

Organic Chemistry

1st year students

Lecture No. 6

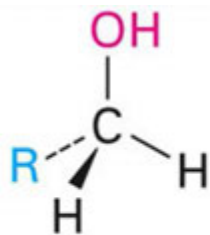
Ahmed Mohamad Jawad

Introduction:-

- **Alcohol** is a compound that has a hydroxyl group(OH) bounded to a saturated sp^3 hybridized carbon atom with a chemical formula of ROH.
- **An ether** has an oxygen atom bounded to two organic groups (R- group), with a chemical formula of ROR .

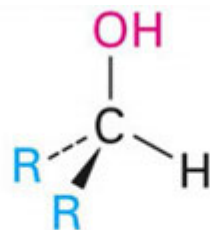
Classification of alcohols:

Alcohols are classified as primary (1°), secondary (2°) or tertiary (3°), depending on the number of carbon substituents bounded to hydroxyl-bearing carbon.

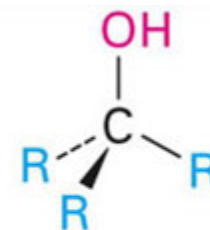


A primary (1°) alcohol

© 2007 Thomson Higher Education



A secondary (2°) alcohol



A tertiary (3°) alcohol

Naming of alcohols and ethers:

- **Alcohols:**

- Simple alcohols are named in the IUPAC system as derivatives of the parent alkane, using the suffix- *ol*.

Step1:

- Select the longest carbon chain containing the hydroxyl group, and replace the *-e* ending of the corresponding alkane with *-ol*.
- The *-e* is deleted to prevent the occurrence of two adjacent vowels ie, propanol rather than propaneol, for example.

Step2 :

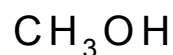
- Number the carbons of the parent chain beginning at the end nearer the hydroxyl group.

Step3 :

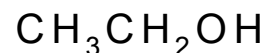
- Number all substituents according to their position on the chain, and write the name listing the substituents in alphabetical order and identifying the position to which the *-OH* is bounded.

Naming of alcohols and ethers:

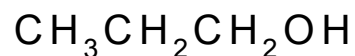
- Some well-known alcohols also have common names that are accepted by IUPAC. For example:



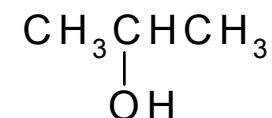
Methanol
Methyl alcohol



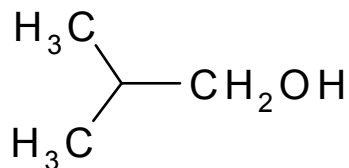
Ethanol
ethyl alcohol



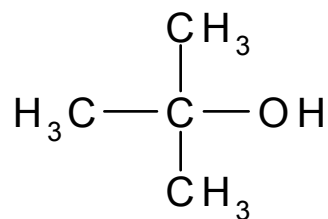
1-propanol
propyl alcohol



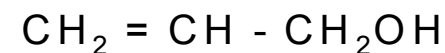
2-propanol
isopropyl alcohol



2-methyl-1-propanol
isobutyl alcohol



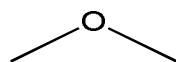
2-methyl-2-propanol
tert-butyl alcohol



2-propen-1-ol
allyl alcohol

Naming of alcohols and ethers:

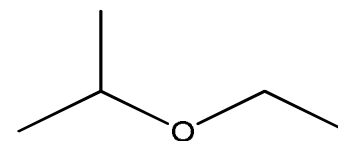
- **Ethers:**
- Simple ethers that contain no other functional groups are named by identifying the two organic groups and adding the word *ether*.



Dimethyl Ether



Ethyl Methyl Ether

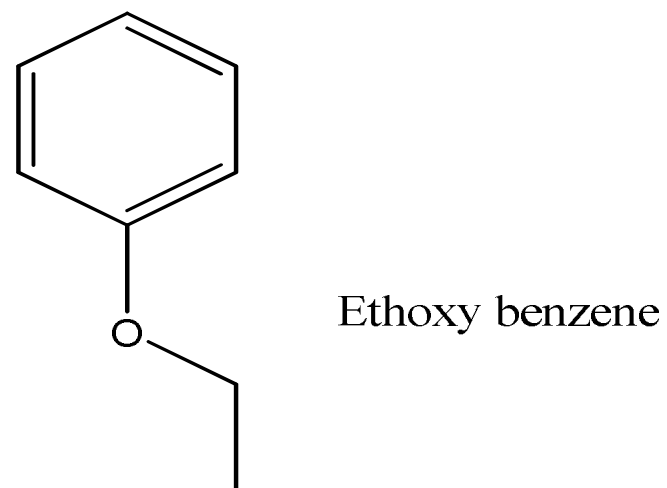
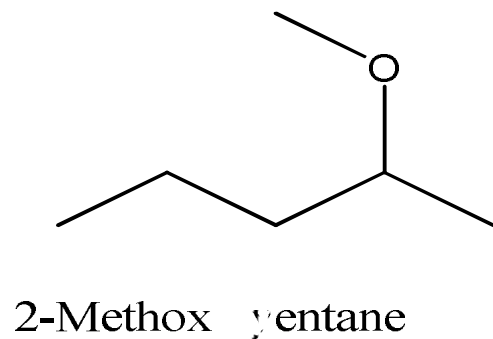
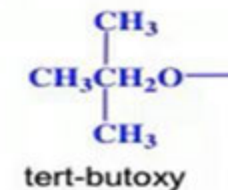
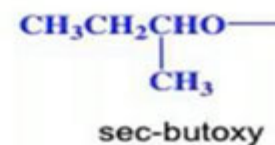
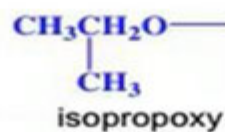
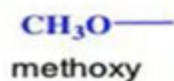


Iso propyl Ethyl Ether

- If other functional groups are present, the ether part is named as an *alkoxy* substituent, for example:

Naming of alcohols and ethers:

As substituents:

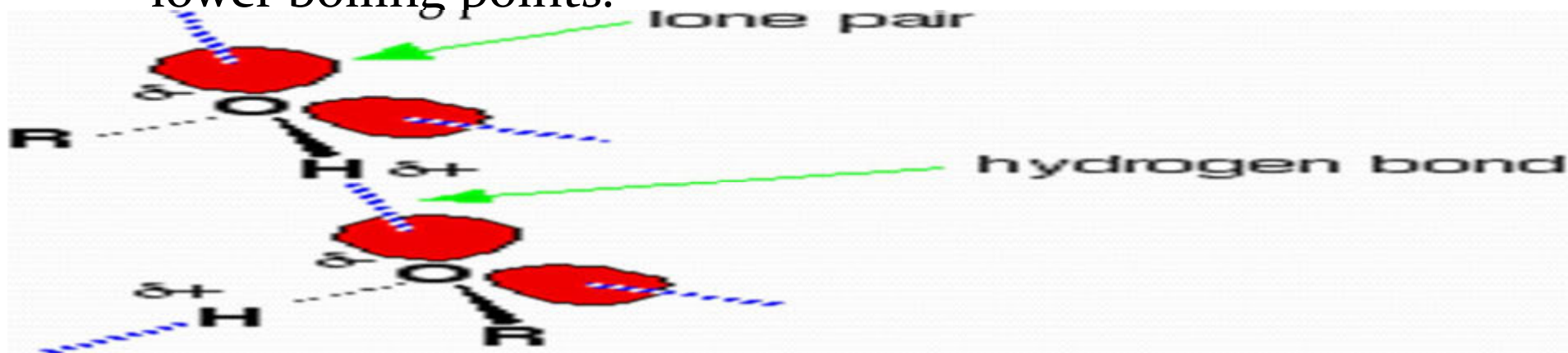


Properties of alcohols hydrogen bonding and acidity:

- Alcohols and ethers can be supposed as an organic derivatives of water in which one or both of the hydrogen have been replaced by organic parts:
- HOH becomes ROH or ROR. Thus, the two classes of compounds have nearly the same geometry as water. The C-O-H or C-O-C bond angles are approximately tetrahedral 109° in methanol and 112° in dimethyl ether, for instance- and the oxygen atoms are sp^3 -hybridized.
- Also like water, alcohols have higher boiling points than might be expected. Propan-1-ol and butane have similar molecular weights, for instance, yet propan-1-ol boils at 97.2°C and butane boils at -0.5°C .

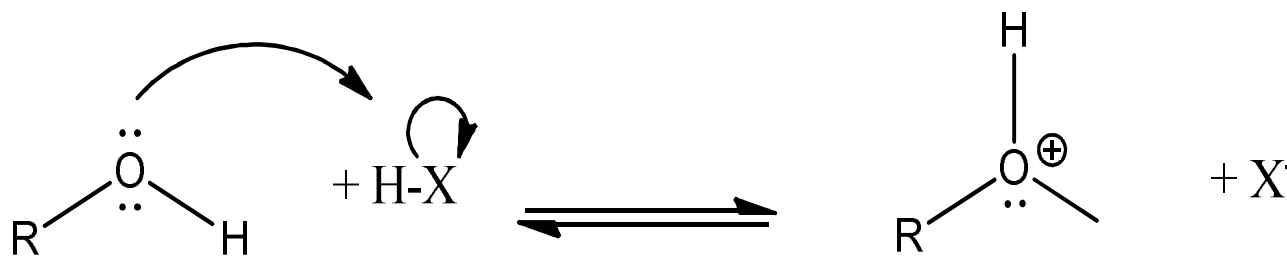
Properties of alcohols hydrogen bonding and acidity:

- Alcohols have unusually high boiling points because, like water, they form hydrogen bonds. The positively polarized $-OH$ hydrogen of one molecule is attracted to lone pair of electrons on the negatively polarized oxygen of another molecule, resulting in a weak force that holds the molecules together. Ethers, because they lack hydroxyl groups, can not form hydrogen bonds and therefore have lower boiling points.



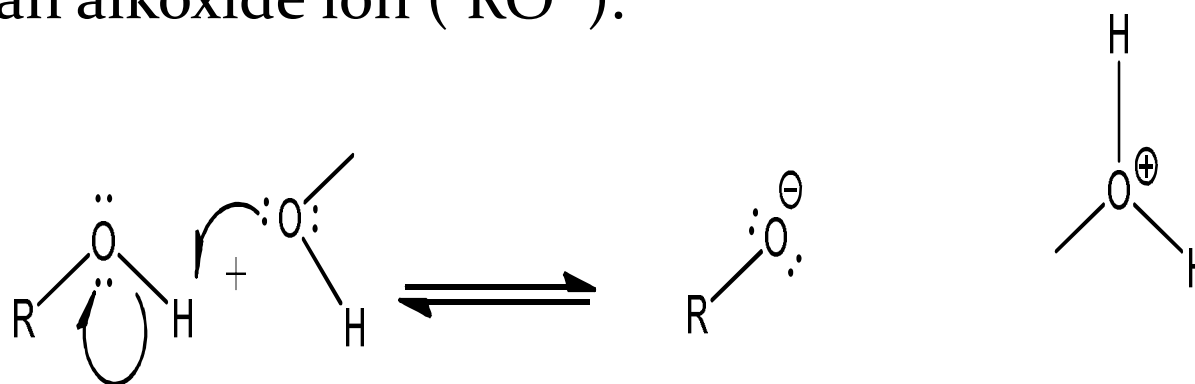
Properties of alcohols hydrogen bonding and acidity:

- Another similarity to water is that alcohols are weakly basic and weakly acidic.
- As weak Lewis bases, alcohols are reversibly protonated by strong acids to yield oxonium ions, ROH_2^+ .



Properties of alcohols hydrogen bonding and acidity:

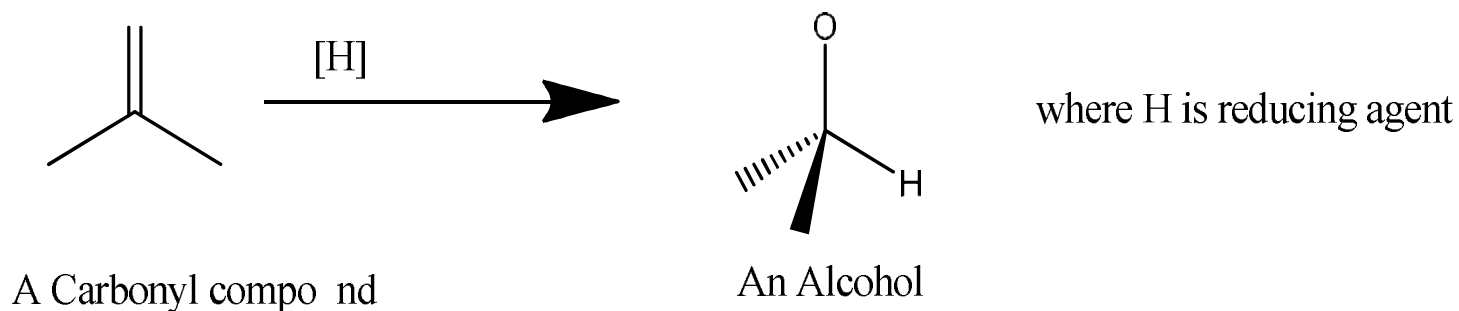
- As weak acids, alcohols dissociate to a slight extent in dilute aqueous solution by donating a proton to water, generating H_3O^+ and an alkoxide ion (RO^-).



- Alkoxides are named commonly by replacing the *-ane* suffix of the corresponding alkane with *-oxide*; methane gives methoxide, for example. They are named systematically by adding the *-ate* suffix to the name of alcohol. Methanol becomes methanolate, for instance.

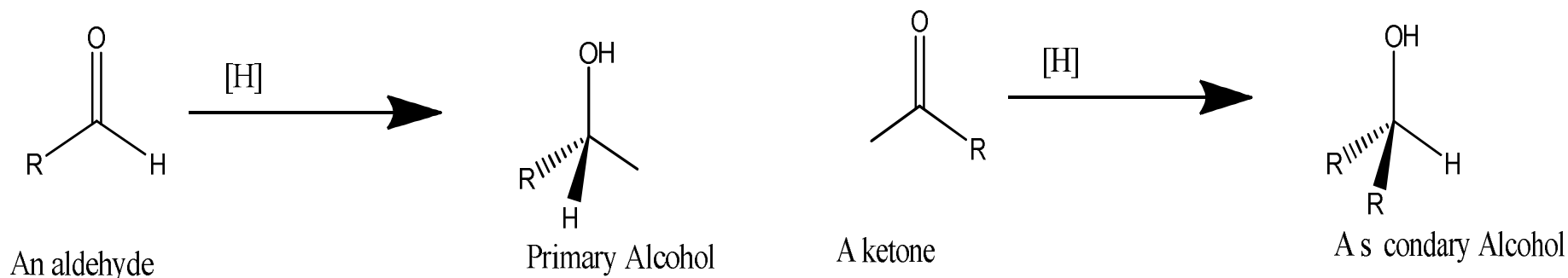
Synthesis of alcohols

- **Synthesis of alcohols from carbonyl compounds:**
- 1- Reduction of carbonyl compounds:
- Reduction of a carbonyl compound adds hydrogen to a C=O bond to give an alcohol. All kinds of carbonyl compounds can be reduced, including aldehydes, ketones, carboxylic acids and esters.



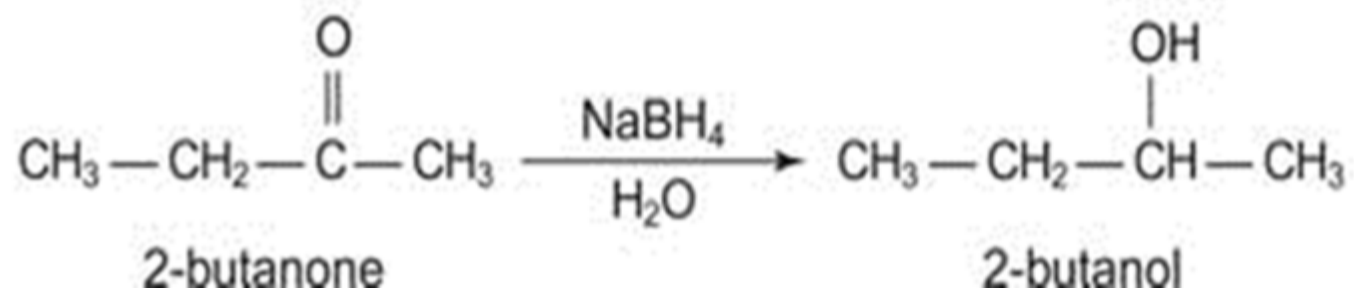
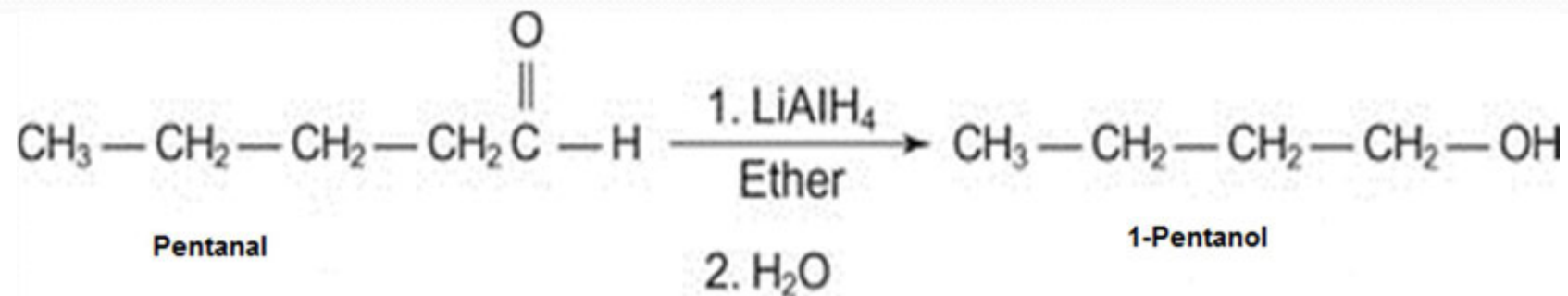
Synthesis of alcohols

- **A- reduction of aldehydes and ketones:**
- Aldehydes are reduced to give primary alcohols, and ketones are reduced to give secondary alcohols.



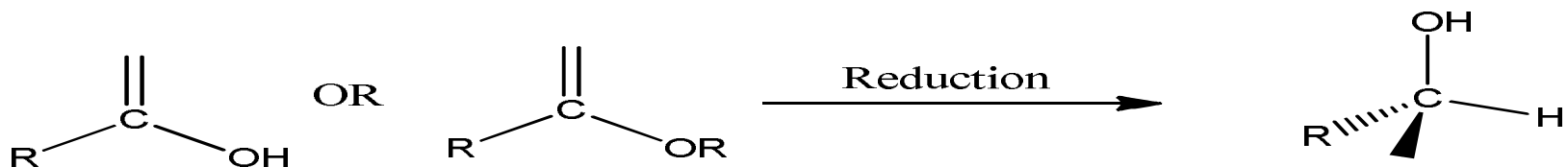
- Many reducing reagents are available, but sodium borohydride (NaBH_4) is usually chosen because of its safety. It is a white, crystalline solid that can be weighed in the open atmosphere and used in either water or alcohol solution.

Synthesis of alcohols



Synthesis of alcohols

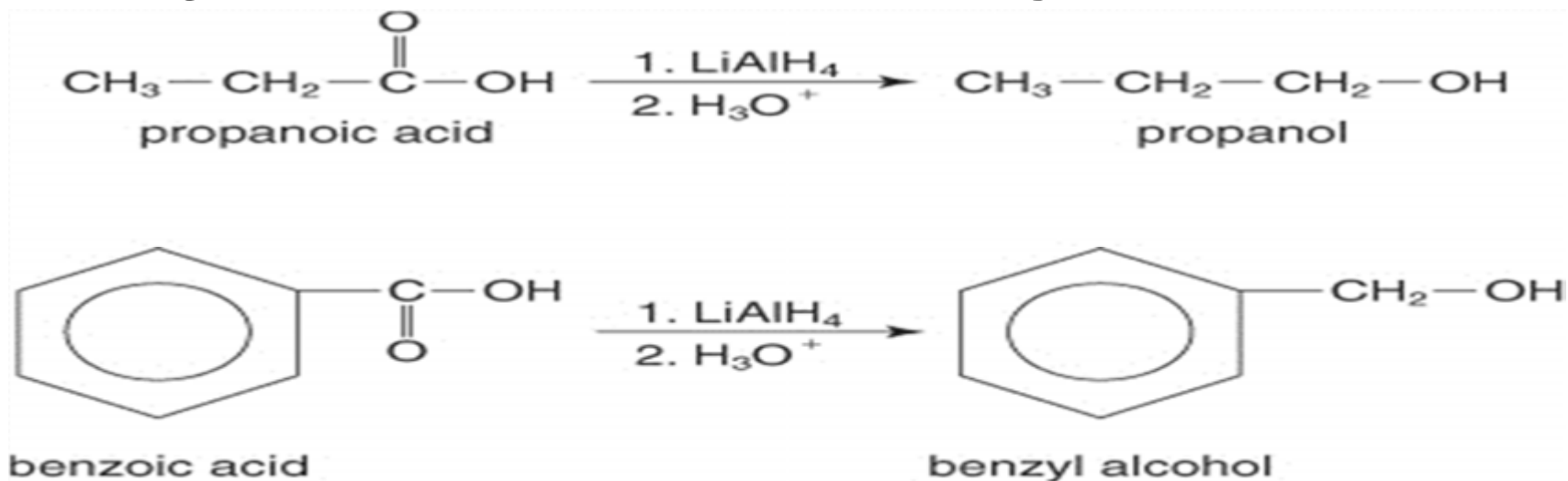
- **B- Reduction of Carboxylic acids and Esters:**
- Esters and Carboxylic acids are reduced to give primary alcohols.



- These reactions aren't as rapid as the reductions of aldehydes and ketones, so that more powerful reducing agent lithium aluminum hydride (LiAlH_4) is used rather than (NaBH_4). (LiAlH_4 will also reduce aldehydes and ketones).

Synthesis of alcohols



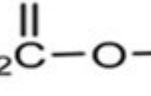

- Note that **only one hydrogen** is added to the carbonyl carbon atoms during the reduction of an **aldehyde** or **ketone**.
- but **two hydrogens** are added to the carbonyl carbon during reduction of an **ester** or **carboxylic acid**.



Synthesis of alcohols

(C) Reduction of ester

□ When reduced using strong reducing agent such as LiAlH_4 , ester will form alcohol as products

Ester	LiAlH_4	Alcohol	Alcohol
$\text{CH}_3\text{CH}_2\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_3$	$\xrightarrow[\text{H}^+]{\text{LiAlH}_4}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{OH}$
 - $\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_3$	$\xrightarrow[\text{H}^+]{\text{LiAlH}_4}$	 - CH_2OH	CH_3OH
$\text{CH}_3\text{CH}_2\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$ 	$\xrightarrow[\text{H}^+]{\text{LiAlH}_4}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	 - OH

Synthesis of alcohols

- **2-Grignard reaction of carbonyl compounds:**
- Grignard reagents (RMgX), prepared by reaction of organohalides with magnesium, react with carbonyl compounds to yield alcohols in much the same way that



Preparing Alcohols from Carbonyl Compounds

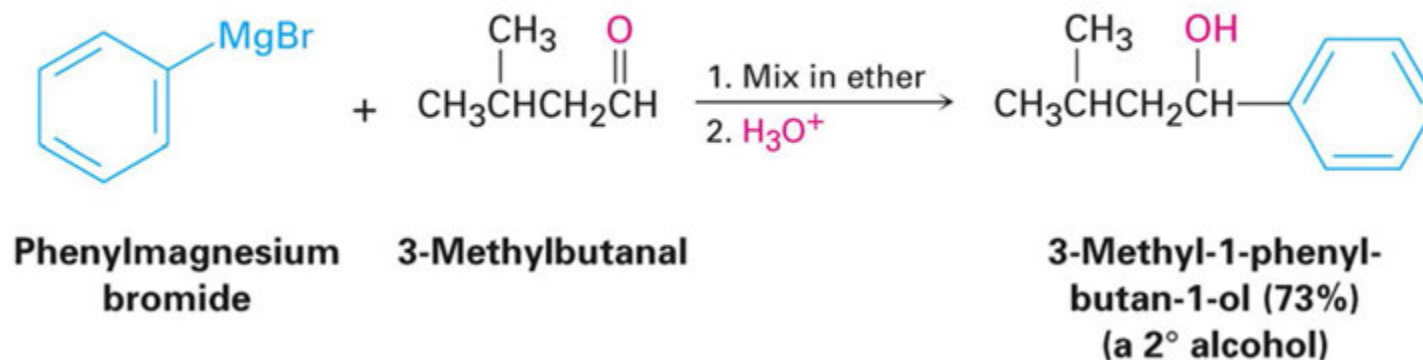
- Grignard reagents react with formaldehyde $\text{H}_2\text{C}=\text{O}$, to yield primary alcohols

Formaldehyde reaction



- Grignard reagent react with aldehydes to yield secondary alcohols

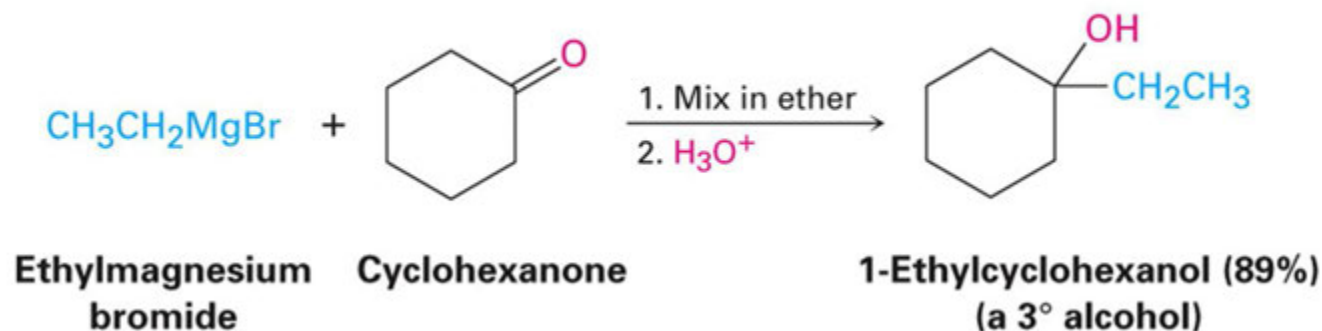
Aldehyde reaction



Preparing Alcohols from Carbonyl Compounds

- Grignard reagents react with ketones to yield tertiary alcohols

Ketone reaction



- Grignard reagents react with esters to yield tertiary alcohols
 - Two of the substituents bonded to the hydroxyl-bearing carbon have come from the Grignard reagent

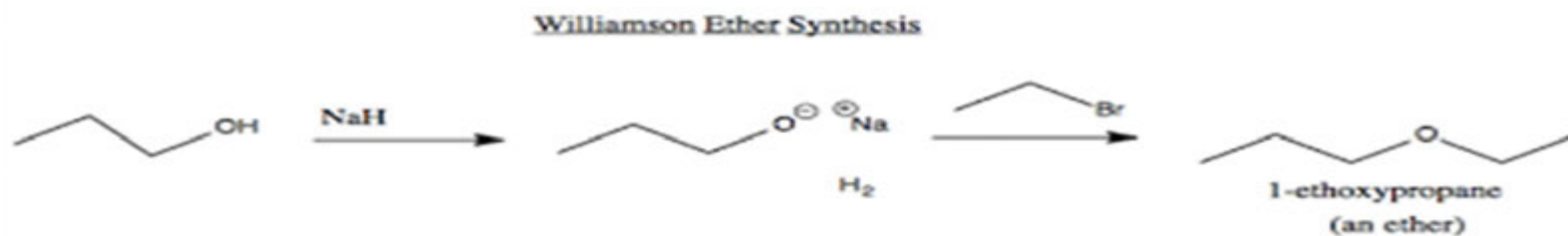
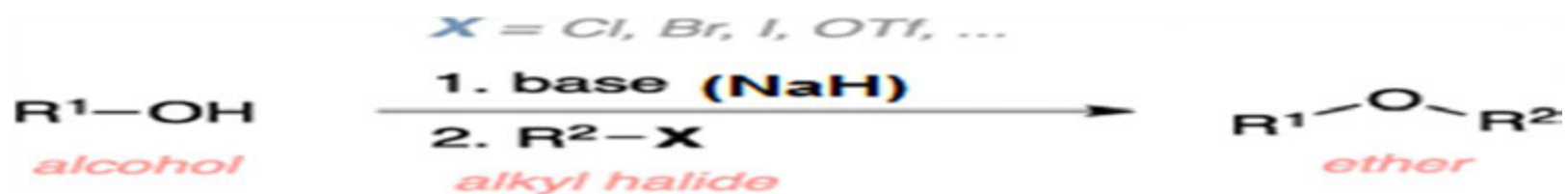




Preparation of ethers

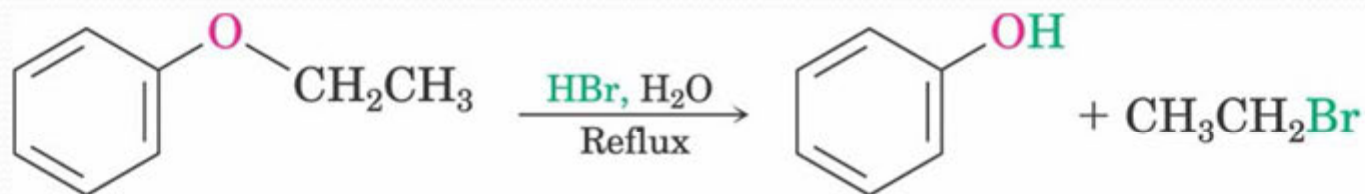
- **Conversion in to Ethers:**
- Alcohols are converted in to ethers by formation of the corresponding alkoxide ion followed by reaction with an alkyl halide, a reaction known as the *Williamson ether synthesis*. As noted previously, the alkoxide ion needed in the reaction can be prepared either by reaction of an alcohol with an alkali metal or by reaction with a strong base such as sodium hydride (NaH).

Alcohol and Ethers



Reactions of Ethers: Acidic Cleavage

- Ethers are generally unreactive
- Strong acid will cleave an ether at elevated temperature
- HI, HBr produce an alkyl halide from less hindered component by S_N2 (tertiary ethers undergo S_N1)

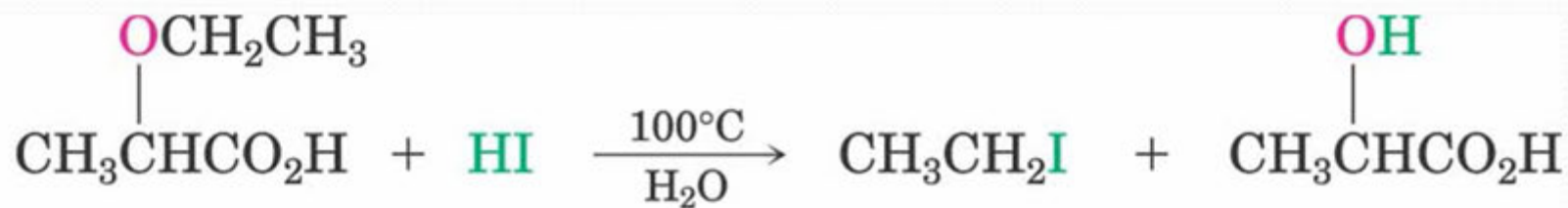


Ethyl phenyl ether

©2004 Thomson - Brooks/Cole

Phenol

Bromoethane



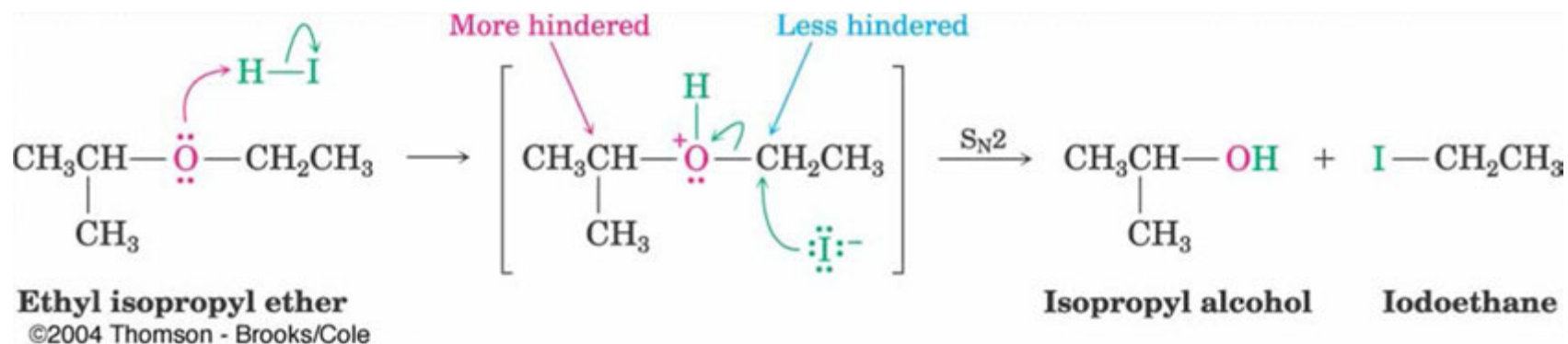
2-Ethoxypropanoic acid

©2004 Thomson - Brooks/Cole

Iodoethane

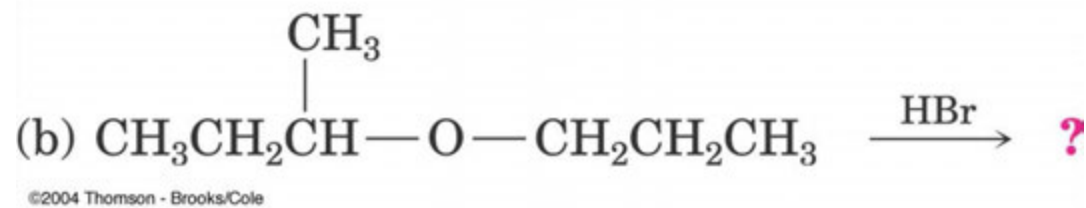
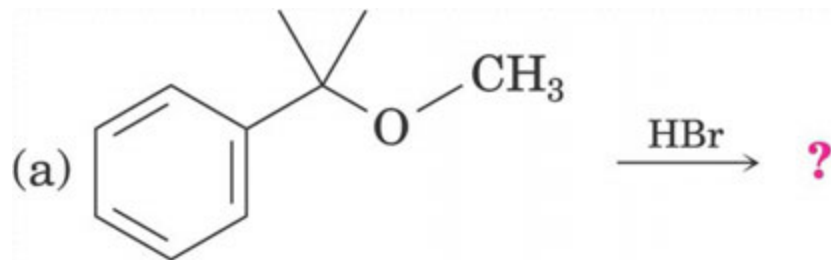
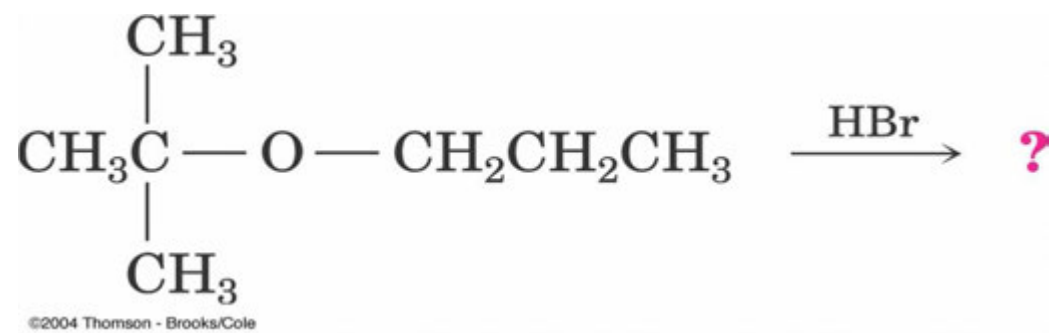
Lactic acid

Mechanism : Acidic Cleavage



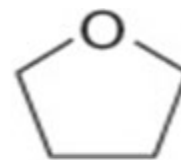
Note that the halide attacks the protonated ether at the less highly substituted site.

Home work:



Alcohol and Ethers

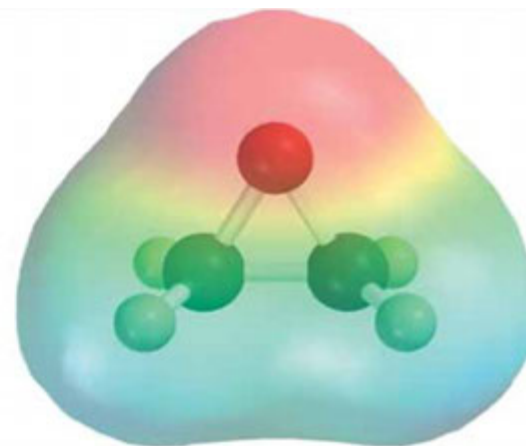
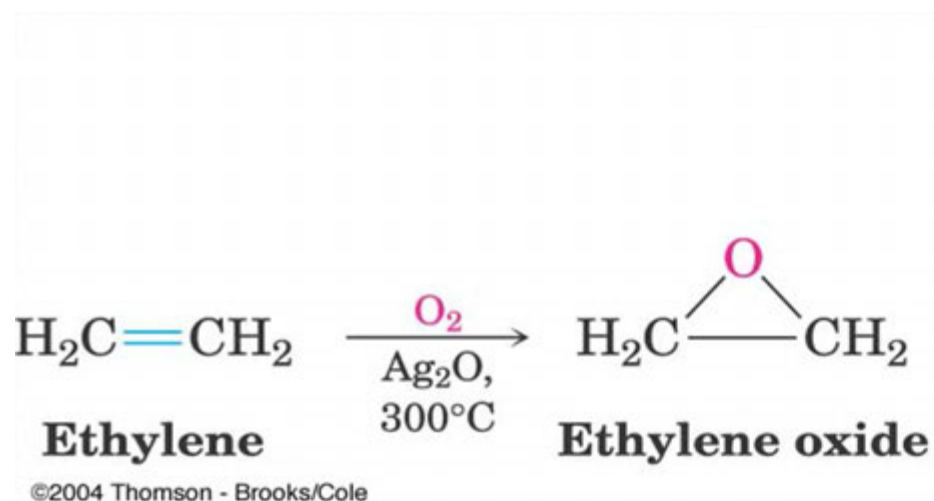
- **Cyclic ethers: Epoxides**
- For the most part, cyclic ethers behave like acyclic ethers. The chemistry of the ether functional group is the same whether its in an open chain or in a ring. Thus, the cyclic ether tetrahydrofuran (THF) is often used as a solvent because of its inertness.



tetrahydrofuran
THF

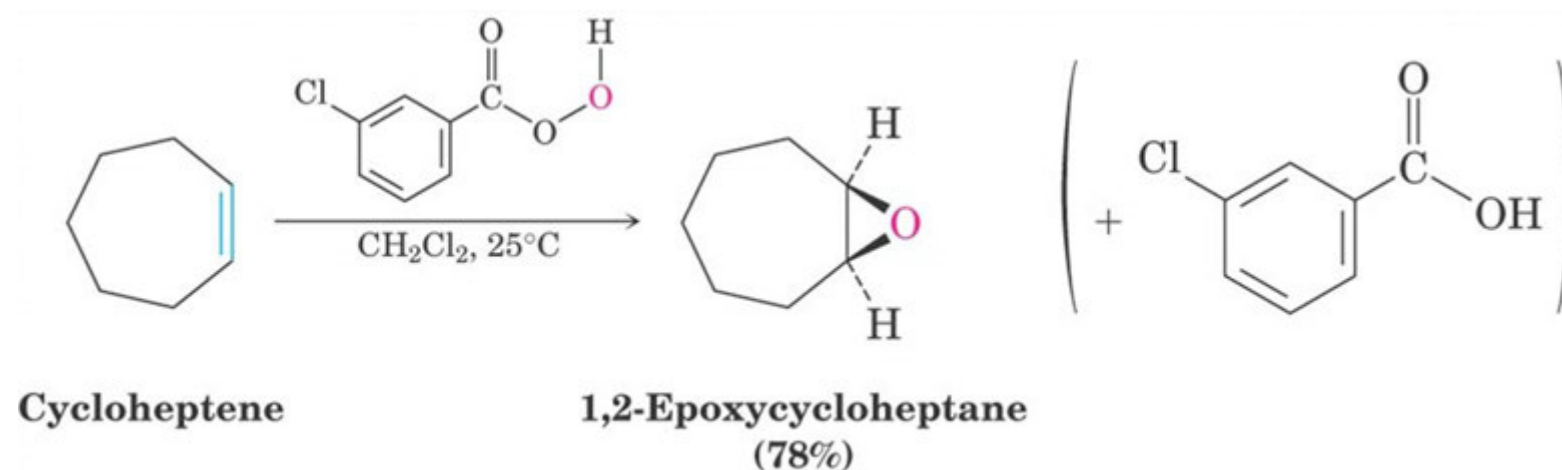
Epoxides (Oxiranes)

- The three-membered-ring ethers, called epoxides, make up the one group of cyclic ethers that behave differently from open-chain ethers. The strain of the three-membered ring makes epoxides much more reactive than other ethers.

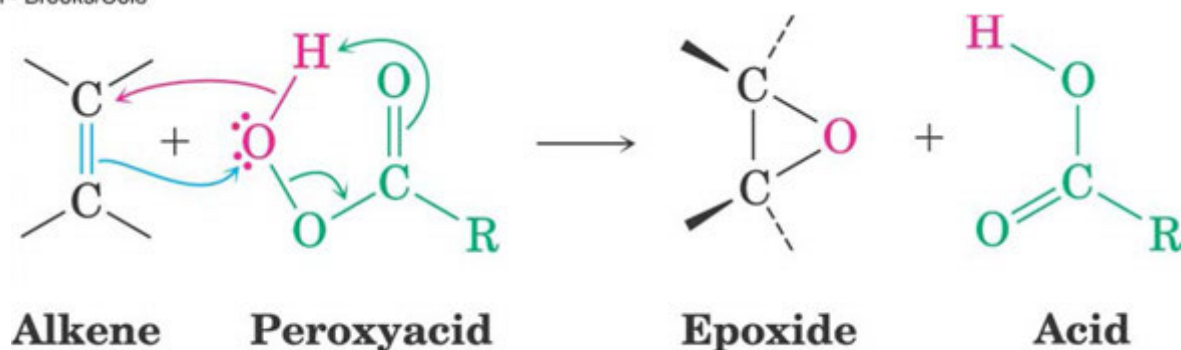


Preparation of Epoxides Using a Peroxy acid

- Treat an alkene with a peroxy acid



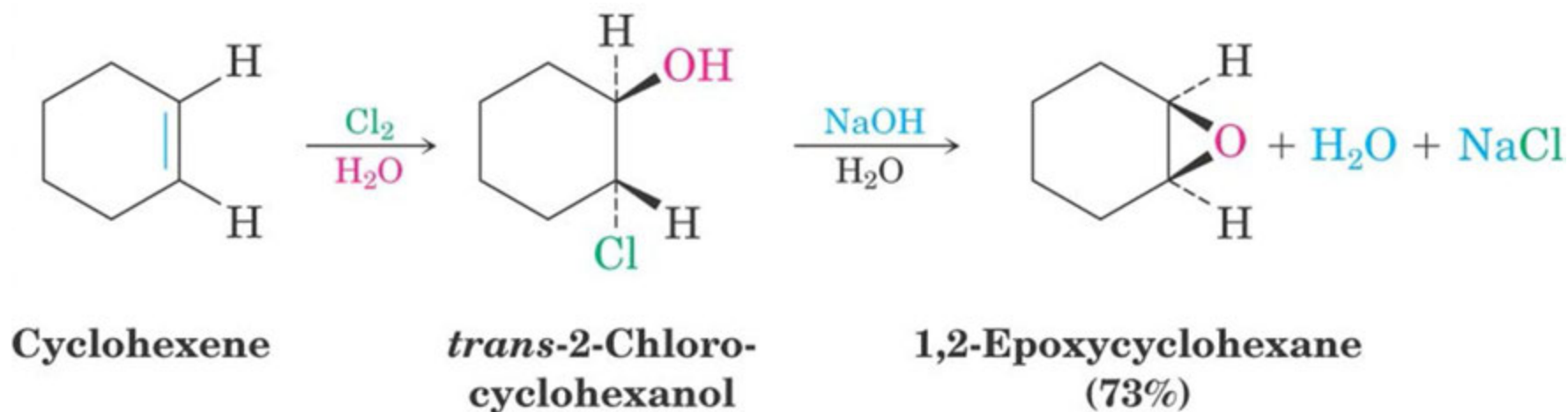
© 2004 Thomson - Brooks/Cole



©2004 Thomson - Brooks/Cole

Epoxides from Halohydrins

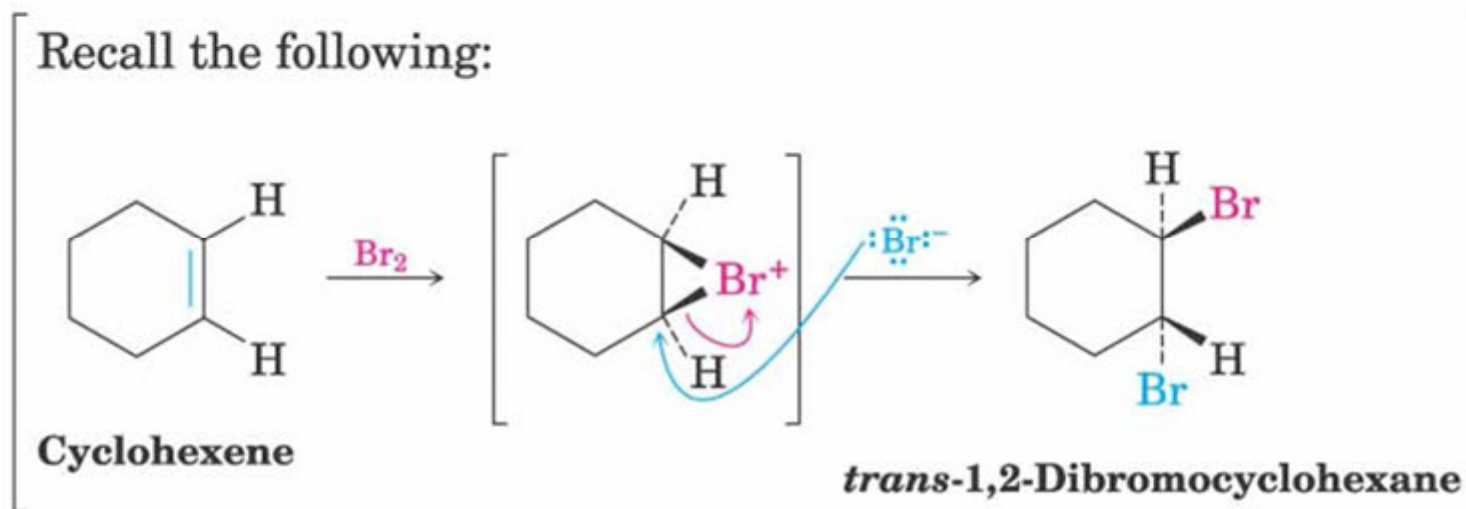
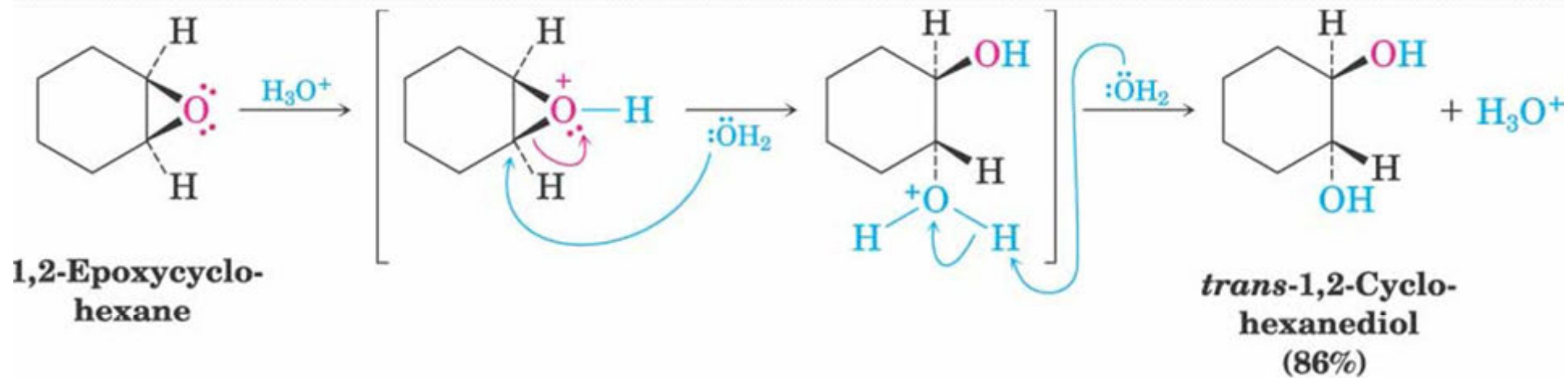
- Addition of HO-X to an alkene gives a halohydrin
- Treatment of a halohydrin with base gives an epoxide
- Intramolecular Williamson ether synthesis





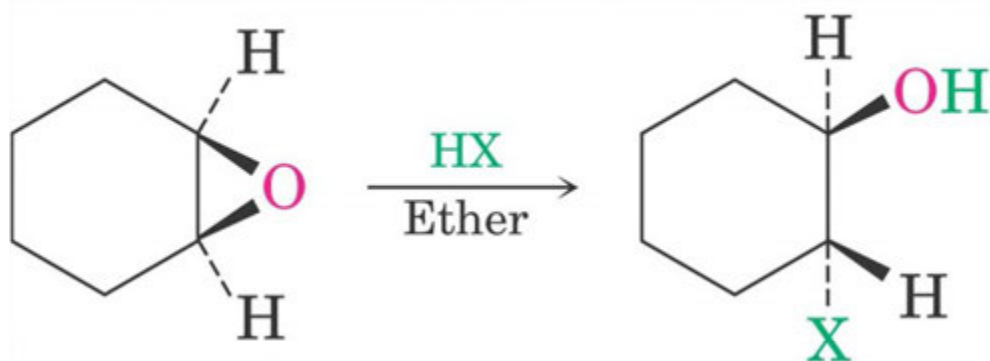
Ring-Opening Reactions of Epoxides

- Water adds to epoxides with dilute acid at room temperature
- Product is a 1,2-diol (on adjacent C's: *vicinal*)
- Mechanism: acid protonates oxygen and water adds to opposite side (anti-addition)



Halohydrins from Epoxides

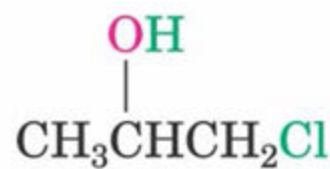
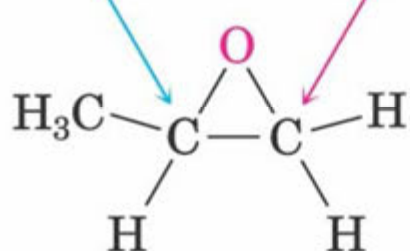
- Anhydrous HF, HBr, HCl, or HI combines with an epoxide
- Gives trans product



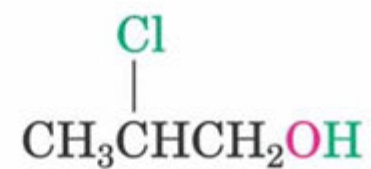
A trans 2-halocyclohexanol

where **X = F, Br, Cl, or I**

Secondary Primary



+

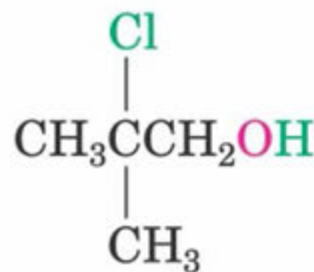
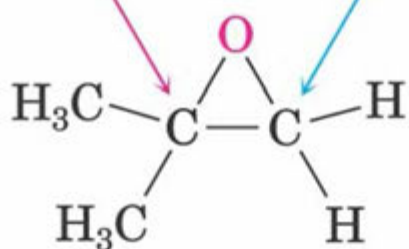


1,2-Epoxypropane

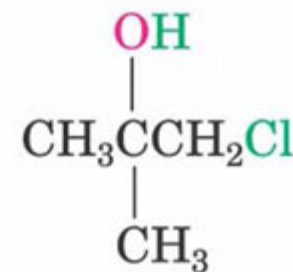
**1-Chloro-2-propanol
(90%)**

**2-Chloro-1-propanol
(10%)**

Tertiary Primary



+

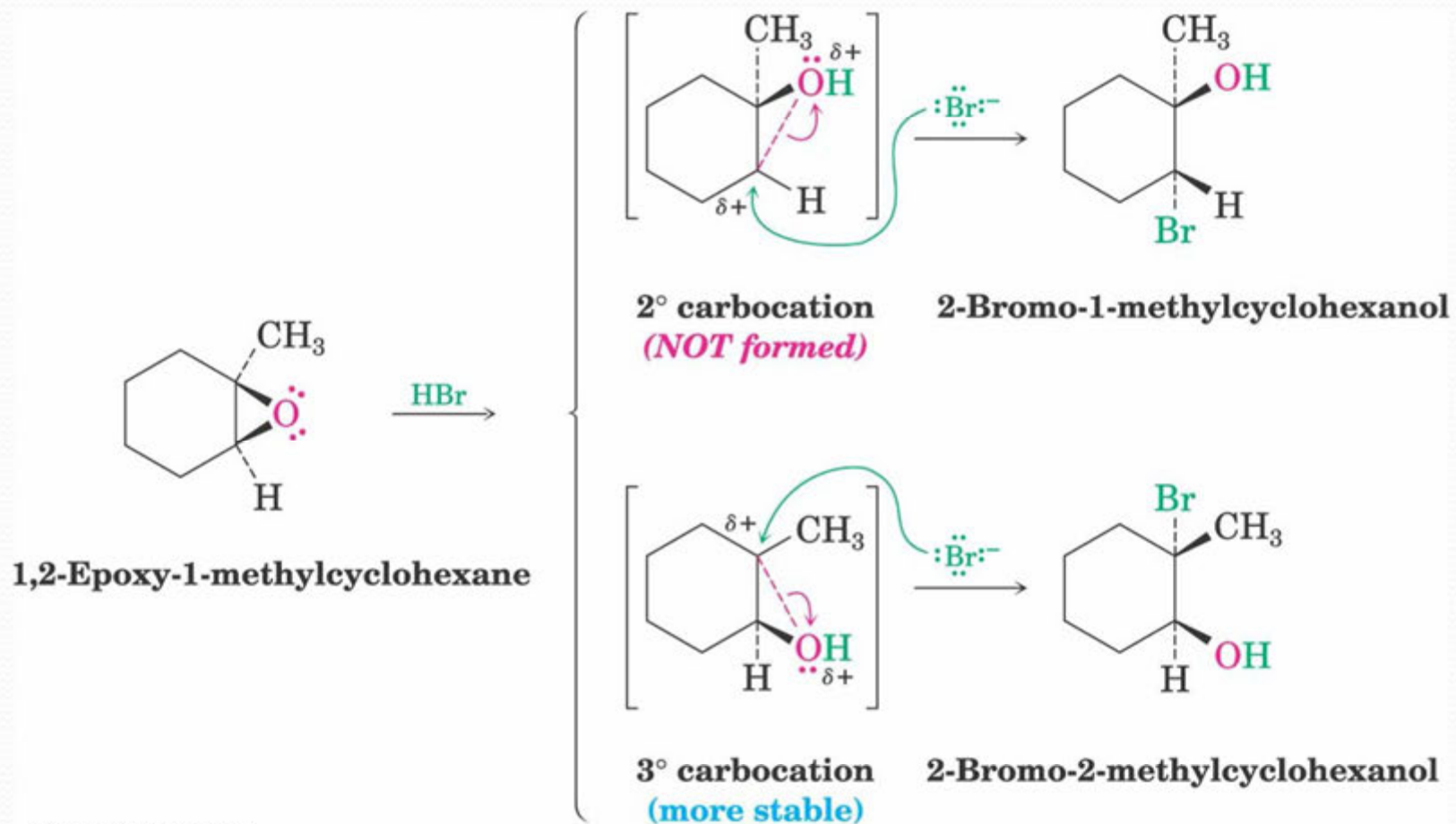


2-Methyl-1,2-epoxypropane

**2-Chloro-2-methyl-
1-propanol (60%)**

**1-Chloro-2-methyl-
2-propanol (40%)**

©2004 Thomson - Brooks/Cole



©2004 Thomson - Brooks/Cole