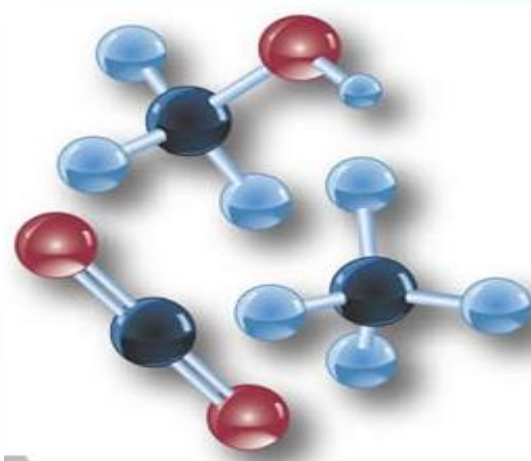




# Organic Chemistry



Le Liu

[le.liu@xjtu.edu.cn](mailto:le.liu@xjtu.edu.cn)



# **Chapter 9**

## **Organic Compounds**

### **—— Alcohols and Ethers**



## Outline:

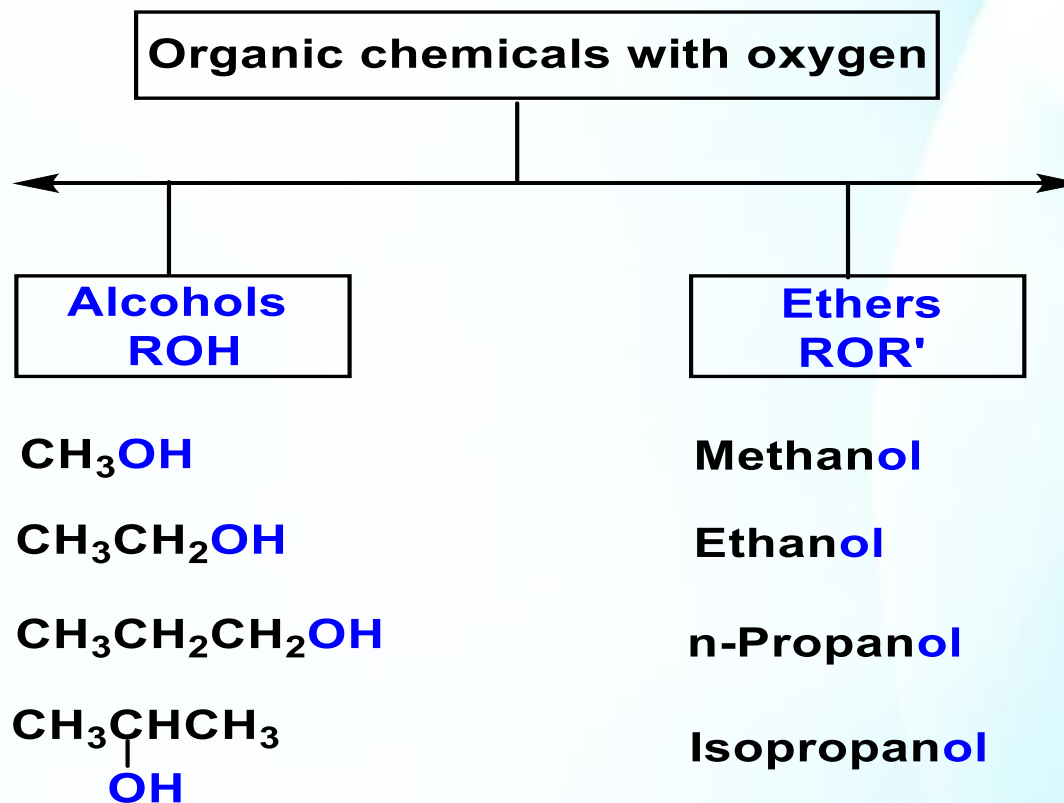
- 1. What are alcohols?**
- 2. What are the characteristic reaction of alcohols?**
- 3. What are ethers?**
- 4. What are the characteristic reaction of ethers?**
- 5. What are epoxides?**
- 6. What are the characteristic reactions of epoxides?**



The general alcohol structure would be **R-OH**.

The common system for naming alcohols is :

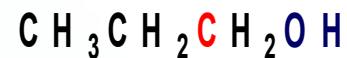
Name of R-group + “alcohol”





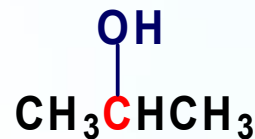
# 1. Classification of Alcohols

① 按与 - OH相连的碳原子的类型分：伯、仲、叔醇。



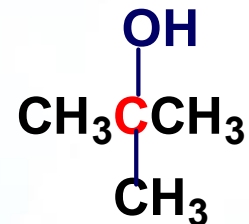
一级醇 (伯醇)

Primary ( $1^\circ$ )



二级醇 (仲醇)

Secondary ( $2^\circ$ )



三级醇 (叔醇)

Tertiary ( $3^\circ$ )

② 按 - OH的数目不同：一元醇、二元醇、三元醇。

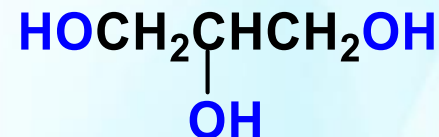


乙醇



乙二醇

ethylene glycol



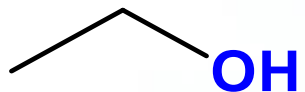
丙三醇 (甘油)

Glycerin



## 2. Nomenclature

Alcohols are named by the IUPAC system as derivatives of the parent alkane, using the suffix **-ol**.

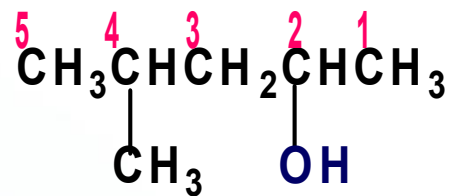


Ethan**ol**

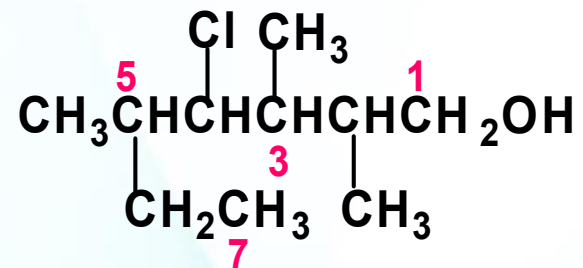
**step1:** Select the longest carbon chain containing *the hydroxyl group*, and derive the parent name by replacing the **-e** ending of the corresponding alkane with **-ol**;

**step2:** Number the alkane chain beginning at the end nearer the *hydroxyl* group;

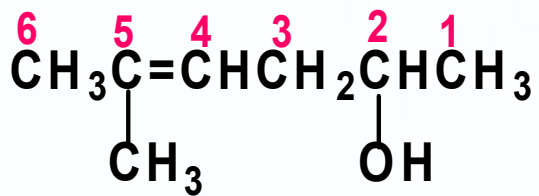
**step3:** Number the substituents according to their position on the chain and write the name listing the substituents on **alphabetical order**.



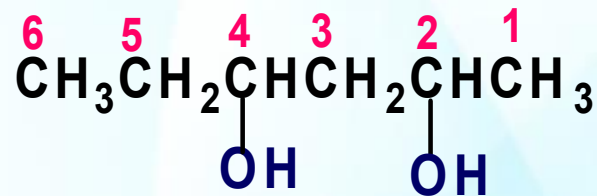
4-Methylpentan-2-ol



4-Chloro-2,3,5-trimethylheptan-1-ol



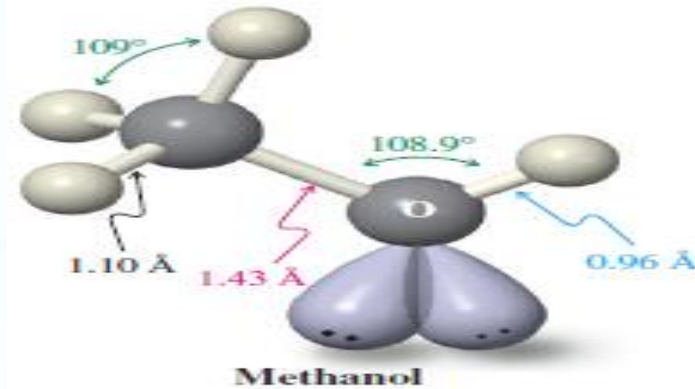
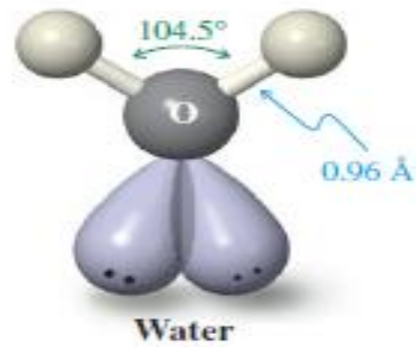
5-methylhex-4-en-2-ol



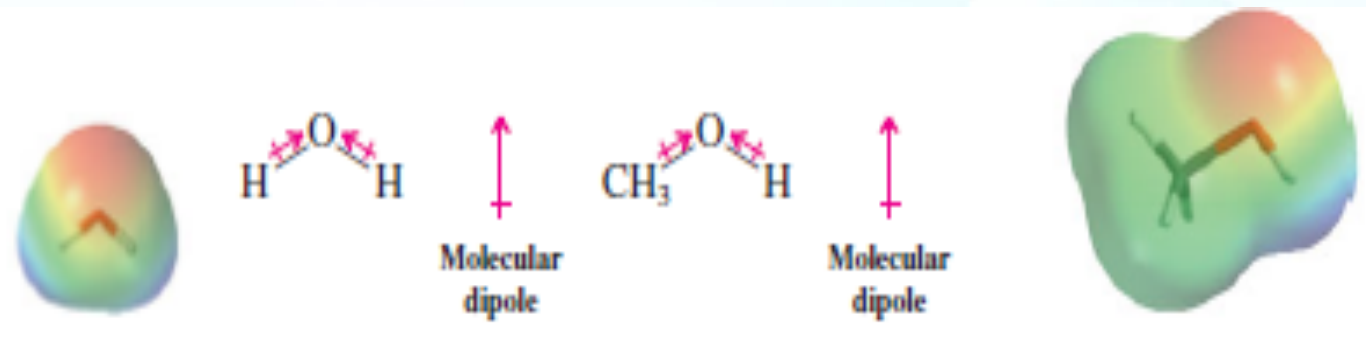
Hexane-2,4-diol



### 3. Structure



The carbon and oxygen atoms of the alcohol group are  $sp^3$  hybridized such that the C-O-H bond angle is approximately  $108.9^\circ$ .

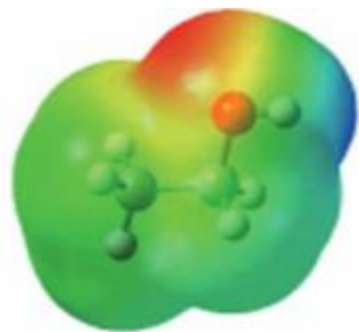


由于氧的电负性大于碳，醇分子中的C-O键是**极性键**, ROH是**极性分子**。  
**C(EN=2.5), H(EN=2.1), O(EN=3.5)**

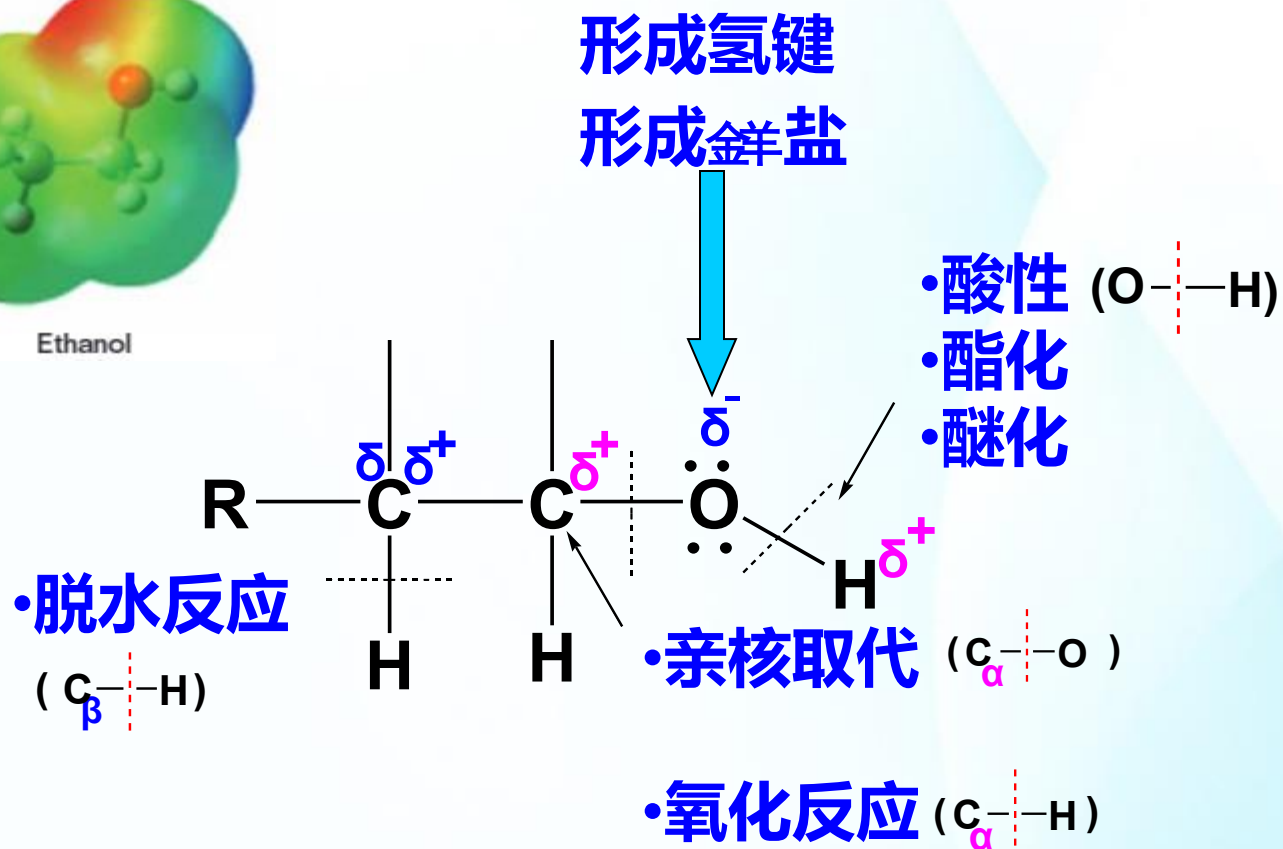




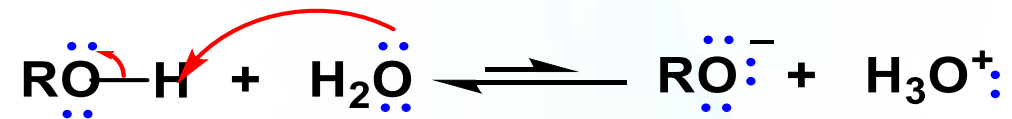
## 结构—化学性质



Ethanol



### (1) Acid-base reactions



Compound	pKa	Compound	pKa
HOH	15.7	ClCH <sub>2</sub> CH <sub>2</sub> OH	14.3
CH <sub>3</sub> OH	15.5	CF <sub>3</sub> CH <sub>2</sub> OH	12.4
CH <sub>3</sub> CH <sub>2</sub> OH	15.9	CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	14.6
(CH <sub>3</sub> ) <sub>2</sub> CHOH	17.1	CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	15.4
(CH <sub>3</sub> ) <sub>3</sub> COH	18		

pKa:           H<sub>2</sub>O>CH<sub>3</sub>CH<sub>2</sub>OH

CH<sub>3</sub>OH < 1° ROH < 2° ROH < 3° ROH

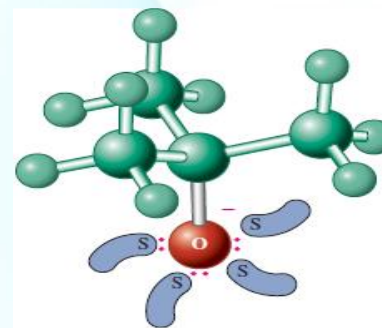
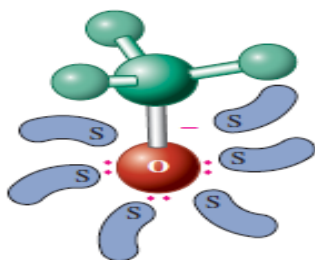


Alcohols are slightly weaker acids than water.



Strongest acid

Weakest acid

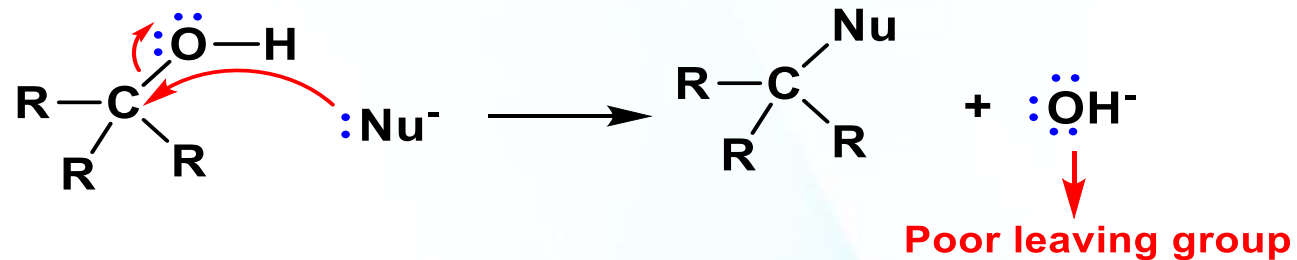


Alcohols do not react with sodium bicarbonate or amines, and a **stronger base** such as sodium hydride or sodium amide is required to generate the alkoxide ion.

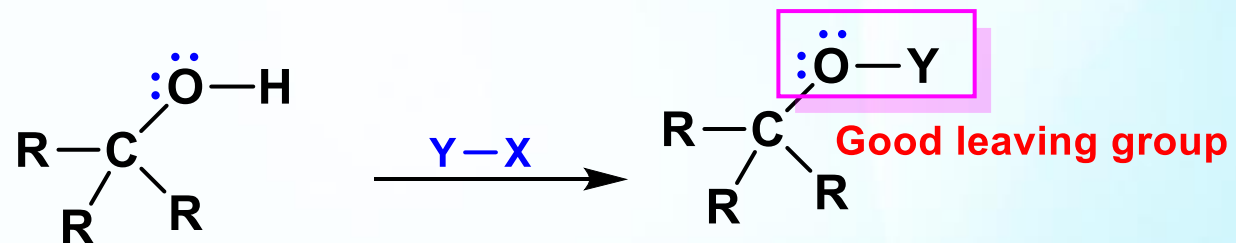
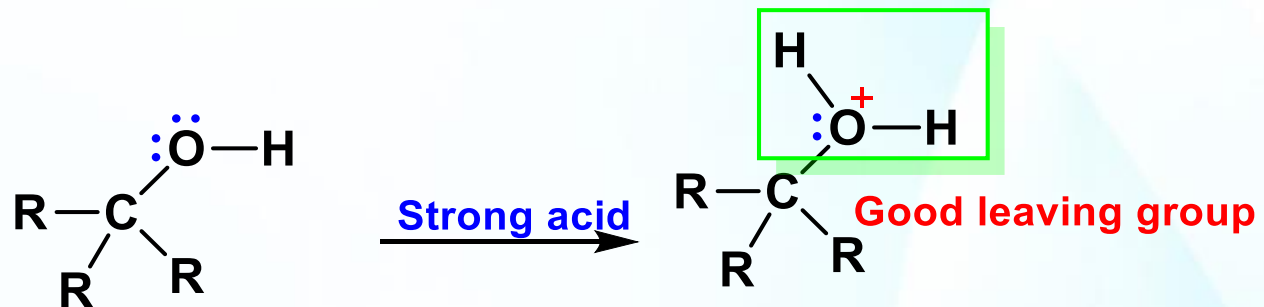
	Alcohol	Ethyne	Ammonia	Ethane
pKa	15.5-18.0	25	38	50

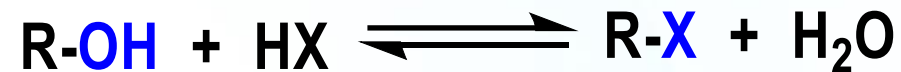


## (2) Synthesis of alkyl halides

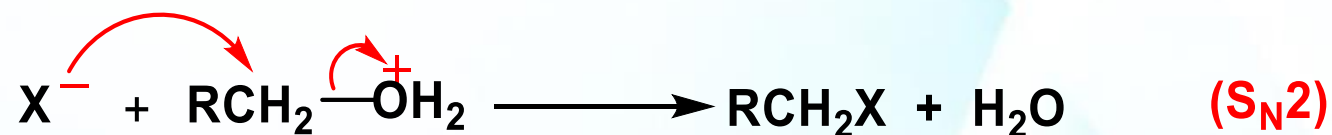
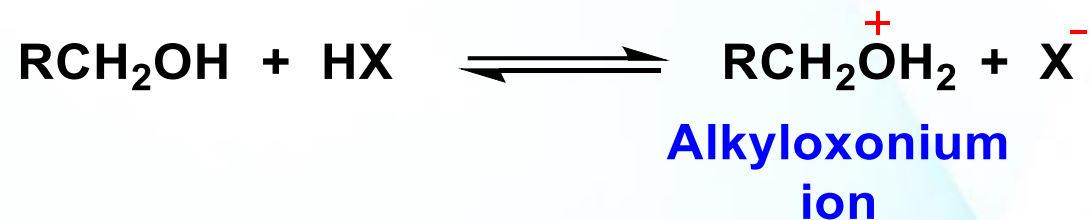


The reagents serve to convert the hydroxyl group into a better leaving group.

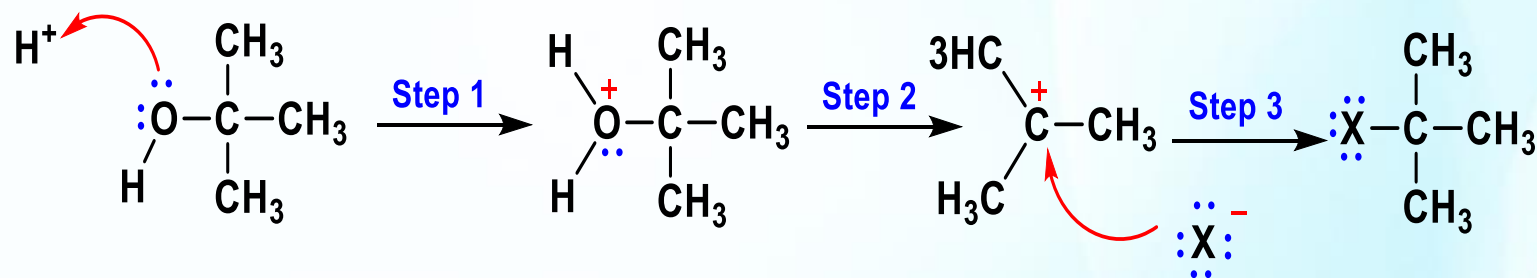




✧ Mechanism:

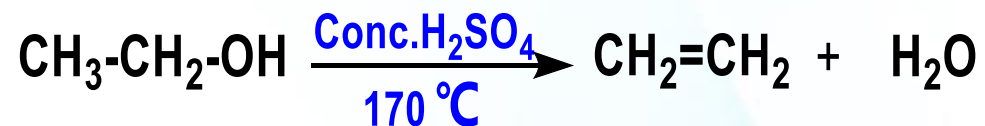


Tertiary alcohols can undergo the  $\text{S}_{\text{N}}1$  reaction to produce tertiary alkyl halides.

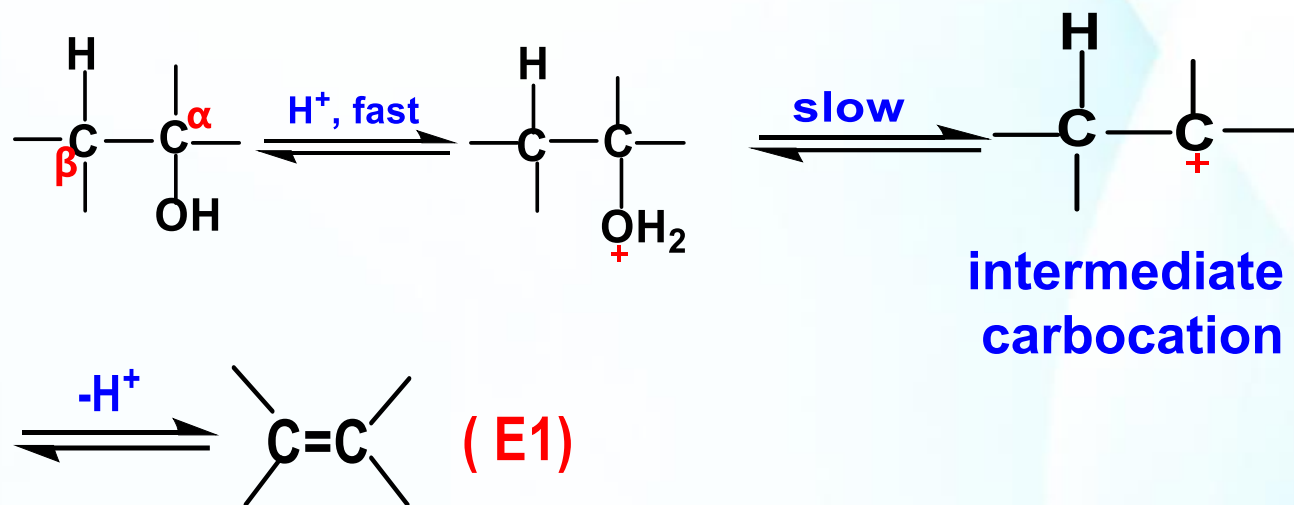




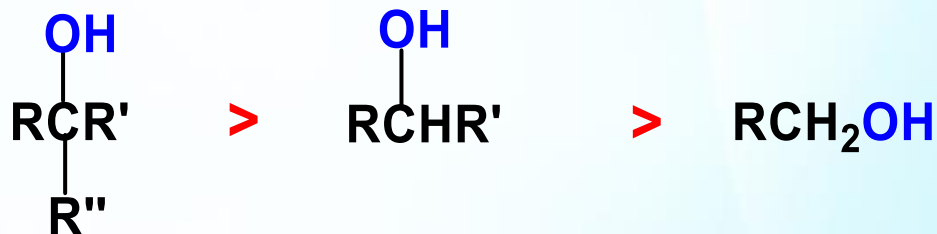
Alcohols are dehydrated to alkenes by heating with sulfuric acid.



#### \* Mechanism



#### \* Reactivity

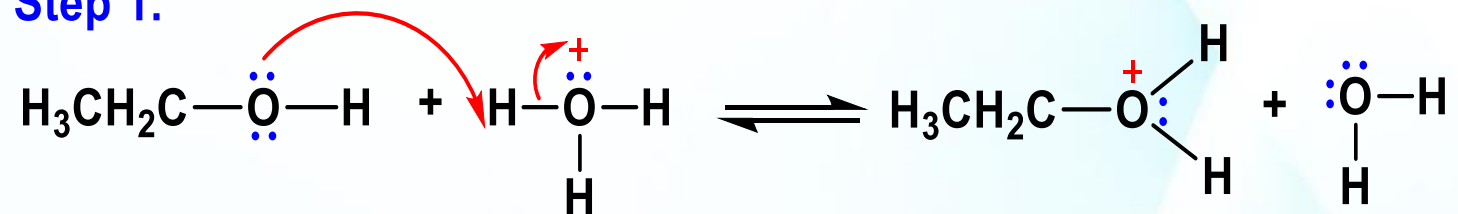




Primary alcohols react by the two-step mechanism, in which Step 2 is the rate-determining step.

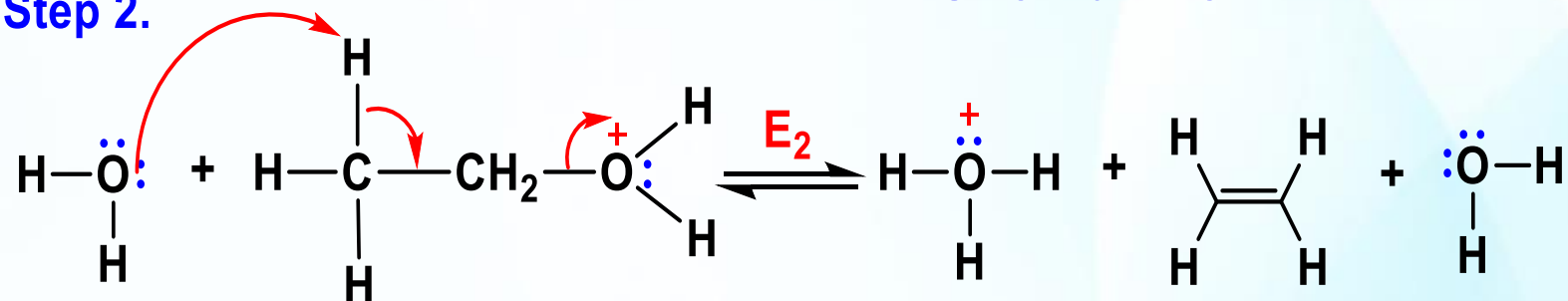
### \* Mechanism

Step 1.



Oxonium ion

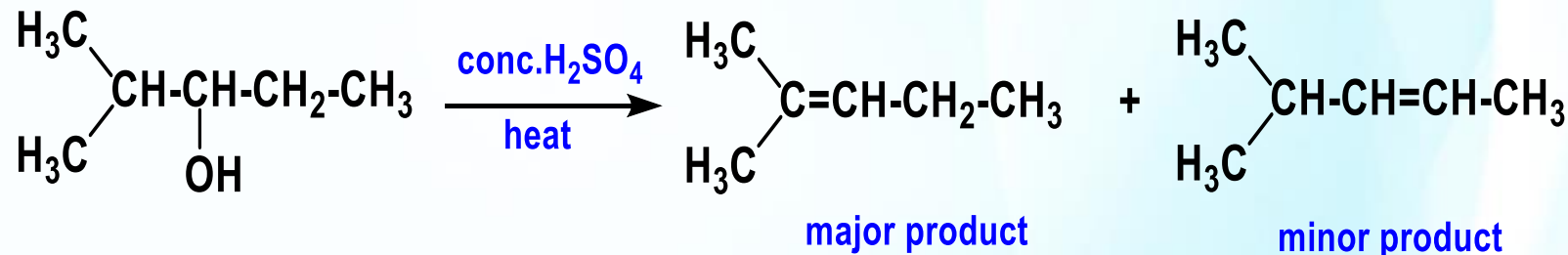
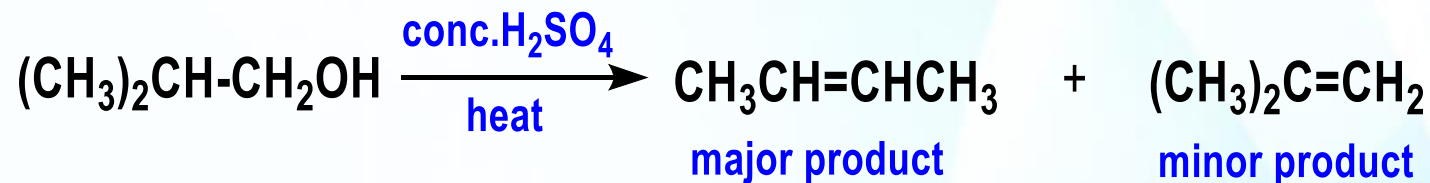
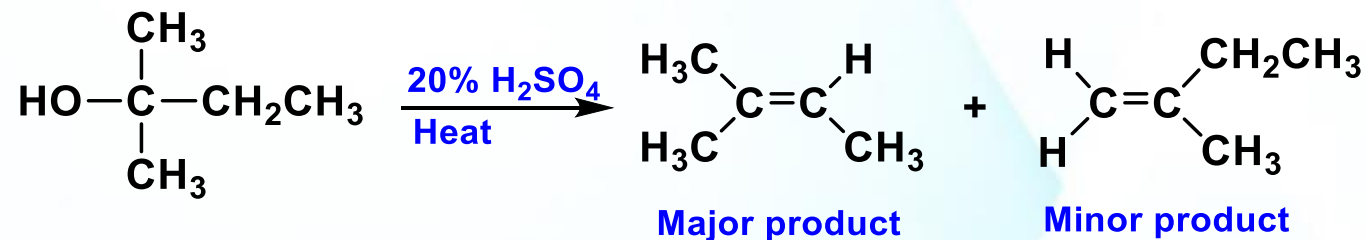
Step 2.



Alkene



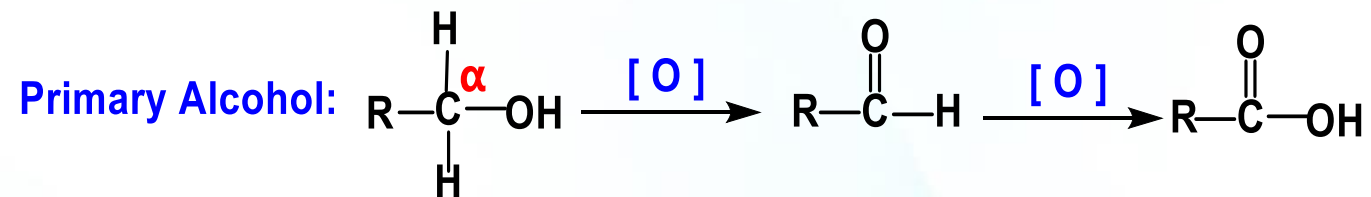
If a choice of alkenes is possible, **the most substituted alkene is preferred** (Zaitsev's rule).



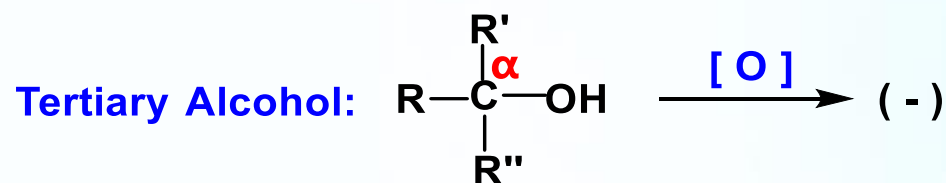
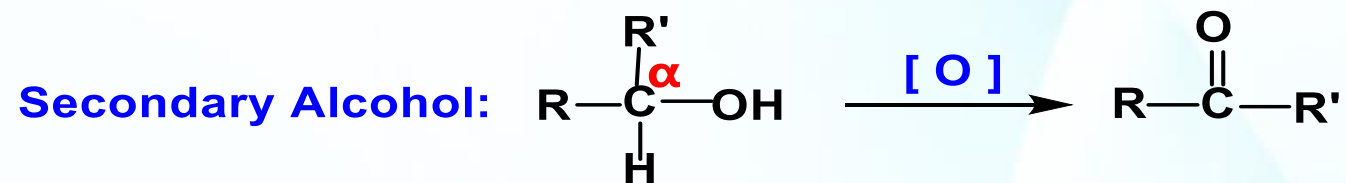




## (4) Oxidation



Primary alcohols are oxidized to **aldehydes** with pyridinium chlorochromate (PCC) in dichloromethane, and oxidized to **carboxylic acids** with CrO<sub>3</sub> in aqueous acid.



$[\text{O}]$ : K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, CrO<sub>3</sub>, KMnO<sub>4</sub>, etc.

Secondary alcohols are oxidized to ketones while tertiary alcohols are resistant to oxidation.

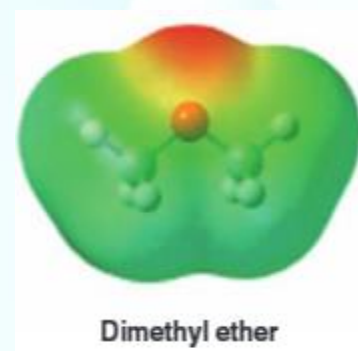
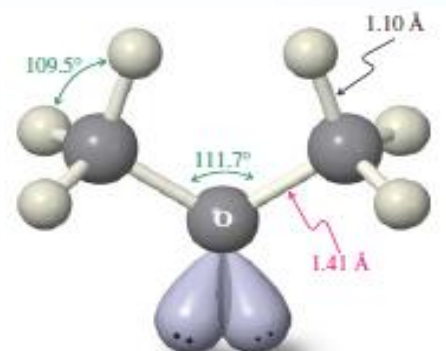


Ethers are named as alkoxy derivatives of alkanes.



Aryl ethers are ethers where the oxygen is linked to one or two aromatic rings ( $\text{ArOR}$  or  $\text{ArOAr}$ ) in which case the attached carbon(s) is  $\text{sp}^2$  hybridized.

## 1. Structure of Ethers



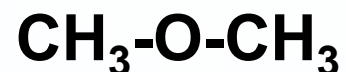
In dimethyl ether, two  $\text{sp}^3$  hybrid orbitals of oxygen form sigma bonds to carbon atoms. The other two  $\text{sp}^3$  hybrid orbitals of oxygen each contain an unshared pair of electrons.



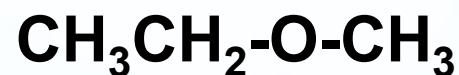
## 2. Nomenclature of Ethers

Ethers may be named by specifying the two alkyl groups in alphabetical order as separate words, then adding the word **ether** at the end.

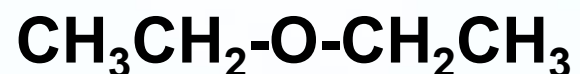
When both alkyl groups are the same, the **prefix di-** precedes the name of the alkyl group.



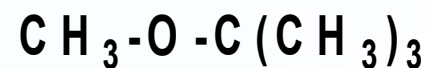
**Dimethyl ether**



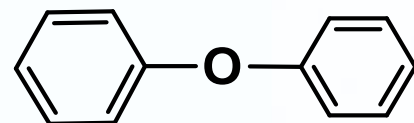
**Ethyl methyl ether**



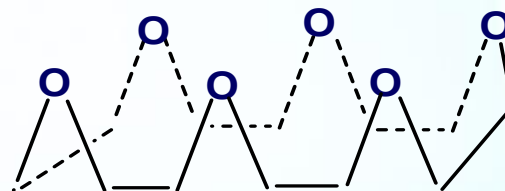
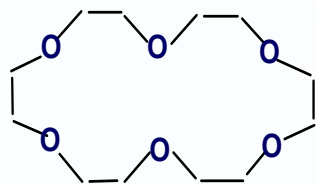
**Diethyl ether**



**tert-Butyl methyl ether**



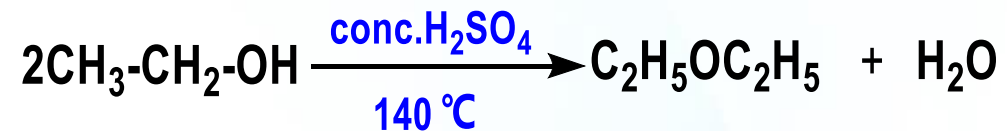
**Diphenyl ether**



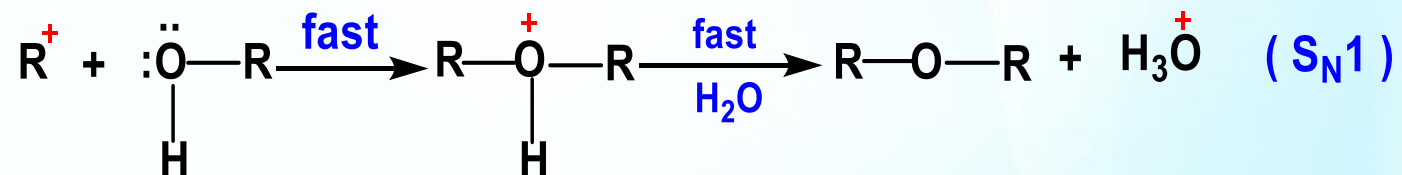
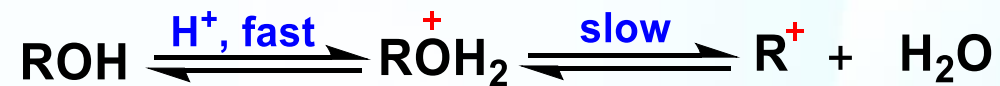
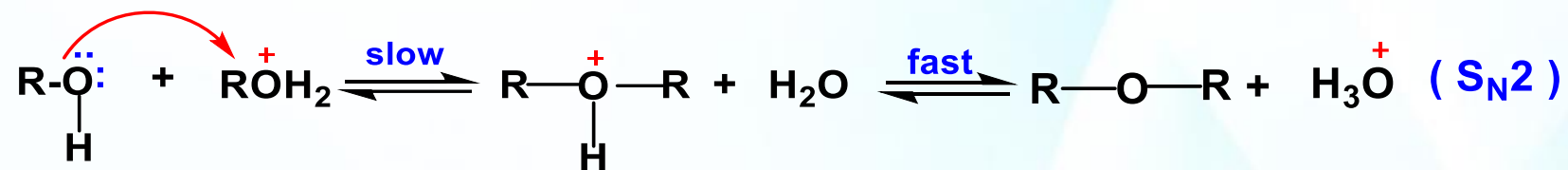
**18-Crown-6-ether**



### 3. Preparation of Ethers



✳ Mechanism:



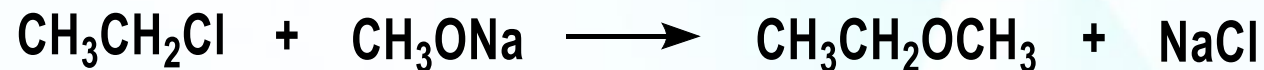


## Williamson Ether Synthesis

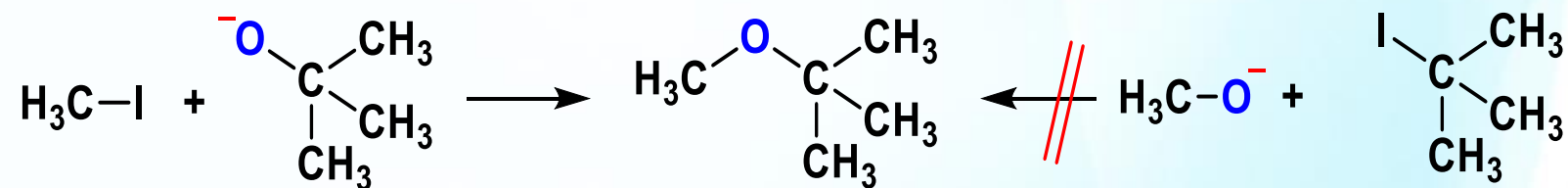
The procedure involves the  $S_N2$  reaction between a metal alkoxide and a primary alkyl halide or tosylate.



The alkoxide required for the reaction is prepared by treating an alcohol with a strong base such as sodium hydride.

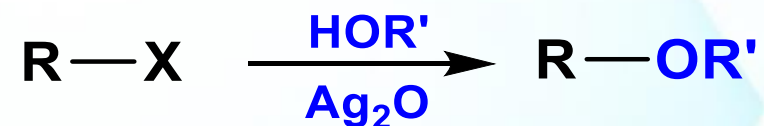


Since this is an  $S_N2$  reaction, primary alkyl halides react better than secondary or tertiary alkyl halides.

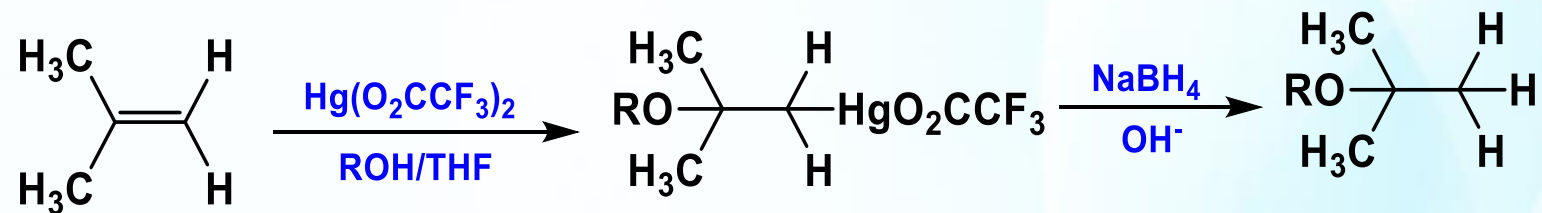




An alternative procedure is to treat the alcohol directly with the alkyl halide in the presence of silver oxide, thus avoiding the need to prepare the alkoxide beforehand.



Alkenes can be converted to ethers by the electrophilic addition of mercuric trifluoroacetate, followed by addition by addition of an alcohol.



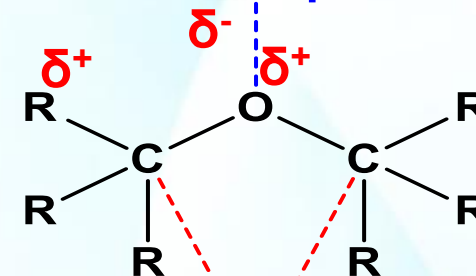
An organomercuric intermediate is obtained which can be reduced with sodium borohydride to give the ether.

## 4. Reactions of Ethers

Ethers, resemble hydrocarbons in their resistance to chemical reaction. They do not react with oxidizing agents, such as potassium dichromate (重铬酸钾) or potassium permanganate (高锰酸钾). They are not affected by most acids or bases at moderate temperatures.

Ethers are relatively unreactive since they have weak nucleophilic and electrophilic centers.

Weak nucleophilic center

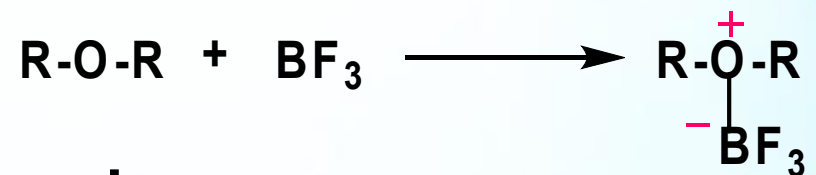
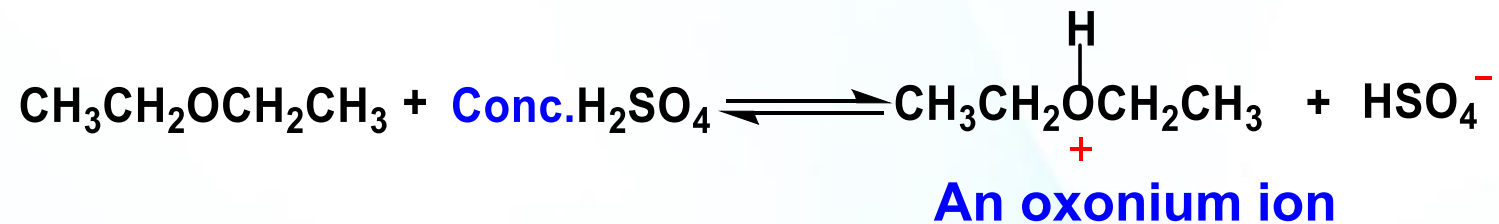


Weak electrophilic centers

Because of their good solvent properties and general inertness to chemical reaction, ethers are excellent solvents in which to carry out many organic reaction.

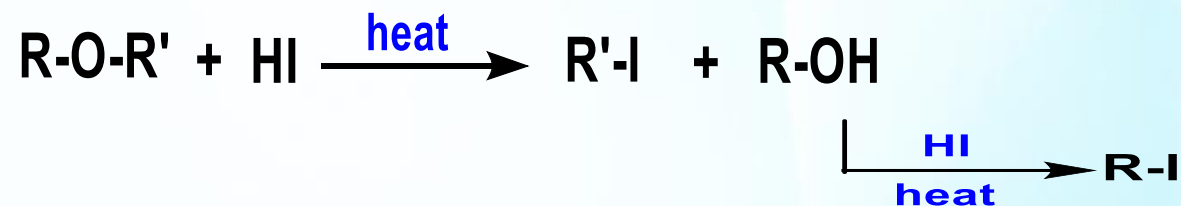


## (1) Oxonium Salts

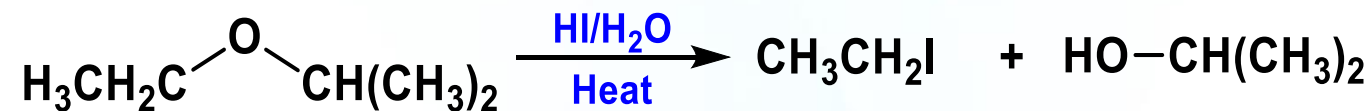


## (2) Cleavage of ether bond

Ethers are unreactive functional groups, but can be cleaved by strong acids such as HI or HBr.

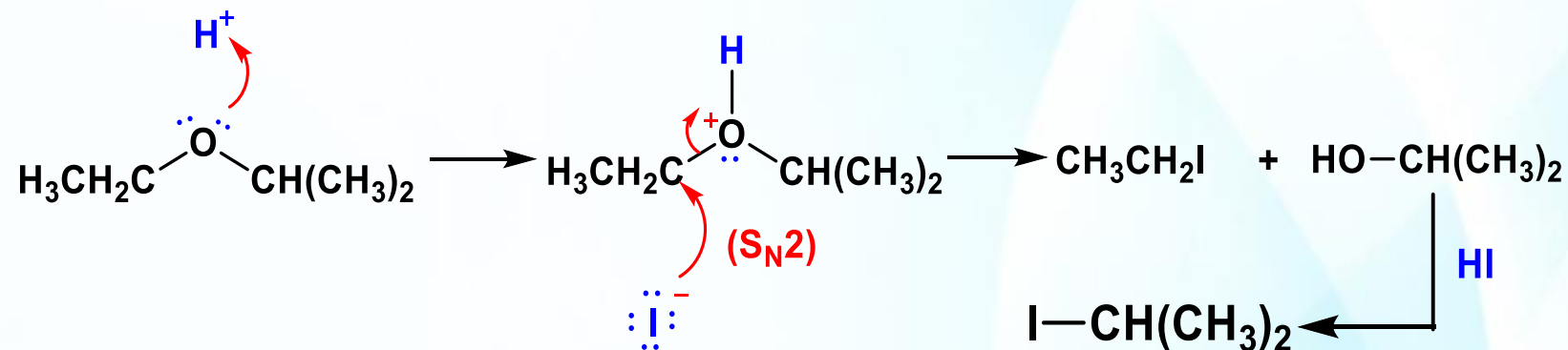






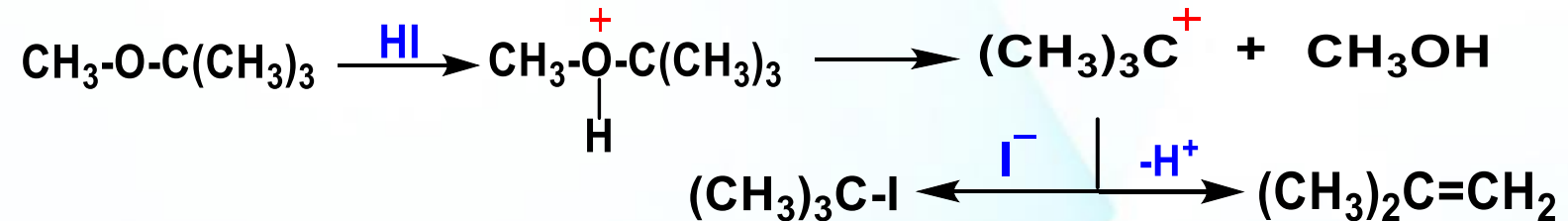
Primary and secondary ethers react by the  **$\text{S}_{\text{N}}2$  mechanism** to produce the least substituted alkyl halide and an alcohol.

✧ Mechanism:

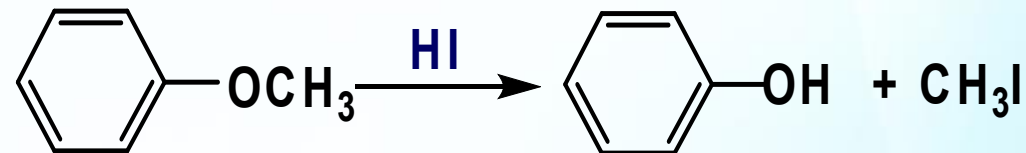
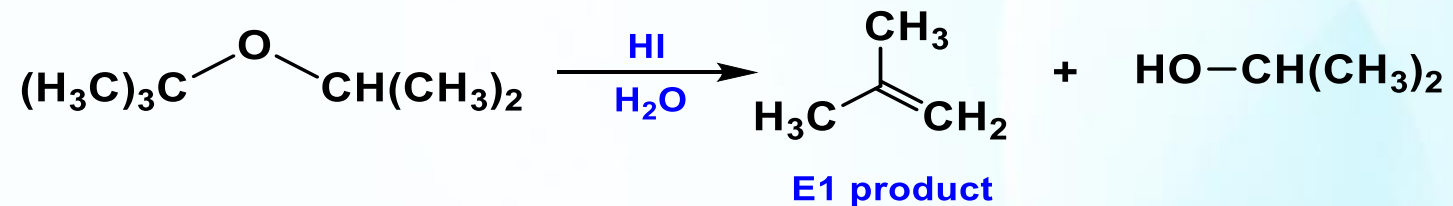


The initial protonation is essential since it converts a poor leaving group (an alkoxide ion) into a good leaving group (the alcohol).

**Tertiary ethers are cleaved by the S<sub>N</sub>1 reaction under milder conditions.**



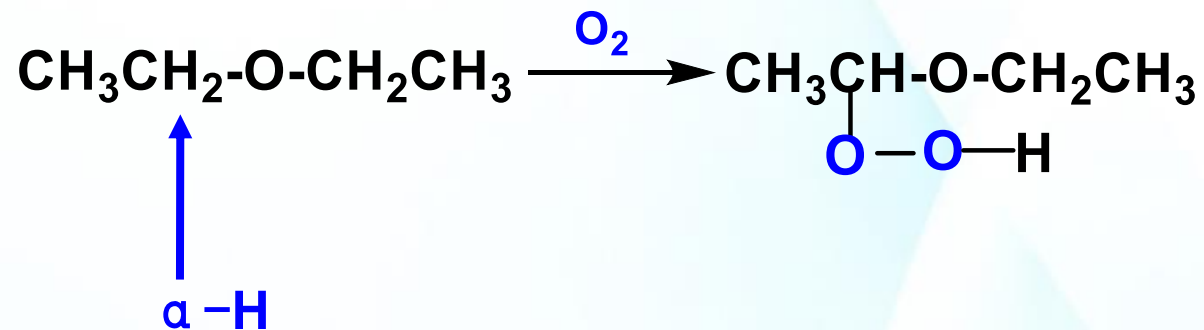
**However, an elimination reaction (E1) may occur in preference to the S<sub>N</sub>1 reaction resulting in formation of an alcohol and an alkene.**





### (3) Oxidation of ethers

Most ethers react slowly with atmospheric oxygen by a radical process to form hydroperoxides (ROOH) and peroxides (ROOR).

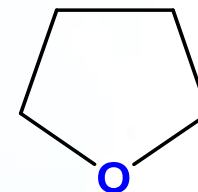
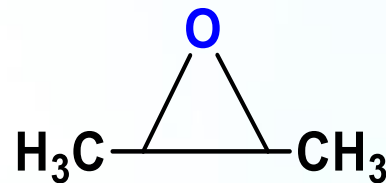
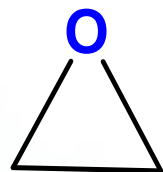


These products can prove to be explosive if old solvents are concentrated to dryness.



# Epoxides

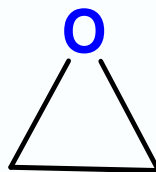
Epoxides are cyclic ethers.



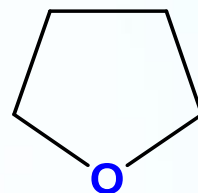
Cyclic ethers are heterocyclic compounds in which the ether oxygen is one of the atoms in a ring.

## 1. Nomenclature

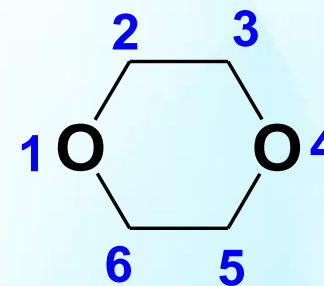
Cyclic ethers are generally known by their common names.



Ethylene oxide



Tetrahydrofuran (THF)

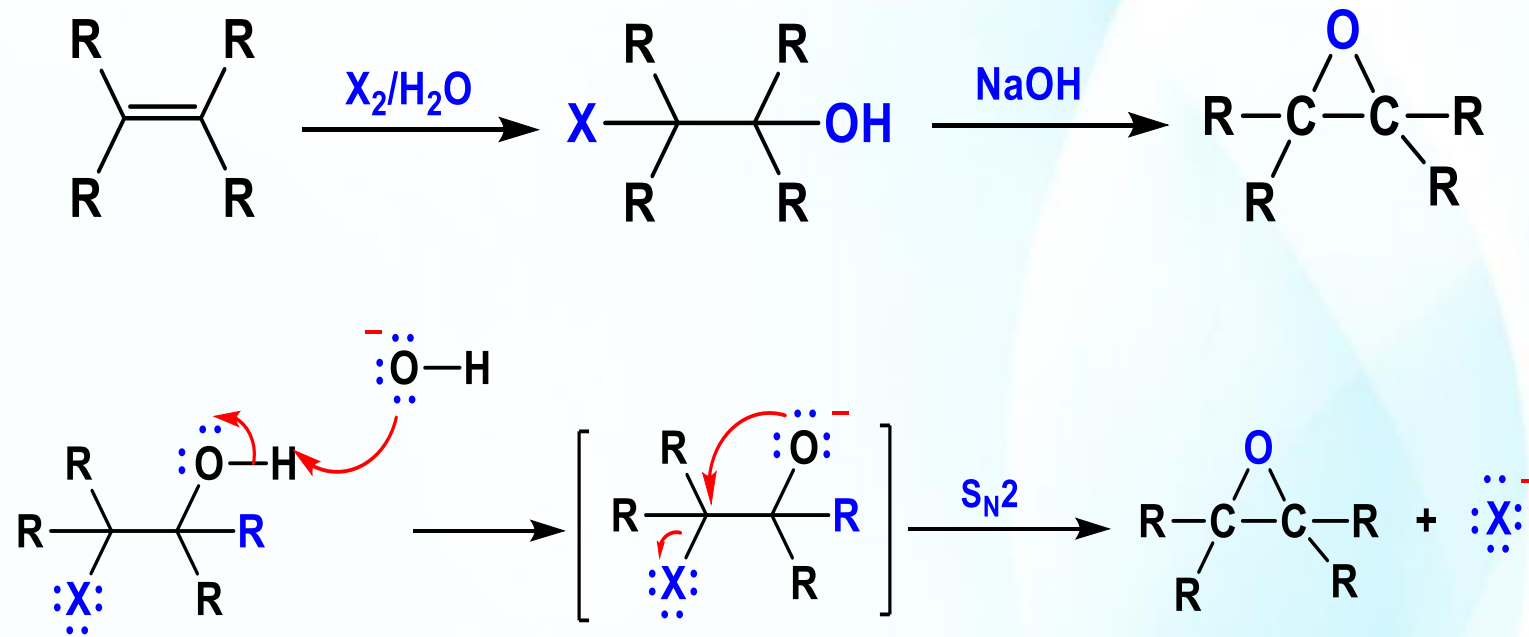


1,4-dioxane



## 2. Preparation of Epoxide

They can be obtained from alkenes in a two-step process. The first step involves electrophilic addition of a halogen in aqueous solution to form a halohydrin. Treatment of the halohydrin with base then ionizes the alcohol group, which can then act as a nucleophile.

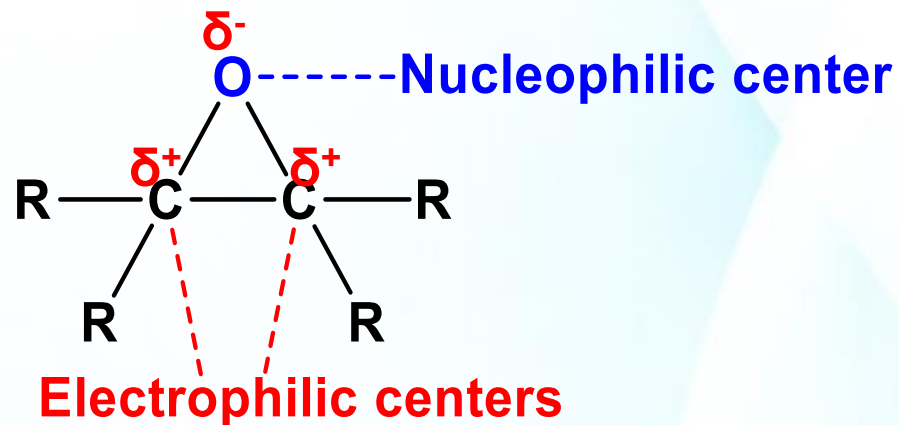


intramolecular S<sub>N</sub>2 reaction



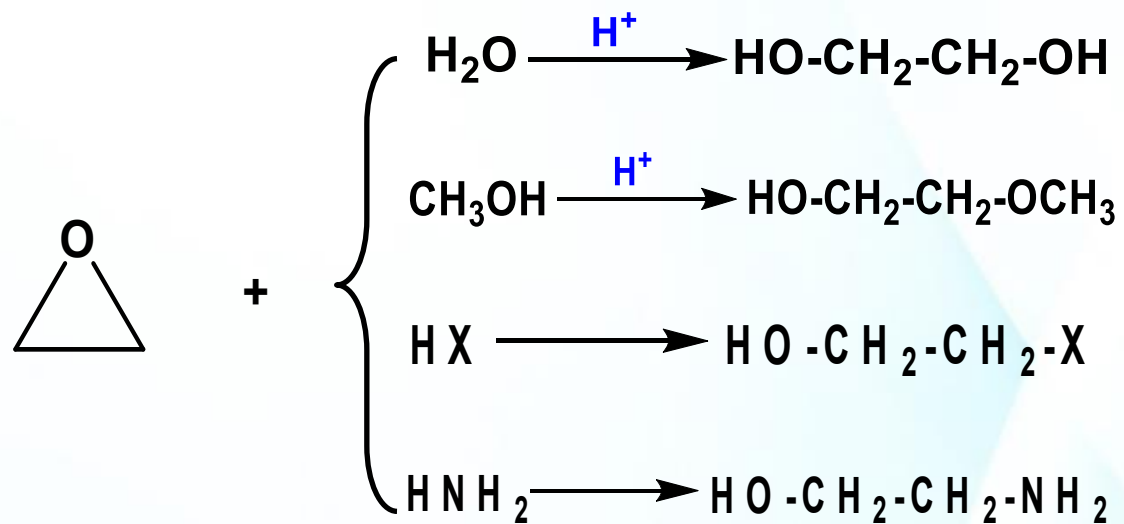
### 3. Structure

Epoxides are three-membered cyclic ethers which are more reactive than other cyclic or acyclic ethers due to the ring strain inherent in three-membered rings.



Reactions with nucleophiles can result in ring opening and relief of strain.

Nucleophiles will attack either of the electrophilic carbons present in an epoxide by an  $S_N2$  reaction.

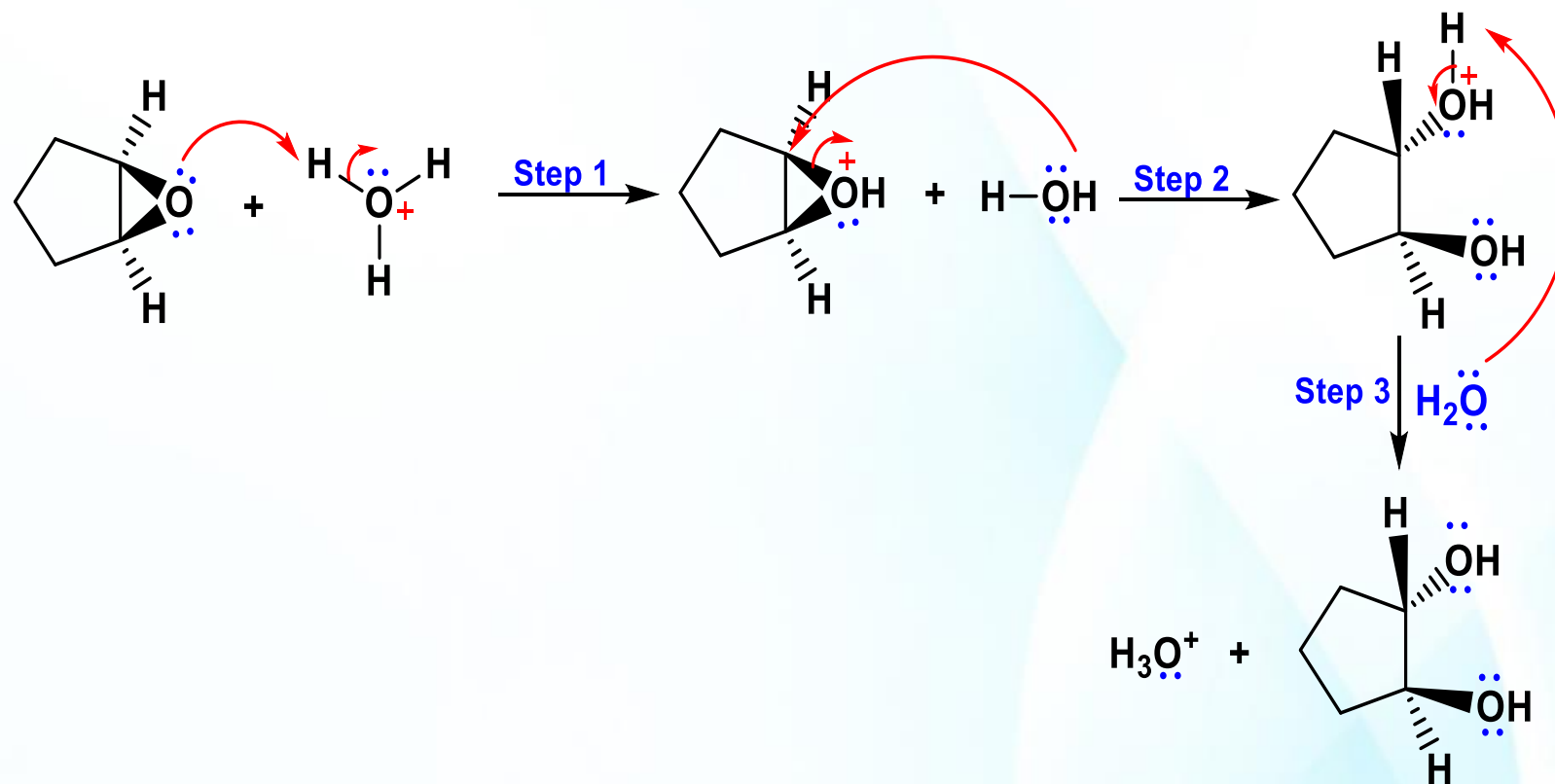


The reaction involves an  $\text{S}_{\text{N}}2$  mechanism with the incoming nucleophile attacking the epoxide from the opposite direction of the epoxide ring.

**Epoxides can be ring-opened under acidic or basic conditions.**



## Acid-Catalyzed Epoxide Ring Opening



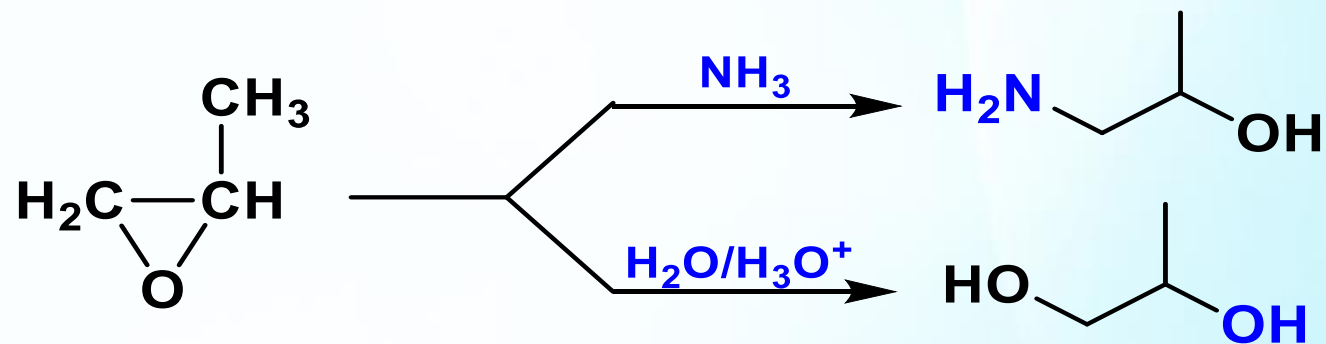
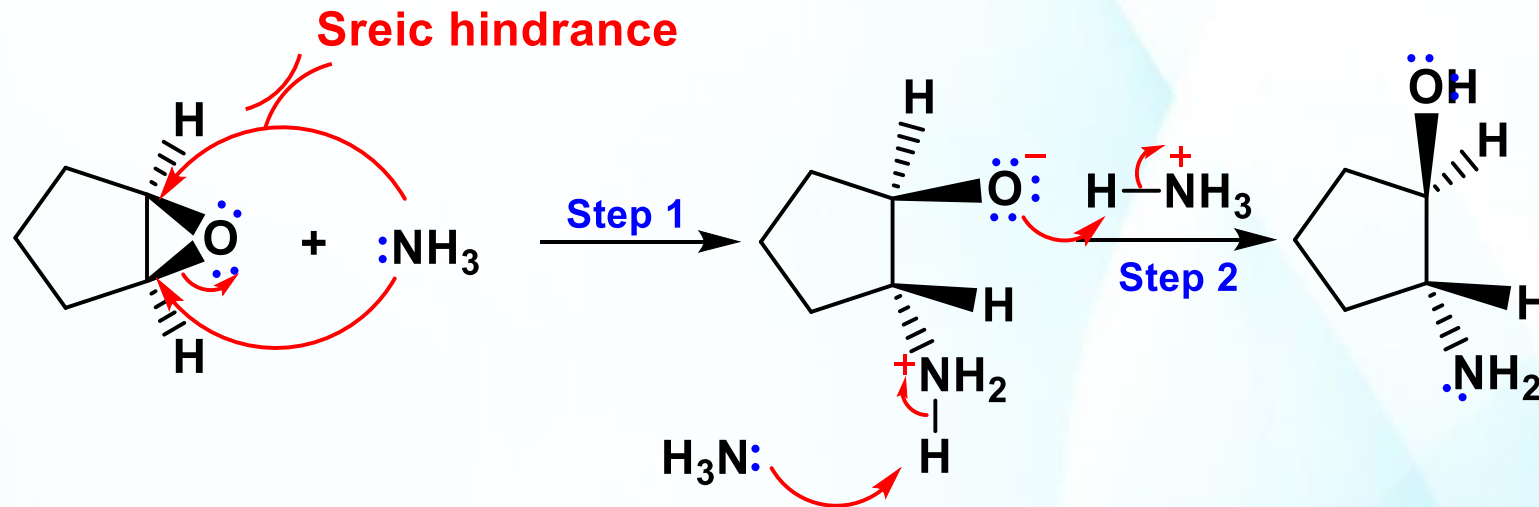
**Under acidic conditions, the epoxide oxygen is first protonated, turning it into a better leaving group.**

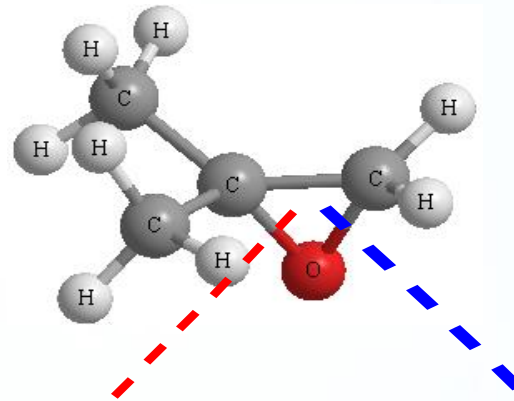




## Base-Catalyzed Epoxide Ring Opening

Good nucleophiles attack the ring by an  $S_N2$  mechanism and show a stereoselectivity for attack of the nucleophile at the less hindered carbon of the three-membered ring.





**Under acidic reaction conditions, nucleophiles will prefer to attack the most substituted carbon atom.**

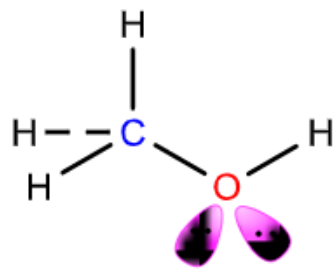
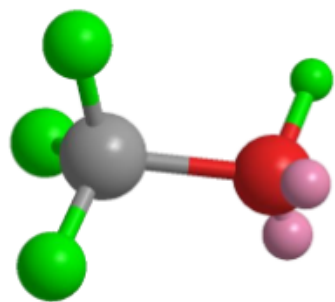
**Nucleophiles will attack unsymmetrical epoxides at the least substituted carbon when basic reaction conditions are employed.**

**This is because the positive charge in the protonated intermediate is shared between the oxygen and the most substituted carbon. This makes the more substituted carbon more reactive to nucleophiles.**

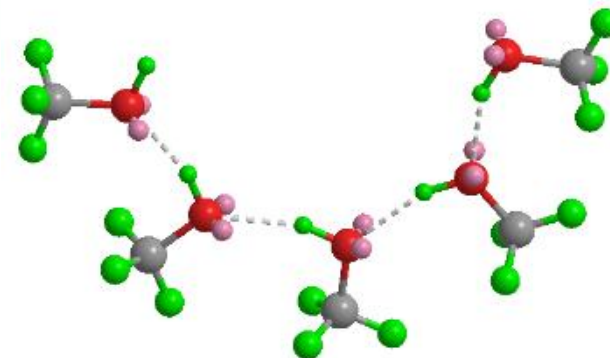
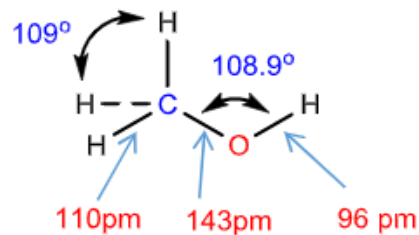


- 1. 醇的结构、命名及相关性质；**
- 2. 醚的结构、命名及相关性质；**
- 4. 环氧化合物的结构、命名及相关性质。**

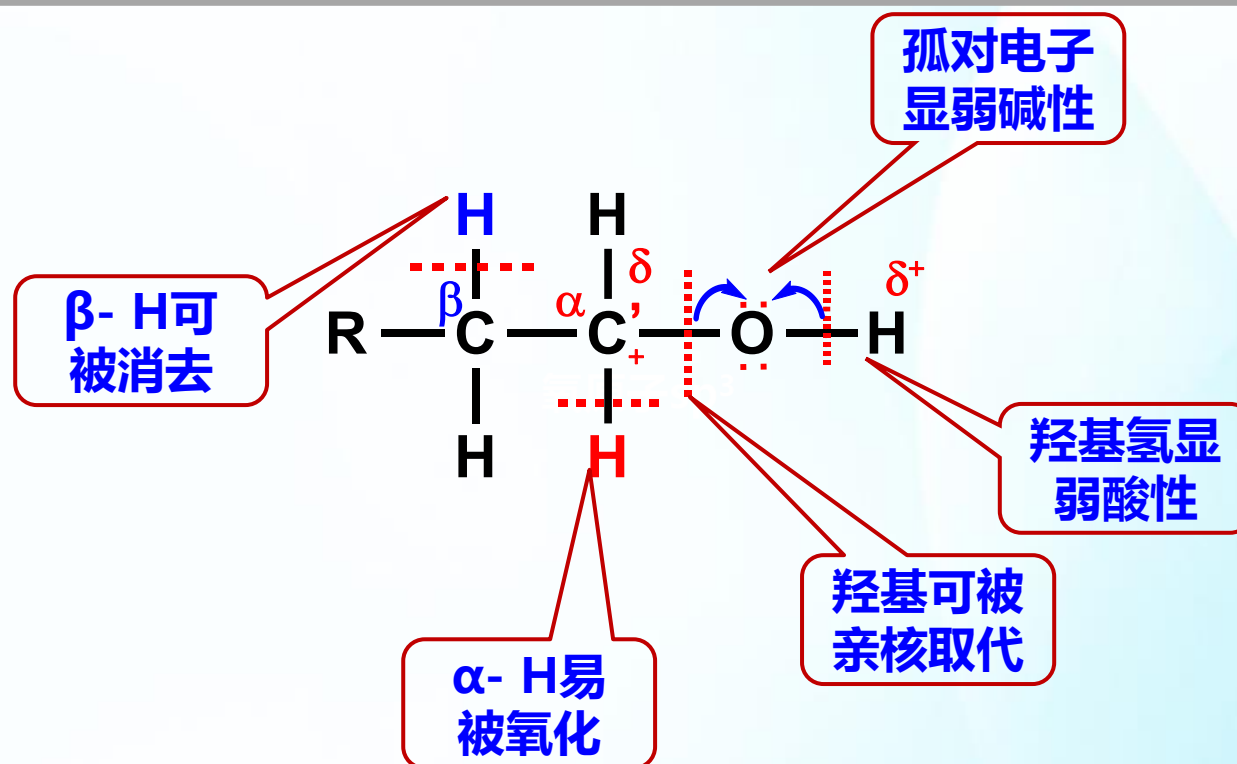
## 1. 醇的结构



甲醇分子

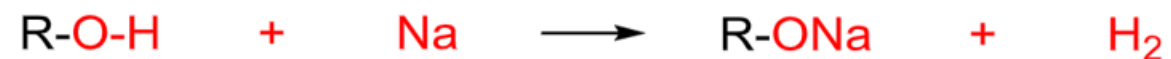


甲醇分子间氢键



## 2. 醇的化学性质

### ① 与活泼金属的反应



### ② 与无机酸的反应

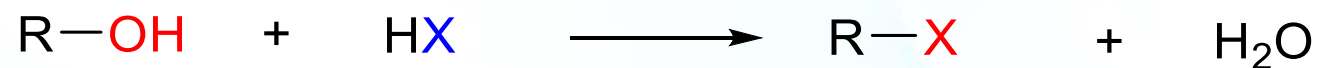


硝酸甘油



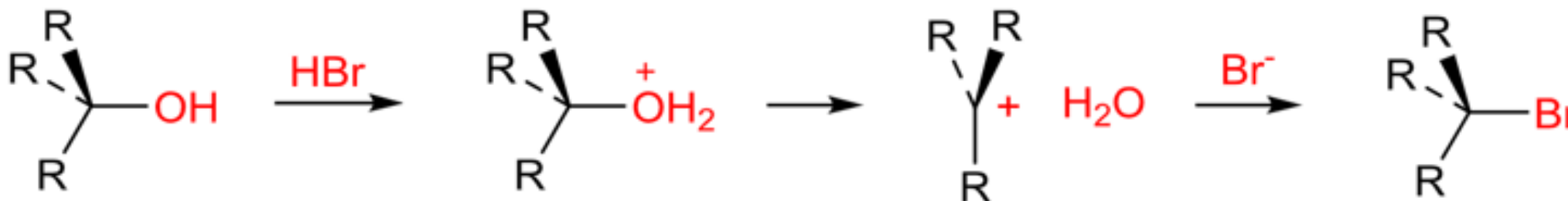
## 2. 醇的化学性质

### ③ 与卤化氢反应

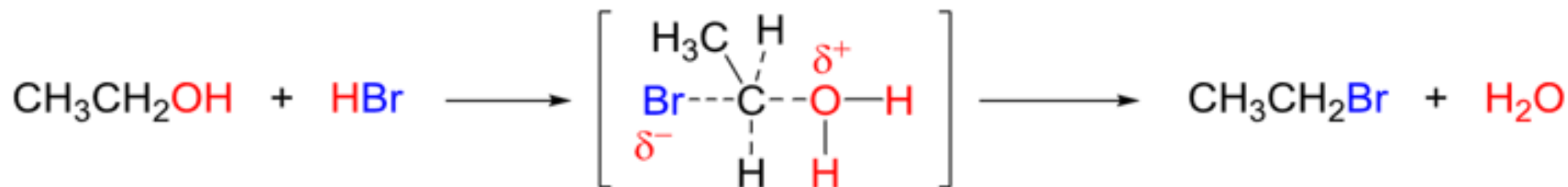


利用醇与氢卤酸反应是实验室制备卤代烷烃的重要方法之一

叔醇按照 $\text{S}_{\text{N}}1$ 反应历程进行

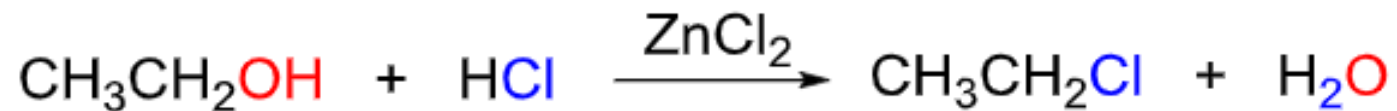


伯醇按照 $\text{S}_{\text{N}}2$ 反应历程进行



## 2. 醇的化学性质

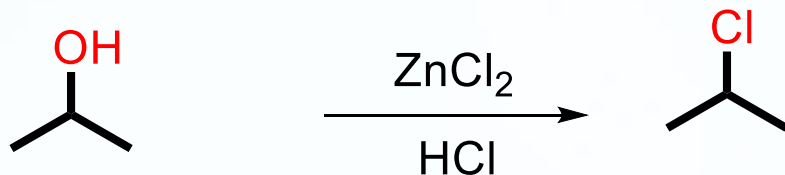
$\text{ZnCl}_2$  与浓盐酸组合，成为Lucas试剂，可以将醇转化为烷基氯代物



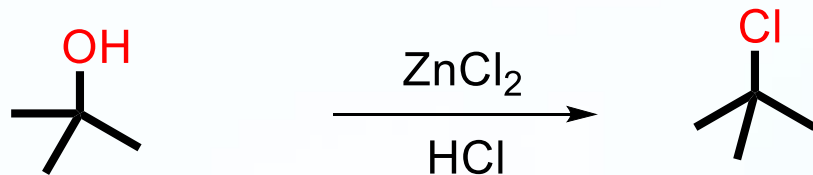
不同结构的低级醇 ( $\text{C} < 6$ ) 与Lucas试剂反应时速率不同，区分不同醇的结构：



伯醇：室温下不反应



仲醇：几分钟内发生反应

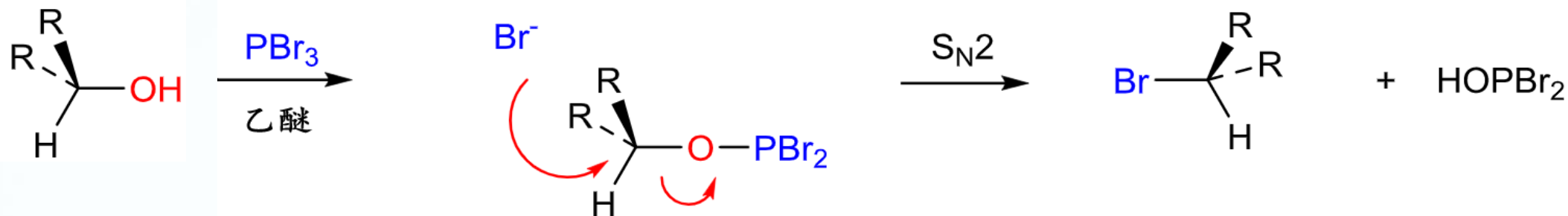
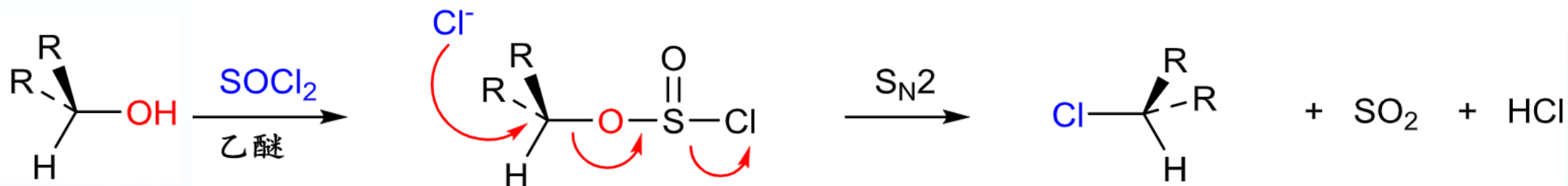


叔醇：立即反应

## 2. 醇的化学性质

### ④ 与其他卤代试剂反应

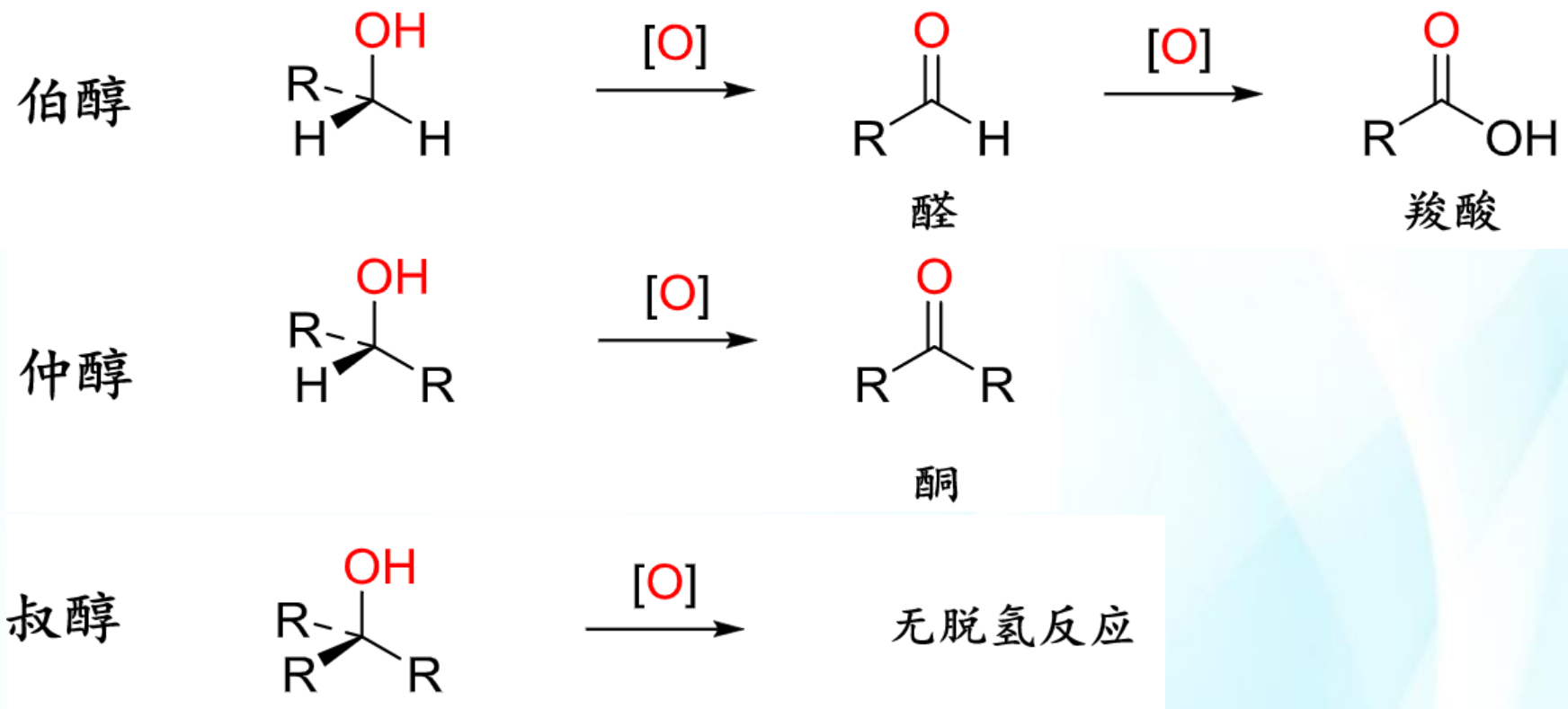
伯醇和仲醇还可与 $\text{SOCl}_2$ 或者 $\text{PBr}_3$ 反应，生成相应的烷基卤代物。





## 2. 醇的化学性质

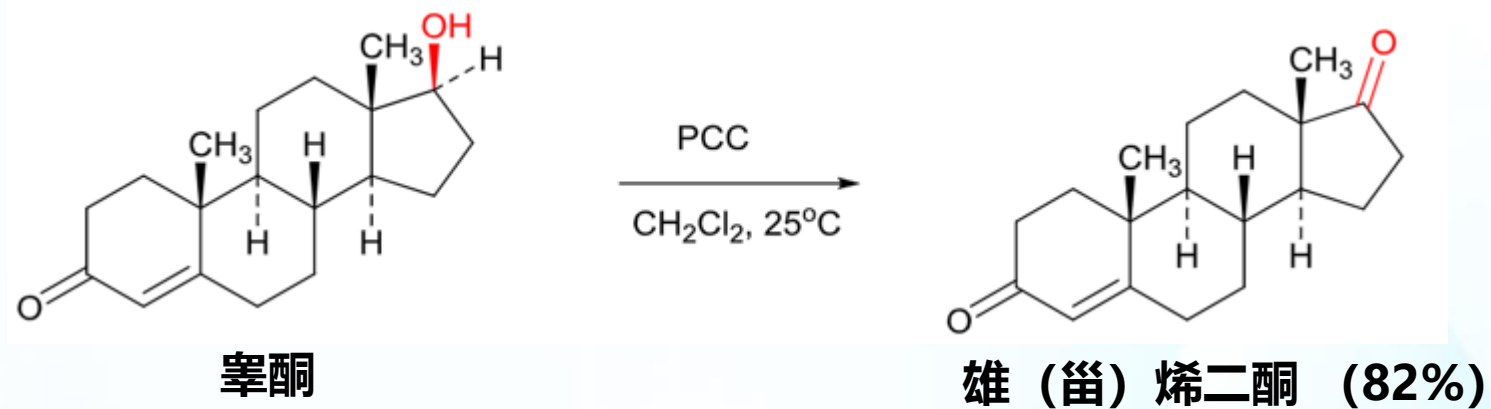
### ⑤ 氧化反应



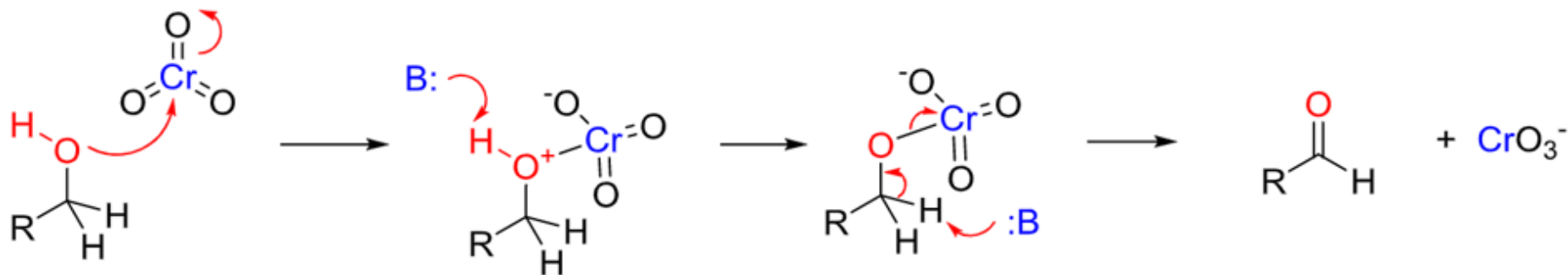
常用氧化剂:  $\text{KMnO}_4$ 、 $\text{K}_2\text{Cr}_2\text{O}_7$ 、PCC (吡啶氯铬酸盐)、琼斯试剂 ( $\text{CrO}_3$ +稀硫酸)等

## 2. 醇的化学性质

**PCC (吡啶氯铬酸盐) 对仲醇的氧化:**



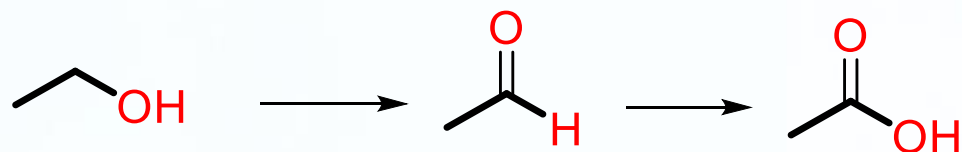
**铬酸氧化反应历程:**



## 酒在人体中的代谢——醇的氧化反应

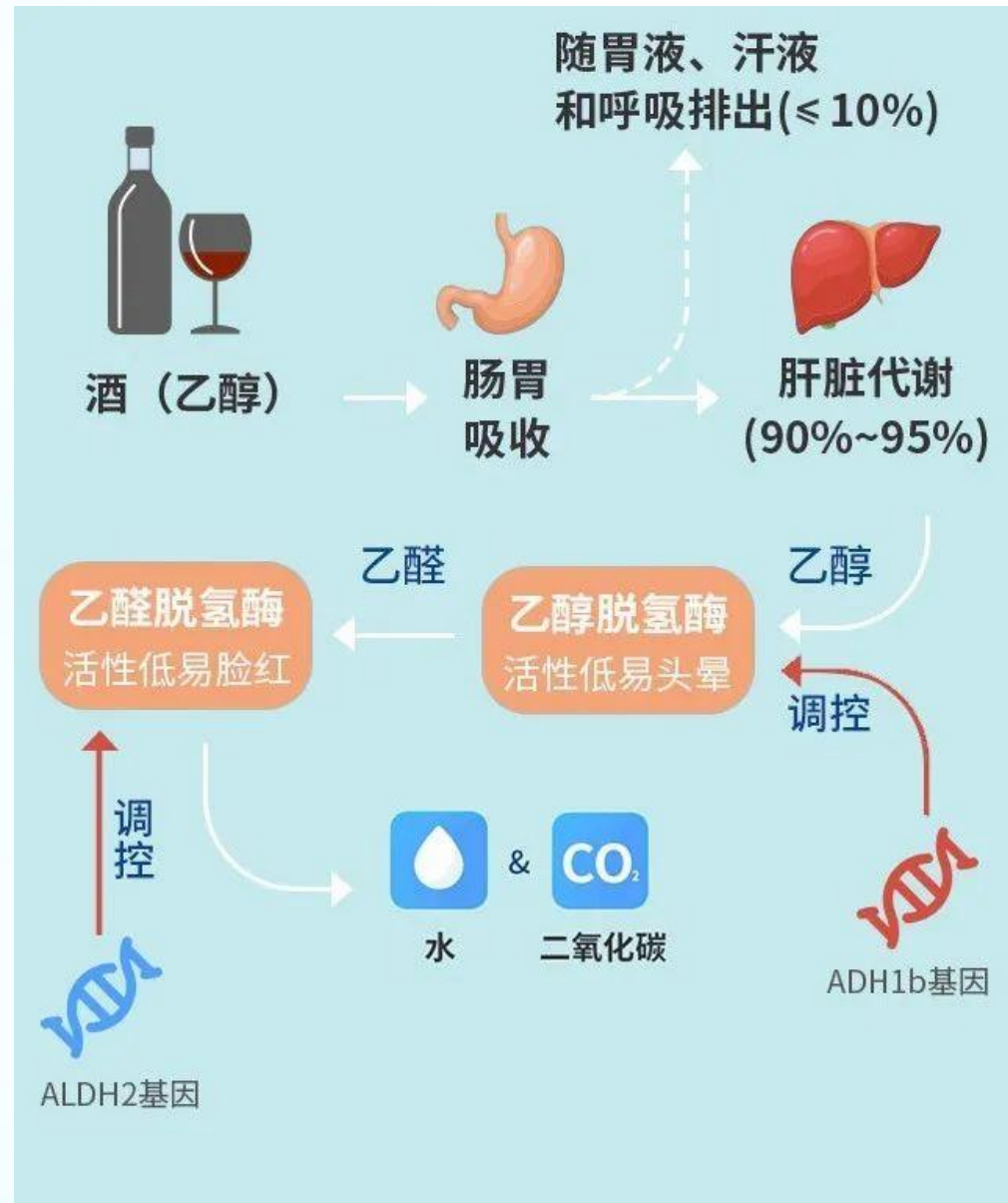
- ◆ 酒精——中枢神经抑制剂（抑制大脑皮层，使人失去部分自我控制能力，暂时忘掉烦恼，缓解压力，进入兴奋状态）

### ◆ 酒在人体内的代谢过程

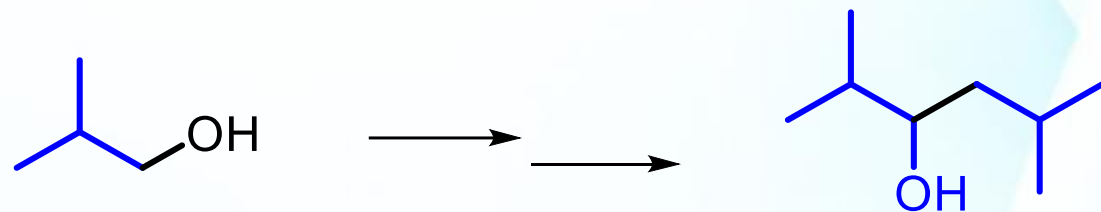


- ◆ 酒量大小，取决于个体内的乙醛脱氢酶

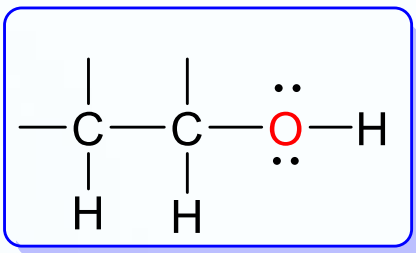
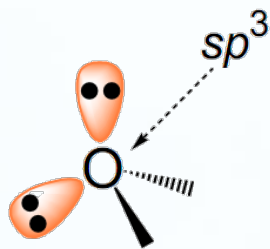
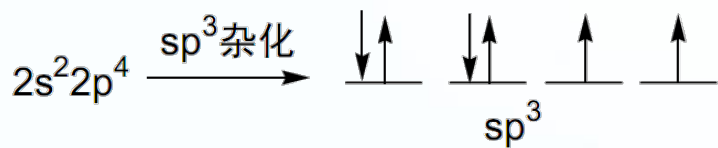
适量饮酒，不可贪杯！



思考题：如何实现下列转化？



## 本章小结

◆ 氧原子 $sp^3$ 杂化;◆ 电负性 $O > H$ ;

◆ 有孤电子对;

◆ 电负性 $O > C$ ;

## ◆ 醇的化学性质

- ① 与金属反应
- ② 与无机酸反应
- ③ 与卤化氢反应
- ④ 与其他卤化试剂反应
- ⑤ 脱氢反应 (氧化反应)



## 电视剧中常见的场景

✓ 吸入式麻醉

### 常见的几类醚类吸入式全麻药



异氟氯甲乙醚



恩氟烷



甲氧氟烷





【产品名称】高露洁光感劲白牙膏

【规格】113g

【香型】沁亮薄荷香型

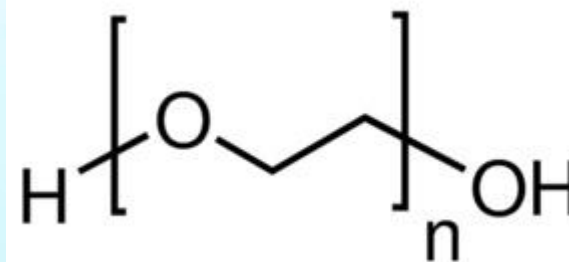
【产地】中国【欧洲研发配方】

【功效】帮助重现牙齿亮白\*

【成分】水，水合硅石(含高清洁型)，山梨(糖)醇，甘油，聚乙二醇-12，三聚磷酸五钠，焦磷酸四钾，月桂醇硫酸酯钠，香精(沁亮薄荷香型)，纤维素胶，椰油酰胺丙基甜菜碱，糖精钠，氢氧化钠，氟化钠(0.10%氟)，黄原胶，云母，CI 77891，CI 420

【使用方法】每天餐后刷牙或至少刷牙三次，每次至少2分钟，以达到美白效果

【注意】建议六岁及以下儿童每次使用豌豆般大小的牙膏，并在成人指导下刷牙，以减少吞咽。含氟化钠



聚乙二醇

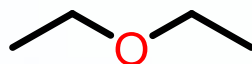


## 1. 醚的结构

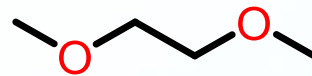
**醚：醇或者酚发生分子间脱水而形成的一类含氧化合物。**

依据结构分为：

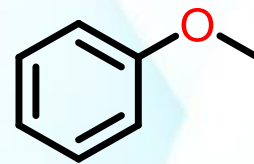
脂肪醚和芳香醚



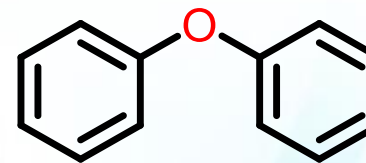
乙醚



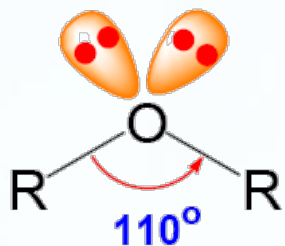
乙二醇二甲醚



苯甲醚



二苯醚



◆ 氧原子 $sp^3$ 杂化

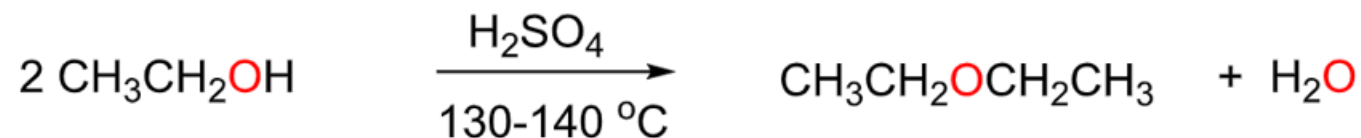
◆ 有孤电子对

◆ 无活泼氢，分子间作用力弱

◆ 极性较小，易挥发

## 2. 醚的制备方法

### 醇的分子间脱水反应

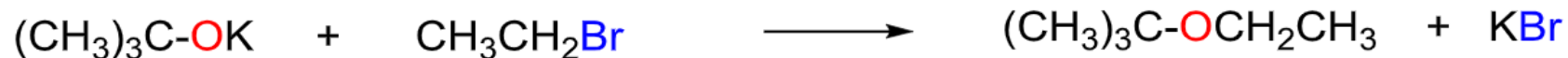
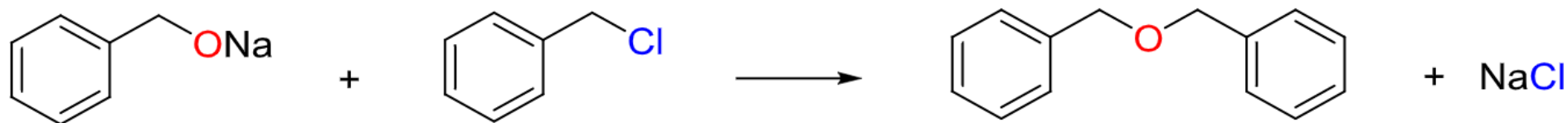


◆ 多用于制备对称性醚

◆ 适用于伯醇

◆ 仲醇、叔醇易发生分子内脱水

### 醇钠与卤代烃反应 (威廉姆森合成法)

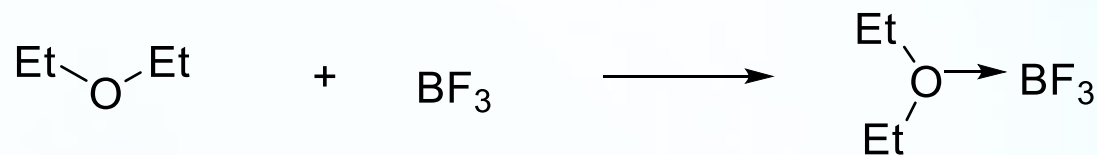




## 3. 醚的性质

### ① 醚的碱性

□ 醚中的孤对电子可以与强酸（质子酸或者Lewis酸）反应



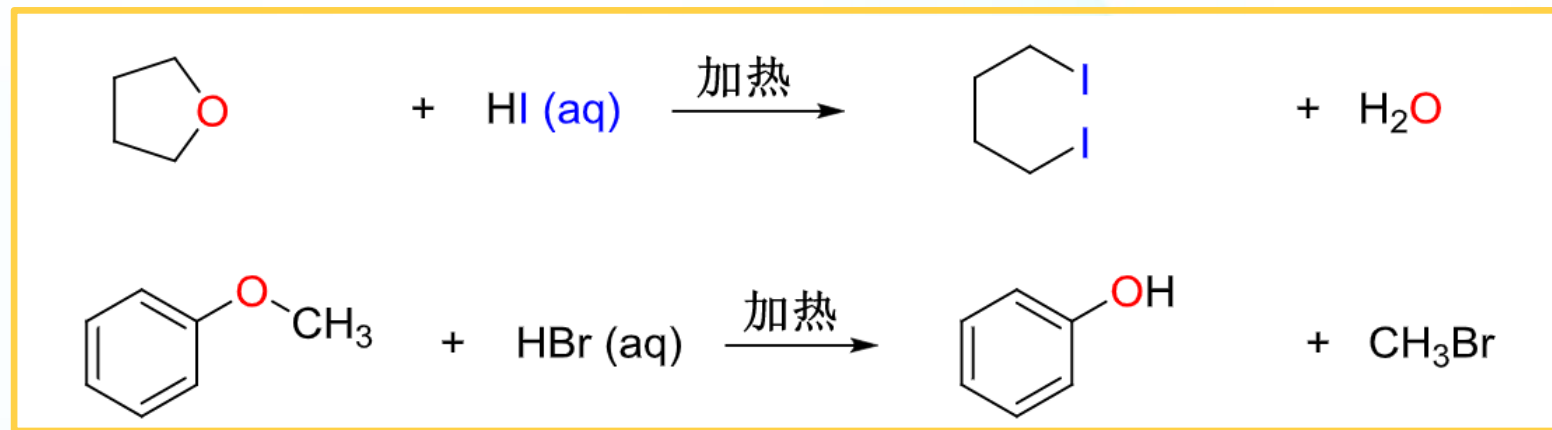
三氟化硼乙醚络合物



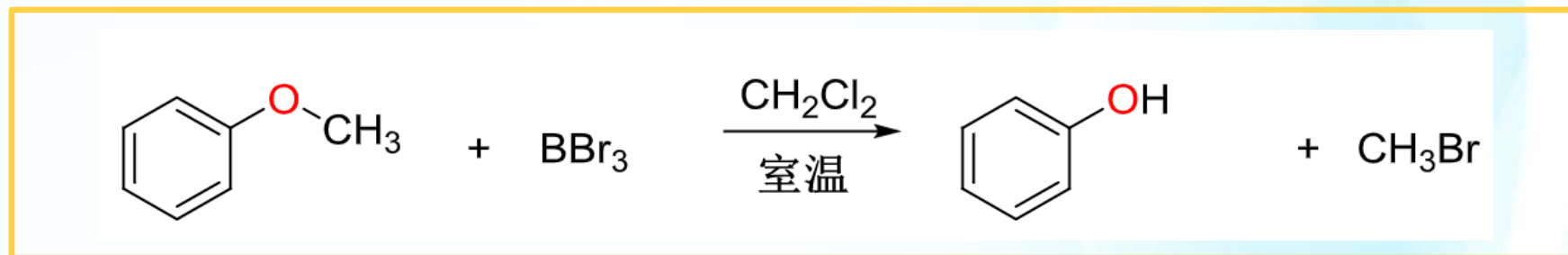
格式试剂醚络合物

## 3. 醚的性质

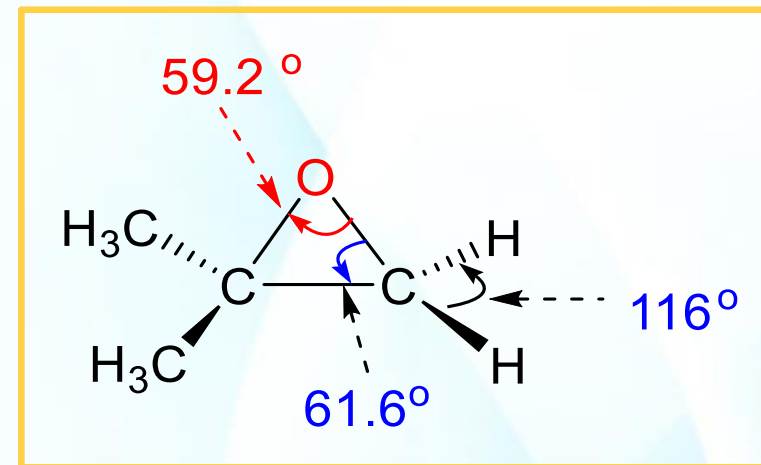
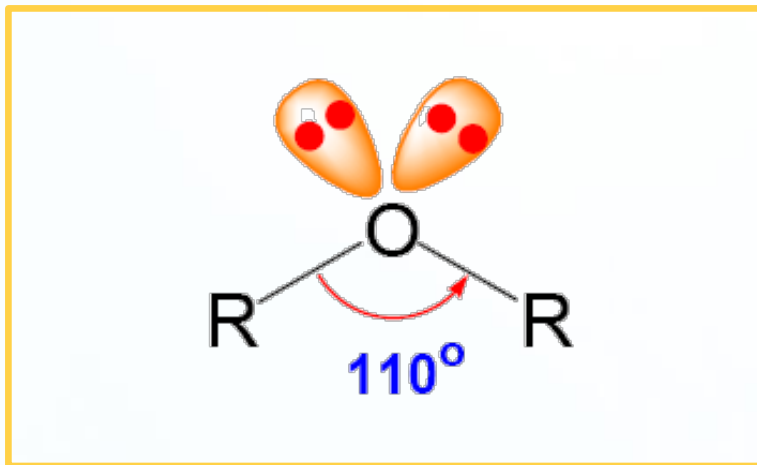
□ 醚质子化反应导致醚键被弱化，可以发生 $S_N1$ 或 $S_N2$ 取代反应：



□ 醚与Lewis酸反应也会导致醚键裂解：



## 3. 醚的性质

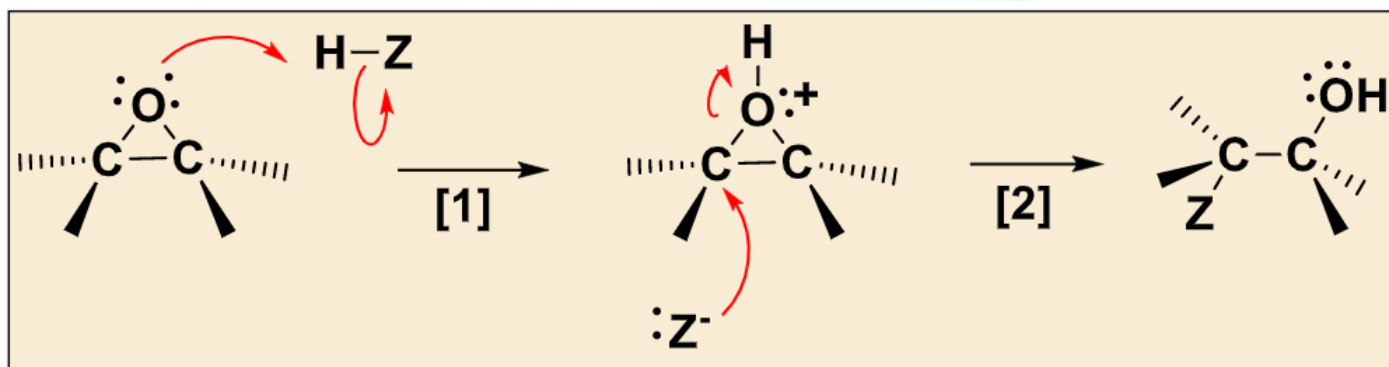


环醚：环张力增大、 $C-O$ 键易断裂，发生开环

## 3. 醚的性质

### 1,2-环氧乙烷的开环反应

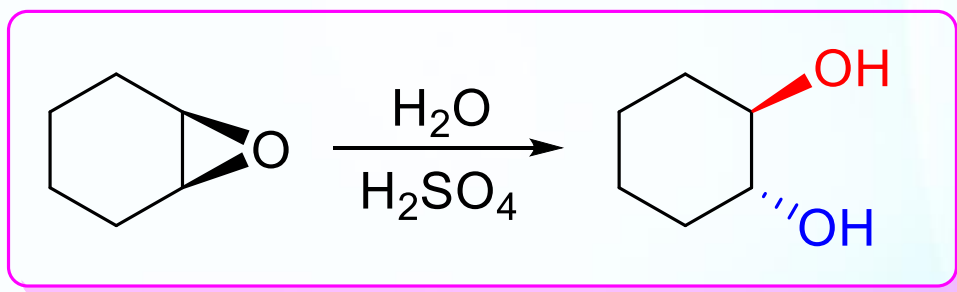
#### ① 与氢卤酸开环—— $S_N2$ (类似 $S_N1$ ) 机理



□ HZ常为HCl、HBr、HI，也可能是酸性 $H_2O$ 或ROH

□ 当环氧乙烷不对称时，断裂取代基多的碳上碳氧键

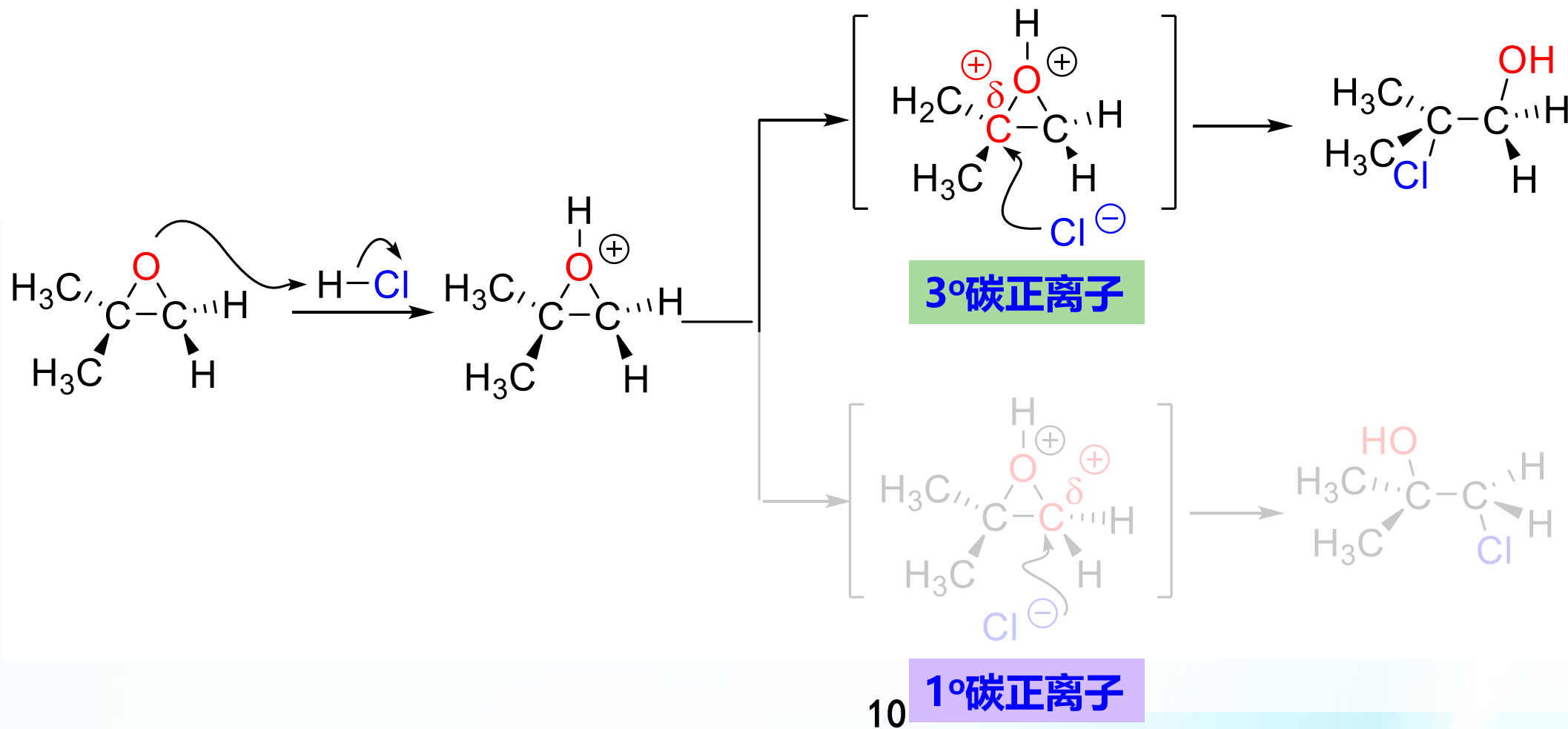
□ 反式产物为主





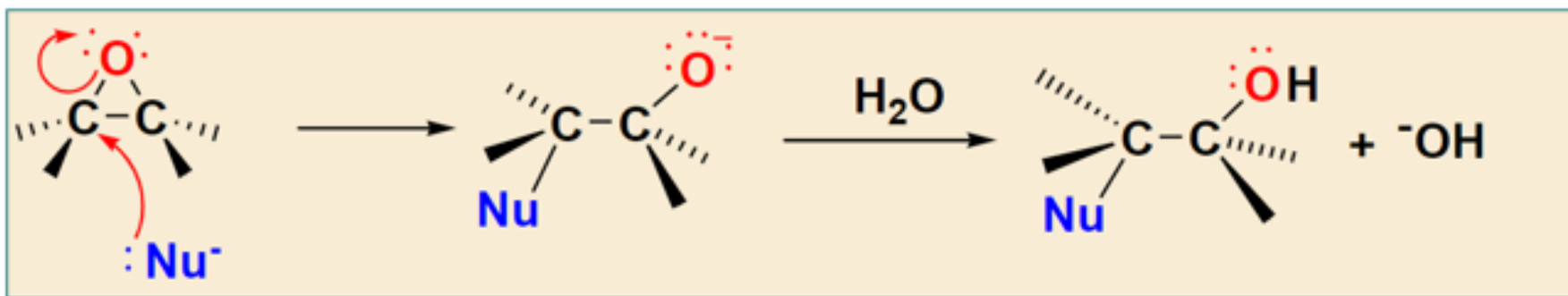
## 3. 醚的性质

非对称性环氧乙烷酸性条件下开环选择性如何？



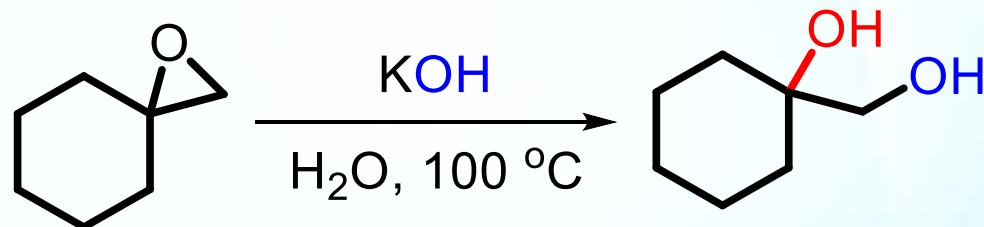
## 3. 醚的性质

### ② 在碱性条件下开环—— $S_N2$ 机理

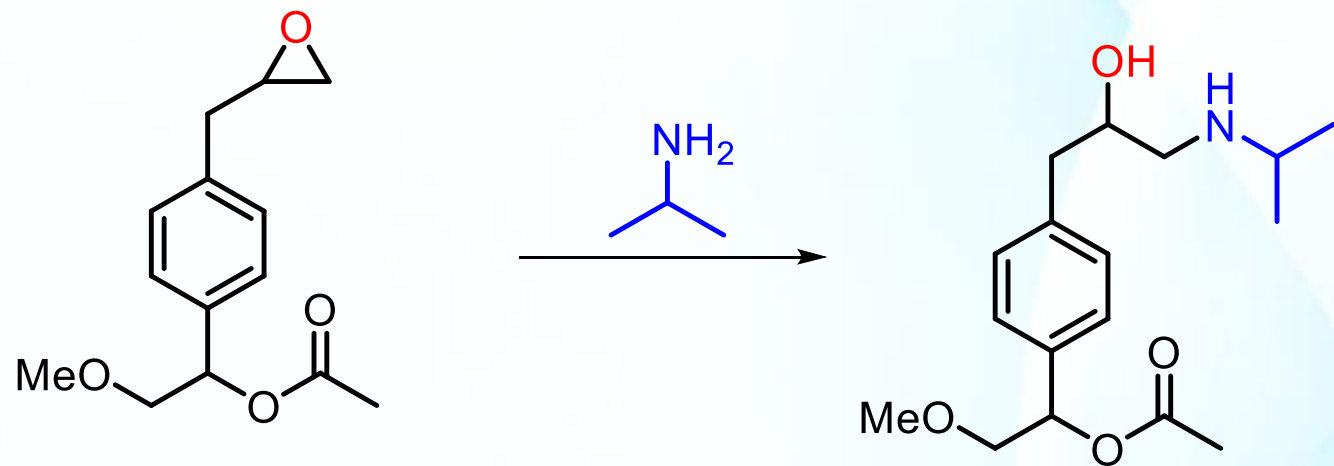


□  $\text{Nu}^-$  可为  $\text{OH}^-$ ,  $\text{OR}^-$ ,  $\text{CN}^-$ ,  $\text{SR}^-$ , and  $\text{NH}_3$

□ 当环氧乙烷不对称时，断裂位阻小的碳上碳氧键

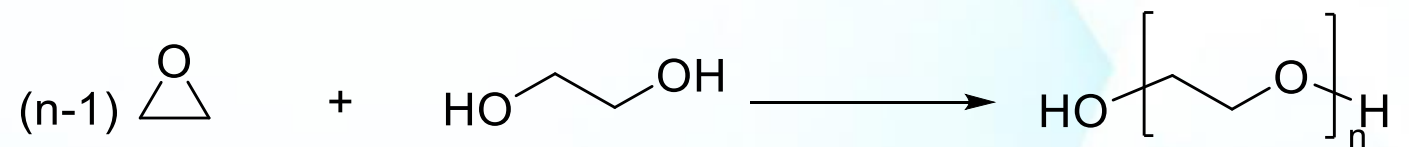


### 3. 醚的性质



降压药：美托洛尔

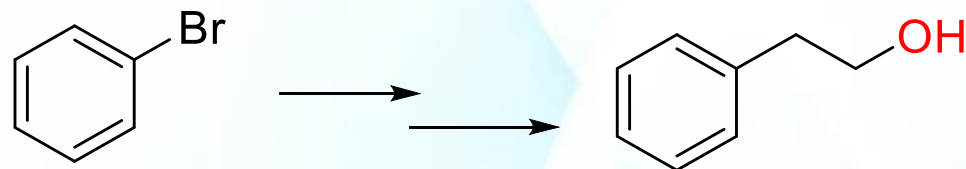
## 工业生产聚乙二醇的工艺路线之一：



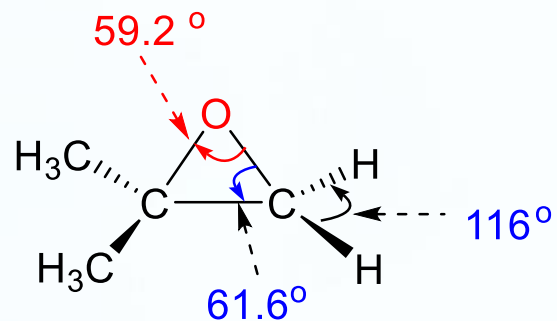
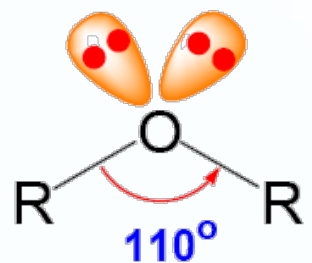




随堂练习题:



## 本章小结



- ◆ 氧原子 $sp^3$ 杂化;
- ◆ 有孤电子对;
- ◆ 性质稳定
- ◆ 环醚张力大, 易开环

- ① 醚的制备方法
- ② 冠醚的基本知识
- ③ 环醚的开环反应及机理



## 作业:

**P275 8.14 (a)(b)(c)(e) (f)(h)**

**P276 9.16(a)(b)(c)(d);**

**P277 8.28;8.38**

**P278 8.39**

**P280 8.53**



**也许有一天, 不知不觉, 你将渐渐活出写满答案的人生!**