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# Organic Chemistry

# Alcohols, Ethers and Epoxides

by
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# Expected Outcomes

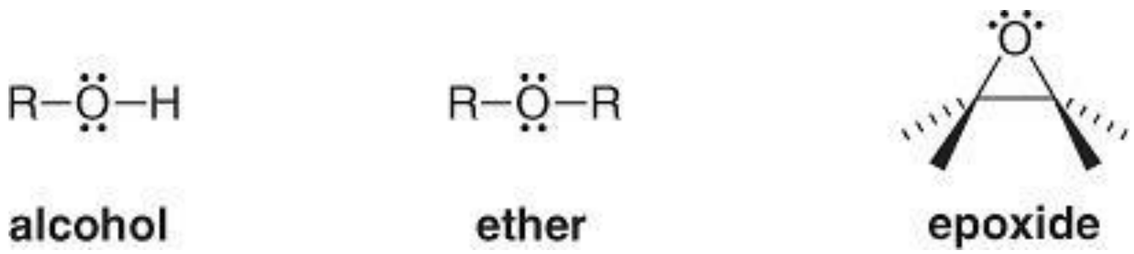
In the completion of this chapter, student will have the ability to:

- Compare and name alcohols, ethers and epoxides
- Describe reaction feature of alcohols, ethers and epoxides

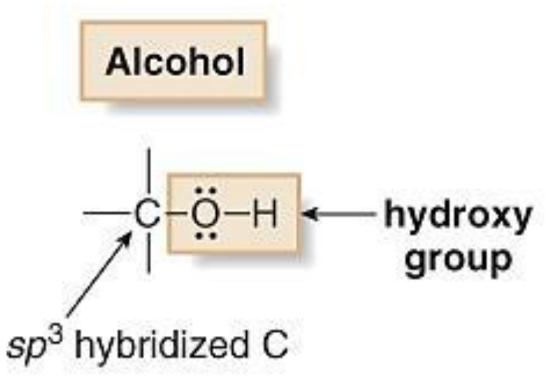
# Contents

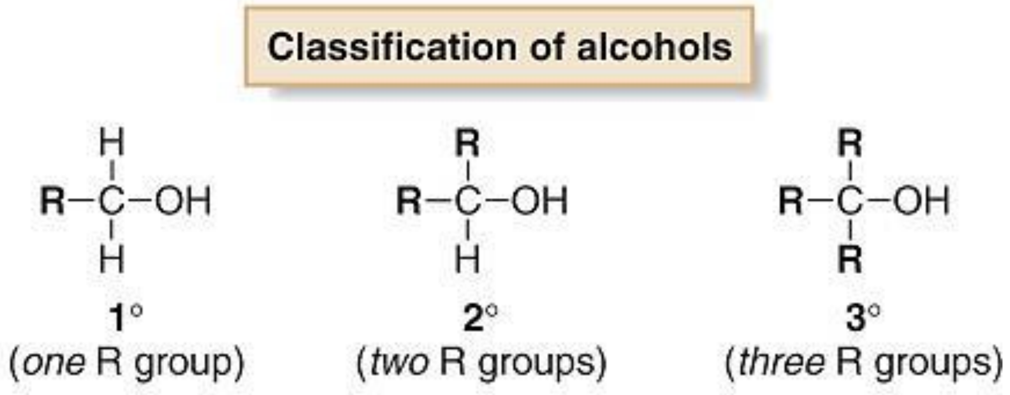
- Alcohol and reaction mechanism
- Ethers and reaction mechanism
- Epoxides and reaction mechanism

# Introduction—Structure and Bonding



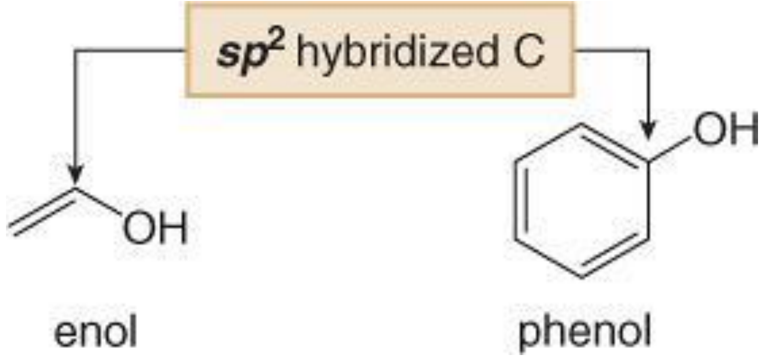

- **Alcohols** contain a hydroxy group (OH) bonded to an $sp^3$ hybridized carbon.



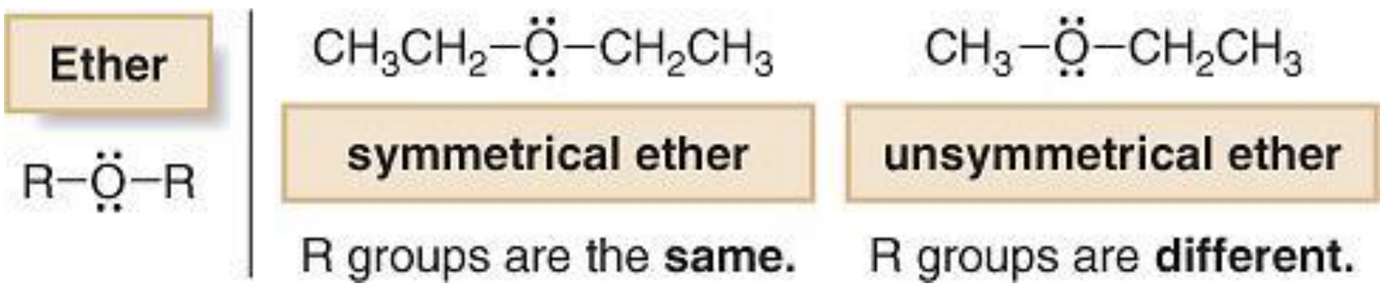



# Introduction—Structure and Bonding

- Compounds having a hydroxy group on a $sp^2$ hybridized carbon—enols and phenols—undergo different reactions than alcohols.




- **Ethers** have two alkyl groups bonded to an oxygen atom.



# Introduction—Structure and Bonding

- **Epoxides** are ethers having the oxygen atom in a three-membered ring. Epoxides are also called **oxiranes**.

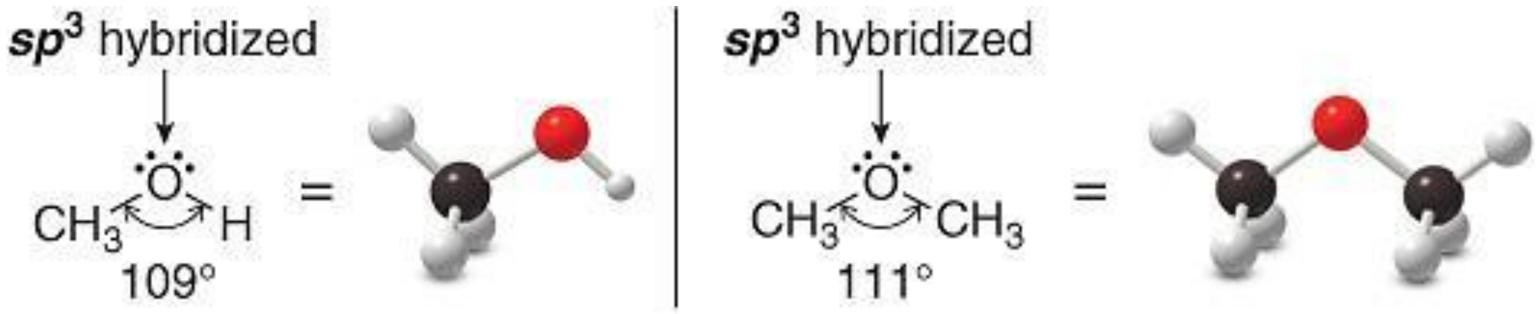
**epoxide** or **oxirane**

An epoxide is a special type of ether.

- The C—O—C bond angle for an epoxide must be 60°(triangle geometry), a considerable deviation from the tetrahedral bond angle of 109.5°($sp^3$ orbital angles). Thus, epoxides have angle strain, making them more reactive than other ethers.

# Introduction—Structure and Bonding

- The oxygen atom in alcohols, ethers and epoxides is *sp*$^3$ hybridized. Alcohols and ethers have a bent shape like that in $H_2O$.
- The bond angle around the O atom in an alcohol or ether is similar to the tetrahedral bond angle of 109.5°.
- Because the O atom is much more electronegative than carbon or hydrogen, the C—O and O—H bonds are all polar.

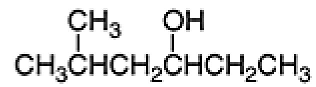


# Nomenclature of Alcohols

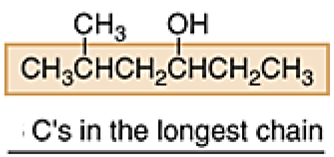


## *How To* Name an Alcohol Using the IUPAC System

**Example** Give the IUPAC name of the following alcohol:



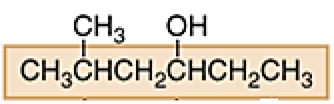

**Step [1]** Find the longest carbon chain containing the carbon bonded to the OH group.



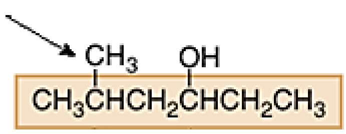

- Change the **-e** ending of the parent alkane to the suffix ***-ol.***

**Step [2]** Number the carbon chain to give the OH group the lower number, and apply all other rules of nomenclature.

a. **Number** the chain.




b. **Name** and **number** the substituents.



# Nomenclature of Alcohols

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## *How To* Name an Alcohol Using the IUPAC System

**Example** Give the IUPAC name of the following alcohol:

$$\begin{array}{c} \quad CH_3 \qquad OH \\ CH_3\overset{|}{C}HCH_2\overset{|}{C}HCH_2CH_3 \end{array}$$

**Step [1]** Find the longest carbon chain containing the carbon bonded to the OH group.

$$\begin{array}{c} \quad CH_3 \qquad OH \\ \boxed{CH_3\overset{|}{C}HCH_2\overset{|}{C}HCH_2CH_3} \end{array}$$

**6** C's in the longest chain

**6 C's** ⟶ **hexane** ⟶ **hexan*ol***

- Change the ***-e*** ending of the parent alkane to the suffix ***-ol.***

**Step [2]** Number the carbon chain to give the OH group the lower number, and apply all other rules of nomenclature.

a. **Number** the chain.

$$\begin{array}{c} \quad CH_3 \qquad OH \\ \boxed{CH_3\overset{|}{C}HCH_2\overset{|}{C}HCH_2CH_3} \\ 6 \quad 5 \quad 4 \quad 3 \quad 2 \quad 1 \end{array}$$

- Number the chain to put the OH group at C3, not C4.

3-hexanol

b. **Name** and **number** the substituents.

methyl at C5

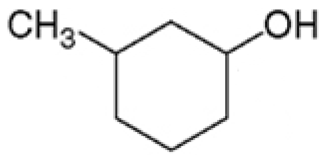
$$\begin{array}{c} \quad CH_3 \qquad OH \\ \boxed{CH_3\overset{|}{C}HCH_2\overset{|}{C}HCH_2CH_3} \\ 5 \qquad\quad 3 \end{array}$$

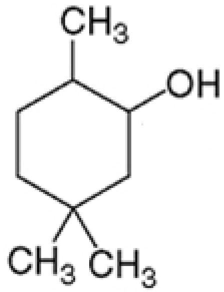
**Answer: 5-methyl-3-hexanol**

# Nomenclature of Alcohols

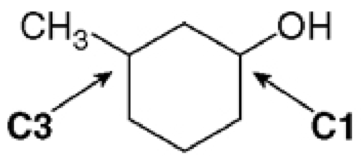
- When an OH group is bonded to a ring, the ring is numbered beginning with the OH group.
- Because the functional group is at C1, the 1 is usually omitted from the name.
- The ring is then numbered in a clockwise or counterclockwise fashion to give the next substituent the lowest number.

**Examples: Naming cyclic alcohols**



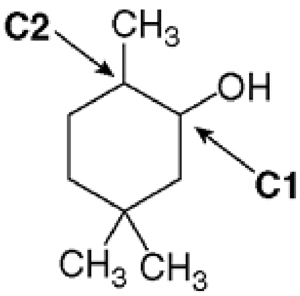



# Naming of cyclic alcohols




**3-methylcyclohexanol**

The OH group is at C1; the second substituent ($CH_3$) gets the lower number.




**2,5,5-trimethylcyclohexanol**

The OH group is at C1; the second substituent ($CH_3$) gets the lower number.

# Unsaturated Alcohols

- Hydroxyl group takes priority over double bond. Assign that carbon the lowest number.
- Use alkene or alkyne name.

$$\begin{array}{c} \qquad\qquad\qquad\quad OH \\ \qquad\qquad\qquad\quad | \\ CH_2{=}CHCH_2CHCH_3 \end{array}$$

4-penten-2-ol

# Naming Priority of functional groups

- Carboxylic acids
- Esters
- Aldehydes
- Ketones
- Alcohols

- Alkenes , Alkynes
- Alkanes , Ethers , Halides

# Hydroxy Substituent

- When -OH is part of a higher priority class of compound, it is named as hydroxy.
- Example:

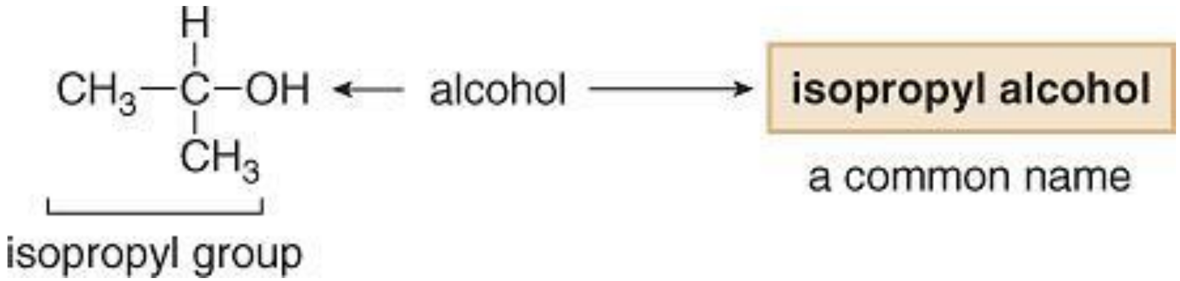
OH
|
$CH_2CH_2CH_2COOH$

OH
|
4 3 2 1
$CH_2CH_2CH_2COOH$
1 2 3 4

4-hydroxybutanoic acid

# Nomenclature of Alcohols

- **Common names** are often used for simple alcohols. To assign a common name:
  - Name all the carbon atoms of the molecule as a single alkyl group.
  - Add the word alcohol, separating the words with a space.

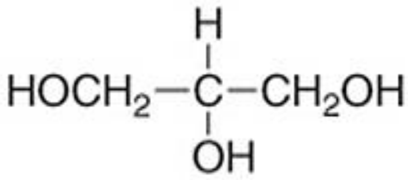


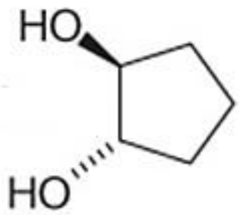

2-propoanol

# Nomenclature of Alcohols

- Compounds with two hydroxy groups are called diols or glycols. Compounds with three hydroxy groups are called triols and so forth.

$HOCH_2CH_2OH$





# Nomenclature of Alcohols

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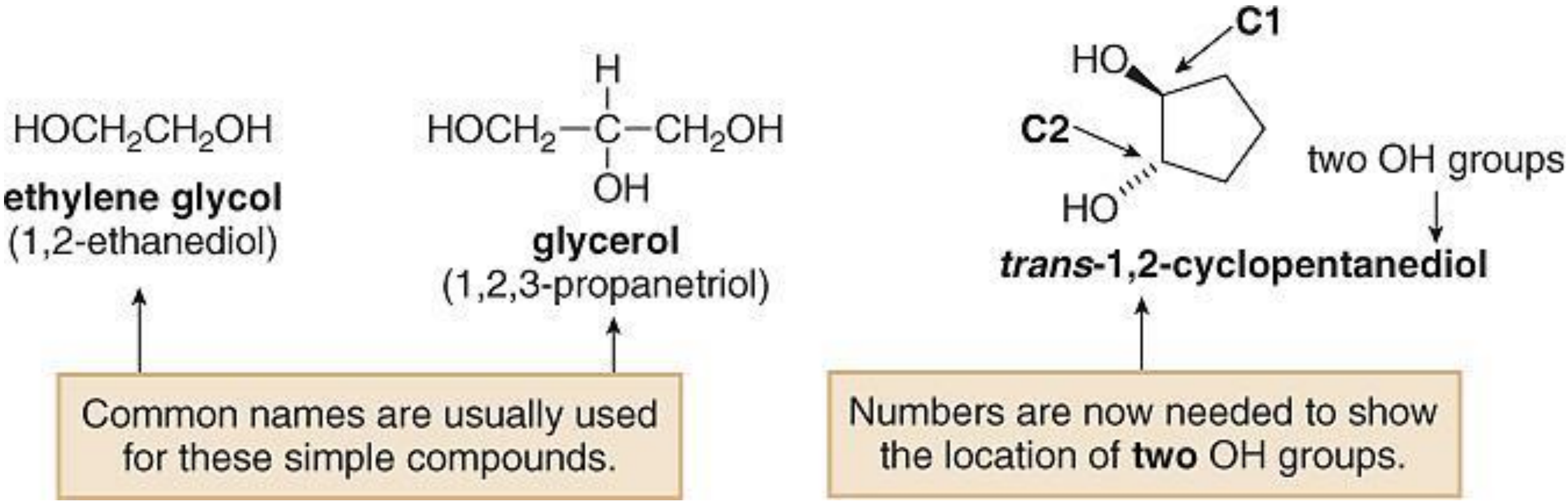
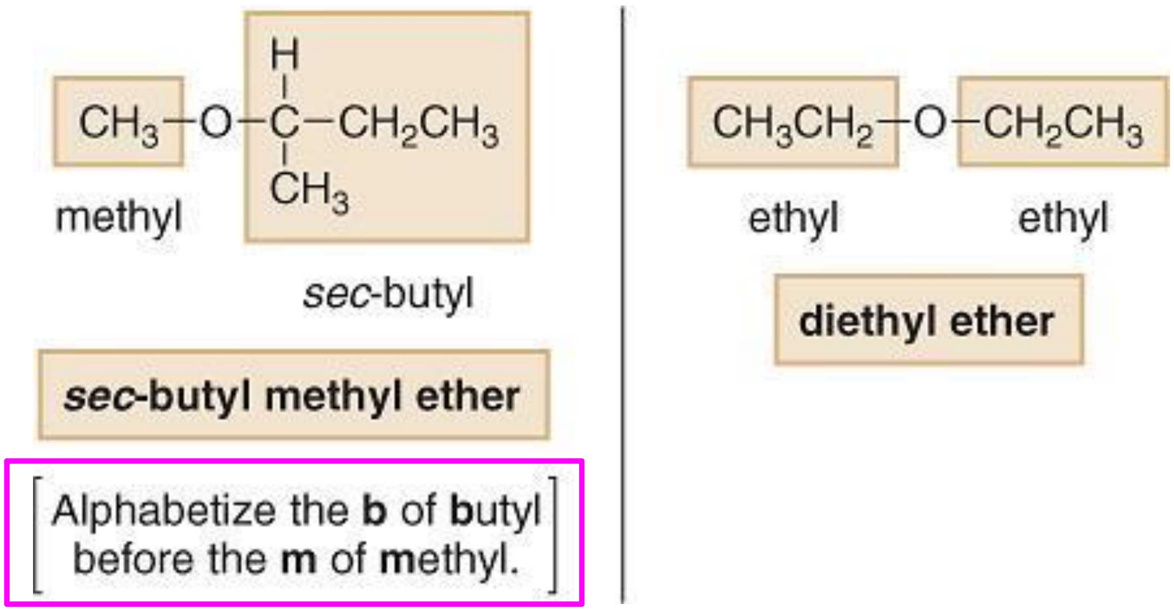


# Nomenclature of Ethers

- Simple ethers are usually assigned common names. To do so:
  - Name both alkyl groups bonded to the oxygen, arrange these names alphabetically, and add the word ether.
  - For symmetrical ethers, name the alkyl group and add the prefix "di-".



# Nomenclature of Ethers

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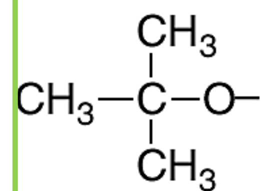
- More complex ethers are named using the **IUPAC system**. One alkyl group is named as a hydrocarbon chain, and the other is named as part of a substituent bonded to that chain:
  - Name the simpler alkyl group as an alkoxy substituent by changing the –yl ending of the alkyl group to –oxy.
  - Name the remaining alkyl group as an alkane, with the alkoxy group as a substituent bonded to this chain.

**Common alkoxy groups**

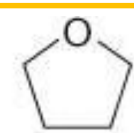
$CH_3O–$
methoxy

$CH_3CH_2O–$
ethoxy



*tert*-butoxy

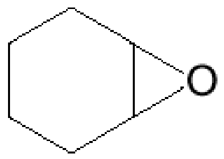
- Cyclic ethers have an O atom in the ring. A common example is tetrahydrofuran (THF).



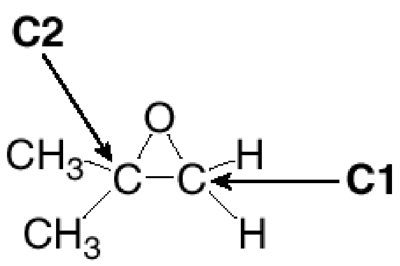
tetrahydrofuran
**THF**

# Nomenclature of Epoxides

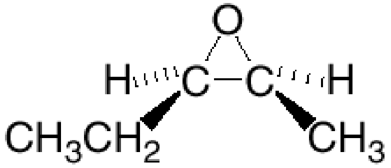
- Epoxides can be named in three different ways—As epoxyalkanes, oxiranes, or alkene oxides.
- To name an epoxide as an epoxyalkane, first name the alkane chain or ring to which the O atom is attached, and use the prefix “epoxy” to name the epoxide as a substituent. Use two numbers to designate the location of the atoms to which the O’s are bonded.




1,2-epoxycyclohexane



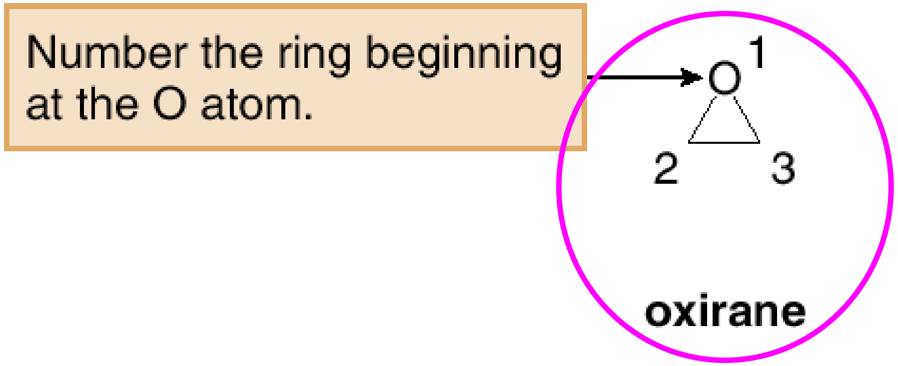

1,2-epoxy-2-methylpropane

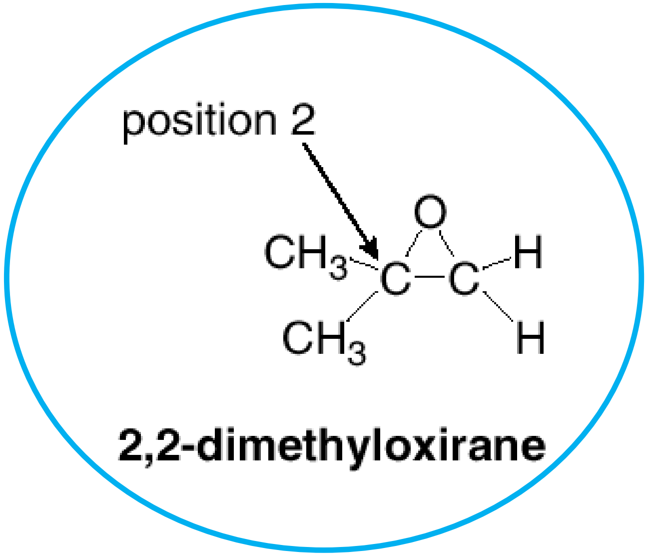



*cis*-2,3-epoxypentane

# Nomenclature of Epoxides

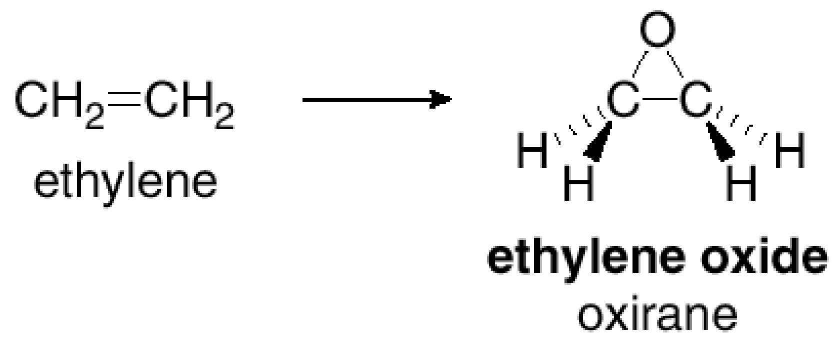
- Epoxides bonded to a chain of carbon atoms can also be named as derivatives of oxirane, the simplest epoxide having two carbons and one oxygen atom in a ring.
- The oxirane ring is numbered to put the O atom at position one, and the first substituent at position two.
- No number is used for a substituent in a monosubstituted oxirane.



# Nomenclature of Epoxides

- Epoxides are also named as alkene oxides, since they are often prepared by adding an O atom to an alkene. To name an epoxide in this way:
  - Mentally replace the epoxide oxygen with a double bond.
  - Name the alkene.
  - Add the word oxide.



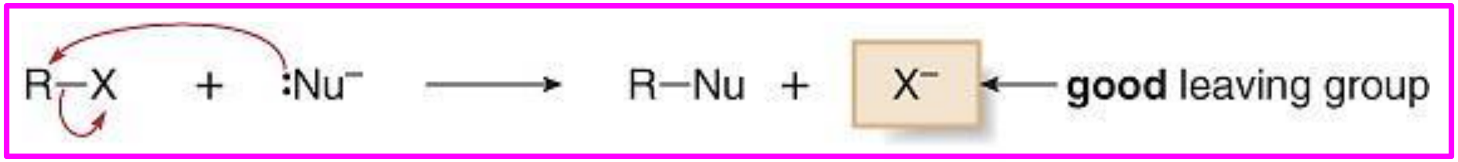
# Physical Properties of Alcohols, Ethers, and Epoxides

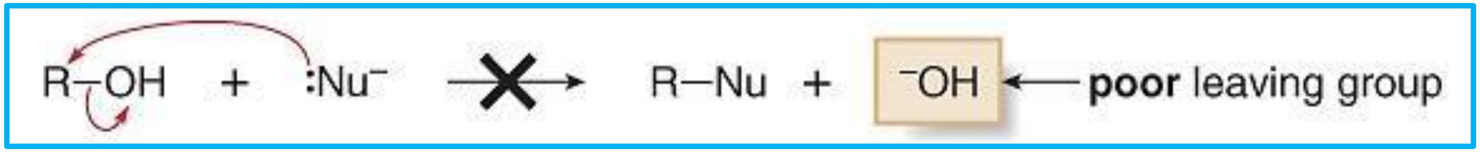
| Property | Observation |
|---|---|
| Boiling point (bp) and melting point (mp) | • For compounds of comparable molecular weight, the **stronger** the intermolecular forces, the **higher** the bp or mp.<br>$CH_3CH_2CH_2CH_3$ — VDW — bp 0 °C<br>$CH_3OCH_2CH_3$ — VDW, DD — bp 11 °C<br>$CH_3CH_2CH_2OH$ — VDW, DD, HB — bp 97 °C<br>**Increasing boiling point** →<br>• Bp's **increase** as the extent of hydrogen bonding **increases.**<br>$(CH_3)_3C{-}OH$ — 3° — bp 83 °C<br>$CH_3CH_2CH(OH)CH_3$ — 2° — bp 98 °C<br>$CH_3CH_2CH_2CH_2{-}OH$ — 1° — bp 118 °C<br>**Increasing ability to hydrogen bond**<br>**Increasing boiling point** → |
| Solubility | • Alcohols, ethers, and epoxides having ≤ 5 C's are $H_2O$ soluble because they each have an oxygen atom capable of hydrogen bonding to $H_2O$.<br>• Alcohols, ethers, and epoxides having > 5 C's are $H_2O$ insoluble because the nonpolar alkyl portion is too large to dissolve in $H_2O$.<br>• Alcohols, ethers, and epoxides of any size are soluble in organic solvents. |

Key: VDW = van der Waals forces; DD = dipole–dipole; HB = hydrogen bonding

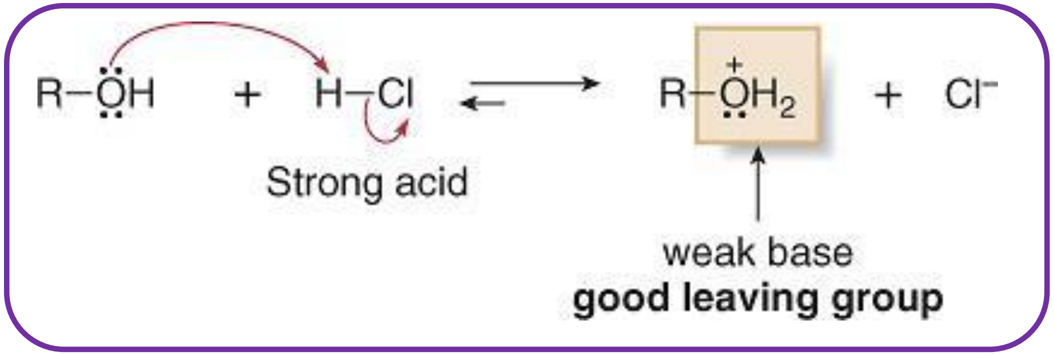
# Reactions of Alcohols

- Recall that, unlike alkyl halides in which the halogen atom serves as a good leaving group, the OH group in alcohols is a very poor leaving group.



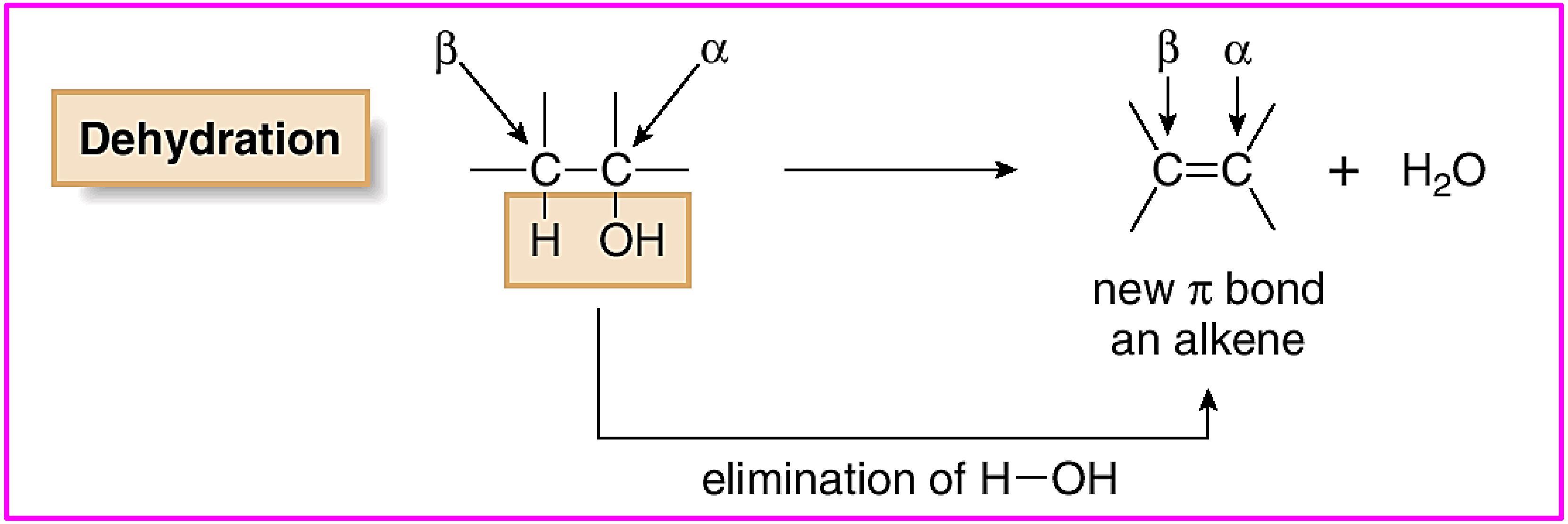




- For an alcohol to undergo nucleophilic substitution, OH must be converted into a better leaving group. By using acid, ⁻OH can be converted into $-OH_2$, a good leaving group.



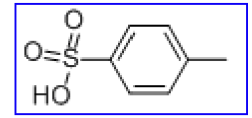
# Reactions of Alcohols—Dehydration

- Dehydration, like dehydrohalogenation, is a β elimination reaction in which the elements of OH and H are removed from the α and β carbon atoms respectively.

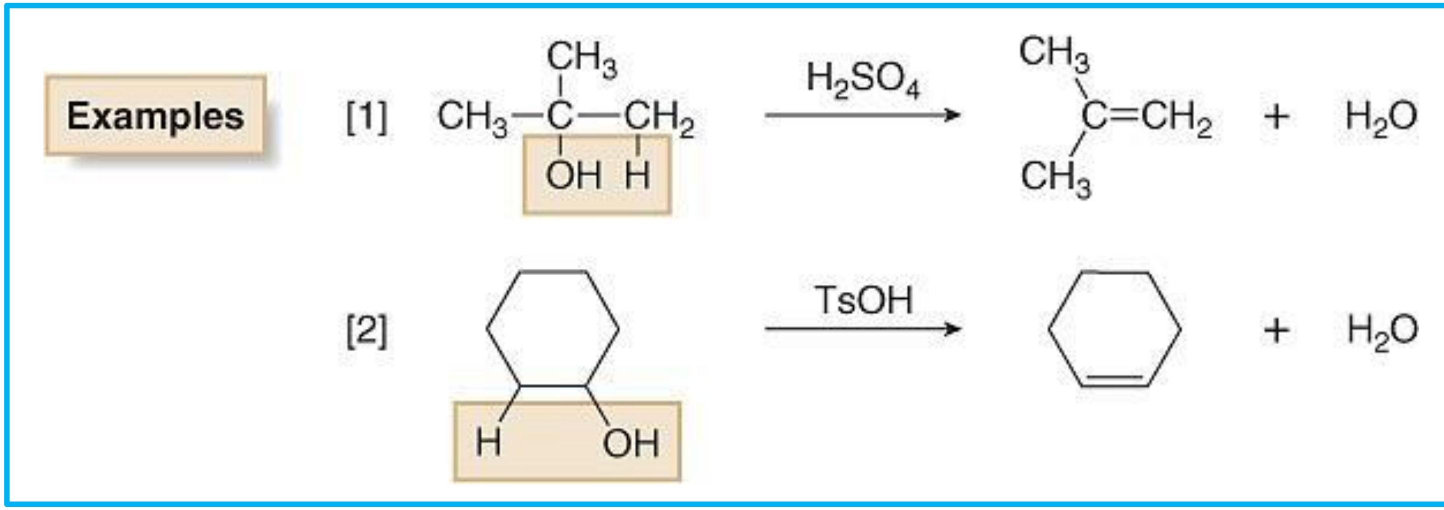



- Dehydration is typically carried out using $H_2SO_4$ and other strong acids, or phosphorus oxychloride ($POCl_3$) in the presence of an amine base.

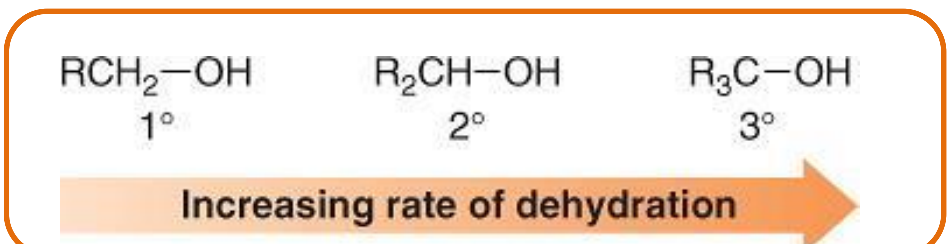
# Reactions of Alcohols—Dehydration




- Typical acids used for alcohol dehydration are $H_2SO_4$ or *p*-toluenesulfonic acid (TsOH).

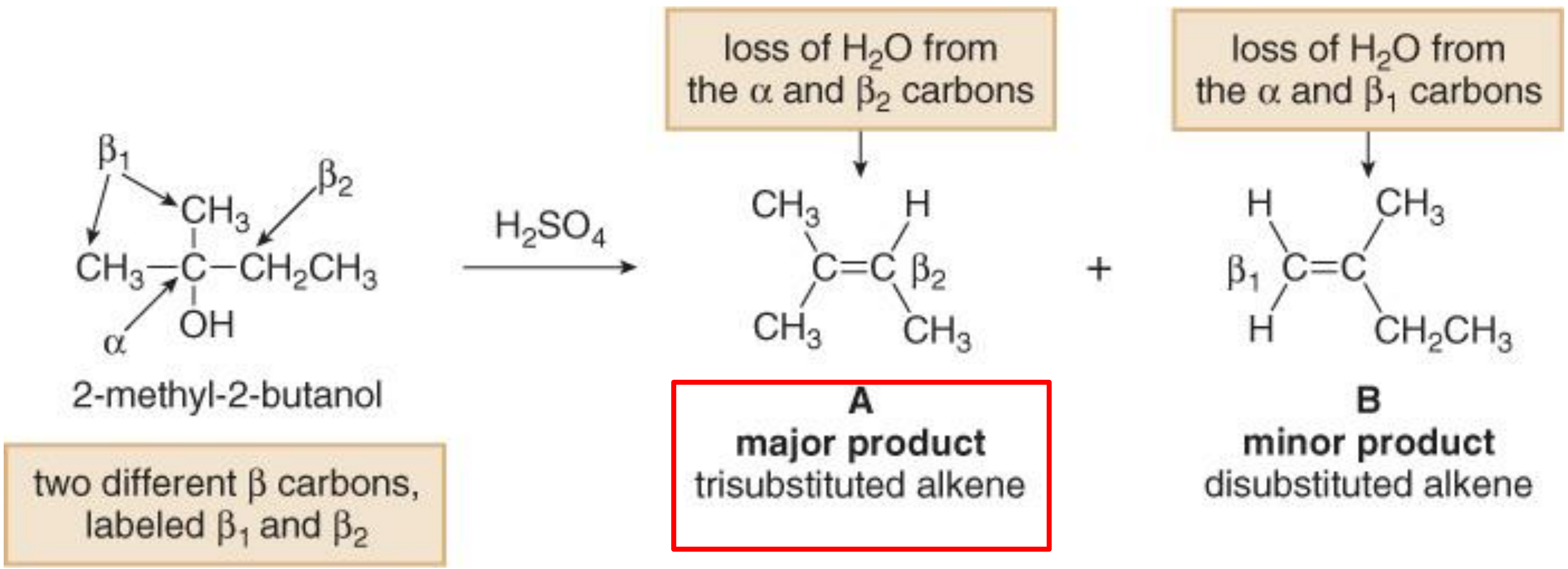



- More substituted alcohols dehydrate more easily, giving rise to the following order of reactivity.



# Reactions of Alcohols—Dehydration

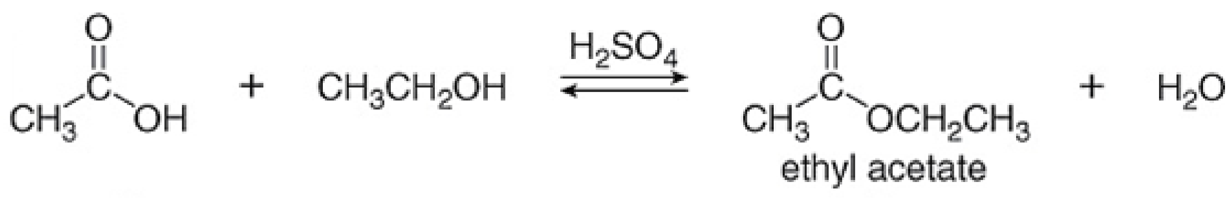
- When an alcohol has two or three β carbons, dehydration is follows Zaitsev (Saytseff) rule:
- The more substituted alkene is the major product when a mixture of constitutional isomers is possible.

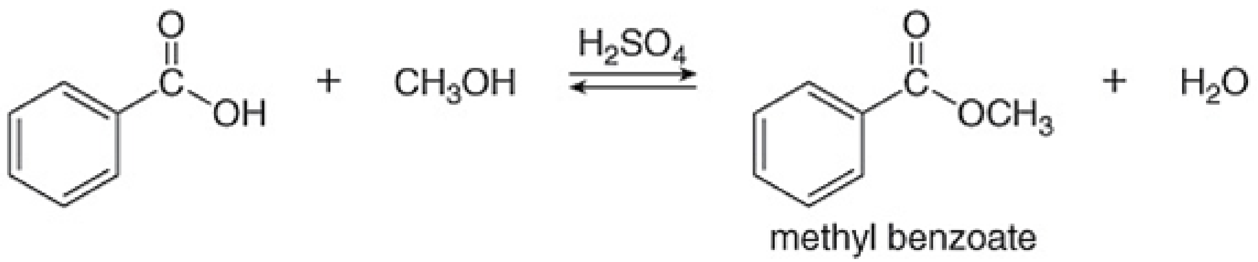


# Reactions with Carboxylic Acids- esterification

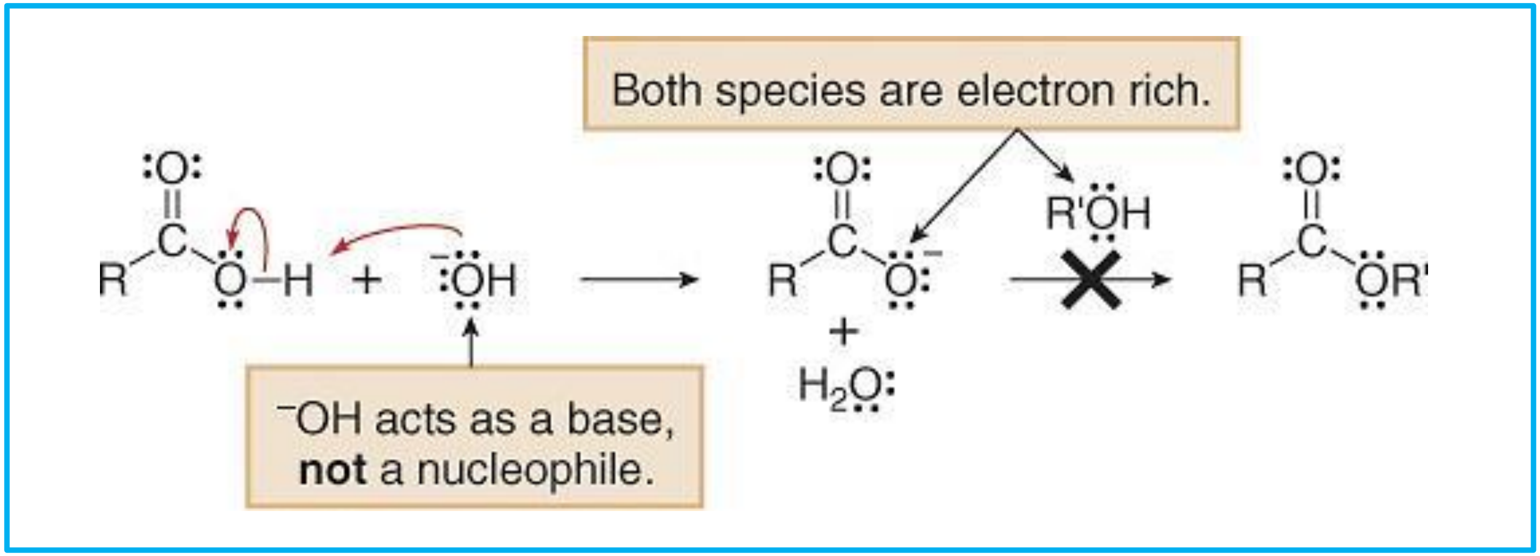
- Treatment of a **carboxylic acid** with an **alcohol** in the presence of an acid catalyst forms an ester.
- This reaction is called a **Fischer esterification**.
- The reaction is an equilibrium, so it is driven to the right by using excess alcohol or by removing water (a product) as it is formed ( Recall: Dean  & Stark's apparatus) .

**Examples**



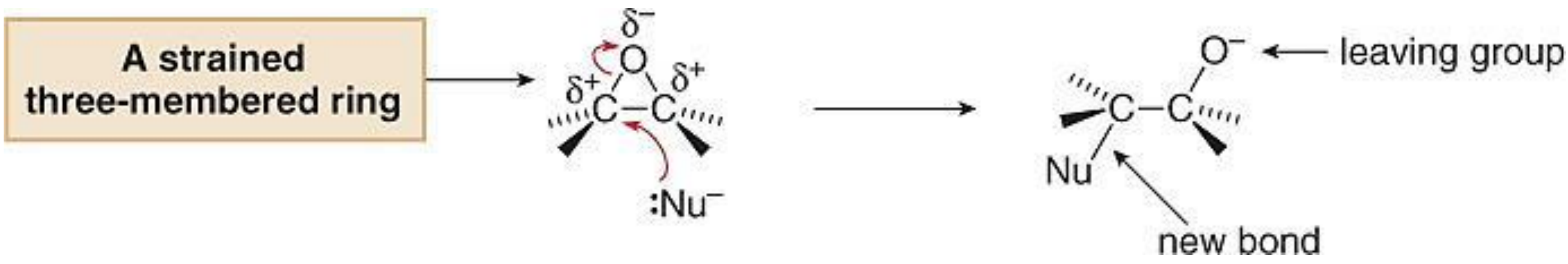



- Esterification of a carboxylic acid occurs in the presence of acid but not in the presence of base.
- Base removes a proton from the carboxylic acid, forming the carboxylate anion, which does not react with an electron-rich nucleophile.



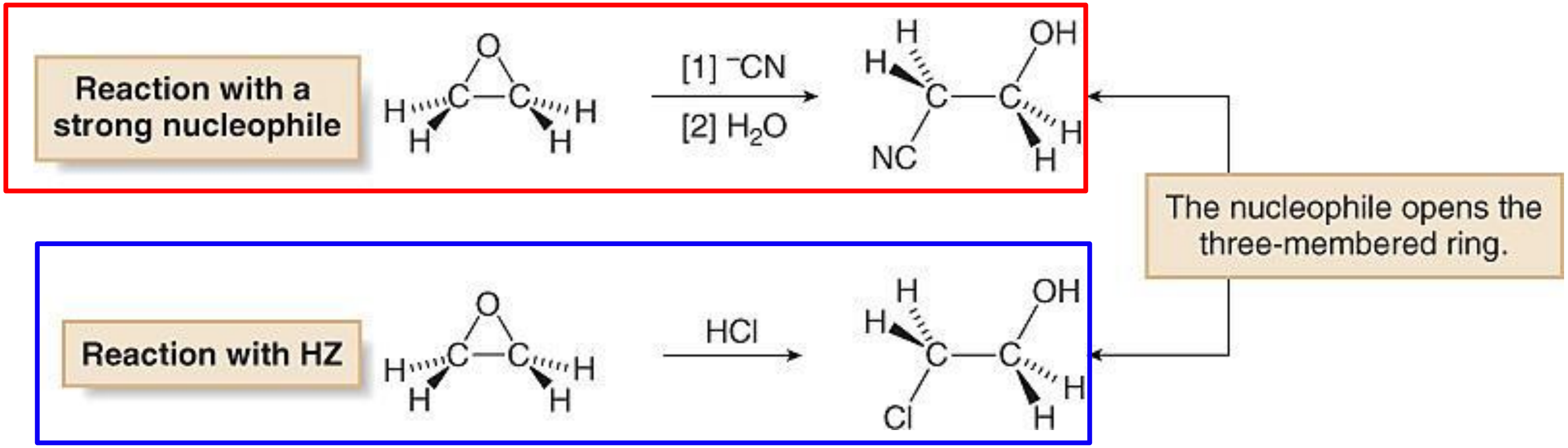
# Reactions of Epoxides

- Epoxides do not contain a good leaving group.
- Epoxides do contain a strained three-membered ring with two polar bonds.
- Nucleophilic attack opens the strained three-membered ring, making it a favorable process even with a poor leaving group.



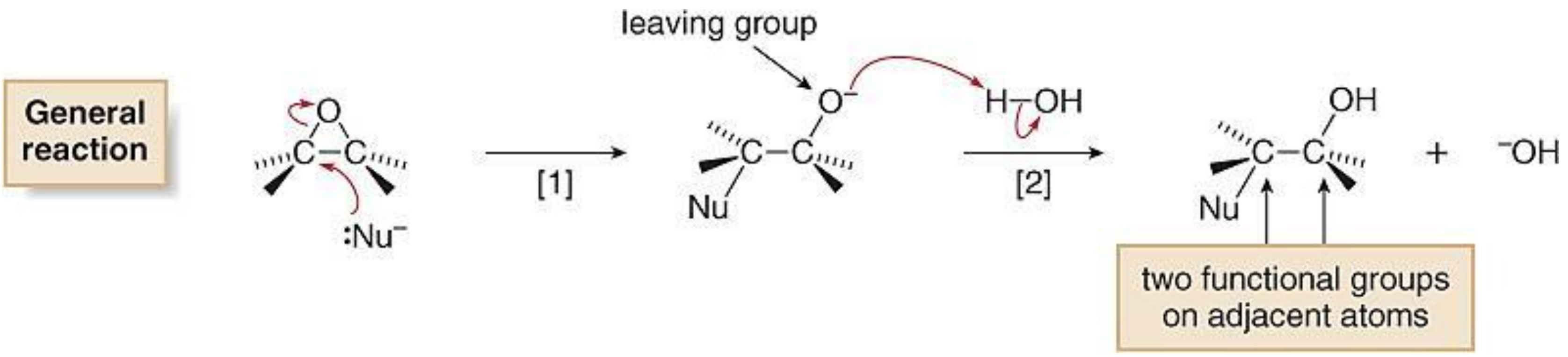
# Reactions of Epoxides

- The reaction occurs readily with **strong nucleophiles** and **with acids** like **HZ**, where **Z** is a nucleophilic atom.



# Reactions of Epoxides

- Virtually all strong nucleophiles open an epoxide ring by a two-step reaction sequence:



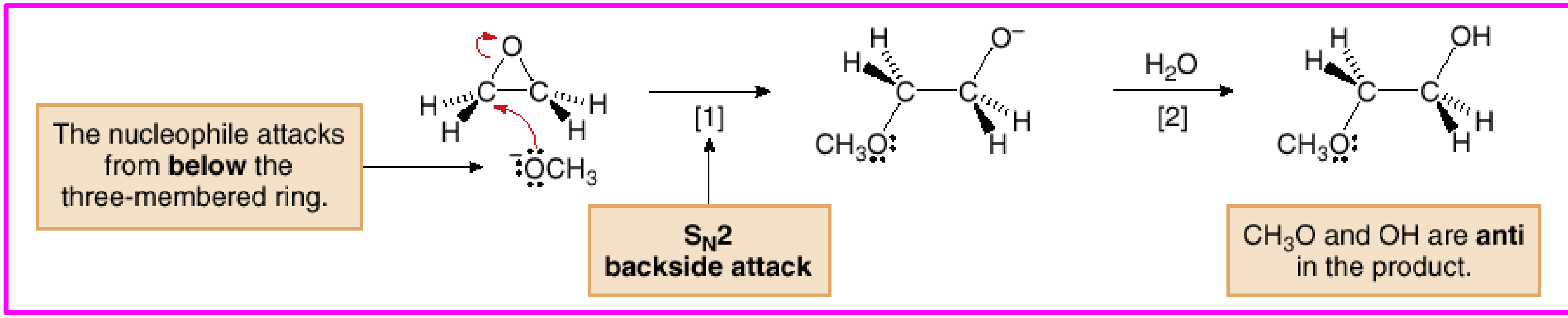

- In step 1, the nucleophile attacks an electron-deficient carbon, thus cleaving the C—O bond and relieving the strain of the three-membered ring.
- In step 2, the alkoxide is protonated with water to generate a neutral product with two functional groups on adjacent atoms.
- Common nucleophiles that open the epoxide ring include $^{-}OH$, $^{-}OR$, $^{-}CN$, $^{-}SR$ and $NH_3$. With these strong nucleophiles, the reaction occurs by an $S_N2$ mechanism.

# Reactions of Epoxides

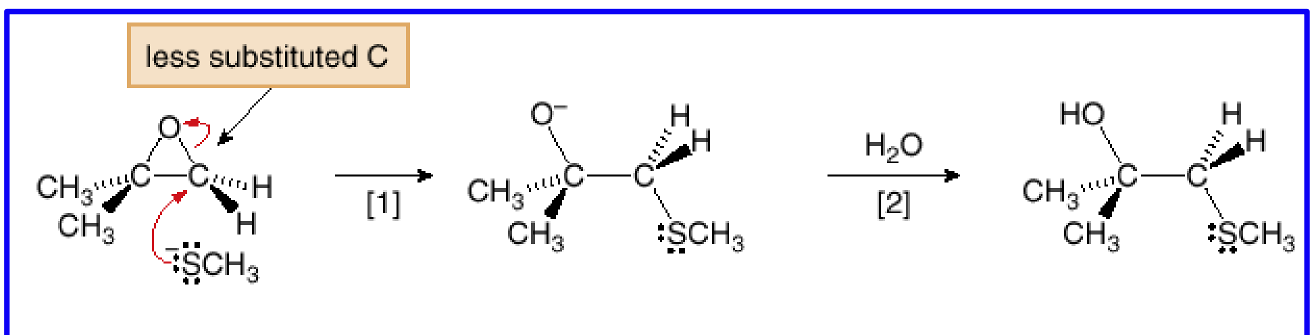


Consider the following examples:

- The nucleophile opens the epoxide ring from the back side.

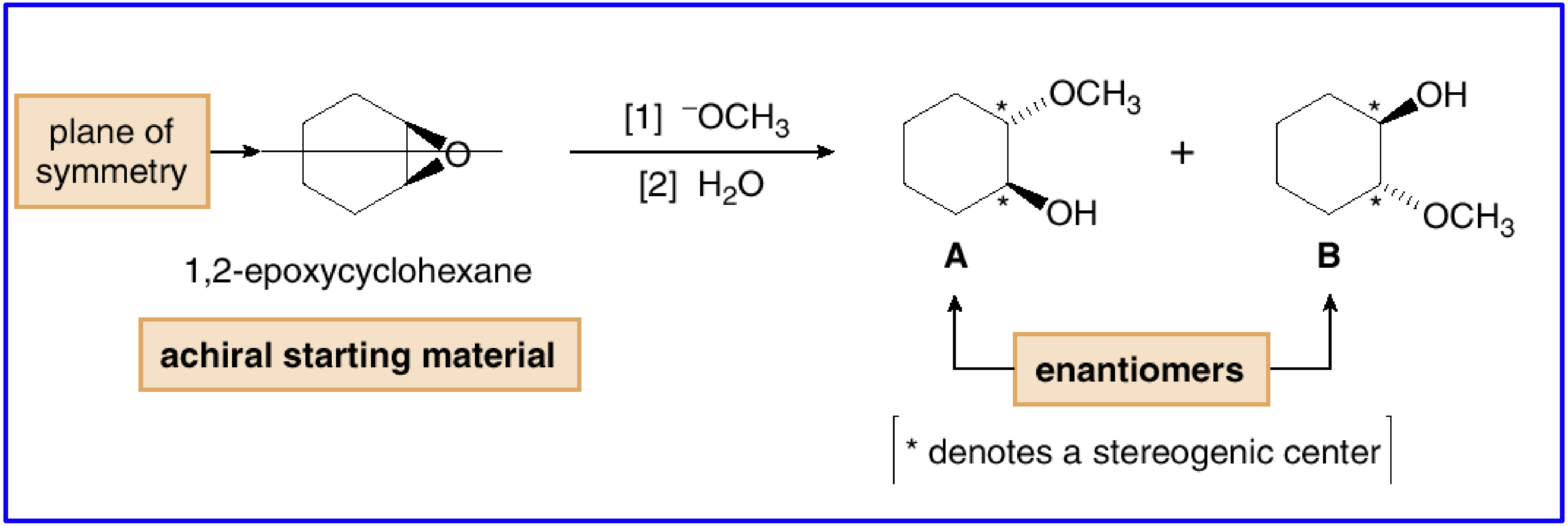



- In an unsymmetrical epoxide, the nucleophile attacks at the less substituted carbon atom.



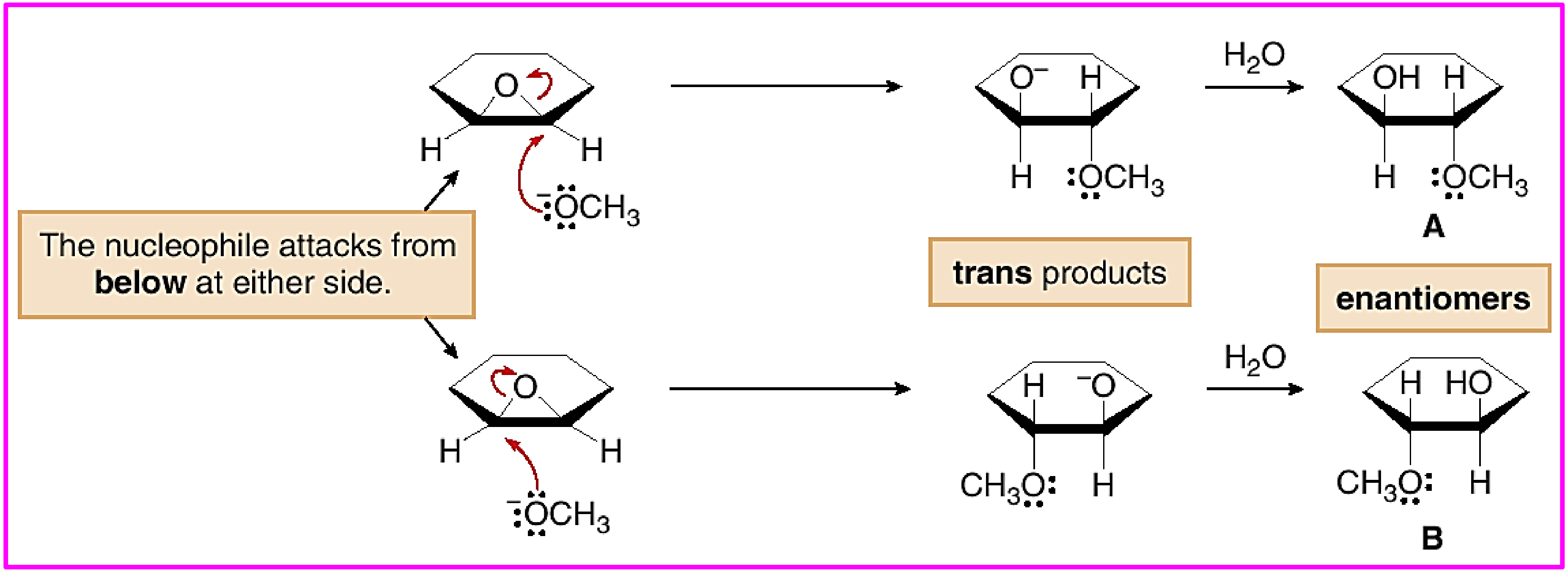
# Reactions of Epoxides

Let's now consider the stereochemical consequences of the reaction of 1,2-epoxycyclohexane with $^{-}OCH_3$.




Nucleophilic attack of $^{-}OCH_3$ occurs from the backside at either C—O bond, because both ends are similarly substituted. Since attack at either side occurs with equal probability, an equal amount of the two enantiomers (i.e., a racemic mixture) is formed.

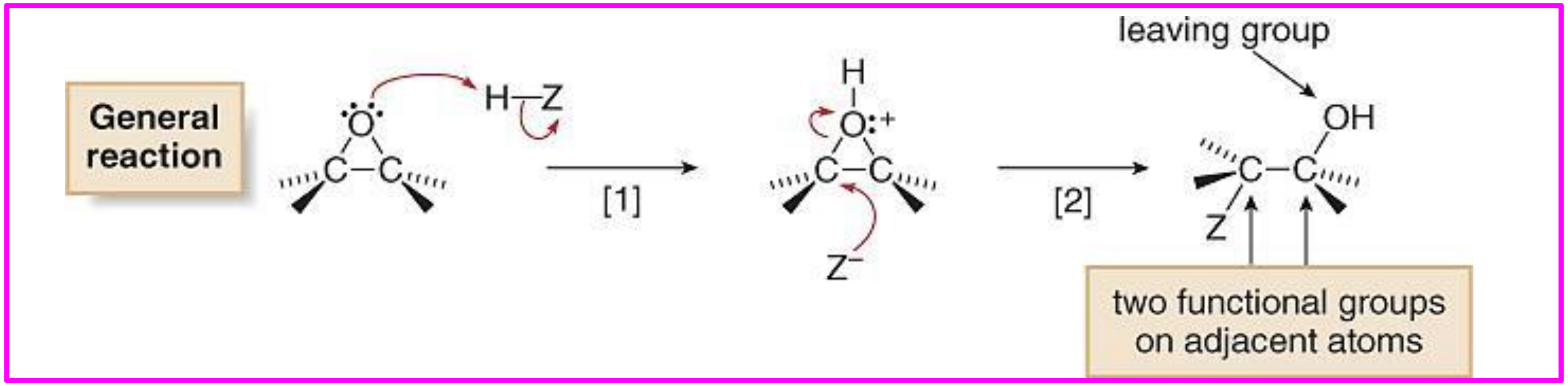
# Reactions of Epoxides




- Whenever an achiral reactant yields a product with stereogenic centers, the product must be achiral (meso) or racemic.

# Reactions of Epoxides

- Acids HZ that contain a nucleophile Z also open epoxide rings by a two-step sequence.
- HCl, HBr and HI, as well as $H_2O$ and ROH in the presence of acid, all open an epoxide ring in this manner.




**Examples**