

第十章 醇 酚 醚



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第一节 醇

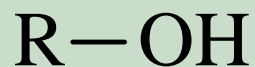
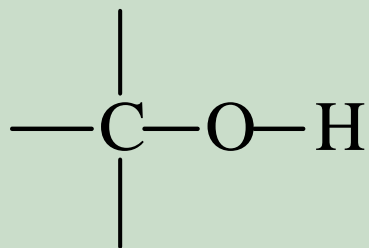
第二节 酚

第三节 醚

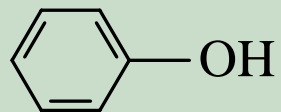


第十章 醇 酚 醚 —O—

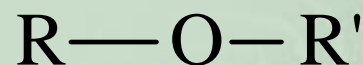
醇



酚



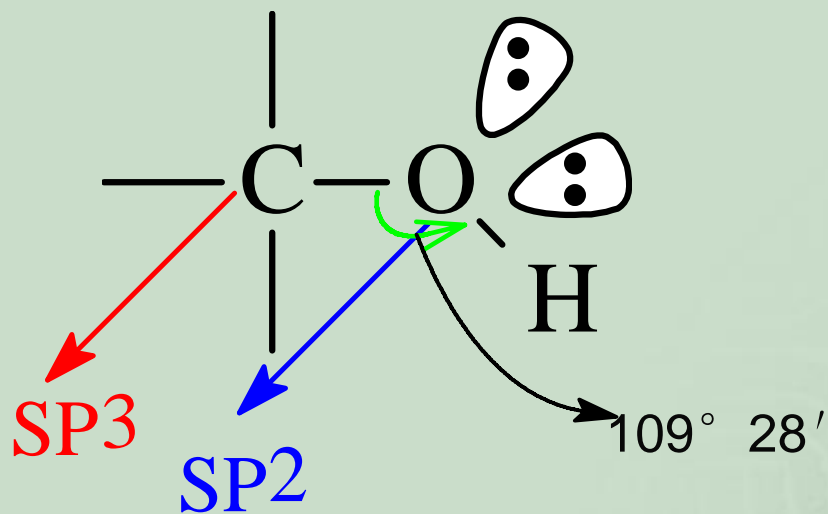
醚



第一节 醇

一 结构与分类

1. 结构



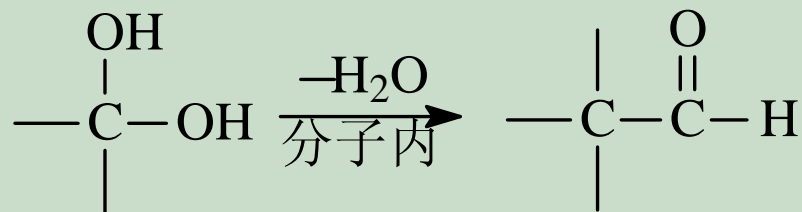
2. 分类

根据含羟基数目的不同分为



一元醇 $\text{CH}_3\text{CH}_2\text{OH}$

二元醇 $\text{HOCH}_2-\text{CH}_2\text{OH}$



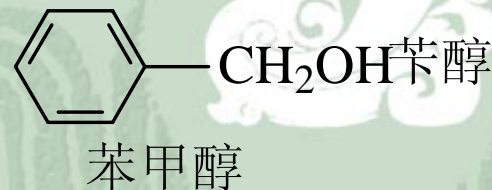
多元醇 $\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_2 \\ | \quad | \quad | \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$ 甘油

伯醇(1°) RCH_2OH $\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{OH} \\ | \\ \text{CH}_3 \end{array}$ 异丁醇

仲醇(2°) R_2CHOH $\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_3 \\ | \\ \text{OH} \end{array}$ 仲丁醇

叔醇(3°) R_3COH $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ | \\ \text{OH} \end{array}$ 叔丁醇

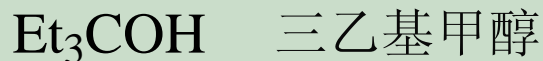
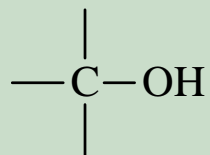
烯丙醇 $\begin{array}{c} | \quad | \quad | \\ -\text{C}=\text{C}-\text{C}-\text{OH} \\ | \end{array}$ $\text{CH}_2=\text{CHCH}_2\text{OH}$ 烯丙醇



二 命名

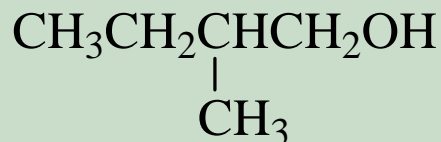
1. 普通命名法

2. 衍生物

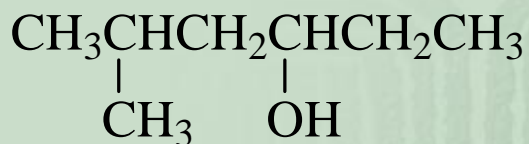


3. 系统命名法

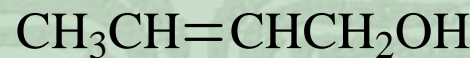
结构较复杂的醇,选含羟基的最长碳链作主链,以离羟基最近的一端开始编号,根据主链中碳原子数称为”某醇”



2-甲基-1-丁醇

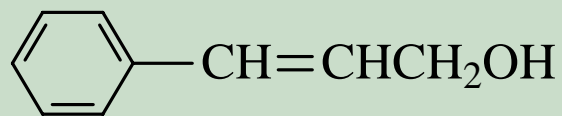


5-甲基-3-己醇

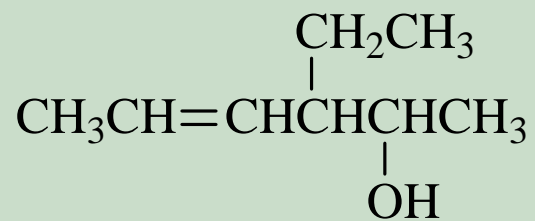


2-丁烯(-1-)醇

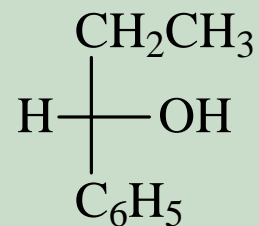




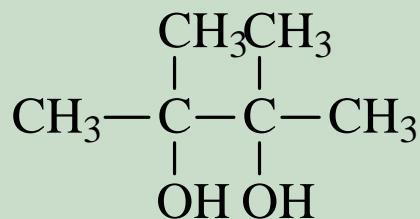
3-苯基-2-丙烯醇



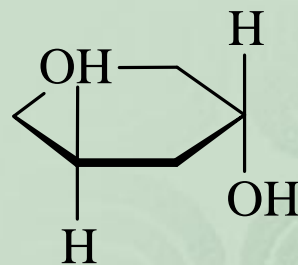
3-乙基-4-己烯-2-醇



(S)-1-苯基-1-丙醇



2,3-二甲基-2,3-丁二醇

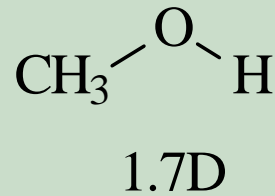
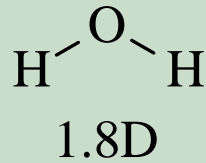


反-1,3-环己二醇



三. 物理性质

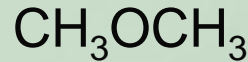
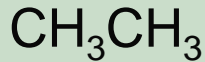
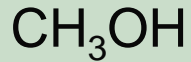
1. 极性 (弱)



2. 沸点

低级醇

{ 较高的沸点 (分子间氢键)
在水里有较大的溶解度



正十七烷

正十六醇

分子量 32

30

46

46

240

242

b.p. 65° C

-88.6° C

78.2° C

-25° C

301.8° C

344° C

烃基对缔合作用产生阻碍, R基增大, 分子间氢键难形成

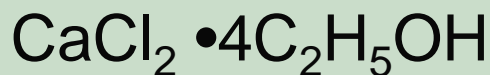


3. 溶解性

C \leq 3及叔丁醇溶于水

R-OH 极性小, 质子性溶剂

4. 醇合物



溶于水, 不溶于有机溶剂

分离应用
制醇 不可用 $CaCl_2$ 干燥

四光谱性质

1. IR 醇 ν O-H 未缔合 3640---3610 cm^{-1} 中(尖) } 特征峰
缔合 3600---3200 cm^{-1} 强(宽)

ν C-O 1000---2000 cm^{-1}

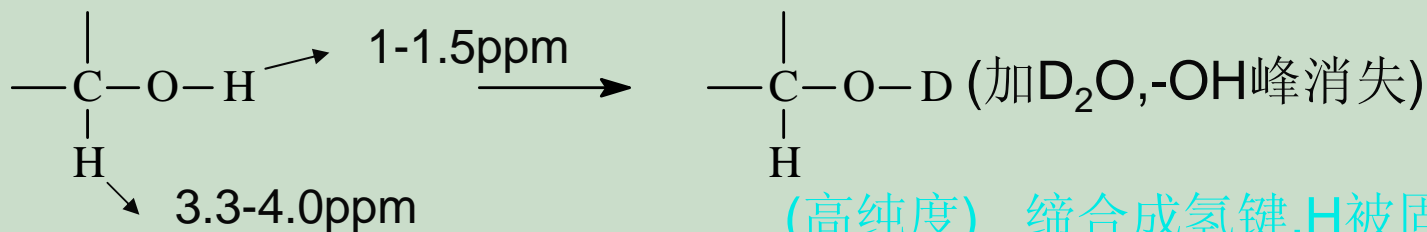
伯醇 1060---1030 cm^{-1}
仲醇 ---1100 cm^{-1} } 相关峰
叔醇 ---1140 cm^{-1}

酚 C-O 1230 cm^{-1}

醚 C-O 有C-O吸收峰, 但无-OH吸收峰

因此可以区别醇, 酚, 醚.

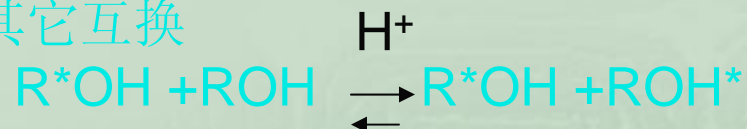
2. ^1H NMR



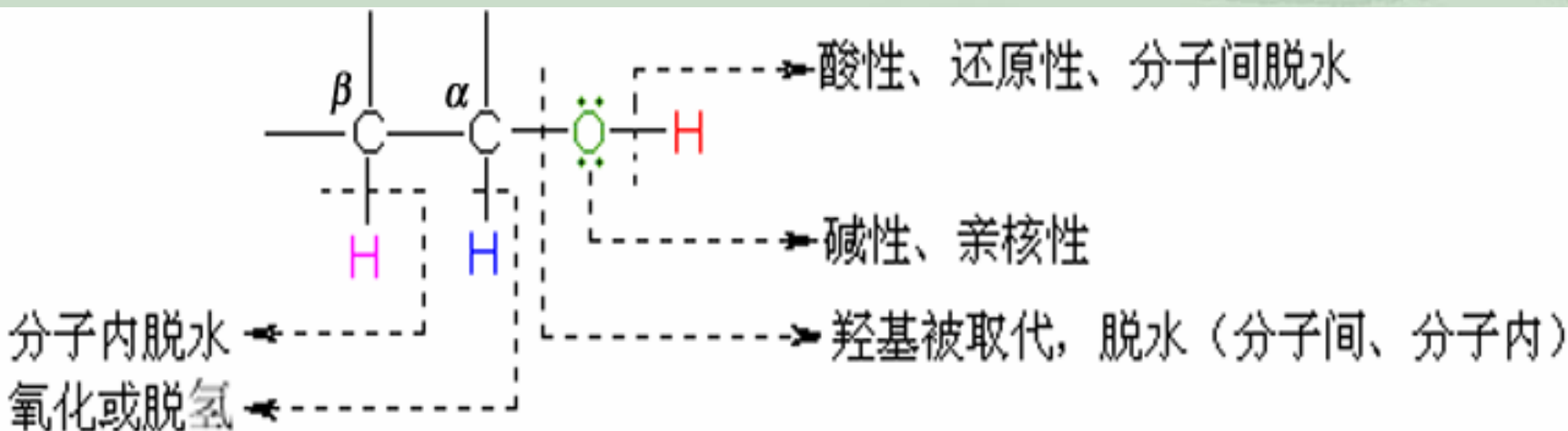
1.22	3.70	5.42	ppm
三重峰	八重	三重	
三	四	单峰	

(高纯度) 缔合成氢键, H被固定
或 $\text{CH}_3\text{-S(=O)-CH}_3$ (DMSO) 也可被固定

微量其它互换

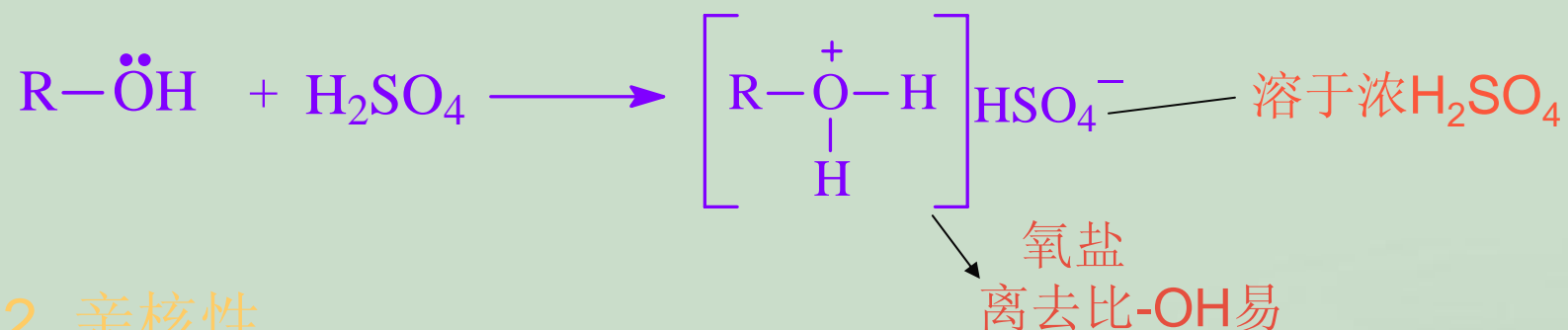


五. 化学性质

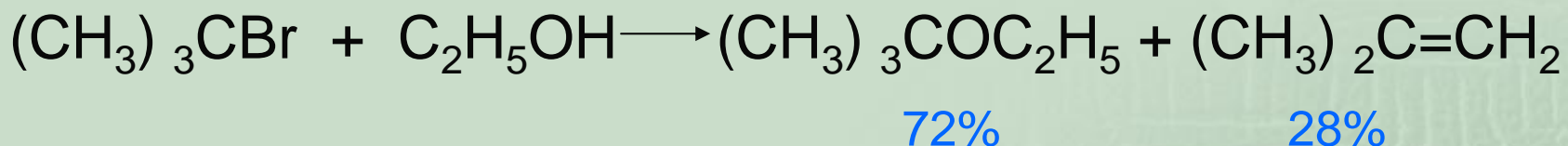


(一) 碱性和亲核

1. 碱性

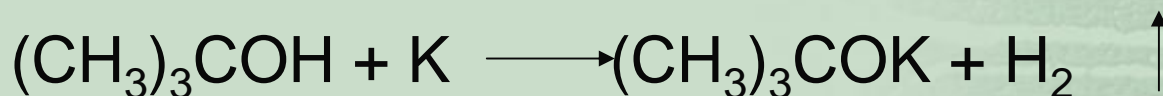
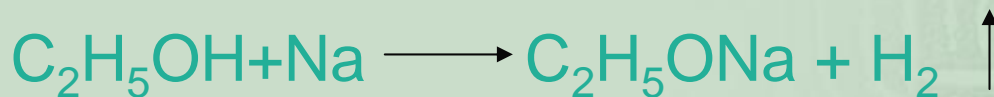


2. 亲核性



(二) 酸性

1. 与活泼金属反应



2. 酸性强度

1) $\text{H}_2\text{O} > \text{ROH}$ 反应性 $\text{H}_2\text{O} > \text{ROH}$

2) $\text{CH}_3\text{OH} > 1^\circ > 2^\circ > 3^\circ$ (液态)
 $\text{CH}_3\text{OH} > 1^\circ > 2^\circ > 3^\circ$ RO^- 的溶剂化

	CH_3OH	$\text{CH}_3\text{CH}_2\text{OH}$	$\text{CH}_3\underset{\text{OH}}{\text{C}}\text{CH}_3$	$(\text{CH}_3)_3\text{C-OH}$
Pka	15	16	~18	>19

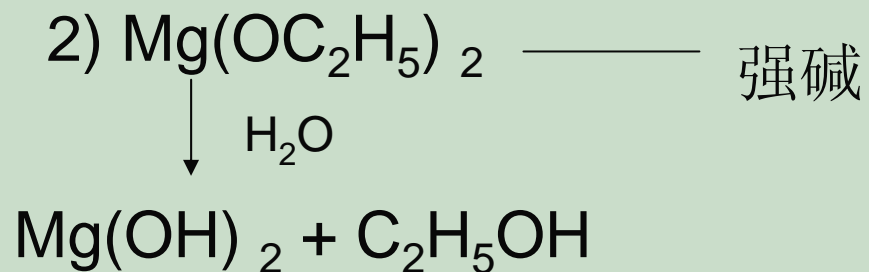
3) $\text{CH}_3\text{OH} < 1^\circ < 2^\circ < 3^\circ$ (气相)

用离子回旋共振谱测电子效应

3. 烷基电子效应和醇的酸性

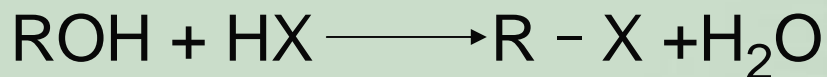
烷基电子效应: 1) 与不饱和键相连, 给电子 δ 超共轭效应
2) 与饱和键相连, 吸电子诱导效应

4.应用 1)有机合成 $\text{Al}[\text{OCHCC}(\text{CH}_3)_2]_3$

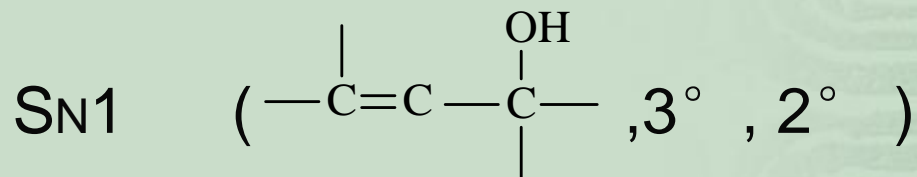


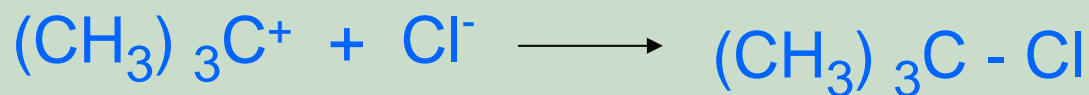
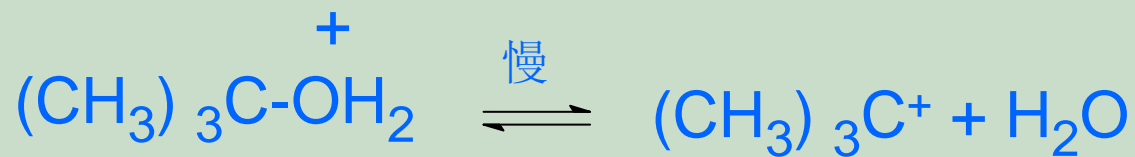
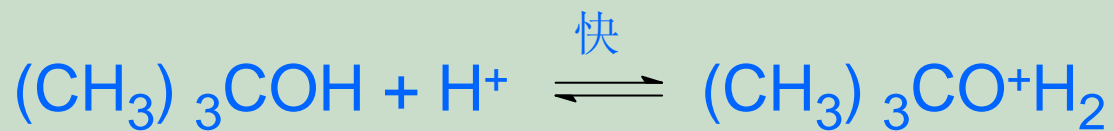
(三) 被卤原子取代 (HX , PX_3 , SOCl_2)

1.与HX反应

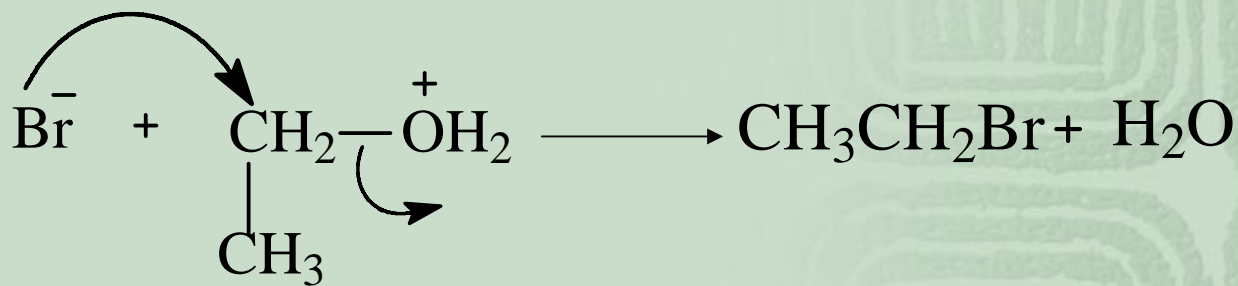
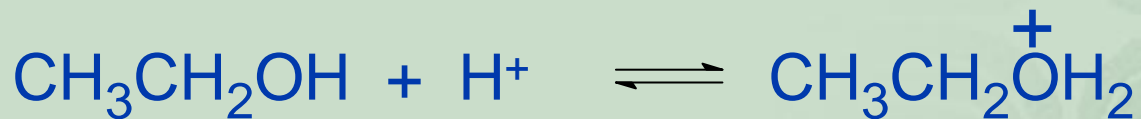


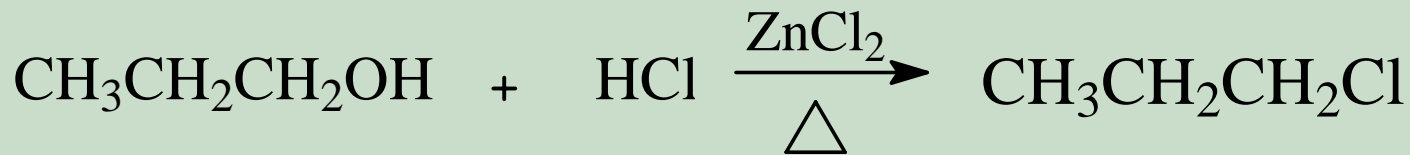
1) 历程





SN2 (1°, CH₃OH)





4. 应用

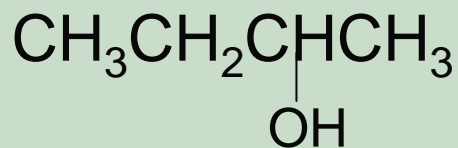


2 卢卡斯试剂鉴别 $< \text{C}_6$ 醇

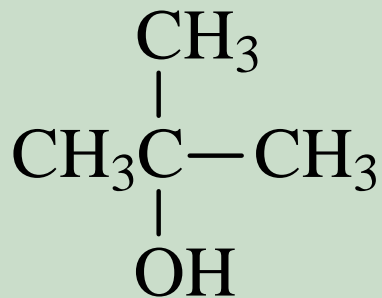
lucas 试剂：无水 $\text{ZnCl}_2 + \text{HCl}$ (浓)

lucas试剂

(一)



(+) 5~10分钟，出现浑浊



(+) 立即浑浊，3~5分钟分层

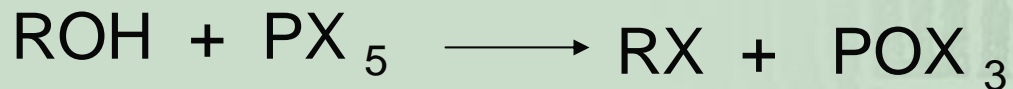
烯丙醇不可用:

因为产物 $\text{CH}_2=\overset{+}{\text{C}}\text{HCH}_2$ 易溶于试剂, 形成 $[\text{ZnCl}_3]$

< C_6 反应物溶, 产物不可溶, 可鉴别

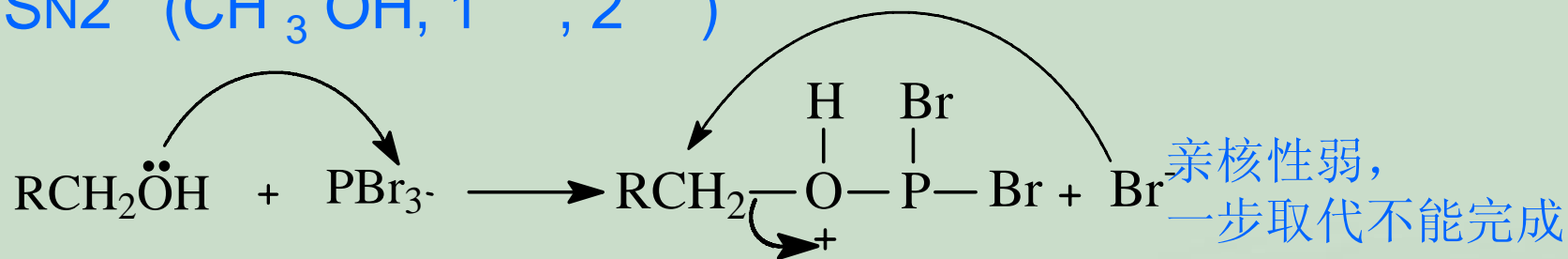
> C_6 反应物产物皆不溶现象不明显

2. 与 PX_3 , PX_5 反应:



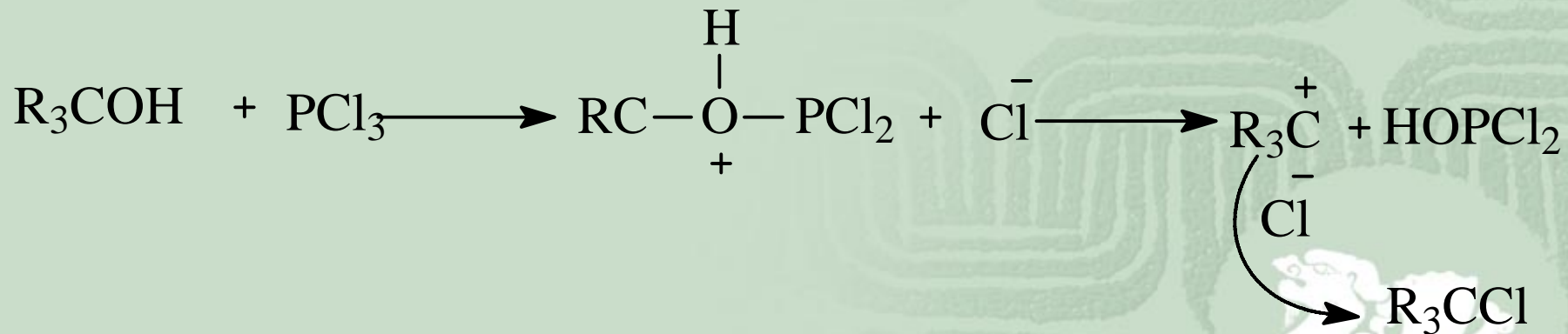
1) 历程

S_N2 (CH_3OH , 1° , 2°)



离去易于-OH

S_N1 (3°)

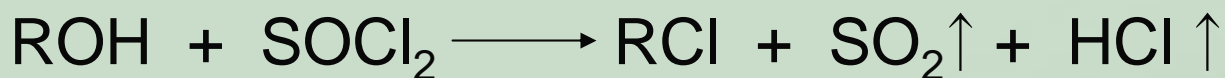


2) 特点: 不发生重排

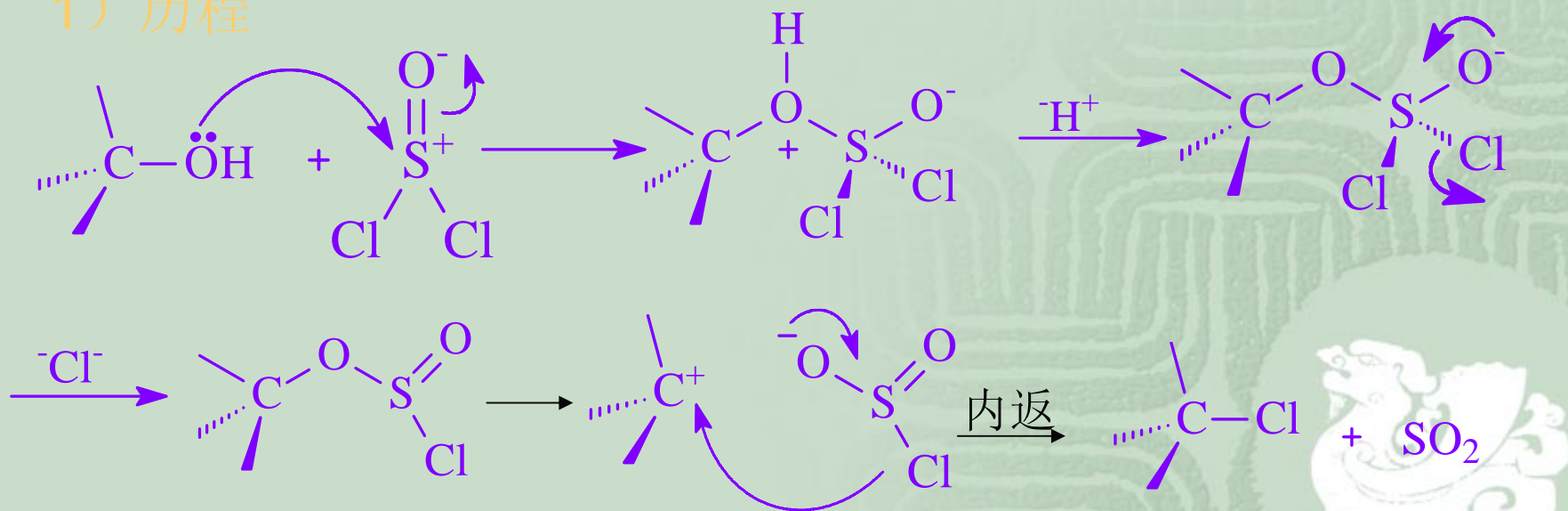
3) 应用: $\text{ROH} \longrightarrow \text{RBr}, \text{RI}$

$\text{R}_3\text{COH} \longrightarrow \text{R}_3\text{COH}$

3. 与 SOCl_2 的反应



1) 历程

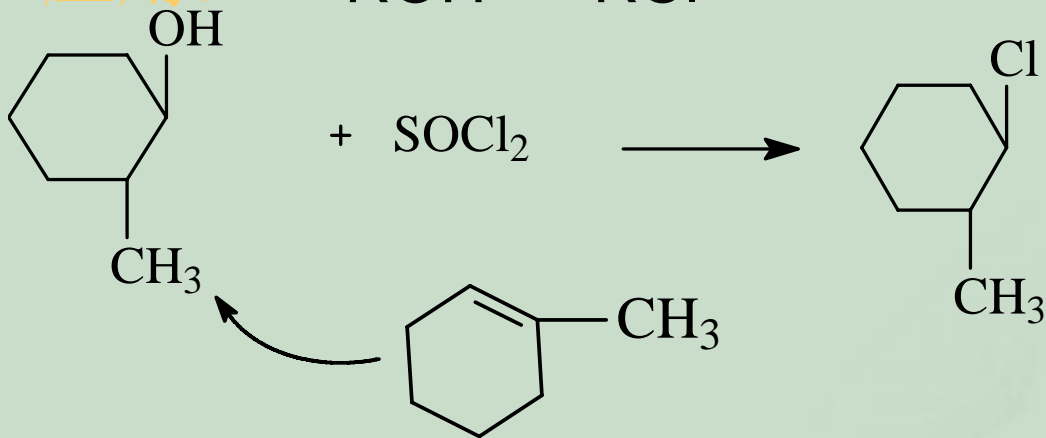
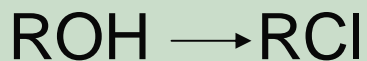


2) 特点

1. 构型保持

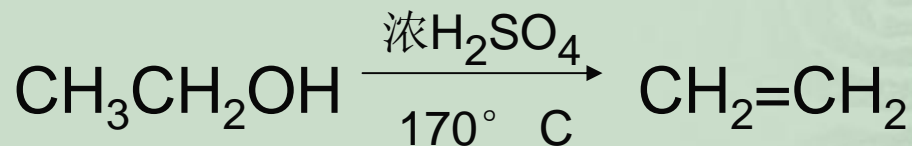
2. 不发生重排

3) 应用:

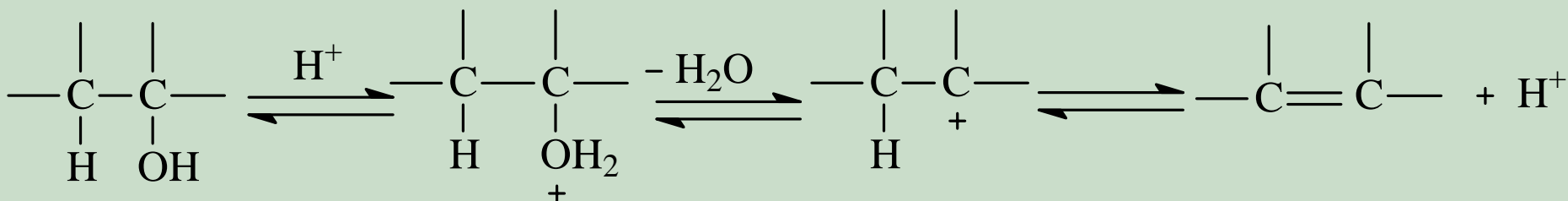


(四) 脱水反应

1. 分子内脱水成烯



1) 历程(E1)

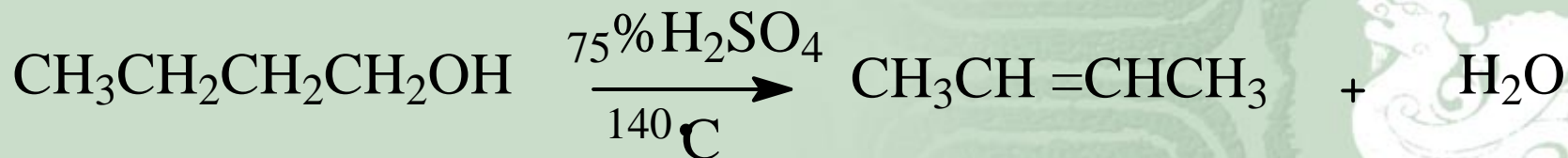


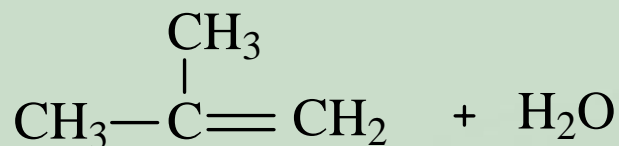
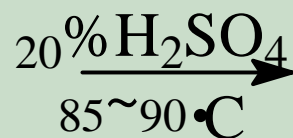
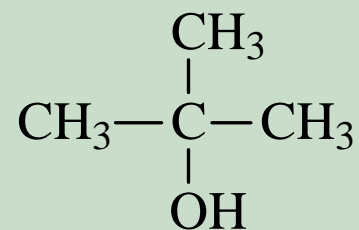
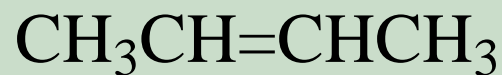
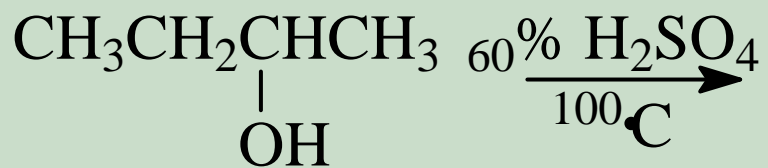
为何不E2

- OH 离去性不好，且 O-H > β-H 酸性
- $\ddot{\text{O}}\text{H}$ \rightarrow - $\overset{+}{\text{O}}\text{H}_2$ 需强酸，则不可能同时存在强碱

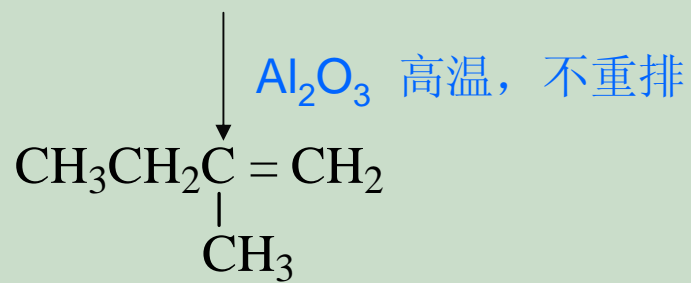
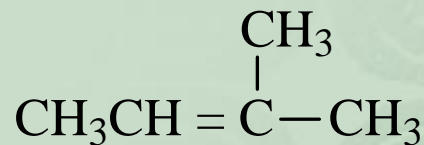
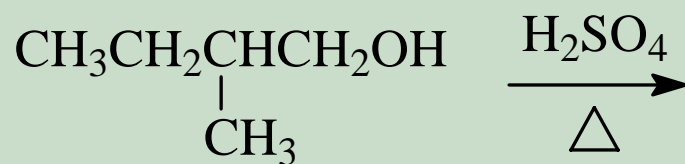
2) 反应活性:

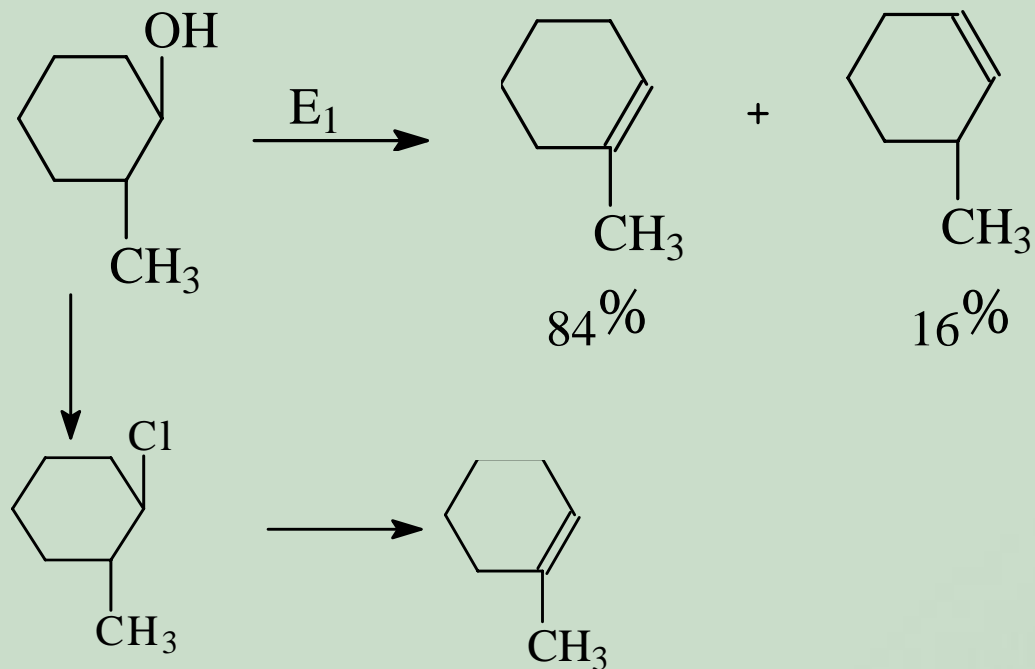
烯丙型醇 > 3° > 2° > 1°



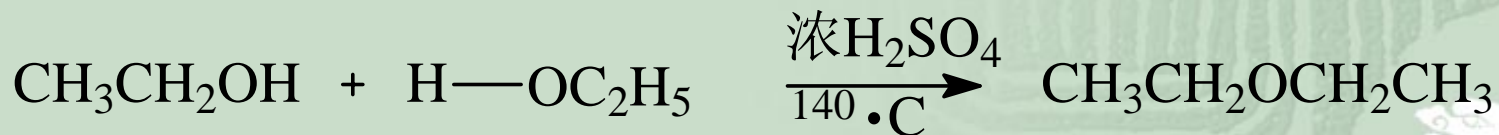


4) 重排

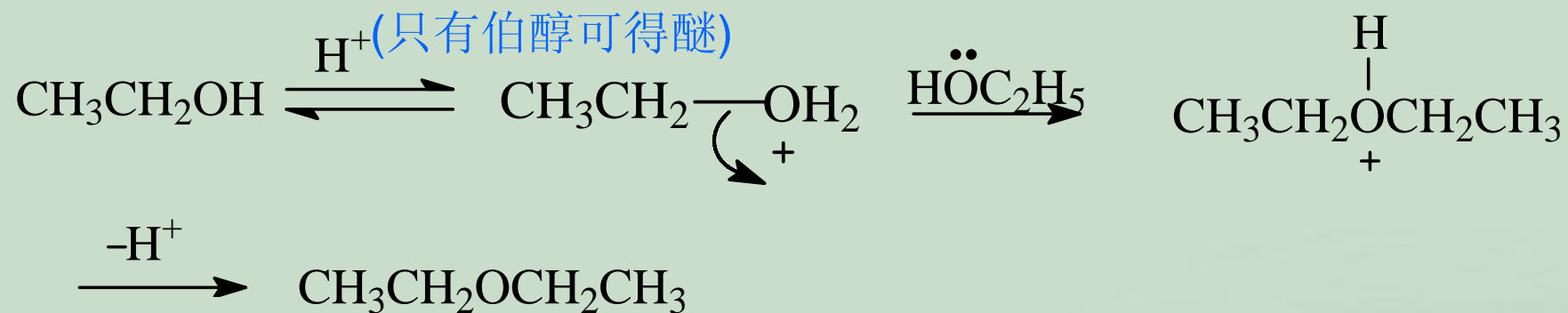




2. 分子间脱水反应



1) 历程 (S_N2)



2) 成烯与成醚之间竞争

1. 3° , 2° 倾向成烯, 1° 倾向成醚
2. 高温倾向成烯, 低温成醚

3 应用

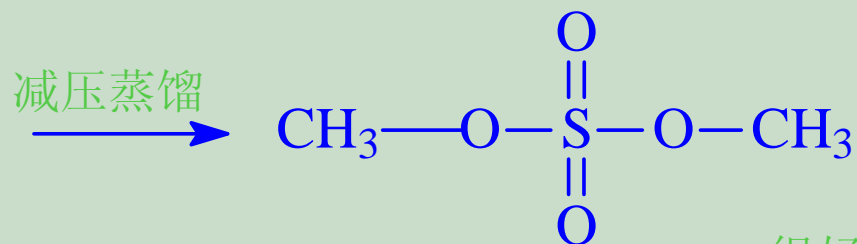
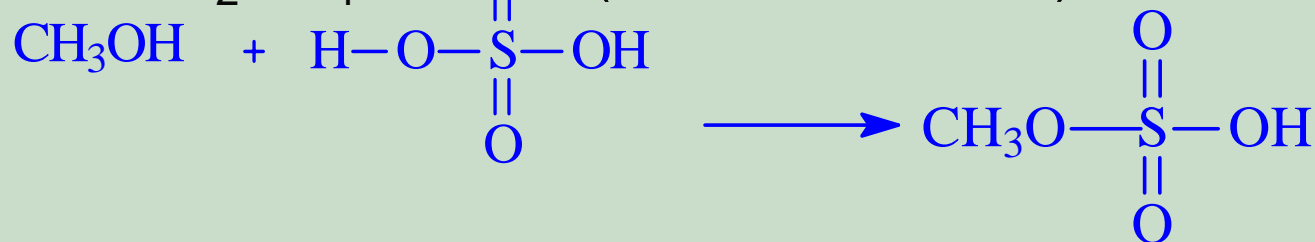
制烯 (重排)

制醚 (1° , RCH₂OCH₂R)



(五) 成酯反应

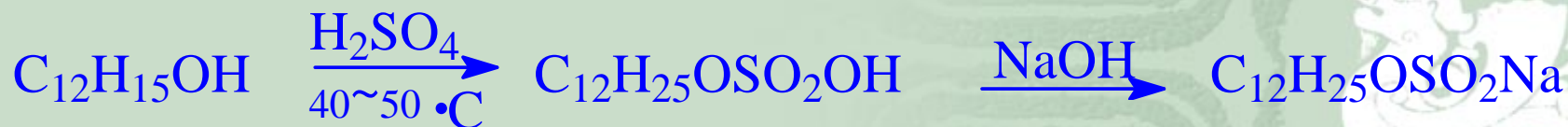
1. 与 H_2SO_4 反应 (SN2 简单伯醇)



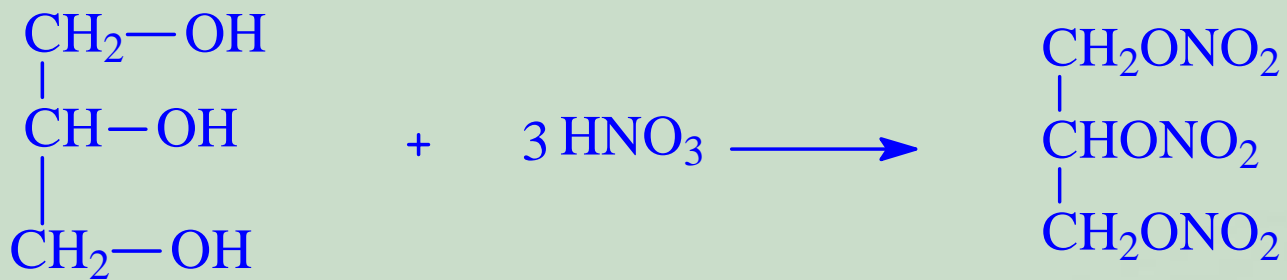
很好的离去基团

应用: 1) 产物: 甲基化试剂

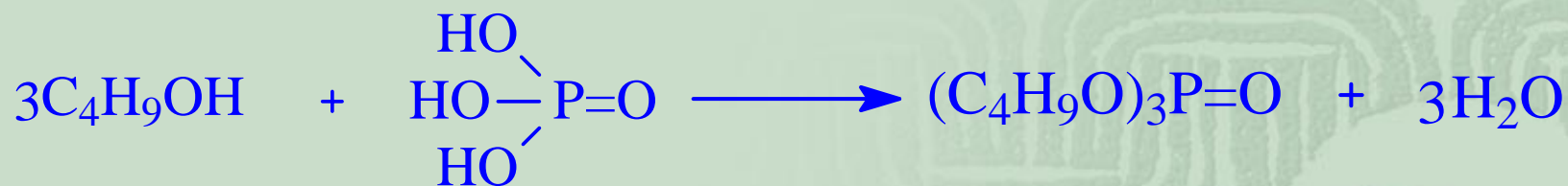
2) 洗涤剂



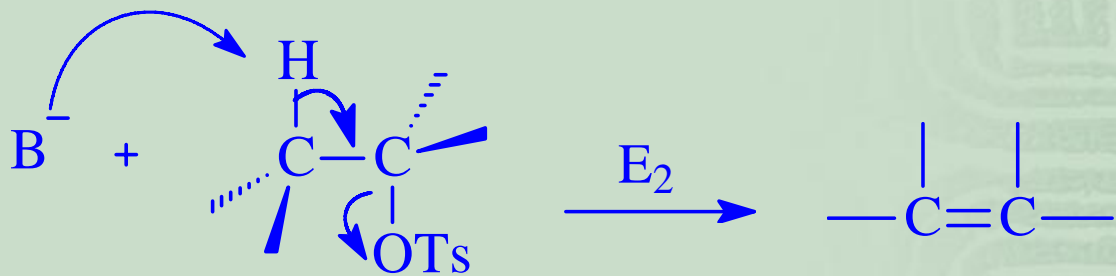
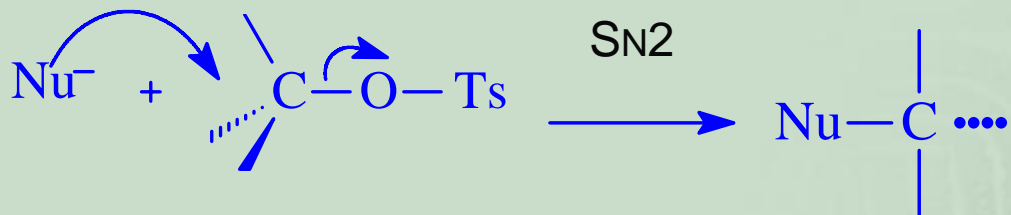
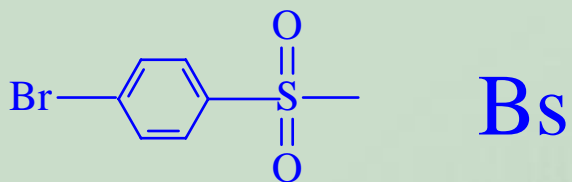
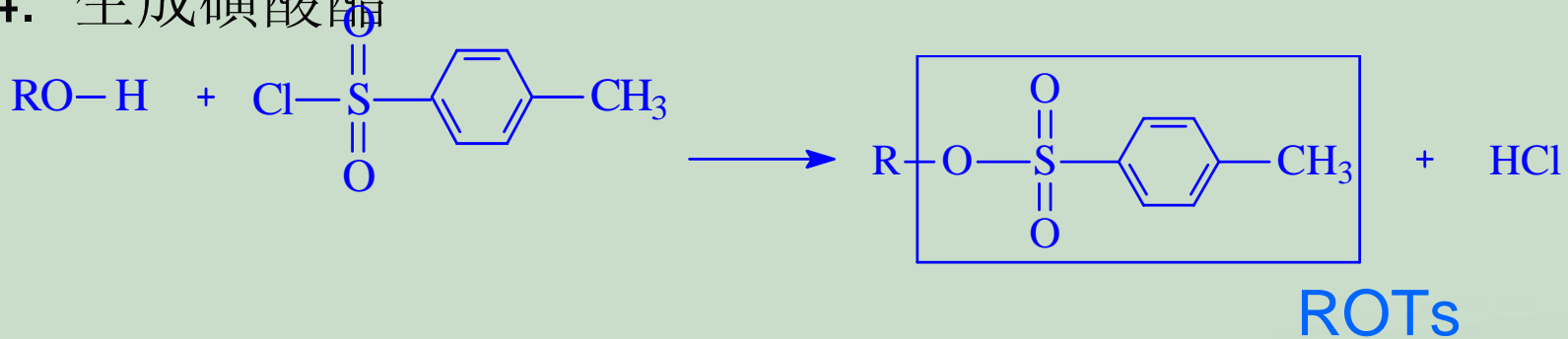
2. 与HNO₃



3. 与H₃PO₄反应



4. 生成磺酸酯



反式共平面消除



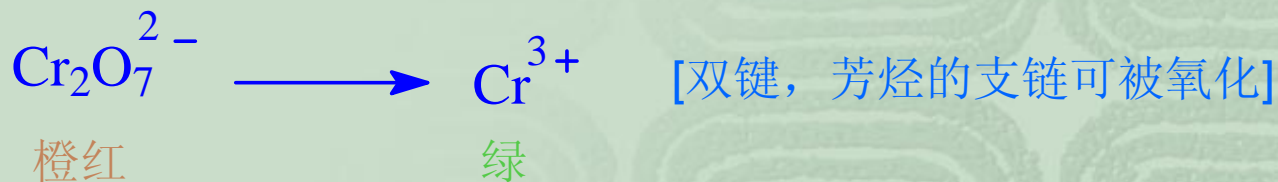
(六) 氧化和脱氢

1. 氧化 ($\text{K}_2\text{Cr}_2\text{O}_7 - \text{H}_2\text{SO}_4$)

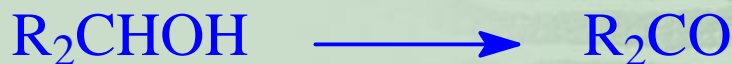
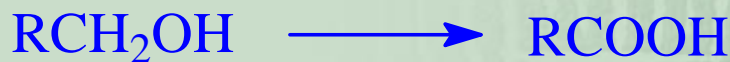


应用:

1) 用于鉴别



2) 有机合成

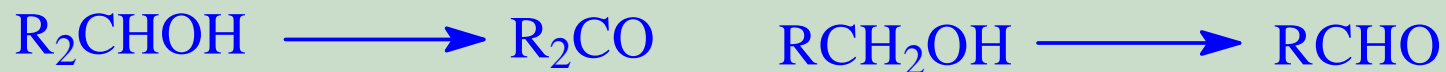


可制分子量较小, 沸点低的醛, 反应过程中被蒸发, 不再被氧化



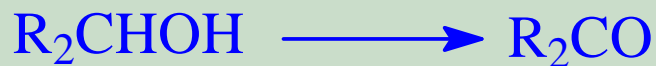
其他氧化剂:

1) Sarrett 试剂 : CrO_3 吡啶 $\text{CrO}_3 \cdot (\text{C}_5\text{H}_4\text{N}_2)_2$

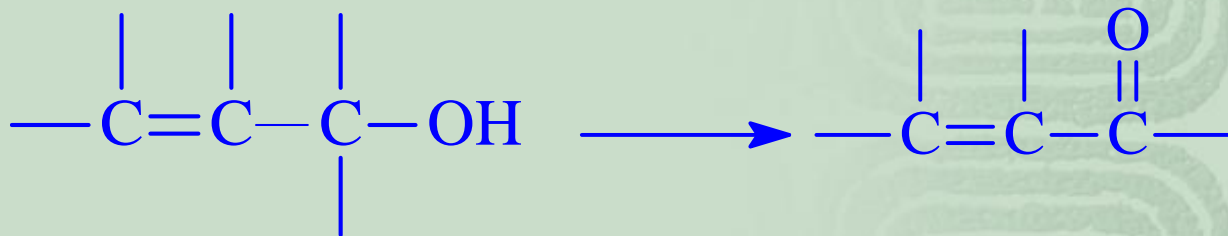


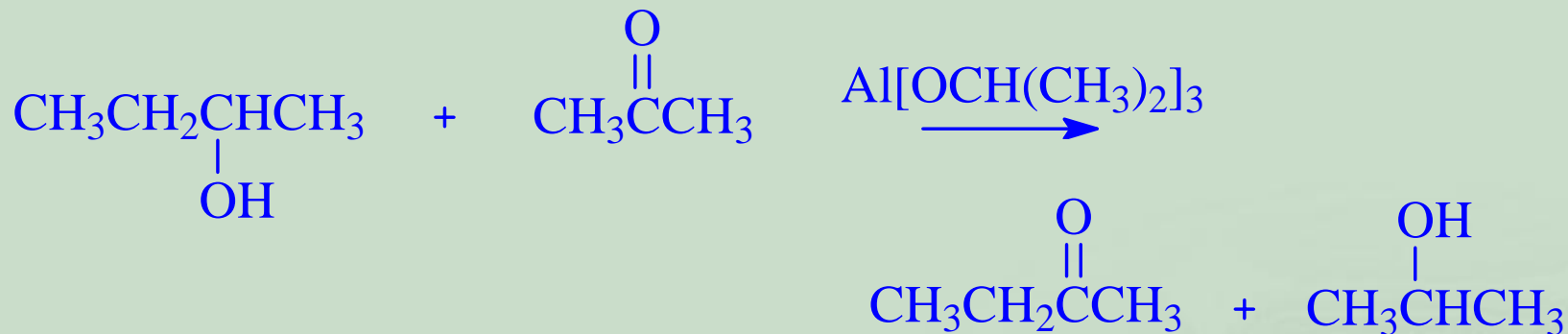
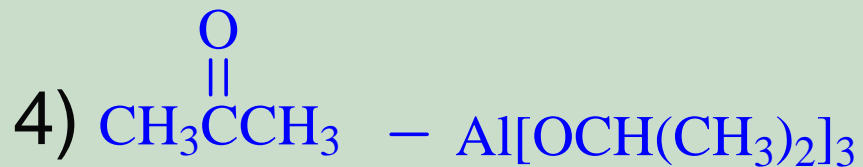
试剂中双键或三键可保留, 不被氧化

2) Jones 试剂 : $\text{CrO}_3 \cdot \text{稀H}_2\text{SO}_4$



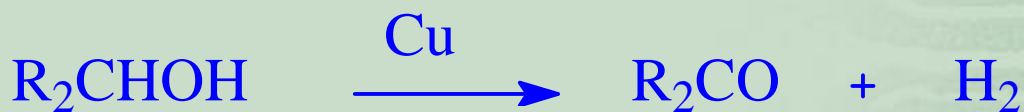
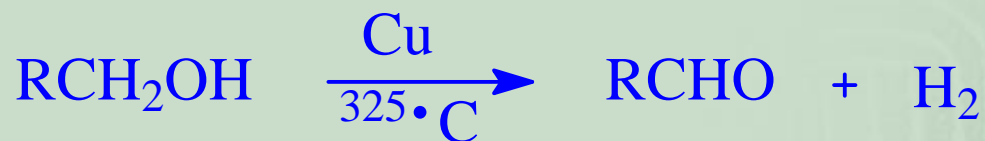
3) 新制 MnO_2





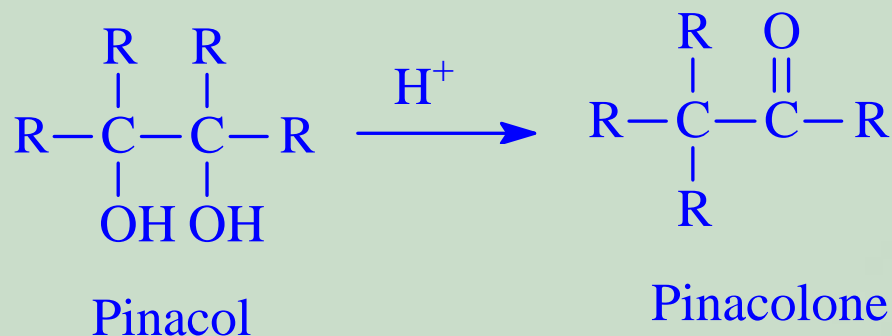
双键不受影响

2. 脱氢

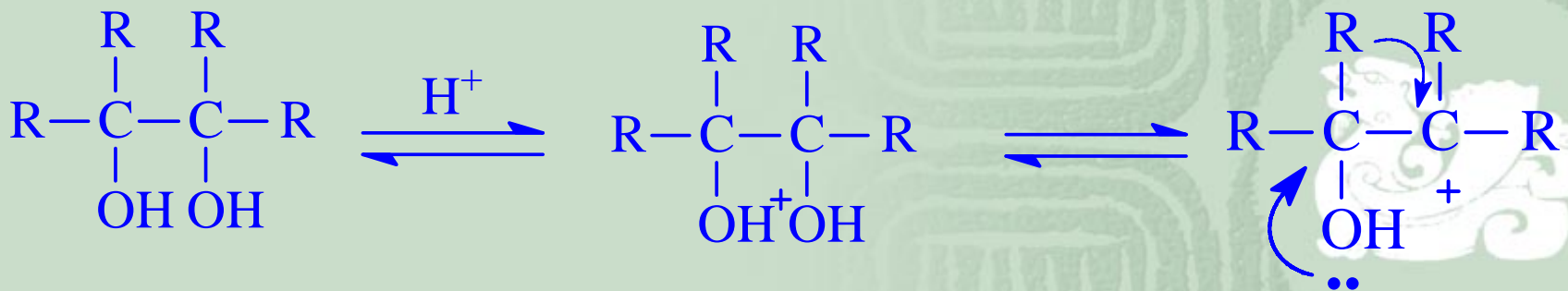


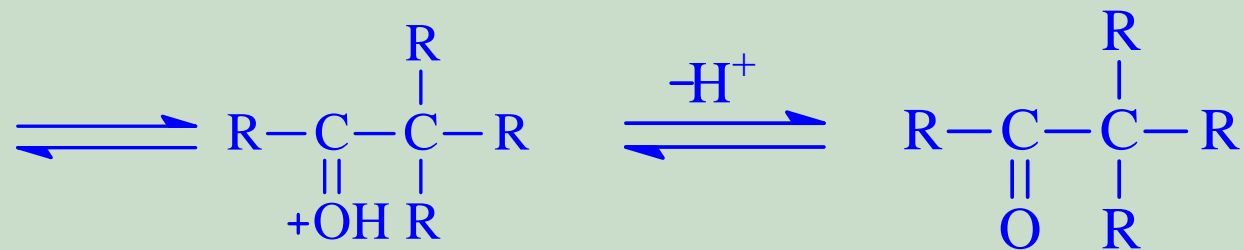


3. 嘮呐醇重排

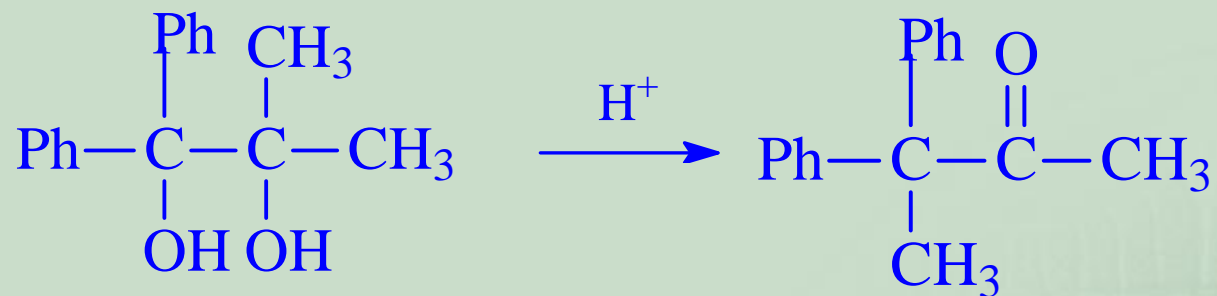


1) 历程

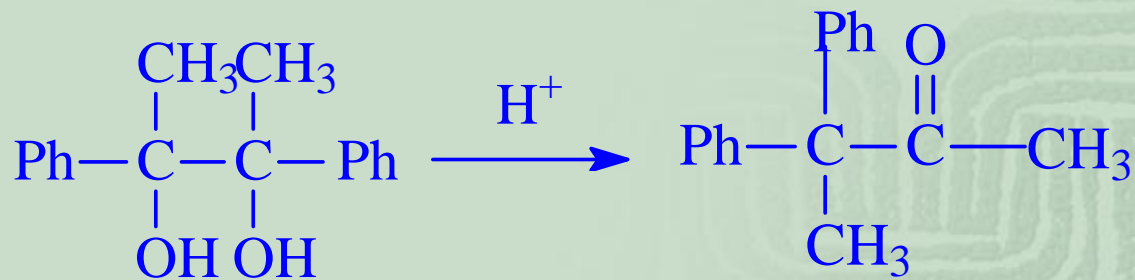




1



2



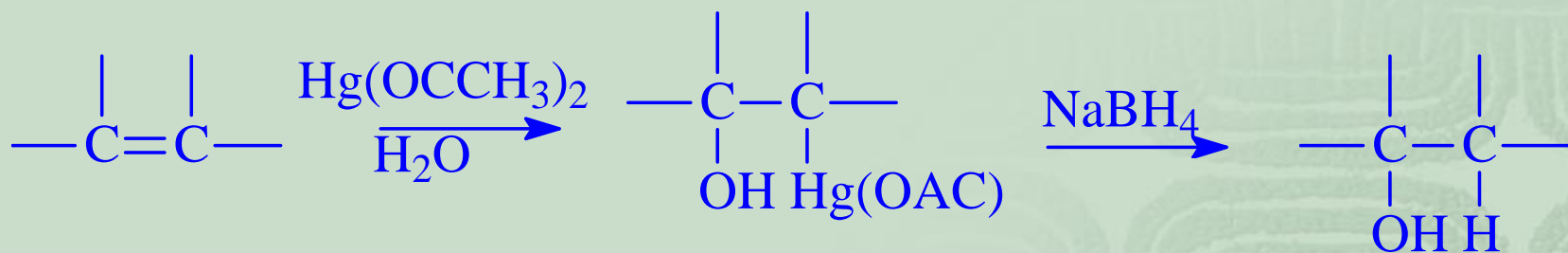
迁移功能 $\text{Ph} \cdot > \text{CH}_3$



六. 醇的制法

(一) 由烯烃制备

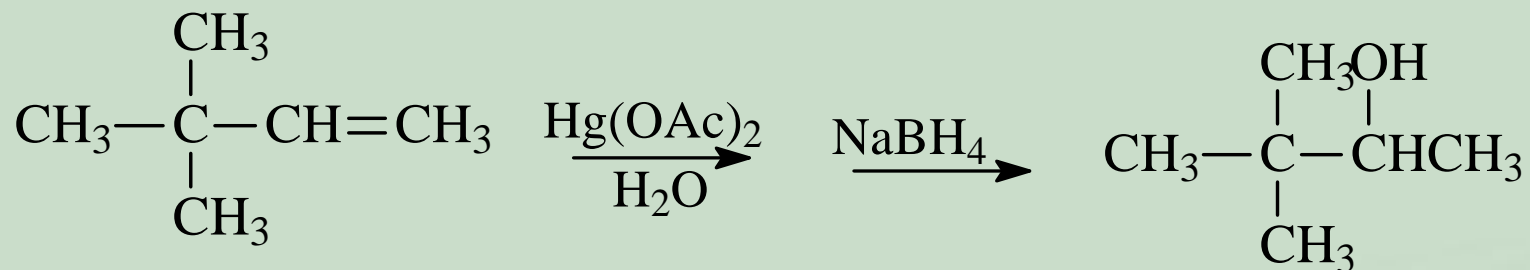
1. 酸性水合 (碳正离子发生重排)
2. 硼氢化氧化
3. 汞化 —— 脱汞反应 (不重排, 其他同酸性水合)



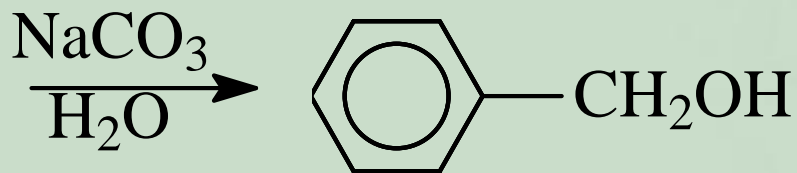
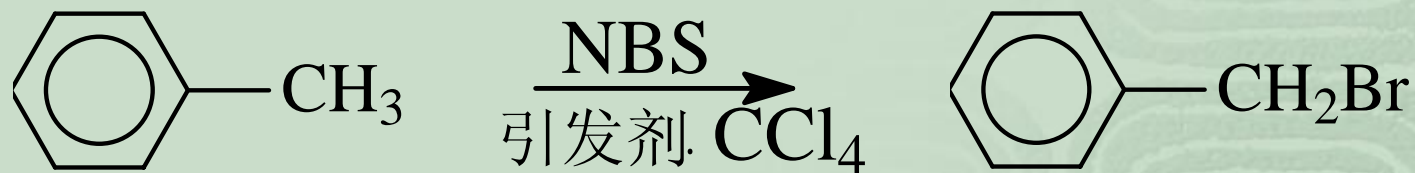
第一步：反式，中间体 $\left[\begin{array}{c} | \quad | \\ \text{---C---C---} \\ \diagdown \quad / \\ \text{Hg} \end{array} \right]^+ +$ ，因此不重排



第二步： 不一定，整个过程无立体专一性

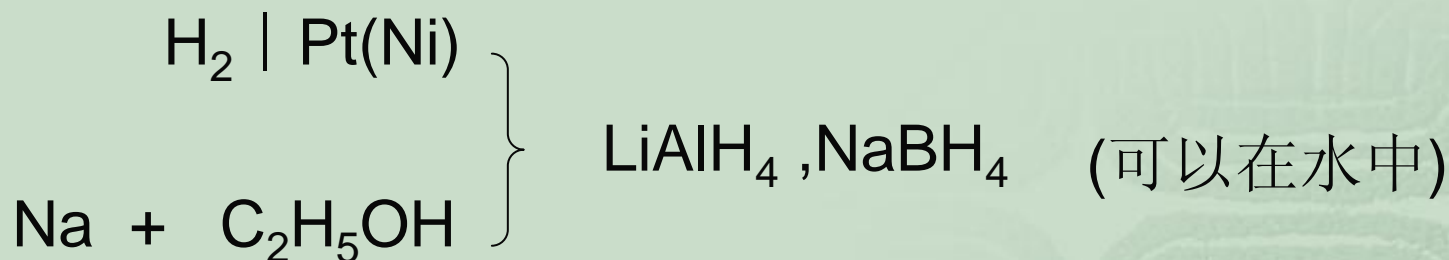
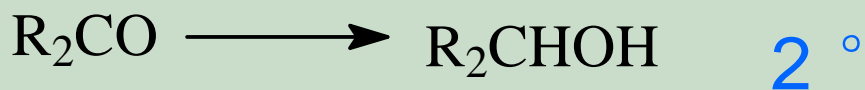


(二) RX 的水解 (只适于RCH₂OH)

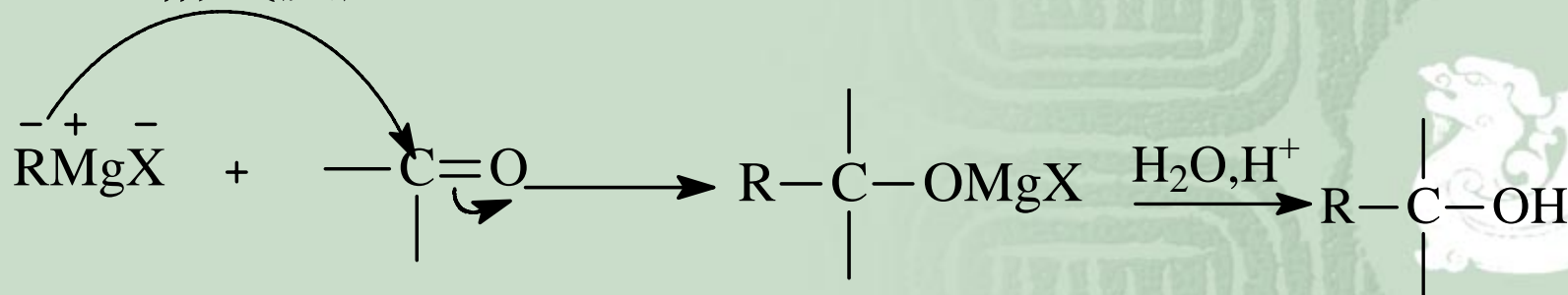


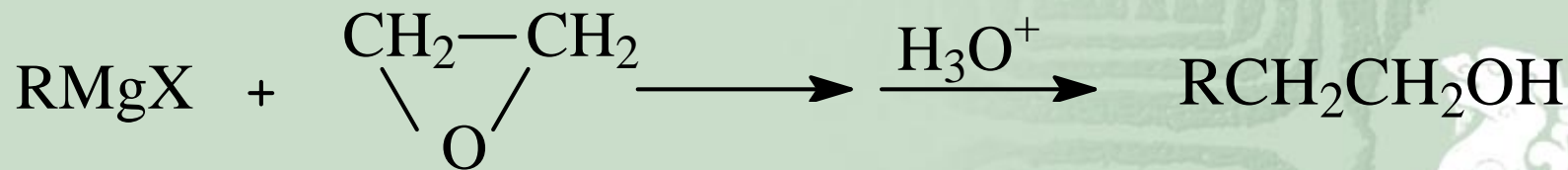
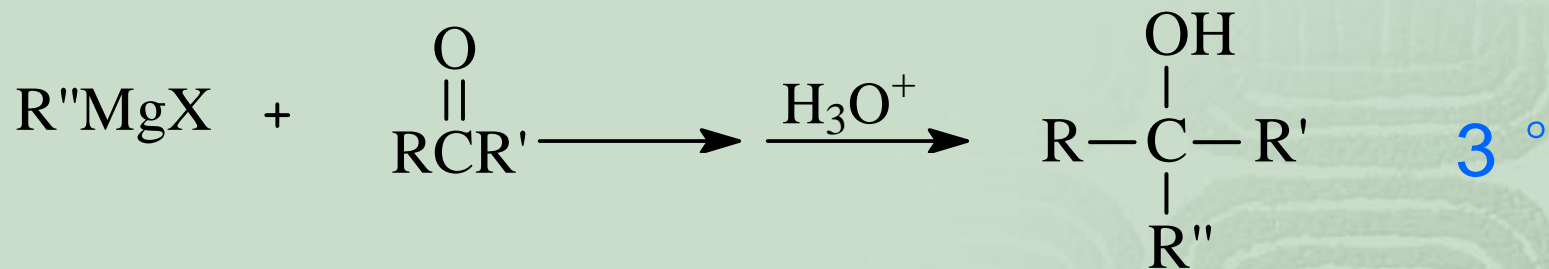
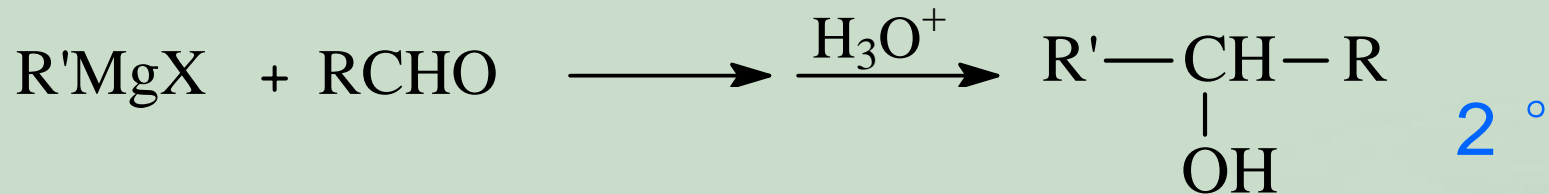
(三) 由醛. 酮制备

1. 还原反应



2. 格式反应





注意: RX中不得含-OH, -COOH, $-\text{C}\equiv\text{CH}$, $-\text{NO}_2$, -CN

吸电子基, -X(Br, I)

(有活性H或氧化性)

C=O不得含-OH, -COOH, $-\text{C}\equiv\text{CH}$, $-\text{NO}_2$, -CN,

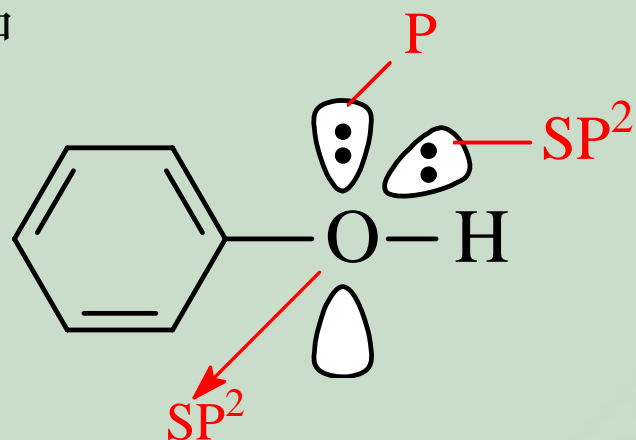
RX中只能含有-R, -Ar, -OR,和 -Cl



第二节 酚

一 结构和命名

1、结构



2、命名

二 物理性质

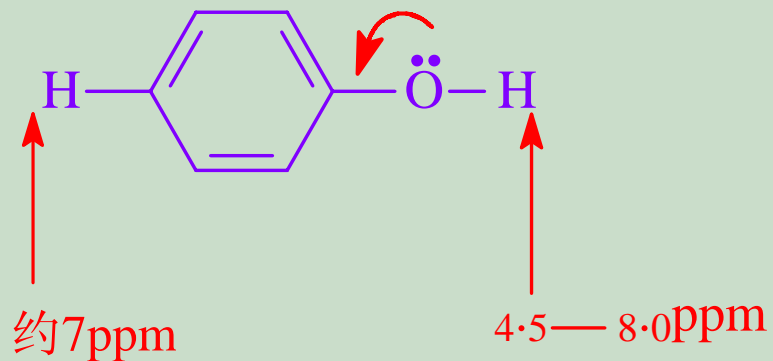
沸点高，固体，微溶于水，溶于热水

三 光谱性质

1、 IR:	γ O-H	3640—3600cm ⁻¹
	γ C-O	1250—1200cm ⁻¹



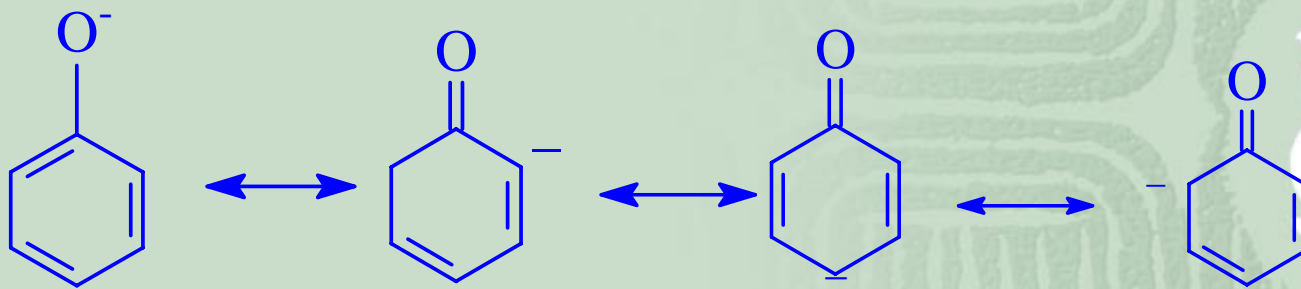
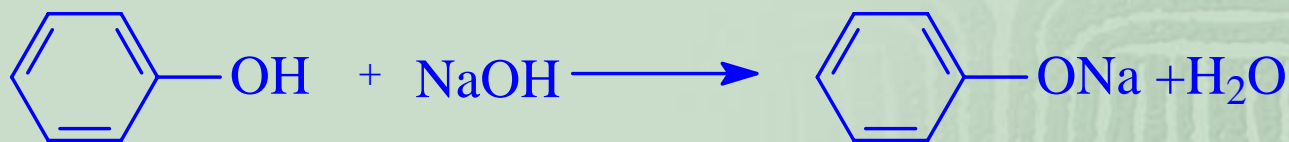
2、 ^1H NMR

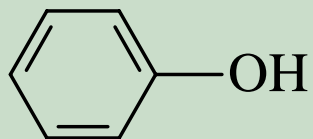
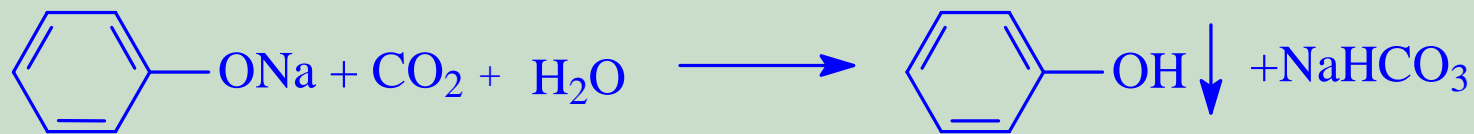


四 化学性质

(一) 羟基反应

1、酸性



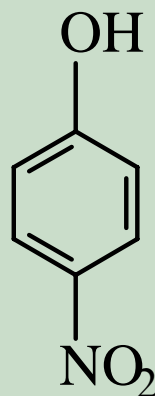


PKa

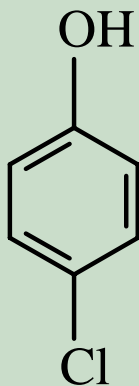
10

6.4

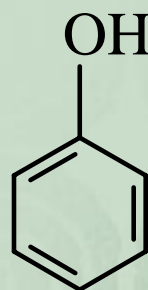
酸性



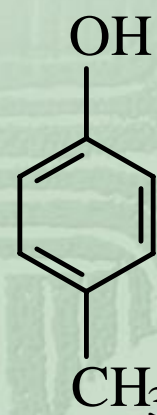
>



>



>



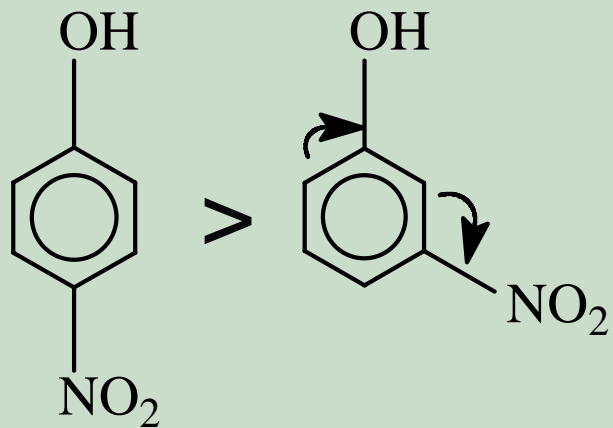
PKa

7.15

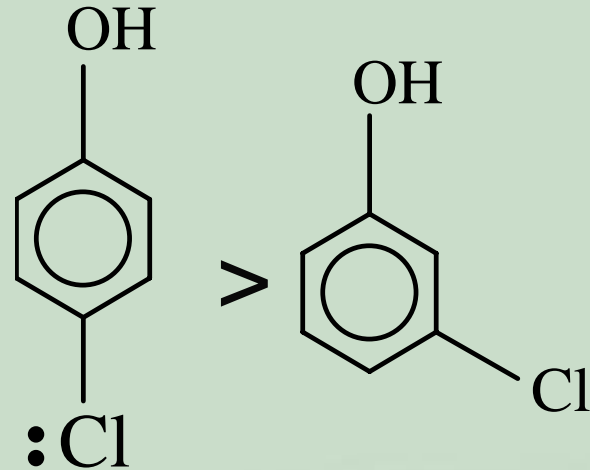
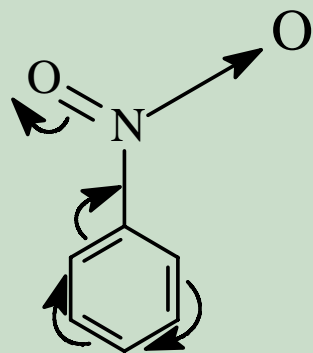
9.38

10

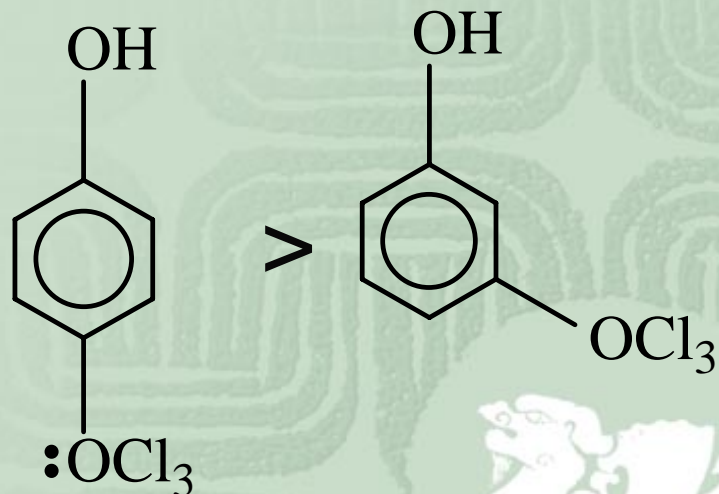
10.26



PKa 7.15 8.39
 -C, -I -I



9.38 9.02
 +C < -I -I



10.21 9.65
 +C > -I -I



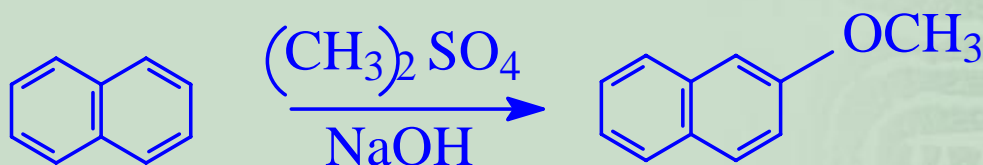
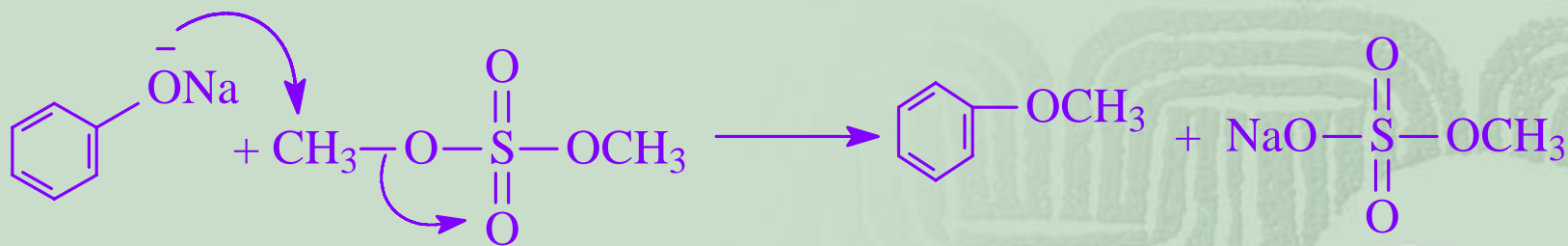
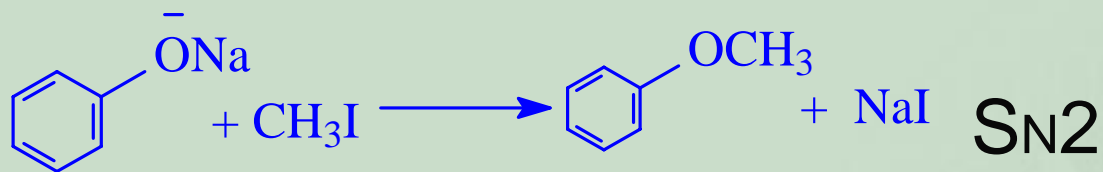
2、与FeCl₃的显色反应 [烯醇也可显色]



α - 萘酚 β - 萘酚

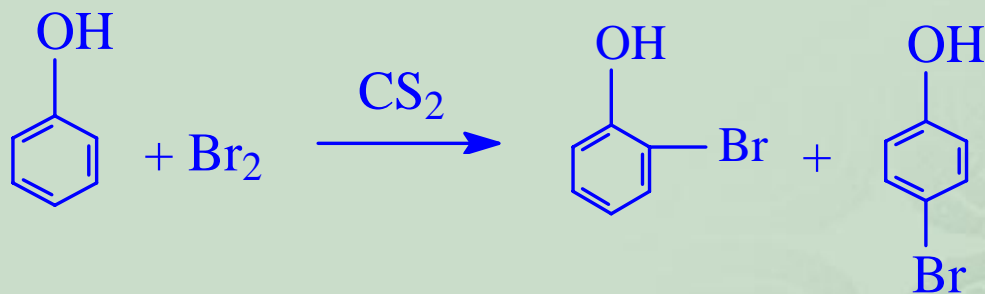
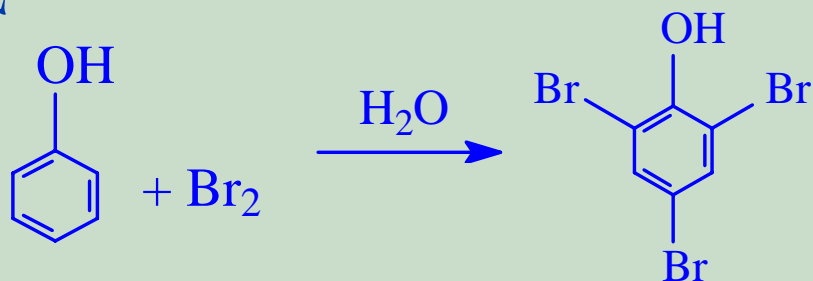
紫红色 ↓ 绿色 ↓

3、酚醚的形成

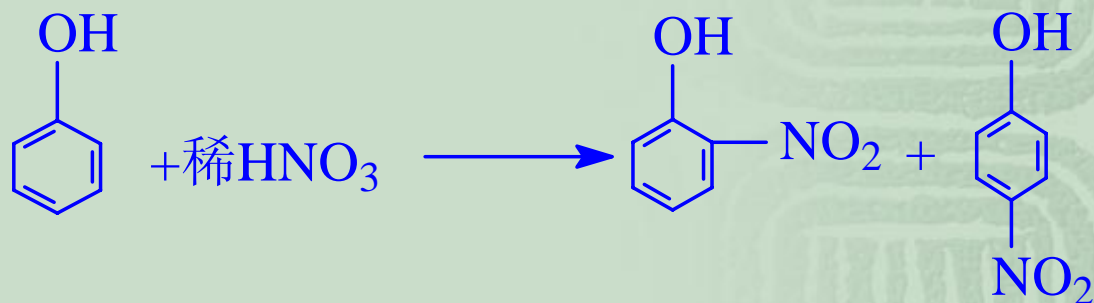


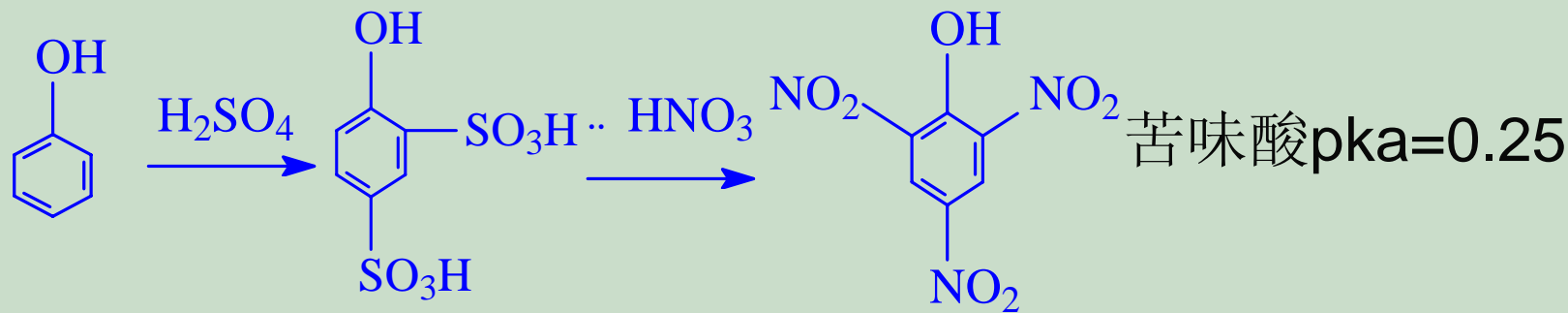
(二) 芳环上的亲电取代反应

1. 卤代



2. 硝化

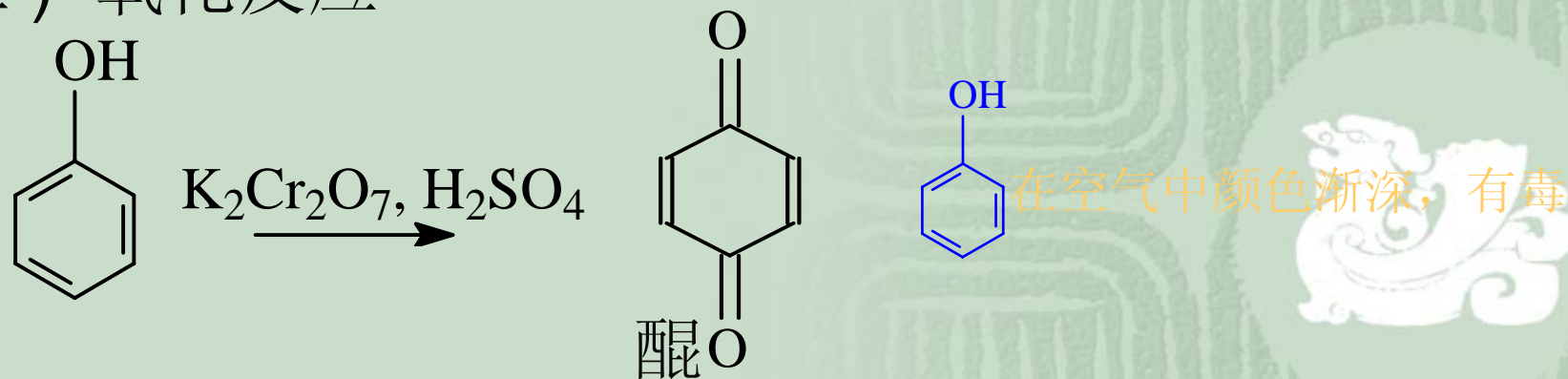




3. 亚硝化反应

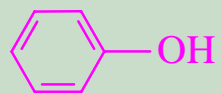


(三) 氧化反应

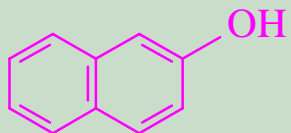
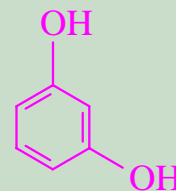


五. 制法

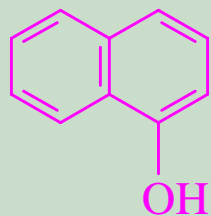
1. 苯磺酸盐碱熔法：适用于



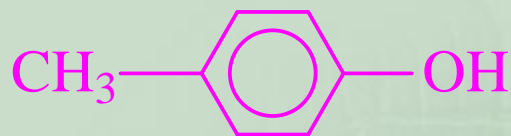
烷基酚



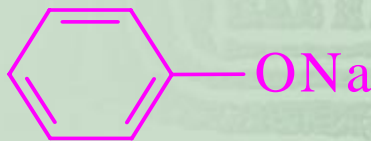
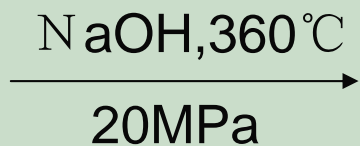
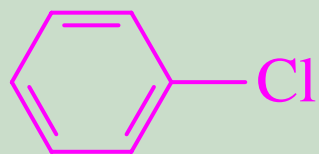
或



碱熔



2. 氯苯水解



$\xrightarrow{\text{H}^+}$



第三节

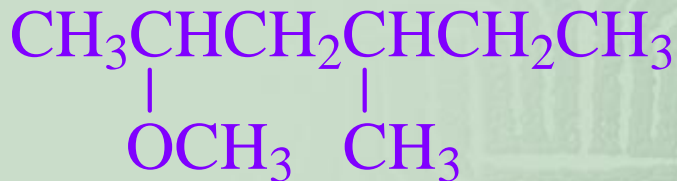
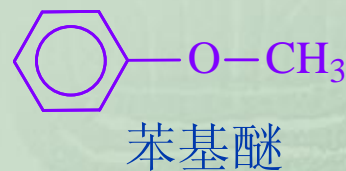
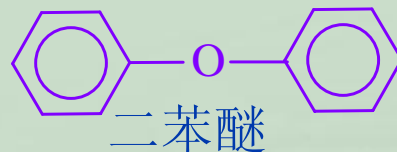
醚

一 概述

1 结构: $R-O-R$ $C-\ddot{O}-C$

2 分类

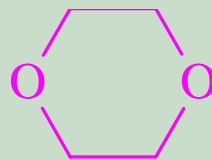
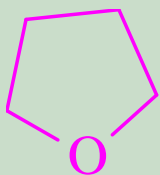
链醚 { 简单醚
混合醚



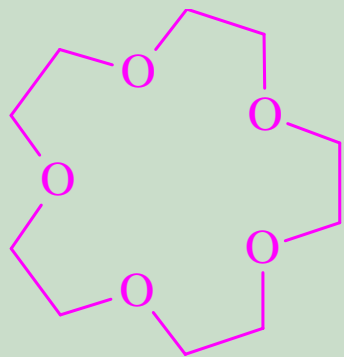
4-甲基-2-甲氧基醚



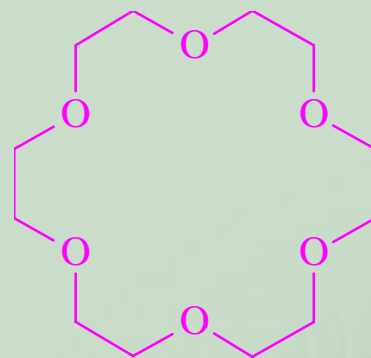
环醚（环氧化合物）



大环多醚
(冠醚)



15-冠-5

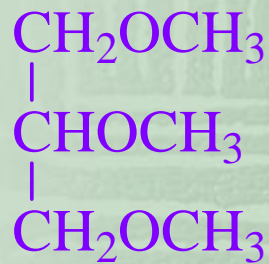


18-冠-6

3. 命名

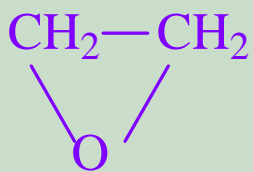


乙二醇甲醚

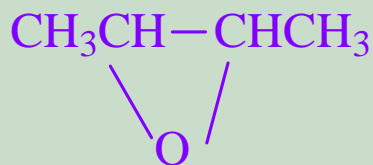


丙三醇三甲醚

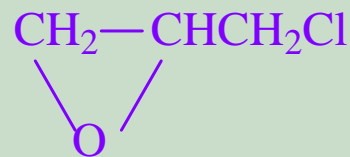




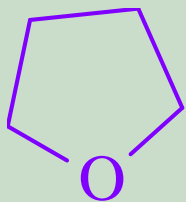
环氧乙烷



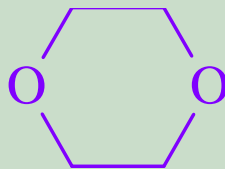
2,3-环氧丁烷



3-氯-1,2-环氧丙烷



1,4-环氧丁烷



1,4-二氧六环

二. 物理性质

1. 极性: 弱极性(非质子型)

2. 沸点: CH_3OCH_3 -23°C

$\text{CH}_3\text{CH}_2\text{OH}$ 78.5°C



3. 溶解性

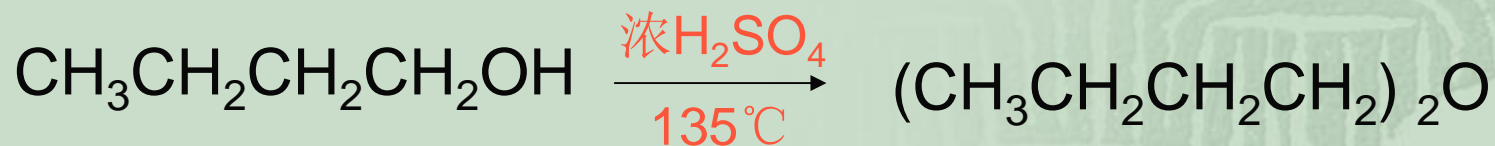
三. 光谱性质

IR: $\nu_{\text{C-O-C}}$ 1275~1020 cm^{-1}

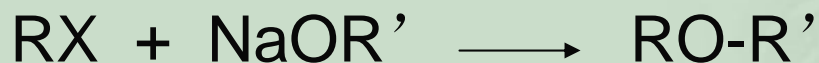
$^1\text{HNMR}$: $\begin{array}{c} | \\ -\text{C}-\text{O}-\text{C}- \\ | \quad | \\ \quad \text{H} \end{array}$ 3~4ppm

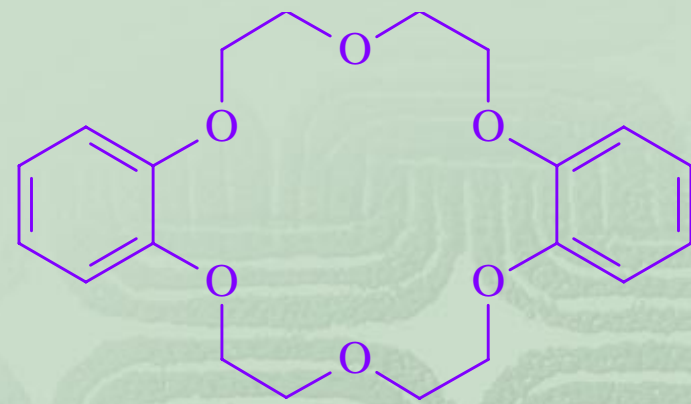
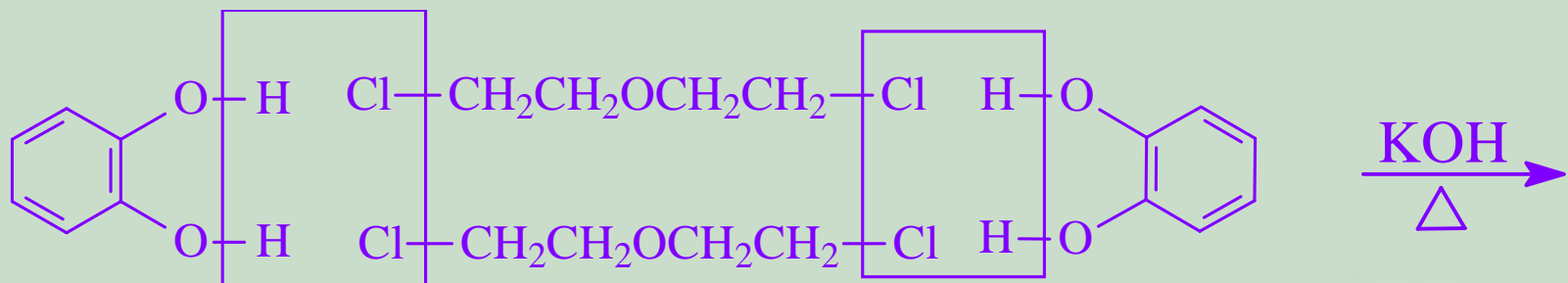
四. 制法

1. 醇的脱水 (RCH₂OH 低级伯醇)

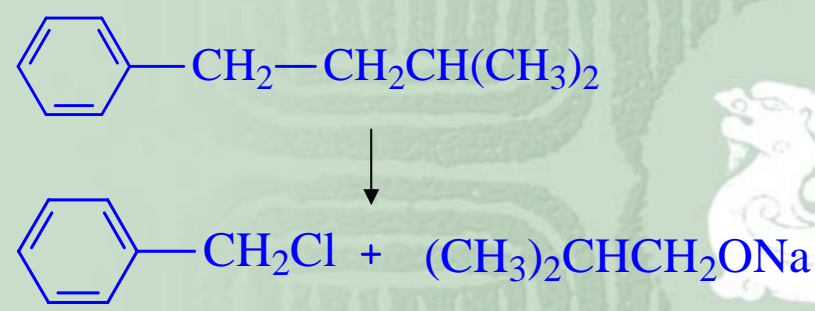
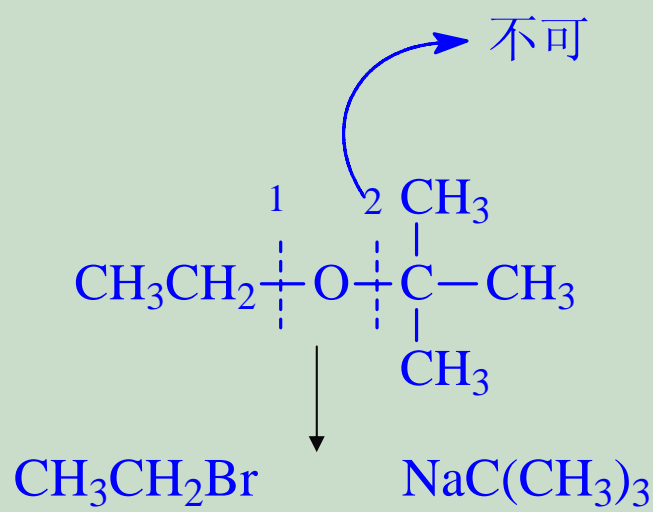


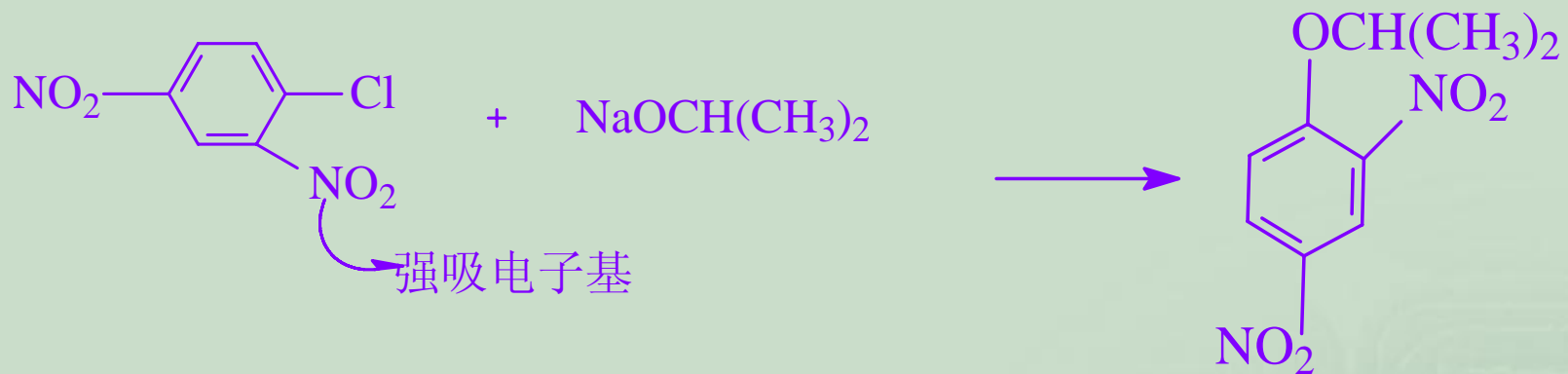
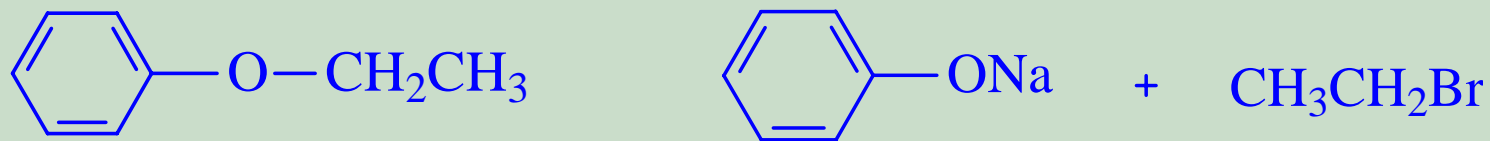
2. Williamson 合成法 $\text{RX}=\text{RCH}_2\text{X}$



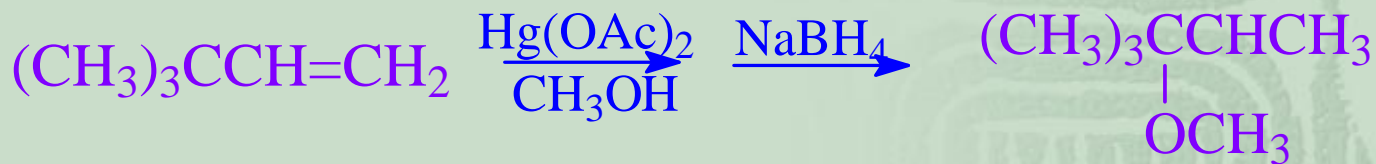
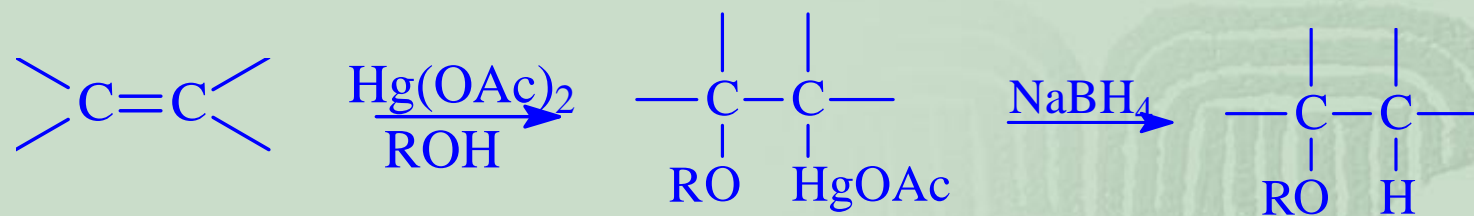


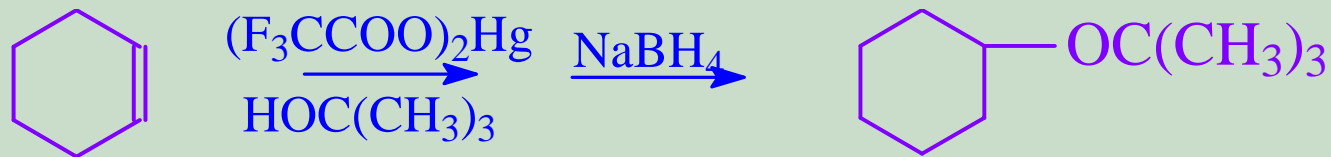
二苯基-18-冠-6





3. 环氧汞化--- 脱汞反应

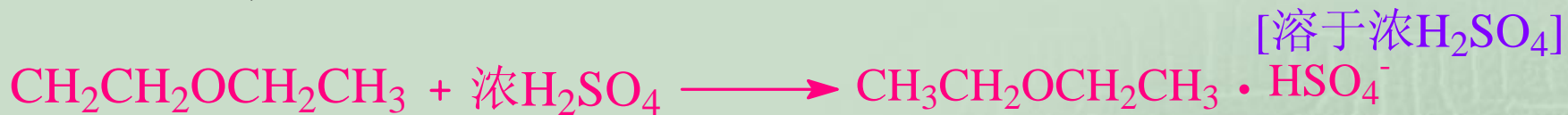




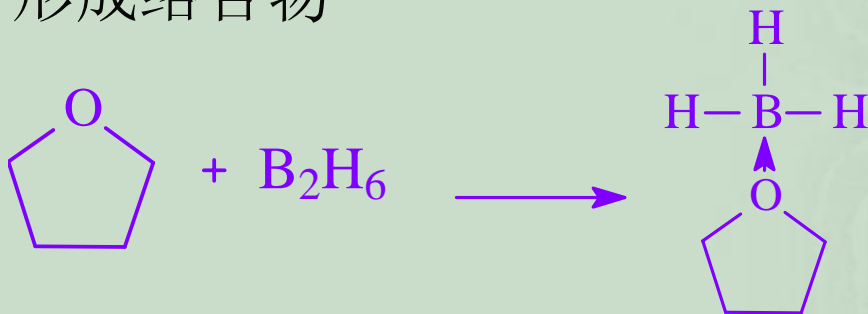
五. 化学性质

(一) 碱性 $\text{—}\ddot{\text{O}}\text{—}$

1. 生成氧盐

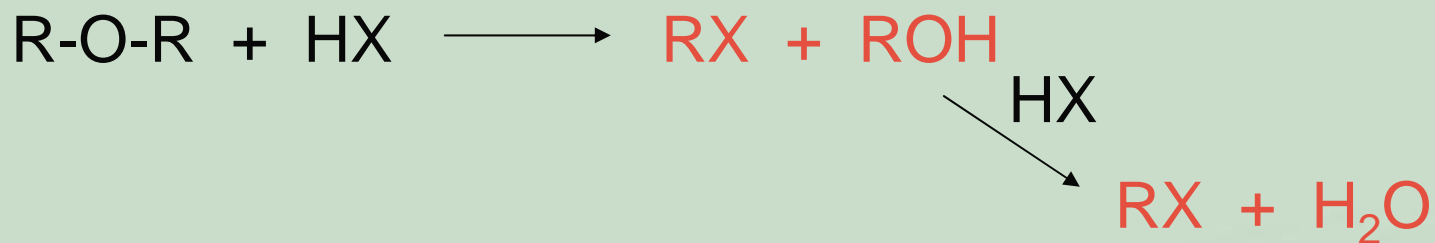


2. 形成络合物



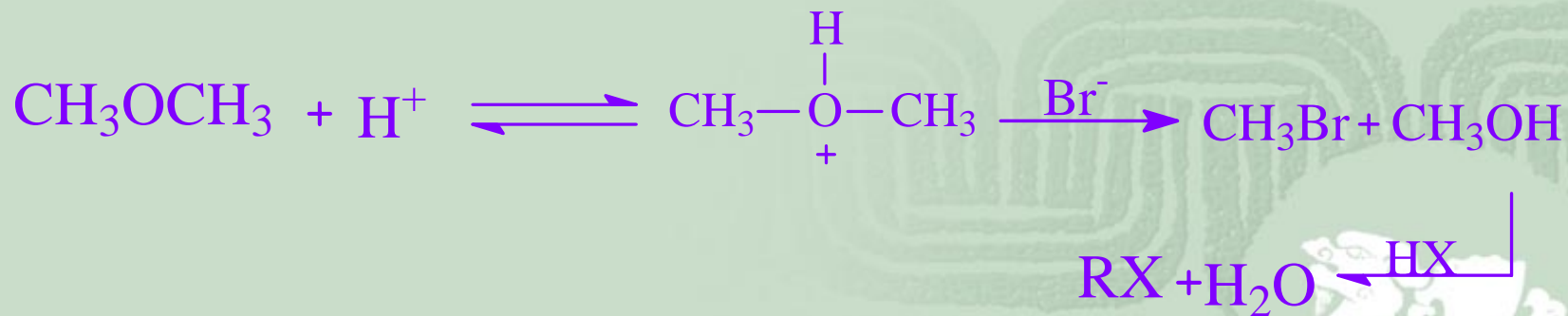
(二) 醚键的断裂

1. 与氢卤酸 亲核取代

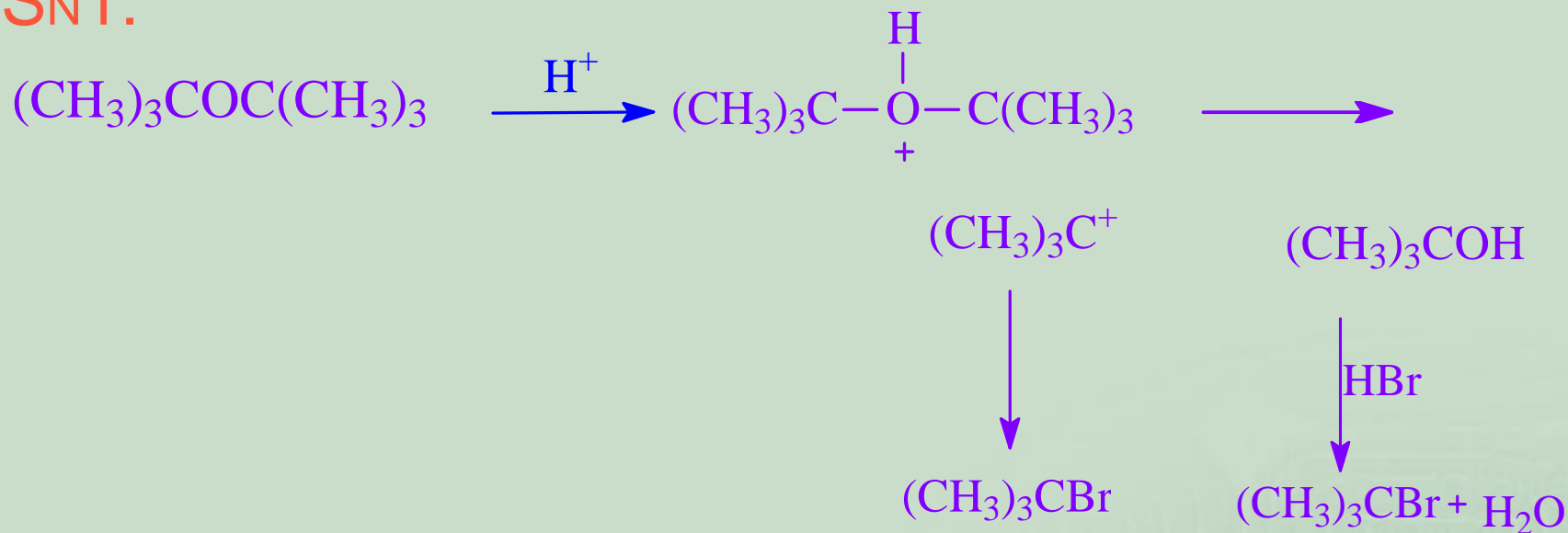


2. 历程

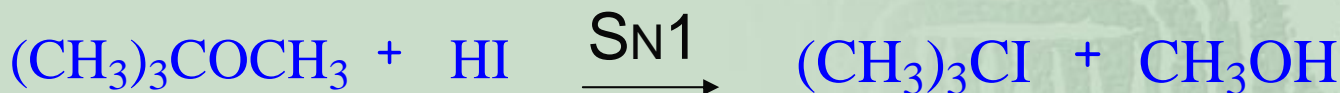
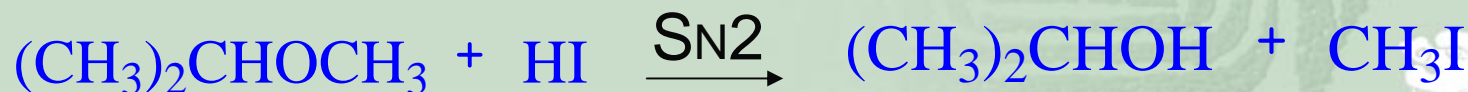
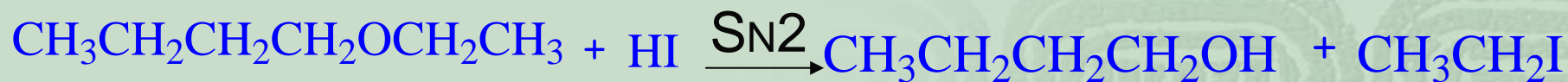
SN2:

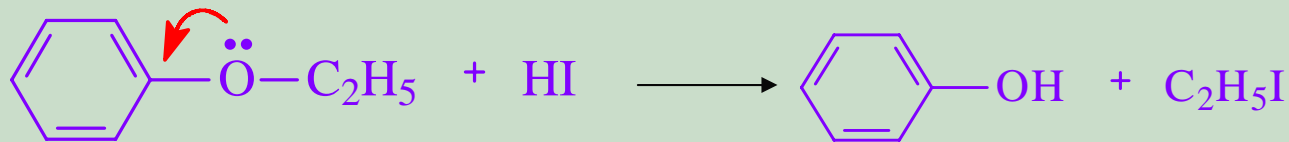


SN1:

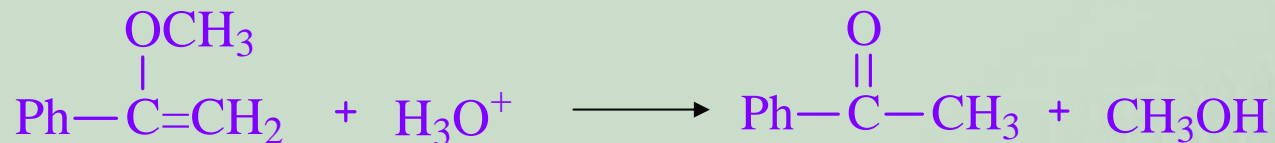


3. 混合醚的断链取向：分裂形成酸性较强的醇

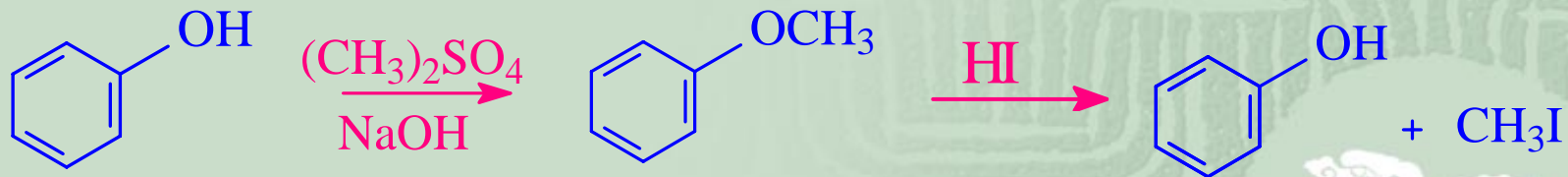


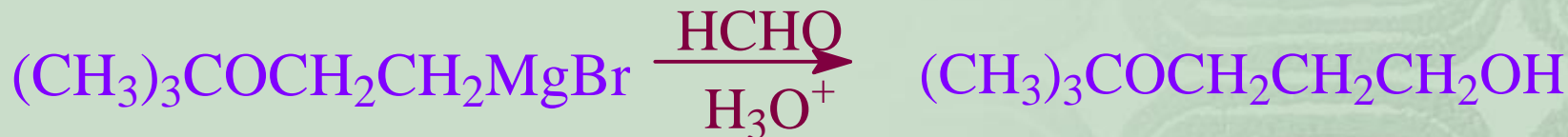
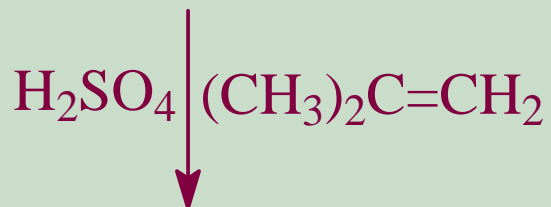
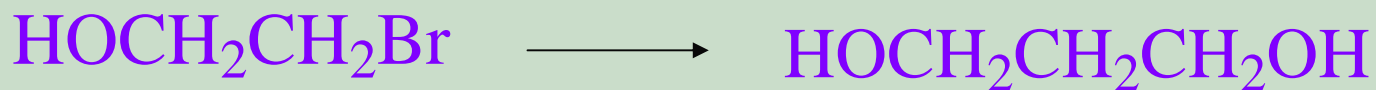


P-π共轭, 加强

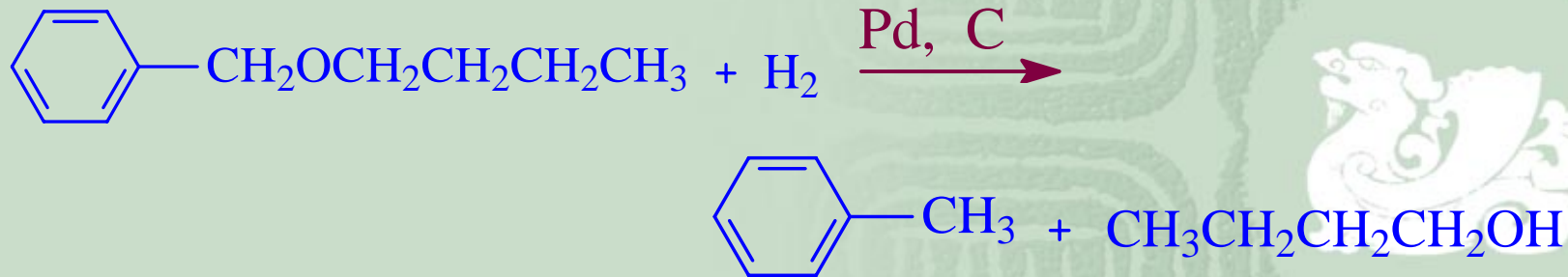


4. 应用: 保护羟基

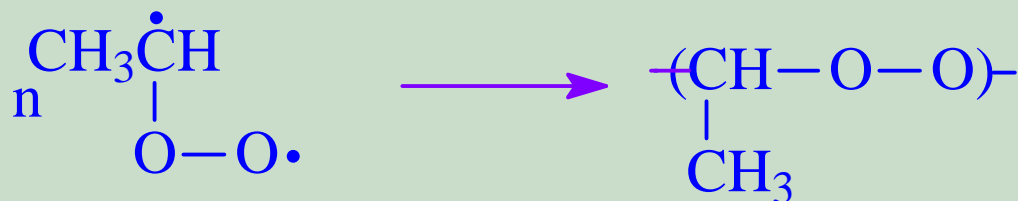
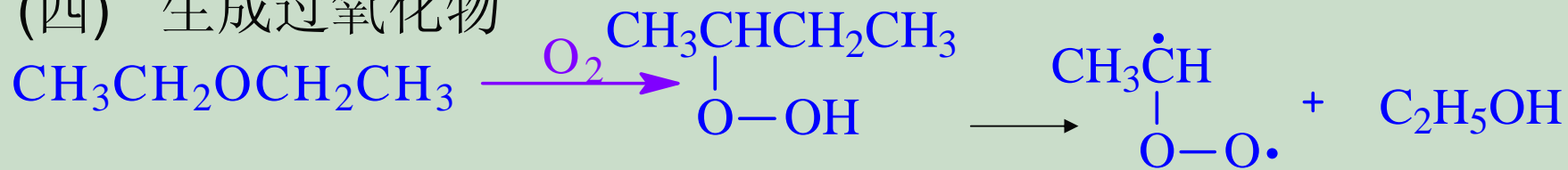




(三) 苜醚的催化氢解



(四) 生成过氧化物

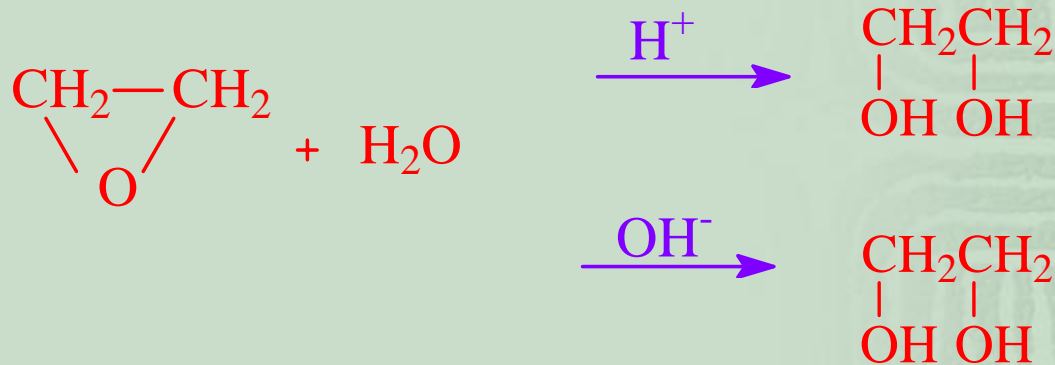


a. KI - 淀粉 蓝色

b. $\text{FeSO}_4 \cdot \text{KCNS}$ $\xrightarrow{\text{过氧}}$ Fe^{3+} 血红色

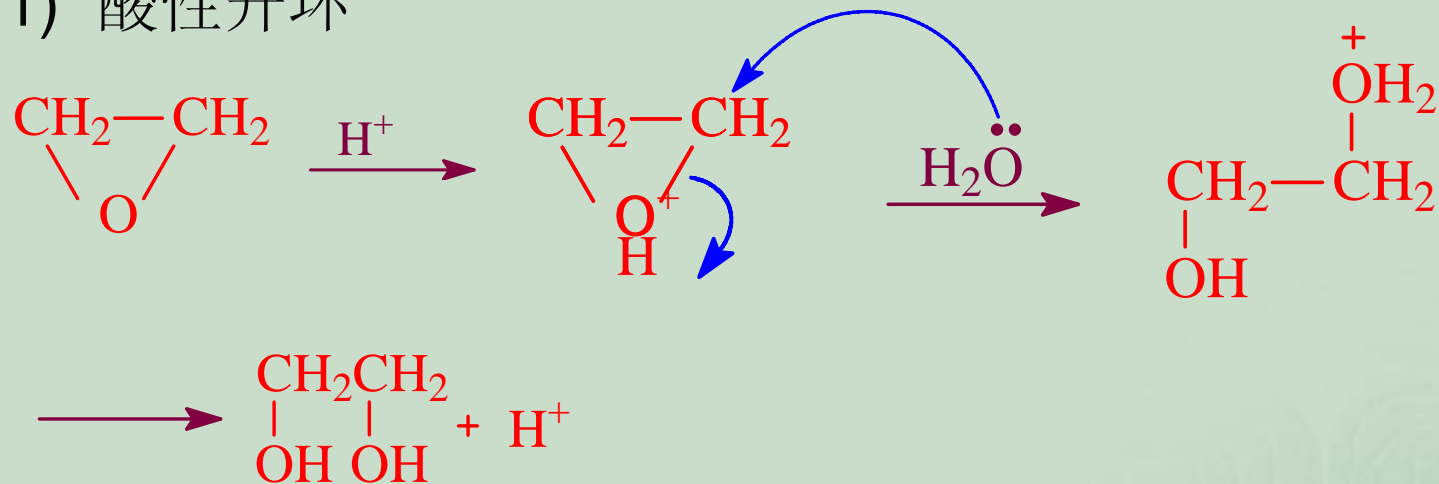
可检验醚中是否有过氧化物

(五) 环氧化合物的开环反应

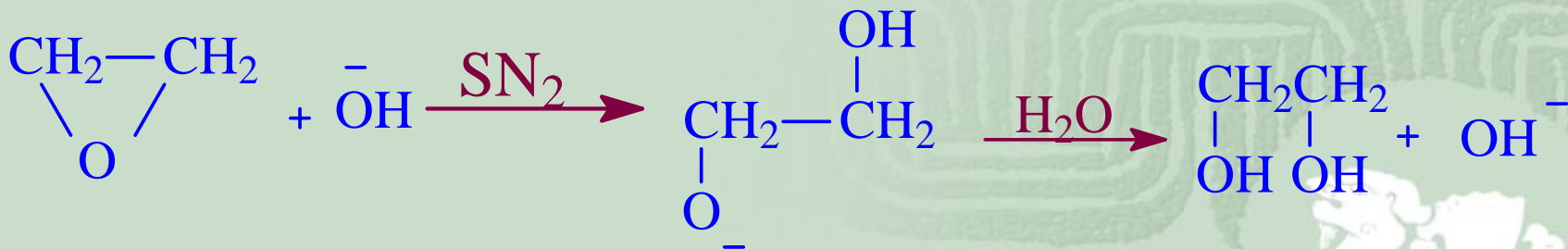


1. 历程

1) 酸性开环

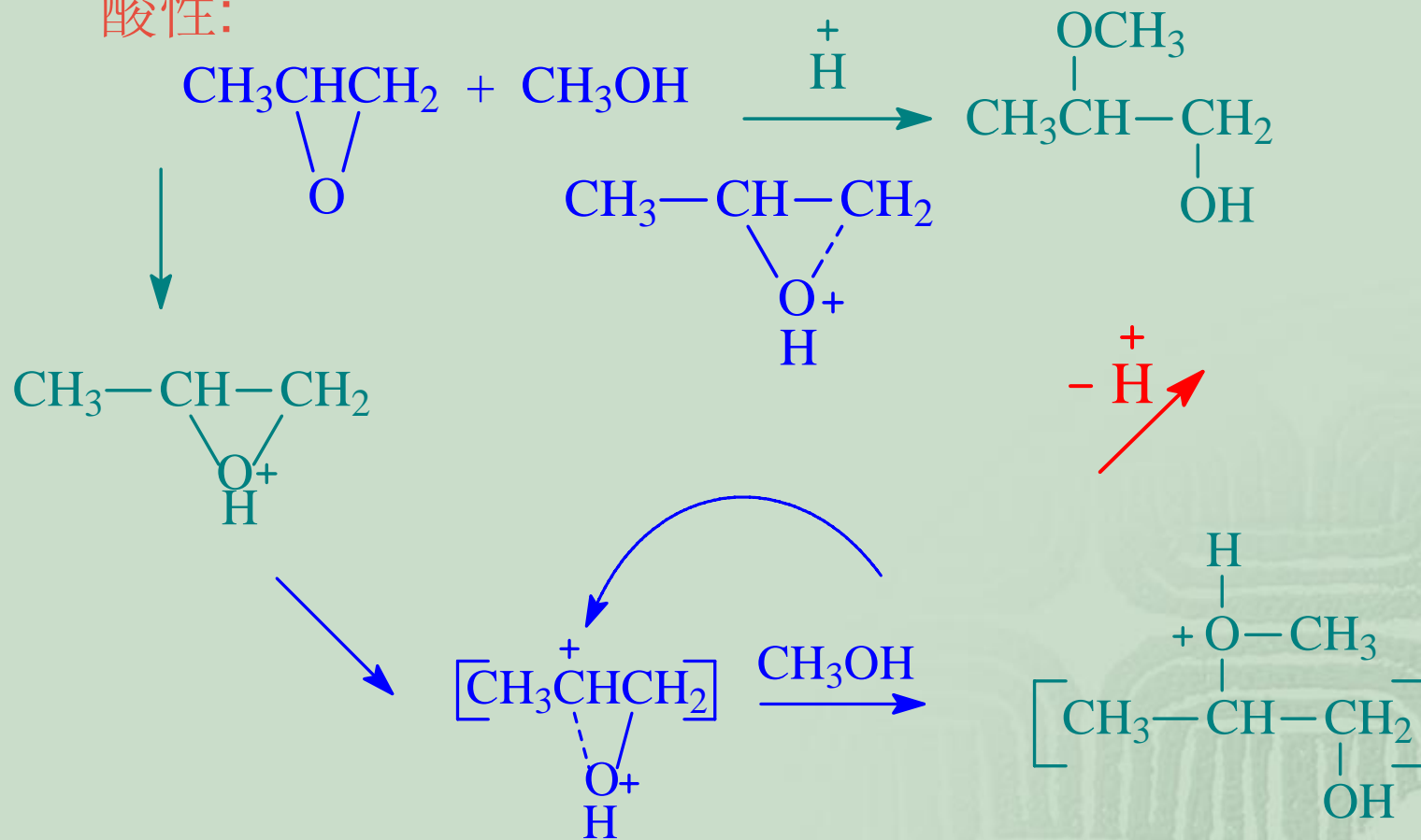


2) 碱性开环

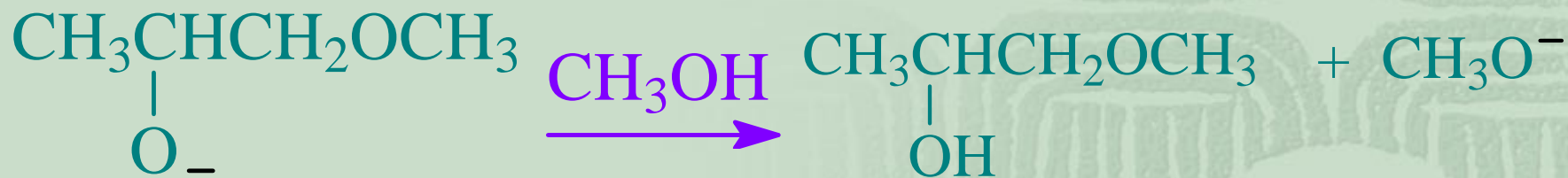
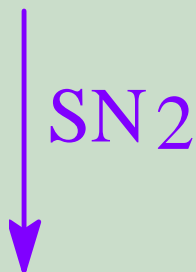
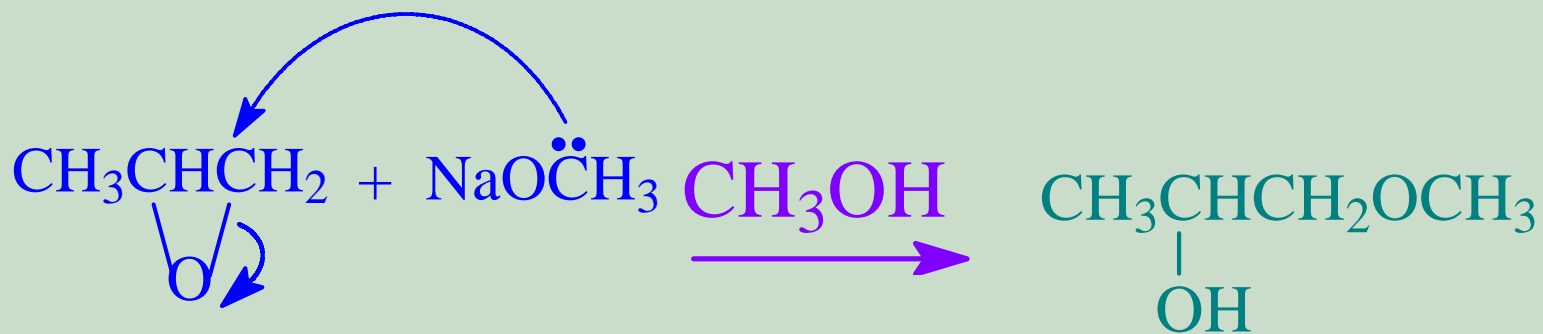


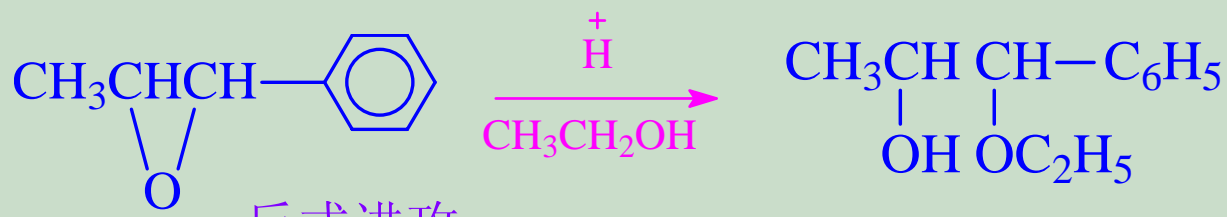
2. 开环取向

酸性:

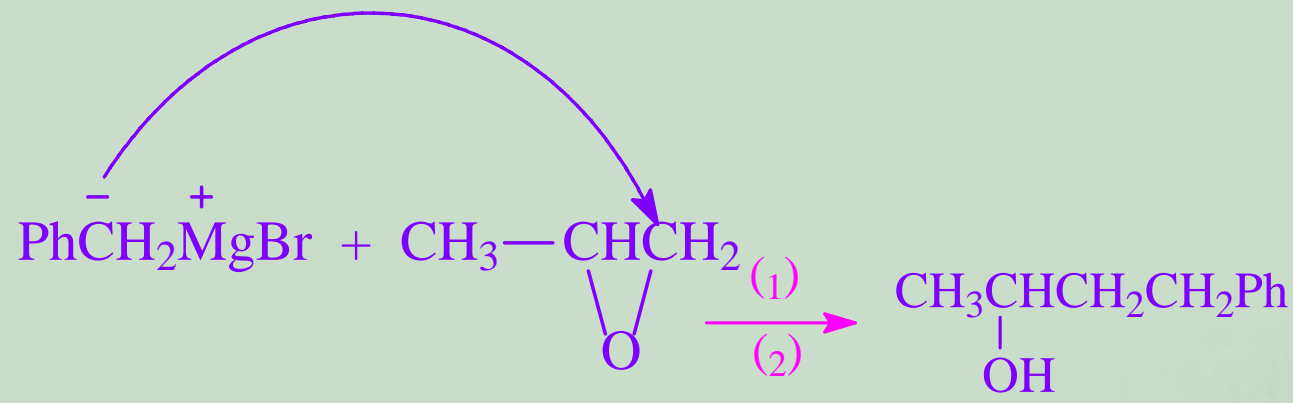


碱性

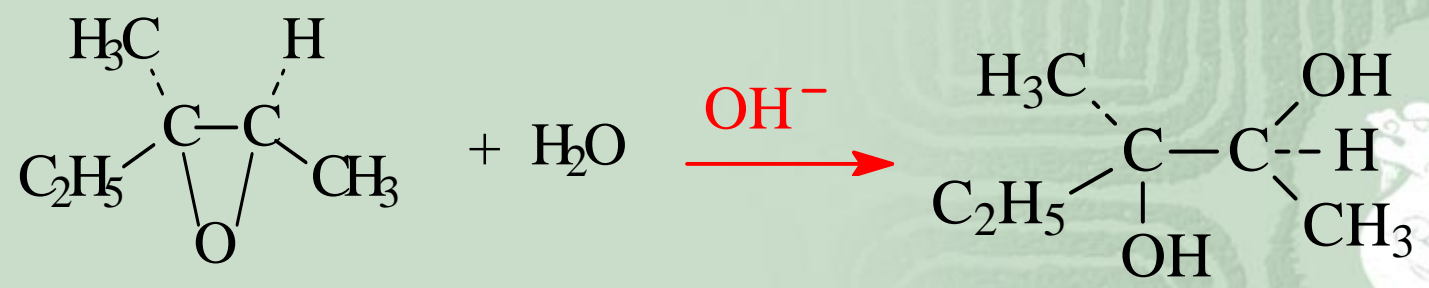


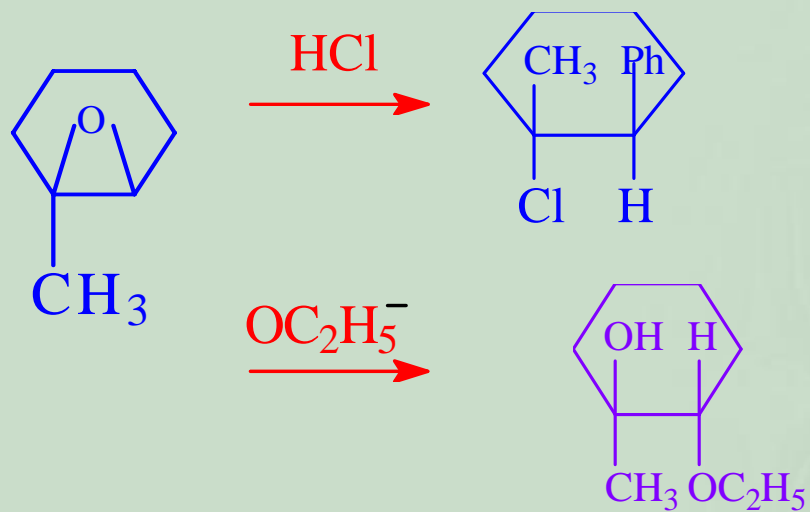
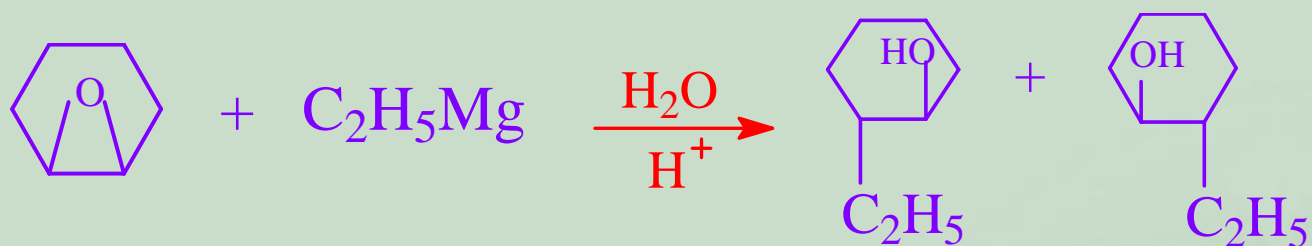
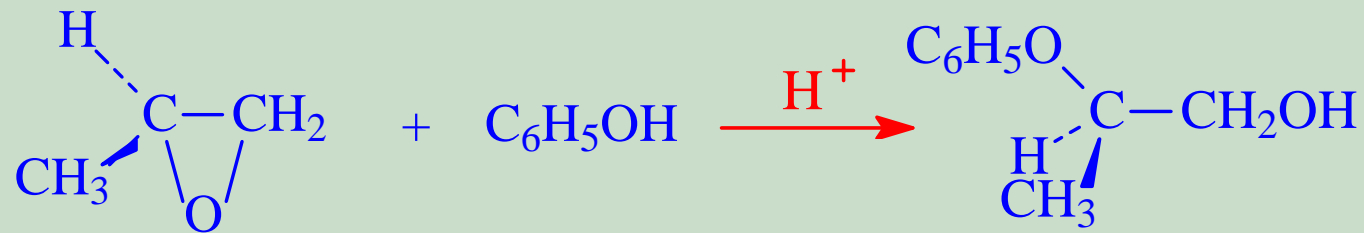


反式进攻



3. 立体化学（反式开环产物为主）



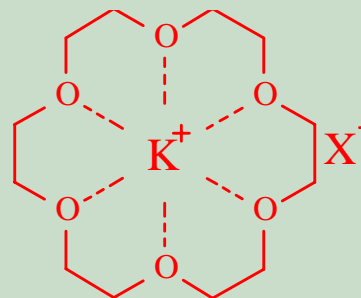
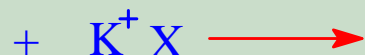
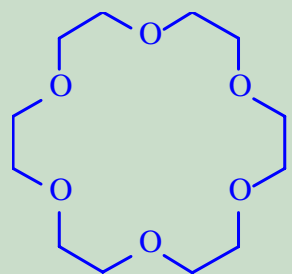


(六) 冠醚的特性

18-冠-6

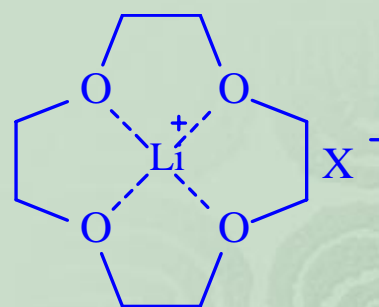
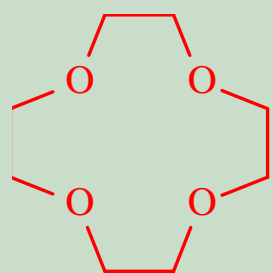
0.26—0.32nm

K+0.226



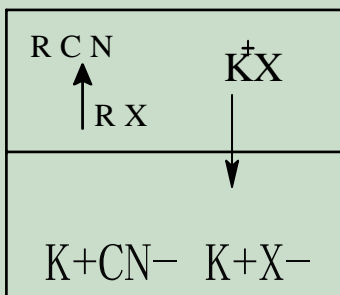
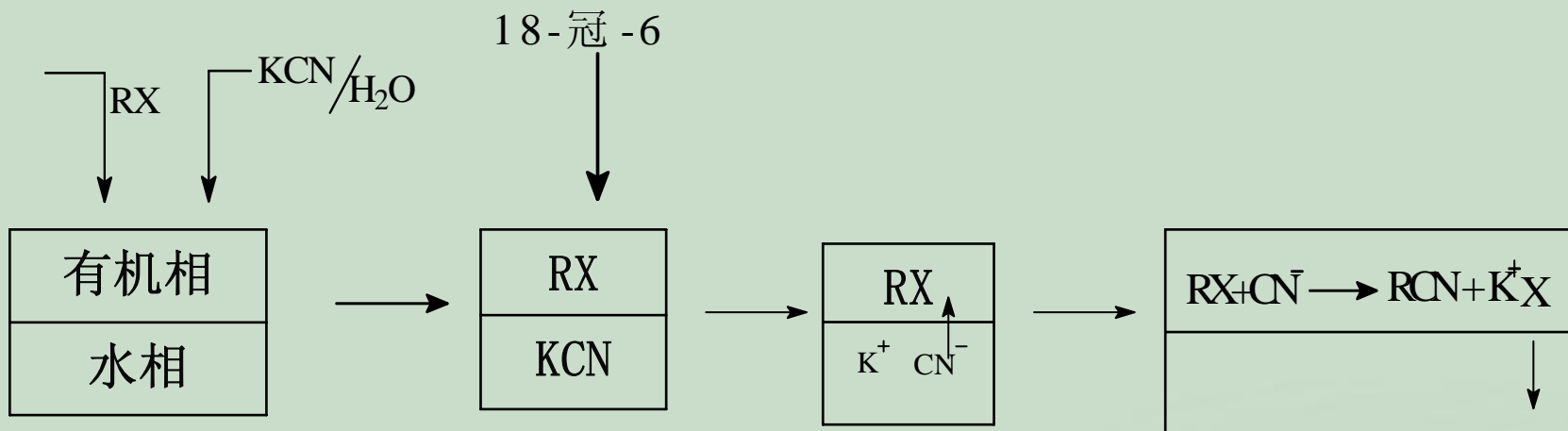
X-: CN-, OH-

I-, F-, MnO₄-



作用: 相转移催化 PTC





总结:

- 一 醇、酚、醚的结构特征、分类和命名
- 二 醇、酚、醚的化学特征，根据路易斯酸碱理论比较醇、酚的酸性
- 三 消除反应历程和消除反应立体化学
- 四 醇、酚、醚的制备方法、鉴别方法及用途



THE END

