Ethers

R-O-R

Ethereal oxygen

Darshan Kumar Assoc. Prof. GC Amb

Classification of Ethers

Symmetrical Ethers

$CH_3—O—CH_3$

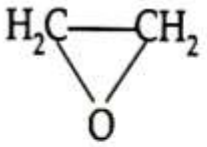
Dimethyl ether

Unsymmetrical Ethers

$CH_3—O—C_2H_5$

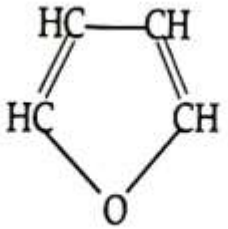
Ethyl methyl ether

Cyclic ethers

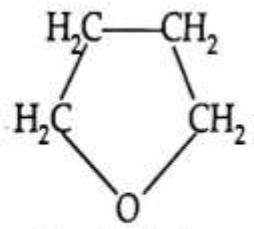


Epoxide

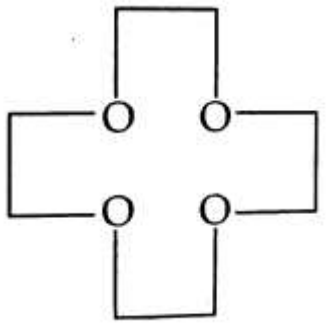
Ethylene oxide



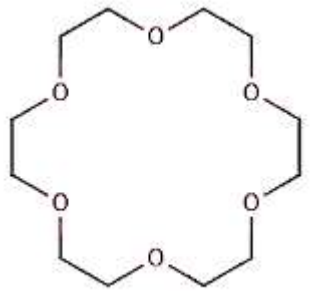
Furan



Tetrahydrofuran



12-Crown-4

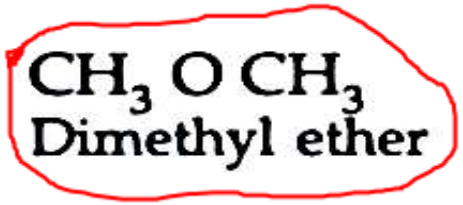


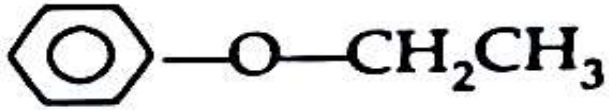
18-Crown-6

Crown Ethers

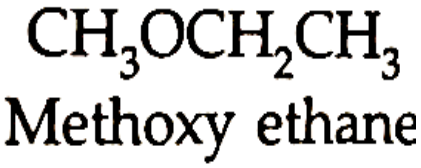
Nomenclature of Ethers

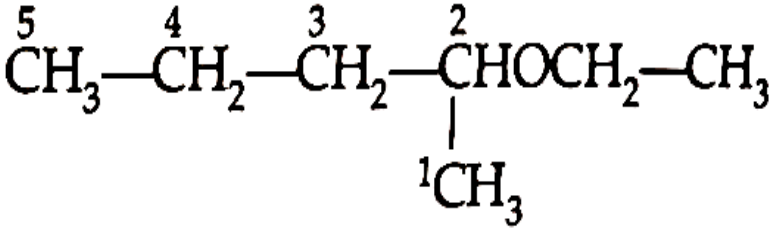
➢ Common System

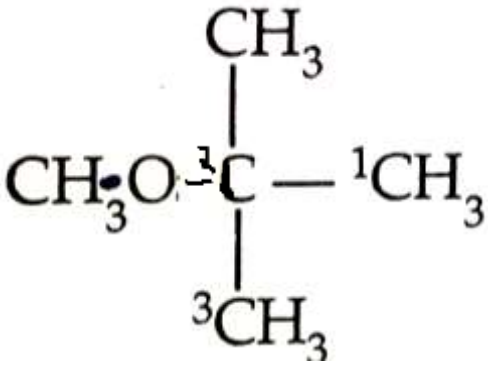


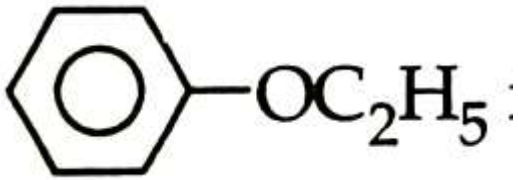


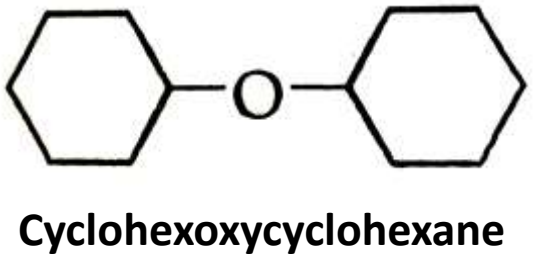
➢ IUPAC System

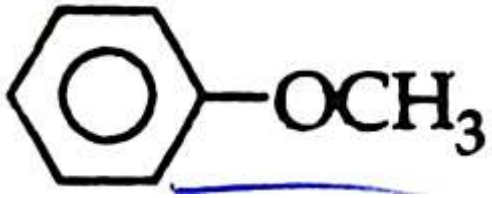








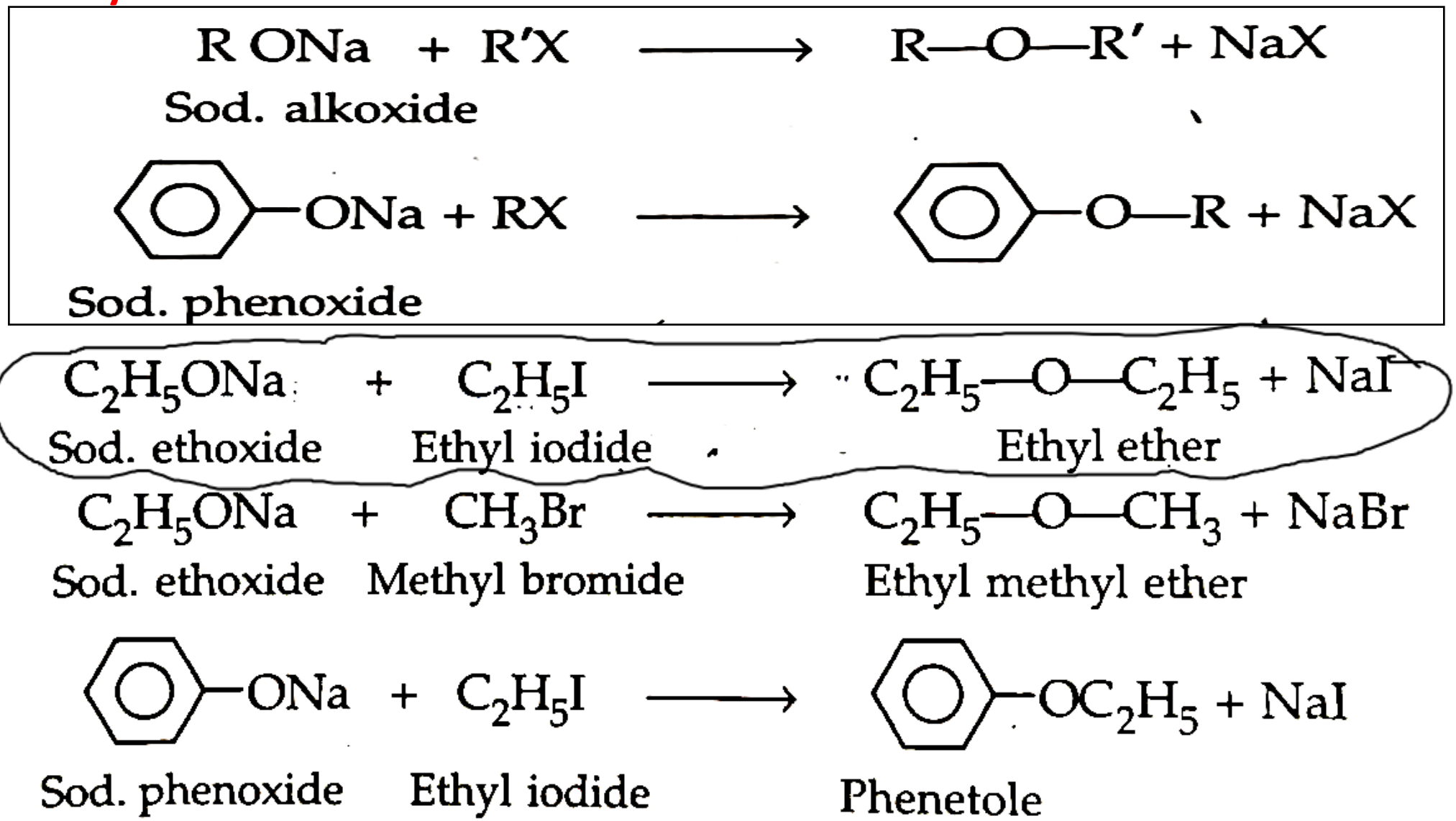




$CH_3CH_2O\text{-}CH=CH_2$
Ethyl vinyl ether
Ethoxyethene

Methods of preparation of Ethers

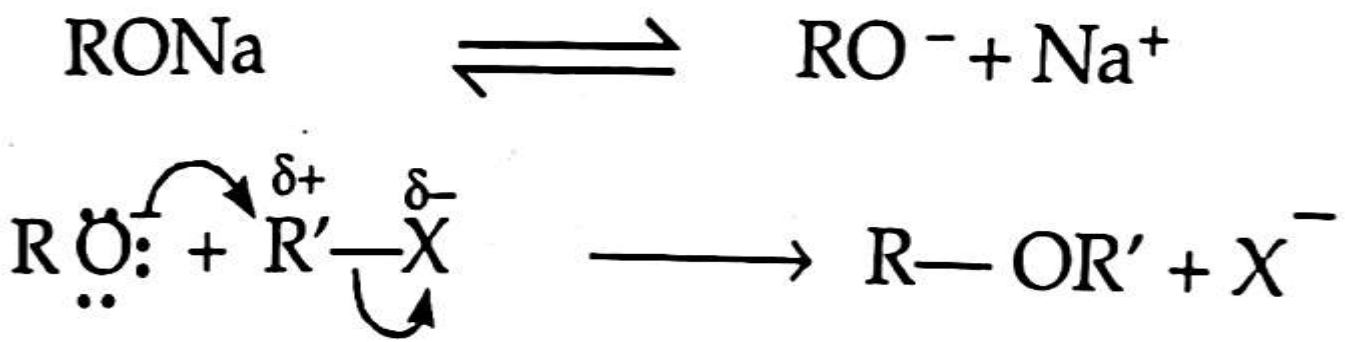
- **Williamson's Synthesis**



Methods of preparation of Ethers

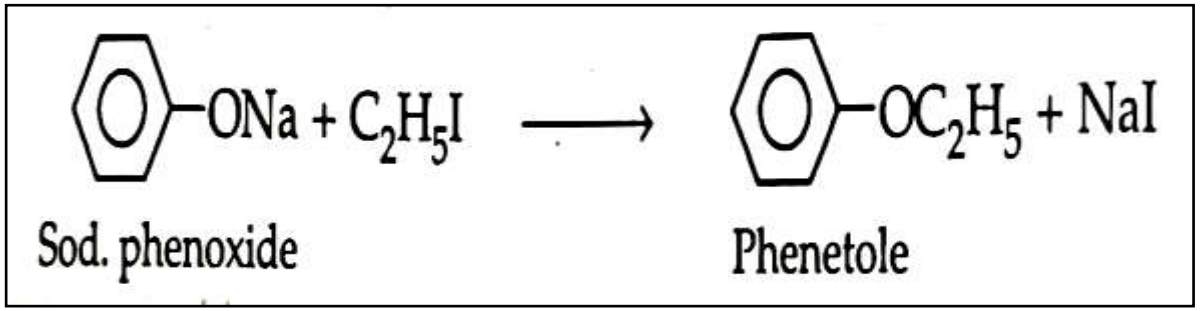
❑ Mechanism of Williamson's Synthesis

➢ Involves nucleophilic substitution of halide ion by the alkoxide ion



❑ Limitations

1. We can not take aryl halides for the synthesis of alkyl phenyl ethers since aryl halides are less reactive. Diaryl ethers can not be prepared by this method

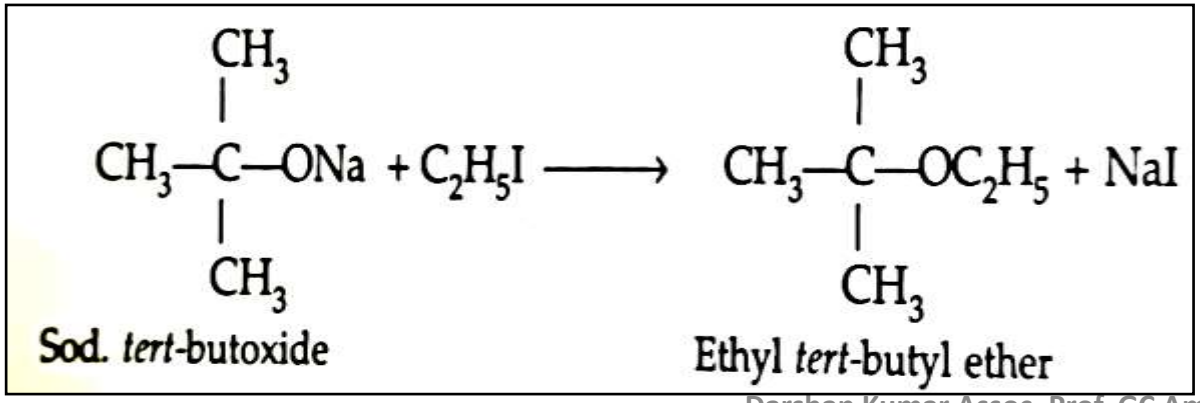


2. Due to the attack of strongly basic alkoxide ion, elimination of alkyl halide can also take place, particularly in the case of tertiary alkyl halides

Order of preference

➢ Pr. Alkyl halide > Sec. Alkyl halide > Tert. Alkyl halide

➢ Tert. Alkoxides > Sec. alkoxides > Pr. Alkoxides



Physical properties of Ethers

❑ Boiling points

➢ Have much lower boiling points than alcohols of comparable molecular masses ?

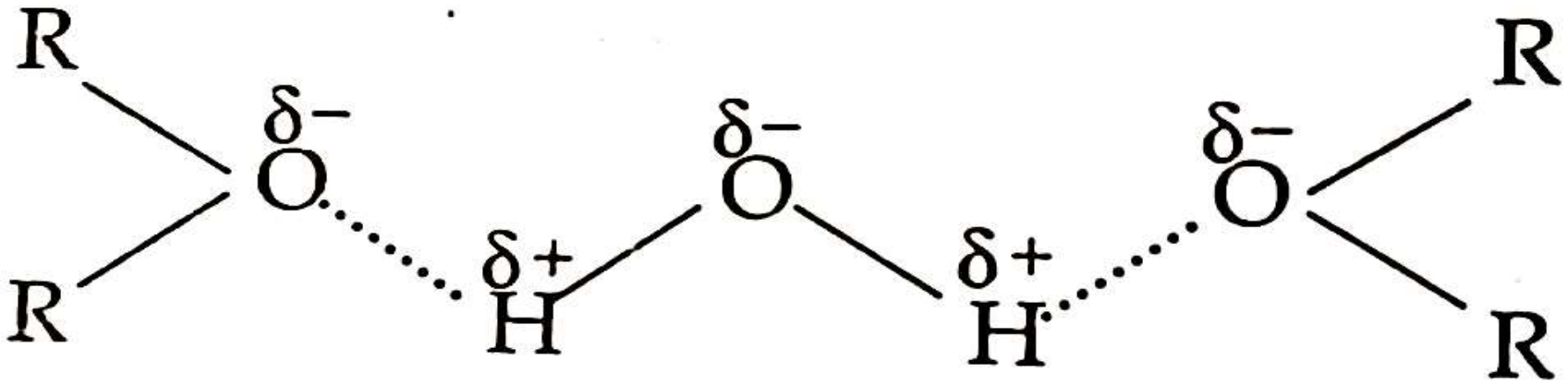
✓ It is due to absence of intermolecular hydrogen bonding

➢ Have higher boiling points than alkanes of comparable molecular masses ?

✓ Due to their polar nature

❑ Solubility

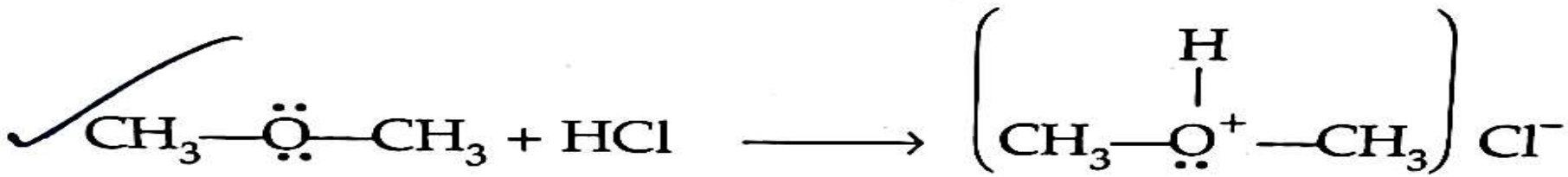
➢ Lower ethers dissolve in water due to formation of hydrogen bonding with water molecules.



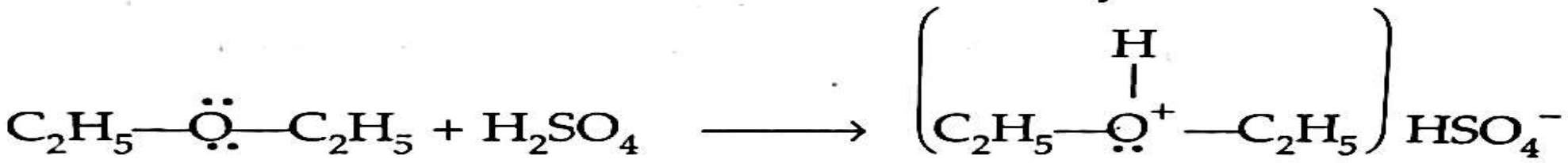
Chemical properties of Ethers

❑ Basic character (Formation of oxonium salts)

- Lone pair on oxygen can be donated to proton



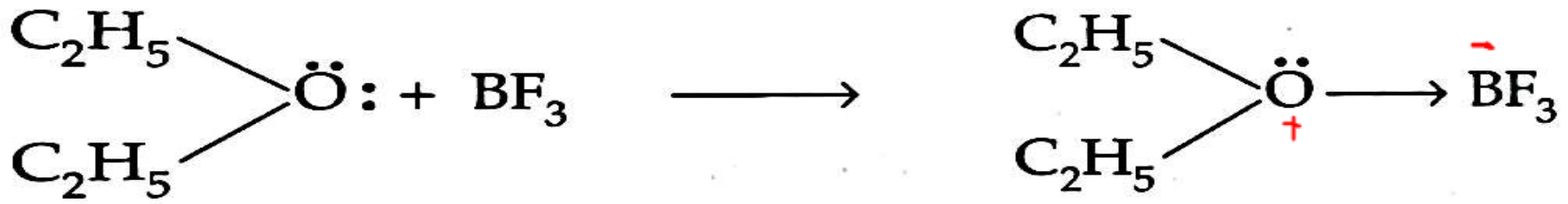
Dimethyl oxonium chloride



Diethyl oxonium hydrogen sulphate

❑ Formation of coordinate complexes

- Due to donation of lone pair of electrons on oxygen atom (Lewis base character)

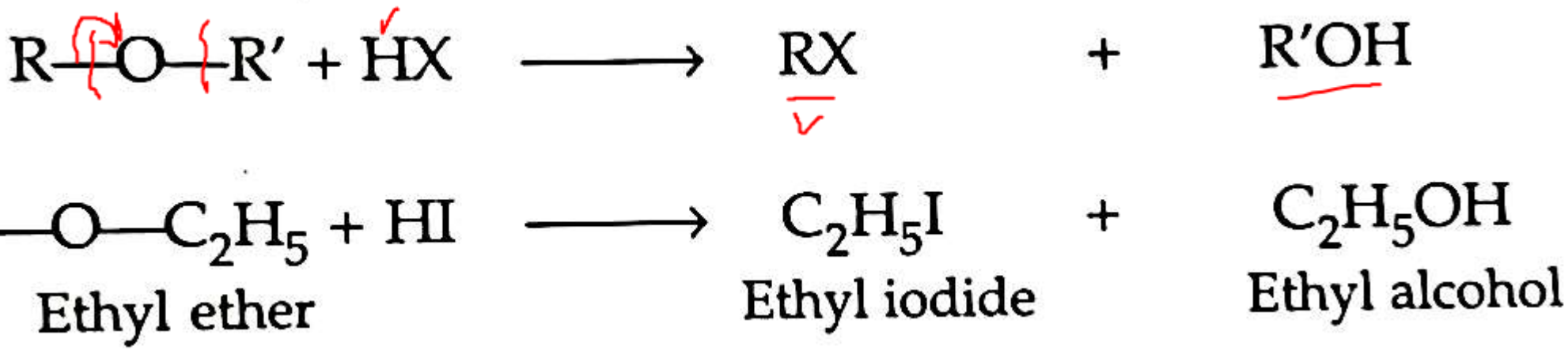


Boron trifluoride etherate

Chemical properties of Ethers

❑ Cleavage by halogen acids

- ➢ On heating with equimolar amount of halogen acids, ethers cleave to give alkyl halide and alcohol

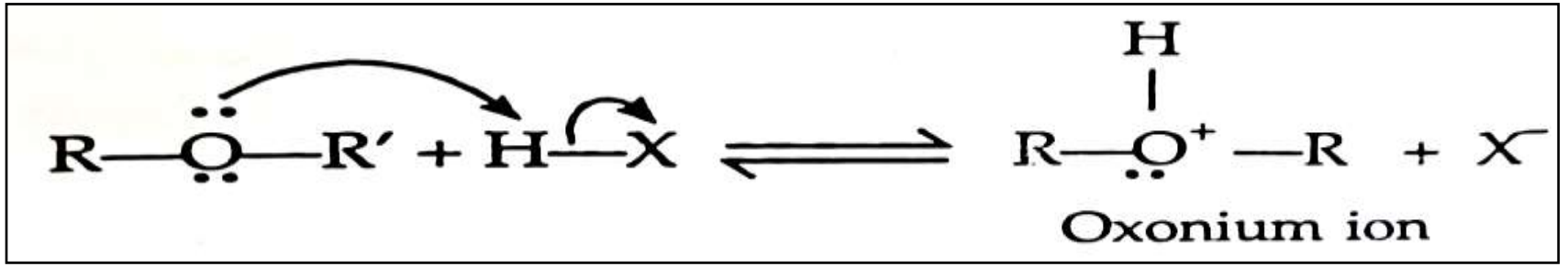


- ➢ In the presence of excess of an acid

Chemical properties of Ethers

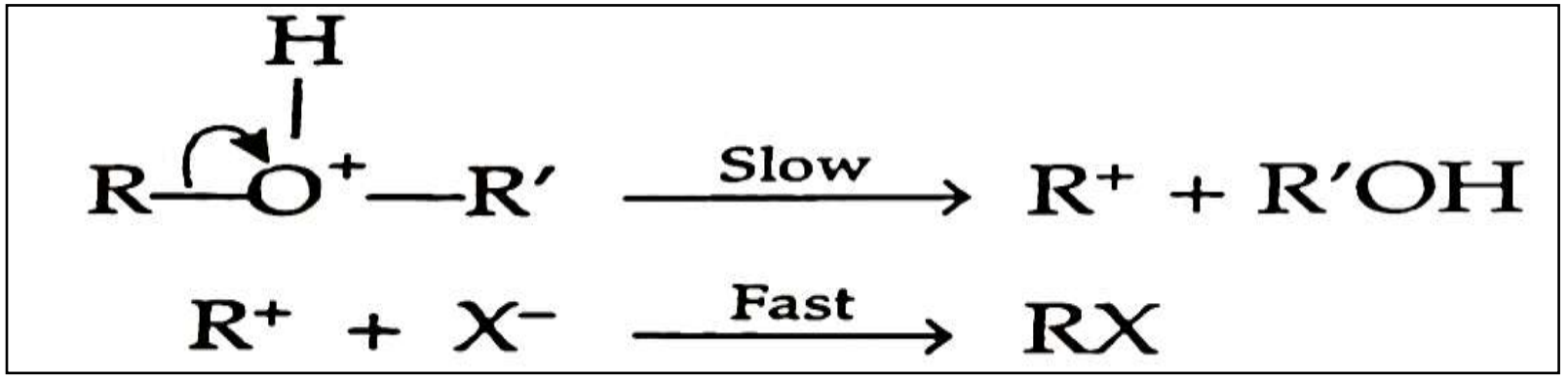
❑ Mechanism of Cleavage by halogen acids

➢ Formation of oxonium ion

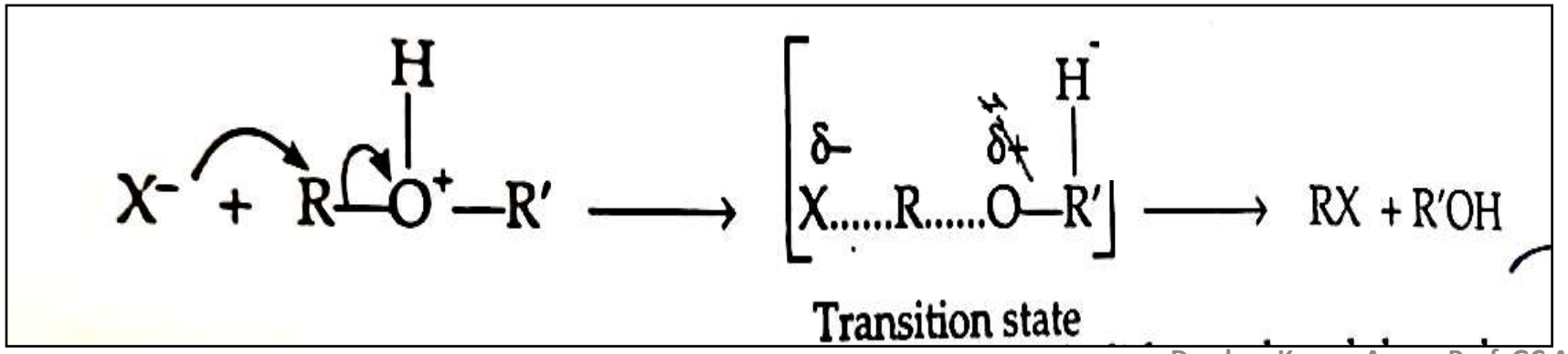


➢ Attack of halide ion by SN_1 manner

OR



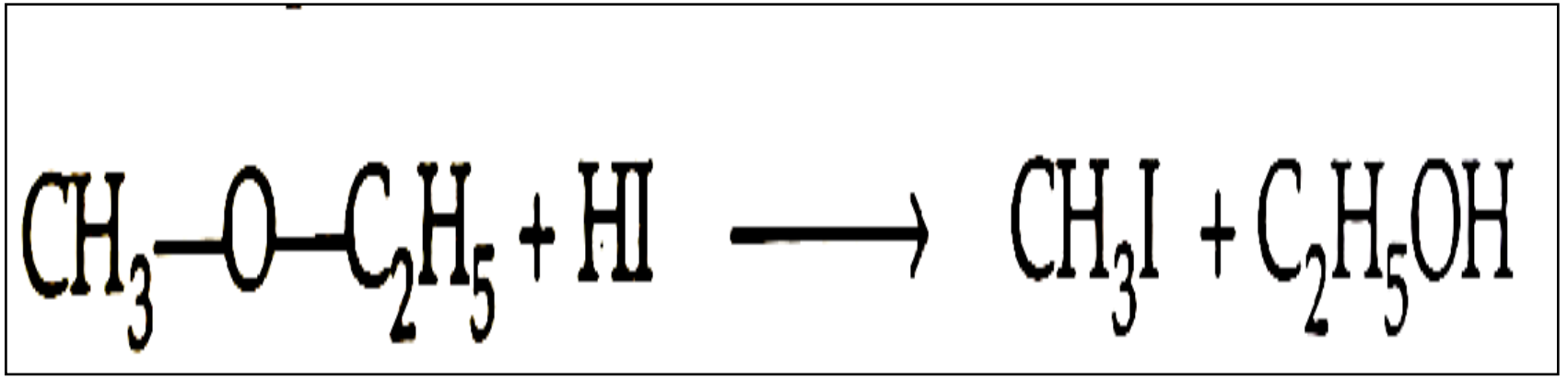
➢ Attack of halide ion by SN_2 manner



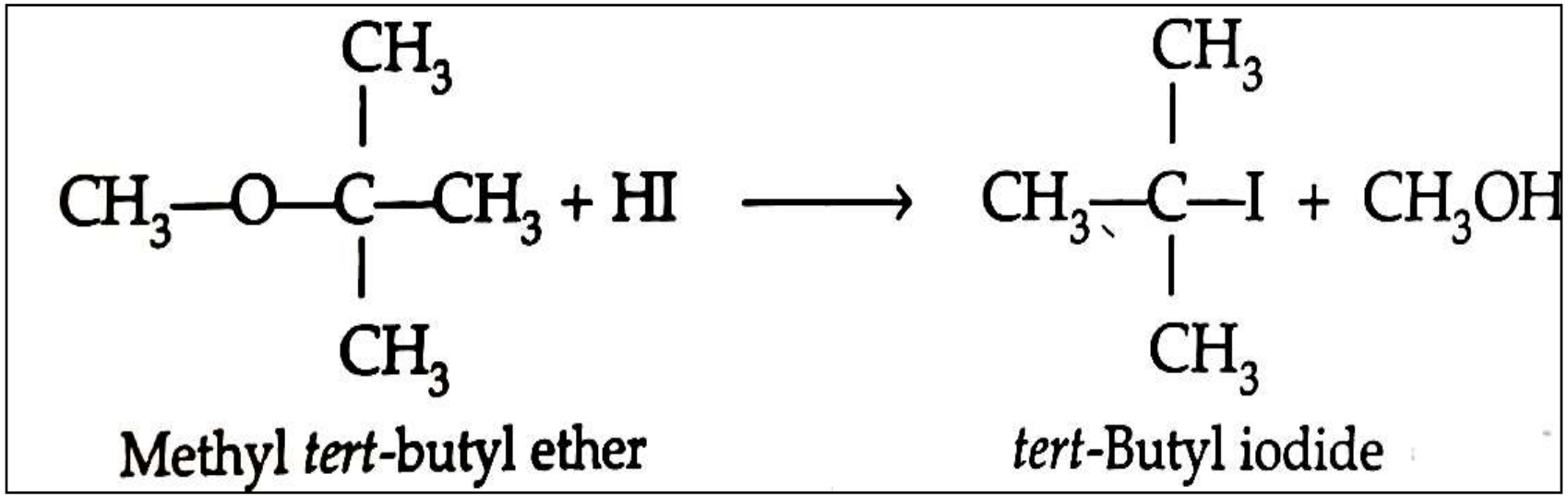
Chemical properties of Ethers

❑ Point of cleavage

- In case of mixed ethers, alkyl halide is formed from smaller alkyl group



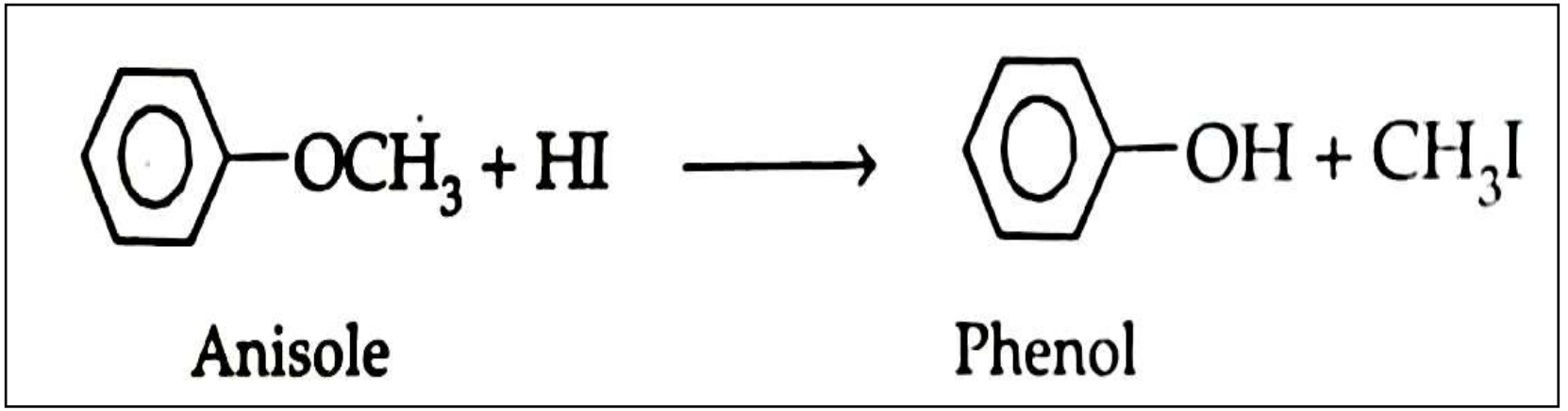
- If ether contains tertiary alkyl group, then tert. Alkyl halide is formed



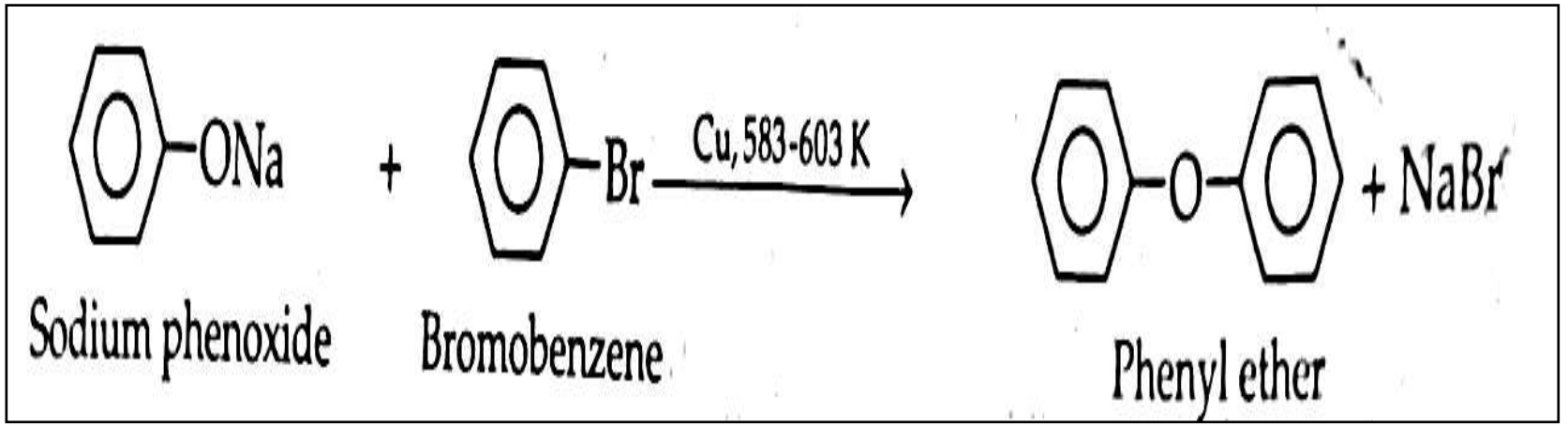
Chemical properties of Ethers

❑Point of cleavage contd.....

- In the case of alkyl aryl ethers, Phenol is formed rather than alcohol



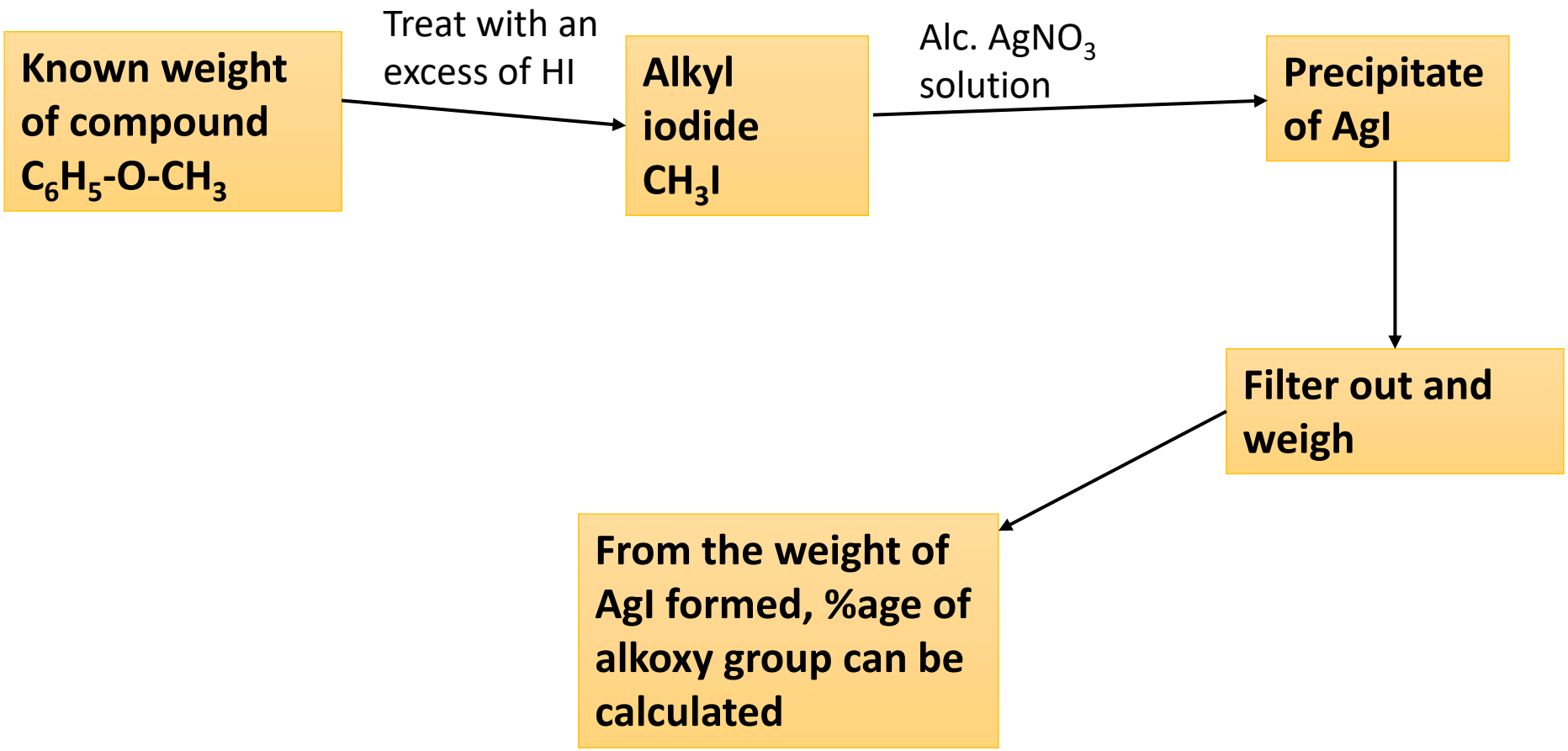
- Diaryl ethers are difficult to cleave



Chemical properties of Ethers

❑ Ziesel Method for estimation of alkoxy groups

➢ **Based upon cleavage of alkyl aryl ethers by with hydroiodic acid**



Questions

I. What is the point of cleavage on cleavage of methyl propyl ether by HCl? Give mechanism.

II. Arrange the following in increasing order of their boiling points giving reasons:

1. Dimethyl ether 2. Propane 3. Ethyl alcohol

iii. What happens when

1. Methyl tert. Butyl ether is reacted with Hydroiodic acid
2. Phenetole is treated with HI