西安交通大学化学学院
XI'AN JIAOTONG UNIVERSITY SCHOOL OF CHEMISTRY

Organic Chemistry

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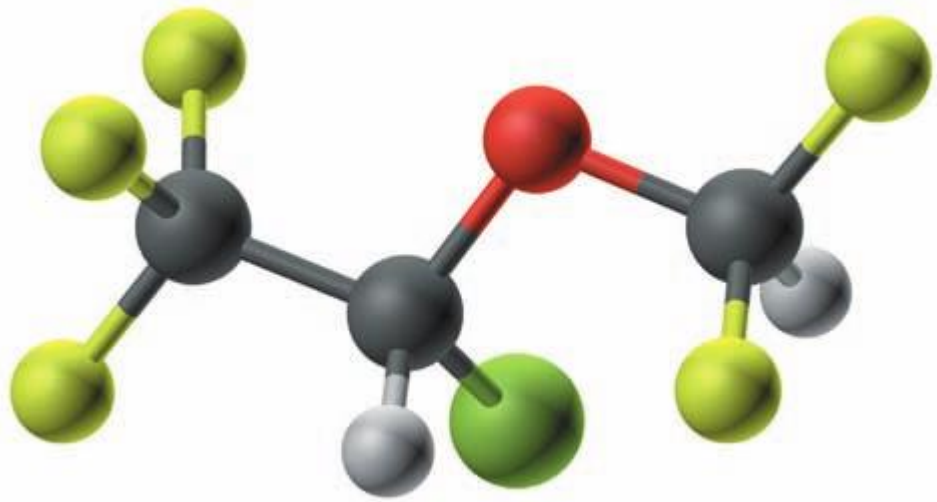
Chapter 8

Alcohols, Ethers, and Thiols



8.1 What Are Alcohols（醇）?

8.2 What Are the Characteristic Reactions of Alcohols?

8.3 What Are Ethers（醚）?

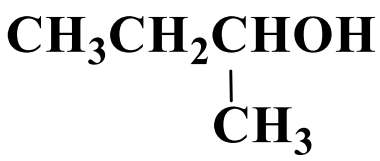
8.4 What Are Epoxides（环氧化物）?

8.5 What Are Thiols（硫醇）?（略）

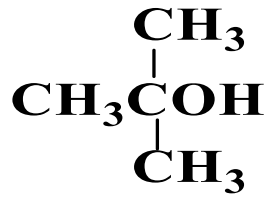
8.6 What Are the Characteristic Reactions of Thiols?（略）

8.1 What Are Alcohols?

一级醇（伯醇）



二级醇（仲醇）

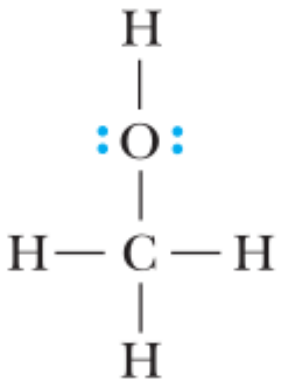


三级醇（叔醇）

A. Structure

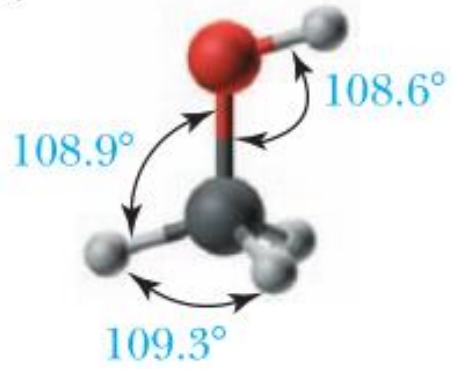
Alcohol A compound containing an -OH (hydroxyl) group bonded to an *sp3* hybridized carbon.

(a)



O: *sp3*
C : *sp3*

(b)



C-O : 3.5 - 2.5 = 1.0
H-O : 3.5 - 2.1 = 1.4

极性分子

B. Nomenclature

IUPAC Names： the ending of the parent alkane is changed from -e to -ol.

1. Select, as the parent alkane, the longest chain of carbon atoms that contains the -OH, and number that chain from the end closer to the -OH group. In numbering the parent chain, the location of the -OH group takes precedence over alkyl groups and halogens.

(选含羟基在内的最长碳链作为母体，称为x醇，优先保证-OH 位次最小)

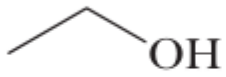
2. Change the suffix of the parent alkane from -e to -ol (Section 3.5), and use a number to show the location of the -OH group. For cyclic alcohols, numbering begins at the carbon bearing the - OH group.

(英文母体名称后缀为-ol，标出羟基位次，环醇从羟基开始编号)

3. Name and number substituents and list them in alphabetical order.

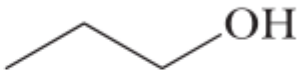
(取代基名称和位次按字母顺序列出)

Common names: **alkyl group + alcohol**



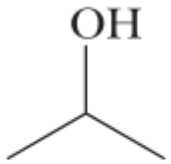
Ethanol
(Ethyl alcohol)

乙醇、乙（基）醇



1-Propanol
(Propyl alcohol)

1-丙醇、丙醇

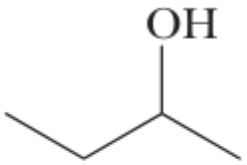


2-Propanol
(Isopropyl alcohol)

2-丙醇、异丙醇

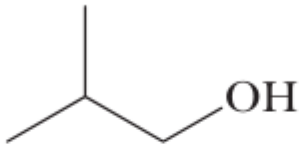
1-Butanol
(Butyl alcohol)

1-丁醇、丁醇



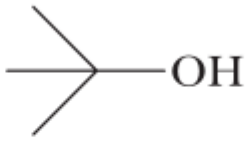
2-Butanol
(*sec*-Butyl alcohol)

2-丁醇、仲丁醇



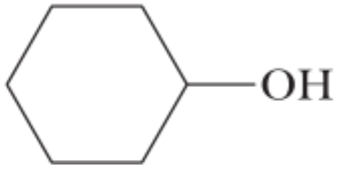
2-Methyl-1-propanol
(Isobutyl alcohol)

2-甲基-1-丙醇、
异丁醇



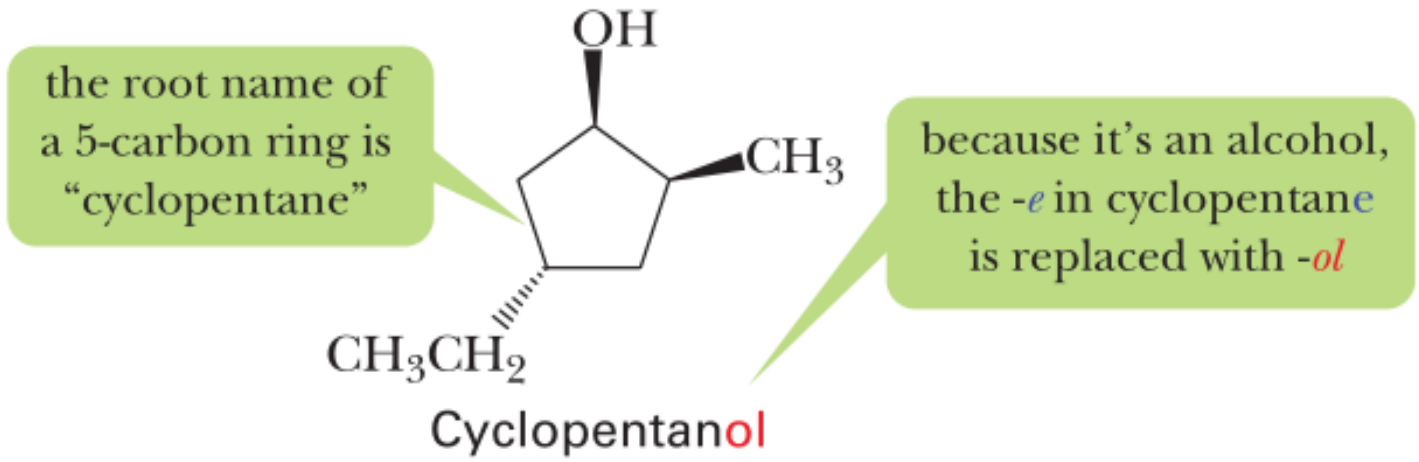
2-Methyl-2-propanol
(*tert*-Butyl alcohol)

2-甲基-2-丙醇
叔丁醇

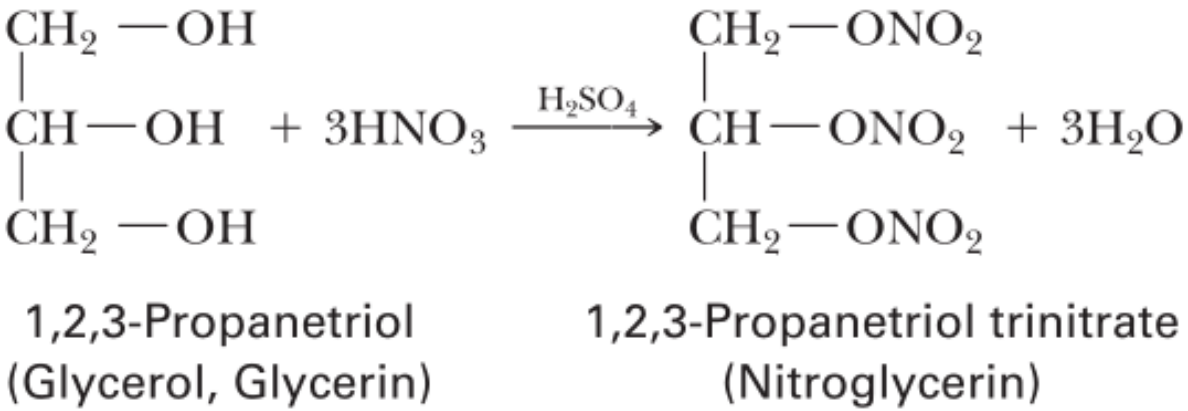


Cyclohexanol
(Cyclohexyl alcohol)

环己醇、环己基醇



NitroglyceriN: An explosive and a drug



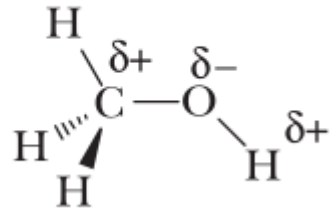
1,2,3-Propanetriol (Glycerol, Glycerin)

1,2,3-Propanetriol trinitrate (Nitroglycerin)

Nobel, 1833–1896, builton the manufacture of dynamite, now funds the Nobel Prizes.

C. Physical Propert

(a)



(b)

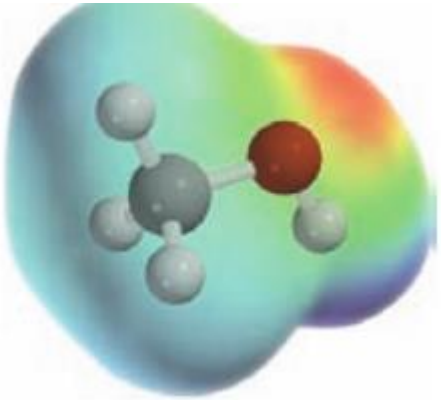
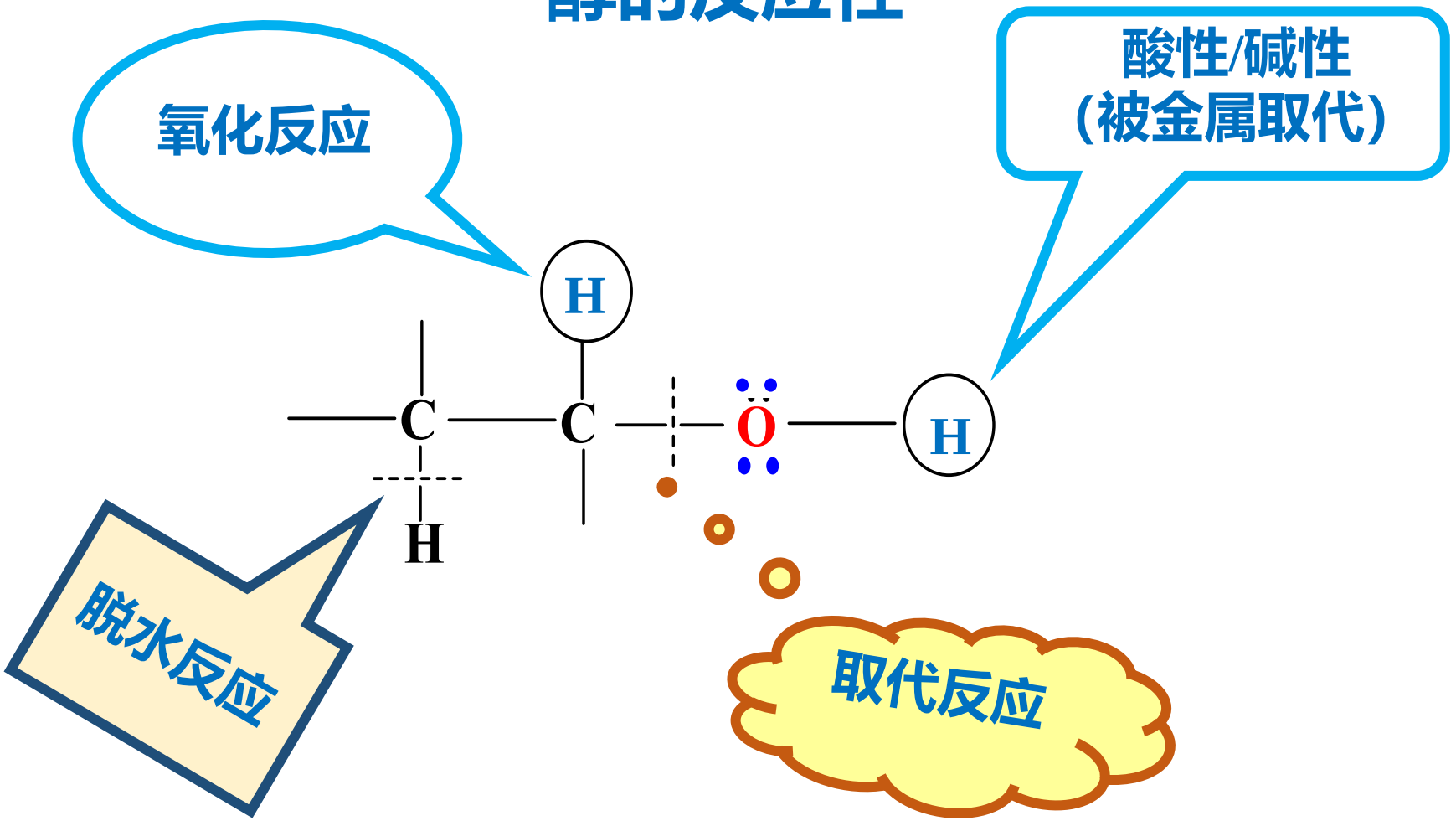


TABLE 8.1 Boiling Points and Solubilities in Water of Five Groups of Alcohols and Alkanes of Similar Molecular Weight

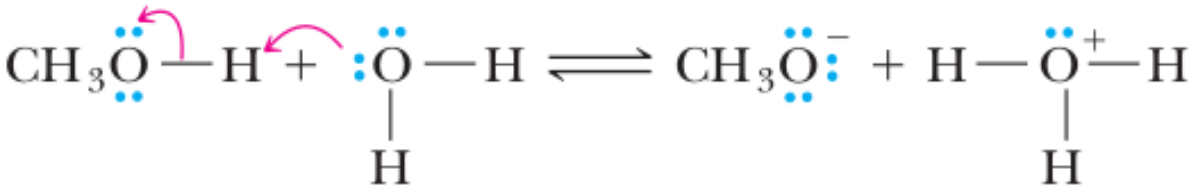
Structural Formula	Name	Molecular Weight	Boiling Point (°C)	Solubility in Water
CH_3OH	methanol	32	65	infinite
CH_3CH_3	ethane	30	−89	insoluble
CH_3CH_2OH	ethanol	46	78	infinite
$CH_3CH_2CH_3$	propane	44	−42	insoluble
$CH_3CH_2CH_2OH$	1-propanol	60	97	infinite
$CH_3CH_2CH_2CH_3$	butane	58	0	insoluble
$CH_3CH_2CH_2CH_2OH$	1-butanol	74	117	8 g/100 g
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	36	insoluble
$CH_3CH_2CH_2CH_2CH_2OH$	1-pentanol	88	138	2.3 g/100 g
$HOCH_2CH_2CH_2CH_2OH$	1,4-butanediol	90	230	infinite
$CH_3CH_2CH_2CH_2CH_2CH_3$	hexane	86	69	insoluble

醇的反应性



8.2 What Are the Characteristic Reactions of Alcohols?

A. Acidity of Alcohols（醇的酸性）



$$K_a = \frac{[CH_3O^-][H_3O^+]}{[CH_3OH]} = 3.2 \times 10^{-16}$$

$$pK_a = 15.5$$

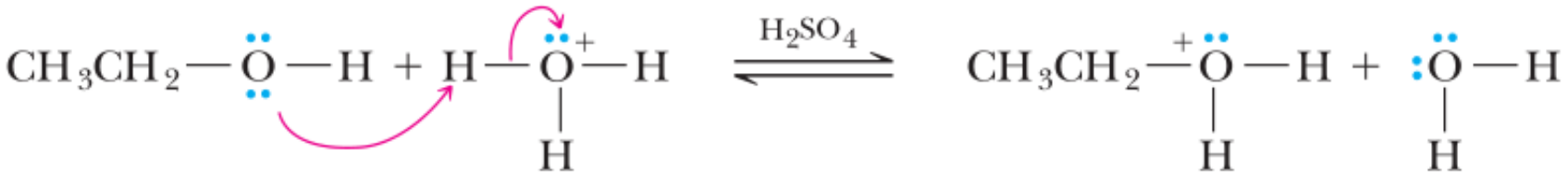
TABLE 8.2 pK_a Values for Selected Alcohols in Dilute Aqueous Solution*

Compound	Structural Formula	pK_a	
hydrogen chloride	HCl	−7	Stronger acid
acetic acid	CH_3COOH	4.8	
methanol	CH_3OH	15.5	
water	H_2O	15.7	
ethanol	CH_3CH_2OH	15.9	
2-propanol	$(CH_3)_2CHOH$	17	Weaker acid
2-methyl-2-propanol	$(CH_3)_3COH$	18	

*Also given for comparison are pK_a values for water, acetic acid, and hydrogen chloride.

B. Basicity of Alcohols

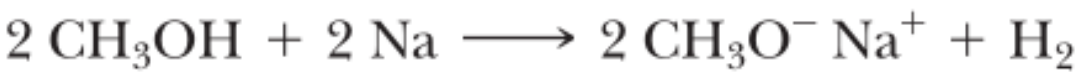
alcohols can function as both weak acids and weak bases



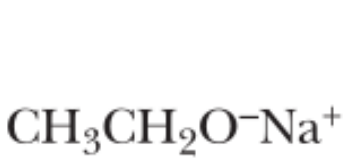
Ethanol　Hydronium ion (pK_a −1.7)　Ethyloxonium ion (pK_a −2.4)

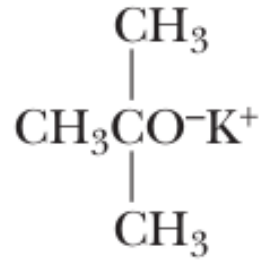
C. Reaction with Active Metals

Li, Na, K, Mg, and other active metals



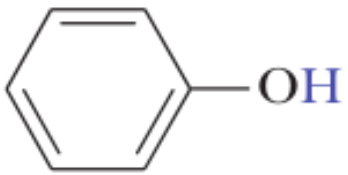
Sodium methoxide



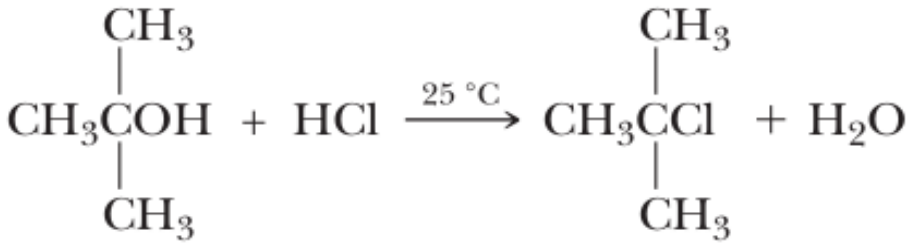


Sodium ethoxide　Potassium *tert*-butoxide

强碱、亲核试剂

	Example	pKa
Higher acidity		
mineral acids	HCl, H_2SO_4	
carboxylic acids	$RCOOH$	
phenols		
water	H_2O	15.7
alcohols	ROH	
alkynes (terminal)	$R-C\equiv C-H$	
ammonia and amines	NH_3, RNH_2, R_2NH	
Lower acidity		
alkenes and alkanes	$R_2C=CH_2$, RH	

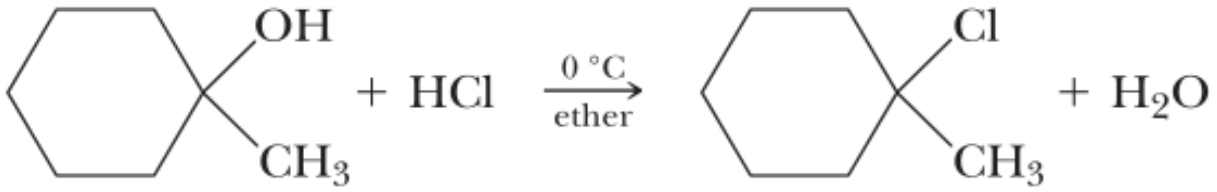
D. Conversion to Haloalkanes（亲核取代）



2-Methyl-2-propanol　　2-Chloro-2-methylpropane

氢卤酸的反应活性：

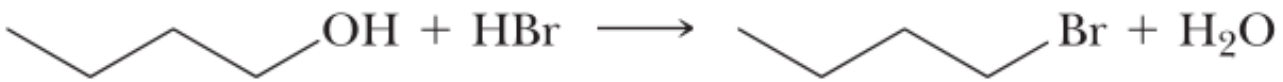
HI＞HBr＞HCl



1-Methyl-cyclohexanol　　1-Chloro-1-methyl cyclohexane

醇的反应活性：

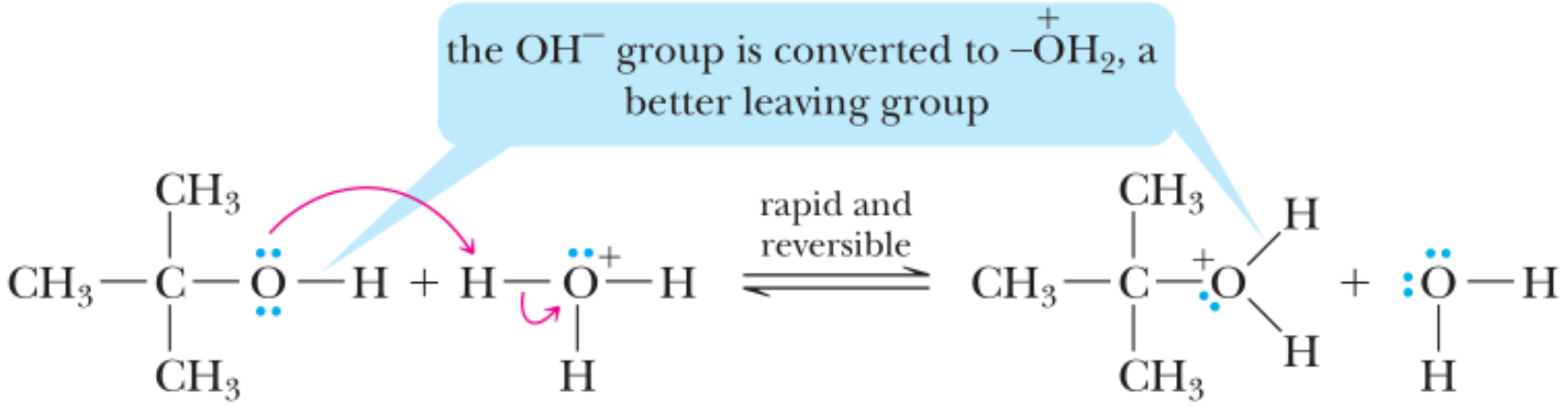
烯丙型醇＞叔醇＞仲醇＞伯醇



1-Butanol　　1-Bromobutane (Butyl bromide)

Reaction of a tertiary Alcohol with Hcl: An S_N1 reaction

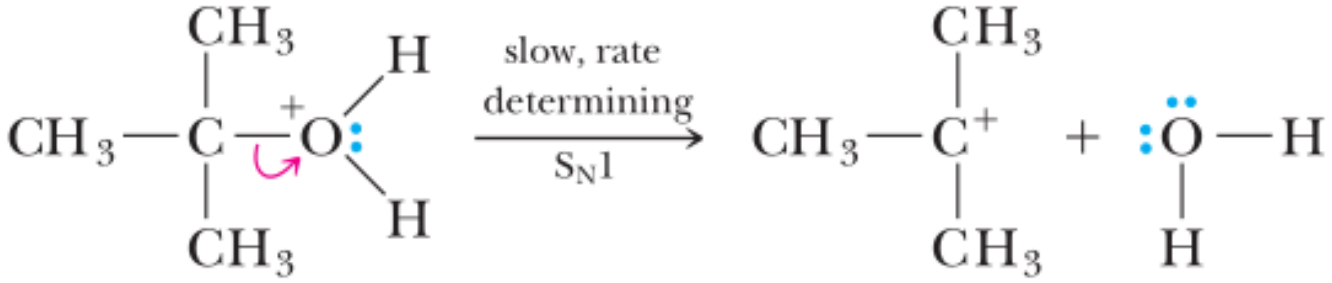
Step1:



2-Methyl-2-propanol (*tert*-Butyl alcohol)

An oxonium ion

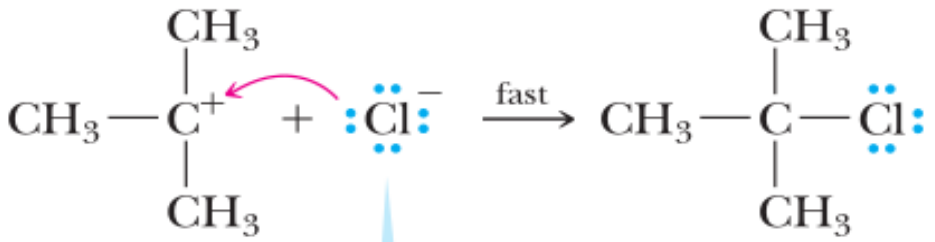
Step2:



An oxonium ion

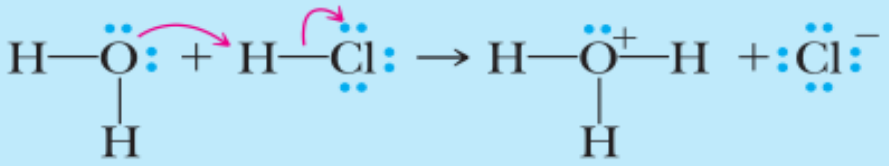
A 3° carbocation intermediate

Step3:



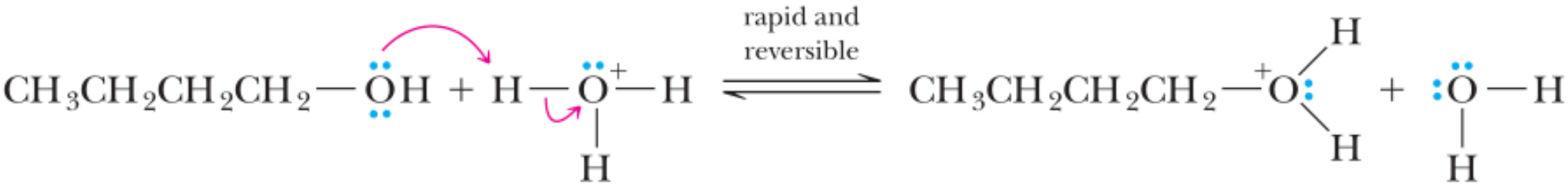
2-Chloro-2-methylpropane
(*tert*-Butyl chloride)

chloride ion is produced in the initial reaction of H_2O with HCl



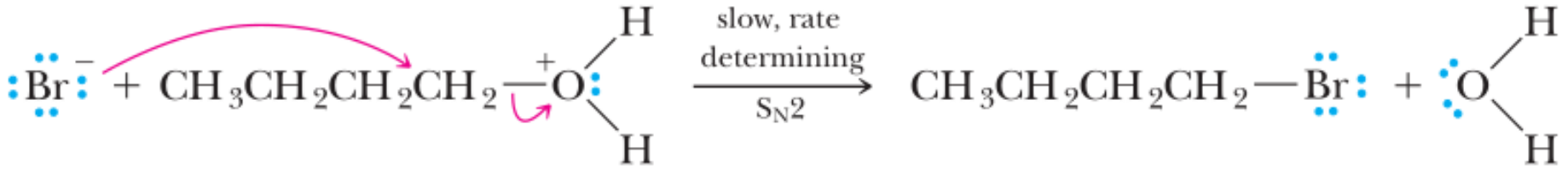
Reaction of a Primary Alcohol with HBr: An S_N2 Reaction

Step1:

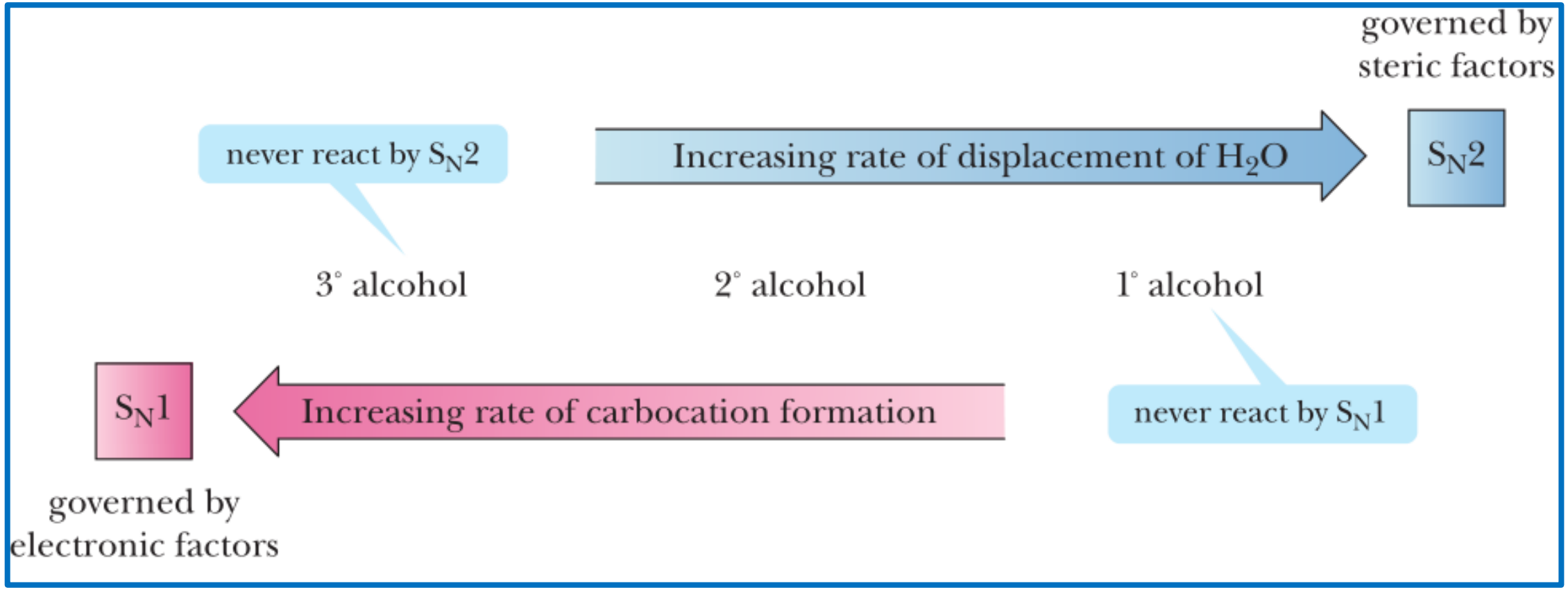


An oxonium ion

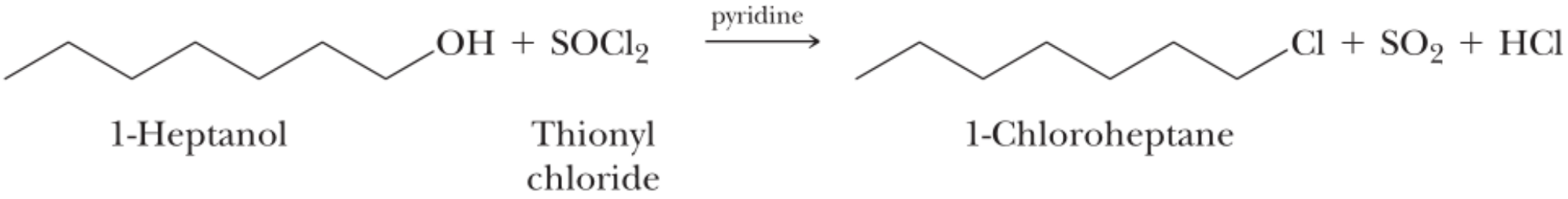
Step2:


slow, rate determining
S_N2

Why?

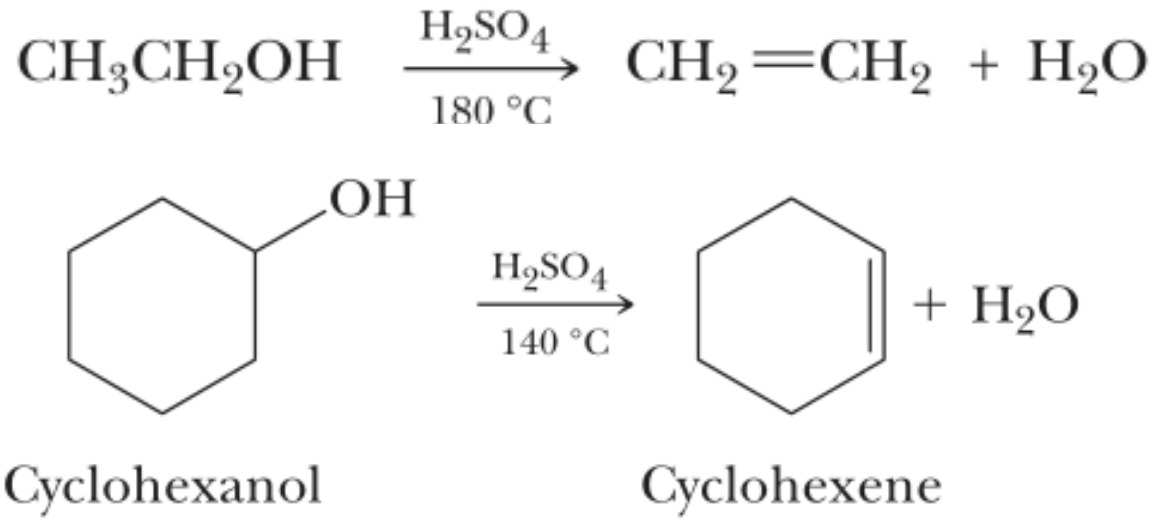

governed by steric factors
never react by S_N2
Increasing rate of displacement of H_2O
S_N2
3° alcohol
2° alcohol
1° alcohol
S_N1
Increasing rate of carbocation formation
never react by S_N1
governed by electronic factors

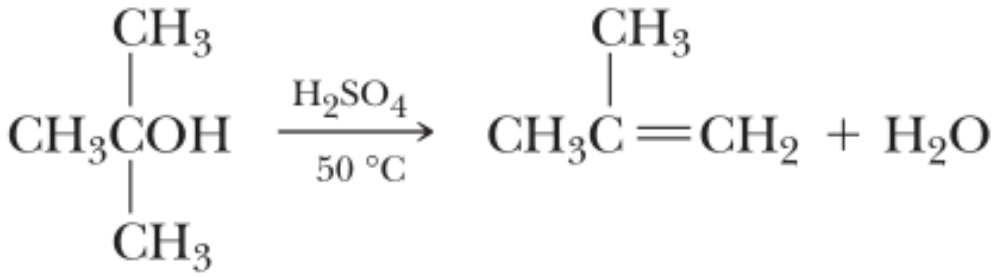
Reaction with Thionyl Chloride



E. Acid-Catalyzed Dehydration to Alkenes(酸催化脱水-消除反应)

Dehydration： Elimination of a molecule of water from a compound.



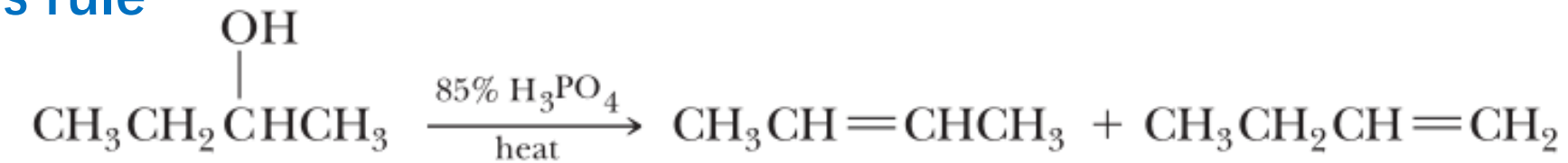


2-Methyl-2-propanol (*tert*-Butyl alcohol)　　2-Methylpropene (Isobutylene)

小结：醇脱水的难易顺序

1° alcohol < 2° alcohol < 3° alcohol

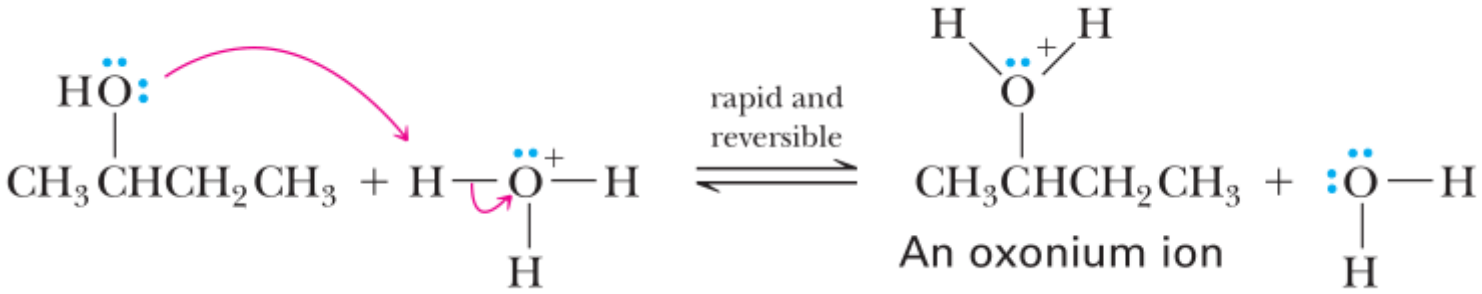
规律：Zaitsev's rule



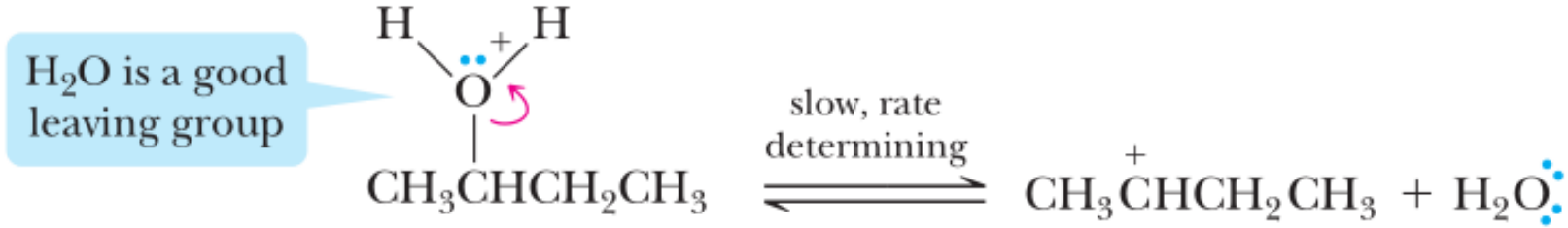
2-Butanol　　2-Butene (80%)　　1-Butene (20%)

Acid-catalyzed dehydration of 2-Butanol: An E1 Mechanism

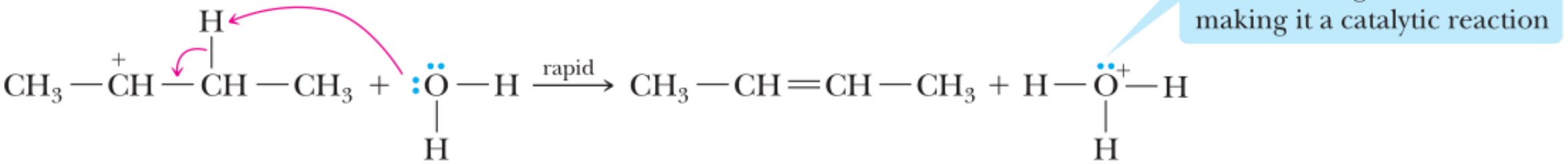
STEP 1: Add a proton.



STEP 2: Break a bond to form a stable molecule or ion.



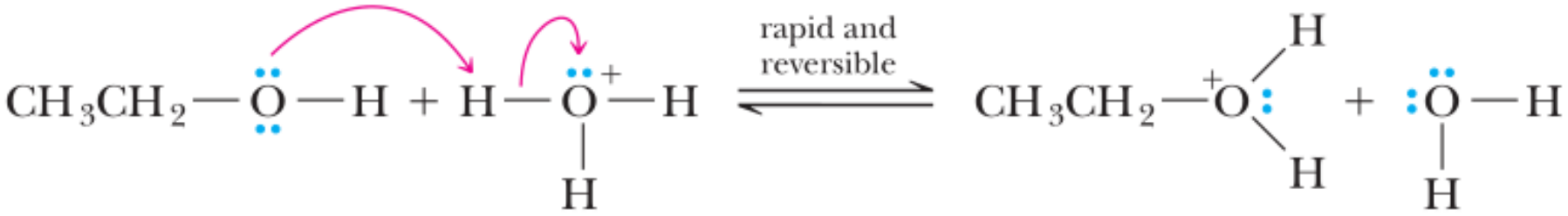
STEP 3: Take away a proton.



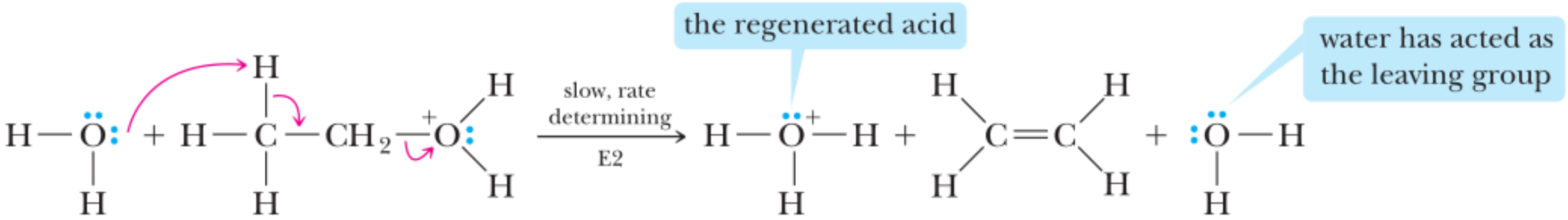
Acid-catalyzed dehydration of a primary Alcohol:

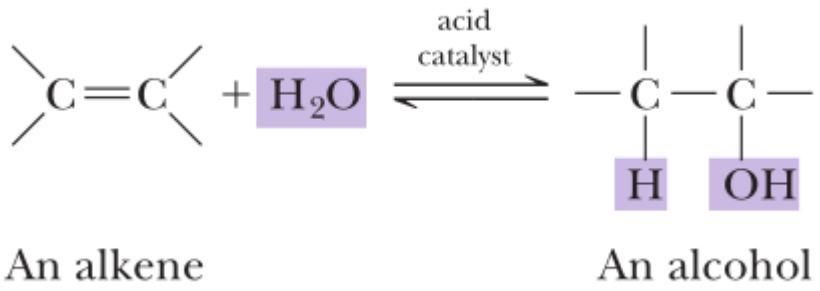
An E2 Mechanism

STEP 1: Add a proton.

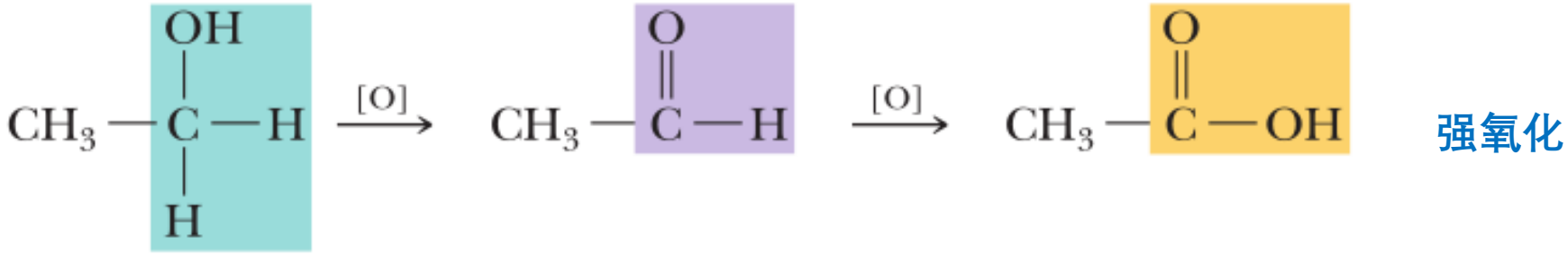


STEP 2: Take a proton away and break a bond to form a stable molecule or ion.





F. Oxidation of Primary and Secondary Alcohols（伯醇和仲醇的氧化）



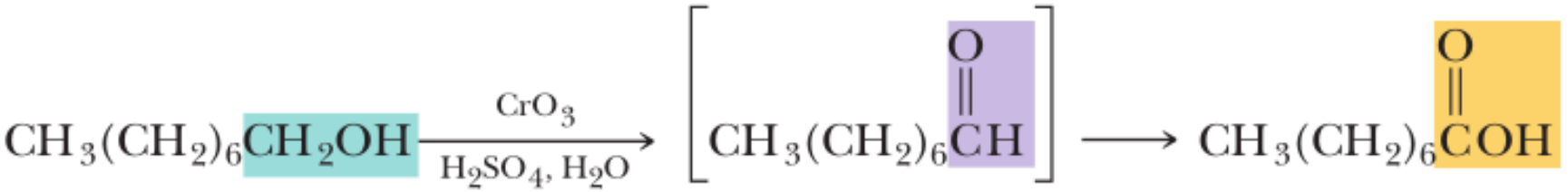
A primary alcohol

伯醇

An aldehyde

A carboxylic acid

强氧化

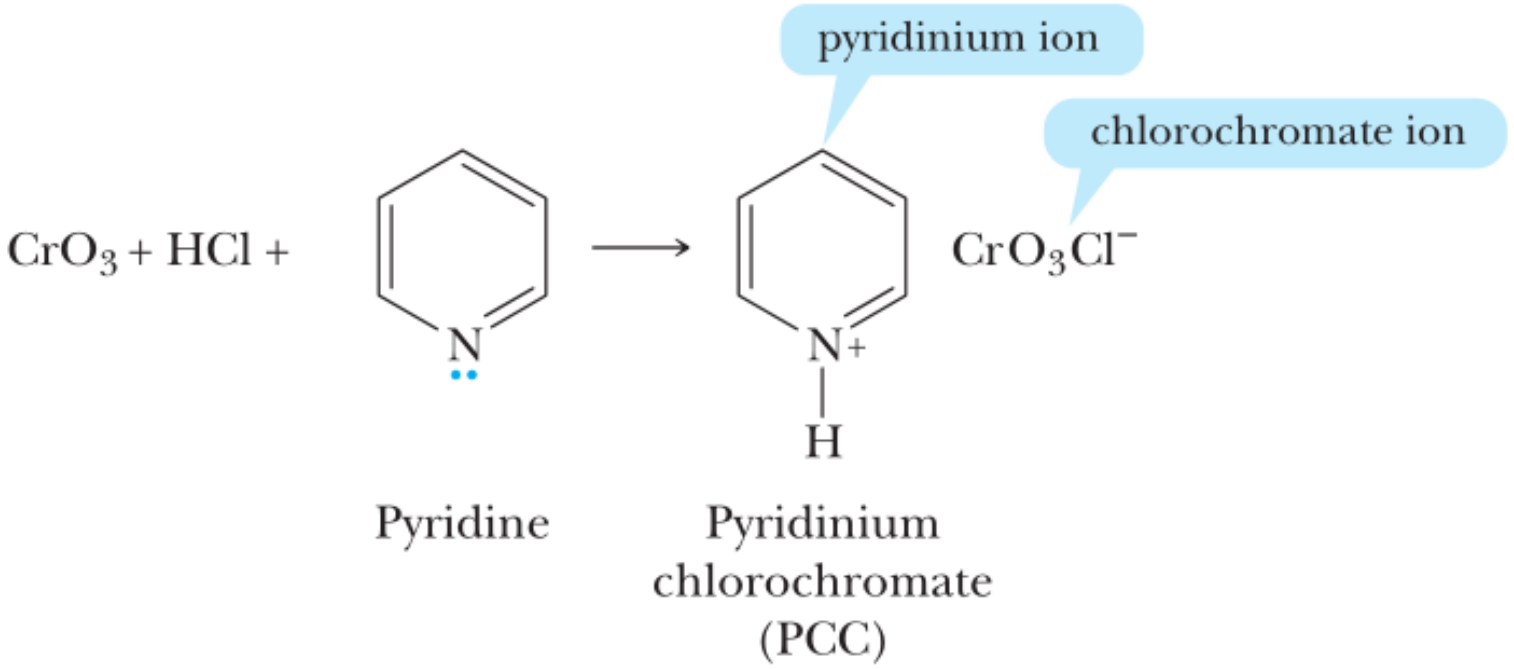


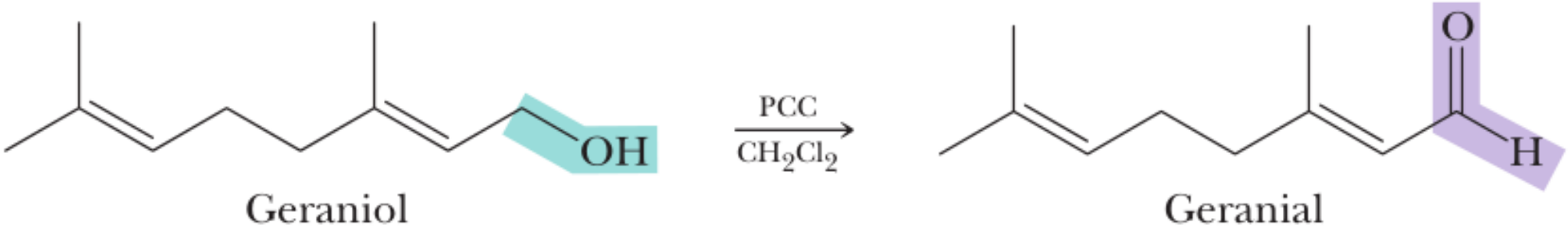
1-Octanol

Octanal (not isolated)

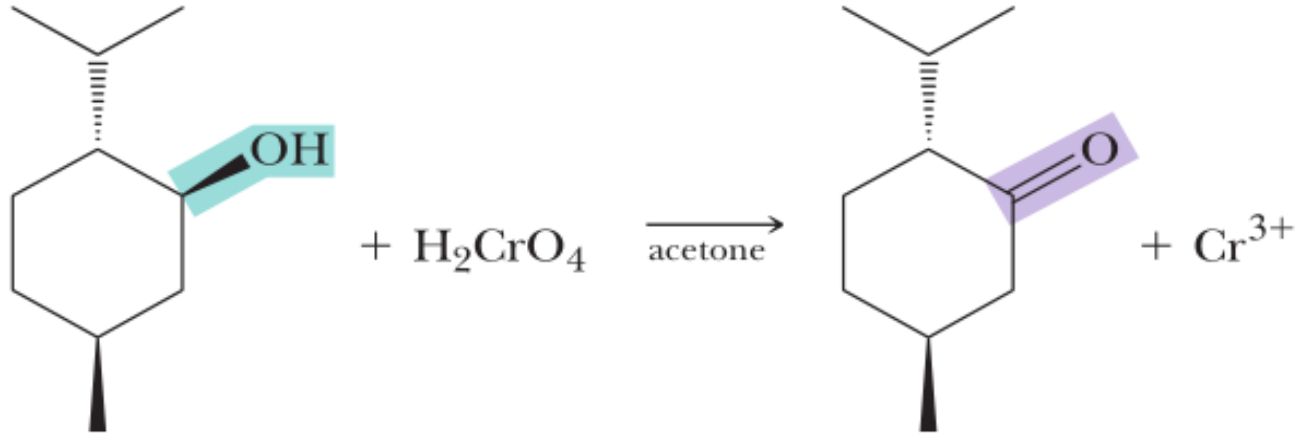
Octanoic acid

选择性氧化


pyridinium ion
chlorochromate ion
$CrO_3 + HCl +$
N
N+
H
CrO_3Cl^-
Pyridine
Pyridinium chlorochromate (PCC)


OH
PCC
CH_2Cl_2
O
H
Geraniol
Geranial

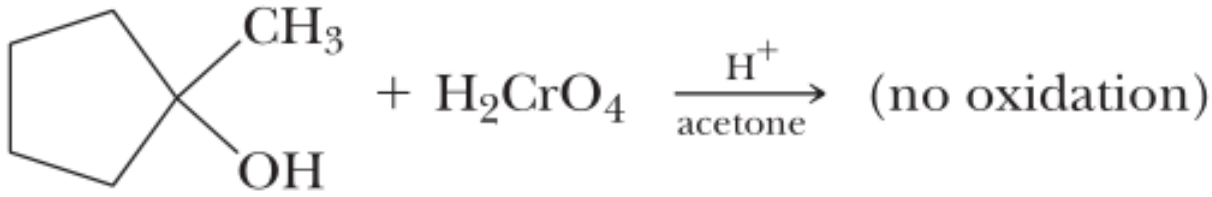
仲醇



2-Isopropyl-5-methyl-cyclohexanol (Menthol)

2-Isopropyl-5-methyl-cyclohexanone (Menthone)

叔醇

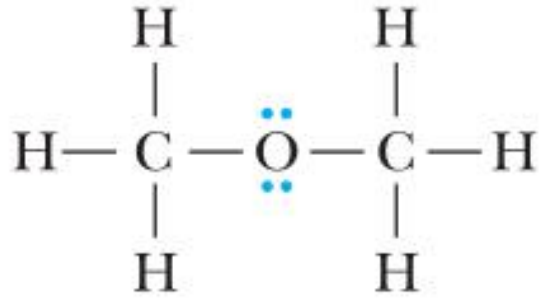


1-Methylcyclopentanol

8.3 What Are Ethers（醚）?

A. Structure

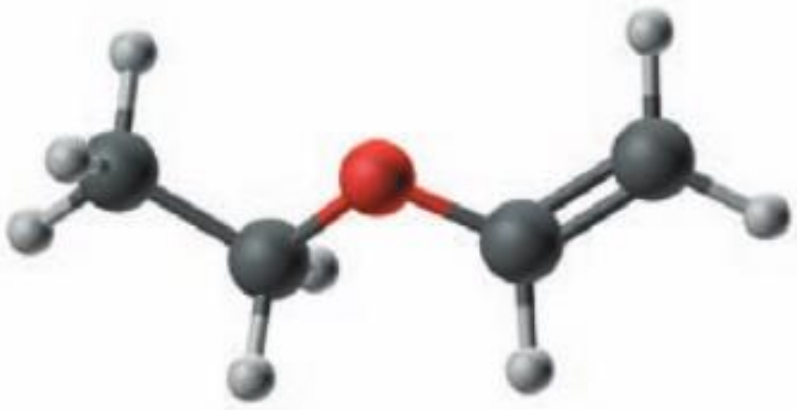
(a)



(b)

$CH_3CH_2—O—CH=CH_2$

Ethyl vinyl ether

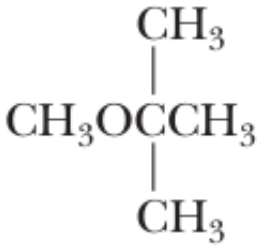


B. Nomenclature

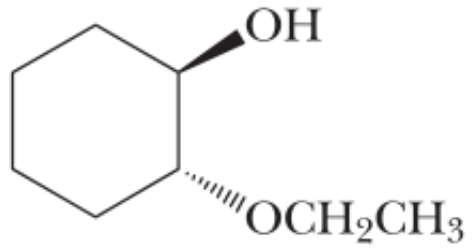
IUPAC system： 最长碳链 + RO-（烷氧基）

Common names: 按字母顺序列出与氧结合的烷基，并加上“醚”.

Ethoxyethane
(Diethyl ether)



2-Methoxy-2-methylpropane
(methyl *tert*-butyl ether, MTBE)



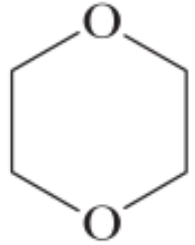
(1*R*,2*R*)-2-Ethoxycyclohexanol
(*trans*-2-Ethoxycyclohexanol)

Cyclic ethers：环醚

Ethylene oxide

Tetrahydrofuran (THF)

四氢呋喃



1,4-Dioxane

1,4-二恶烷/二氧六环

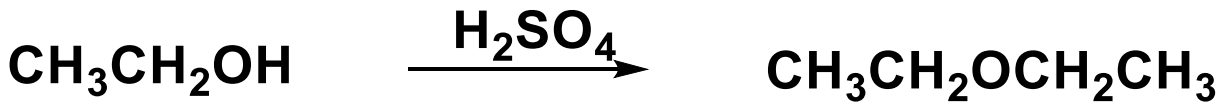
C. Physical Properties

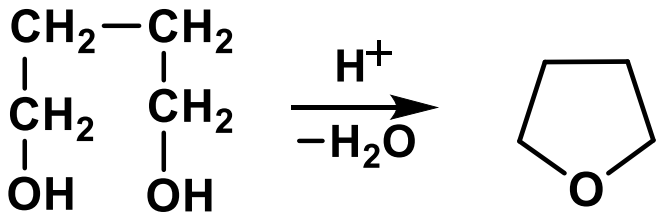
TABLE 8.3 Boiling Points and Solubilities in Water of Some Alcohols and Ethers of Comparable Molecular Weight

Structural Formula	Name	Molecular Weight	Boiling Point (°C)	Solubility in Water
CH_3CH_2OH	ethanol	46	78	infinite
CH_3OCH_3	dimethyl ether	46	−24	7.8 g/100 g
$CH_3CH_2CH_2CH_2OH$	1-butanol	74	117	7.4 g/100 g
$CH_3CH_2OCH_2CH_3$	diethyl ether	74	35	8 g/100 g
$CH_3CH_2CH_2CH_2CH_2OH$	1-pentanol	88	138	2.3 g/100 g
$HOCH_2CH_2CH_2CH_2OH$	1,4-butanediol	90	230	infinite
$CH_3CH_2CH_2CH_2OCH_3$	butyl methyl ether	88	71	slight
$CH_3OCH_2CH_2OCH_3$	ethylene glycol dimethyl ether	90	84	infinite

Preparation of Ethers

A. 醇脱水



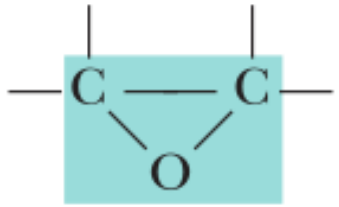


THF

B. 威廉森 (Williamson)合成法

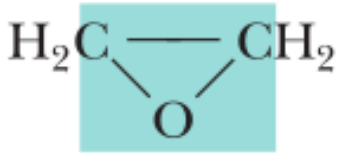
8.4 What Are Epoxides?

A. Structure and Nomenclature



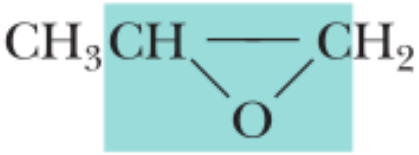
Functional group of an epoxide

官能团



Ethylene oxide

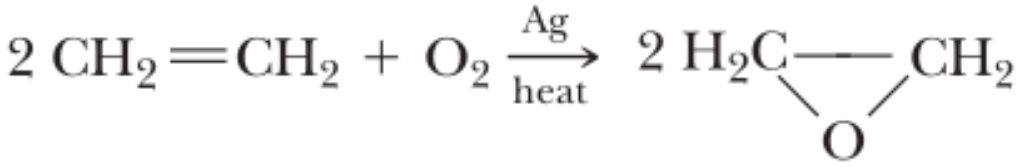
环氧乙烷



Propylene oxide

氧化丙烯

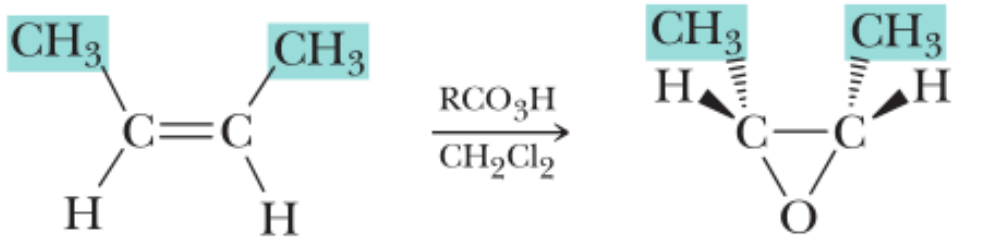
B. Synthesis from Alkenes



Ethylene

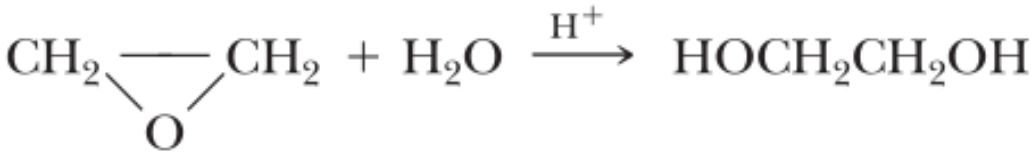
Ethylene oxide

过氧酸氧化

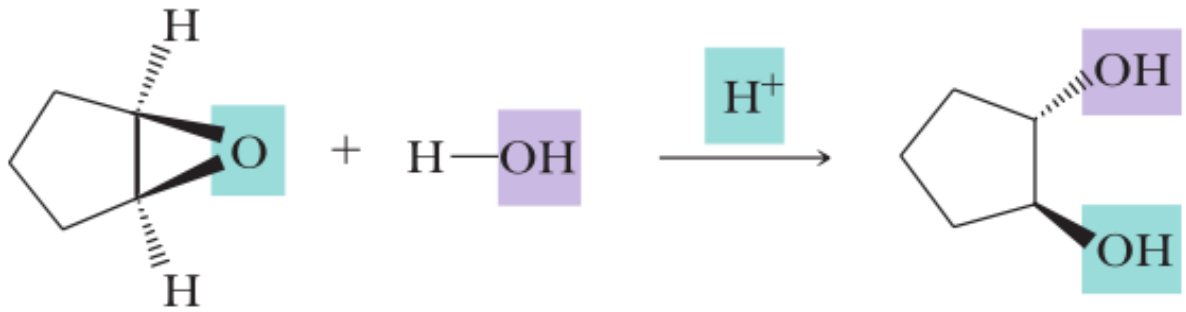


cis-2-Butene　　*cis*-2-Butene oxide

C. Ring-opening Reactions（开环反应）



Ethylene oxide　　1,2-Ethanediol (Ethylene glycol)



作 业

8.14（a、c、e）、8.15（a、c、e）、

8.18（a、b、c）、8.24、8.35、

8.41（a、b）、8.46