241 Chem

CH-4

Ethers and Epoxides

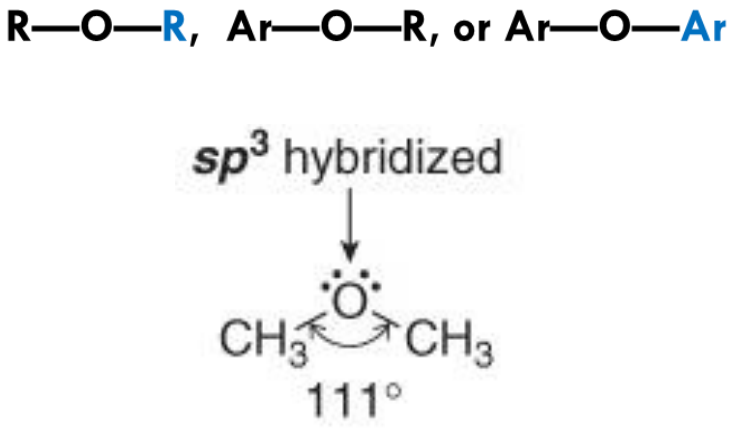
Learning Objectives

By the end of this chapter the student will Know:

- The structure of Ethers and Epoxides.
- The nomenclature of Ethers and Epoxides.
- The physical properties of Ethers.
- The different methods used in preparation of ethers and Epoxides
- The reactions of Ethers and Epoxides.

Structure of Ethers

- Ethers are organic derivatives of water, where alkyl groups replace both hydrogen atoms. Thus, ethers have two hydrocarbons bonded to an oxygen atom.
- The general formula for an ether is R-O-R`, where R and R` may be identical or different, and they may be alkyl or aryl groups



- The ether is classified as
  - A symmetrical ether , When the organic groups attached to the oxygen are identical.
  - An unsymmetrical ether , When the organic groups attached to the oxygen are different.

Nomenclature of Ethers

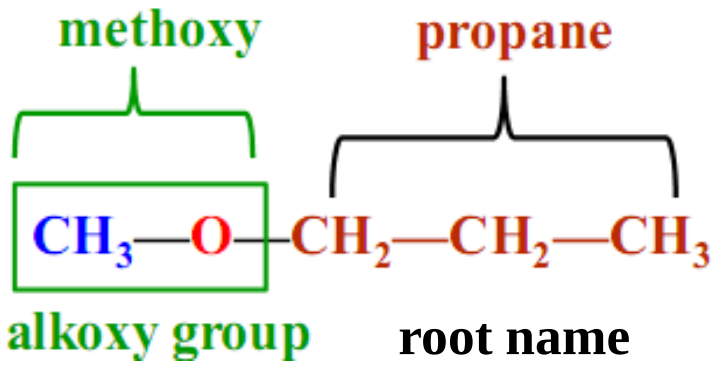
The common name

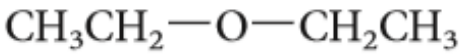
The common names of ethers are derived by naming the alkyl groups bonded to the oxygen then listing them in alphabetical order followed by the word "ether".

The IUPAC System

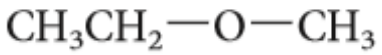
The shorter alkyl group and the oxygen are named as an alkoxy group attached to the longer alkane.

They are named as alkoxyalkanes

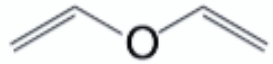




Common name: Diethyl ether
IUPAC name: Ethoxyethane

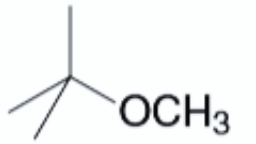


Ethyl methyl ether
Methoxyethane

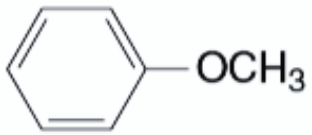


Divinyl ether
Vinyloxyethene

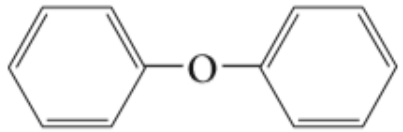
Allyl methyl ether
3-Methoxypropene



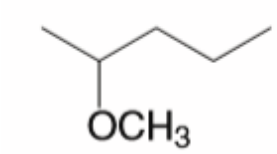
Common name: tert-Butyl methyl ether
IUPAC name: 2-Methoxy-2-methylpropane



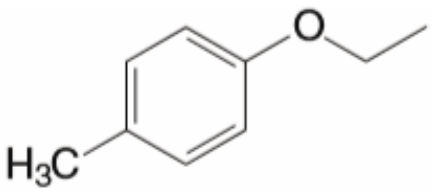
Methyl Phenyl ether (anisole)
Methoxy benzene



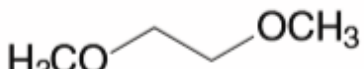
Diphenyl ether
Phenoxybenzene



2-Methoxypentane



1-Ethoxy-4-methylbenzene



1,2-Dimethoxyethane (DME)

Physical Properties of Ethers

- Ethers are colorless compounds with characteristic, relatively pleasant odors.

Boiling Points:

- They have lower boiling points than alcohols with an equal number of carbon atoms. Because of their structures (no O-H bonds), ether molecules cannot form hydrogen bonds with one another
- An ether has nearly the same boiling point as the corresponding hydrocarbon in which a -CH_2- group replaces the ether's oxygen.

Solubility in water

- Ethers are able to form hydrogen bonds with compounds such as water.
- Ethers have solubility in water that are similar to those of alcohols of the same molecular weight and that are very different from those of hydrocarbons.

	$CH_3CH_2OCH_2CH_3$	$CH_3CH_2CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2OH$
	Diethyl ether	Pentane	1-Butanol
Boiling point:	35°C	36°C	117°C
Solubility in water:	7.5 g/100 mL	Insoluble	9 g/100 mL

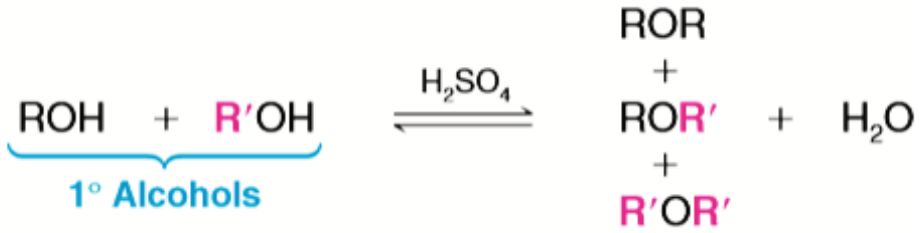
Preparation Of Ethers

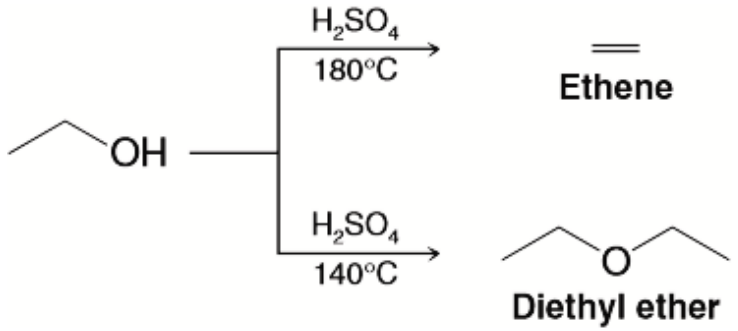
1. Dehydration of Alcohols
2. The Williamson Synthesis of Ethers
3. Alkoxymercuration-Demercuration

1. Dehydration of Alcohols

- Intermolecular dehydration of alcohols takes place in the presence of acid catalysts (H_2SO_4, H_3PO_4) under controlled temperature (140 °C).

- Intermolecular dehydration is not useful for the preparation of unsymmetrical ethers from primary alcohols because the reaction leads to a mixture of products:

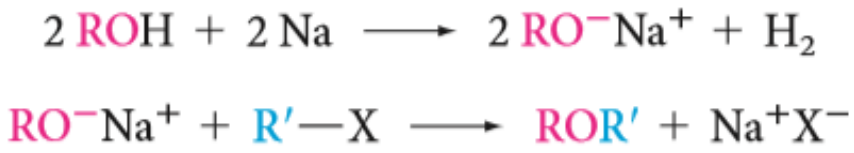




Preparation Of Ethers

2. The Williamson Synthesis of Ethers

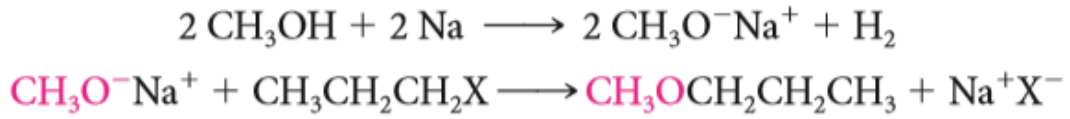
- This method is usually used for preparation of unsymmetrical ethers.



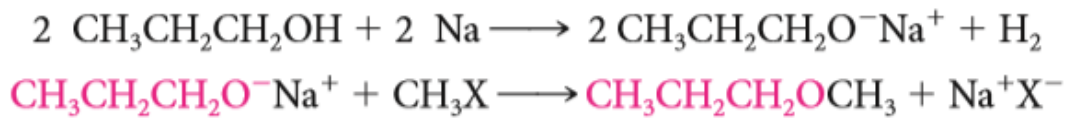
Nucleophilic Substitution Reaction

- The second step is an S_N2 reaction, it works best if R´ in the alkyl halide is primary and not well at all if R´ is tertiary.

$CH_3OCH_2CH_2CH_3$

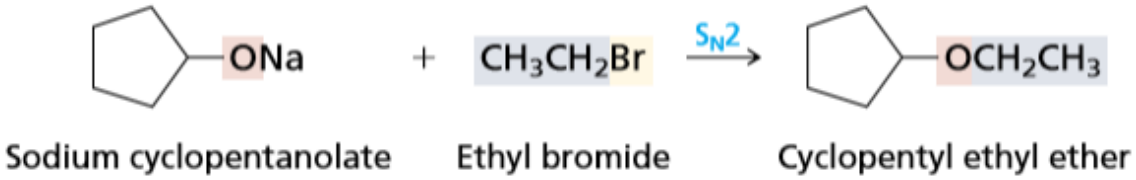


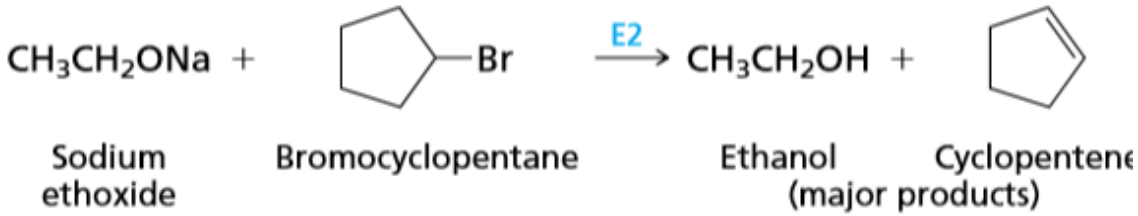
or



X is usually Cl, Br, or I.

CH_3CH_2O

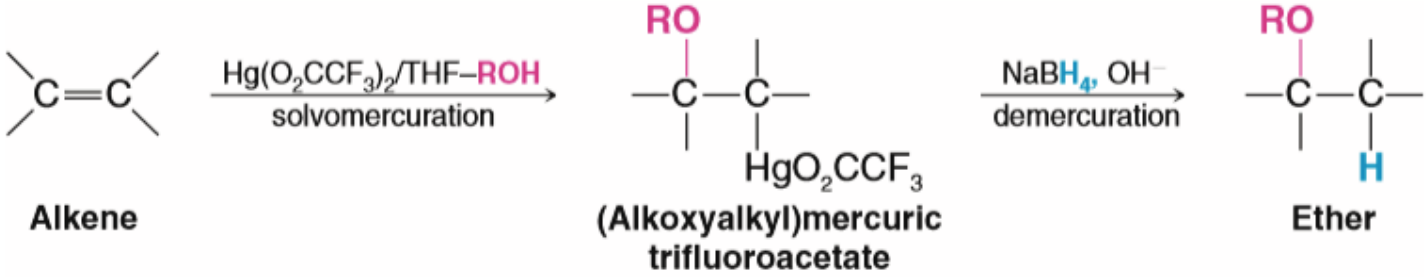


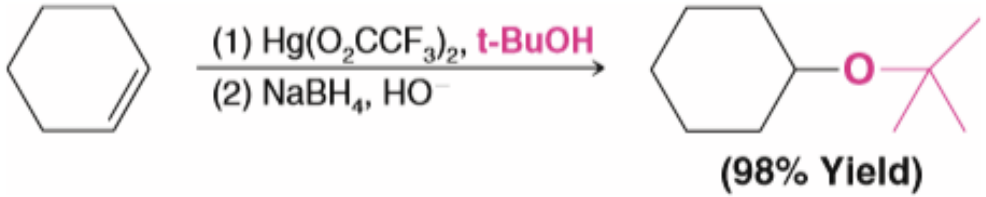


Preparation Of Ethers

3. Alkoxymercuration-Demercuration

- The reaction of an alkene with an alcohol in the presence of a mercury salt such as mercuric acetate $Hg(OAc)_2$ or mercuric trifluoroacetate $Hg(O_2CCF_3)_2$, in alcohol leads to an alkoxymercury intermediate, which on reaction with sodium borohydride $NaBH_4$ yields an ether.

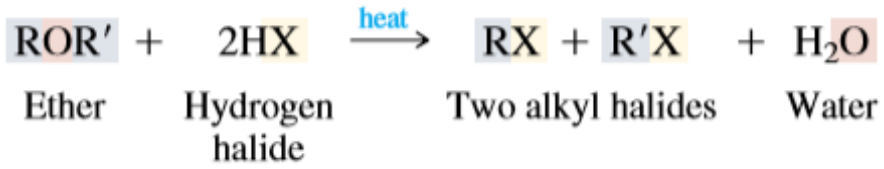




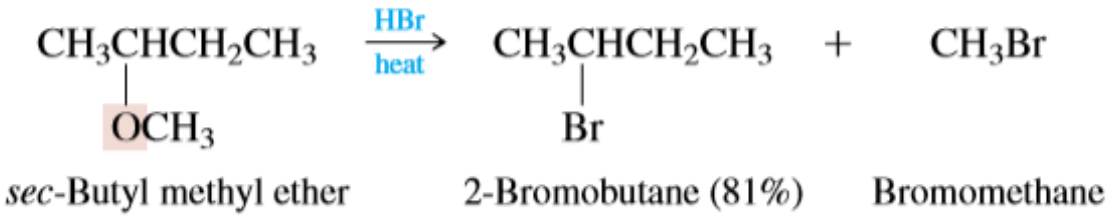
Reactions Of Ethers

- The ether linkage does not react with bases, reducing agents, oxidizing agents, or active metals.
- Ethers react only under strongly acidic conditions.

1- Cleavage of Ethers by Hot Concentrated Acids



X= Br and I



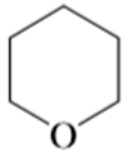
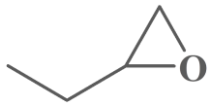
Structure of Epoxides (or Oxiranes)

- Epoxides (or oxiranes) are cyclic ethers with a three-membered ring containing one oxygen atom.

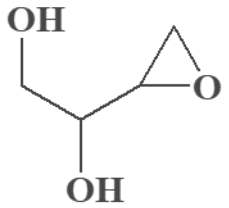
epoxide or oxirane

Nomenclature of Epoxides

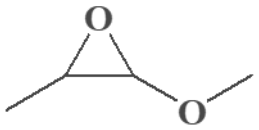
- Although cyclic ethers have IUPAC names, their common names are more widely used.
- IUPAC: prefix ox- shows oxygen in the ring the suffixes -irane, -etane, -olane, and -ane show three, four, five, and six atoms in a saturated ring.

					
Common name:	Oxirane (Ethylene oxide)	Oxetane	Oxolane (Tetrahydrofuran)	Oxane (Tetrahydropyran)	2-Ethyloxirane
IUPAC name:	Oxacyclopropane	Oxacyclobutane	Oxacyclopentane	Oxacyclohexane	

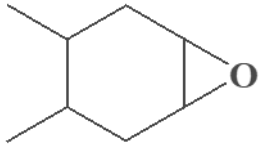
- One systematic method for naming epoxides is to name the rest of the molecule and use the term epoxy as a substituent, giving the numbers of the two carbon atoms bonded to the epoxide oxygen.



3,4-epoxy-1,2-butanediol



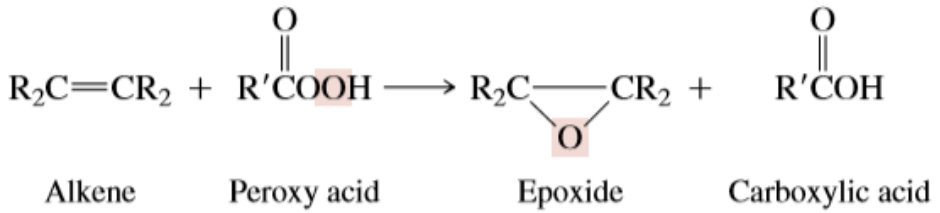
2-Methoxy-3-methyl-oxirane
1-methoxy1,2-epoxypropane

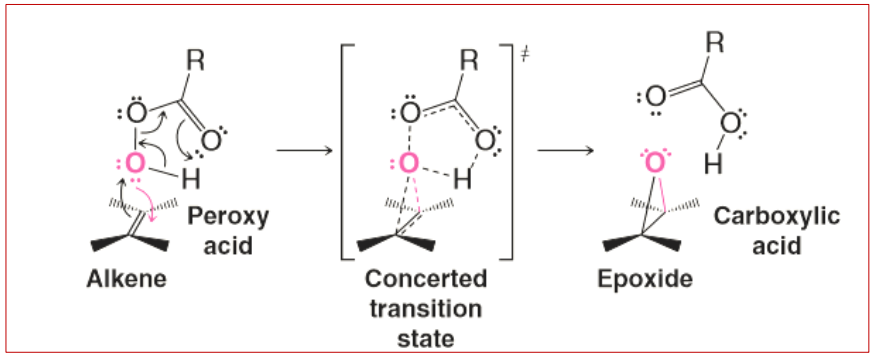


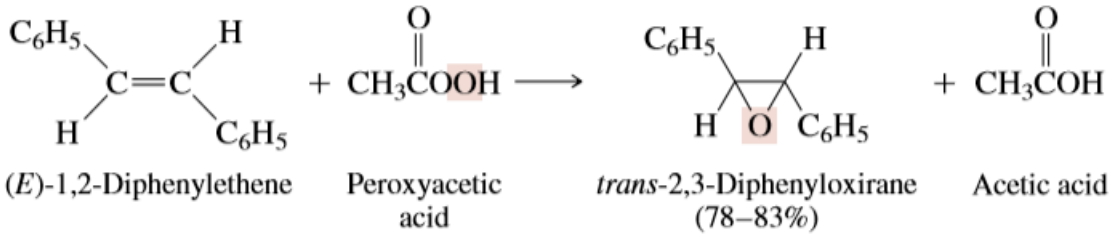
4,5-dimethyl-1,2-epoxycyclohexane

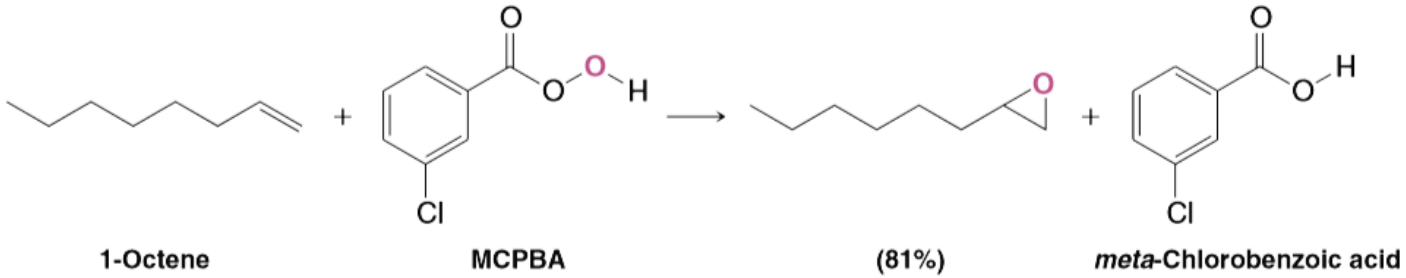
Preparation Of Epoxides

Epoxidation of alkenes by reaction with Peroxy acids (sometimes called peracid)







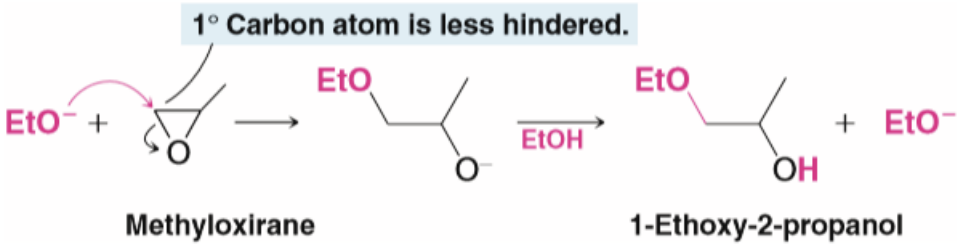


Reactions Of Epoxides

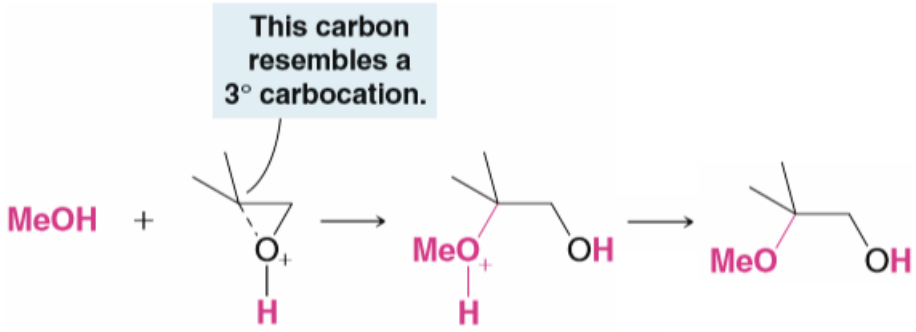
- Epoxides are much more reactive toward nucleophilic substitution than other ethers, because of the strain in the three-membered ring.
- Ring-Opening Reactions:
    1. Acid –Catalyzed ring opening reaction of epoxides in water to form glycols
    2. Acid –Catalyzed ring opening reaction of epoxides in alcohol to form alkoxy alcohols
    3. Acid –Catalyzed ring opening reaction of epoxides with a hydrohalic acid
    4. Ring opening reaction of epoxides with Grignard reagents to give longer alcohols

If the epoxide is unsymmetrical

- In the base-catalyzed ring opening, the nucleophile attacks primarily at the less substituted carbon atom (S_N2)

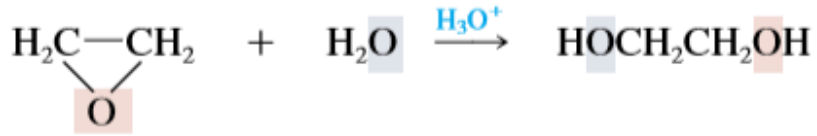


- In the acid-catalyzed ring opening, the nucleophile attacks primarily at the more substituted carbon atom (S_N1)

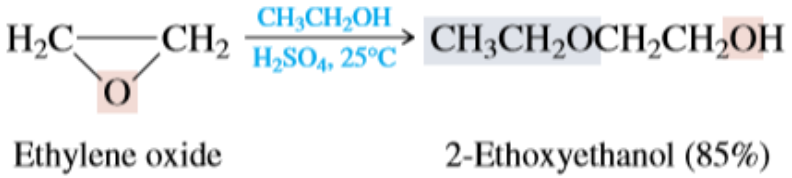


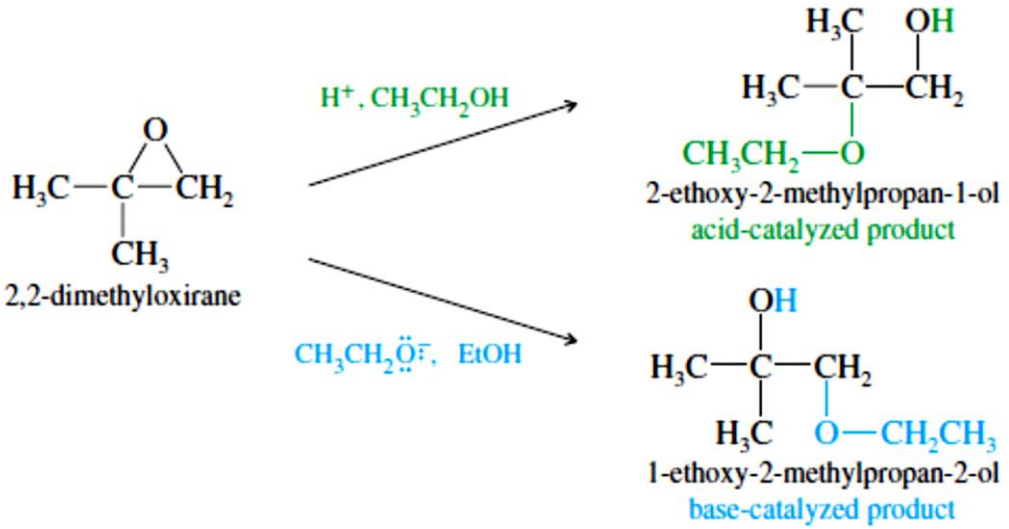
Reactions Of Epoxides

1- Acid –Catalyzed ring opening reaction of epoxides in water to form glycols.



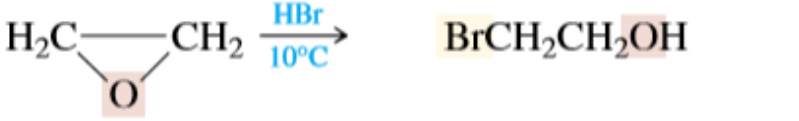
2- Acid –Catalyzed ring opening reaction of epoxides in alcohol to form alkoxy alcohols



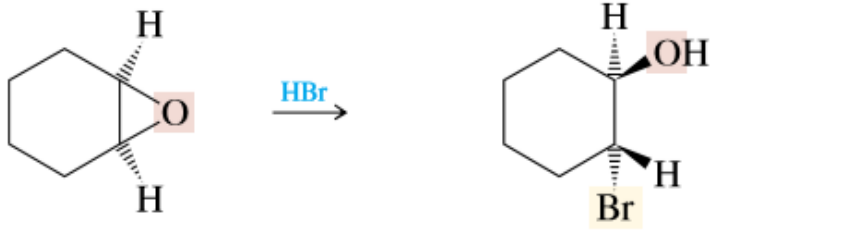


Reactions Of Epoxides

3- Acid –Catalyzed ring opening reaction of epoxides with a hydrohalic acid

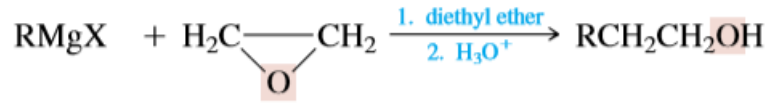


Ethylene oxide — 2-Bromoethanol (87–92%)

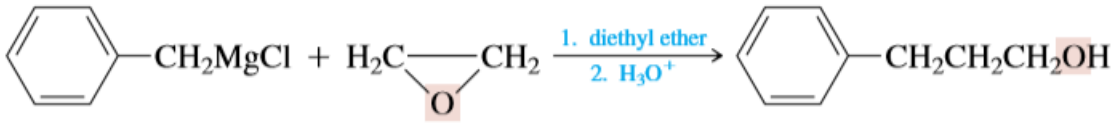


1,2-Epoxycyclohexane — *trans*-2-Bromocyclohexanol (73%)

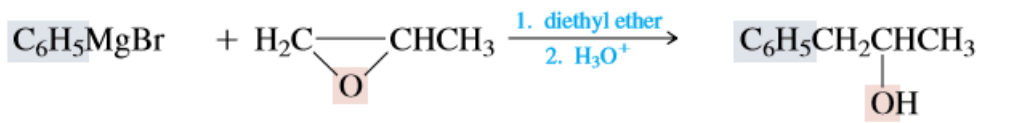
4- Ring opening of epoxides with Grignard reagents to give longer alcohols



Grignard reagent — Ethylene oxide — Primary alcohol



Benzylmagnesium chloride — Ethylene oxide — 3-Phenyl-1-propanol (71%)



Phenylmagnesium bromide — 1,2-Epoxypropane — 1-Phenyl-2-propanol (60%)