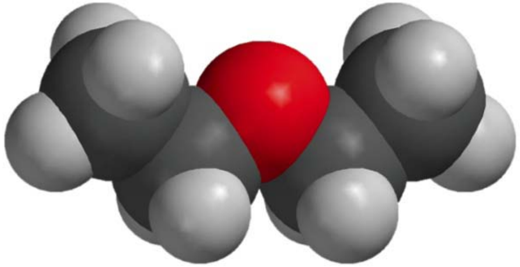
Chapter 8: Ethers and Epoxides



Diethyl ether in starting fluid

8.1 Nomenclature of Ethers

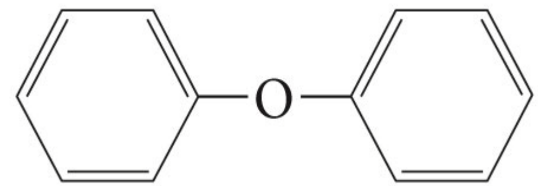
Ethers are usually named by giving the name of each alkyl or aryl group, in alphabetical order, followed by the word *ether.*

$CH_3CH_2—O—CH_3$

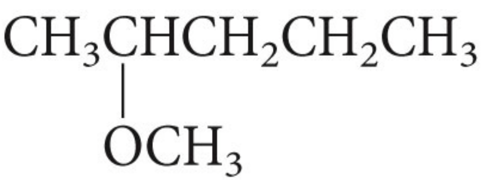
ethyl methyl ether

$CH_3CH_2—O—CH_2CH_3$

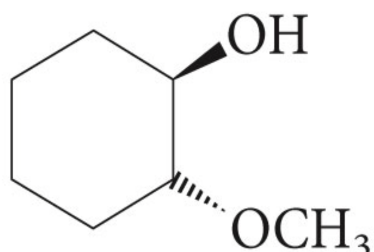
diethyl ether (the prefix *di*- is sometimes omitted)



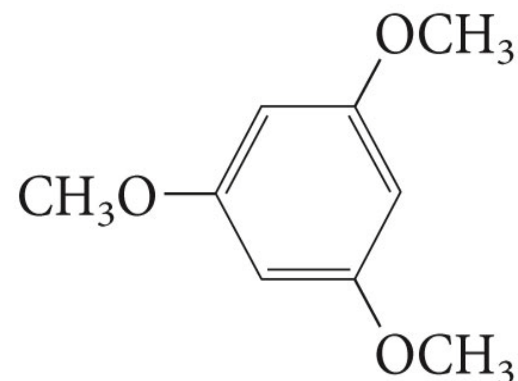
diphenyl ether



2-methoxypentane

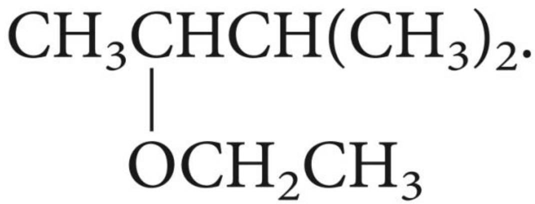


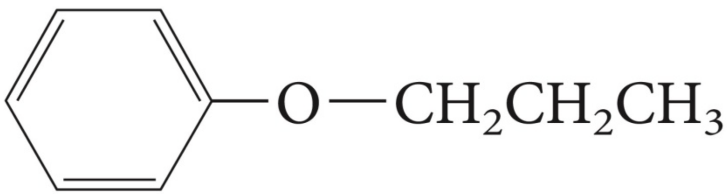
trans-2-methoxycyclohexanol



1,3,5-trimethoxybenzene

What are the correct names for the following ethers?





8.2 Physical Properties of Ethers

Ethers are colorless compounds with characteristic, relatively pleasant odors. They have lower boiling points (bp's) than alcohols with an equal number of carbon atoms. In fact, an ether has nearly the same bp as the corresponding hydrocarbon in which a -CH_2- group replaces the ether's oxygen.

Table 8.1 Properties of Alcohols, Ethers, and Hydrocarbons of Similar Molecular Weight

Compound	Formula	bp	mol wt	Water solubility (g/100 mL, 20°C)
1-butanol	$CH_3CH_2CH_2CH_2OH$	118°C	74	7.9
diethyl ether	$CH_3CH_2—O—CH_2CH_3$	35°C	74	7.5
pentane	$CH_3CH_2—CH_2—CH_2CH_3$	36°C	72	0.03

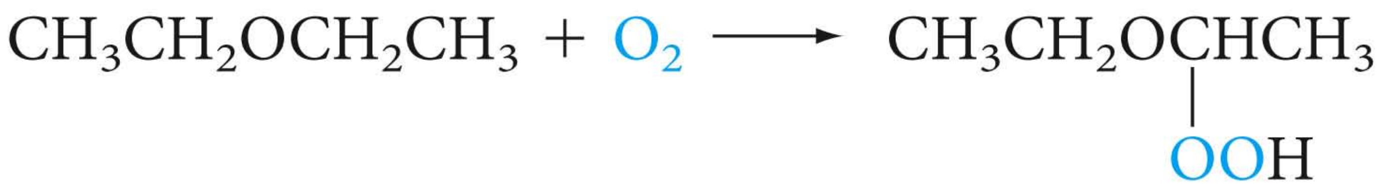
Because of their structures (no O-H bonds), ether molecules cannot form hydrogen bonds with one another. This is why they boil at much lower temperatures than their isomeric alcohols

Although ethers cannot form hydrogen bonds with one another, they do form hydrogen bonds with alcohols. This explains why ethers and alcohols are mutually soluble.

Ethers as Solvents

Ethers are relatively inert compounds. They do no usually react with dilute acids or bases or common oxidizing and reducing agents. They do not react with metallic sodium unlike alcohols. Their inert nature and the fact that most organic compounds are ether-soluble makes them excellent solvents for organic reactions.

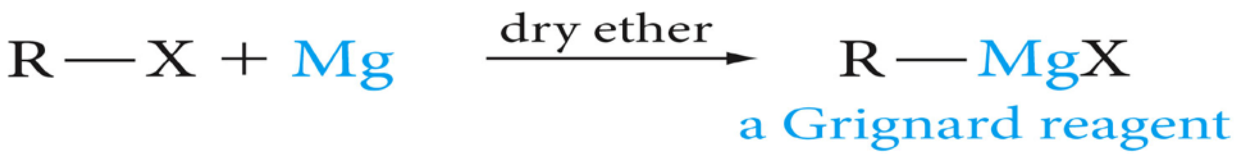
When ethers are exposed to air for a long time, they form peroxides and may result to explosives. $FeSO_4$ is usually added to destroy the peroxides.

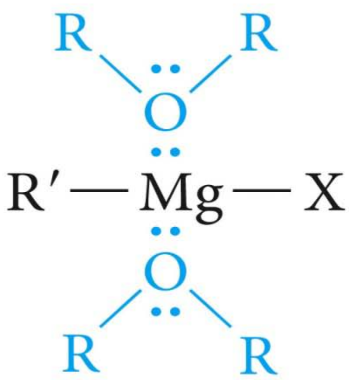


an ether hydroperoxide

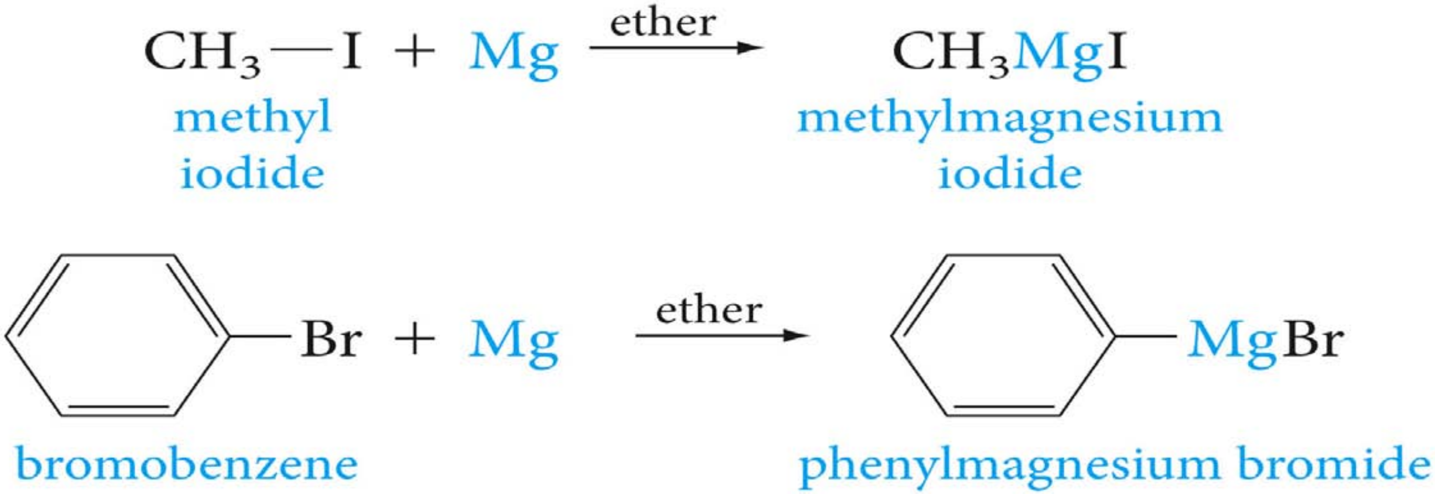
The Grignard Reagent : an Organometallic Compound

Pronounced greenyar(d)





Acting as a Lewis base, ether stabilizes a Grignard reagent.

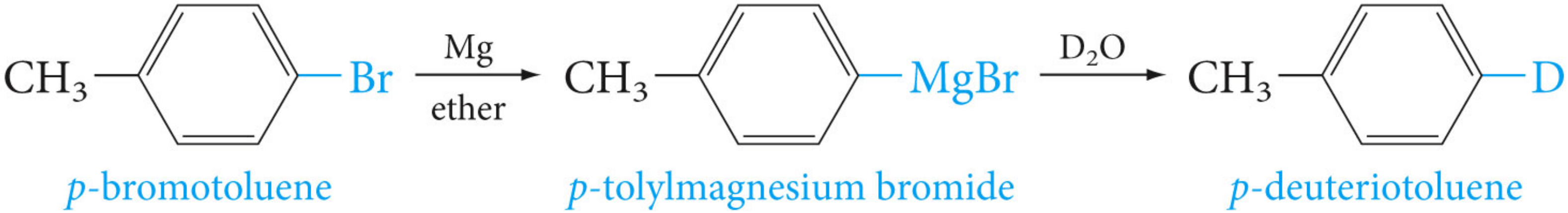


A carbanion is an alkyl or aryl group with a negatively charged carbon atom. Carbanions are strong bases

$$\overset{\delta-}{R}\text{—MgX} + \overset{\delta+}{H}\text{—OH} \longrightarrow \text{R—H} + Mg^{2+}(OH)^{-}X^{-}$$

stronger base | stronger acid | weaker acid | weaker base

Grignard reagent reaction with water



Reaction of Grignard reagent with water can be used to place deuterium isotopes by reacting them with heavy water (D_2O), where the deuterium substitutes the halogen

Question: Show how to prepare CH_3CHDCH_3 from $CH_2{=}CHCH_3$

$$CH_2{=}CHCH_3 \xrightarrow{HBr} CH_3\underset{\displaystyle |\atop \displaystyle Br}{C}HCH_3 \xrightarrow[\text{ether}]{Mg} CH_3\underset{\displaystyle |\atop \displaystyle MgBr}{C}HCH_3 \xrightarrow{D_2O} CH_3CHDCH_3$$

$$\overset{\delta+}{R}-\overset{\delta-}{X} + 2\,Li \xrightarrow{\text{ether}} \overset{\delta-}{R}-\overset{\delta+}{Li} + Li^+\,X^-$$

an alkyllithium

These compounds contain carbon- metal (lithium) bond. They react in a similar manner to Grignard reagents, and are very useful in synthesis

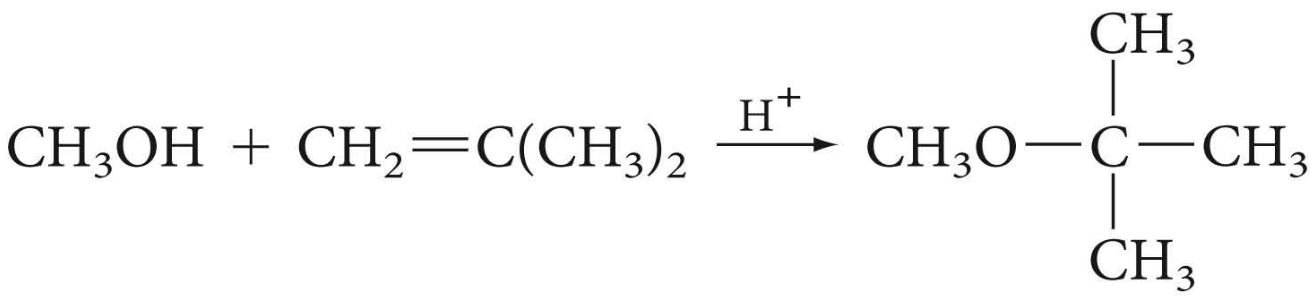
8.5 Preparation of Ethers

1. Commercial diethyl ether is prepared from ethanol and sulfuric acid.

$$CH_3CH_2OH + HOCH_2CH_3 \xrightarrow[140^\circ C]{H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$$

ethanol → diethyl ether

2. Methyl *tert* Butyl Ether (MTBE) has a high octane value of about 110, it is used as an octane number enhancer in unleaded gasoline. It is prepared by the acid-catalyzed addition of methanol to 2-methylpropene



methanol 2-methylpropene *t*-butyl methyl ether

Williamson Synthesis for unsymmetrical ether

This method has two:

The first step, an alcohol is converted to its alkoxide by treatment with a reactive metal (sodium or potassium) or metal hydride

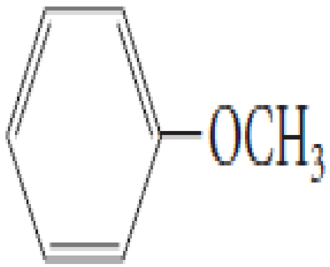
$$2\,ROH + 2\,Na \longrightarrow 2\,RO^{-}Na^{+} + H_2$$

In the second step, an S_N2 displacement is carried out between the alkoxide and an alkyl halide

$$RO^{-}Na^{+} + R'{-}X \longrightarrow ROR' + Na^{+}X^{-}$$

Since 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

PROBLEM 8.11 Write equations for the synthesis of the following ethers by the Williamson method:

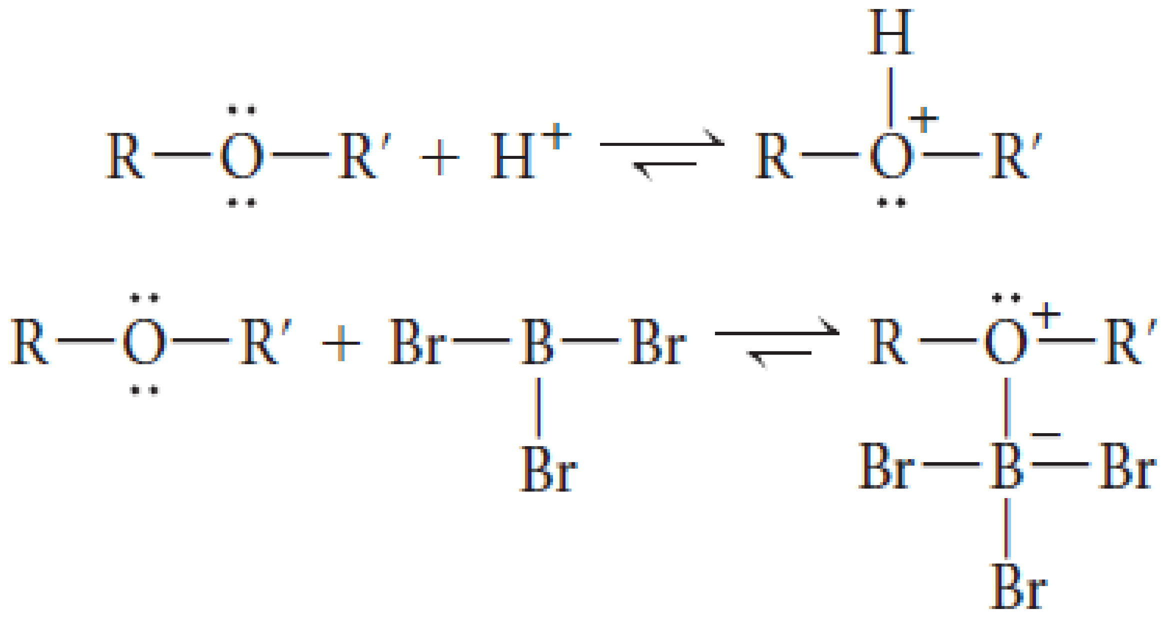
a. 

b. $(CH_3)_3COCH_3$

c. $C_6H_5CH_2OC(CH_3)_3$

8.6 Cleavage of Ethers

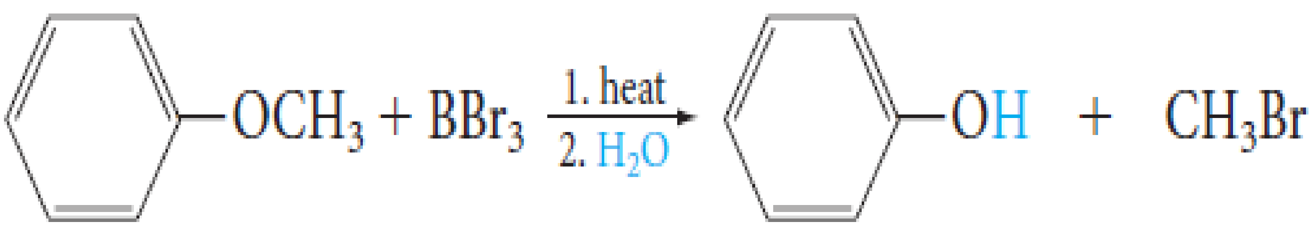
Ethers have unshared electron pairs on the oxygen atom and are therefore Lewis bases .They react with strong proton acids and with Lewis acids such as the boron halides.



These reactions are similar to the reaction of alcohols with strong acids . If the alkyl groups R and/or R´ are primary or secondary, the bond to oxygen can be broken by reaction with a strong nucleophile such as I^- or Br^- (by an S_N2 process)

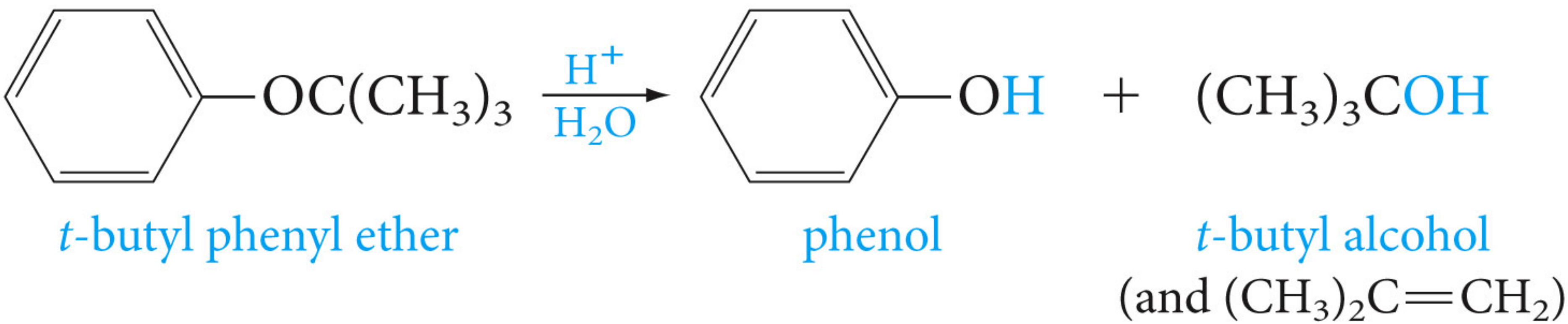
$$CH_3CH_2OCH(CH_3)_2 + HI \xrightarrow{\text{heat}} CH_3CH_2I + HOCH(CH_3)_2$$

ethyl isopropyl ether — ethyl iodide — isopropyl alcohol



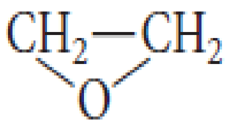
anisole — phenol — methyl bromide

If R or R' is tertiary, a strong nucleophile is not required since reaction will occur by an S_N1 (or E1) mechanism.

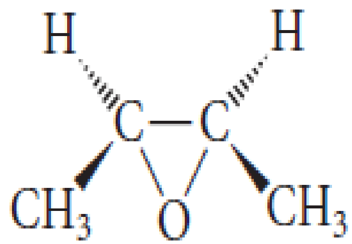


8.7 Epoxides (Oxiranes)

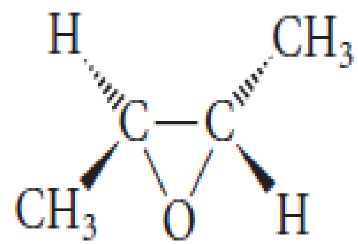
Epoxides (or oxiranes) are cyclic ethers with a three-membered ring containing one oxygen atom.



ethylene oxide
(oxirane)
bp 13.5°C

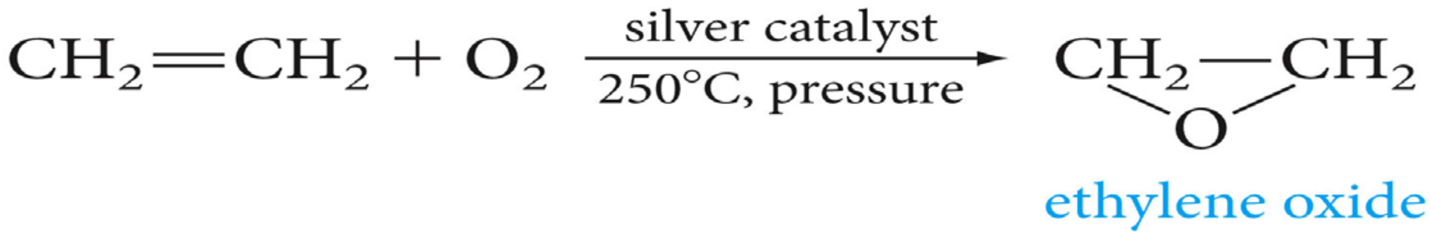


cis-2-butene oxide
(*cis*-2,3-dimethyloxirane)
bp 60°C

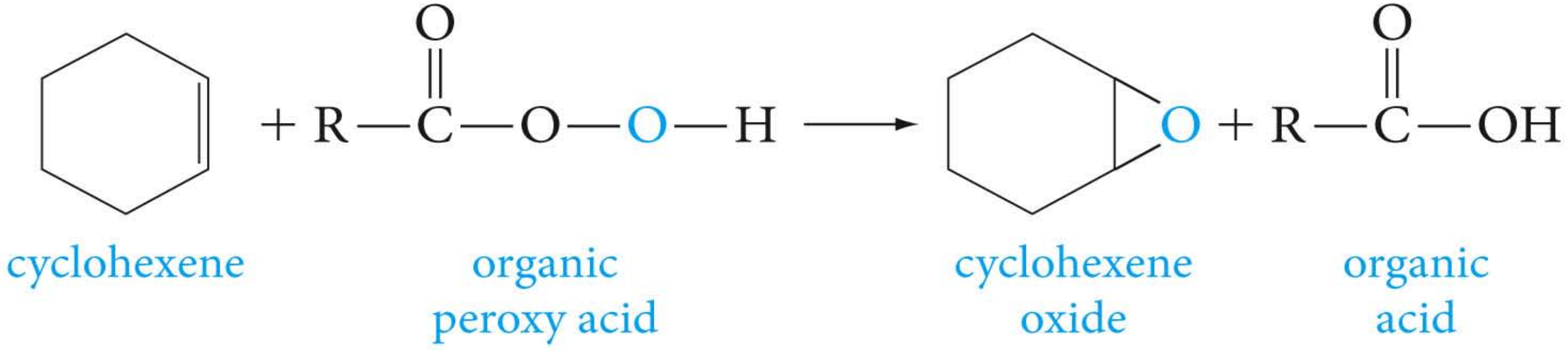


trans-2-butene oxide
(*trans*-2,3-dimethyloxirane)
bp 54°C

The most important commercial epoxide is ethylene oxide, produced by the silver-catalyzed air oxidation of ethylene.



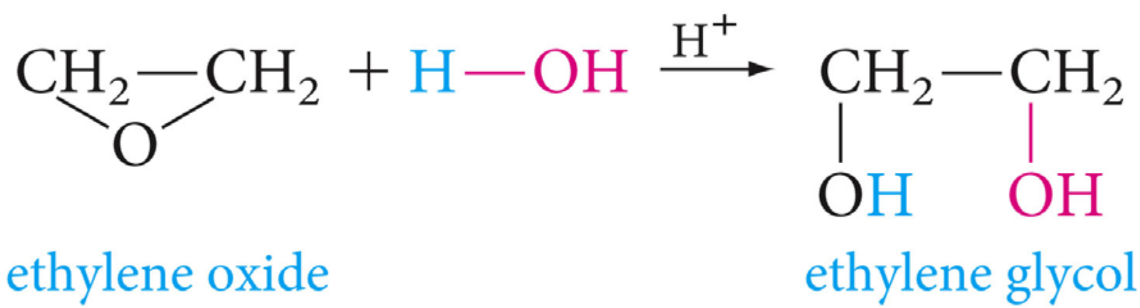
Other epoxides are usually prepared by the reaction of an alkene with an organic peroxyacid (often called simply a *peracid*)



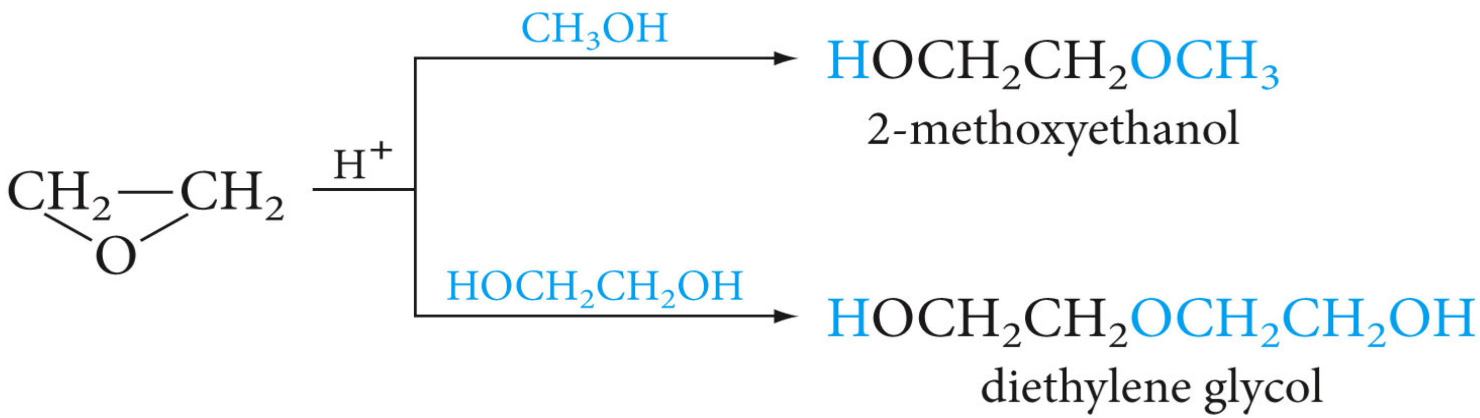
8.8 Reactions of Epoxides

Because of the strain in the three-membered ring, epoxides are much more reactive than ordinary ethers and give products in which the ring has opened.

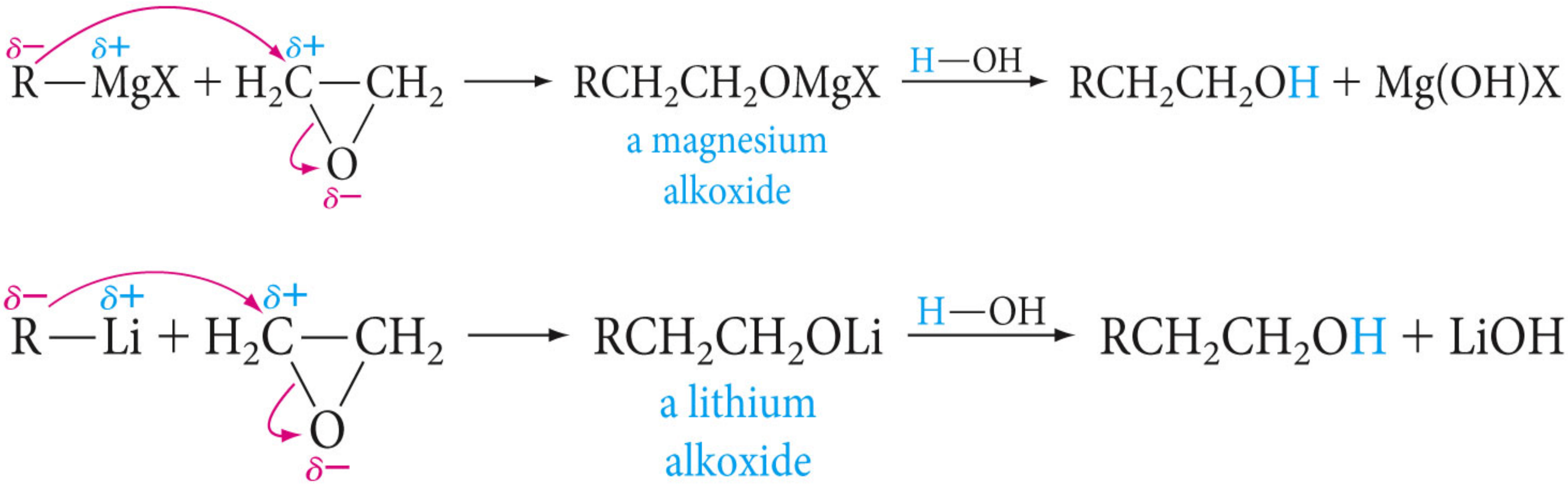
1. Reaction with water they undergo acid-catalyzed ring opening to give glycols.



2.Other nucleophiles add to epoxides in a similar way.



Grignard reagents and organolithium compounds are strong nucleophiles capable of opening the ethylene oxide (epoxide) ring. The initial product is a magnesium alkoxide of lithium alkoxide, but after hydrolysis, we obtain a primary alcohol with two carbon atoms than the organometallic reagent.



PROBLEM 8.15 Write an equation for the reaction between ethylene oxide and

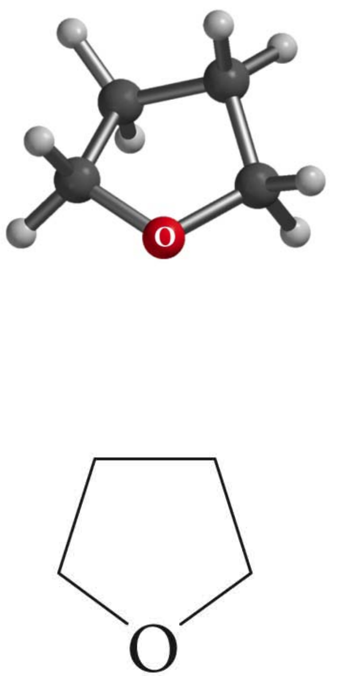
a. $CH_3CH_2CH_2CH_2MgCl$ followed by hydrolysis

b. $C_6H_5CH_2MgBr$ followed by hydrolysis

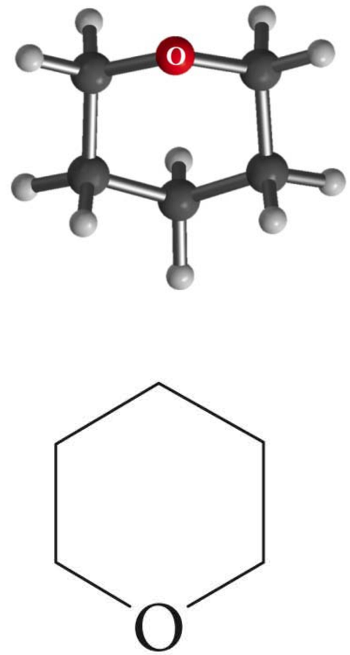
c. $H_2C{=}CHLi$ followed by hydrolysis

d. $CH_3C{\equiv}C^-Na^+$ followed by hydrolysis

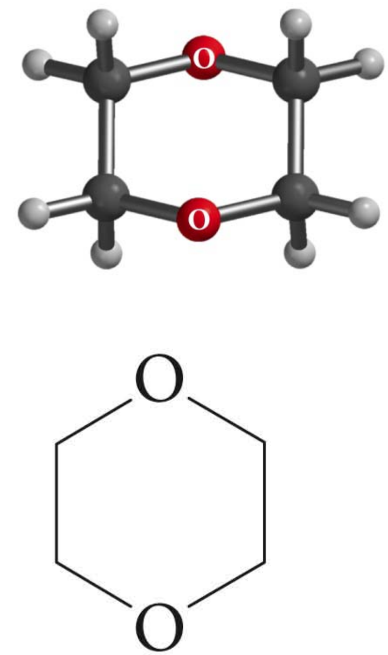
8.9 Cyclic Ethers



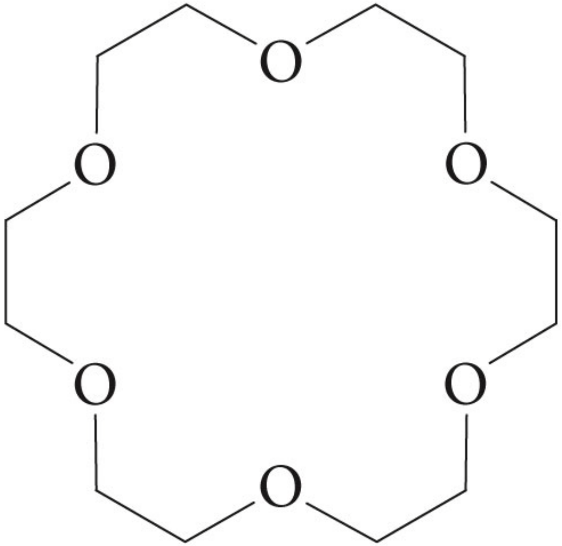
tetrahydrofuran
(oxolane)
bp 67°C



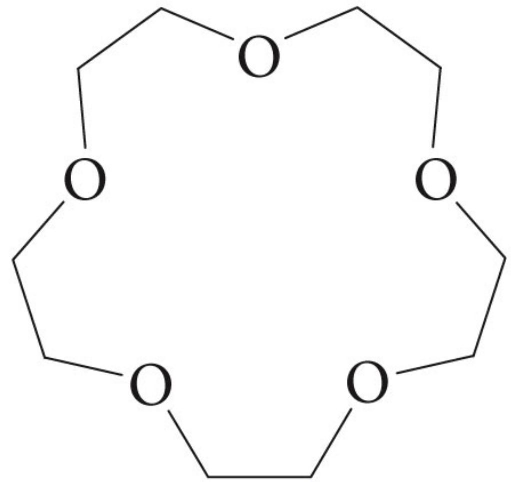
tetrahydropyran
(oxane)
bp 88°C



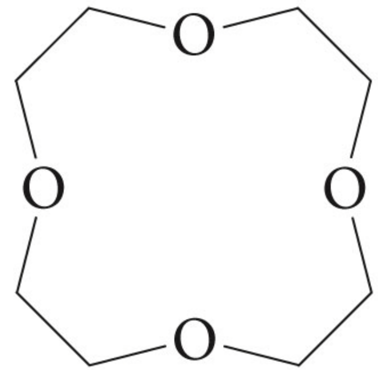
1,4-dioxane
bp 101°C



[18]crown-6
mp 39–40°C

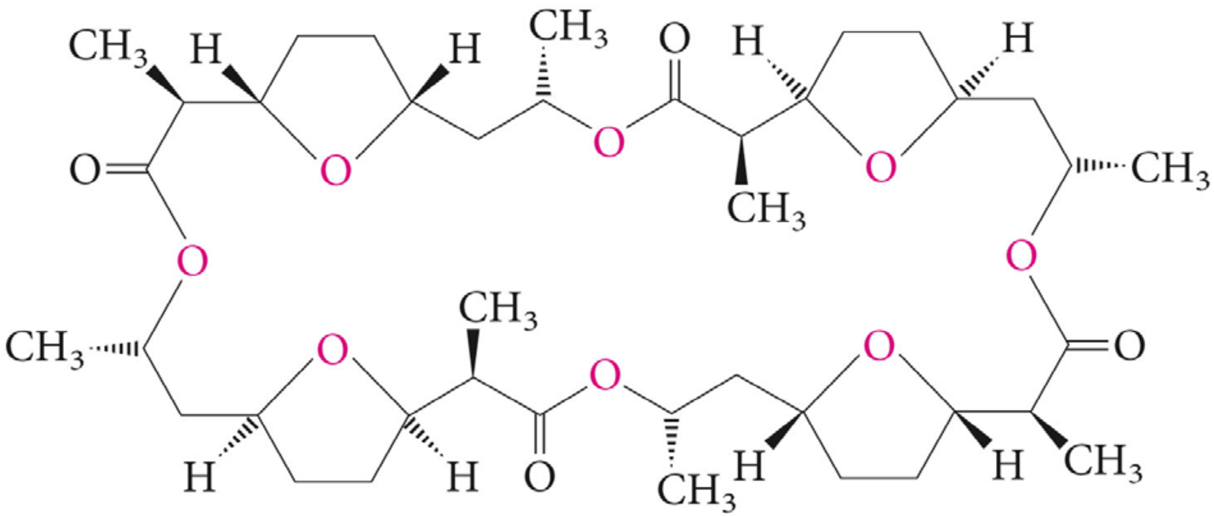


[15]crown-5
(liquid)



[12]crown-4

These compounds are called **Crown ethers** because their molecule have a crown-like shape. The bracket number represents the ring size and the terminal numbers gives the number of oxygens. The oxygens are usually separated by two carbons.



The selective binding of metallic ions by macrocyclic compounds is important in nature. Several antibiotics, such as **nonactin**, have large rings that contain regularly spaced oxygen atoms. Nonactin (which contains four tetrahydrofuran rings joined by four ester links) selectively binds K^+ (in the presence of Na^+) in aqueous media. Thus allowing selective transport of K^+ (but not Na^+) through the cell membranes

Homework 7

26,29,33,34,36,38,40,47,48,52

Homework 8

17,21,23,27,31,33,42