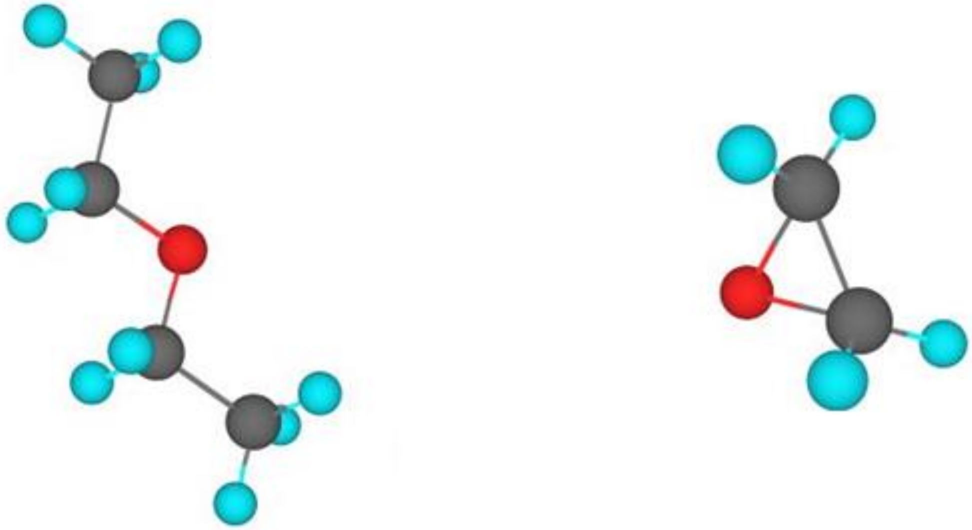
Ethers & Epoxides



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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

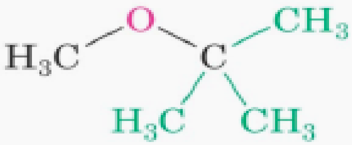
Oxygen is *sp*^{3} hybridized

Nearly tetrahedral angle, depends on the R group

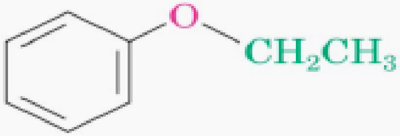
Oxygen atom gives a slight dipole moment

Naming Ethers

Simple ethers are named by identifying the two organic substituents and adding the word *ether*



***tert*-Butyl** methyl ether



Ethyl phenyl ether

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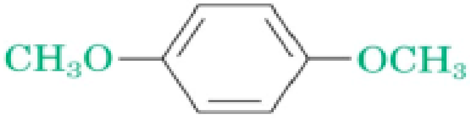
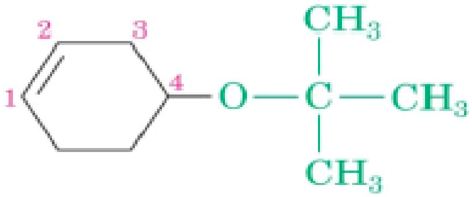
If other functional groups are present, the ether part is considered an alkoxy substituent



***p*-Dimethoxy**benzene



4-*tert*-Butoxy-1-cyclohexene

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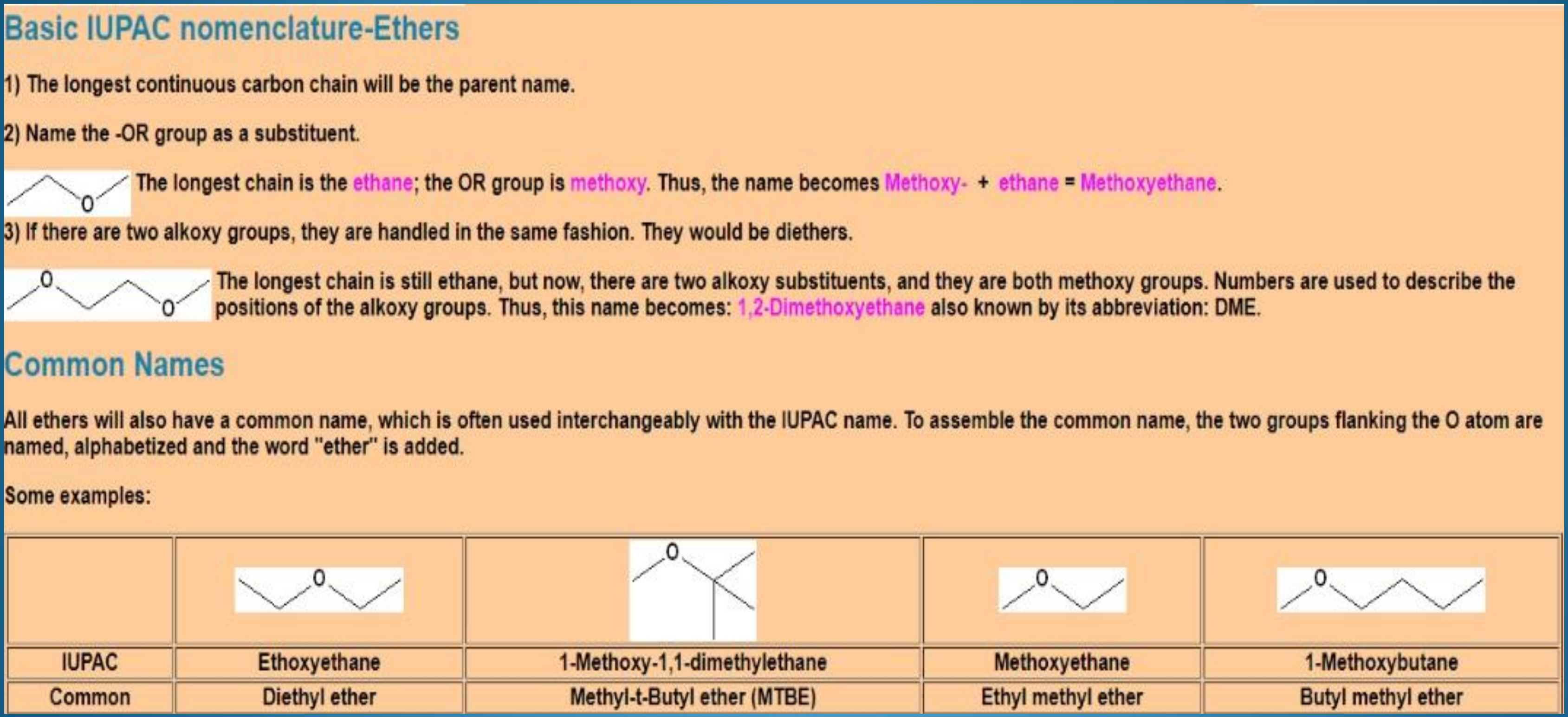


Basic IUPAC nomenclature-Ethers

1) The longest continuous carbon chain will be the parent name.

2) Name the -OR group as a substituent.

The longest chain is the ethane; the OR group is methoxy. Thus, the name becomes Methoxy- + ethane = Methoxyethane.

3) If there are two alkoxy groups, they are handled in the same fashion. They would be diethers.

The longest chain is still ethane, but now, there are two alkoxy substituents, and they are both methoxy groups. Numbers are used to describe the positions of the alkoxy groups. Thus, this name becomes: 1,2-Dimethoxyethane also known by its abbreviation: DME.

Common Names

All ethers will also have a common name, which is often used interchangeably with the IUPAC name. To assemble the common name, the two groups flanking the O atom are named, alphabetized and the word "ether" is added.

Some examples:

IUPAC	Ethoxyethane	1-Methoxy-1,1-dimethylethane	Methoxyethane	1-Methoxybutane
Common	Diethyl ether	Methyl-t-Butyl ether (MTBE)	Ethyl methyl ether	Butyl methyl ether

Preparation of Ethers

1. Dehydation of Alcohols: Symmetrical ethers are prepared by heating an excess of alcohol with Conc. H_2SO_4 at 140^0C.

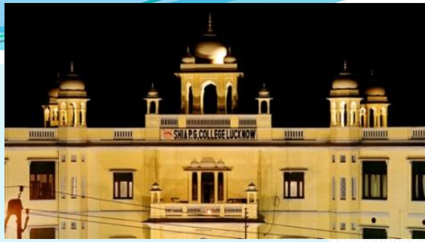
$$R—OH + H—OR \xrightarrow[140^0C]{H_2SO_4} R—O—R + H_2O$$

Alcohol (2 molecules) Ether

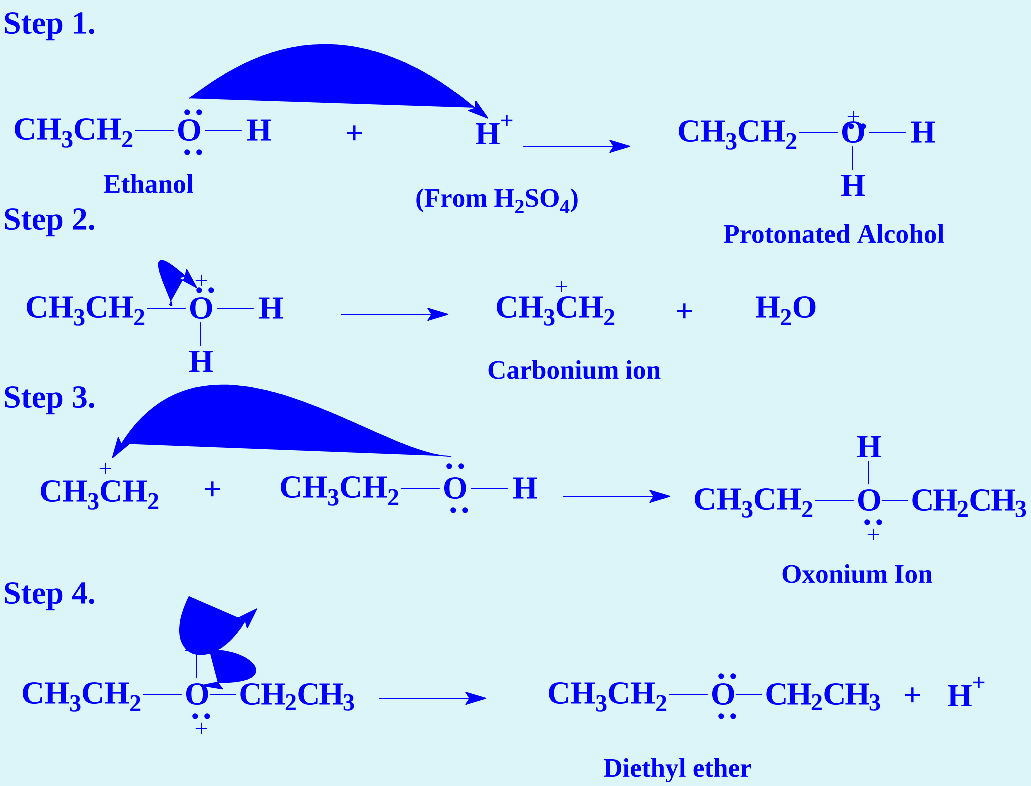
$$C_2H_5—OH + H—OC_2H_5 \xrightarrow[140^0C]{H_2SO_4} C_2H_5—O—C_2H_5 + H_2O$$

Ethanol Ethanol Diethyl Ether

The starting alcohol in the above reaction must be primary and the rection temperature must be kept at 140^0C. This is because *alkene* formation is favored at high temperature and with secondary or tertiary alcohol.



Mechanism of dehydation of alcohols:



Step 1.

$CH_3CH_2-\ddot{\underset{\cdot\cdot}{O}}-H \quad + \quad H^+ \longrightarrow CH_3CH_2-\underset{\substack{|\\H}}{\overset{+}{O}}-H$

Ethanol

(From H_2SO_4)

Protonated Alcohol

Step 2.

$CH_3CH_2-\underset{\substack{|\\H}}{\overset{+}{\ddot{O}}}-H \longrightarrow CH_3\overset{+}{C}H_2 \quad + \quad H_2O$

Carbonium ion

Step 3.

$CH_3\overset{+}{C}H_2 \quad + \quad CH_3CH_2-\ddot{\underset{\cdot\cdot}{O}}-H \longrightarrow CH_3CH_2-\overset{\substack{H\\|}}{\underset{\substack{\cdot\cdot\\+}}{O}}-CH_2CH_3$

Oxonium Ion

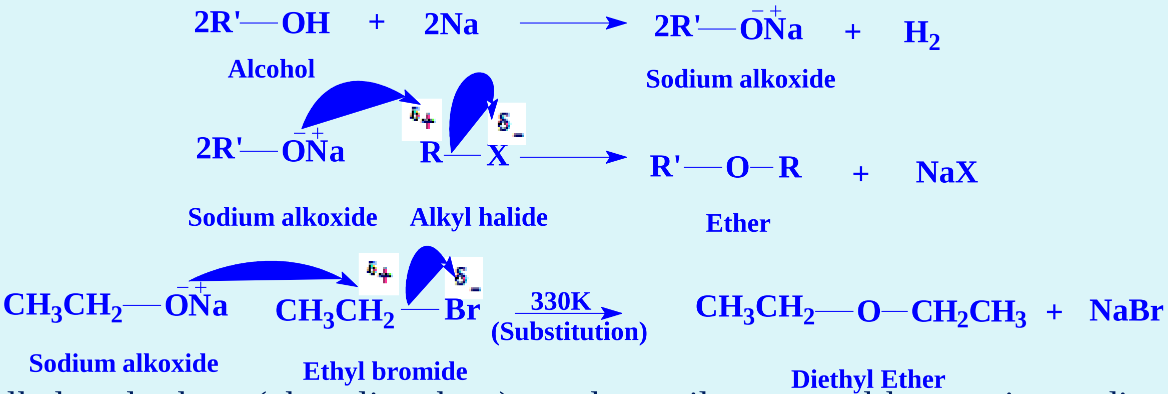
Step 4.

$CH_3CH_2-\overset{\substack{H\\|}}{\underset{\substack{\cdot\cdot\\+}}{O}}-CH_2CH_3 \longrightarrow CH_3CH_2-\ddot{\underset{\cdot\cdot}{O}}-CH_2CH_3 \quad + \quad H^+$

Diethyl ether

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.

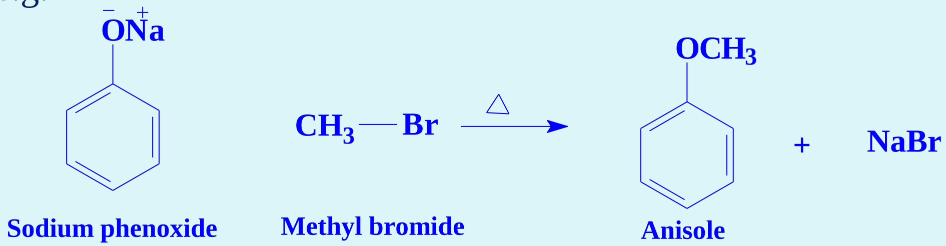


$$\underset{\text{Alcohol}}{2R'{-}OH} + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2R'{-}\overset{-}{O}\overset{+}{Na}} + H_2$$

$$\underset{\text{Sodium alkoxide}}{2R'{-}\overset{-}{O}\overset{+}{Na}} \quad \underset{\text{Alkyl halide}}{\overset{\delta+}{R}{-}\overset{\delta-}{X}} \longrightarrow \underset{\text{Ether}}{R'{-}O{-}R} + NaX$$

$$\underset{\text{Sodium alkoxide}}{CH_3CH_2{-}\overset{-}{O}\overset{+}{Na}} \quad \underset{\text{Ethyl bromide}}{CH_3\overset{\delta+}{CH_2}{-}\overset{\delta-}{Br}} \xrightarrow[\text{(Substitution)}]{330K} \underset{\text{Diethyl Ether}}{CH_3CH_2{-}O{-}CH_2CH_3} + NaBr$$

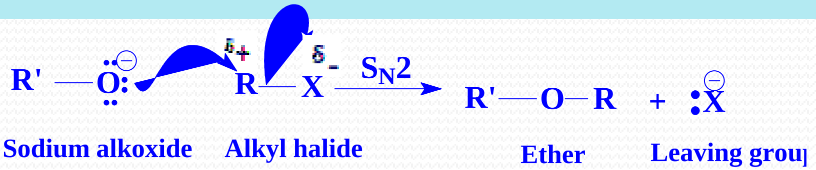
Similarly, alkyl aryl ethers (phenolic ethers) can be easily prepared by treating sodium phonoxide with alkyl halides. For e.g.



$\overset{-}{O}\overset{+}{Na}$ (Sodium phenoxide) + $CH_3{-}Br$ (Methyl bromide) $\xrightarrow{\triangle}$ OCH_3 (Anisole) + $NaBr$

Mechanism of Williamson synthesis:

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



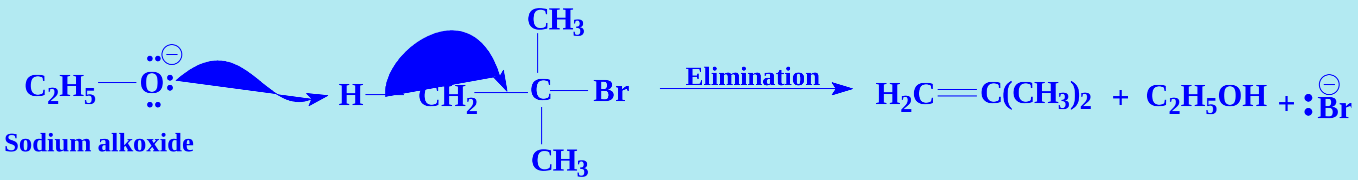
$$R'-\ddot{O}:^{\ominus} + \overset{\delta+}{R}-\overset{\delta-}{X} \xrightarrow{S_N2} R'-O-R + :X^{\ominus}$$

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.

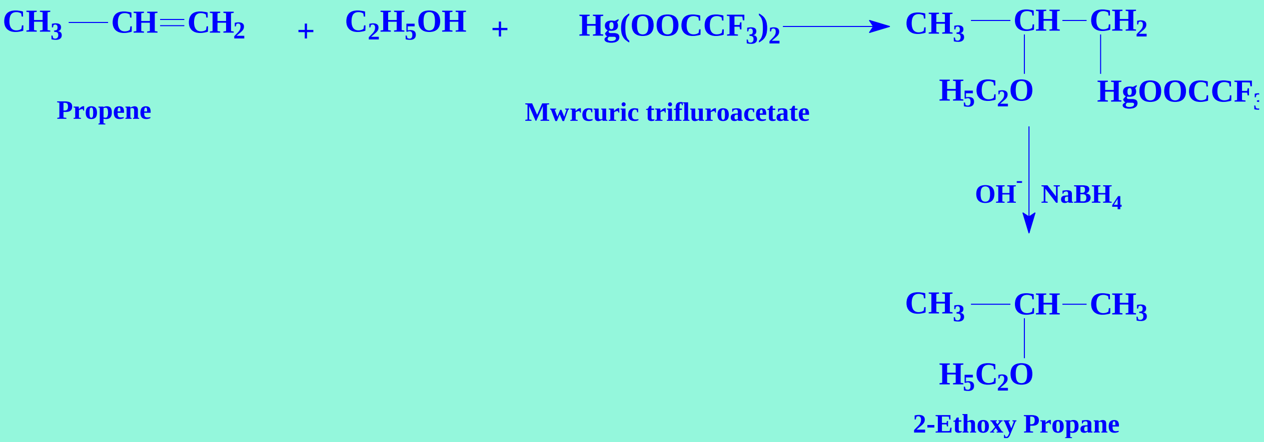
The primary alkyl halide (C_2H_5Br) as substrate is preferable than tert-alkyl halides [$(CH_3)_3C-Br$] as the substrate, since the latter halide is prone to elimination.



$$C_2H_5-\ddot{O}:^{\ominus} + H-CH_2-C(CH_3)_2-Br \xrightarrow{\text{Elimination}} H_2C=C(CH_3)_2 + C_2H_5OH + :Br^{\ominus}$$

Preparation of Ethers

3. Alkoxymercuration-demercuration:: In this method alkenes react with mercuric trifluoroacetate in the presence of an alcohol , followed by reduction with $NaBH_4$ in basic conditions gives ethers. The reaction is *Makovnikov's* addition of alcohols to alkenes.



$$CH_3-CH=CH_2 + C_2H_5OH + Hg(OOCCF_3)_2 \longrightarrow \underset{H_5C_2O}{\underset{|}{CH_3-CH}}-\underset{HgOOCCF}{\underset{|}{CH_2}} \xrightarrow{OH^-\ NaBH_4} \underset{H_5C_2O}{\underset{|}{CH_3-CH}}-CH_3$$

Propene

Mwrcuric trifluroacetate

2-Ethoxy Propane

The reaction has advantages over Williamson's synthesis:

- ✓ **High yield of ethers**
- ✓ **No rearrangement**
- ✓ **No Competing elimination reactions**

Preparation of Ethers

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

$$R-OH + CH_2N_2 \xrightarrow{HBF_4} R-O-CH_3 + N_2$$

$$CH_3CH_2-OH + CH_2N_2 \xrightarrow{HBF_4} CH_3CH_2-O-CH_3 + N_2$$

Ethyl methyl ether

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

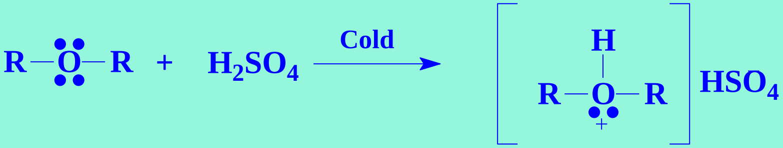
$$CH_3CH_2-Cl + Ag_2O + Cl-CH_2CH_3 \xrightarrow{\Delta} CH_3CH_2-O-CH_2CH_3 + 2AgCl$$

Ethyl chloride   Ethyl chloride   Diethyl ether

Chemical Reactions of Ethers

A. Reactions of the ethereal oxygen:

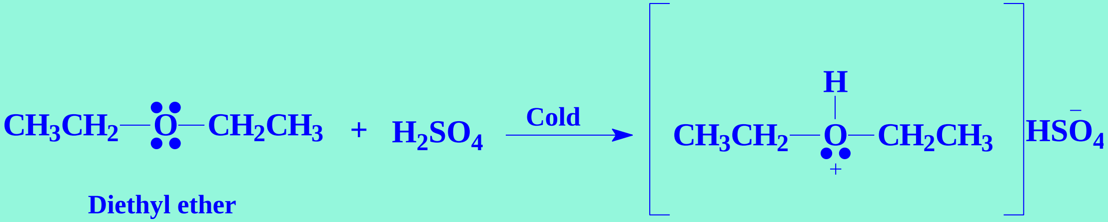
1. **Action of concentrated acids:** Due to the presence of two loan pairs of electrons on oxygen, ether behave as ***Lewis bases*** and thus react with cold H_2SO_4 or HCl to give **Oxonium salts**.



$$R-\ddot{\underset{\cdot\cdot}{O}}-R + H_2SO_4 \xrightarrow{\text{Cold}} \left[R-\underset{+}{\overset{H}{\overset{|}{\ddot{O}}}}-R\right]HSO_4$$

Ether

An oxonium salt



$$CH_3CH_2-\ddot{\underset{\cdot\cdot}{O}}-CH_2CH_3 + H_2SO_4 \xrightarrow{\text{Cold}} \left[CH_3CH_2-\underset{+}{\overset{H}{\overset{|}{\ddot{O}}}}-CH_2CH_3\right]H\overset{-}{S}O_4$$

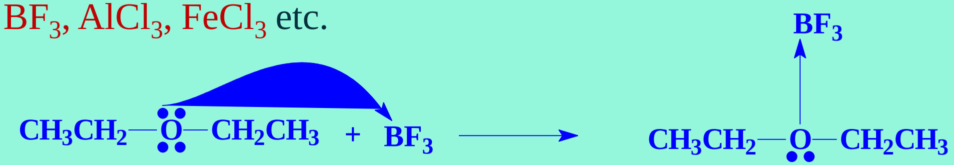
Diethyl ether

Oxonium salt of diethyl ether

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 BF_3, $AlCl_3$, $FeCl_3$ etc.



$$CH_3CH_2-\ddot{\underset{\cdot\cdot}{O}}-CH_2CH_3 + BF_3 \longrightarrow CH_3CH_2-\underset{\cdot\cdot}{\overset{\overset{BF_3}{\uparrow}}{O}}-CH_2CH_3$$

Diethyl ether

Boron trifluoride etherate

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.

$$R-\ddot{\underset{\cdot\cdot}{O}}-R' + HX \xrightarrow{373K} R-OH + R'X$$

Ether

Alcohol

Alkyl halide

$$CH_3CH_2-\ddot{\underset{\cdot\cdot}{O}}-CH_2CH_3 + HI \xrightarrow{373K} CH_3CH_2-OH + CH_3CH_2-I$$

Diethyl ether

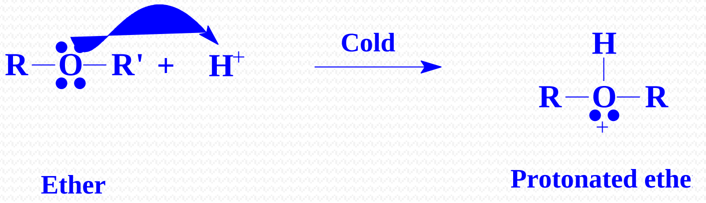
Ethanol

Ethyl halide

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

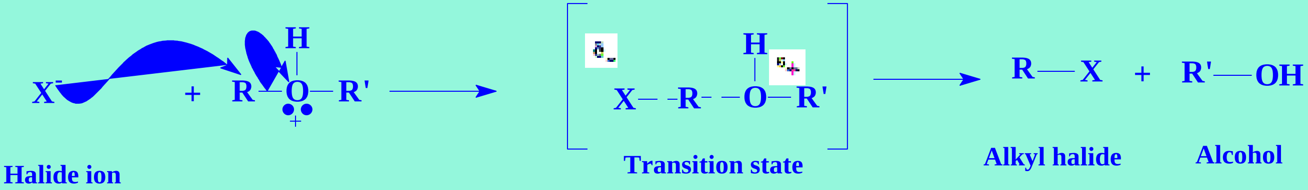
$$R-OH + HX \xrightarrow{373K} R-X + H_2O$$

Mechanism:

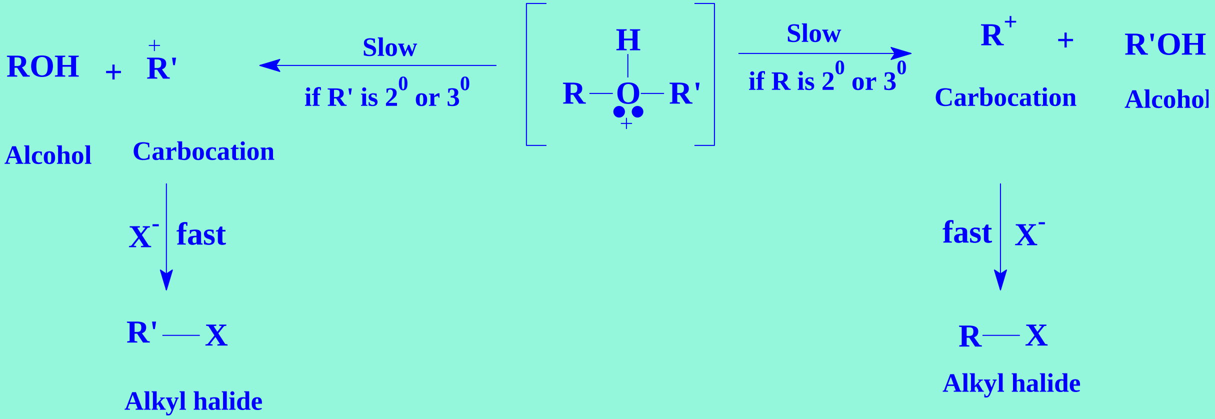


The protonated ether undergoes nucleophilic attack by the halide ion either by S_N1 or S_N2 mechanism depending upon the nature of the alkyl groups attached to ether. If the alkyl groups are

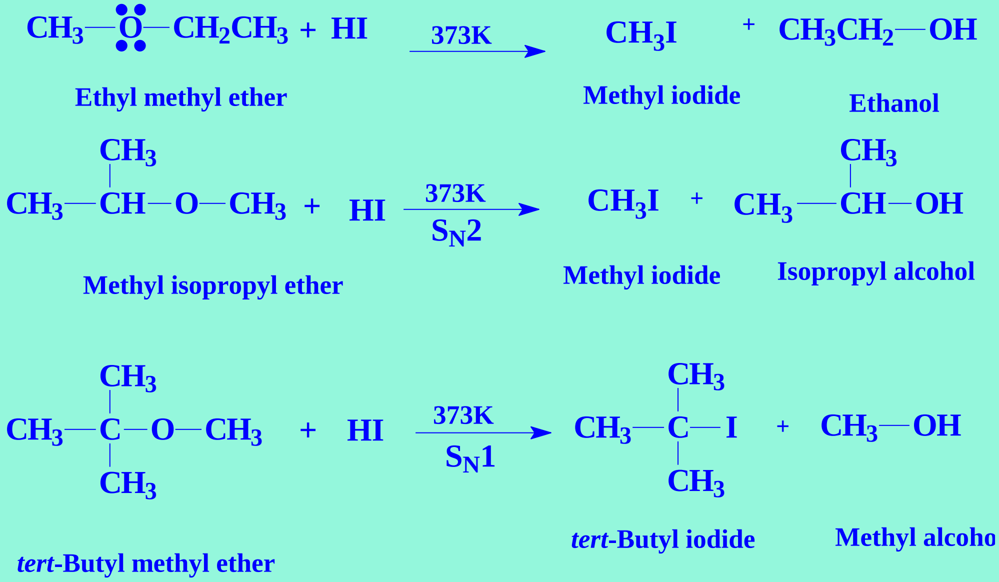
S_N2 mechanism:



S_N1 mechanism



Side of cleavage:



$$CH_3-\ddot{\underset{\cdot\cdot}{O}}-CH_2CH_3 + HI \xrightarrow{373K} CH_3I + CH_3CH_2-OH$$

Ethyl methyl ether Methyl iodide Ethanol

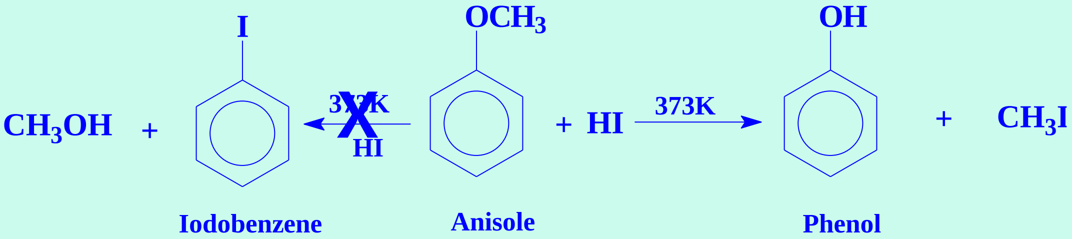
$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-O-CH_3 + HI \xrightarrow[S_N2]{373K} CH_3I + CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-OH$$

Methyl isopropyl ether Methyl iodide Isopropyl alcohol

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-O-CH_3 + HI \xrightarrow[S_N1]{373K} CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-I + CH_3-OH$$

tert-Butyl methyl ether *tert*-Butyl iodide Methyl alcoho

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. $AgNO_3$ to form AgI ppt.

(a) $ROCH_3 + HI \longrightarrow ROH + CH_3I$

$CH_3I + AgNO_3 \longrightarrow CH_3NO_3 + \underset{\text{ppt}}{AgI\downarrow}$

(b) $ROC_2H_5 + HI \longrightarrow ROH + C_2H_5I$

$C_2H_5I + AgNO_3 \longrightarrow C_2H_5NO_3 + \underset{\text{ppt}}{AgI\downarrow}$

Calculation of -OCH_3 Group
Wt. of samle taken = W_1 gm
Wt. of AgI formed = W_2 gm
1 mole of AgI ≡ one OCH_3 group
234 gm of AgI ≡ 31 gm of CH_3 group
So % of –OCH_3 group ≡

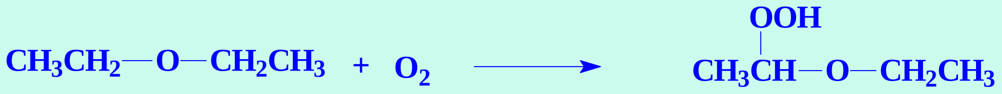
$$\frac{31}{234} \times \frac{W_2}{W_1} \times 100$$

Calculation of -OC_2H_5 Group
1 mole of AgI = one -OC_2H_5 group
234 gm of AgI = 45 gm of -OC_2H_5 group–OCH_3
So % of -OC_2H_5 group ≡

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

C. Reaction involving the alkyl group:

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

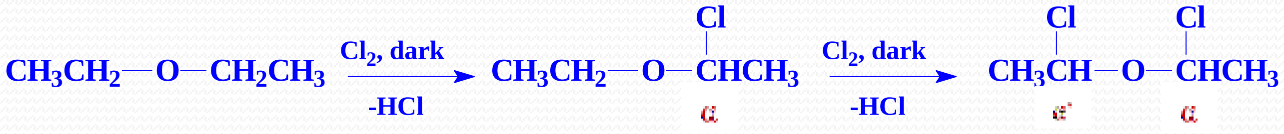


$$CH_3CH_2{-}O{-}CH_2CH_3 + O_2 \longrightarrow CH_3\overset{OOH}{\overset{|}{C}H}{-}O{-}CH_2CH_3$$

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.

2. Halogenation: When ethers are treated with Cl_2 or Br_2 in the dark, substitution products are obtained. The extent of the substitution depends upen the reaction conditions. *for e.g.*, diethyl ether reacts with chlorine in the dark to give α,α'-dichlorodiethyl ether.

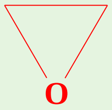


$$CH_3CH_2-O-CH_2CH_3 \xrightarrow[-HCl]{Cl_2,\ dark} CH_3CH_2-O-\underset{\alpha}{\overset{Cl}{C}}HCH_3 \xrightarrow[-HCl]{Cl_2,\ dark} CH_3\underset{\alpha'}{\overset{Cl}{C}}H-O-\underset{\alpha}{\overset{Cl}{C}}HCH_3$$

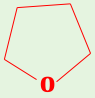
Diethyl Ether α-chlorodiethyl ether α,α'-dichlorodiethyl ether

Epoxides

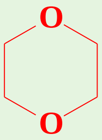
Three membered cyclic ethers are called epoxides also called alkylene oxides, epoxyalkanes or oxiranes.



Ethylene oxide



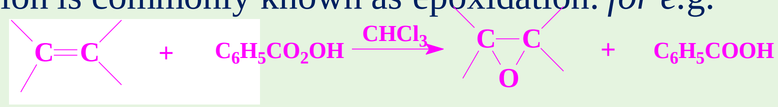
Tetrahydrofuran



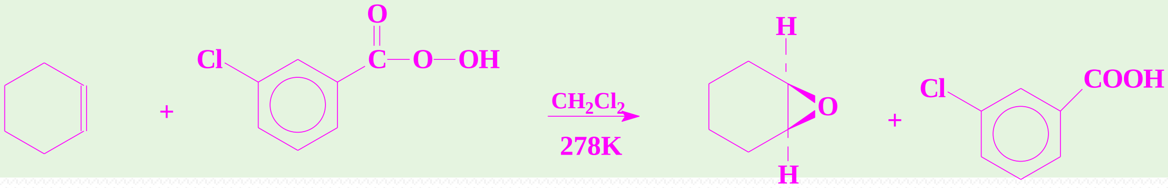
1, 4-Dioxane

Synthesis of epoxides:

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

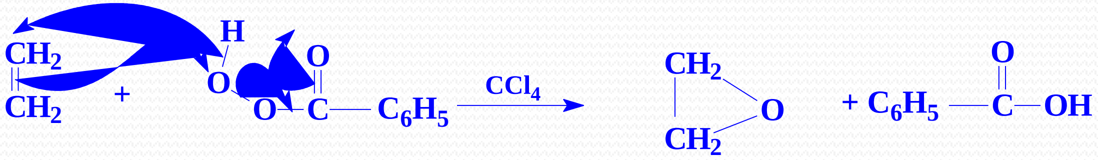


Alkene **Perbenzoic acid** **Epoxide** **Benzoic Acid**



Cyclohexene **m-chloroperoxy benzoic acid** **1,2-epoxycyclohexane**

Mechanism:



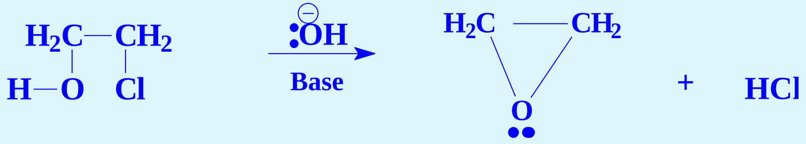
Ethylene

Peroxy benzoic acid

Ethylene epoxide

benzoic acid

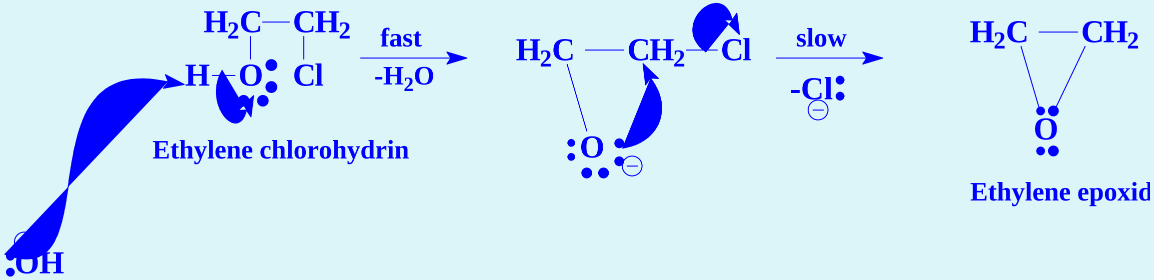
2. From Halohydrins: When halohydrins are treated with a base like NaOH or KOH, epoxide is formed with the elimination of HX. *for e.g.*



Ethylene chlorohydrin

Ethylene epoxide

Mechanism:



Ethylene chlorohydrin

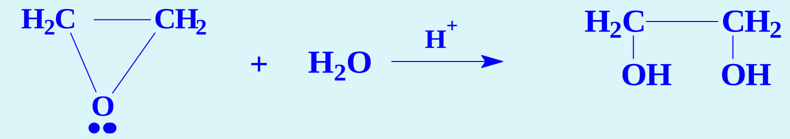
Base

Ethylene epoxid

Chemical Properties:

Epoxide ring has angle strain because the bond angle is about 60^0 much smaller than the tetrahedral bond angle of 109.5^0. As a result most of the epoxides reactions are ring opening reactions.

Acid catalysed ring opening: When an epoxide is treated with a nucleophile (H_2O, 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.

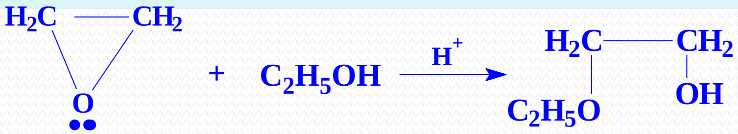


Ethylene epoxide

Ethylene glyco

Ethylene epoxide

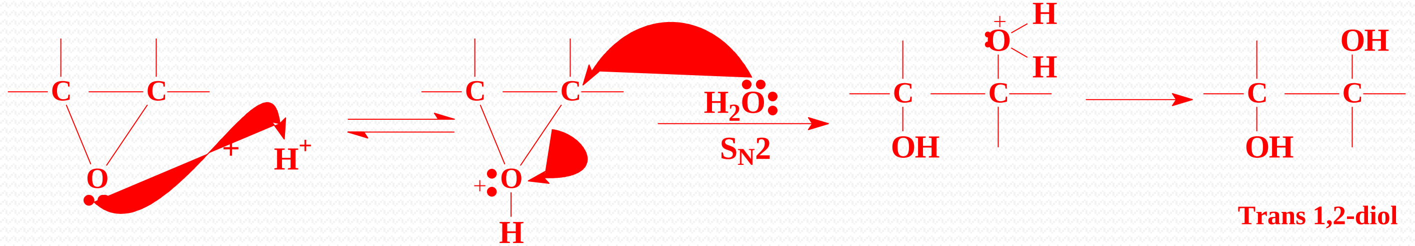
Ethylene bromohydri



Ethylene epoxide

2-Ethoxyethanol

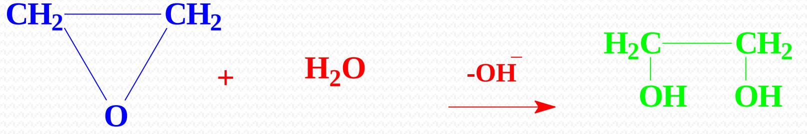
Mechanism:



Epoxide

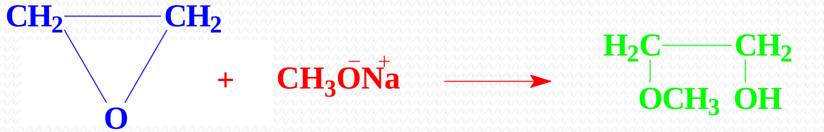
Protonated Epoxide

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



Ethylene epoxide

Ethylene glycol



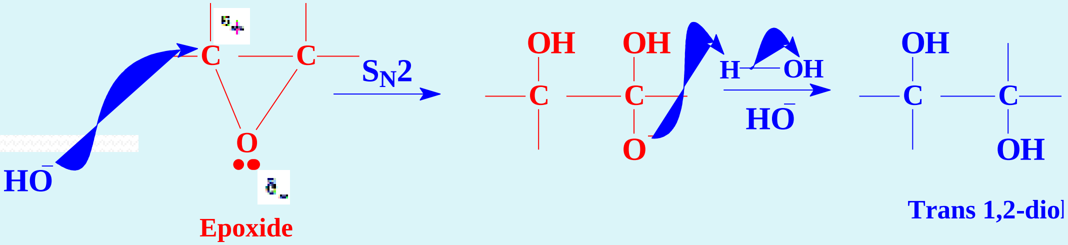
Ethylene epoxide

2-methoxyethanc

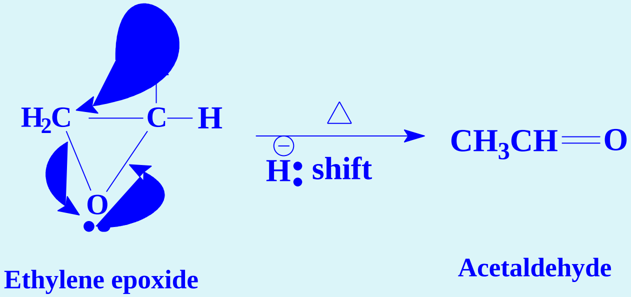
Ethylene epoxide

2-aminoethanol

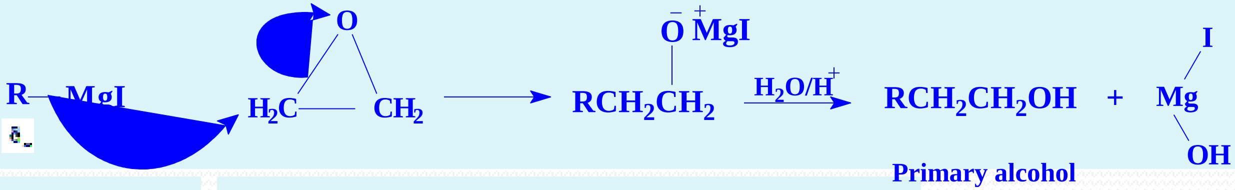
Mechanism:



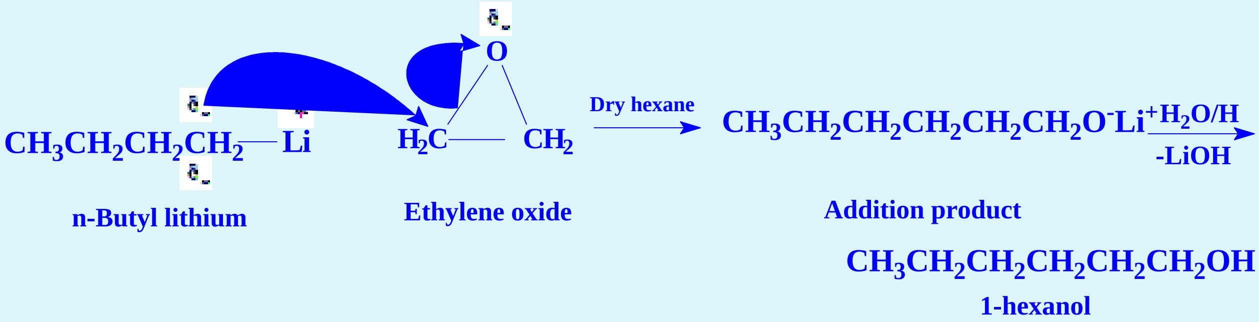
3. Molecular rearrangement: Ethylene oxide undergoes molecular rearrangement on heating to form acetaldehyde.



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:



$CH_3CH_2CH_2CH_2—Li$

n-Butyl lithium

$H_2C—CH_2$ (O)

Ethylene oxide

$\xrightarrow{\text{Dry hexane}}$ $CH_3CH_2CH_2CH_2CH_2CH_2O^-Li^+$ $\xrightarrow[\text{-LiOH}]{H_2O/H}$

Addition product

$CH_3CH_2CH_2CH_2CH_2CH_2OH$

1-hexanol