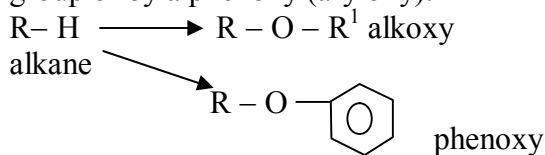


## Ethers

### Definition:

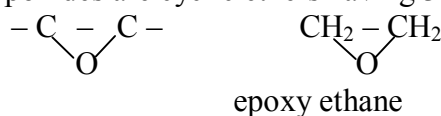
1) Ethers are defined as derivatives of alkanes in which hydrogen atom is replaced by either alkoxy group or by a phenoxy (aryloxy).



\* Ethers are organic oxides

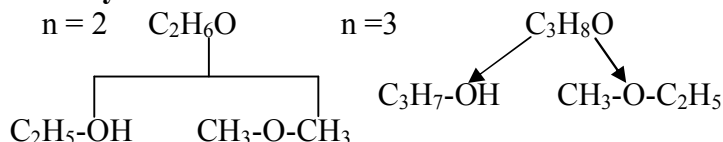
\* In ethers bivalent oxygen is attached to two alkyl or two aryl or alkyl & aryl radicals.

\* Expoxides are cyclic ethers having 3 membered closed ring



### \* General formula for aliphatic Ethers.

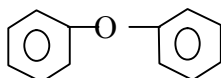
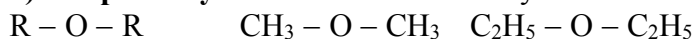
The general formula of aliphatic ethers is  $\text{C}_n\text{H}_{2n+2}\text{O}$  (minimum value of  $n = 2$ ) So ethers are isomeric with **monohydric alcohols**.



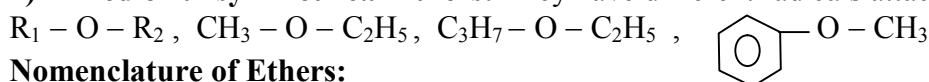
### Classification of Ethers:

Ethers are classified on the basis of alkyl radicals.

1) **Simple or symmetrical Ethers:** They have same alkyl/aryl radicals.

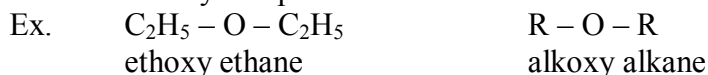


2) **Mixed or unsymmetrical Ethers:** They have different radicals attached to oxygen.



### Nomenclature of Ethers:

Common names of ethers are given on the basis of alkyl radicals attached to oxygen. In the IUPAC system, out of the two alkyl radicals one is considered as parent alkane. Remaining group is then called as alkoxy and prefixed to the name of alkane.



In the case of mixed ethers bigger alkyl radical should be selected as parent alkane and if required numbering may be done.

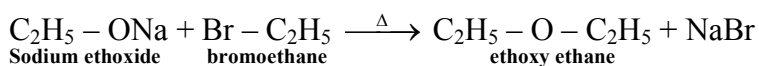
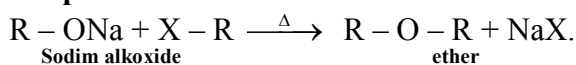
Formula	Common Name	IUPAC Name
$R - O - R$	dialkyl ether	Alkoxy alkane
$CH_3 - O - CH_3$	dimethyl ether	Methoxy methane
$C_2H_5 - O - C_2H_5$	diethyl ether	Ethoxy ethane
$CH_3 - \overset{\overset{H}{ }}{\underset{\underset{CH_3}{ }}{C}} - O - CH_3$	methyl isopropyl ether	2 Methoxy propane
$CH_3 - CH_2 - CH_2 - O - CH_3$	methyl n propyl ether	1 Methoxy propane
$CH_3 - \overset{\overset{CH_3}{ }}{\underset{\underset{H}{ }}{C}} - CH_2 - O - C_2H_5$	isobutyl ethyl ether	1-Ethoxy 2 methyl propane
	Anisole or methyl phenyl ether	Methoxy benzene
	Phenetole or ethyl phenyl ether	Ethoxy benzene
	Cyclohexyl ethyl ether	ethoxy cyclohexane.
	_____	Methoxy cyclobutane

### Methods of Preparation:

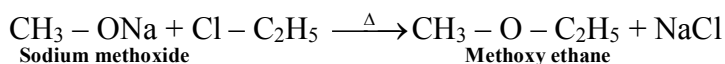
#### 1) By Williamson's Synthesis (From sodium alkoxide & alkyl halide or aryl halide):

When sodium alkoxide is heated with alkyl halide ethers are formed. The reaction is called **Williamson's Synthesis**. By this method all types of ethers such as simple ethers, mixed ethers, aromatic ethers etc can be obtained.

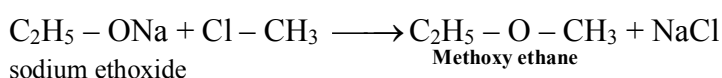
##### a) Simple ether:



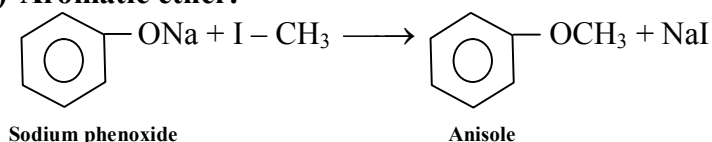
##### b) Mixed ether:



**OR**



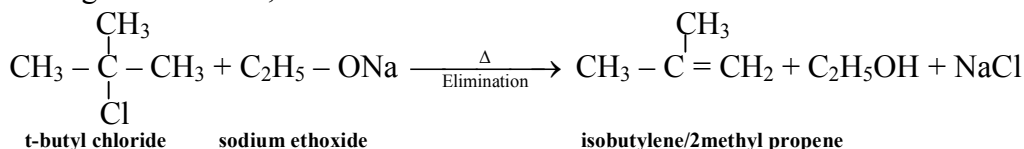
**c) Aromatic ether:**



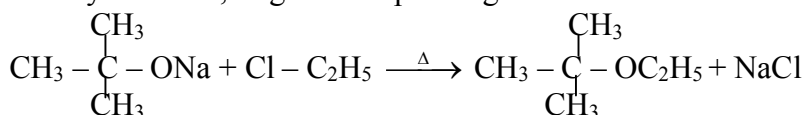
**Limitations of Williamson's Synthesis:**

In the preparation of unsymmetrical ethers having secondary or tertiary alkyl radicals, the reactants **must be properly selected**.

A secondary or tertiary alkyl halide should be avoided because they have greater tendency to undergo elimination, as follows.

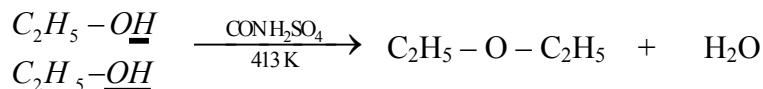
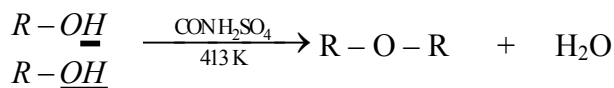


Therefore in Williamson's Synthesis, a primary alkyl halide should be heated with a secondary or tertiary alkoxide, to get corresponding ether.



**2) By intermolecular dehydration of alcohols (continuous etherification process):**

When large excess of alcohol is heated with a dehydrating agent such as 95% or concentrated  $\text{H}_2\text{SO}_4$  at 413K, intermolecular dehydration takes place. This gives corresponding ethers. The reaction is completed in two steps as follow.

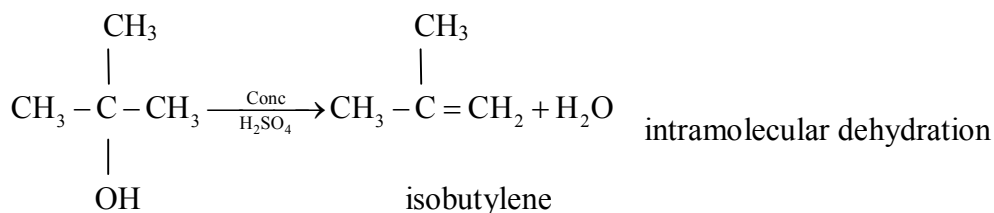


Sulphuric acid can be again & again used as dehydrating agent, and ether formed can be distilled out. So the method is called **Continuous Etherification**.

\* Alcohol is continuously added while ether and water are continuously distilled out.

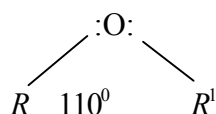
**Limitations:**

- 1) The temperature must be maintained at 413K. Because at higher temperature alkenes are formed.
- 2) This method is useful for the preparation of simple ethers only. For ex. ethoxy ethane is obtained industrially as well as in the laboratory by this method.  
If two different alcohols are mixed in the dehydration, then at 413K a mixture of three ethers along with water is obtained.
- 3) This method is suitable for intermolecular dehydration of only **primary alcohols**. Because if secondary or tertiary alcohol is taken then elimination. i.e. intramolecular dehydration takes place with the formation of alkenes.



### Structure of ether group (Structure of ether linkage)

In ethers, oxygen is  $\text{sp}^3$  hybridised. It forms two sigma covalent bonds with two different carbon atoms. These bonds are formed by  $\text{sp}^3 - \text{sp}^3$  overlap. Also oxygen atom has two non bonding lone pairs of electrons. Ether molecule gets angular geometry with a bond angle of  $110^\circ$ . Oxygen being more electronegative than carbon these bonds are polar covalent.



\*Bulky alkyl radicals repel each other so tetrahedral bond angle increases to  $110^\circ$ .

### Physical Properties:

- 1) First two members are gases. Next few members are liquids while higher members are solids.
- 2) Boiling point of ethers are higher than alkane. because ethers have dipole attraction. But their boiling points are low than alcohols which have H-bonding. (alkane < ether < alcohol)  
Ethers have a net little dipole moment. But polarity being less, it does not effect the boiling point.
- 3) Ethers are sparingly soluble in water as they may form few H-bonds with water.
- 4) Ethers are highly inflammable and easily catch fire. (This fire can be extinguished by pyrine i-e  $\text{CCl}_4$  and not by water.)

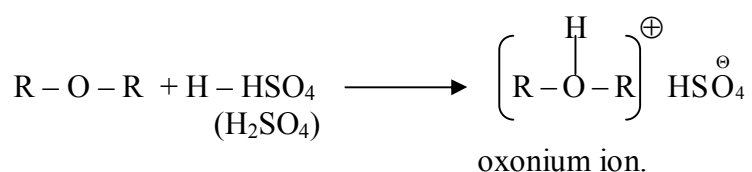
### Chemical Properties:

Ethers are not attacked by common acids alkalies, oxidising agents, reducing agents, Grignard's reagent etc. So ethers are considered as **inert organic compounds**. However, following properties are observed in ethers.

#### 1) Laboratory Test of ethers :

##### (Action of cold concentrated $\text{H}_2\text{SO}_4$ )

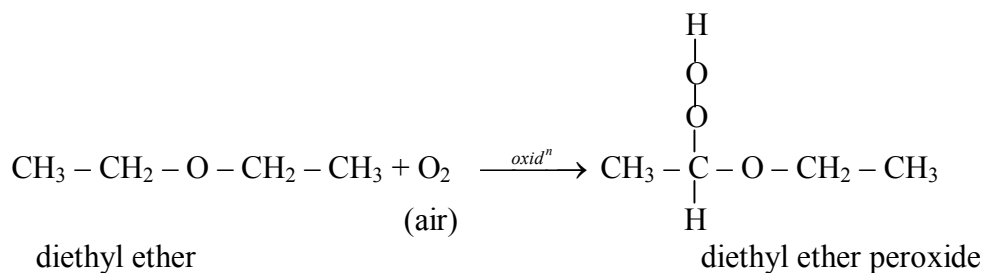
Ether dissolves in cold concentrated  $\text{H}_2\text{SO}_4$  forming oxonium salt.



\* Hydrocarbons (alkanes) do not react with  $\text{H}_2\text{SO}_4$ , only ethers can react.

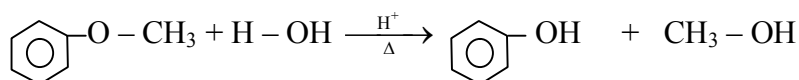
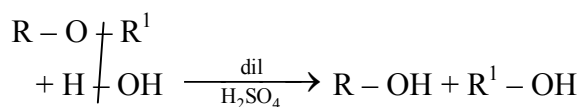
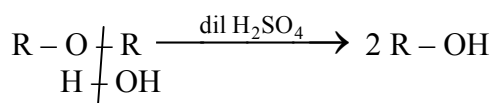
#### 2) Action of air (Formation of peroxide)

Ether reacts with Oxygen in air to form its peroxide. These peroxides are hazardous (poisonous). At high temperature ether- peroxide decompose violently.



### 3) Hydrolysis of ether by dil $\text{H}_2\text{SO}_4$ ,

Simple ethers are hydrolysed on heating with dil  $\text{H}_2\text{SO}_4$  under pressure. They on hydrolysis give single alcohol. A mixed ether on similar hydrolysis gives homologues of alcohol i.e. mixture of two alcohols.

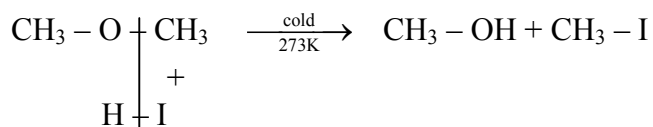
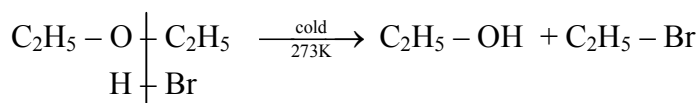
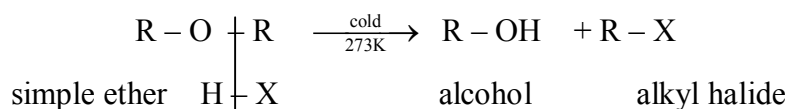


### 4) Reaction with hydrogen halides ( $\text{H} - \text{X}$ ). (Cleavages in ether)

\*  $\text{H} - \text{Cl}$  does not react with ethers. So only  $\text{H} - \text{Br}$  or  $\text{H} - \text{I}$  can react with ethers under two conditions.

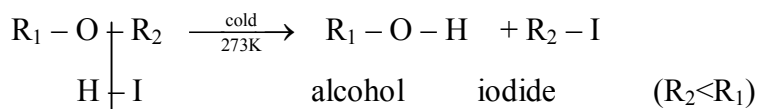
#### A] Cold condition:

Ethers react with  $\text{H} - \text{I}$  or  $\text{H} - \text{Br}$  at 273K i.e. in cold condition giving only one cleavage. This gives alcohol and alkyl halide. In simple ethers any one ether linkage may break giving the products.

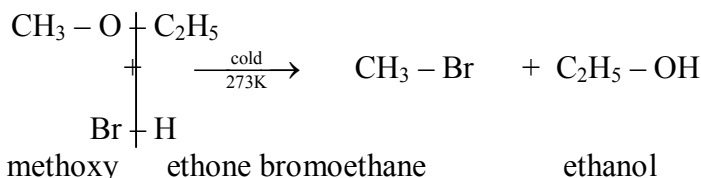


But in case of **mixed ethers** the cleavage occurs in such a way that smaller radical forms alkyl iodide/bromide. This is due to  $S_N^2$  mechanism or backside attack.

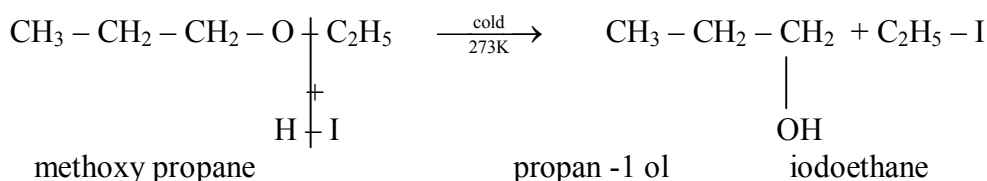
i)



ii)

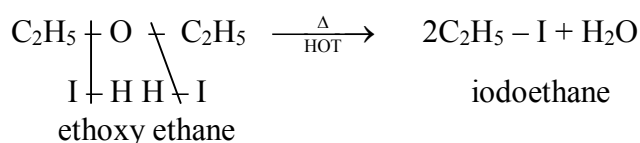
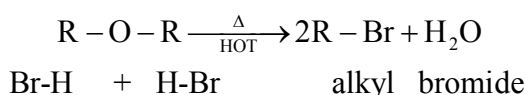


iii)

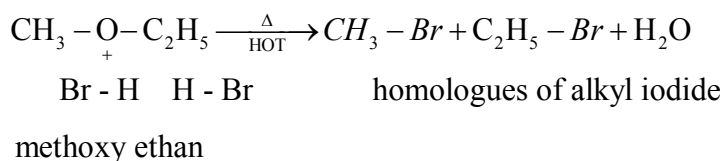
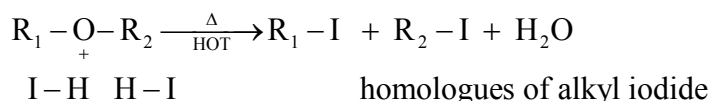


### B) Hot condition:

When ether is heated with solution of H-I or HBr two cleavages occur with the formation of alkyl iodide/bromide and water.



In case of mixed ether similar reaction occurs with the formation of two different alkyl halides and water.

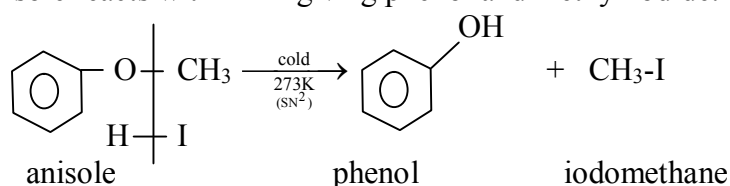


### Properties of aromatic ethers i.e. Anisole

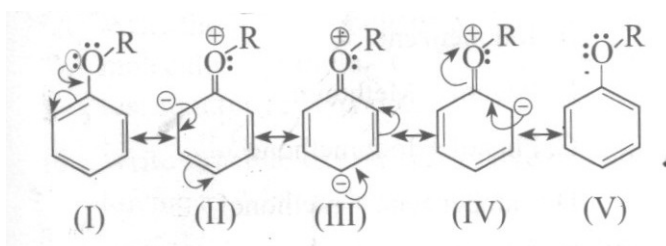
#### 1) Reaction of H - I on anisole

(It is not electrophile reaction)

Anisole reacts with H - I giving phenol and methyl iodide.



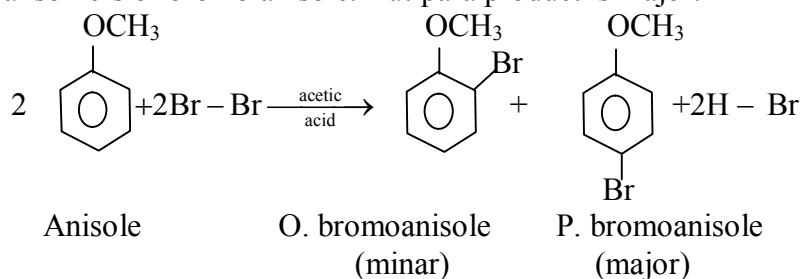
Ether group is responsible for five resonating structures.



\* The methoxy group in anisole ( $R = CH_3$ ) is ortho para directing following are **electrophilic substitution of anisole**. Because due to + R (resonance) negative charge is available on ortho and para position.

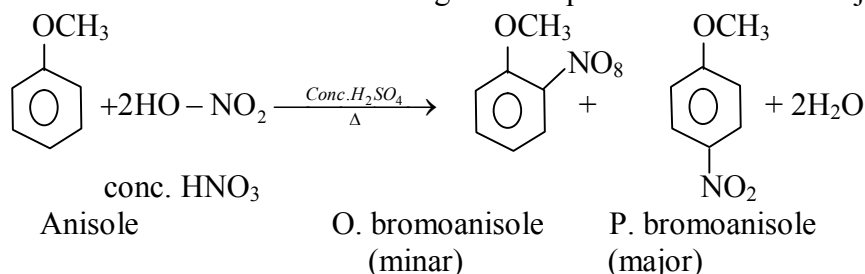
### 1) Bromination of Anisole:

Anisole reacts with bromine in the presence of acetic acid as a solvent giving mixture of ortho and para isomers of bromo anisole. But para product is major.



### 2) Nitration of Anisole:

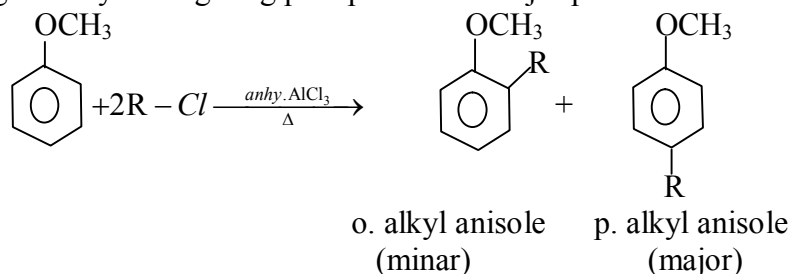
When anisole is heated with nitrating mixture para derivative is a major product.



### 3) Friedel-Crafts Reaction:

#### a) Alkylation:

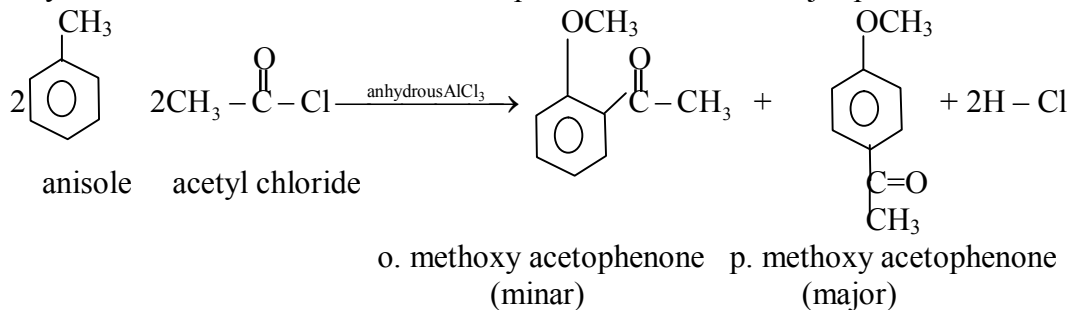
When anisole is heated with alkyl halide in the presence of anhydrous aluminium chloride, it undergoes alkylation giving para product as major product.



### b) Acylation / Acetylation:

If “ $R - \overset{\text{O}}{\parallel}{C} -$ ” group enters the process is acylation. For “ $CH_3 - \overset{\text{O}}{\parallel}{C} -$ ” the process is acetylation. So acetylation is a type of acylation.

When anisole is heated with acetyl chloride in the presence of anhydrous aluminium chloride, acetylation occurs with the formation of para derivative as a major product.



### Uses of ethers (Ethoxy ether)

\* Diethyl ether is generally considered as **Ether**.

- 1) Ether is used as an industrial solvent for fats, oils, resins etc.
- 2) Being inert, diethyl ether is used as a medium in many organic reactions like Wurtz Reaction, Grignard's Reagent etc.
- 3) Diethyl ether is used as an anesthetic agent.

\*\*\*\*\*