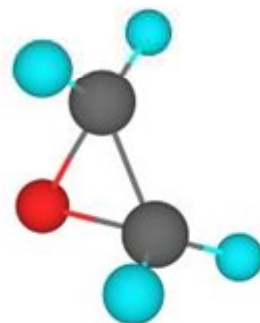


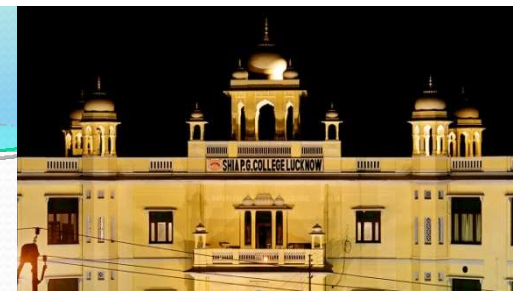
# Ethers & Epoxides



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## Note:

**This is to bring to kind notice that the matter of this e-content is for the B.Sc. IV semester students. It has been taken from the following sources. The students are advised to follow these books as well.**

- **A TEXTBOOK OF ORGANIC CHEMISTRY** by **Arun Bahl & B.S. Bahl**, S. Chand & Company Ltd. Publication.
- **Graduate Organic Chemistry** by **M. K. Jain and S.C. Sharma**, Vishal Publishing Co.
- **Pradeep's Organic Chemistry Vol II** by **R. N. Dhawan**, Pradeep Publication, Jalandhar.



## ETHERS AND EPOXIDES

### STRUCTURE

Ethers have two organic groups (alkyl, aryl, or vinyl) bonded to the same oxygen atom.



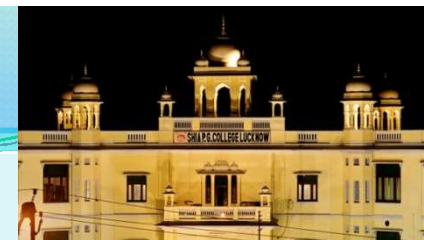
R groups are identical = symmetrical ether

R groups are different = unsymmetrical ether

Oxygen is  $sp^3$  hybridized

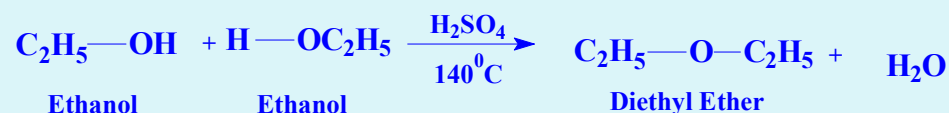
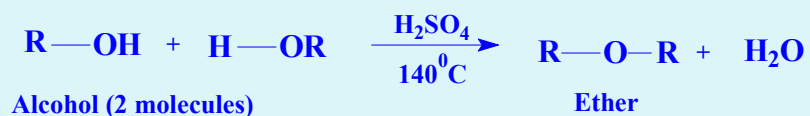
Nearly tetrahedral angle, depends on the R group

Oxygen atom gives a slight dipole moment

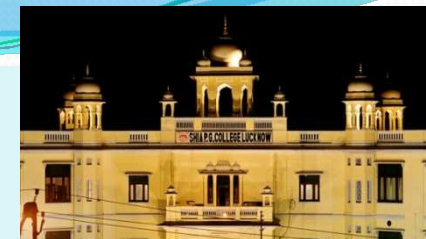


# Preparation of Ethers

**1. Dehydration of Alcohols:** Symmetrical ethers are prepared by heating an excess of alcohol with Conc.  $\text{H}_2\text{SO}_4$  at  $140^\circ\text{C}$ .

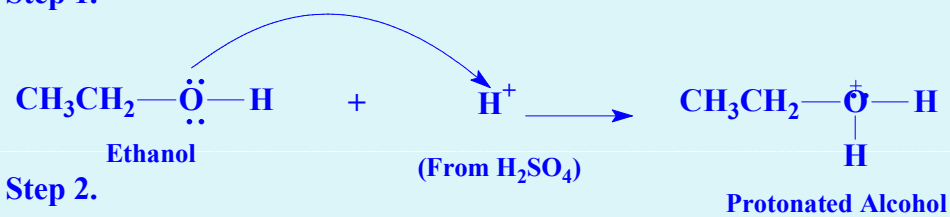


The starting alcohol in the above reaction must be primary and the reaction temperature must be kept at  $140^\circ\text{C}$ . This is because *alkene* formation is favored at high temperature and with secondary or tertiary alcohol.

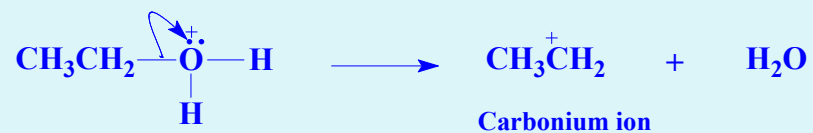


## Mechanism of dehydration of alcohols:

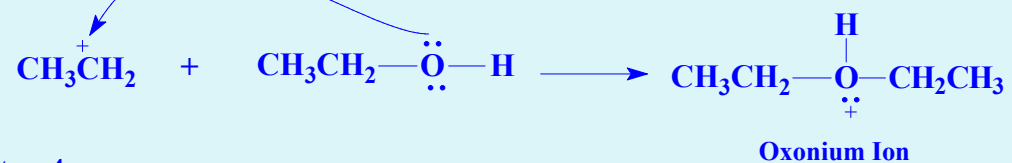
Step 1.



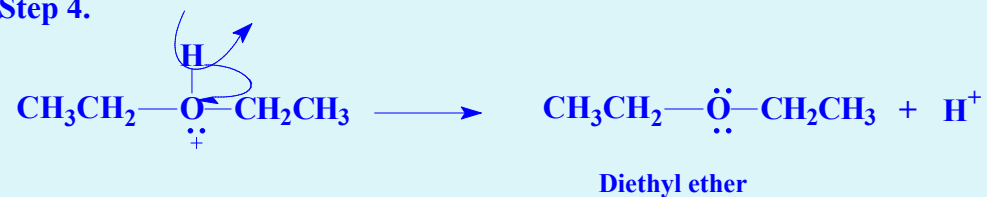
Step 2.



Step 3.



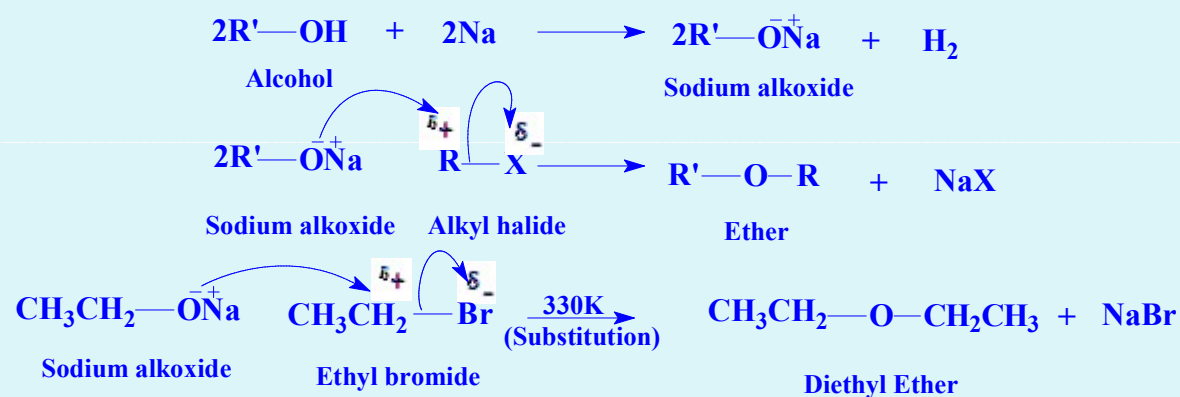
Step 4.



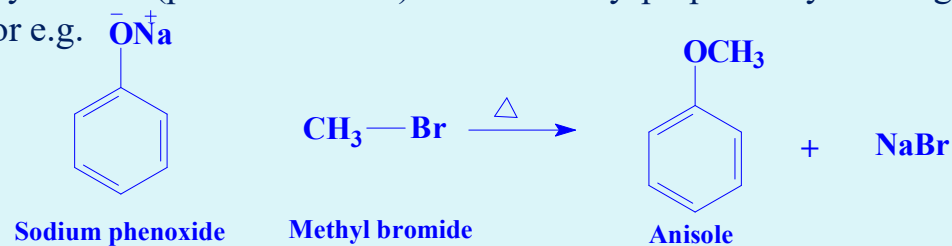


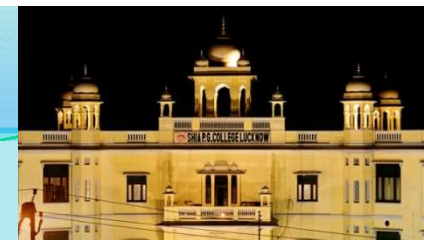
# Preparation of Ethers

**2. From alkyl halides:** This is one of the best method for the preparation of ethers. This involves the treatment of a sodium alkoxide with an alkyl halide. Sodium alkoxide are obtained by treating alcohol with sodium metal. Both symmetrical as well as unsymmetrical ethers can be prepared by this method.



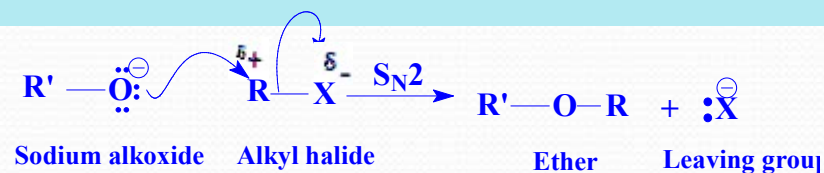
Similarly, alkyl aryl ethers (phenolic ethers) can be easily prepared by treating sodium phenoxide with alkyl halides. For e.g.





## Mechanism of Williamson synthesis:

It involves nucleophilic substitution by alkoxide or phenoxide ion (nucleophile) for the halide ion in alkyl halides.

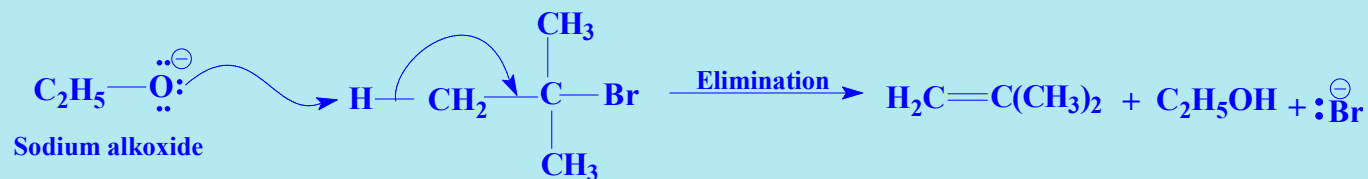


The alkyl halide used in this reaction must be primary. If secondary or tertiary alkyl halides are used, the reaction leads mainly to alkene formation.

Limitations:

1. **Aryl halides** and **vinyl halides** can not be used as substrates in this method because of their low reactivity in nucleophilic substitution.
2. Secondary and tertiary alkyl halides, which are very prone to elimination, should be avoided as substrates. For e.g., tert-Butyl ethyl ether, can be prepared either by the reaction of tert-butoxide ion with ethyl bromide or by the action of the ethoxide ion on tert-Butyl bromide.

The **primary alkyl** halide ( $\text{C}_2\text{H}_5\text{Br}$ ) as **substrate** is preferable than tert-alkyl halides  $[(\text{CH}_3)_3\text{C}-\text{Br}]$  as the substrate, since the latter halide is prone to **elimination**.





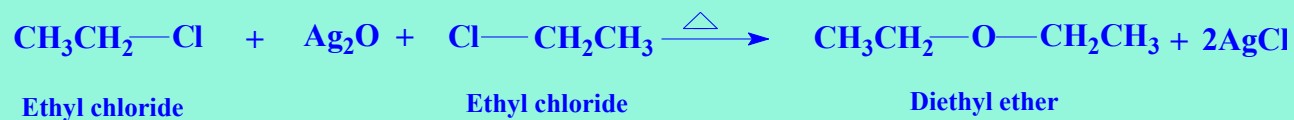


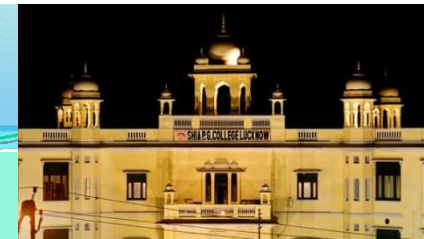
# Preparation of Ethers

**4. By the action of diazomethane on alcohols::** Primary and secondary alcohols on treatment with diazomethane give methyl ether using fluoroboric acid as a catalyst.



**5. By treating an alkyl halide with dry silver oxide:** Heating an alkyl halide with dry silver oxide gives ether. For e.g.

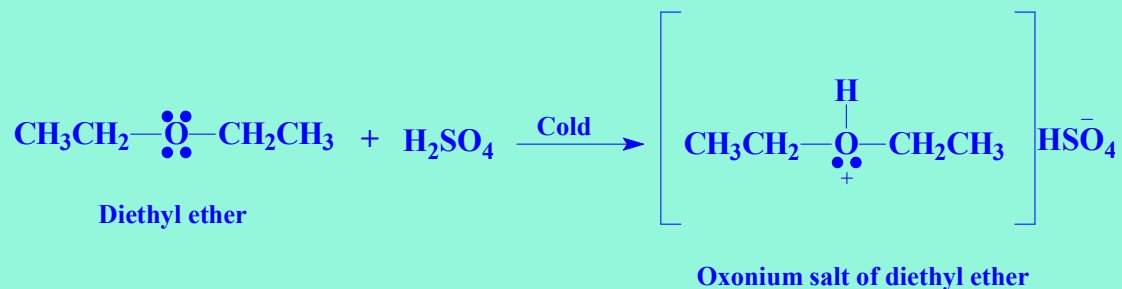
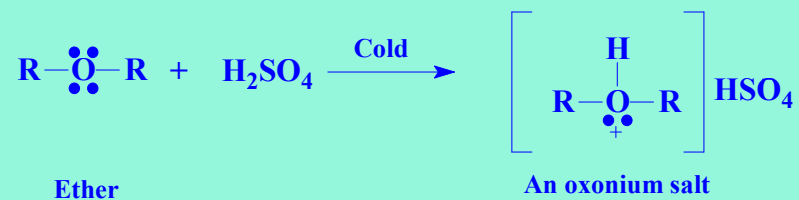




# Chemical Reactions of Ethers

## A. Reactions of the ethereal oxygen:

1. **Action of concentrated acids:** Due to the presence of two lone pairs of electrons on oxygen, ether behave as *Lewis bases* and thus react with cold  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  to give **Oxonium salts**.

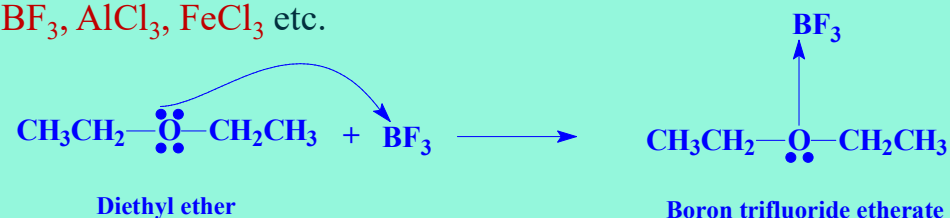




# Chemical Reactions of Ethers

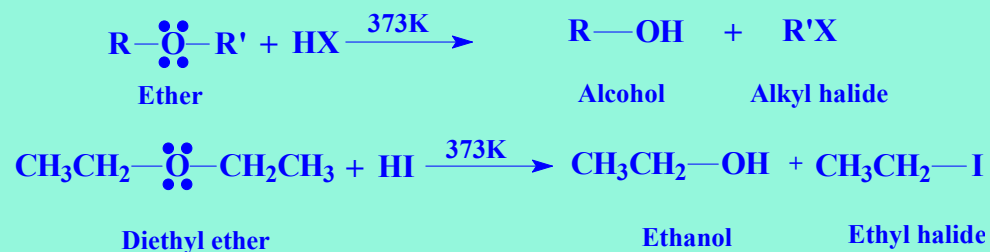
## A. Reactions of the ethereal oxygen:

2. **Formation of coordination complexes:** Being a Lewis base ether form **coordination complexes** with Lewis acids like  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{FeCl}_3$  etc.



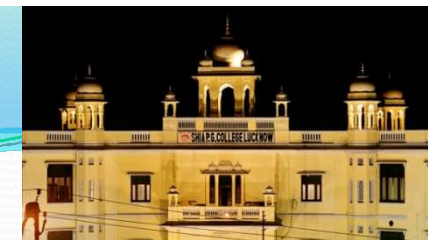
## B. Reactions involving C-O bond:

1. **With halogen acids:** Ethers react with hot concentrated HI or HBr to give an alcohol and an alkyl halide.

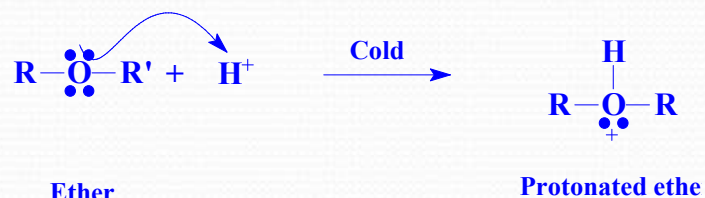


If excess of acid is used, the alcohol first formed which reacts further with acid to form the corresponding alkyl halide.



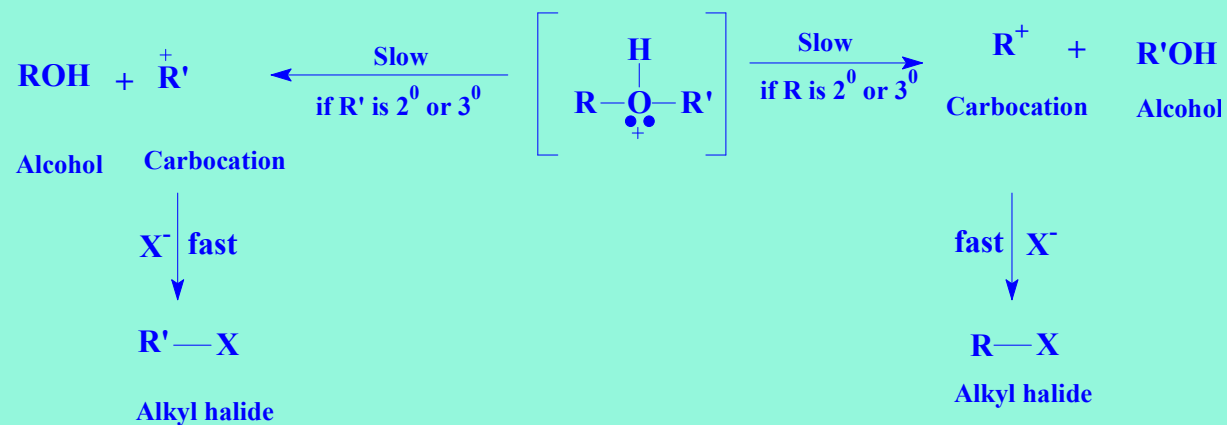
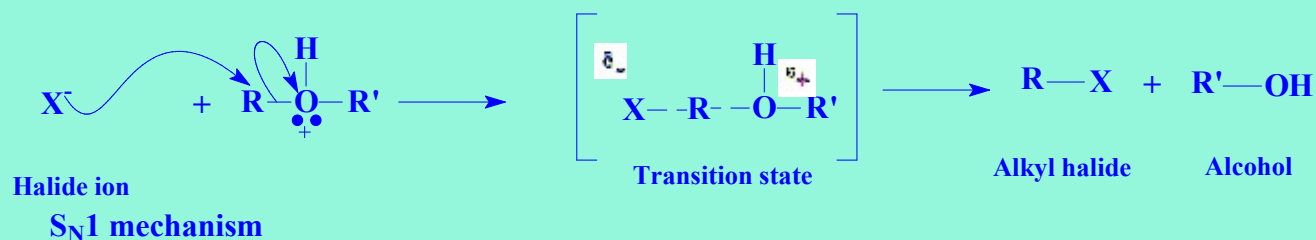


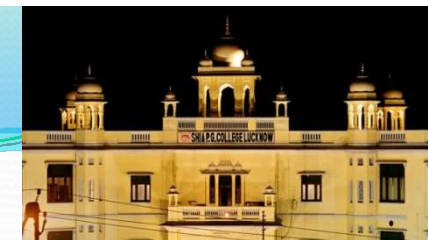
### Mechanism:



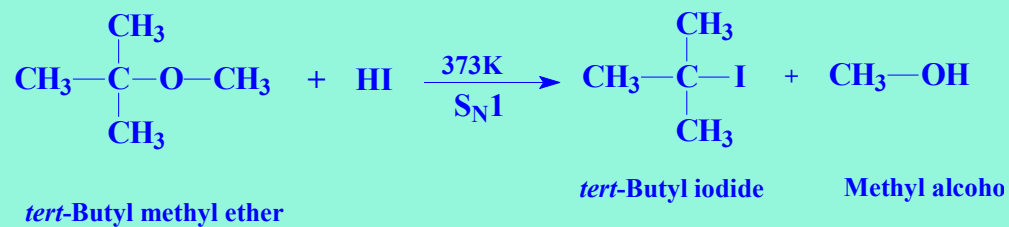
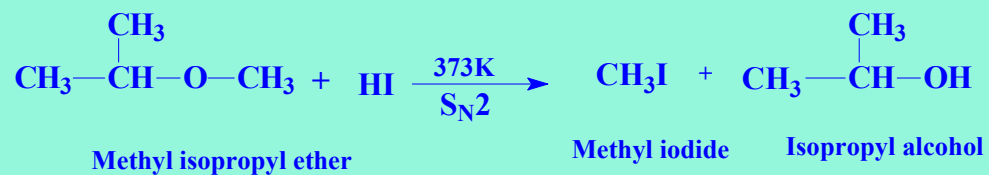
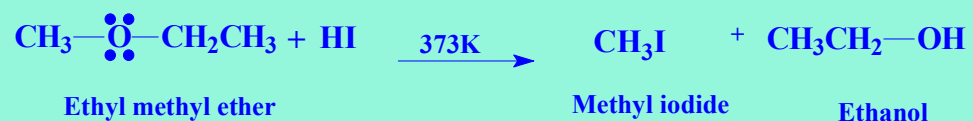
The protonated ether undergoes nucleophilic attack by the halide ion either by S<sub>N</sub>1 or S<sub>N</sub>2 mechanism depending upon the nature of the alkyl groups attached to ether. If the alkyl groups are

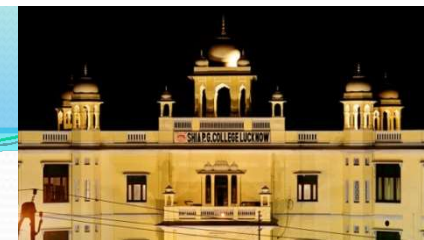
#### S<sub>N</sub>2 mechanism:



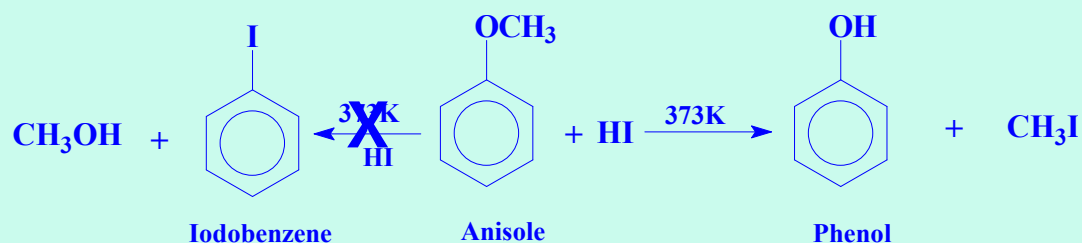


### Side of cleavage:

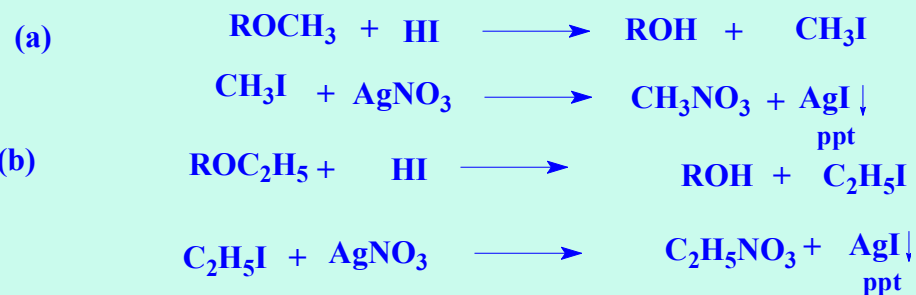


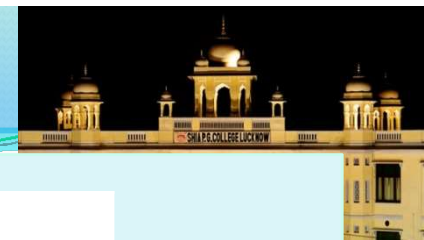


In case of alkyl aryl and diaryl ether s, the products are always phenol and an alkyl halide and never an aryl halide and an alcohol. *For e.g.*



**Ziesel Method:** This method is used for the estimation of methoxy or ethoxy group (Alkoxy group). The methoxy or ethoxy alkane or arene is weighed and heated with conc. HI to form methyl or ethyl iodide. The **methyl** or **ethyl iodide** thus obtained is the treated with alc.  $\text{AgNO}_3$  to form  $\text{AgI}$  ppt.





Calculation of  $-\text{OCH}_3$  Group  
Wt. of sample taken =  $W_1$  gm  
Wt. of AgI formed =  $W_2$  gm  
1 mole of AgI  $\equiv$  one  $\text{OCH}_3$  group  
234 gm of AgI  $\equiv$  31 gm of  $\text{CH}_3$  group  
So % of  $-\text{OCH}_3$  group  $\equiv$

$$\frac{31}{234} \times \frac{W_2}{W_1} \times 100$$

Calculation of  $-\text{OC}_2\text{H}_5$  Group  
1 mole of AgI = one  $-\text{OC}_2\text{H}_5$  group  
234 gm of AgI = 45 gm of  $-\text{OC}_2\text{H}_5$  group  
 $\text{OCH}_3$   
So % of  $-\text{OC}_2\text{H}_5$  group  $\equiv$

$$\frac{45}{234} \times \frac{W_2}{W_1} \times 100$$

## C. Reaction involving the alkyl group:

**Formation of peroxides (Autooxidation).** Ethers react with atmospheric oxygen to form peroxides.



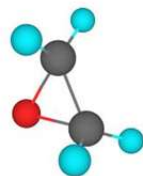
Diethyl ether

peroxide of diethyl ether

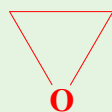
These peroxides are very dangerous because they decompose violently at high temperatures. Ethers should not have evaporated to dryness because serious explosion may take place during distillation of old samples of ethers if peroxides are not removed.



# Epoxides



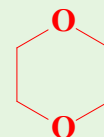
Three membered cyclic ethers are called **epoxides** also called **alkylene oxides**, **epoxyalkanes** or **oxiranes**.



Ethylene oxide



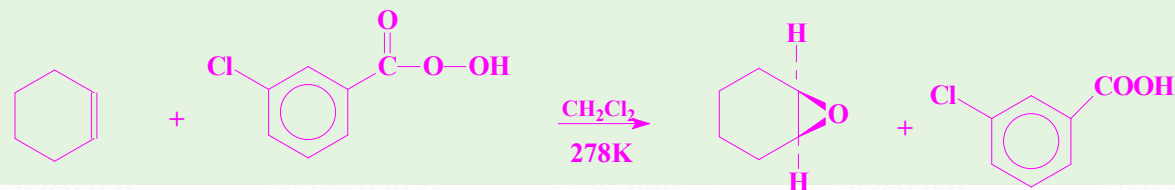
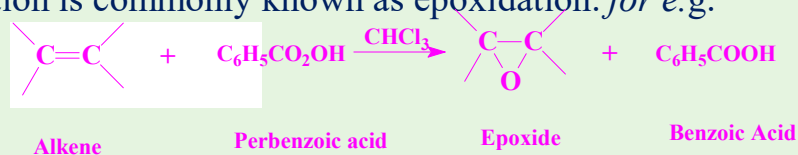
Tetrahydrofuran



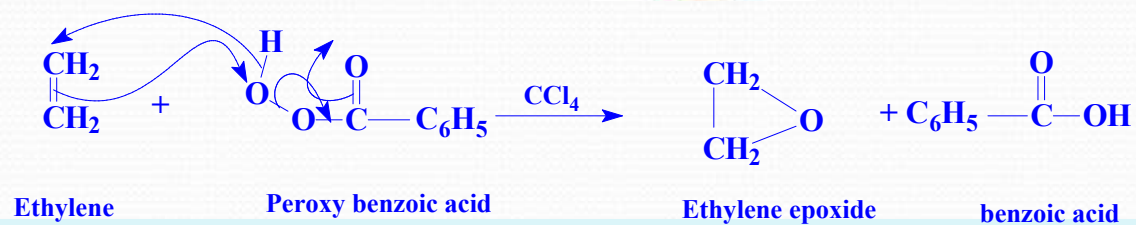
1,4-Dioxane

## Synthesis of epoxides:

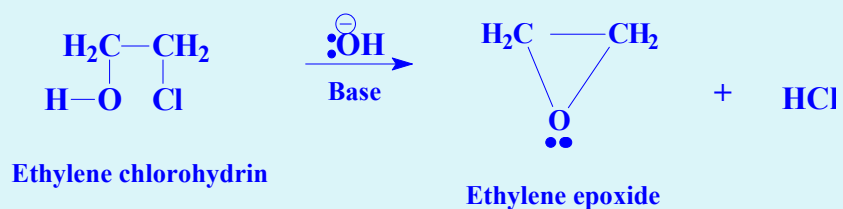
- Epoxidation of alkene:** When an **alkene** is treated with **peracids** like **perbenzoic acid**, **m-chloroperbenzoic acid**, **trifluoroperacetic acid** etc in an inert solvent like dichloromethane, carbon tetrachloride etc, epoxides are formed. This reaction is commonly known as epoxidation. *for e.g.*



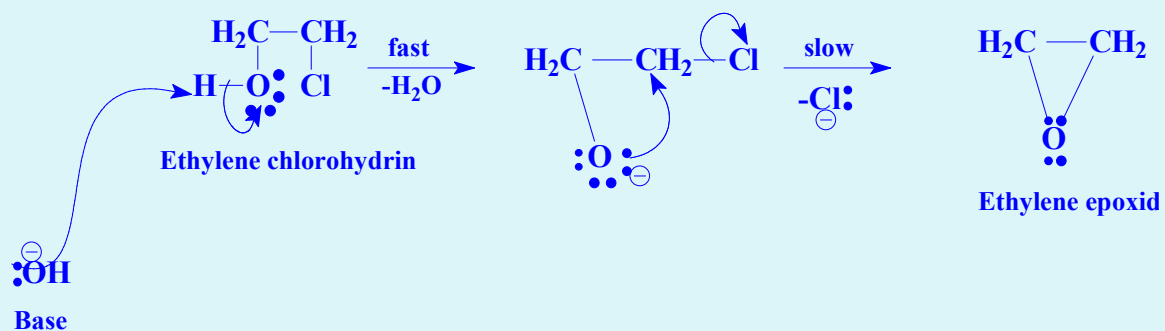
## Mechanism:



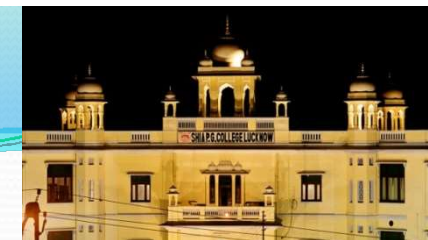
**2. From Halohydrins:** When halohydrins are treated with a base like NaOH or KOH, epoxide is formed with the elimination of HX. *for e.g.*



## Mechanism:

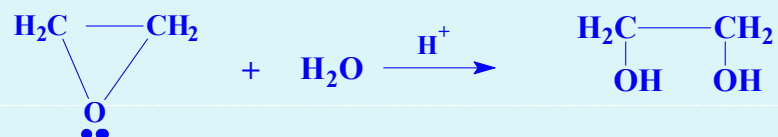


## Chemical Properties:



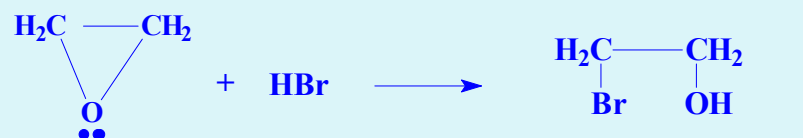
Epoxide ring has **angle strain** because the bond angle is about  $60^\circ$  much smaller than the tetrahedral bond angle of  $109.5^\circ$ . As a result most of the epoxides reactions are ring opening reactions.

**Acid catalysed ring opening:** When an epoxide is treated with a **nucleophile** ( $\text{H}_2\text{O}$ ,  $\text{R-OH}$  etc) in the presence of an acid, **C-O cleavage**. In unsymmetrical epoxides the bond cleavage takes place in such a way that most stable carbocation is formed.



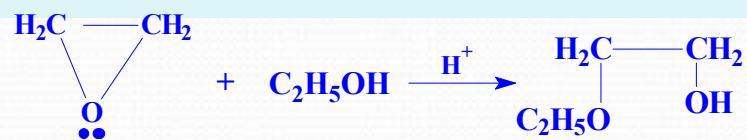
Ethylene epoxide

Ethylene glyco



Ethylene epoxide

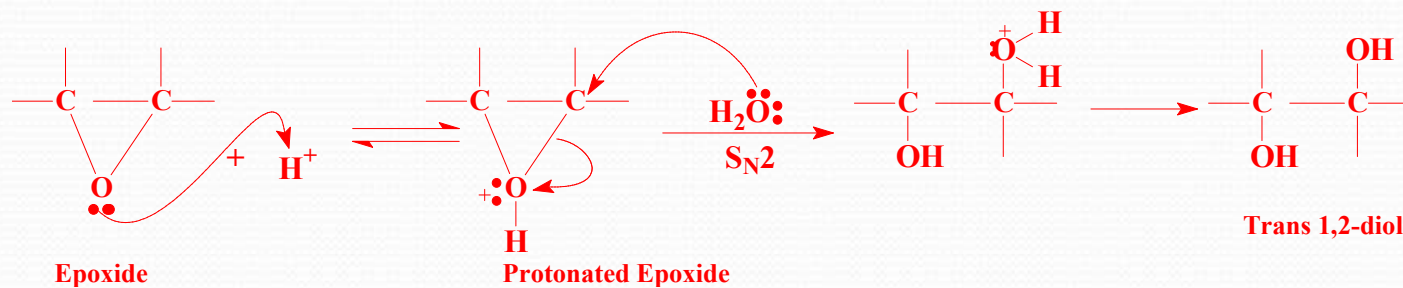
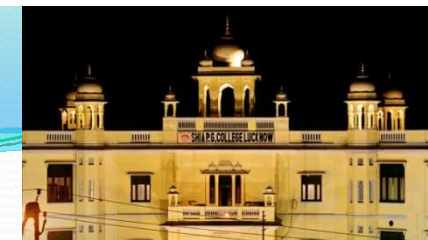
Ethylene bromohydri



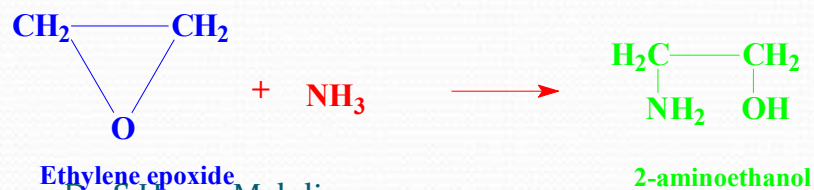
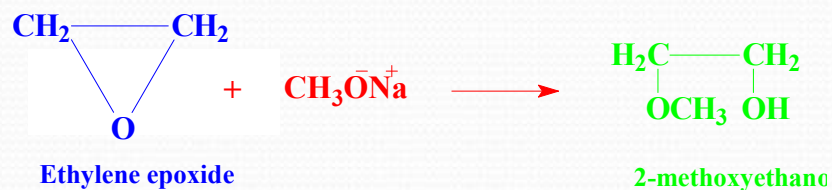
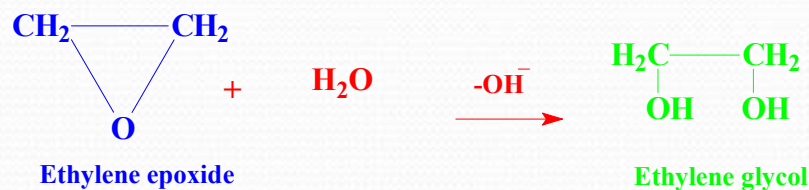
Ethylene epoxide

2-Ethoxyethanol

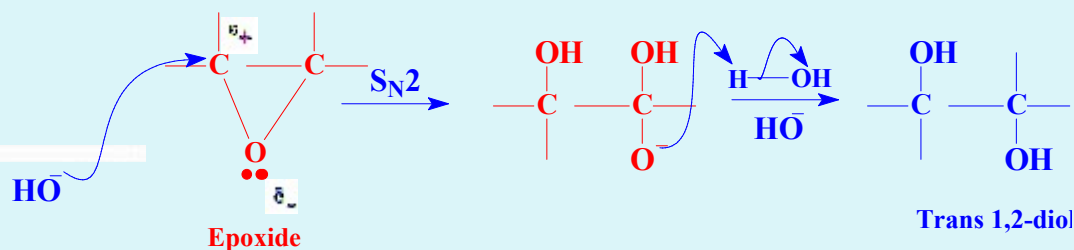
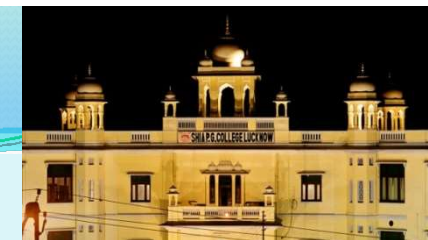
## Mechanism:



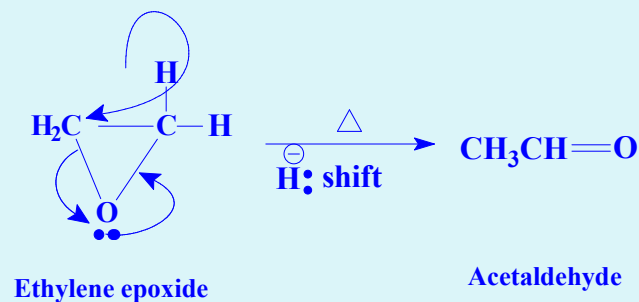
**Base catalysed ring opening:** In the presence of a base like sodium alkoxides, ammonia/amines, nucleophilic attack takes place at less sterically hindered side.



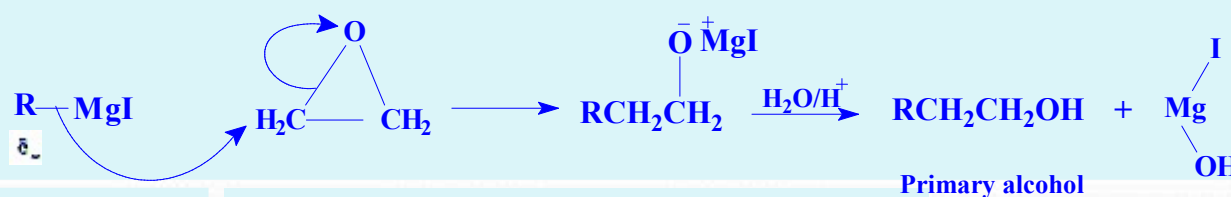
## Mechanism:



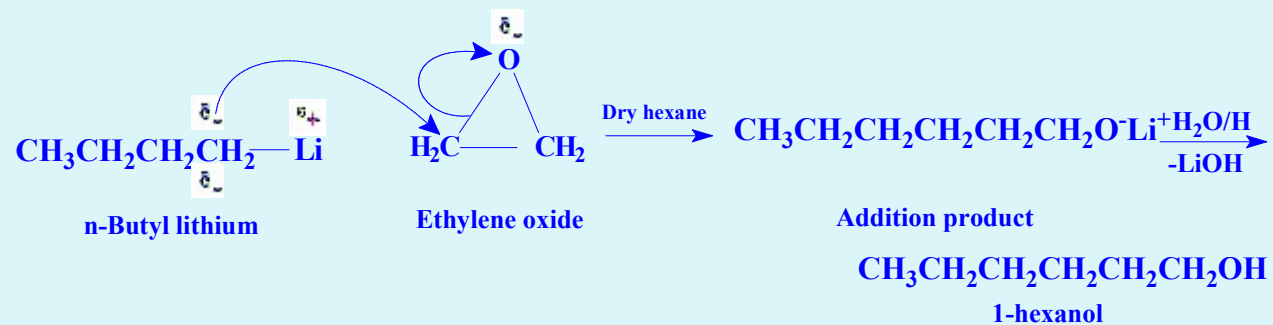
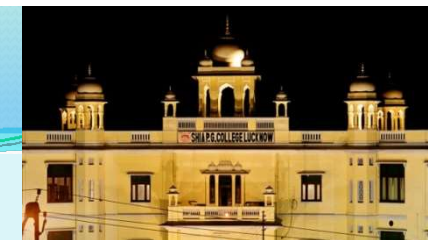
**3. Molecular rearrangement:** Ethylene oxide undergoes molecular rearrangement on heating to form acetaldehyde.



**Reaction with Grignard reagents and organolithium reagents:** Ethylene oxide reacts with Grignard reagent and organolithium reagents to form addition products which on acid hydrolysis give **primary alcohols**. The primary alcohol thus produced having two carbon more than the starting reagent.



# Mechanism:





## References:

- **A TEXTBOOK OF ORGANIC CHEMISTRY** by **Arun Bahl & B.S. Bahl**, S. Chand & Company Ltd. Publication.
- *Graduate Organic Chemistry* by **M. K. Jain and S.C. Sharma**, Vishal Publishing Co.
- **Pradeep's Organic Chemistry Vol II** by **R. N. Dhawan**, Pradeep Publication, Jalandhar.