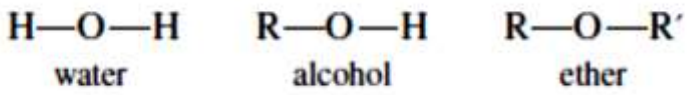
# Ethers

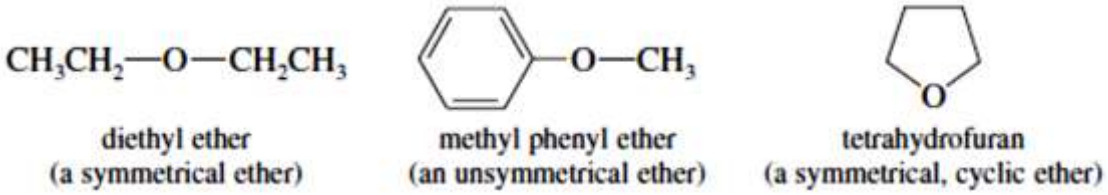
## *Introduction*

Are compounds of formula R-O-R' where R and R' may be alkyl groups or aryl (benzene ring) groups. Like alcohols, ethers are related to water, with alkyl groups replacing the hydrogen atoms. In an alcohol, one hydrogen atom of water is replaced by an alkyl group. In an ether, both hydrogens are replaced by alkyl groups.

The two alkyl groups are the same in a **symmetrical ether** and different in an **unsymmetrical ether.**




### *Examples of ethers*



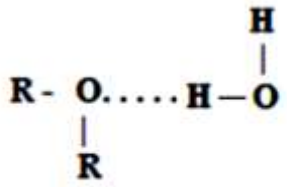

## *Physical Properties of Ethers*

Since the C-O-C bond angle is not 180°, the dipole moment of the two C-O bonds do not cancel each other; consequently, ethers possess a small net dipole moment.


This weak polarity does not appreciably affect the boiling point of the ethers, which are about the same as those of alkanes having comparable molecular weights, and much lower than those of isomeric alcohols. The hydrogen bonding that holds alcohol molecules strongly together is not possible for ethers, since they contain hydrogen bonded only to carbon.

On the other hand, ethers show solubility in water comparable to that of the alcohols, both diethyl ether and *n*-butyl alcohol, for example, being soluble to the extent of about

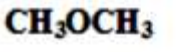
8 g per 100 g water. We attributed the water solubility of the lower alcohols to hydrogen bonding between water molecules and alcohol molecules; the water solubility of ether arises in the same way.



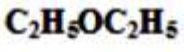
**Hydrogen bonding with water**

***Nomenclature of Ethers:***

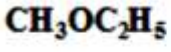
The common names of simple ethers are made by naming the groups attached to oxygen and follow these names by word ether.



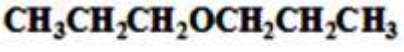
**Dimethyl ether**



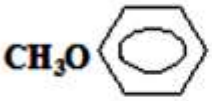
**Diethyl ether**



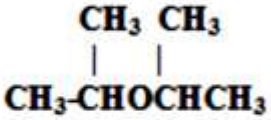
**Ethyl methyl ether**



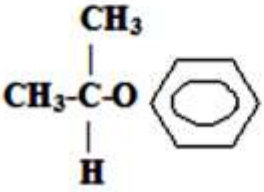
**Dipropyl ether**



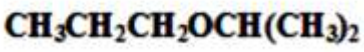
**Methyl phenyl ether**



**Diisopropyl ether**



**Isopropyl phenyl ether**



**Isopropyl *n*-propyl ether**

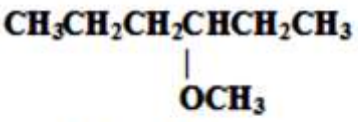
In the IUPAC system, ethers are named by selecting the longest carbon chain as the parent alkane and naming the **–OR** group attached to it as alkoxy group.

**-$OCH_3$ methoxy**

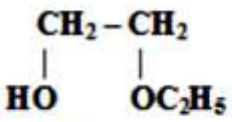
**-$OCH_2CH_3$ ethoxy ……** etc.

1-Methoxypropane

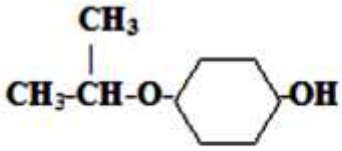
1-Ethoxybutane



3-Methoxyhexane



2-Ethoxyethanol



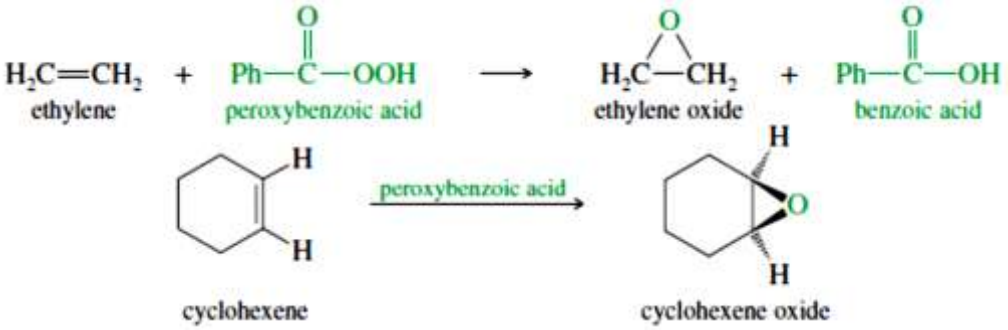
4-Isopropoxycyclohexanol

*p*-Ethoxybenzoic acid

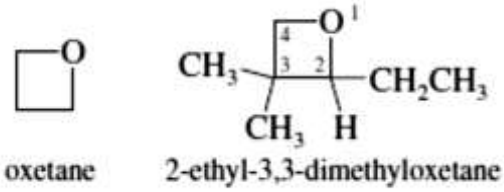
**Nomenclature of Cyclic Ethers:**

Cyclic ethers are our first examples of **heterocyclic compounds,** containing a ring in which a ring atom is an element other than carbon. This atom, called the **heteroatom,** is numbered 1 in numbering the ring atoms. Heterocyclic ethers are especially important and useful ethers.

**Epoxides (Oxiranes)**:



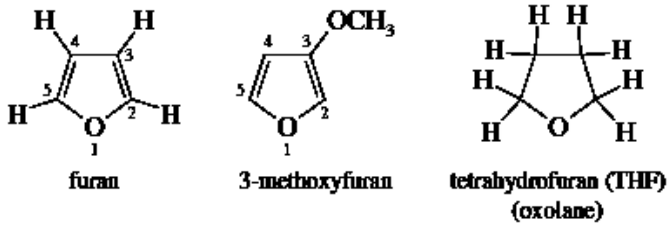

**Oxetanes** the least common cyclic ethers are the four-membered **oxetanes.**



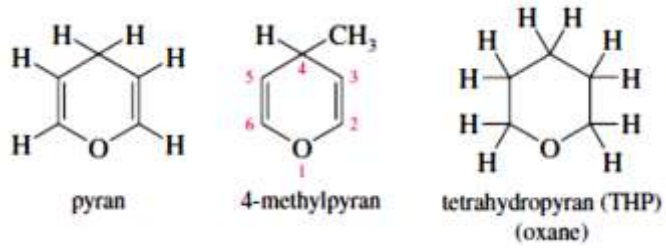
oxetane

2-ethyl-3,3-dimethyloxetane

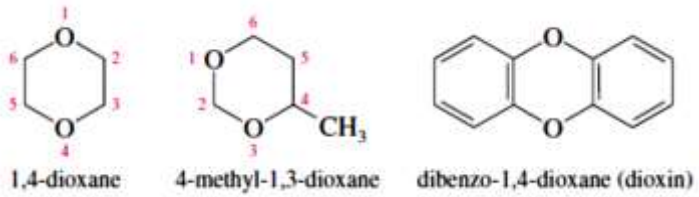
**Furans (Oxolanes)** The five-membered cyclic ethers are commonly named after an aromatic member of this group, **furan.**




**Pyrans (Oxanes)** The six-membered cyclic ethers are commonly named as derivatives of **pyran,** an unsaturated ether.



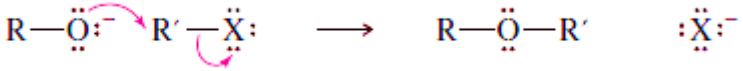

**Dioxanes** Heterocyclic ethers with two oxygen atoms in a six-membered ring are called **dioxanes.**

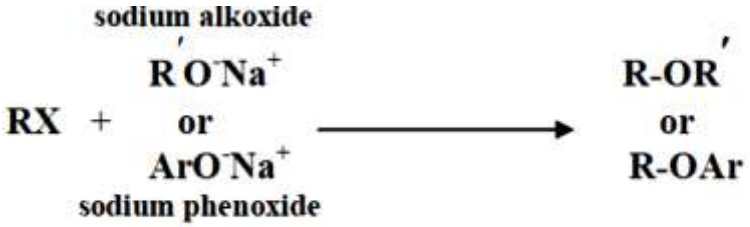


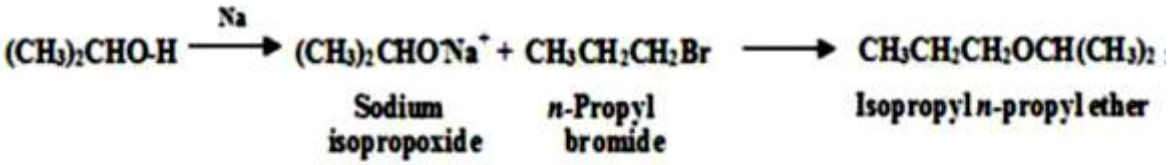

***Syntheses of Ethers:***

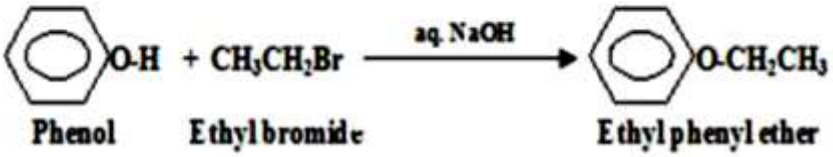
1.The Williamson Ether Synthesis:

In the Williamson synthesis an alkyl halide (or substituted alkyl halide) is allowed to react with a sodium alkoxide or sodium phenoxide.



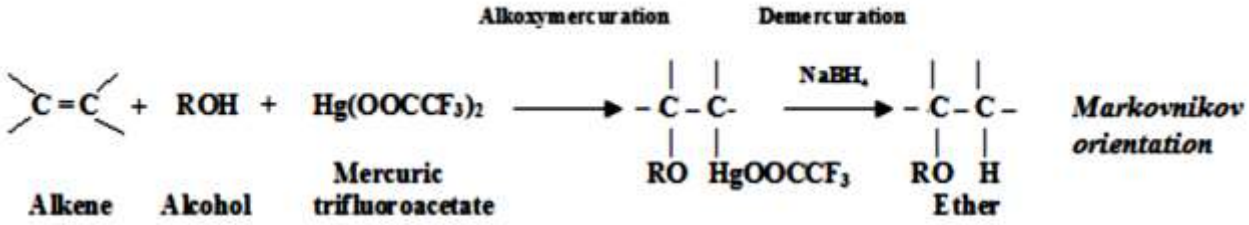


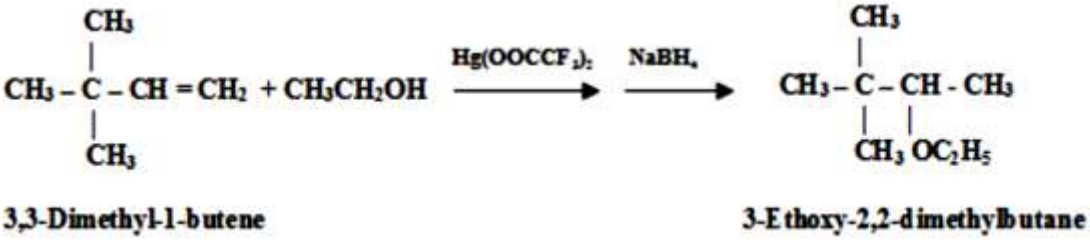



2- Alkoxymercuration – demercuration

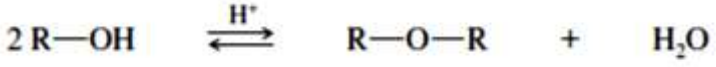
Alkenes react with mercuric trifluoroacetate in the presence of an alcohol to give alkoxymercurial compounds which on reduction yield ether.



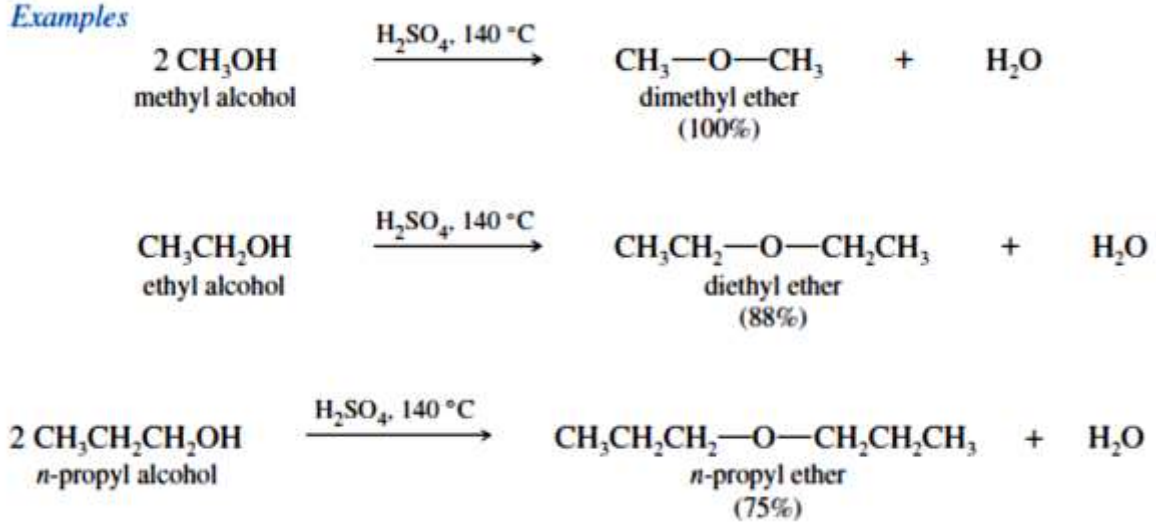




3. Synthesis: Bimolecular Condensation of Alcohols:

*Bimolecular condensation*



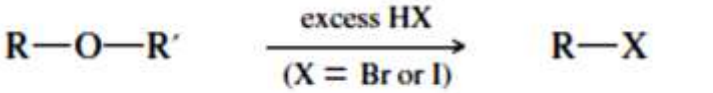
*Examples*

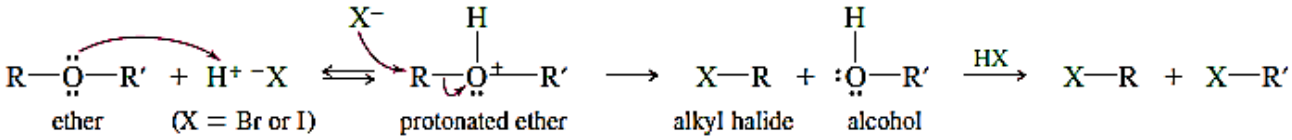



## Reactions of Ethers:

### 1. Cleavage of Ethers by HBr and HI:

Ethers are cleaved by heating with HBr or HI to give alkyl bromides or alkyl iodides.

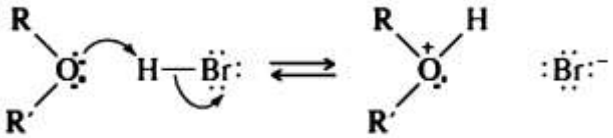


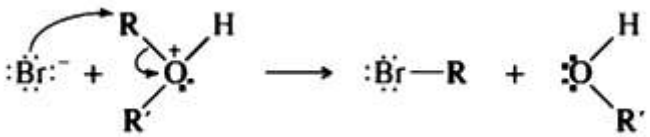

### Mechanism: Cleavage of an Ether by HBr or HI

Ethers are cleaved by a nucleophilic substitution of $Br^-$ or $I^-$ on the protonated ether.

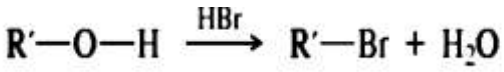
***Step 1:*** Protonation of the ether to form a good leaving group.




***Step 2:*** $SN_2$ cleavage of the protonated ether.

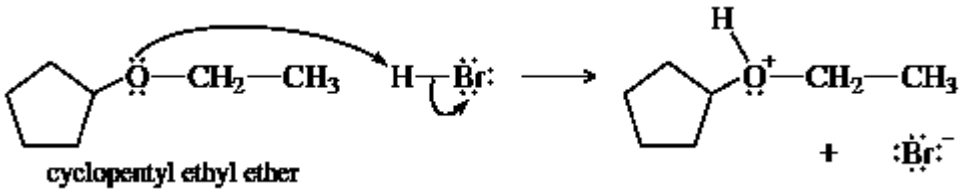


***Step 3:*** Conversion of the alcohol fragment to the alkyl halide. (Does not occur with phenols.)

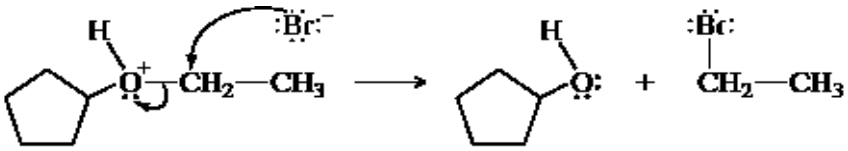



**Example:** Cleavage of cyclopentyl ethyl ether by HBr.

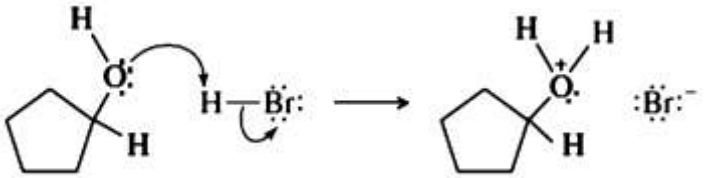
***Step 1:*** Protonation of the ether to form a good leaving group.



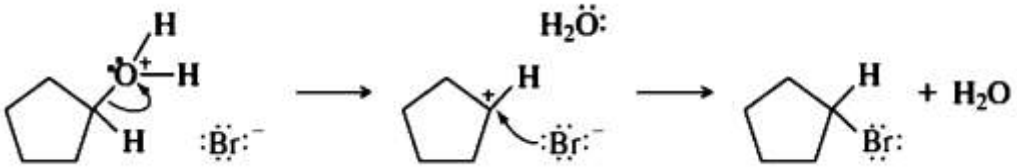

***Step 2:*** Cleavage of the protonated ether.



***Step 3:*** Conversion of the alcohol fragment to the alkyl halide. First, the alcohol is protonated to form a good leaving group.



The protonated alcohol undergoes SN1 or SN2 substitution by bromide ion.



**Autoxidation of Ethers**