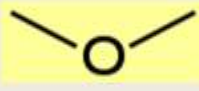


ETHERS

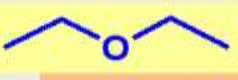
Ether group

Ether

R-O-R

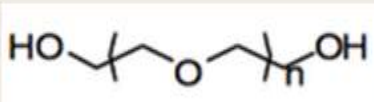


dimethyl ether,
an aerosol spray propellant



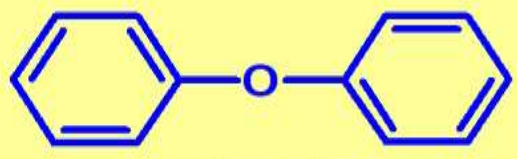
diethyl ether
(ether)

A common low boiling solvent
(b.p. 34.6°C), and an early
anaesthetic.

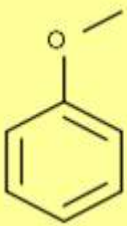


Polyethylene glycol (PEG)

Polyethylene glycol has a low toxicity and is used in a variety of products. It is the basis of a number of laxatives (such as Movicol and polyethylene glycol 3350, or MiraLax or GlycoLax). It is the basis of many skin creams, as *cetomacrogol*, and sexual lubricants,



diphenyl ether

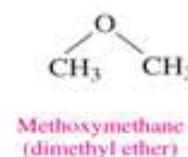


Anisole (methoxybenzene)
An aryl ether and a major constituent of the essential oil of anise seed.

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.

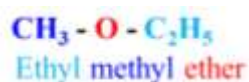


2-Nomenclature for ethers

All/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.

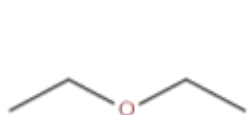
➤ **Unsymmetrical:** (Alkyl alkyl ether).



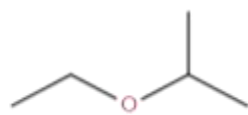
➤ **Symmetrical:** (Dialkyl ether).



Examples:



Diethyl ether



Ethyl isopropyl ether

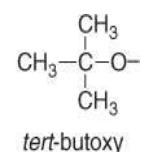
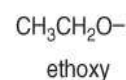


Methyl propyl ether

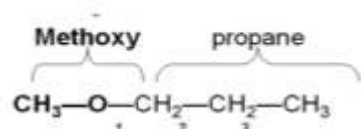
B// IUPAC system:

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

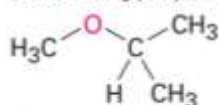
Common alkoxy groups



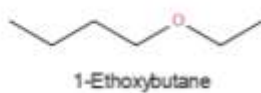
3. Number the longer carbon chain from the end nearer the alkoxy group and give its location.



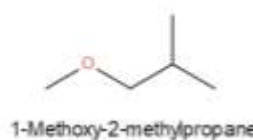
- Numbering the longer alkane gives **1-Methoxypropane**.



Isopropyl methyl ether



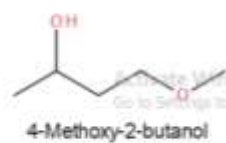
1-Ethoxybutane



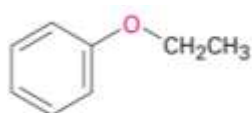
1-Methoxy-2-methylpropane



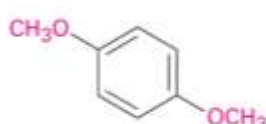
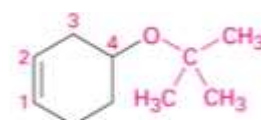
2-methoxypentane



4-Methoxy-2-butanol

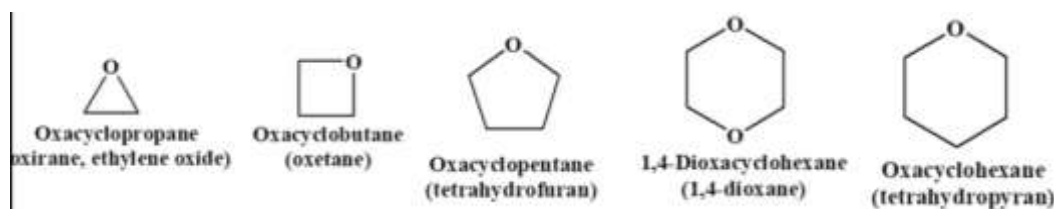


Ethyl phenyl ether

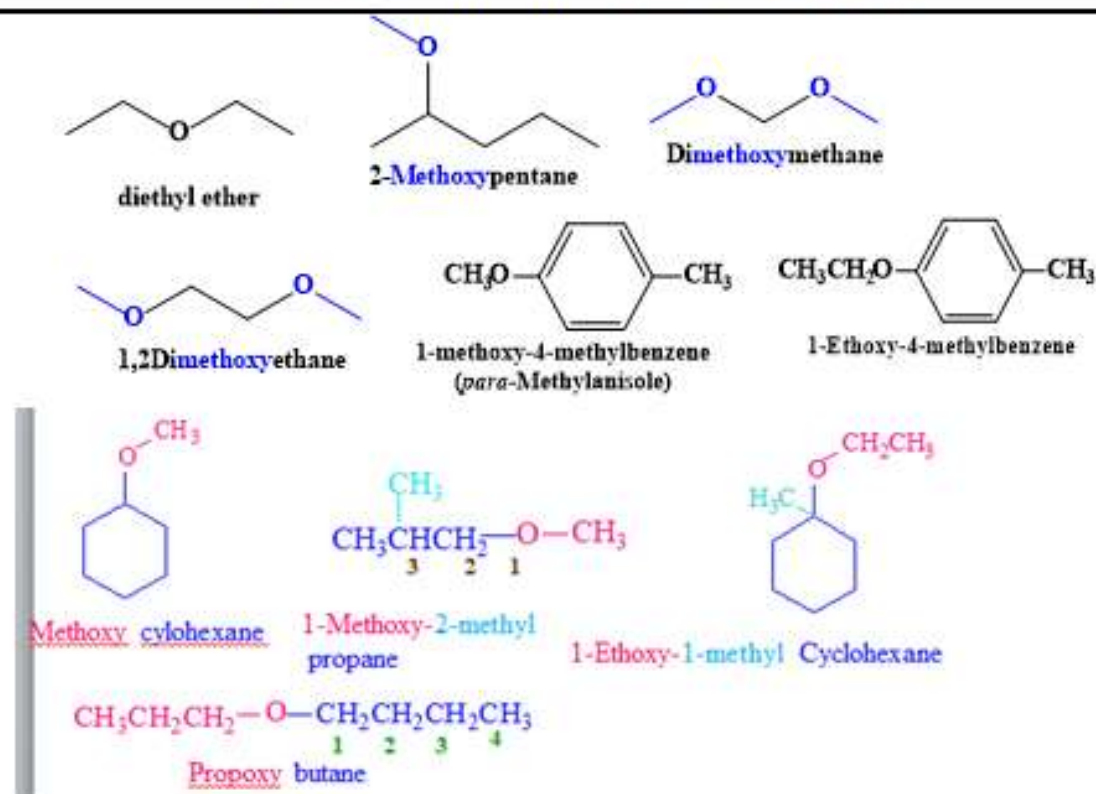
*p*-Dimethoxybenzene4-*tert*-Butoxy-1-cyclohexene
tert-Butyl phenyl ether

C//Naming Cyclic Ethers:

1. Can Use Replacement Nomenclature (oxa → O replaces CH₂) is called a *heterocyclic* compound.
2. Typically has 5 (furan) or 6 atoms (pyran) in the ring.



Ethers: General Nomenclature

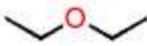
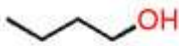



3-Physical Properties of Ethers:

- 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 | <i>n</i> -butanol | Sodium <i>n</i> -butoxide |
| Strongest intermolecular force | DIPOLE-DIPOLE | HYDROGEN BONDING | IONIC |
| Boiling point | 35 °C | 117 °C | > 260 °C |

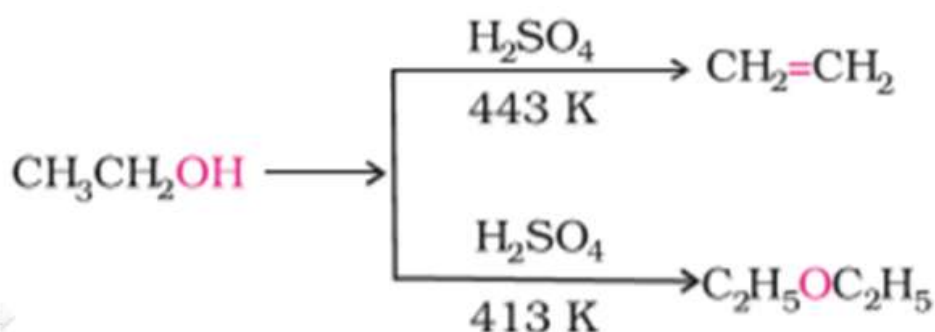
3) They can make hydrogen bonds with water – more soluble than alkanes but less than alcohols.

4-Preparation of Ethers:

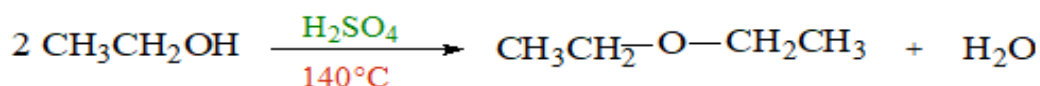
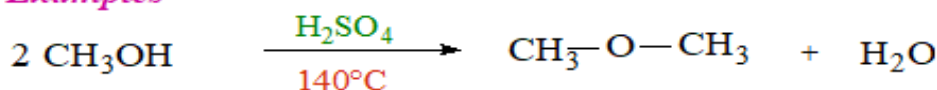
1- By a dehydration reaction:

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 (170 °C), ethanol is dehydrated to ethene in the presence of sulphuric acid. At 413 K (140 °C), ethoxyethane is the main product.

This method is used for *industrially* preparation for symmetric ethers

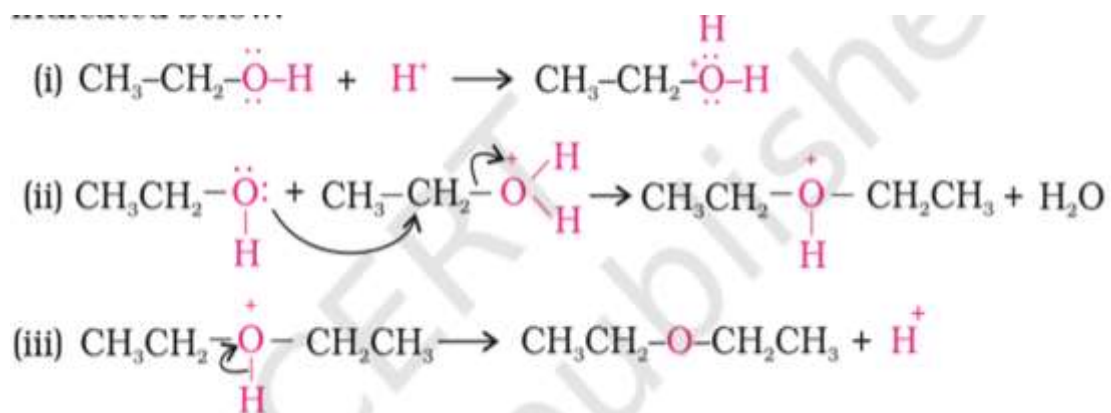


Examples

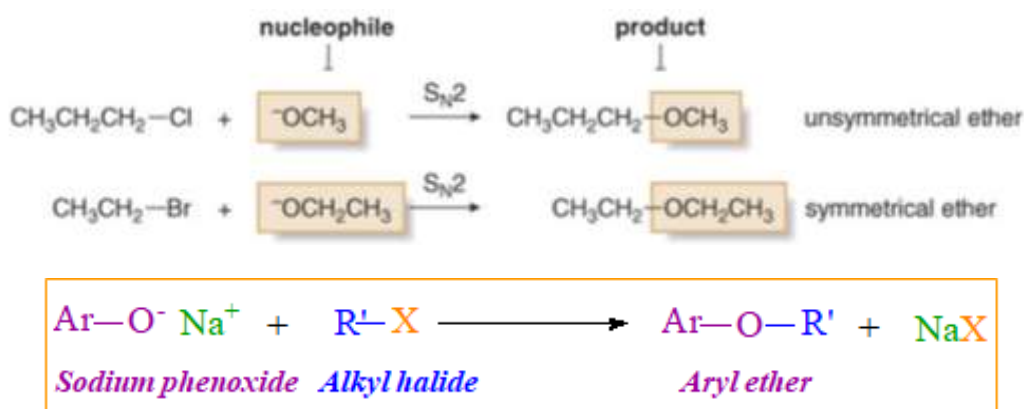


Mechanism:

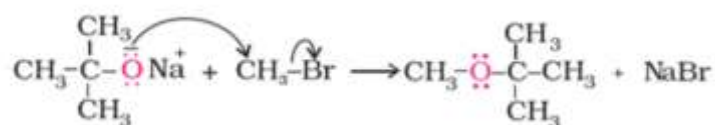
The formation of ether is a nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on a protonated alcohol, as indicated below:

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

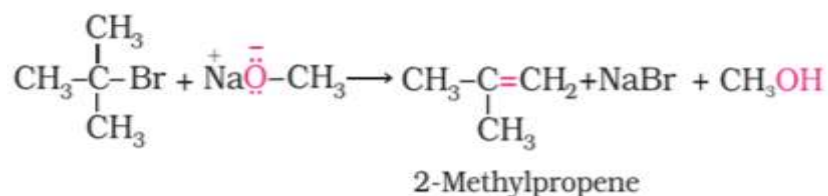
It is an important laboratory method for the preparation of **symmetrical and unsymmetrical ethers**. In this method, an alkyl halide is allowed to react with sodium alkoxide.



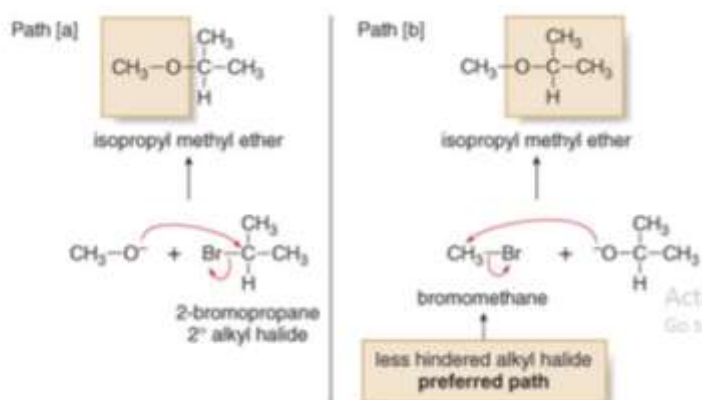
Ethers containing substituted alkyl groups (secondary or tertiary) may also be prepared by this method. The reaction involves S_N2 attack of an alkoxide ion on **primary alkyl halide**.



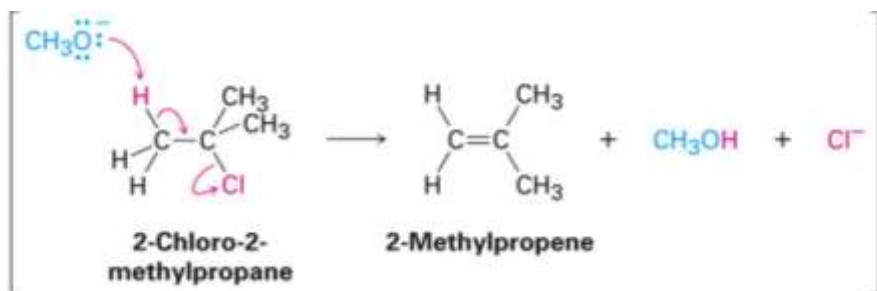
Better results are obtained if the **alkyl halide is primary**. In case of secondary and tertiary alkyl halides, elimination competes over substitution.



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

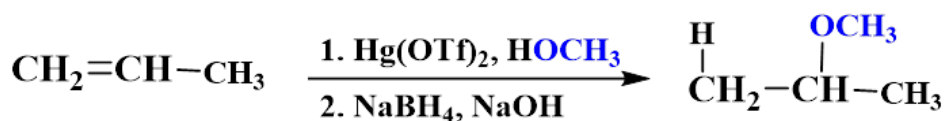


- Competitive E2 elimination can occur with more hindered substrates.



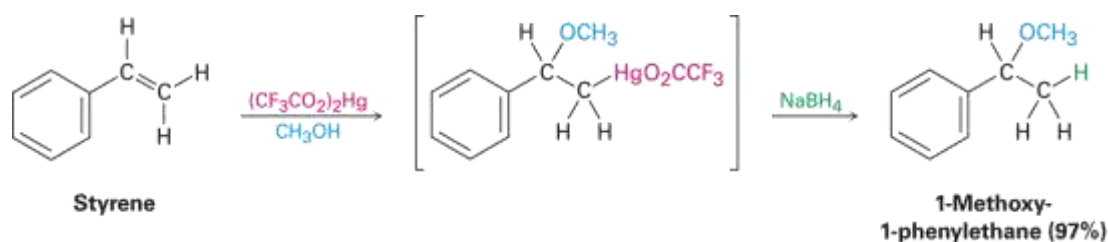
3-Alkoxymercuration-Demercuration:

This Reaction is Analogous to Oxymercuration-Demercuration



Using New Hg Salt Here (Triflate) \rightarrow Can Use $\text{Hg}(\text{OAc})_2$ 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.



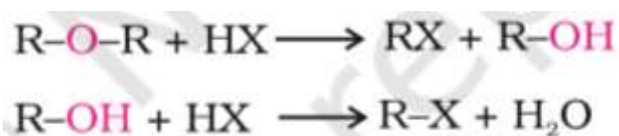
5-Reactions of Ethers:

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

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

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.



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



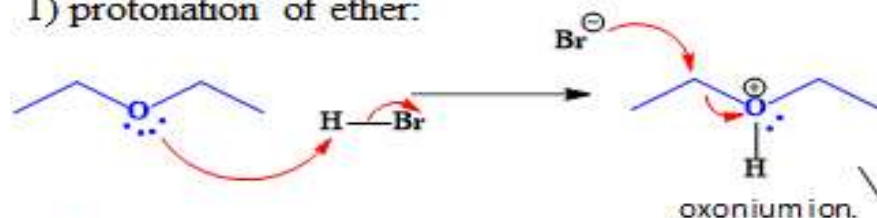
- The order of reactivity of **hydrogen halides** is as follows:

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

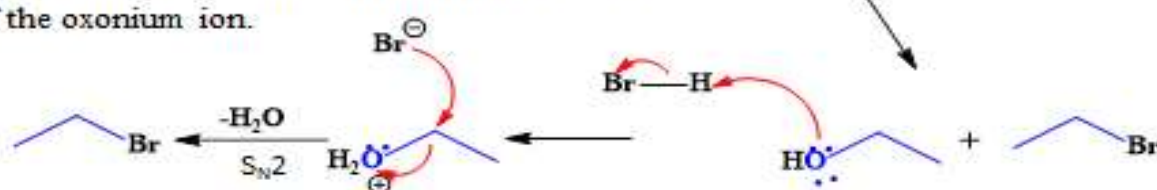
Ether Cleavage by HBr: Mechanism



1) protonation of ether:

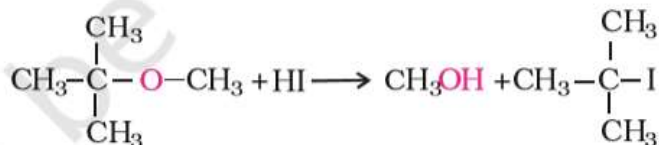


2) Bromide attacks the least substituted carbon of the oxonium ion.

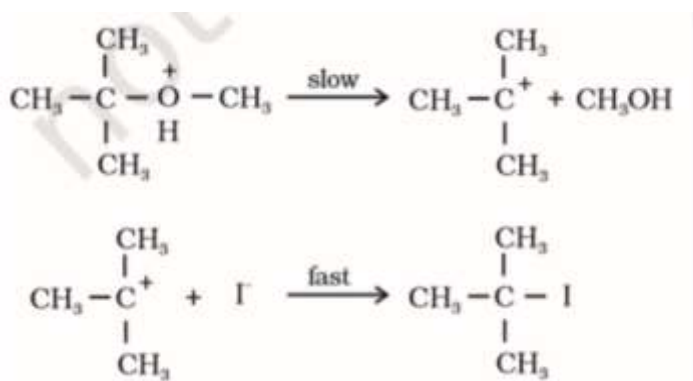


- Two Equivalents of Ethyl bromide Produced (+H₂O)

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

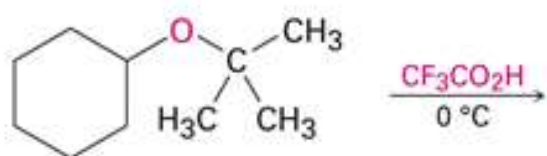
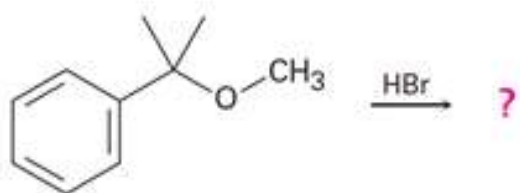


- It is because in step 2 of the reaction, the departure of leaving group (HO-CH₃) creates a more stable carbocation [(CH₃)₃C⁺], and the reaction follows S_N1 mechanism.



In case of anisole, methylphenyl oxonium ion, $\text{C}_6\text{H}_5-\overset{+}{\text{O}}-\text{CH}_3$ is S_N1 Or S_N2 mechanism?????

Q// Predict the product(s) of the following reaction:



tert-Butyl cyclohexyl ether