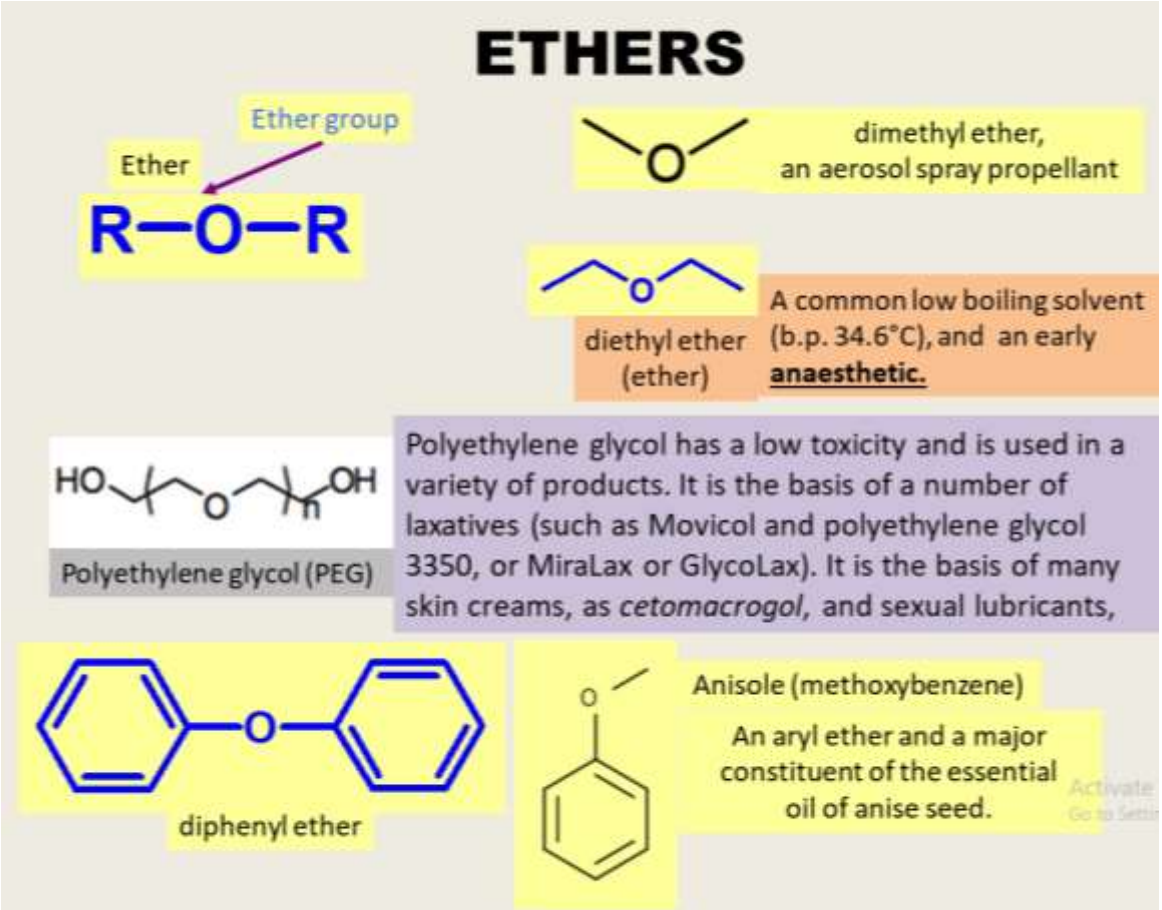
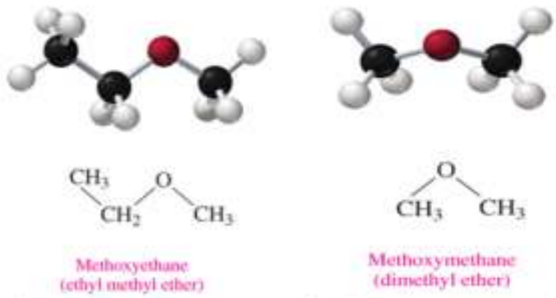


1-Introduction of Ethers (R-O-R)

- Ethers are organic compounds that contain the –OR (alkoxy) functional group attached to the hydrocarbon skeleton.



- -OH group in alcohols is replaced by –OR (alkyl or aryl group instead of hydrogen)
- In other words, *ethers are compounds in which two alkyl (or aryl) groups are linked by a bridging oxygen*

2-Nomenclature for ethers

A//common names:

✓ The ethers are named according to ***the alkyl group bonded to the oxygen atoms***.

✓The two-alkyl groups bonded to the functional group (-O-) are written alphabetically followed by the word ether.

- **Unsymmetrical:** (Alkyl alkyl ether). CH_3 - O - C_2H_5 Ethyl methyl ether

- **Symmetrical:** (Dialkyl ether). CH_3 - O - CH_3 Dimethyl ether

Examples:

Diethyl ether

Ethyl isopropyl ether

CH_3–O—CH_2–CH_2–CH_3

Methyl propyl ether

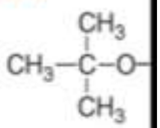
B// IUPAC system:

1. Write the alkane name of the longer carbon chain.
2. Name the oxygen and smaller alkyl group as an alkoxy group.

Common alkoxy groups

CH_3O– methoxy

CH_3CH_2O– ethoxy



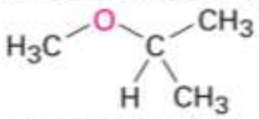
tert-butoxy

3. Number the longer carbon chain from the end nearer the alkoxy group and give its location.

Methoxy propane

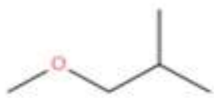
CH_3—O—CH_2—CH_2—CH_3 (1, 2, 3)

- Numbering the longer alkane gives **1-Methoxy**propane.

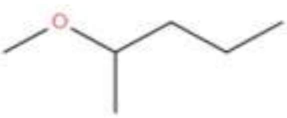


Isopropyl methyl ether

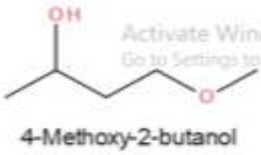
1-Ethoxybutane



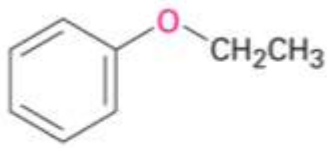
1-Methoxy-2-methylpropane



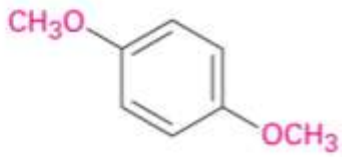
2-methoxypentane



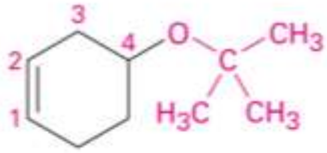
4-Methoxy-2-butanol



Ethyl phenyl ether



p-Dimethoxybenzene



4-*tert*-Butoxy-1-cyclohexene

C//Naming Cyclic Ethers

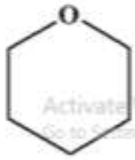
1. Can Use Replacement Nomenclature (oxa → O replaces CH_2) is called a *heterocyclic* compound.
2. Typically has 5 (furan) or 6 atoms (pyran) in the ring

Oxacyclopropane (oxirane, ethylene oxide)

Oxacyclobutane (oxetane)

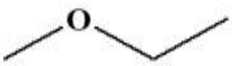
Oxacyclopentane (tetrahydrofuran)

1,4-Dioxacyclohexane (1,4-dioxane)



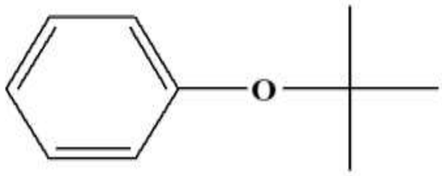
Oxacyclohexane (tetrahydropyran)

Ethers: General Nomenclature

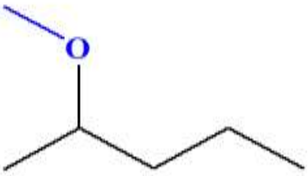


ethyl methyl ether

diethyl ether



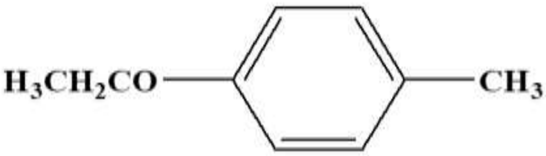
tert-Butyl phenyl ether



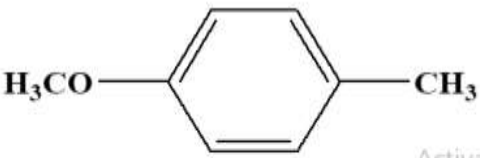
2-Methoxypentane

Dimethoxymethane

1,2Dimethoxyethane



1-Ethoxy-4-methylbenzene



1-methoxy-4-methylbenzene (*para*-Methylanisole)

3-Physical Properties of Ethers

1) Ethers are relatively polar molecules (due to the electronegativity difference of the atoms) results in intermolecular dipole-dipole interactions, but not as polar as alcohols.

2) Unlike alcohols, they can't make hydrogen bonds with itself, why?– so **lower mp and bp** compared to alcohols.

Boiling Points Reflect Intermolecular Attractive Forces

Example - Alcohol derivatives (of similar molecular weight)

Mol. weight	74.12	74.12	96.1
Name	Diethyl ether	*n*-butanol	Sodium *n*-butoxide
Strongest intermolecular force	DIPOLE-DIPOLE	HYDROGEN BONDING	IONIC
Boiling point	35 °C	117 °C	> 260 °C

3) They can make hydrogen bonds with water – more soluble than alkanes but less than alcohols.

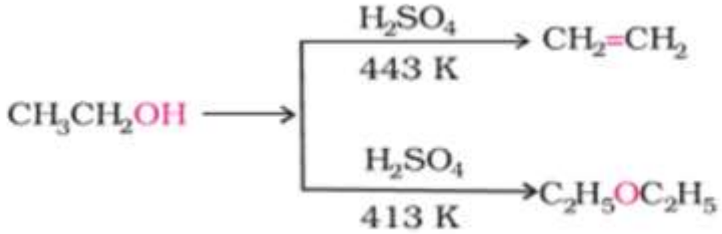
4-Preparation of Ethers:

1-Ethers are moderately inert (not very reactive).

2-Extremely volatile and flammable. (easily oxidized in the air).

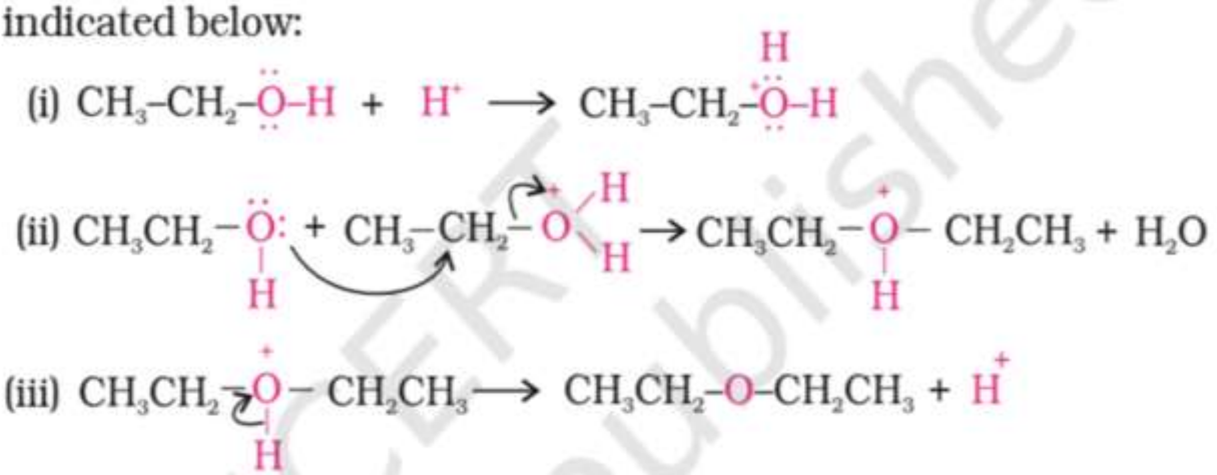
4.1- By a dehydration reaction:

- **Alcohols** undergo dehydration in the presence of protic acids (H_2SO_4, H_3PO_4). The formation of the reaction product, **alkene or ether** depends on the reaction conditions. For example, at 443 K, ethanol is dehydrated to ethene in the presence of sulphuric acid. At 413 K, ethoxyethane is the main product.



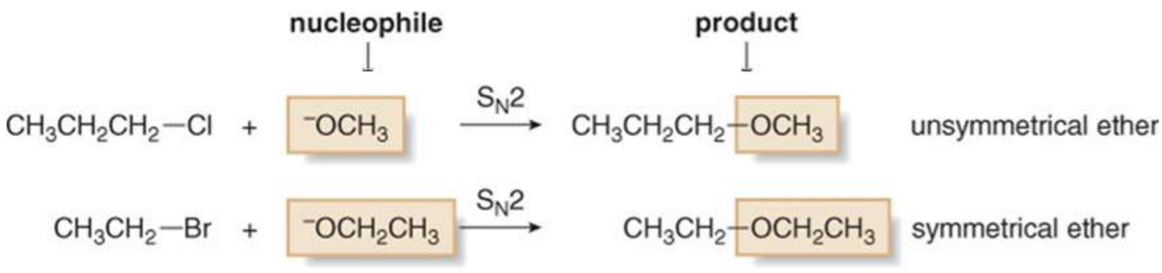
Mechanism:

The formation of ether is a nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on a protonated alcohol, as indicated below:

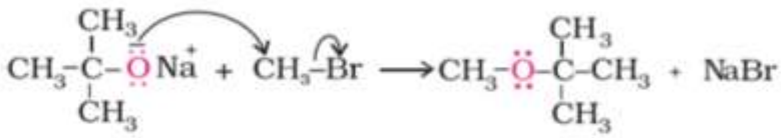


4.2- **Williamson ether synthesis** (nucleophilic substitution).

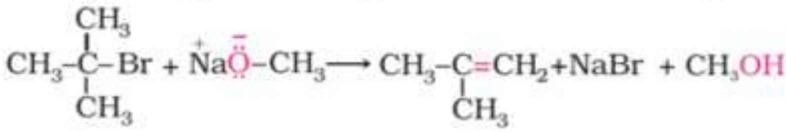
- It is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide.



- Ethers containing substituted alkyl groups (secondary or tertiary) may also be prepared by this method. The reaction involves S_N2 attack of an alkoxide ion on **primary alkyl halide**

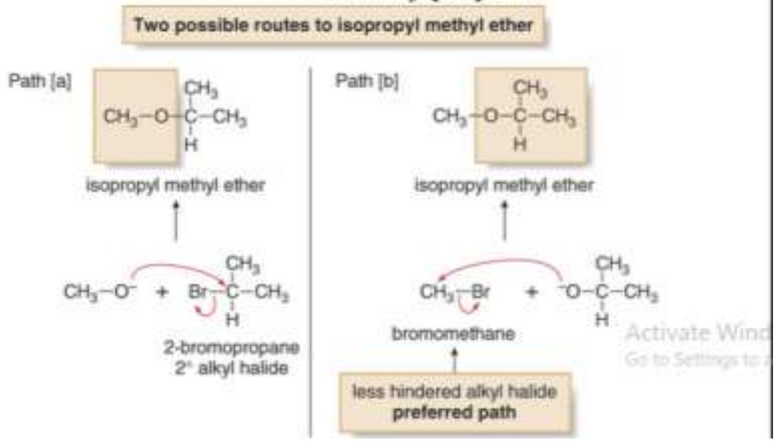


Better results are obtained if the alkyl halide is primary. In case of secondary and tertiary alkyl halides, elimination competes over substitution.

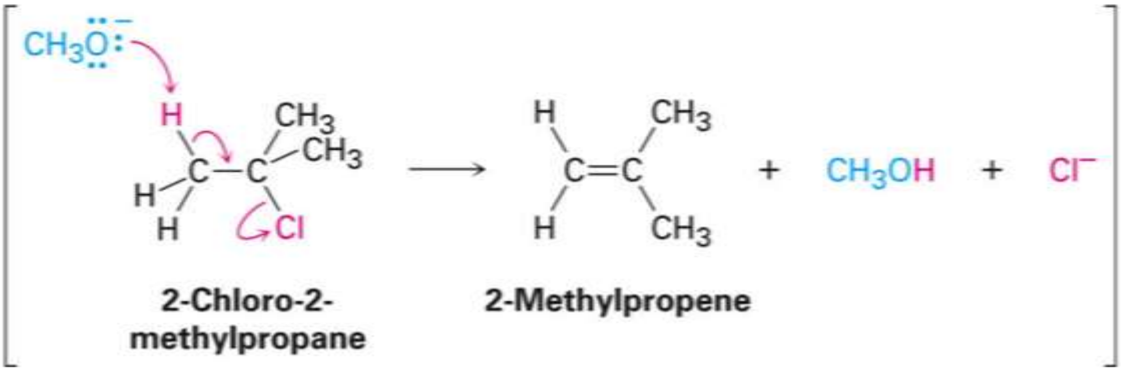


2-Methylpropene

Unsymmetrical ethers can be synthesized in two different ways, but often one path is preferred.

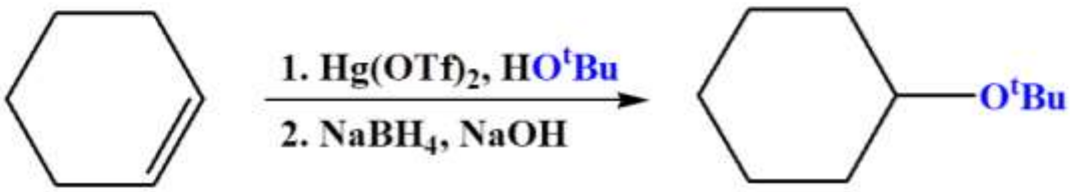


- Competitive E2 elimination can occur with more hindered substrates.



4.3-Alkoxymercuration-Demercuration

This Reaction is Analogous to Oxymercuration-Demercuration



- Using **New Hg Salt** Here (Triflate) → **Can Use $Hg(OAc)_2$** Also

Instead of H_2O in First Step, **We Use an Alcohol**

- Carbocation is Captured by **Alcohol Molecule.** After Loss of

Proton, Alkoxide is Added Instead of Alcohol

5-Reactions of Ethers by Strong Acids

- Ethers are the least reactive of the functional groups. The cleavage of C-O bond in ethers takes place under drastic conditions with excess of **hydrogen halides**. The reaction of dialkyl ether gives two alkyl halide molecules.

$$R{-}O{-}R + HX \longrightarrow RX + R{-}OH$$

$$R{-}OH + HX \longrightarrow R{-}X + H_2O$$

- Ethers with two different alkyl groups are also cleaved in the same manner.

$$R{-}O{-}R' + HX \longrightarrow R{-}X + R'{-}OH$$

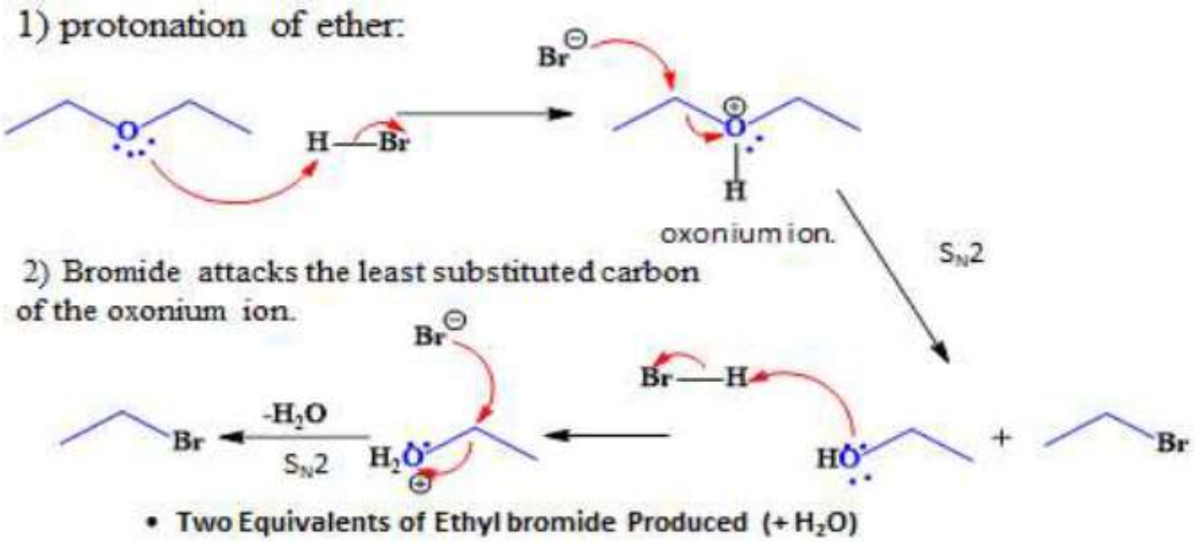
- The order of reactivity of **hydrogen halides** is as follows:

HI > HBr > HCl. The cleavage of ethers takes place with concentrated HI or HBr at **high temperature**.

Ether Cleavage by HBr: Mechanism

$$CH_3CH_2OCH_2CH_3 + 2\,HBr \xrightarrow{Heat} 2\,CH_3CH_2Br + H_2O$$

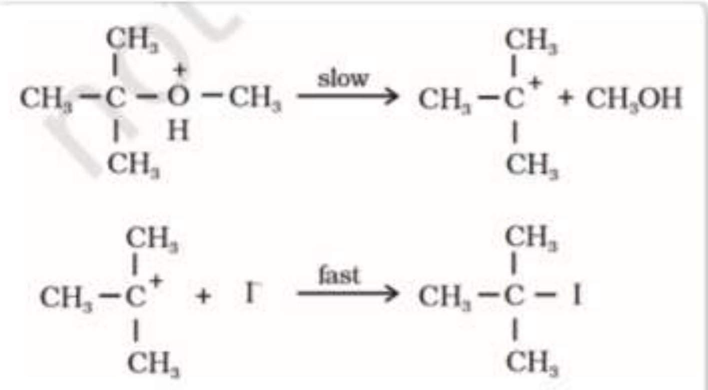
Diethyl ether — *Excess Hydrogen bromide* — *Ethyl bromide*



- However, when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide.

$$(CH_3)_3C-O-CH_3 + HI \longrightarrow CH_3OH + (CH_3)_3C-I$$

It is because in step 2 of the reaction, the departure of leaving group (HO–CH3) creates a more stable carbocation [(CH3)3C+], and the reaction follows S_N1 mechanism.



In case of anisole, methylphenyl oxonium ion, $C_6H_5-\overset{+}{O}H-CH_3$ is S_N1 Or S_N2 mechanism?????