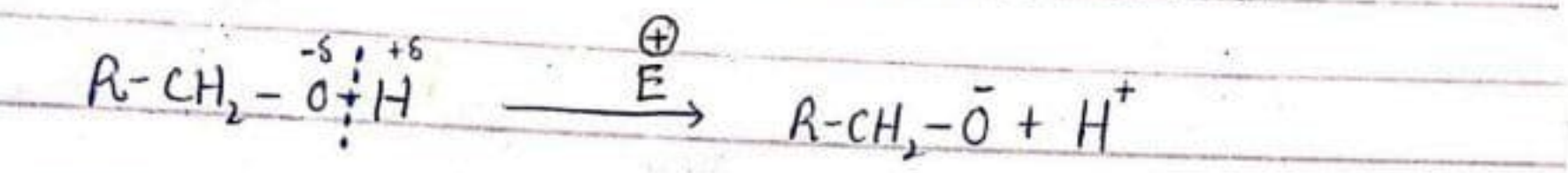


The reactivity order is given by

Ter-alcohol > Sec-alcohol > Pri-alcohol

This stability order is due to stability of carbocation.

2) Reaction in which O-H bond is broken.



The reactivity order is given by

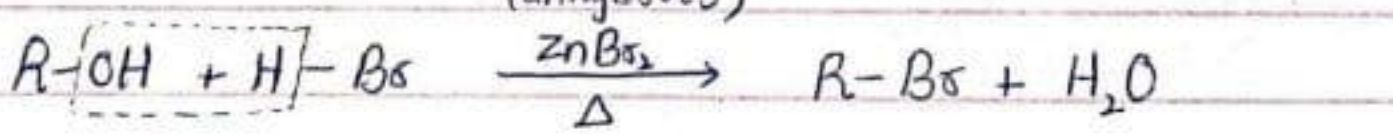
CH_3-OH > Pri-alcohol > Sec-alcohol > Ter-alcohol

This stability order is due to polarity of OH group.

REACTIONS OF ALCOHOLS :-

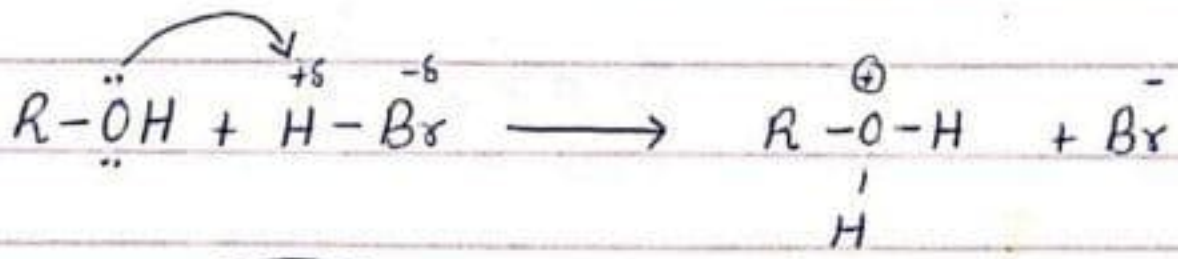
A) Reactions in which C-O bond is broken :-

1) **Reaction with Halogen acid (HX) :-**

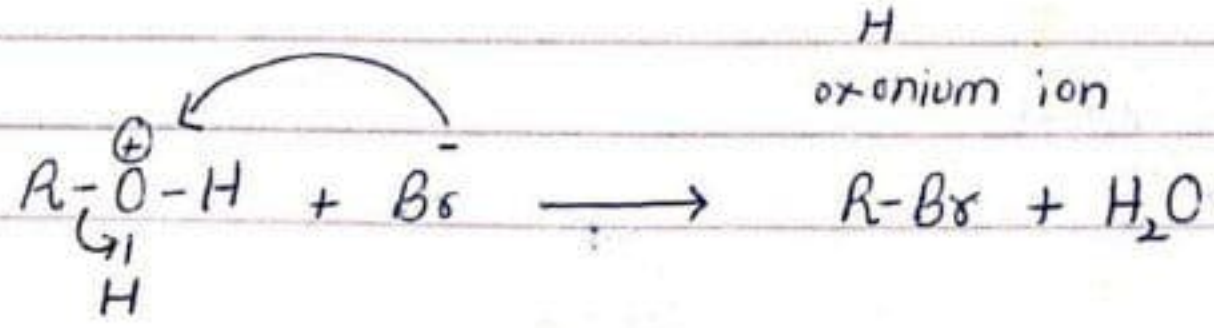


Mechanism :-

Step-1



Step-2



→ $CH_3-OH + HCl \xrightarrow[\Delta]{ZnCl_2} CH_3-Cl + H_2O$

Lucas Test:-

"When alcohol is reacted with conc HCl in the presence of anhydrous $ZnCl_2$ as a catalyst, oily liquids are obtained. This test is called Lucas test" It is used to distinguish b/w primary, secondary and tertiary alcohols.

→ $CH_3-CH_2-CH_2-OH + HCl \xrightarrow[\text{heat}]{ZnCl_2} CH_3-CH_2-CH_2-Cl + H_2O$

1-propanol

→ $CH_2-CH(OH)-CH_3 + HCl \xrightarrow[\text{5-10 min.}]{ZnCl_2} CH_3-CH(Cl)-CH_3 + H_2O$

2-propanol

→ $CH_3-C(CH_3)(OH)-CH_3 + HCl \xrightarrow[\text{immediately}]{ZnCl_2} CH_3-C(CH_3)(Cl)-CH_3 + H_2O$

2-Methyl-2-propanol

Q:- How will you distinguish b/w primary, secondary and tertiary alcohols?

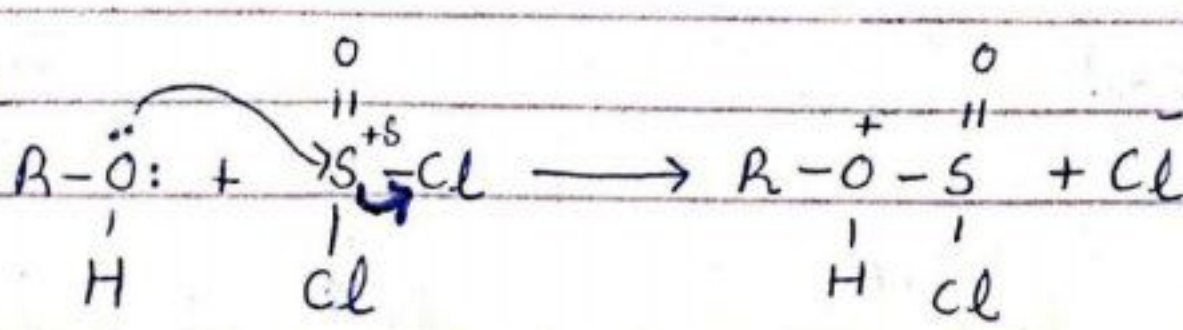
Ans:- Lucas Test

2) Reaction with Thionylchloride ($SOCl_2$):-

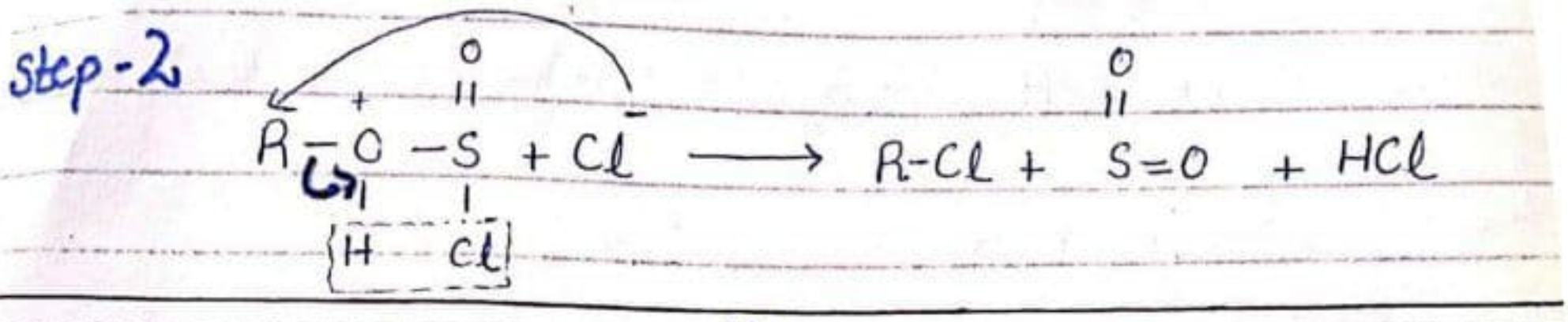
$$R-OH + SOCl_2 \xrightarrow{\text{Pyridine}} R-Cl + HCl + SO_2$$

Mechanism:-

step-1



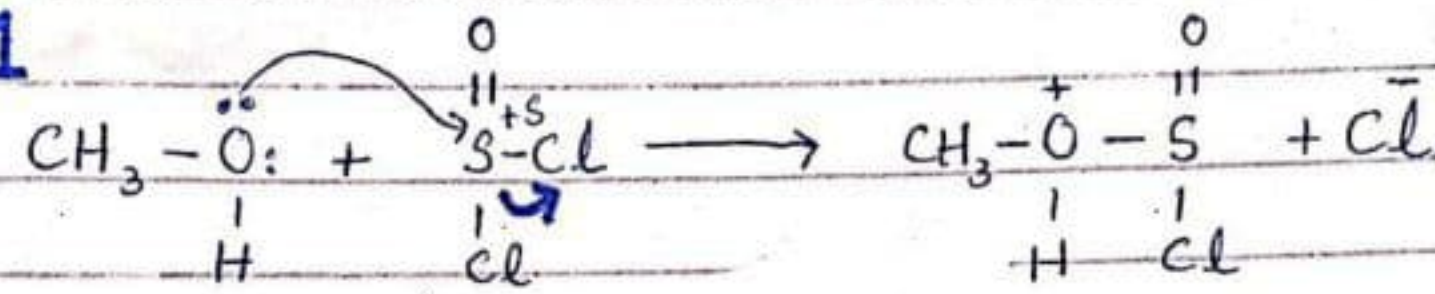
Step-2



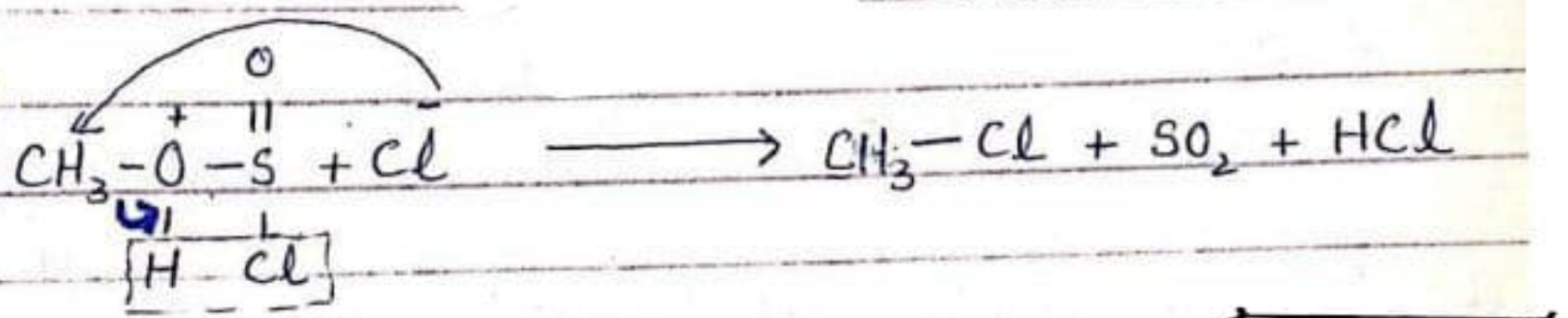
→ $CH_3-OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3-Cl + HCl + SO_2$

Mechanism:-

step-1



step-2



3) Reaction with phosphorus halide:-

→ $3R-OH + PI_3 \longrightarrow 3R-I + H_3PO_3$

phosphorus acid

→ $3R-OH + PBr_3 \longrightarrow 3R-Br + H_3PO_3$

4) Acidic dehydration of Alcohol:- OR Alcohol Condensation

OR

Acid catalyzed Dehydration:-

Best dehydric agent for alcohols is H_2SO_4

→ $CH_3-CH_2-OH + HO-CH_2-CH_3 \xrightarrow[140^\circ C]{H_2SO_4} CH_3-CH_2-O-CH_2-CH_3 + H_2O$

Diethyl ether

$$\rightarrow \overset{\beta}{CH_3}-\overset{\alpha}{CH_2}-OH \xrightarrow[180^\circ C]{H_2SO_4} CH_2=CH_2 + H_2O$$

Mechanism:- (for first reaction)

Step-1

$$CH_3-CH_2-\ddot{O}-H + H^+ \longrightarrow CH_3-CH_2-\overset{\oplus}{\underset{|}{O}}-H$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad H$$
oxonium ion

Step-2

$$CH_3-CH_2-\overset{\oplus}{\underset{|}{O}}-H + H-\ddot{O}-CH_2-CH_3 \longrightarrow CH_3-CH_2-\overset{\oplus}{\underset{|}{O}}-CH_2-CH_3$$
$$\qquad\qquad\qquad\quad H \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad H$$

Step-3

$$CH_3-CH_2-\overset{+}{\underset{|}{\ddot{O}}}-CH_2-CH_3 + H_2\ddot{O} \longrightarrow CH_3-CH_2-O-CH_2-CH_3 + H_3O^+$$
$$\qquad\qquad\qquad\quad H$$

(B) Reactions in which O-H bond is broken:-

1) Preparation of Ester or Esterification:-

When Alcohol is reacted with carboxylic acid in the presence of H_2SO_4 ester is formed. This process is called as Esterification.

$$CH_3-CH_2-O\boxed{H} + CH_3-\overset{O}{\overset{\|}{C}}-\boxed{OH} \underset{\Delta}{\overset{H_2SO_4}{\rightleftharpoons}} CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + H_2O$$
Ethyl acetate

Extra

2) Nitration:-

$$\begin{array}{l} CH_2-O\boxed{H} + HO-NO_2 \\ CH-O\boxed{H} + HO-NO_2 \\ CH_2-O\boxed{H} + HO-NO_2 \end{array} \xrightarrow[\Delta]{H_2SO_4} \begin{array}{l} CH_2-O-NO_2 \\ CH-O-NO_2 \\ CH_2-O-NO_2 \end{array} + 3H_2O$$

Nitro Glycerine
or
Glyceryl trinitrate

Note:-

Nitroglycerine or Glyceryltrinitrate is highly explosive liquid. It is mixed with fine sand and moulded into sticks called **Dynamite**.

C) Other reactions of alcohol:-

Oxidation:-

→ Oxidizing agents are

i) $KMnO_4/H_2SO_4$

ii) $K_2Cr_2O_7/H_2SO_4$ (best oxidizing agent)

→ Primary alcohol first oxidizes to an aldehyde and then further oxidizes to a carboxylic acid.

① $CH_3-\overset{\alpha}{C}H_2-OH + [O] \xrightarrow[H^+\ 50^\circ C]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-H + H_2O$

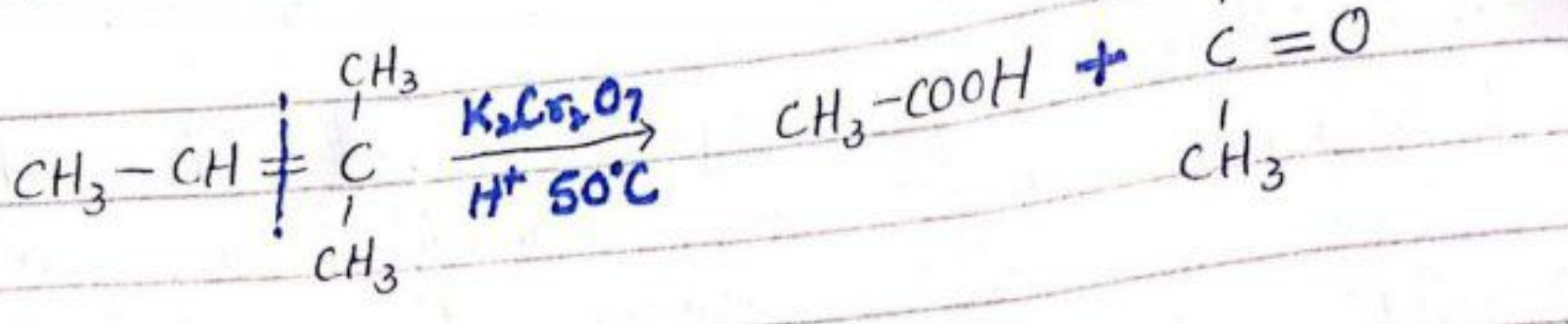
$CH_3-\underset{\underset{O}{\|}}{C}-H + [O] \xrightarrow[H^+\ 50^\circ C]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-OH$

→ Secondary alcohol oxidizes to give Ketone.

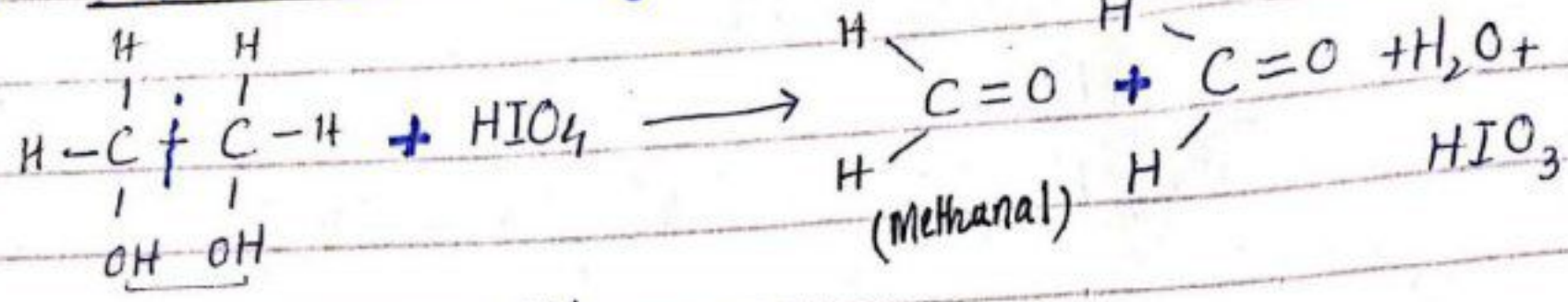
② $CH_3-\underset{OH}{\overset{\alpha}{C}H}-CH_3 + [O] \xrightarrow[H^+\ 50^\circ C]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O$

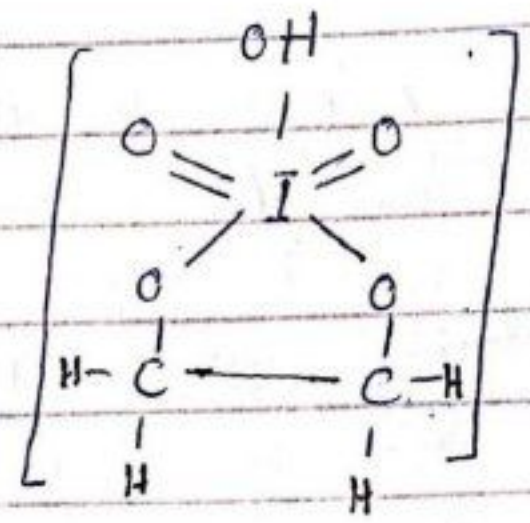
→ Tertiary Alcohol is not oxidized due to non-availability of α-Hydrogen. It reacts with mixture of $K_2Cr_2O_7$ and H_2SO_4 to given alkene. Alkene reacts again with $K_2Cr_2O_7$ and H_2SO_4 to give ketone and carboxylic acid.

③ $CH_3-\overset{\beta}{C}H_2-\underset{CH_3}{\overset{CH_3}{\overset{\alpha}{C}}}-OH \xrightarrow[H_2SO_4\ 50^\circ C]{K_2Cr_2O_7} CH_3-CH=\underset{CH_3}{\overset{CH_3}{C}} + H_2O$



b) Oxidative cleavage of 1,2-diol :-





Reaction Intermediate

Periodate ion

SULPHUR ANALOGUES (Thiols, R-S-H)

→ Sulphur analogues of Alcohols are called Thiols.

→ They are named as Alkanethiol e.g

CH_3-SH — Methanethiol

CH_3-CH_2-SH — Ethanethiol

Properties :-

→ They have low boiling points due to weak H-bonding.

→ S-H bond is less polar than O-H bond because O is more electronegative than S.

→ Thiols are more acidic than alcohols b/c in thiols S-H bond length is large due to low E.N of S. Bond is weak so they are more acidic. But in alcohols O-H bond length is small due to high E.N of O. Bond is strong so they are less acidic.

→ In RSH ($pK_a = 10$) but in ROH ($pK_a = 16-19$)

→ They are oxidized readily to S-O system rather than C=S systems.

PHENOLS :

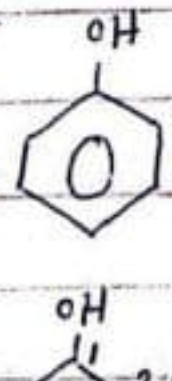
Q:- What are Phenols? How are they classified?

Phenols:-

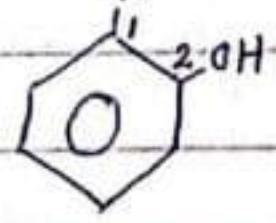
Aromatic compounds containing one or more than one **-OH** group directly attached with the carbon of benzene ring are called Phenols.

It was first obtained from coal tar by **Runge** in **1834**. Phenol is derived from old name of benzene (**phene**).

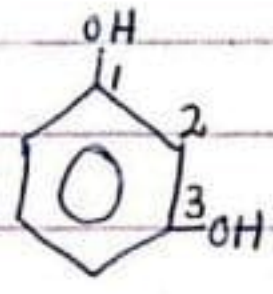
Examples:-

① 

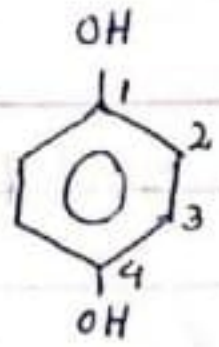
Phenol (IUPAC)
(carbolic acid) (C6N1)

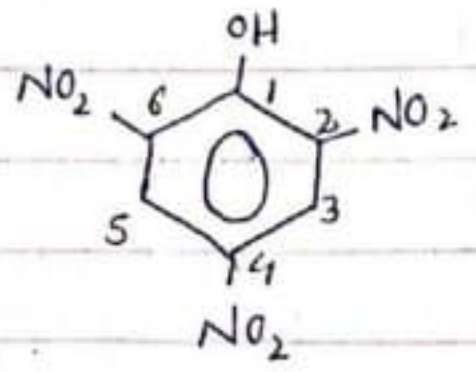
② 

1,2-Dihydroxy benzene (IUPAC)
(catechol) (C6N2)

③ 

1,3-Dihydroxy benzene (IUPAC)
(Resorcinol) (C6N3)

(4)  ... P-Hydroxy phenol or 1,4-Dihydroxy benzene (IUPAC) (Hydroquinone) ... (C·N)

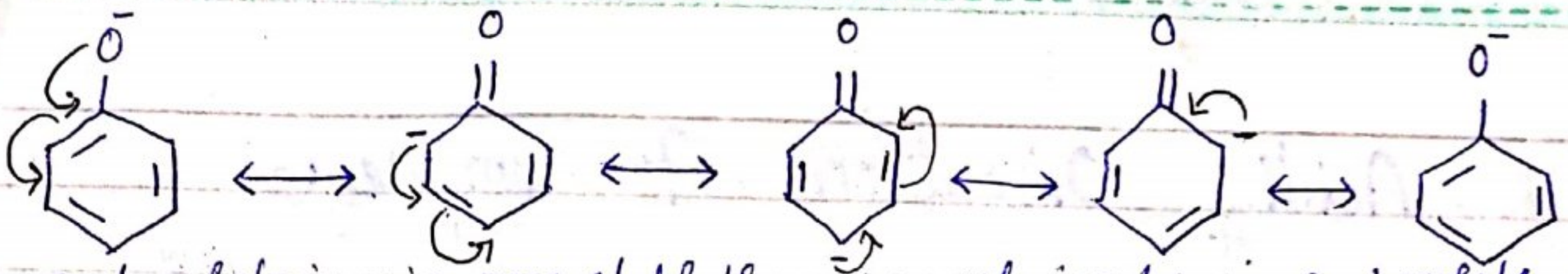
(5)  ... 2,4,6-Trinitrophenol (IUPAC) (Picric acid) ... (C·N)

PHYSICAL PROPERTIES:-

1) Phenol is a colourless, crystalline, poisonous solid.
2) It has phenolic like odour.
3) Its M·P is 41°C and B·P is 182°C
4) It is soluble in water forming pink soln.
5) It is sparingly soluble in water.
6) It is completely soluble in water at 68·5°C.
7) It is poisonous and causes blisters on skin.
8) It is used as disinfectants in washrooms.
9) It is deliquesent solid.

ACIDITY:-

→ Phenols are more acidic than alcohols but less acidic than carboxylic acids.
→ pK_a for Phenols is ($pK_a \approx 10$) and for alcohols is ($pK_a \approx 16-20$); carboxylic acid ($pK_a \approx 5$)
→ It is acidic due to stability of phenoxide or phenolate ion. Alcohol is not stable b/c it has ($R-O^-$) Alkoxide ion but phenol has phenoxide ion which is stable due to delocalization of $\bar{e}$s. It shows resonance.



Carboxylate ion is more stable than phenoxide ion b/c in carboxylate ione -ve charge delocalized from one oxygen atom to other oxygen atom

Substituent Effects on Acidity:- ($R-\overset{O}{\overset{\|}{C}}-\bar{O} \rightleftharpoons R-\overset{O}{\overset{|}{C}}=O$)

→ Substituents increase the acidity of phenol due to resonance.

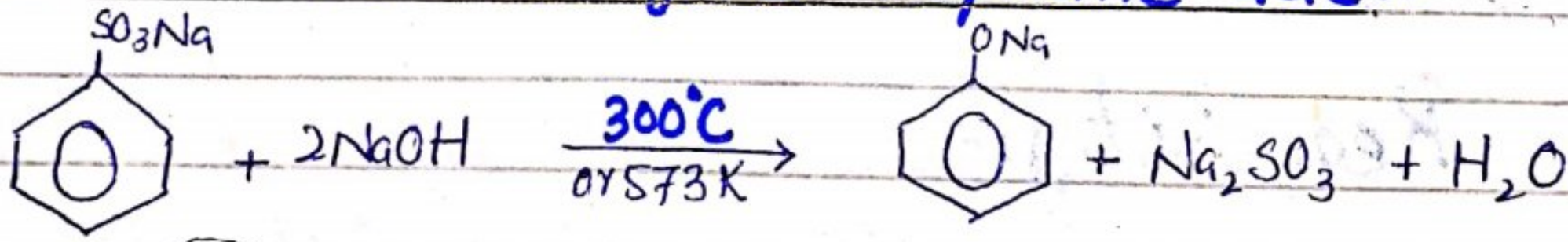
→ Ostho-para- directing groups decreases acidity of phenol due to destabilization of ion.

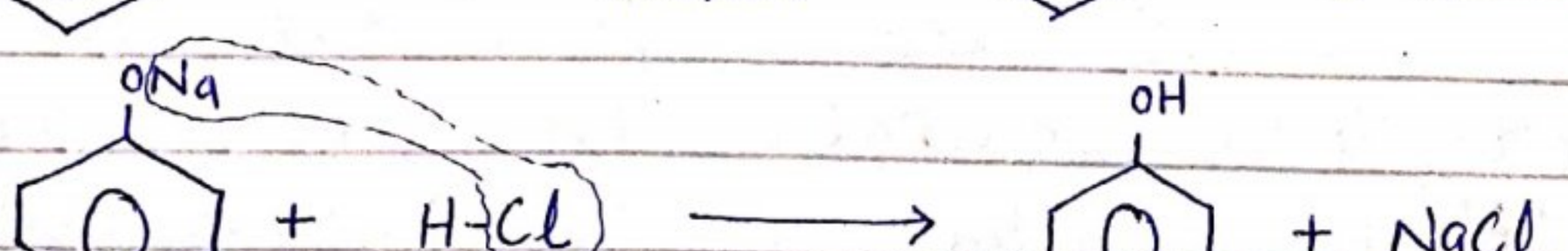
→ Meta- directing groups increases acidity of phenol due to stabilization of ion

Muhammad Javed Iqbal
HOD Chemistry
Askaria Colleges Rwp.

METHODS OF PREPARATION:-

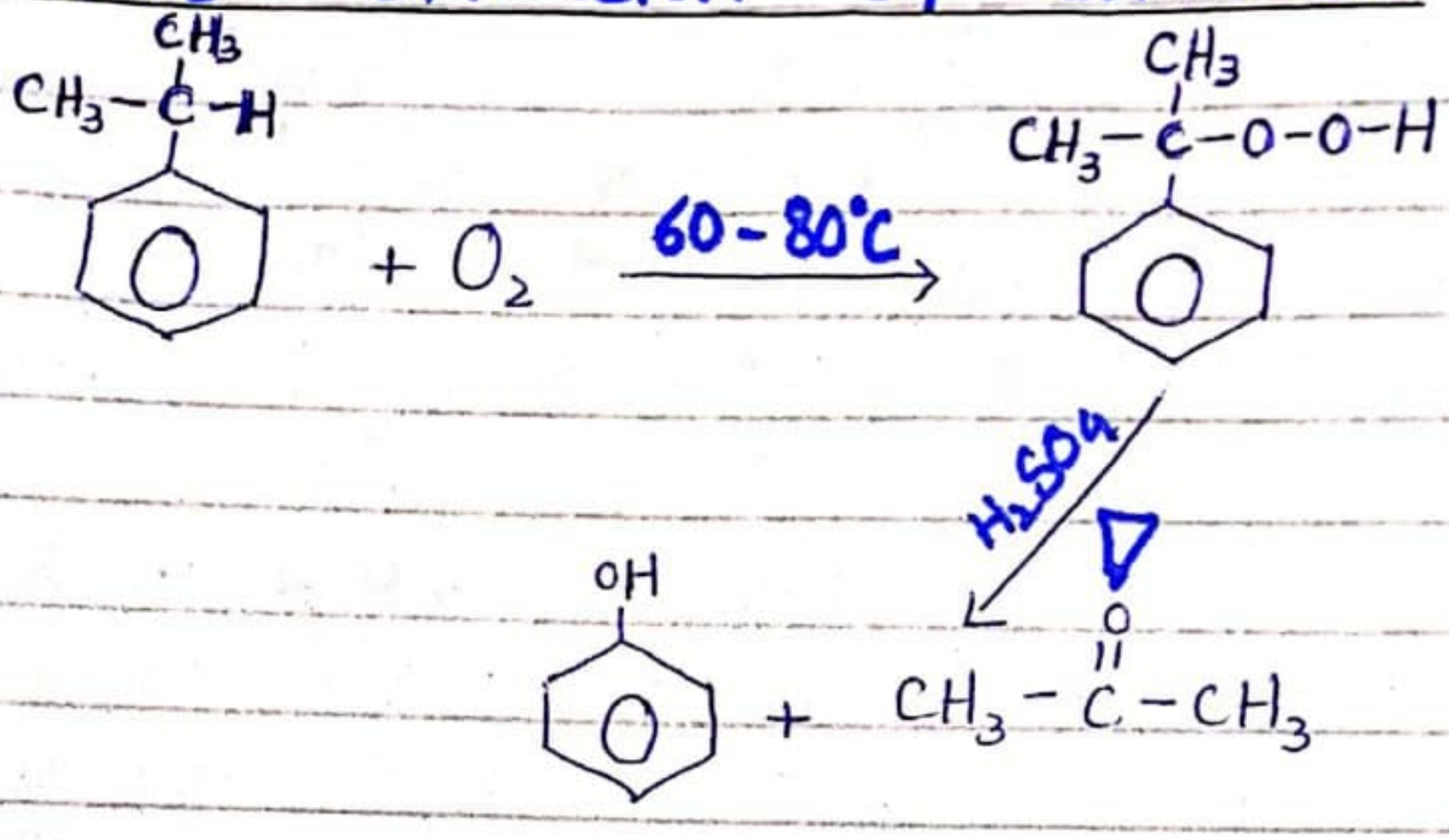
From Sodium salt benzene sulphonic acid:-



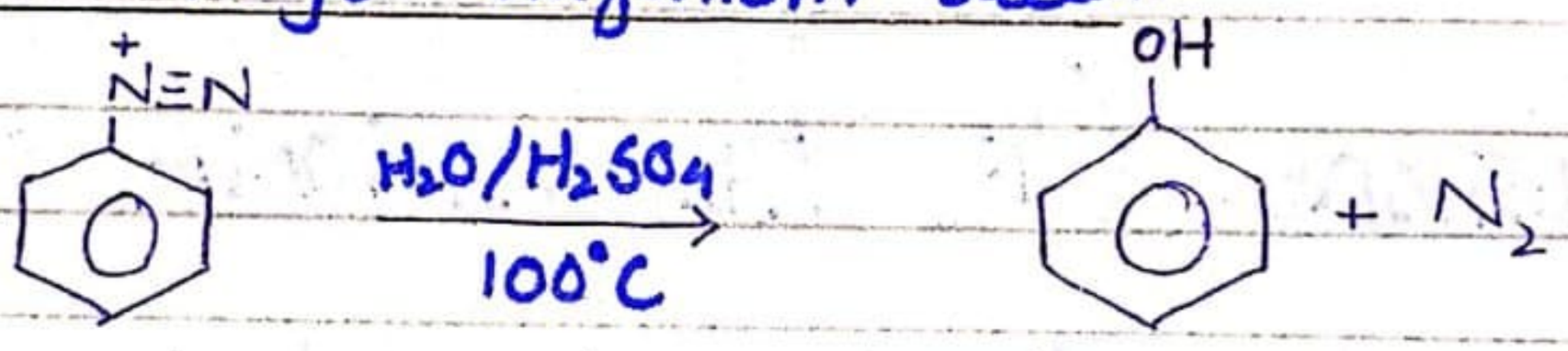


Base Hydrolysis of chlorobenzene:- or Dow's Method:-

Acidic Oxization of Cumene :-



From Asyl diazonium salt :-

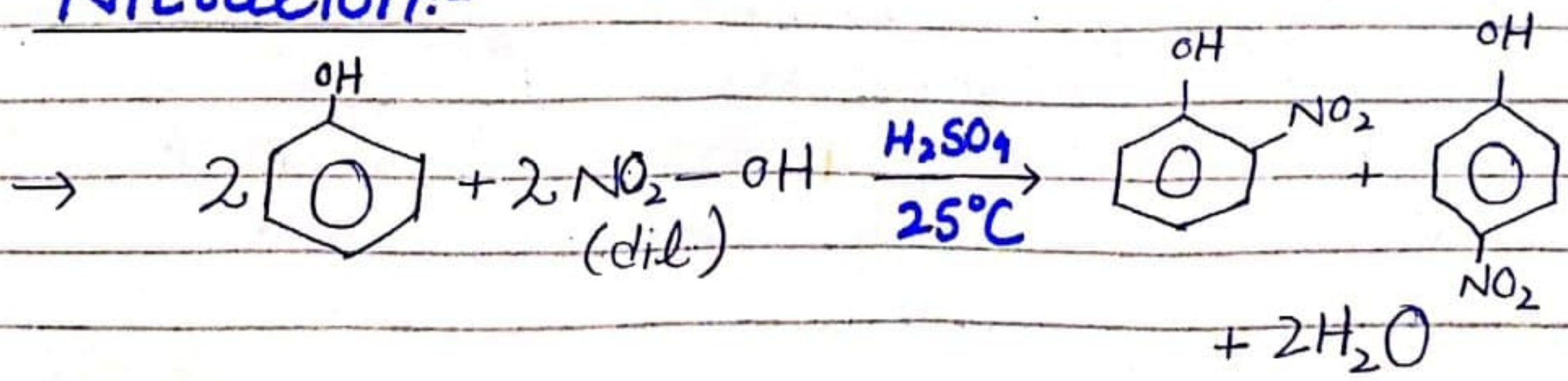


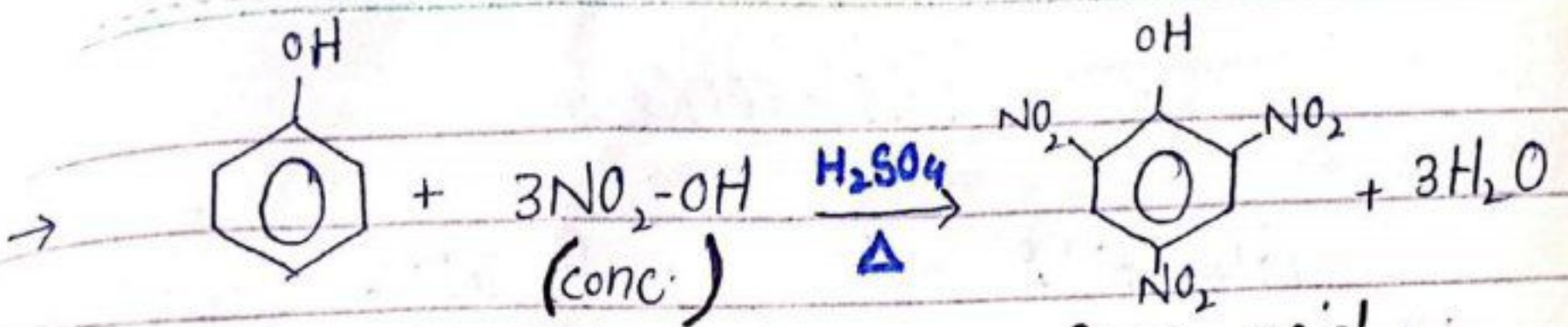
Reactivity :-

Phenols are very reactive towards electrophilic aromatic substitution. They contain **OH** group which is ortho-para-directing substituent.

REACTIONS OF PHENOLS :-

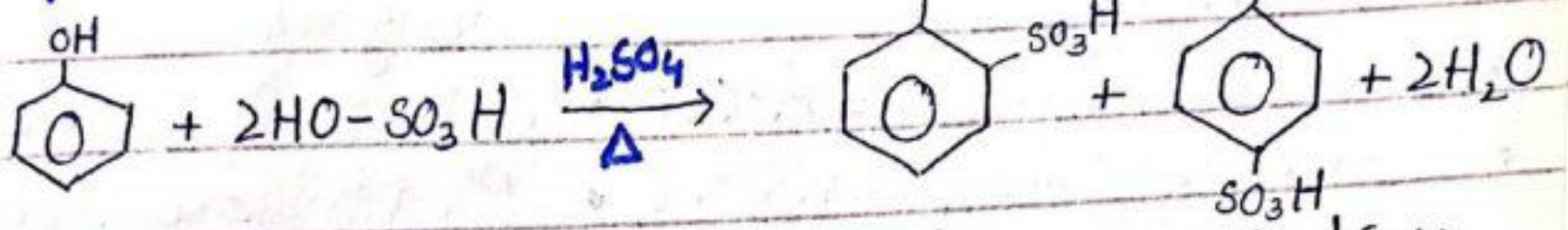
Nitration :-





Picric acid

Sulphonation:-



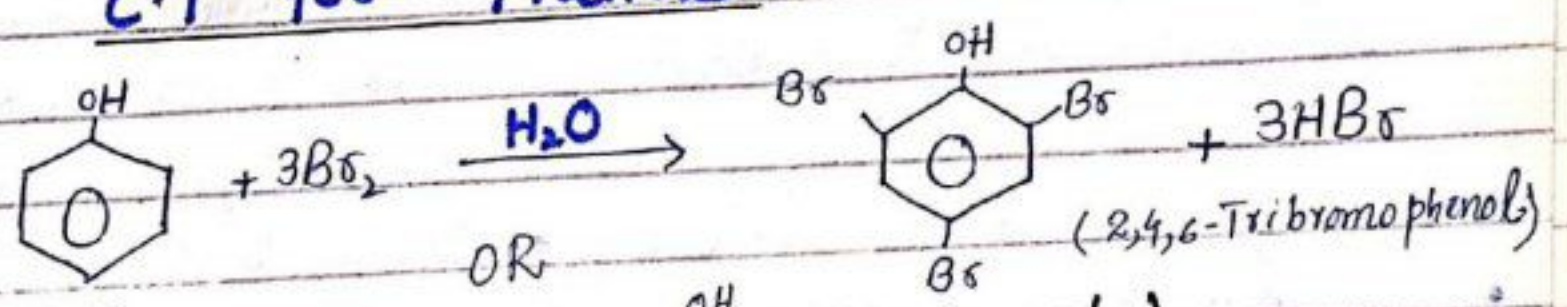
o-hydroxy benzene sulphoic acid

p-hydroxy benezene sulphonic acid

Halogenation:-

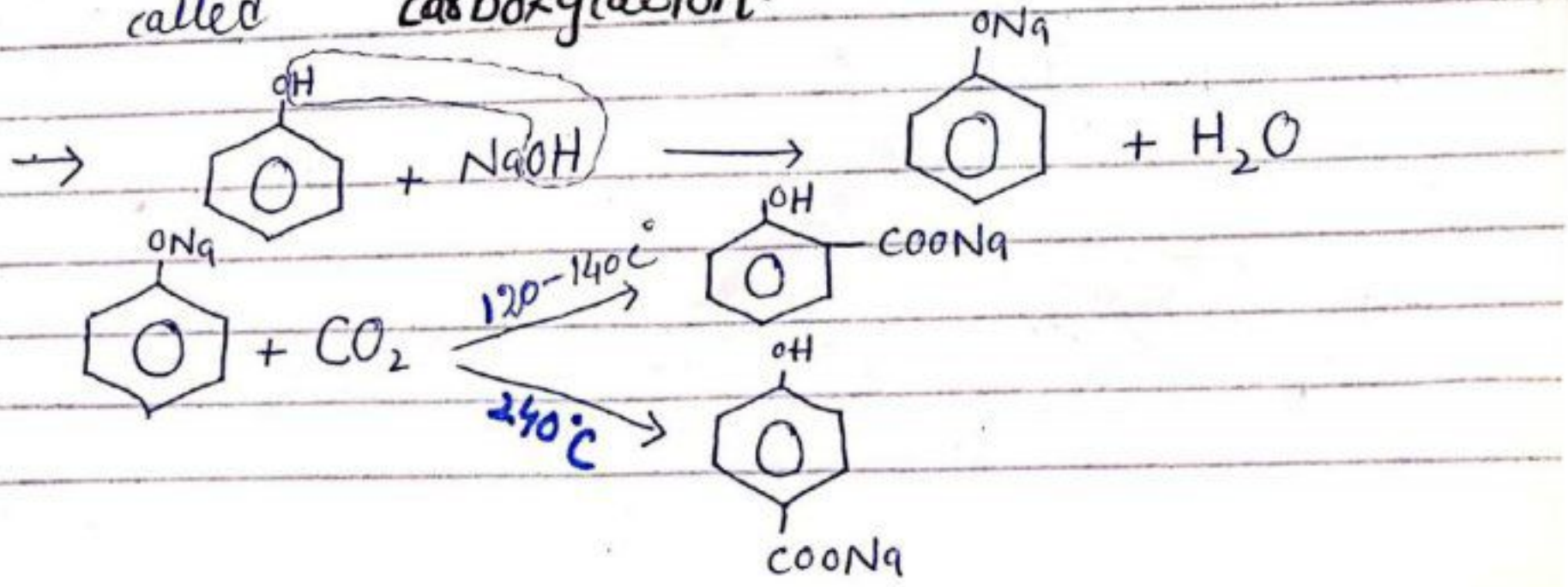
or

C.T for Phenol:-



Reaction with sodium metal & Carboxylation of Phenol:- (Kolbe - schmitt reaction):-

Addition of CO_2 in the molecule is called Carboxylation.



Differences

ALCOHOLS	PHENOLS
• OH group is attached to alkyl group.	• OH group is attached to aryl group.
• Derivatives of Alkanes.	• Derivatives of benzene.
• General formula = R-OH.	• General formula = C_6H_5OH
• Alcohols are monohydric & Polyhydric.	• Phenols are not poly or monohydric.
• Lower alcohols are colourless liquids.	• They are colourless, crystalline, deliquesent solids.
• They have sweet smell & burning taste.	• They have phenolic odour.
• They are readily soluble in water due to H-bonding.	• They are sparingly soluble in water and forms pink solution.
• They are less acidic.	• They are more acidic
• $pK_a \approx 16-20$.	• $pK_a \approx 10$.
• Solubility of alcohols decrease with increase in no. of C-atoms.	• They are completely soluble in water at 68.5°C.
• Alkoxy ions ($R-\bar{O}$) are not stable b/c they don't have resonance structures.	• Phenoxy or Phenolate ions are stable b/c they have resonance structures.

ETHERS

Q:- What are Ethers? How are they classified?

Ether or Alkoxyalkane (R-O-R):-

When oxygen is directly bonded with two alkyl groups, compound form are called ethers. If two alkyl group are same, it is called **symmetrical** ether. If two alkyl groups are **different**, it is called **unsymmetrical** ether.

Examples:-

① CH_3-O-CH_3
Dimethyl ether (C·N)
Methoxy methane (IUPAC)

② $CH_3-O-CH_2-CH_3$
Methyl ethyl ether (C·N)
Methoxy ethane (IUPAC)

③ $CH_3-CH_2-O-CH_2-CH_3$
Diethyl ether (C·N)
Ethoxy ethane (IUPAC)

④ $CH_3-CH_2-O-CH_2-CH_2-CH_3$
Ethyl-n-propyl ether (C·N)
Ethoxy propane (IUPAC)

⑤ $CH_3-\underset{\underset{CH_3}{|}}{CH}-O-\underset{\underset{CH_3}{|}}{CH}-CH_3$

Diisopropyl ether (C·N)
2-isopropoxy propane (IUPAC)

⑥ $CH_3-O-C_6H_5$

Methyl phenyl ether (C·N)
Methoxy benzene (IUPAC)

⑦ $C_6H_5-O-C_6H_5$

Diphenyl ether (C·N)
Phenoxy benzene (IUPAC)

METHODS OF PREPARATION:-

Williamson Synthesis:-

→ This test gives both symmetrical or unsymmetrical ether.

→ $R-OH + Na \longrightarrow R-ONa + \frac{1}{2}H_2$

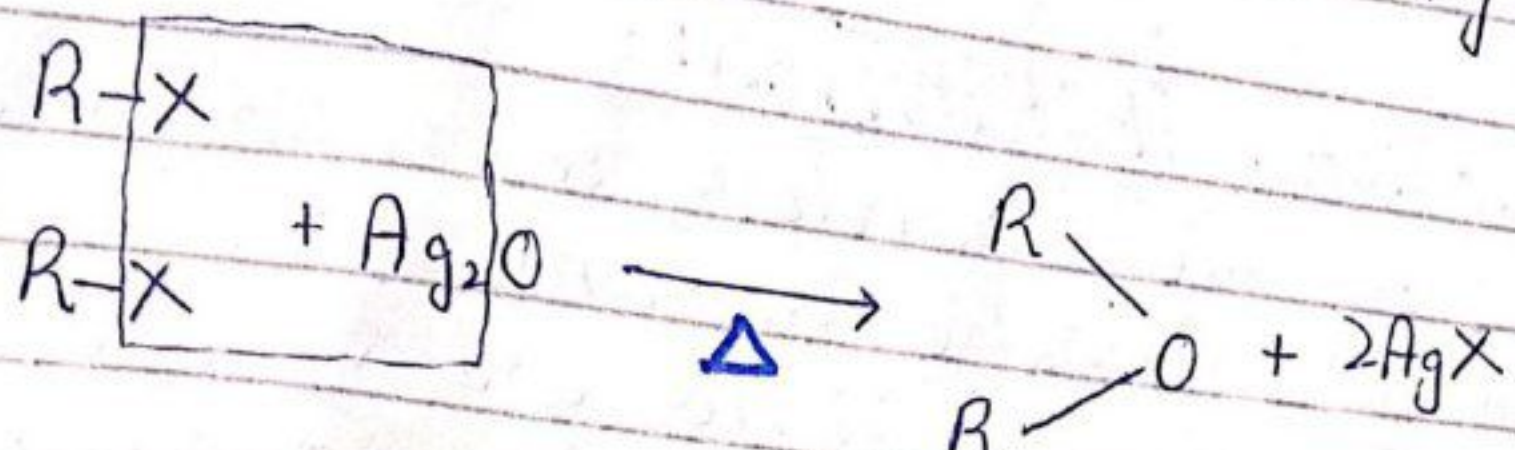
$R-O\boxed{Na + X}-R \longrightarrow R-O-R + NaX$

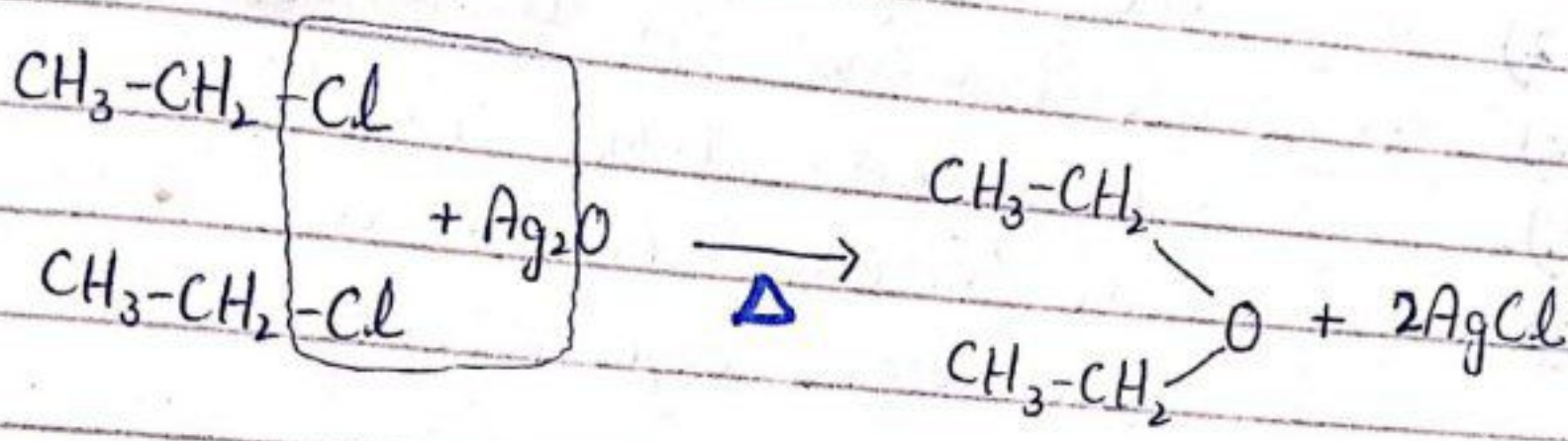
→ $CH_3-OH + Na \longrightarrow CH_3-ONa + \frac{1}{2}H_2$

$CH_3-O\boxed{Na + Cl}-CH_3 \longrightarrow CH_3-O-CH_3 + NaCl$

Reaction of alkyl halides with dry Ag_2O :-

→ This reaction is used to form only symmetrical ethers.

→ 

→ 

Same alkylhalides are reacted with Ag_2O · If same alkylhalides are not used then Ag_2O will give no reaction.

Dehydration of Alcohols :-

1) $CH_3-CH_2-OH + HO-CH_2-CH_3 \xrightarrow[140^\circ C]{H_2SO_4} CH_3-CH_2-O-CH_2-CH_3 + H_2O$

2) $3CH_3-OH + 3CH_3-CH_2-OH \xrightarrow[140^\circ C]{H_2SO_4} CH_3-O-CH_3 + CH_3-CH_2-O-CH_2-CH_3 + CH_3-O-CH_2-CH_3 + 3H_2O$

Note :-

When two different alcohols are dehydrated then 3 moles of each alcohol is used. This is because firstly 2 moles of one alcohol and 2 moles of other alcohol react with themselves and form symmetrical ethers. Then remaining 1 mole is each alcohol react with eachother.

and form unsymmetrical ethers.

PHYSICAL PROPERTIES:-

1) Ethers are colourless, low boiling and highly inflamable compounds.
2) They are oily liquid and volatile.
3) They are soluble in H_2SO_4 on heating.
4) They are lighter than waters.
5) They have ability to dissolve fats, oils, gums and other organic compounds.

CHEMCAL REACTIVITY:-

→ Ethers donot react with acids, bases, oxidizing agents, reducing agents, Na-metal etc.
→ Ethers acts as lewis bases.
→ They have OR group which is poor leaving group.

Q:- How will you distinguish b/w ethers and alcohols?

Ans:- Ether and alcohol can be distinguished by following test.

$$2R\text{-}OH + 2Na \longrightarrow 2R\text{-}\bar{O}Na + \uparrow H_2$$

Alcohols evolve H_2 gas when Na-metal is dissolved in them while ethers give no reaction with Na-metal.

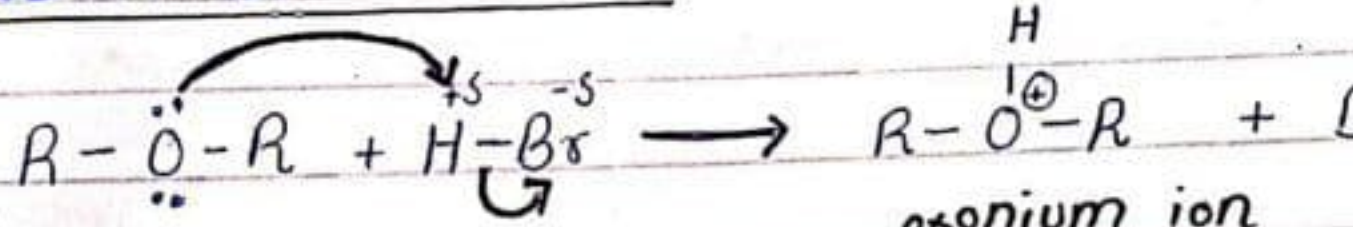
$$2R\text{-}O\text{-}R + 2Na \longrightarrow \text{No reaction.}$$

Q:- How ethers show resistance to oxidation?

Ethers do not react with chemical oxidizing agents. Moreover, reagent like NH_3, Na, alkali and acids have no action on ethers.

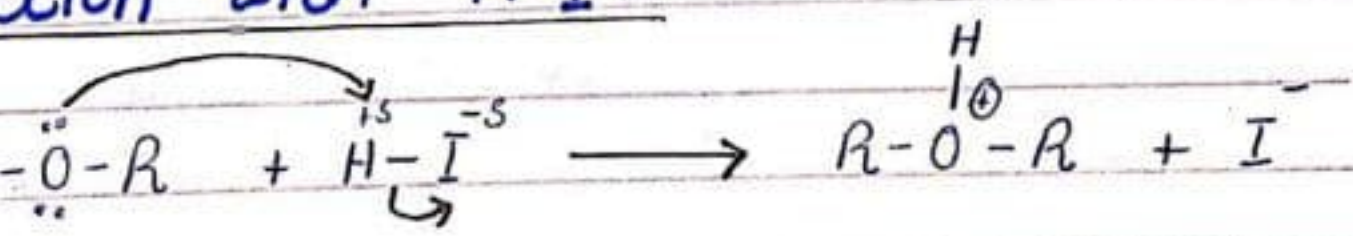
REACTIONS OF ETHERS

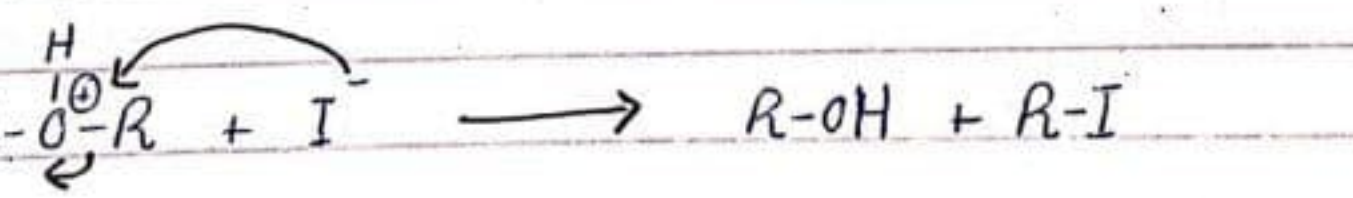
Reaction with H-Br :-



no further reaction occurs.

Reaction with H-I :-





EXERCISE

→ MCQ's

(i) d
(ii) a
(iii) b
(iv) c
(v) a
(vi) d

viij) d

viiij) a

ix) d

x) b & c (both)

xi) a

xii) c

xiii) d

xiv) c

xv) b

Q.2 (i) , (ii) , (v) , (vi) , (vii) , (viii) , (ix) (From notes)

iii) Compare the acidity of pri-, sec-, teri-alcohols.

1°-Alcohol > 2°-Alcohol > 3°-Alcohol

Reason:-

As the no. of Alkyl groups increases on α-Carbon, acidity decreases and vice versa. It is due to electron donor nature of alkyl groups.

iv) 2-Butene is the major product when n-butyl alcohol is heated with conc. H_2SO_4. Explain.

$$CH_3-CH_2-CH_2-CH_2-\ddot{O}H \xrightarrow{H_2SO_4} CH_3-CH_2-CH=CH_2$$

(Minor)

Relatively Less stable carbocation rearrange to stable carbocation before giving elimination product (Major)

$$+\ CH_3-CH=CH-CH_3$$

Explanation:-

$$CH_3-CH_2-CH_2-CH_2-\ddot{O}H \xrightarrow{H^+} CH_3-CH_2-CH_2-CH_2-\overset{\oplus}{O}H_2$$

$$CH_3-CH_2-CH_2-CH_2-\overset{\oplus}{O}H_2 \longrightarrow CH_3-CH_2-\overset{\oplus}{C}H-CH_3 + H_2O$$

1°-carbocation (unstable)

2°-carbocation (stable)

$$CH_3-CH_2-\overset{\oplus}{C}H-CH_3 \longrightarrow CH_3-CH=CH-CH_3 + H^{\oplus}$$

x) Why is phenol more soluble in water than toluene?

Phenol shows polar nature due to presence of OH- group. Water is also polar. So it is soluble in water.

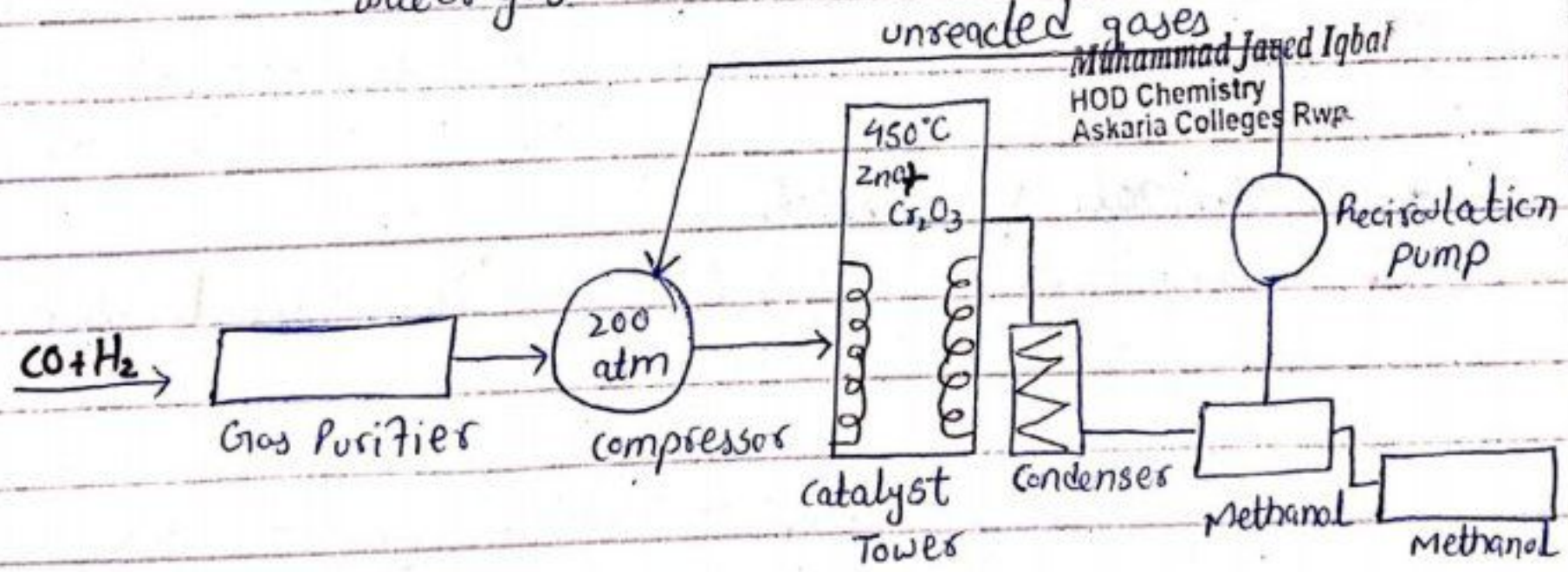
Toluene is non-polar due to the presence of CH_3- (a hydrocarbon). CH_3 is non-polar. So it is insoluble (less soluble) in water than phenol.

Q.3 ③, ④, ⑤, ⑥, ⑦, ⑧, ⑨, ⑩

i) How will you prepare alcohols on industrial scale?

ii) **Methanol :-**

$$\underbrace{CO + 2H_2}_{\text{water gas}} \xrightarrow[450^\circ C \;\; 200 atm]{ZnO + Cr_2O_3} CH_3-OH$$



iii) **Ethanol :-**

From Molasses :-

"The residue obtained after the crystallization of sugar from conc. sugar cane juice is called molasses."

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{yeast}]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow[\text{yeast}]{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

From starch

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow[\text{yeast}]{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{yeast}]{\text{Maltose}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow[\text{yeast}]{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

2) Distinguish ethanol from methanol and ethanol from phenol.

→ **Methanol & Ethanol**

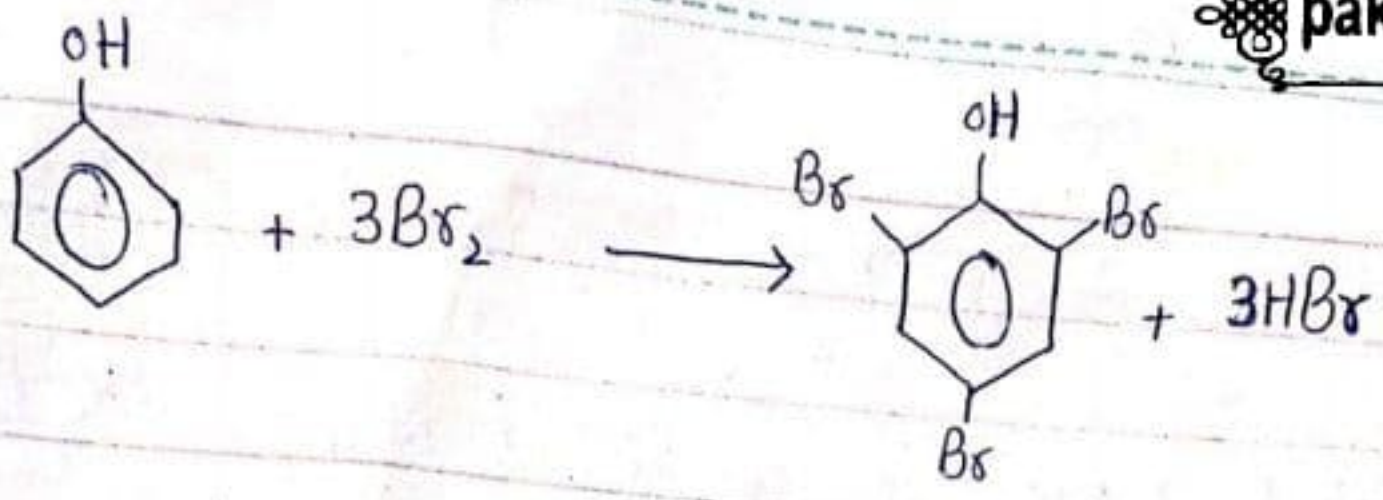
Methanol & Ethanol can be distinguished by iodoform test.

$$CH_3-CH_2-OH + 4I_2 + 6NaOH \longrightarrow \underset{\text{(Yellow ppt.)}}{\underset{\text{Iodoform}}{CHI_3}} + HCOONa + 5NaI + 5H_2O$$

$$CH_3-OH + I_2 + NaOH \longrightarrow \text{No reaction.}$$

→ **Phenol & Ethanol**

Phenol & Ethanol can be distinguished by Bromine water.



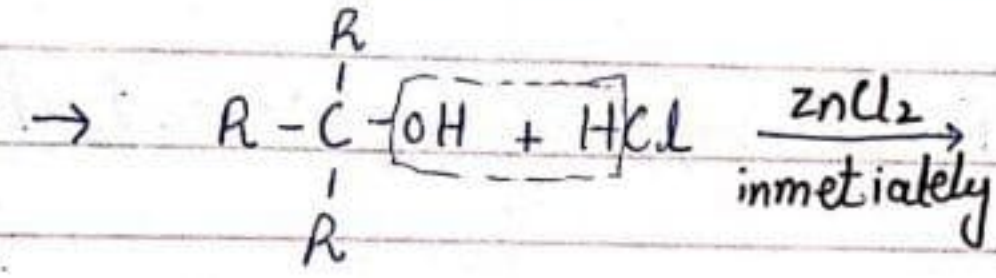
2,4,6-Tribromophenol
(white ppt)

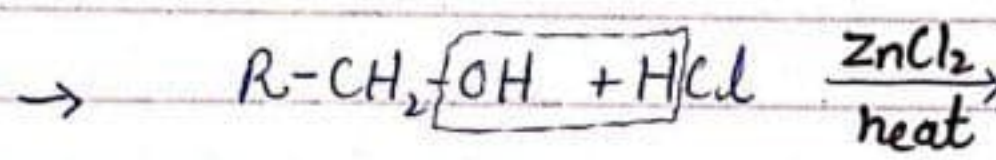
Alcohol does not gives white ppt with Br_2 water.

ii) How will you distinguish b/w

iv) **Ter-Alcohol & Pri-Alcohol**

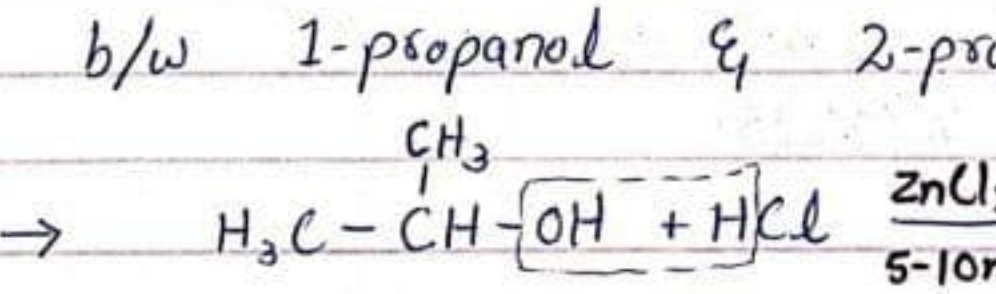
Lucas Test is used to distinguish b/w ter-Alcohol & Pri-Alcohol.

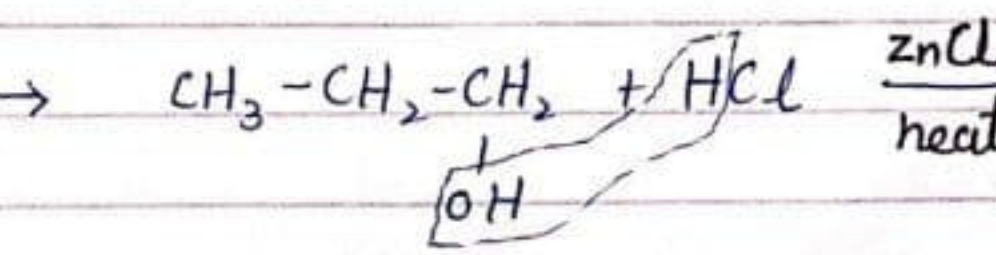




v) **1-propanol & 2-propanol**

Lucas test is used to distinguish b/w 1-propanol & 2-propanol.



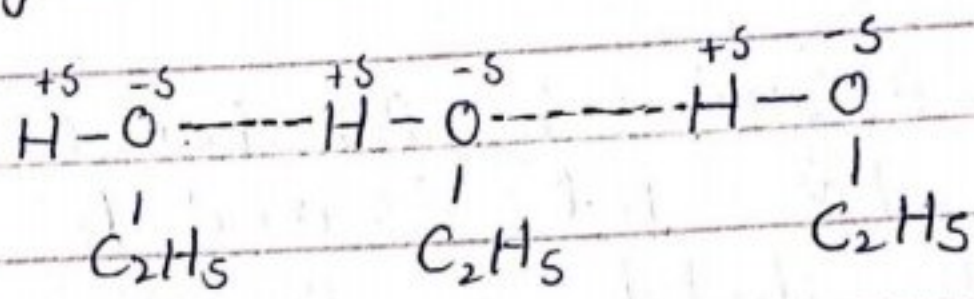


12) Give reason for the followings.

i) Ethyl alcohol is a liquid while ethyl chloride is a gas.

Reason:-

Ethyl chloride has weak dipole-dipole forces while ethyl alcohol has strong H-bonding. Due to strong H-bonding it is a liquid. and ethyl chloride is a gas.



ii) Ethanol has higher b.p than diethyl ether.

Reason:-

Ethanol has strong H-bonding while diethyl ether have weak vander Waal's dispersion forces. Bonds b/w diethyl ether are weak and easily break on boiling. Thus Ethanol has high B.P than Diethyl ether.

iii) Absolute Alcohol cannot be prepared by fermentation process.

Reason:-

This is b/c at higher concentration of alcohol enzyme of yeast becomes inactive and reaction stops.

Alcohol obtained by fermentation process is only 12% - It is further concentrated by distillation to about 95% called rectified

spirit. Rectified spirit is further distilled with **lime** to give absolute alcohol.

iv) Ethanol gives different products with conc. H_2SO_4 under different conditions.

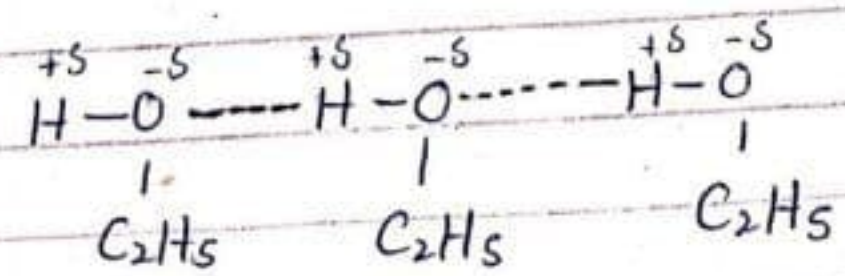
→ $CH_3-CH_2-OH \xrightarrow[180°C]{(conc.)\ H_2SO_4} CH_2=CH_2 + H_2O$

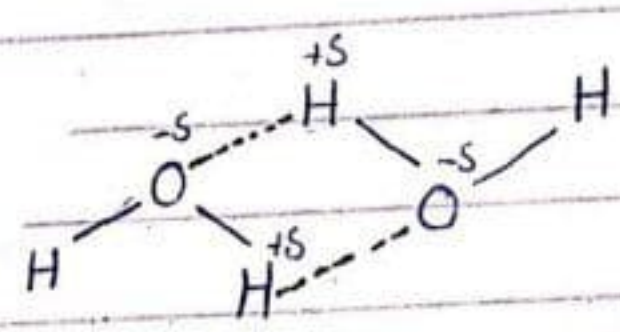
→ $CH_3-CH_2-\boxed{OH}$ / $CH_3-CH_3-\boxed{OH}$ $\xrightarrow[140°C]{conc.\ H_2SO_4}$ $CH_3-CH_2-O-CH_2-CH_3 + H_2O$

v) Water has high B.P than Ethanol.

Reason:-

In water two H-bonds are formed per molecule while in ethanol one H-bond is formed per molecule. Due to stronger H-bonding in H_2O, its boiling point is greater than ethanol.





Chapter 18

Alcohls, Phenols and Esthers

Quick Quiz 1

i) What are monohydric and pdyhdric alcohols?

Monohydric Alcohols :- Alcohols containing one -OH grap are called monohydric alcohols.

Examples :-

CH_3-OH Methanol

CH_3-CH_2-OH Ethanol

Polyhydric Alcohds :- Alcohds containing two or more hydroxyl graps are called polyhydric alcohds.

Examples :-

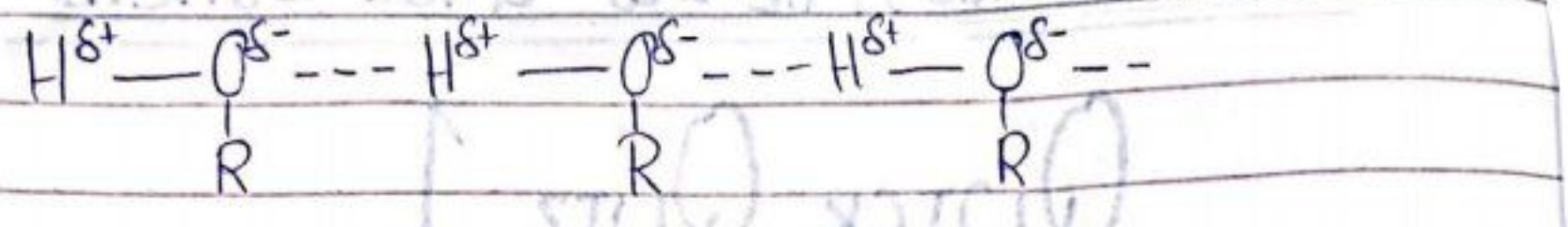
$CH_2(OH)-CH_2(OH)$ 1,2 Ethanediol

$CH_2(OH)-CH(OH)-CH_2(OH)$ 1,2,3-Propanediol

ii) Why are some alcohds readily soluble in water?

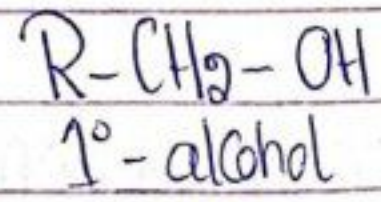
⇒ Small alcohol, eg methand and ethand, are readily solube in water.

⇒ The solubility of alcohds is due to hydrogen bonding which is significant in lower alcohds but decrease in higher alcohols due to increase in non-pdar nature of alkyl (R) grap.

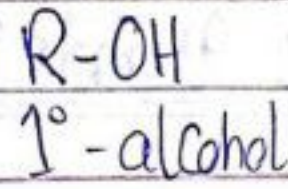


iii) Write general formulas of 1°, 2° and 3° alcohols.

1°-Alcohols :-

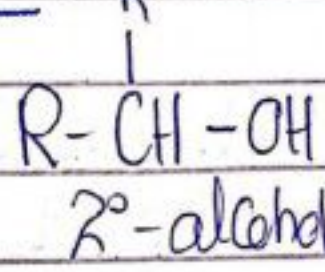


1°-alcohol



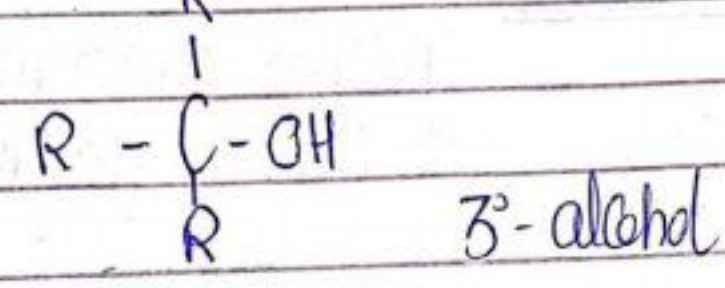
1°-alcohol

2°-Alcohols :-



2°-alcohol

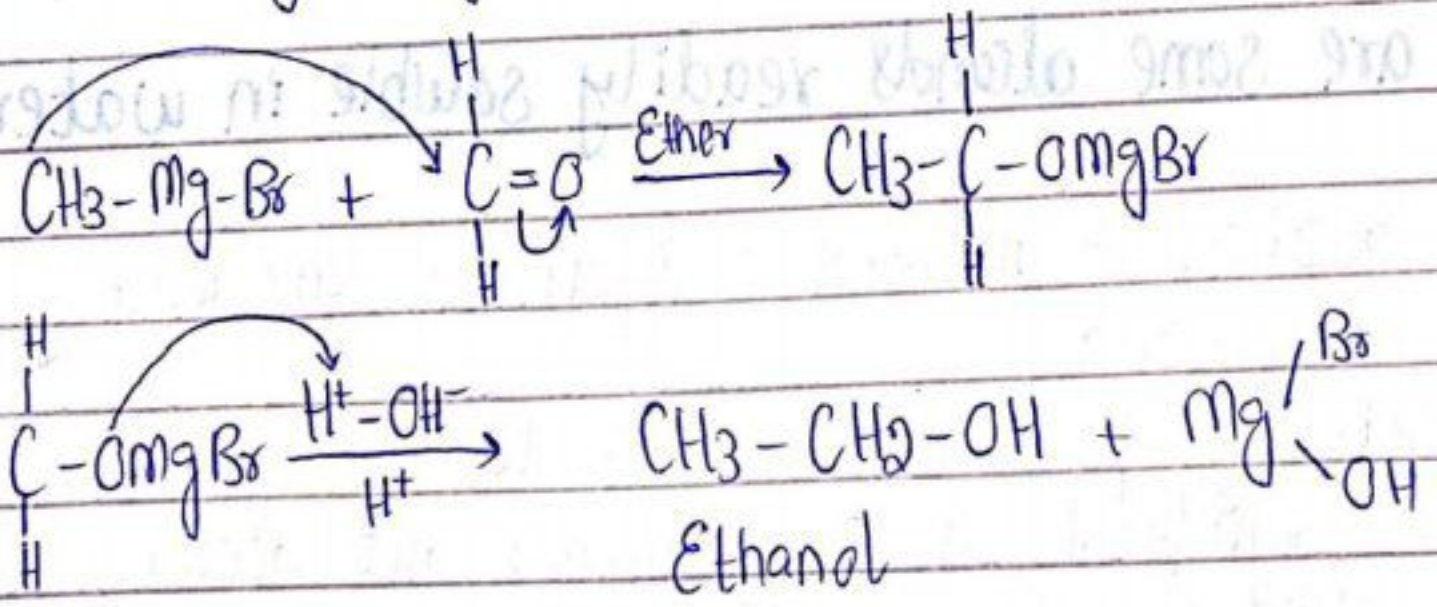
3°-Alcohols :-



3°-alcohol

iv) How Grignard's reagent is used for preparation of 1°-alcohols?

⇒ Formaldehyde give 1°-alcohol with Grignard's reagent



Quack Quaz ?

i) What is acidic order of carboxylic acid, phenol and ether?

Acidity Order

Carboxylic acid > phenol > Ether

ii) Why phenols are reactive towards electrophilic aromatic substitution?

⇒ Phenols are very reative towards electrophilic aromatic substitution.

⇒ The OH group is an ortho-para director therefore it produces ortho-para products.

⇒ The OH group is an activator and it denotes electrons to benzene ring (as ortho-para directing groups are electron donor). Thus it activates the ring.

→ Hence, mild conditions are needed for phenol than that of benzene.

iii) Alcohols & phenols both contain -OH group. What is difference blw them.

Alcohols :-

⇒ The general formula of alcohol is R-OH.

⇒ Alcohols are hydroxyl derivatives of alkanes.

⇒ lower alcohols are generally colourless liquids.

⇒ Alcohols have characteristic sweet smell and burning taste.

Phenols :-

⇒ Phenols are derivates of alcohols.

⇒ It's melting point is 41°C

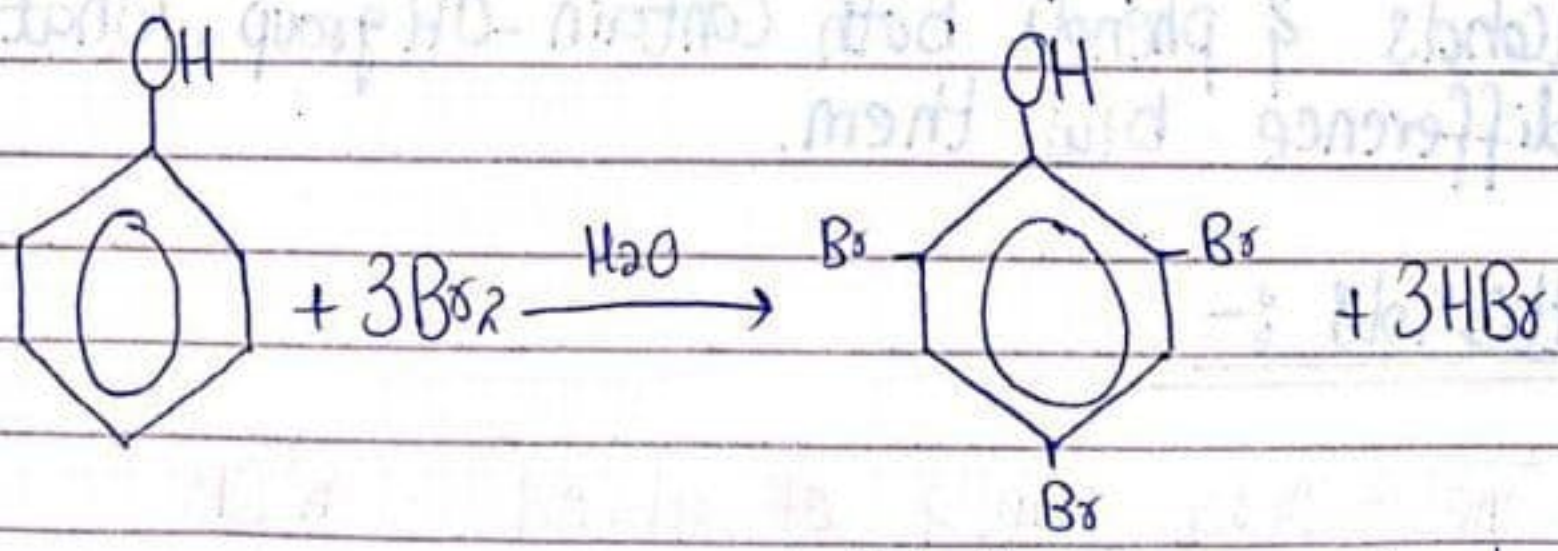
⇒ They have a characteristic phenolic odor.

⇒ They are colourless, crystalline, deliquescent solids.

iv) What happen when phenol is treated with bromine water?

⇒ Aqueous solution of phenol react with bromine water to give white precipitates of 2,4,6-tribromophenol.

⇒ The red color of bromine water is discharged. This test is used for identification of phenol.



2,4,6-tribromo phenol

Quick Quiz 3

i) How is diethyl ether prepared in laboratory?

Conversion of alcohols to ethers:-

$CH_3-CH_2-OH + Na \longrightarrow CH_3-CH_2-ONa + 1/2 H_2$

$CH_3-CH_2-ONa + Cl-CH_2-CH_3 \longrightarrow CH_3-CH_2-O-CH_2-CH_3 + NaCl$

ii) What are symmetrical and unsymmetrical ethers?

Symmetrical Ethers:- Ethers which contain same alkyl groups on both sides of oxygen atom are called symmetrical ethers.

Examples:-

CH_3-O-CH_3 Dimethyl ether

$C_2H_5-O-C_2H_5$ Diethyl ether

Unsymmetrical Ethers:- Ethers which contain different alkyl groups on both sides of oxygen atom are called unsymmetrical ethers.

Examples:-

$CH_3-O-C_2H_5$ Methy Ethyl ether

$CH_3-O-C_3H_7$ Methyl Propyl Ether

iii) What is Williamson's synthesis?

→ This test gives both symmetorcal and unsymmetrical ether

→ $R-OH + Na \longrightarrow R-ONa + 1/2\ H_2$

$R-ONa + X-R \longrightarrow R-O-R + NaX$

→ $CH_3-OH + Na \longrightarrow CH_3-ONa + 1/2\ H_2$

$CH_3-ONa + Cl-CH_3 \longrightarrow CH_3-O-CH_3 + NaCl$