



Chapter 8

Ethers

and

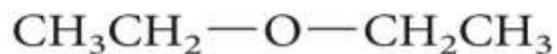
Epoxides

8.1 Nomenclature of Ethers (R-O-R) :

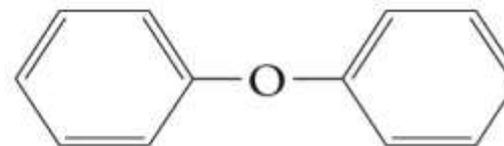
Ethers are named by giving the **name of each alkyl** (or aryl) **group**, in alphabetical order, followed by the word **ether**.



ethyl methyl ether

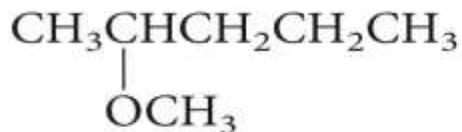


diethyl ether (the prefix *di-* is sometimes omitted)

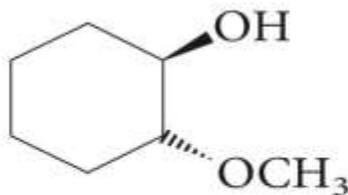


diphenyl ether

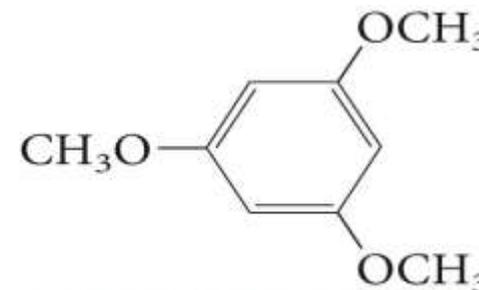
IUPAC : If other functional groups are present, or if more than one ether linkage is present : ether linkage is considered as substituent o the alkane.



2-methoxypentane

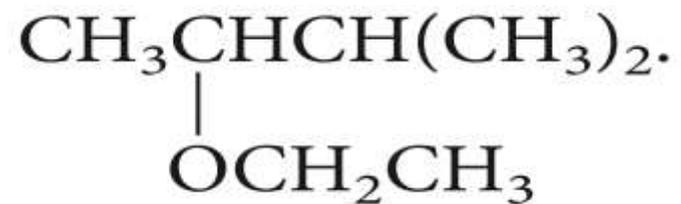


trans-2-methoxycyclohexanol

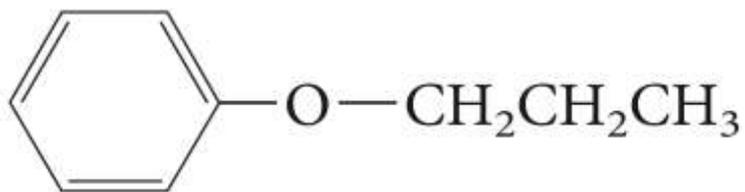


1,3,5-trimethoxybenzene

What are the correct names for the following ethers?



2-Ethoxy-3-methylbutane



Phenyl n-propyl ether

8.2 Physical Properties of Ethers

Boiling Point: much lower than alcohols. (no H-bonding)
Nearly same as hydrocarbons.

Solubility : same as alcohols. (water forms H-bonds with ether like alcohols)

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	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	118°C	74	7.9
diethyl ether	$\text{CH}_3\text{CH}_2\text{—O—CH}_2\text{CH}_3$	35°C	74	7.5
pentane	$\text{CH}_3\text{CH}_2\text{—CH}_2\text{—CH}_2\text{CH}_3$	36°C	72	0.03

8.3 Ethers as Solvents

Ethers are relatively inert (unlike alcohols) :

Ether + dilute acids \longrightarrow No Reaction

Ether + strong bases \longrightarrow No Reaction

Ether + oxidizing agents \longrightarrow No Reaction

Ether + reducing agents \longrightarrow No Reaction

$\text{R-O-R} + (\text{NaOH, Na, NaH, NaNH}_2) \longrightarrow \text{No reaction}$
(strong / very strong bases)

8.4 Grignard Reagents (an organometallic reagent) :

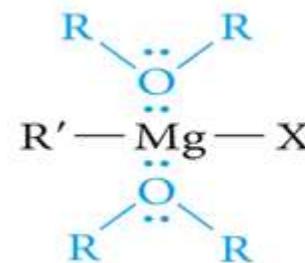
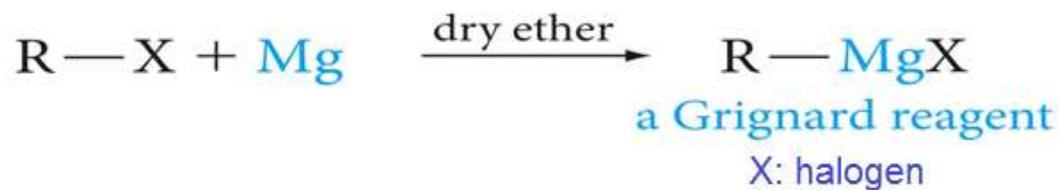
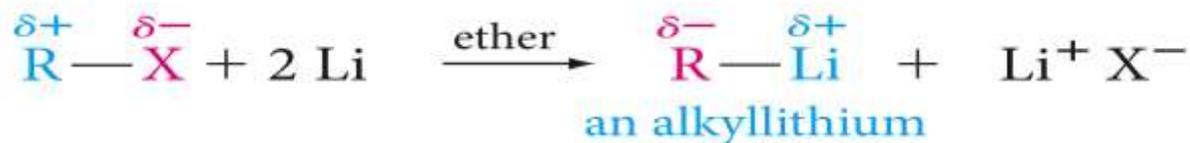
Organometallic Reagents : Organic part + metal

Examples : R-Li (Alkyl lithium Reagents) Formation of Organometallic reagents :

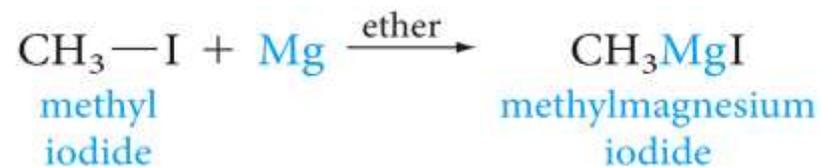
R-MgX (Alkylmagnesium Halides, or **Grignard reagents**)

Organic part **R** has large partial -ve charge, **Strong Nucleophile**

Formation of Organometallic reagents :

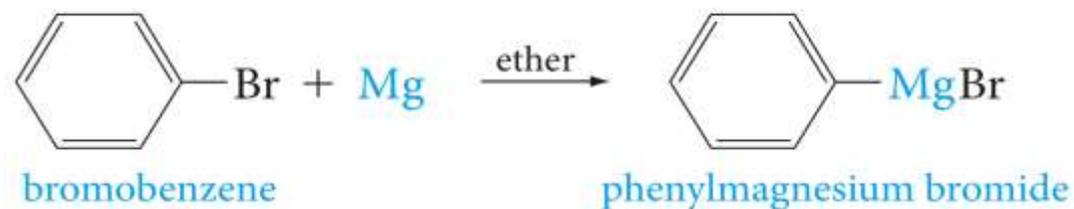


Alkyl halides :

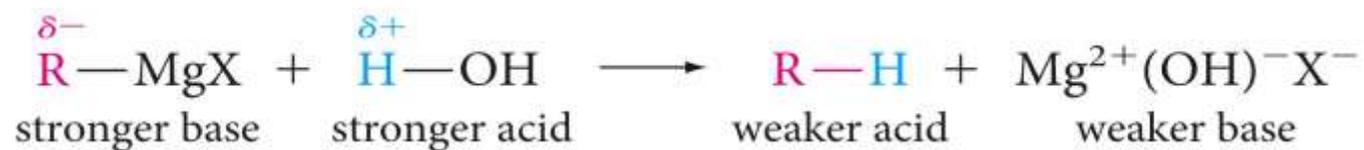


or

Aryl halides :

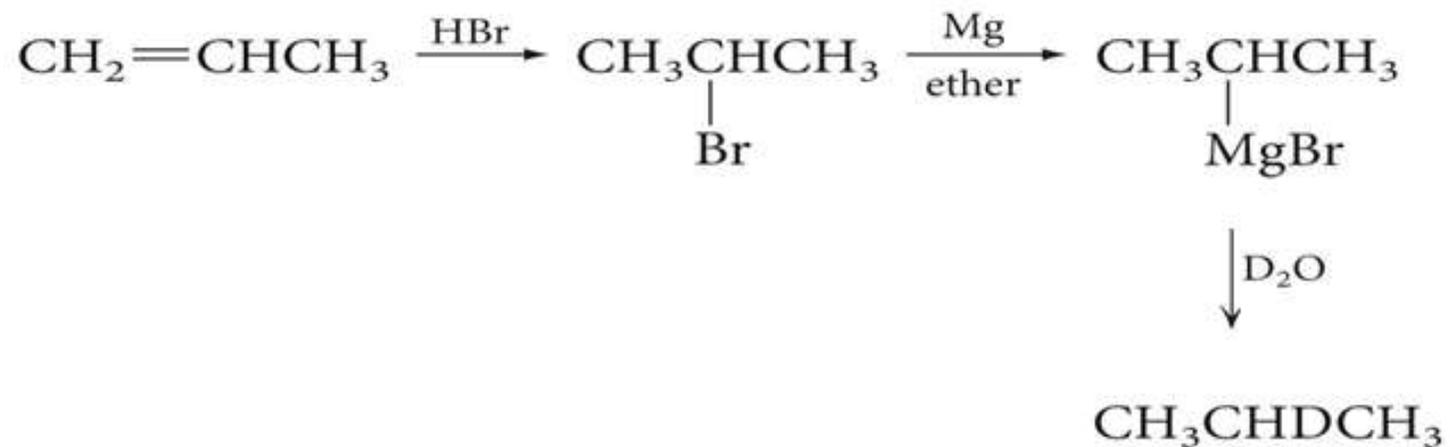


Grignard Reagents are v. strong bases (and v. strong Nucleophiles) :



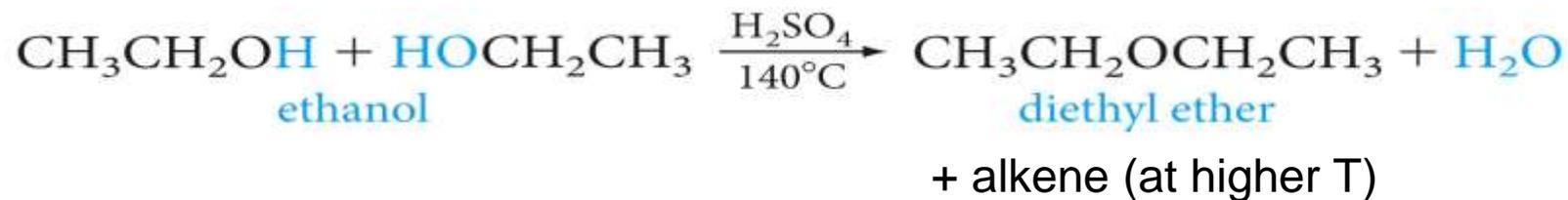
Question:

How to prepare $\text{CH}_3\text{CHDCH}_3$ from $\text{CH}_2=\text{CHCH}_3$

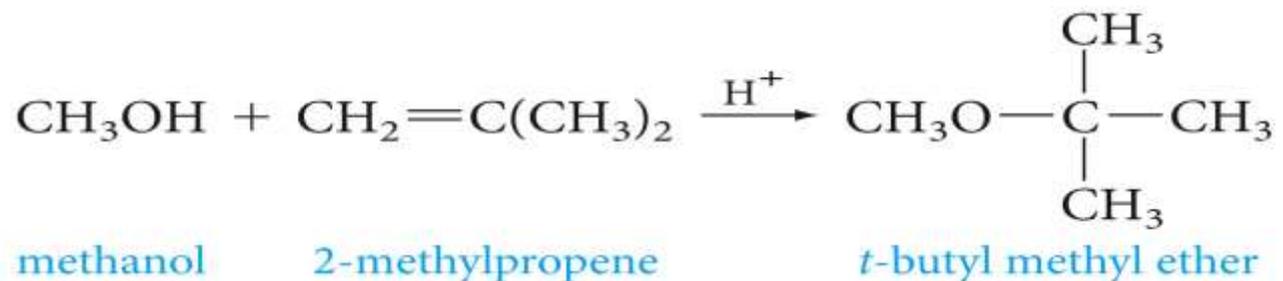


8.5 Preparation of Ethers :

1. From primary alcohols: (example diethyl ether) + alkene (at higher T)



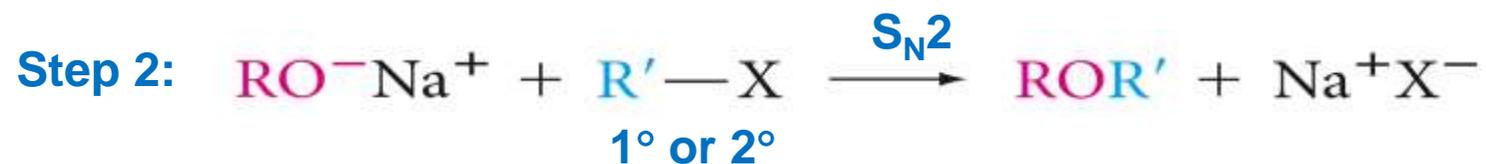
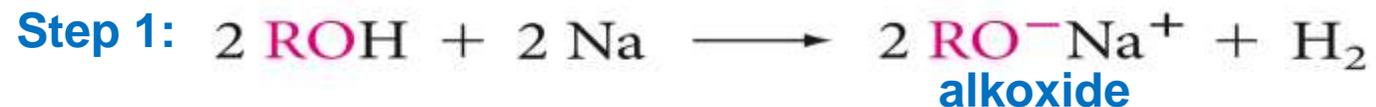
2. Addition of alcohol to an alkene : (example : MTBE)



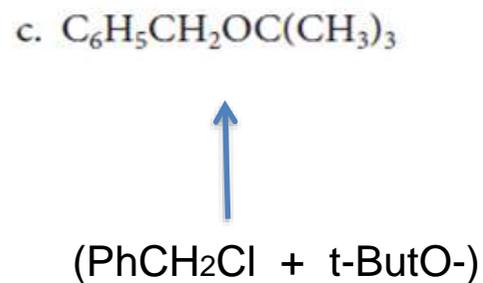
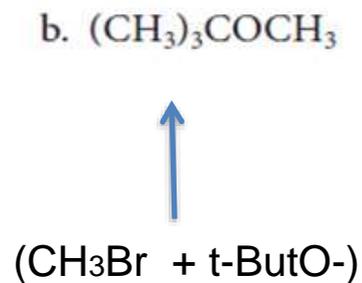
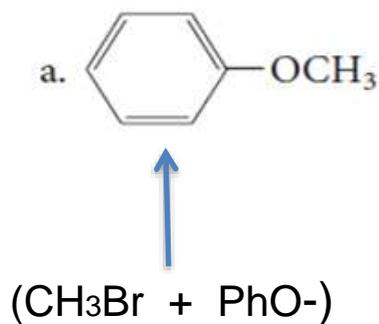
**Reaction
mechanism : ??**

3. Williamson Synthesis – a more general method :

Alkoxide + 1° or 2° alkyl halide (RO⁻ + RX)

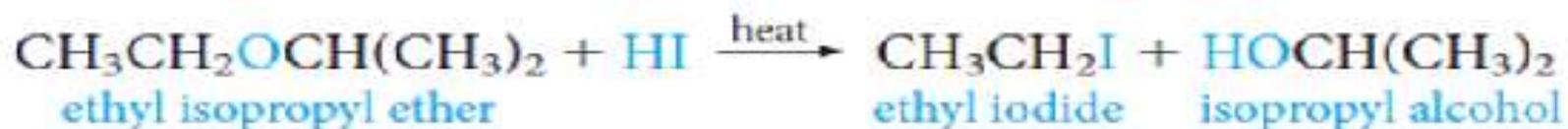
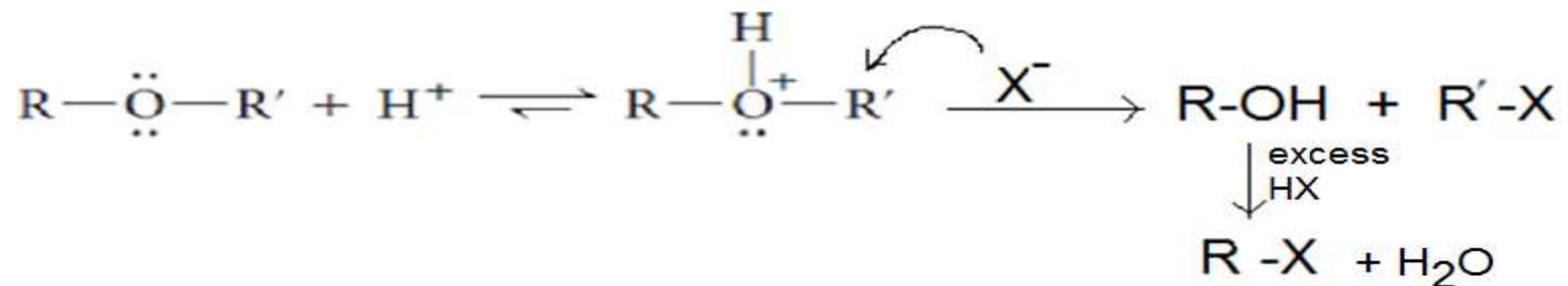


Write equations for the synthesis of the following ethers

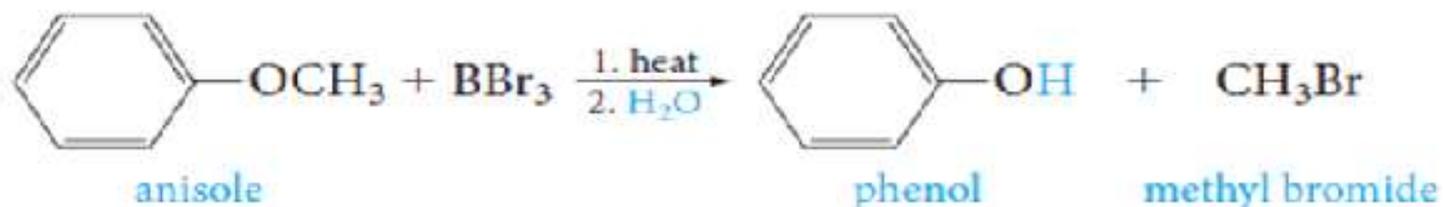


How would you prepare diphenyl ether (Ph-O-Ph)?

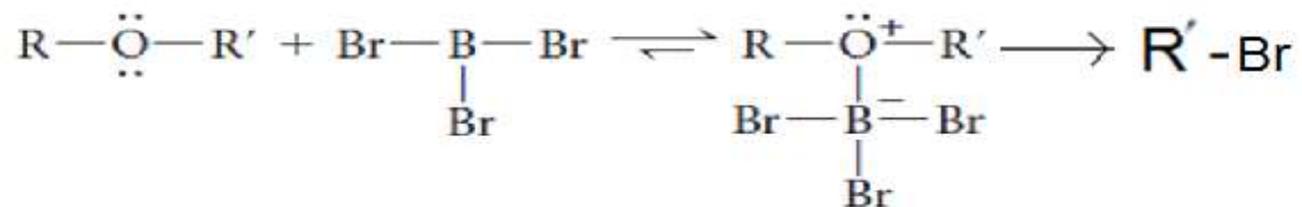
8.6 Cleavage of Ethers (with HX) :



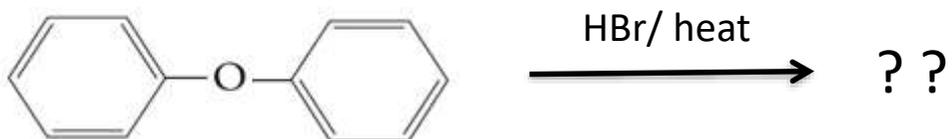
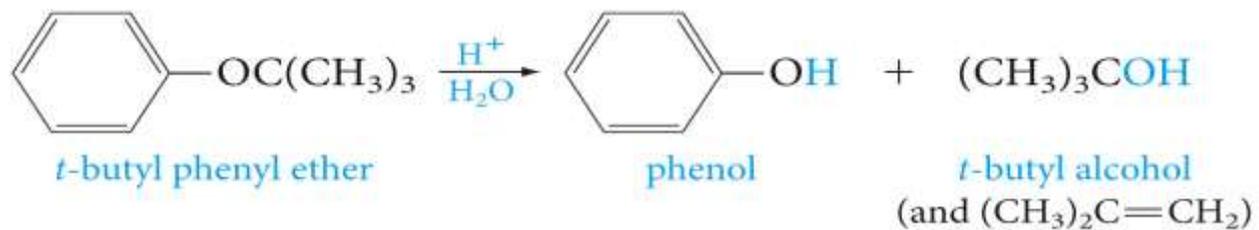
SN2 : iodide ion strong Nu, reacts by SN2 at the less crowded R group



SN2

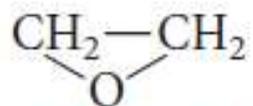


If R or R' is tertiary, a reaction can occur with weak nucleophiles (e.g. H₂O) by S_N1 mechanism.

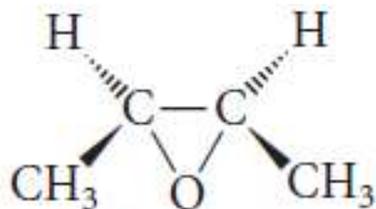


8.7 Epoxides (Oxiranes)

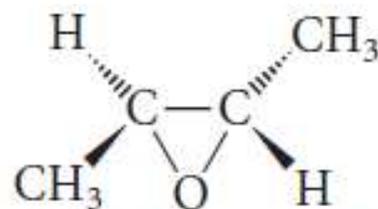
three-membered ring cyclic ethers containing one oxygen atom.



ethylene oxide
(oxirane)
bp 13.5°C

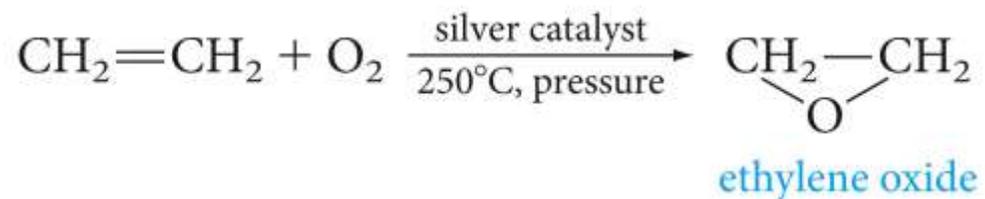


cis-2-butene oxide
(*cis*-2,3-dimethyloxirane)
bp 60°C



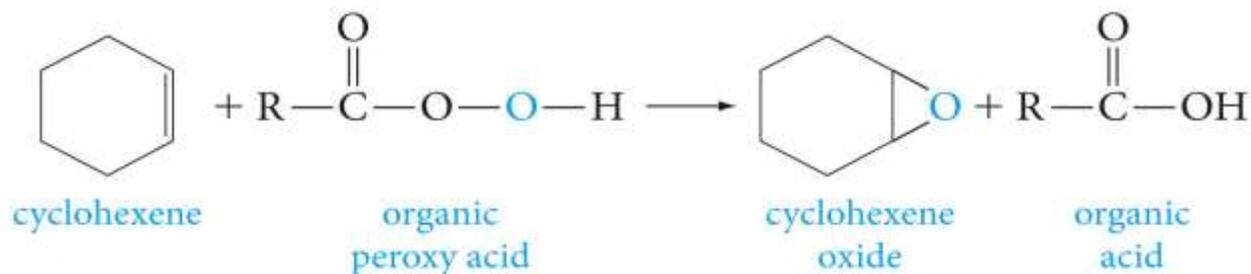
trans-2-butene oxide
(*trans*-2,3-dimethyloxirane)
bp 54°C

ethylene oxide has wide industrial application, and it is industrially produced by oxidation of ethylene :



General method for preparation of epoxides:

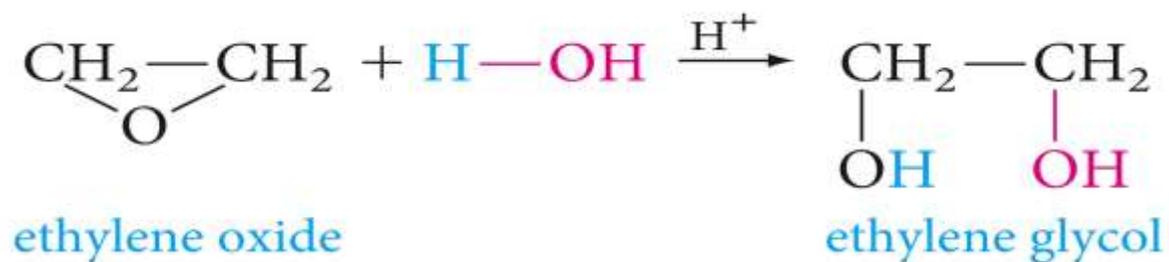
By oxidation of alkenes with organic peroxyacid (peracid) :



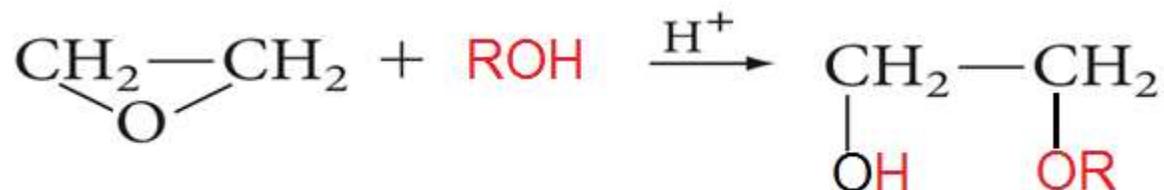
8.8 Reactions of Epoxides

Because the three-membered ring is **highly strained**, epoxides are much more reactive than ordinary ethers and undergo **ring-opening** reactions (to get rid of strain)

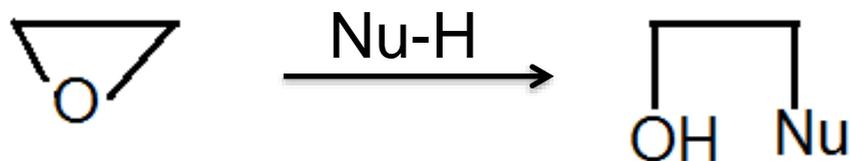
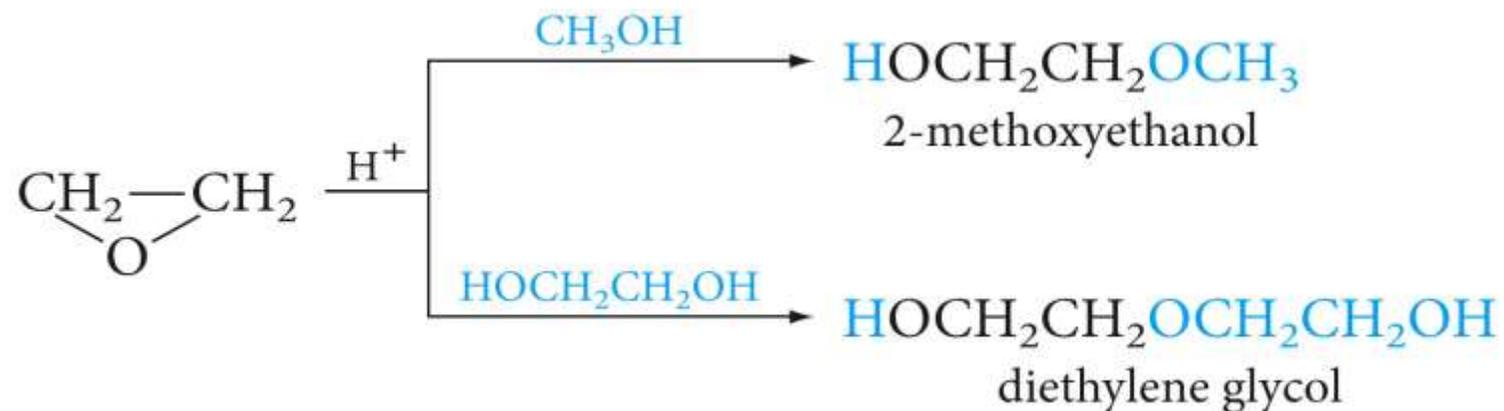
1. Reaction with water : acid-catalyzed ring opening to give glycols.



Reaction with alcohols :



2. Reaction of other weak nucleophiles : add similarly (need acid catalyst)

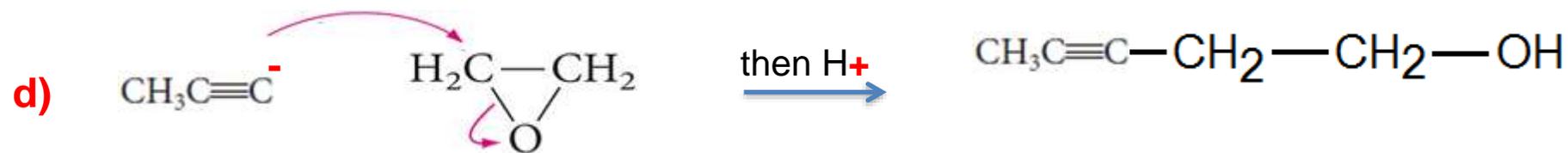
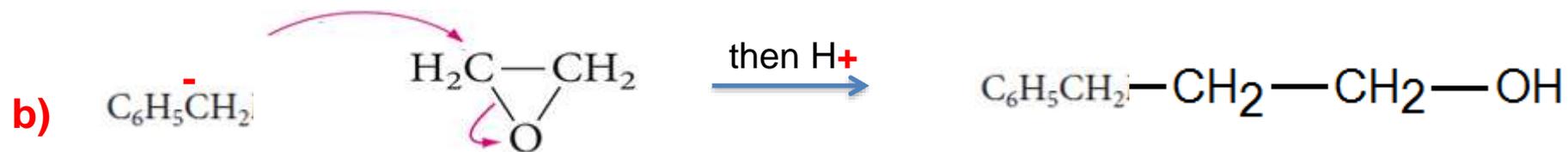


3. Reaction of strong nucleophiles : (No need for catalyst-

Grignard reagent , alkyl lithium , alkoxides , cyanide ion RO^- , CN^- ,

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

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{MgCl}$ followed by hydrolysis
- $\text{C}_6\text{H}_5\text{CH}_2\text{MgBr}$ followed by hydrolysis
- $\text{H}_2\text{C}=\text{CHLi}$ followed by hydrolysis
- $\text{CH}_3\text{C}\equiv\text{C}^- \text{Na}^+$ followed by hydrolysis



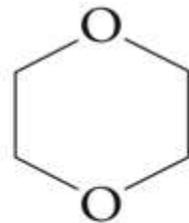
8.9 Cyclic Ethers :



tetrahydrofuran

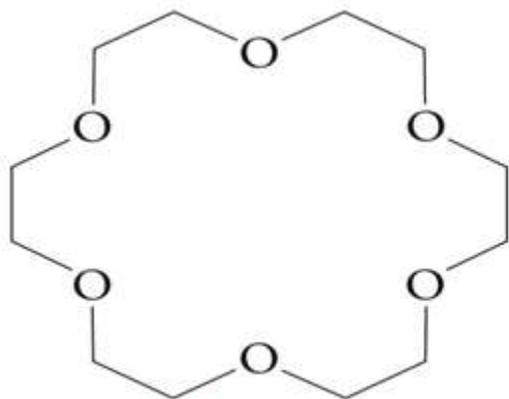


tetrahydropyran

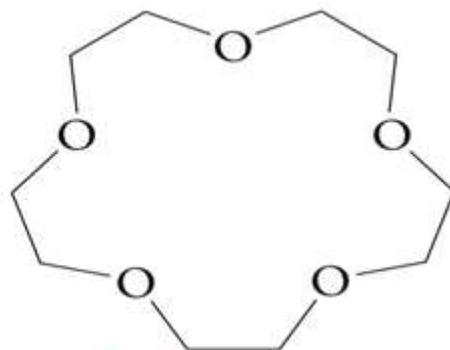


1,4-dioxane

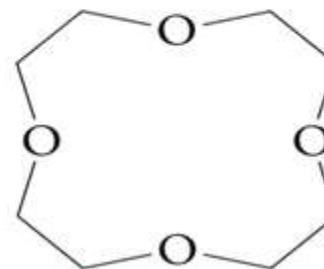
Crown ethers :



[18]crown-6



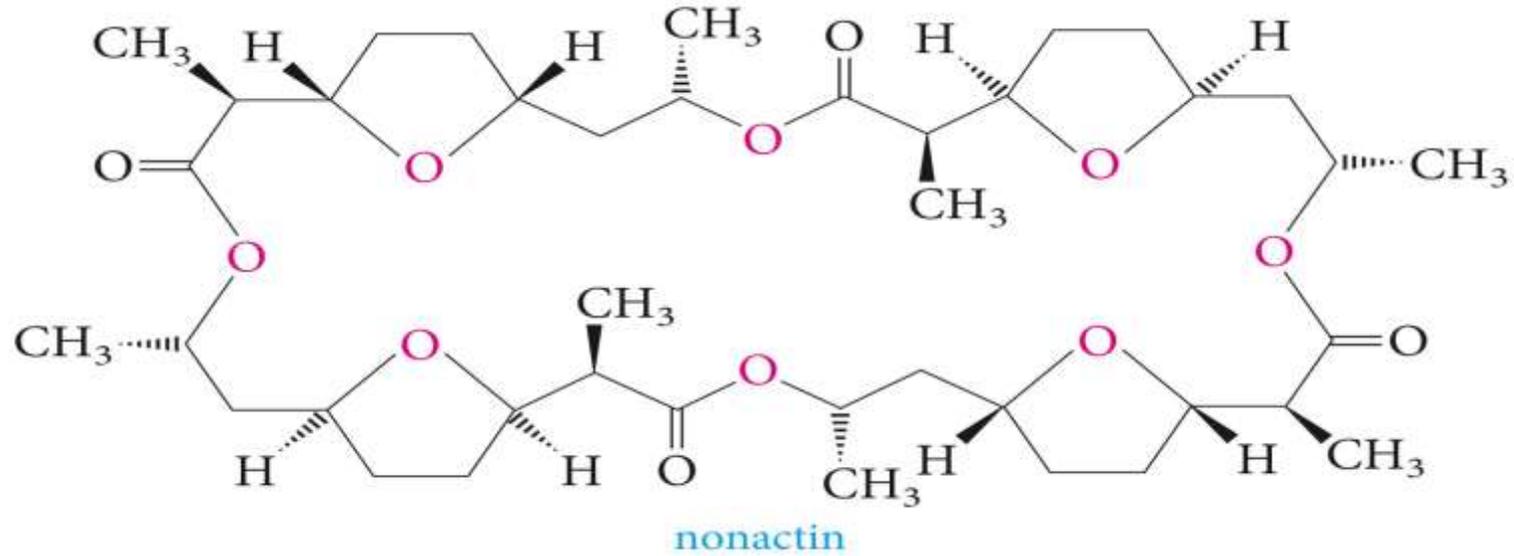
[15]crown-5



[12]crown-4

ring size

No of O atoms



Nonactin is antibiotic.

It selectively binds K⁺ allowing selective transport of K⁺
(but not Na⁺) through the cell membranes