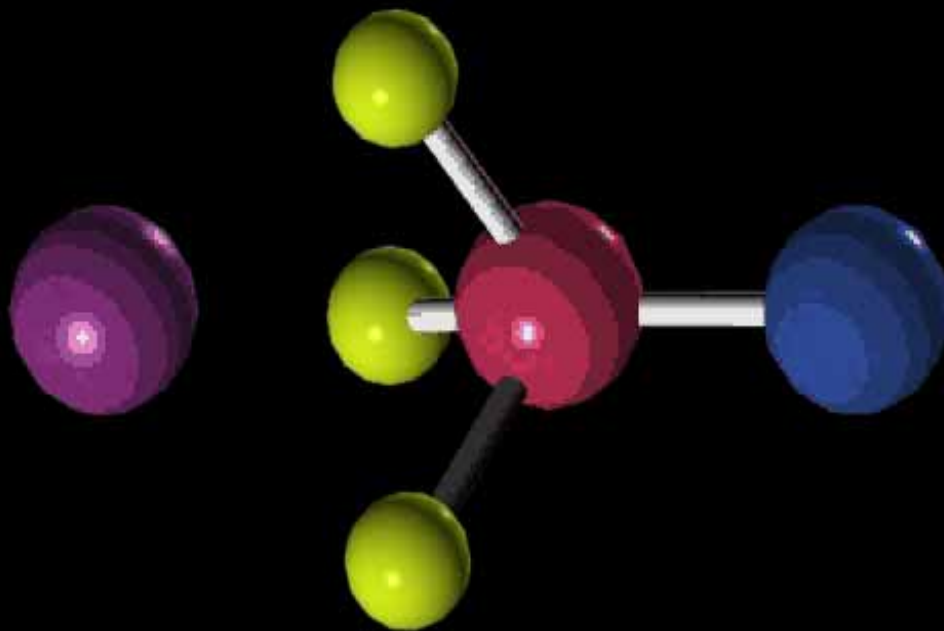
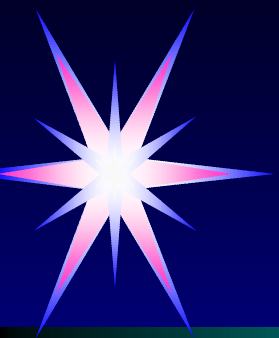


# 有机化学

( Organic Chemistry )

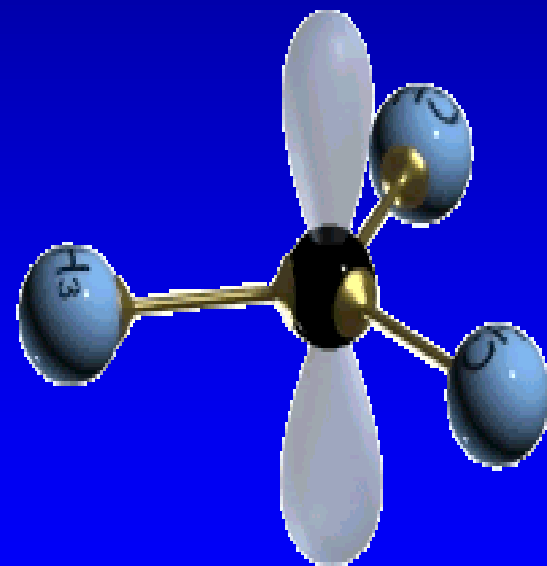


制作：付蕾 朱凤岗

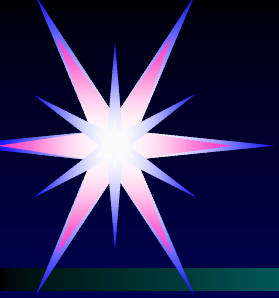


# 有机化学

( Organic Chemistry )

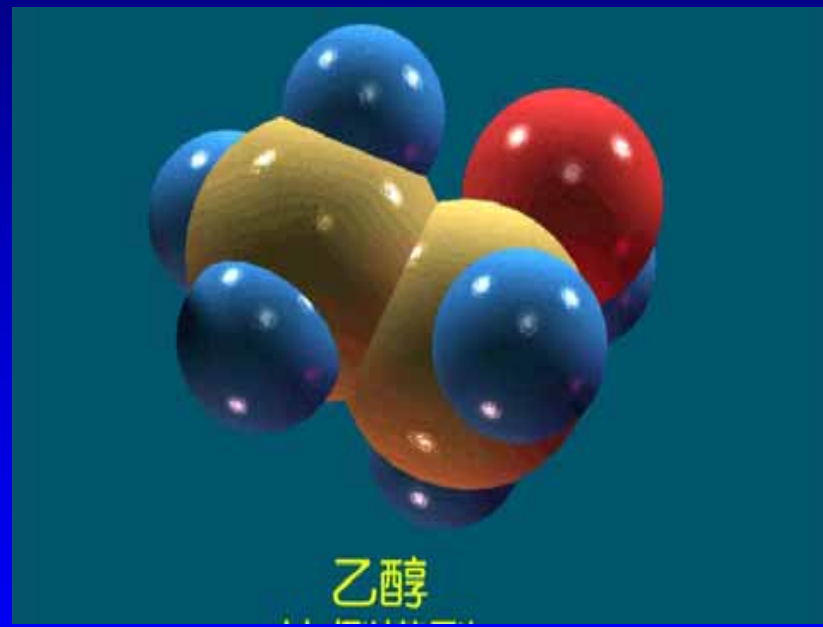
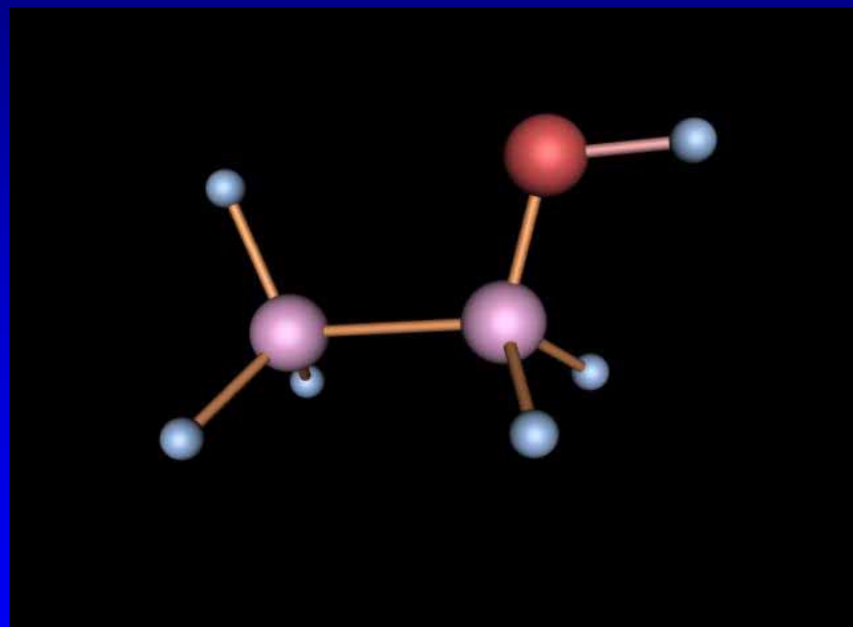


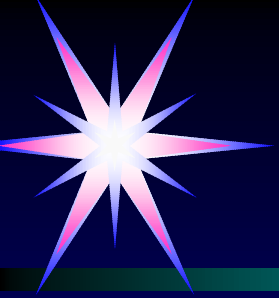
制作：付蕾 朱凤岗



# 第八章 醇 酚 醚

( Alcohols , phenols , ethers )





# 第八章 醇 酚 醚

( Alcohols , phenols , ethers )

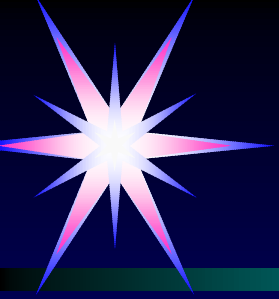
第一节 醇 ( Alcohols )

第二节 酚 ( Phenols )

第三节 醚 ( Ethers )

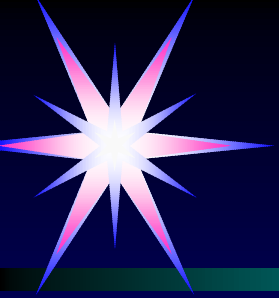
第四节 硫醇、硫酚、硫醚

( Mercaptan , thiophenol , thioether )



# 第一节 醇 ( Alcohols )

- 一、醇的分类和命名  
( Classification and nomenclature )
- 二、醇的物理性质  
( Properties of alcohols )
- 三、醇的化学性质  
( Reactions of alcohols )



# 一、醇的分类和命名

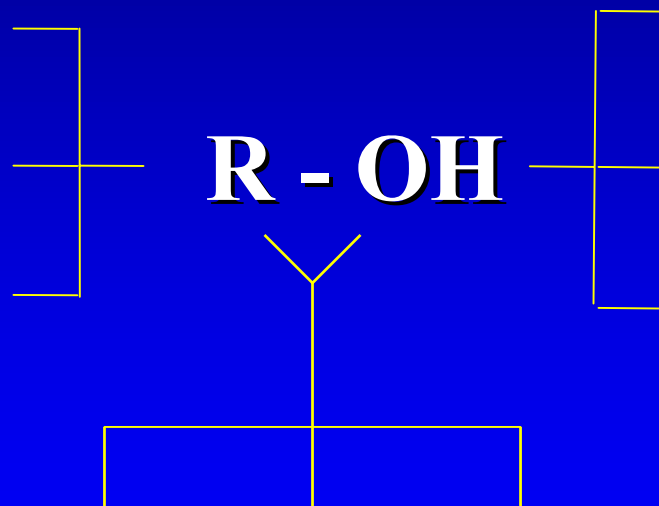
( Classification and nomenclature )

## 1. 分类 ( Classification )

脂肪醇

脂环醇

芳香醇



一元醇

二元醇

多元醇

伯醇

仲醇

叔醇



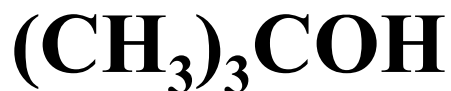
## 2. 命名 ( Nomenclature)

Common name : 先叫烃基 , 后叫醇



乙醇

ethyl alcohol



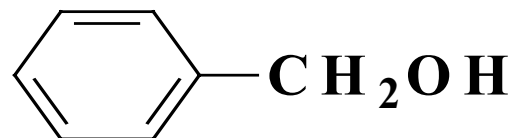
叔丁醇

tert-butyl alcohol



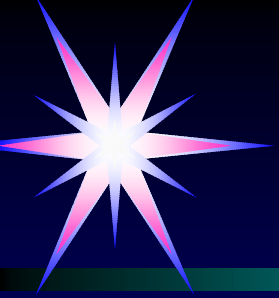
烯丙醇

allyl alcohol



苯甲醇

benzyl alcohol



# 命名 (Nomenclature)

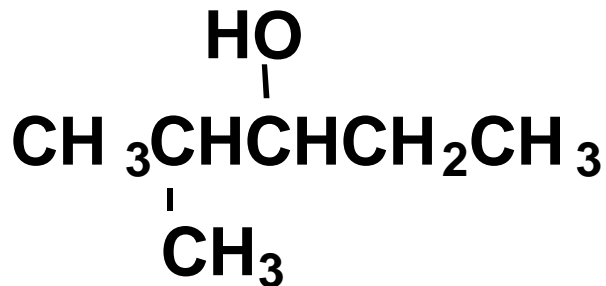
**Systematic name :**

选主链：含 - OH和重键，

Ar - 取代基

编号：近 - OH端，

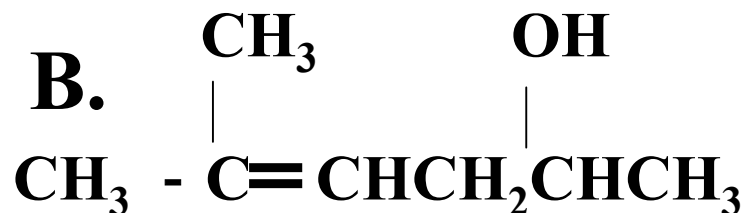
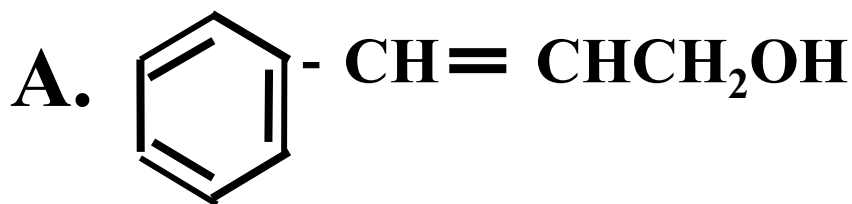
指明 - OH位置和数目



**2-甲基-3-戊醇**  
**2-methyl-3-pentanol**

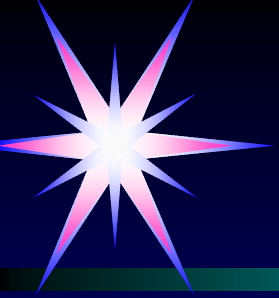


# 命名 (Nomenclature)

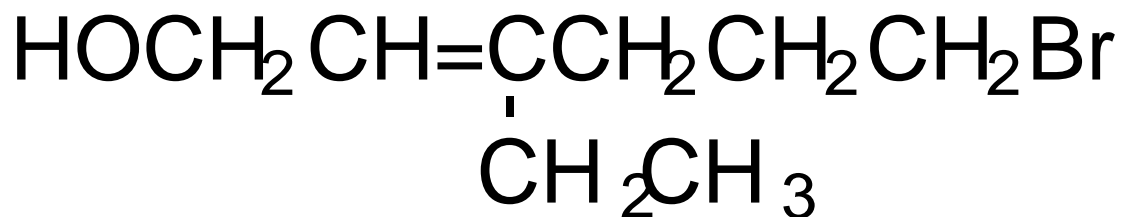


A. 3 - 苯基 - 2 - 丙烯 - 1 - 醇  
3-phenyl-2-propene-1-ol

B. 5 - 甲基 - 4 - 己烯 - 2 - 醇  
5-methyl-4-hexene-2-ol

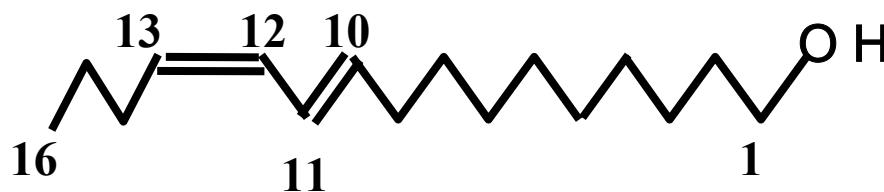


# 命名 ( Nomenclature )



3-乙基 - 6 - 溴 - 2 - 己烯 - 1 - 醇

6-bromo-3-ethyl-2-hexene-1-ol



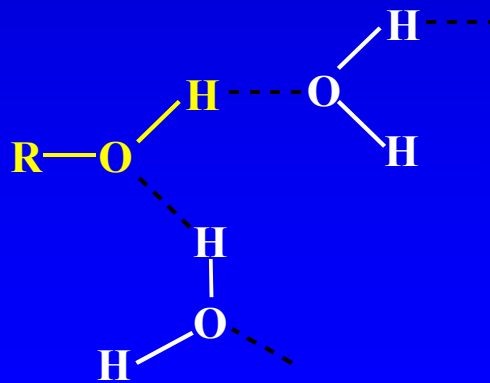
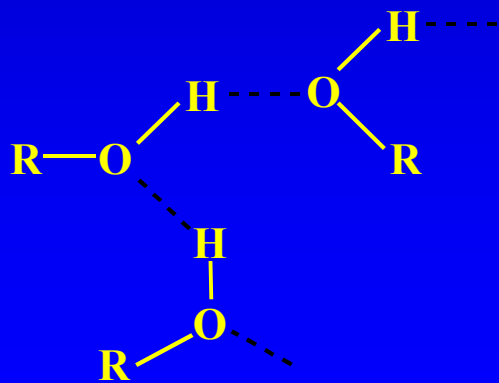
( 10E, 12Z ) - 10, 12 - 十六碳二烯 - 1 - 醇

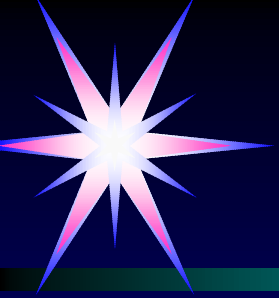
( 10E, 12Z ) - 10, 12 - hexadecadiene-1-ol

## 二、醇的物理性质

### ( Properties of alcohols )

1. 为什么醇的b.p.比相对分子质量近似的烃、卤代烃、醛、醚高？
2. 为什么低相对分子质量的醇溶于水，从丁醇开始  $M_r$  ，水溶性 ？

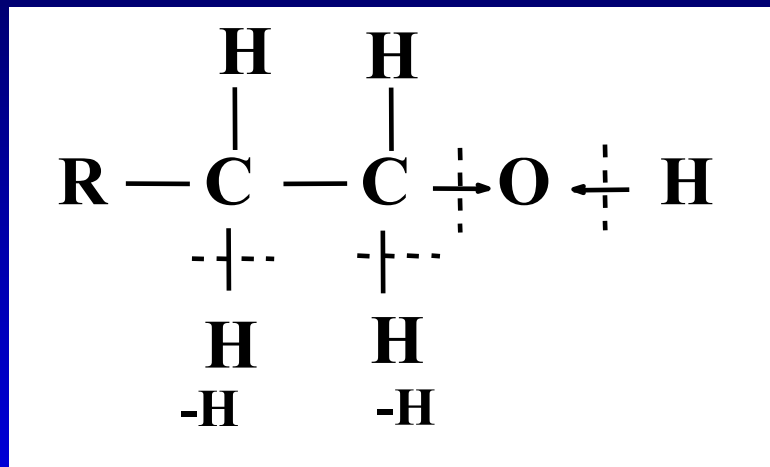
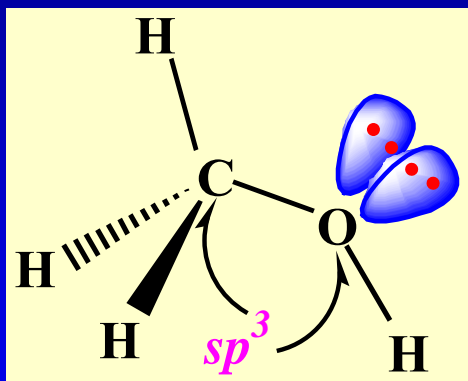




# 三、醇的化学性质

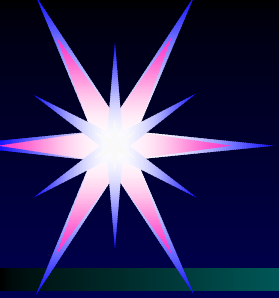
## ( Reactions of alcohols )

结构分析：



反应部位

- O - H (酸碱反应)
- C - O (卤化反应)
- H (氧化反应)
- H (消除反应)



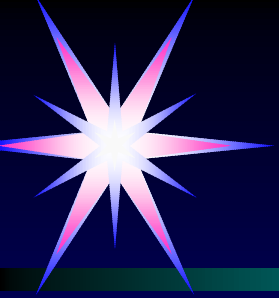
# 1. 与金属Na的反应



讨论：

(1) 活性：甲醇 > 伯 > 仲 > 叔醇

解释：R-CH<sub>2</sub>-O-H，R-是斥电子基，  
R，O e，O-H 不易断。



## 讨论：



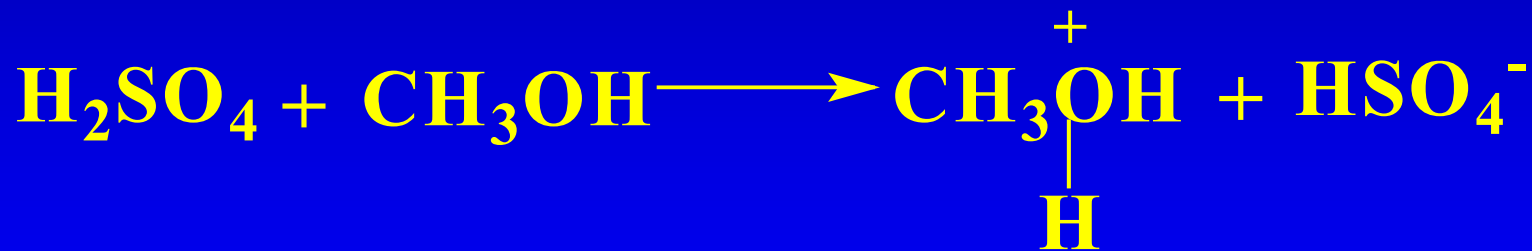
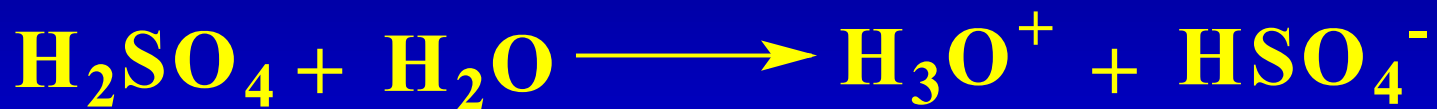
布朗斯特酸

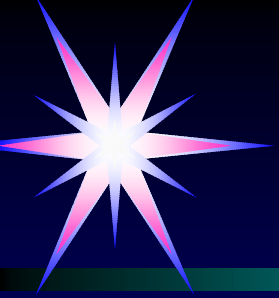
酸强度：水 > 甲醇 > 伯 > 仲 > 叔醇



## 讨论：

(3) 醇既可做酸 ( $\text{H}^+$ )，又可做碱 ( $\ddot{\text{O}}$ )，  
碱性比水弱。





## 2. 与HX（氢卤酸）反应



讨论：

(1)活性

R相同：HI > HBr > HCl

(原子半径大，易异裂)

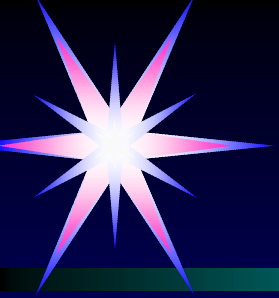
HX相同：

烯丙（苄基）型醇 > 叔 > 仲 > 伯

HCl/ZnCl<sub>2</sub>      立即      1'      10'      1小时

20





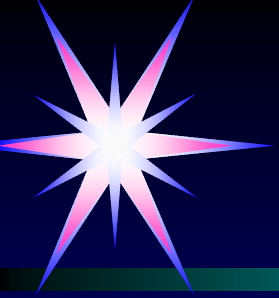
## 讨论：

(2) 卢卡斯(Lucas)试剂：浓HCl / 无水ZnCl<sub>2</sub>



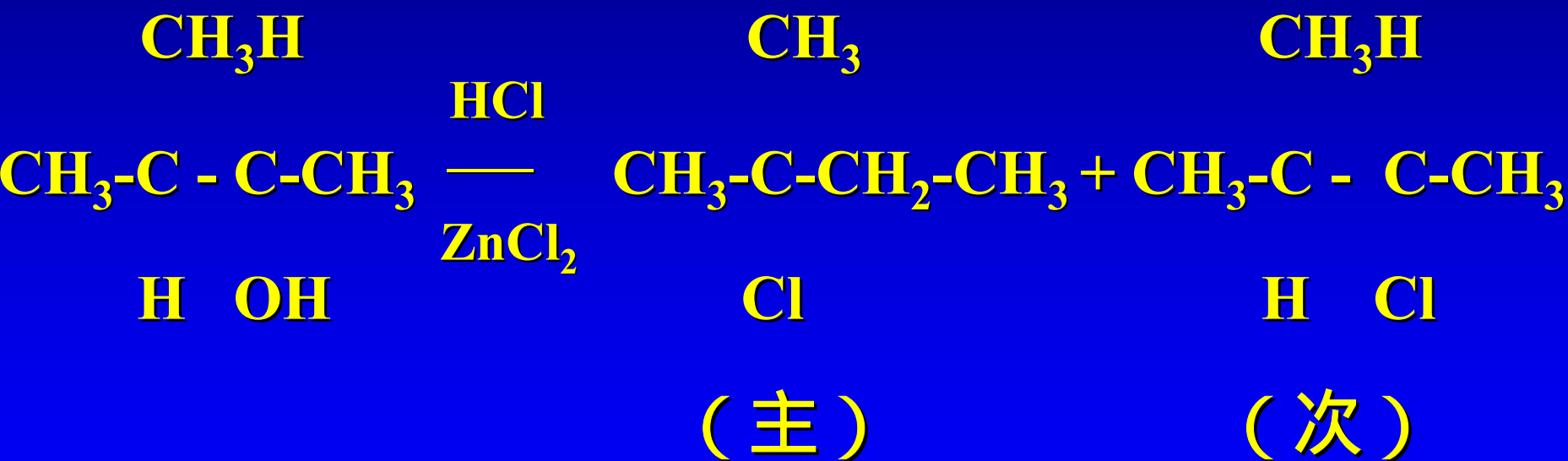
< C<sub>6</sub>卤烃混浊或分层

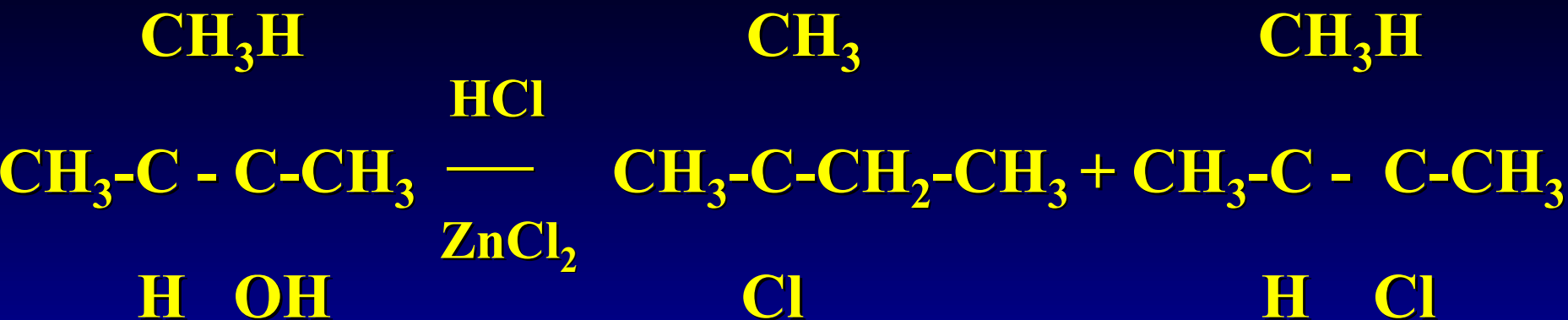
用途：1. 制备氯代烃  
2. 鉴别



# 讨论：

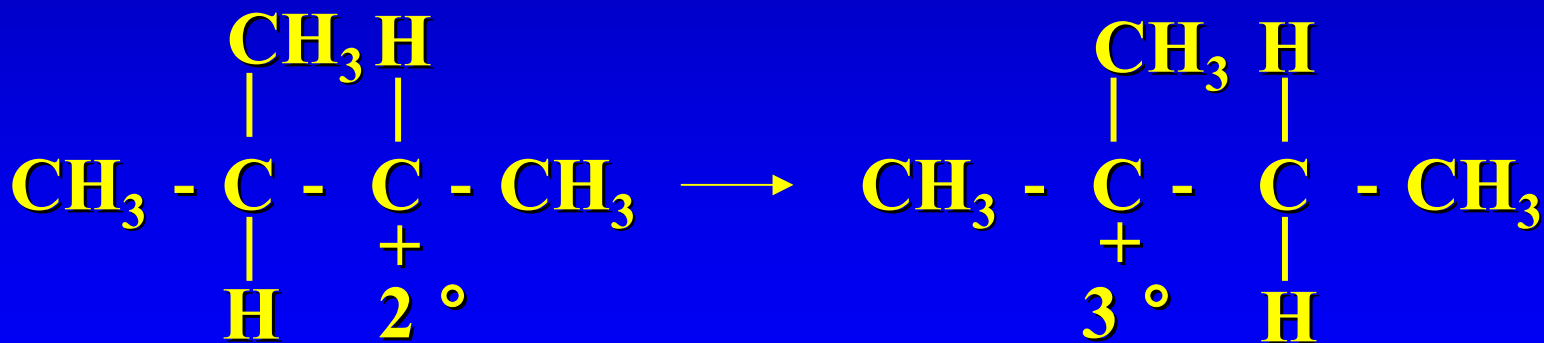
(3) 分子重排：分子中某些原子或基团发生转移的反应。





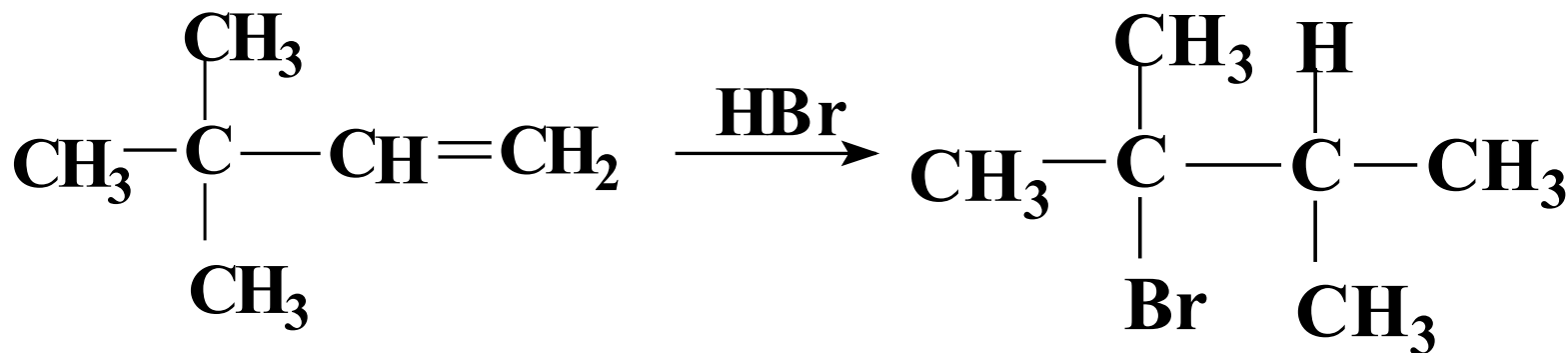
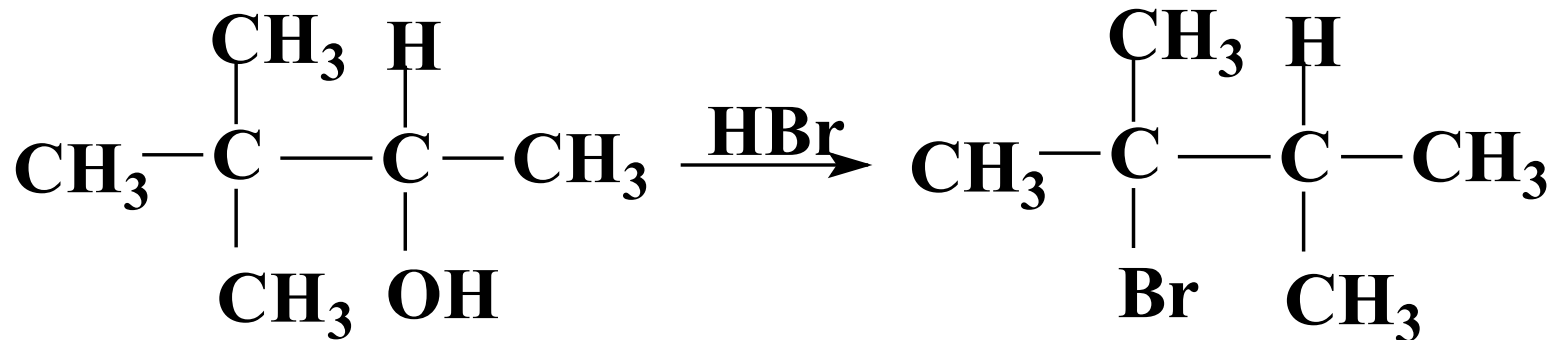
(主)

(次)



(稳定)

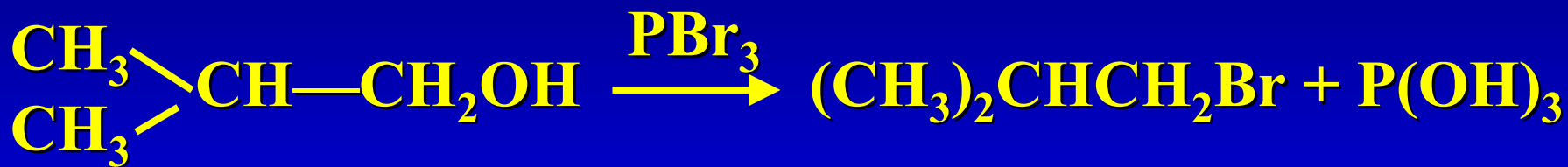
# 练习





### 3. 与无机酰卤反应

$\text{PI}_3$  ,  $\text{PBr}_3$  ,  $\text{SOCl}_2$  ( $\text{Cl} - \overset{\text{Cl}}{\underset{\text{O}}{\text{S}}} = \text{O}$ ) 亚硫酸酰氯

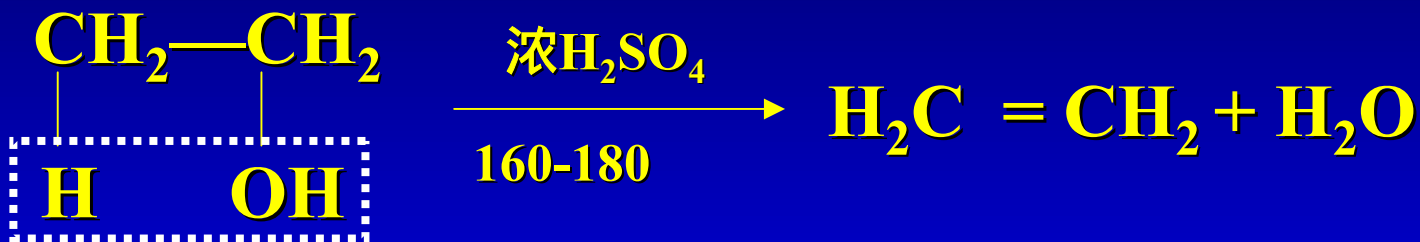


优点：速度快，产量高，副产物少，纯度高



## 4. 脱水反应

### (1) 分子内脱水成烯（消除反应）

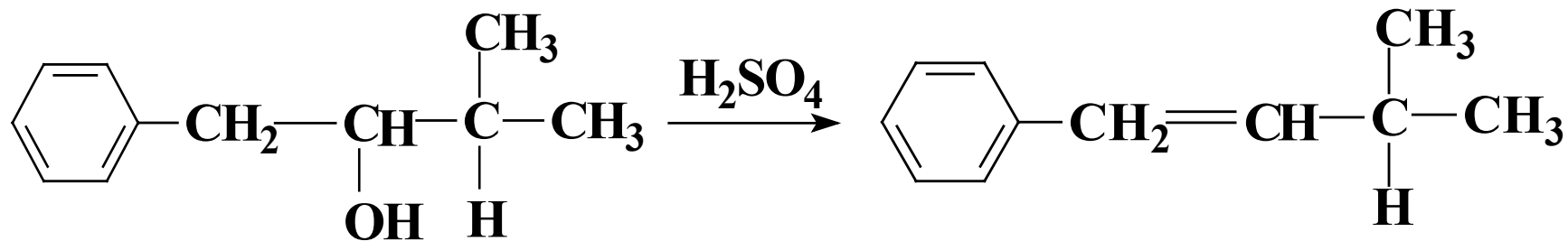
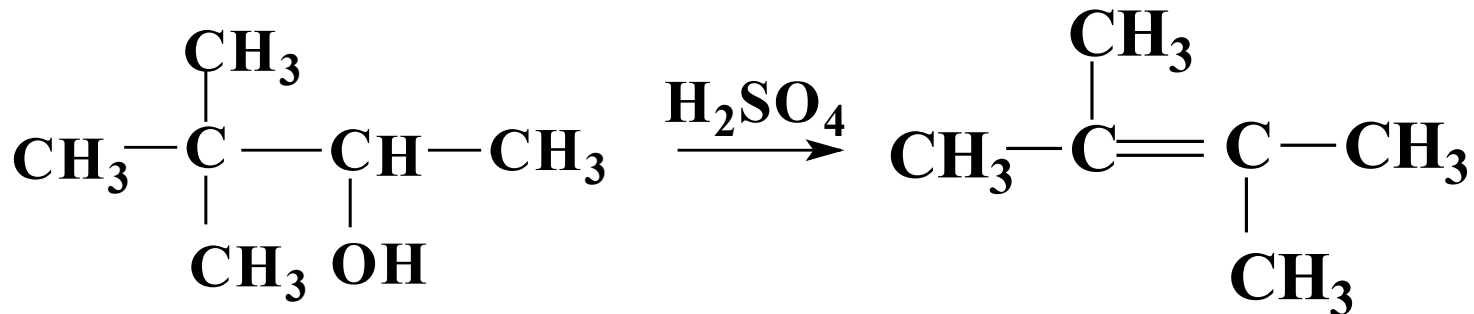


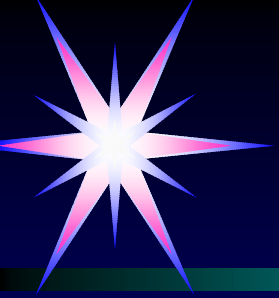
讨论： 活性：叔 > 仲 > 伯

遵守查依采夫规则

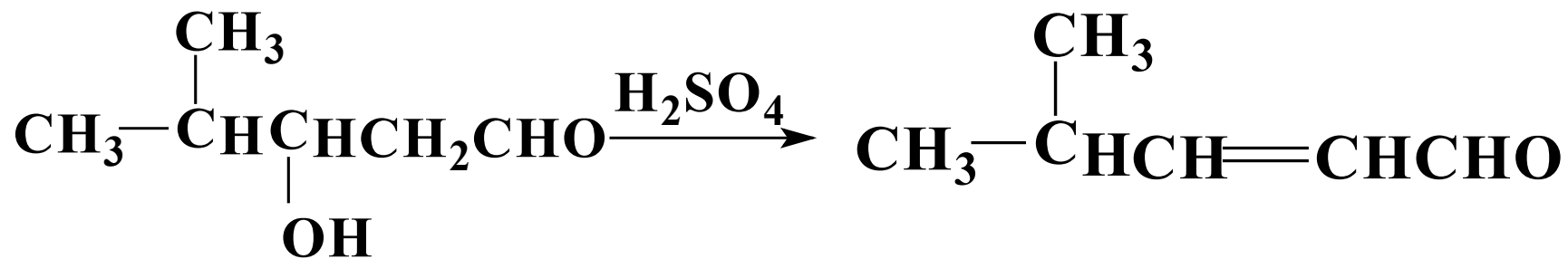
特殊情况

# 特殊情况

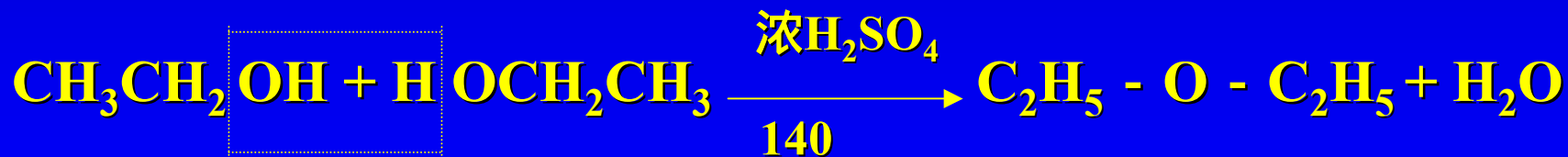




# 特殊情况



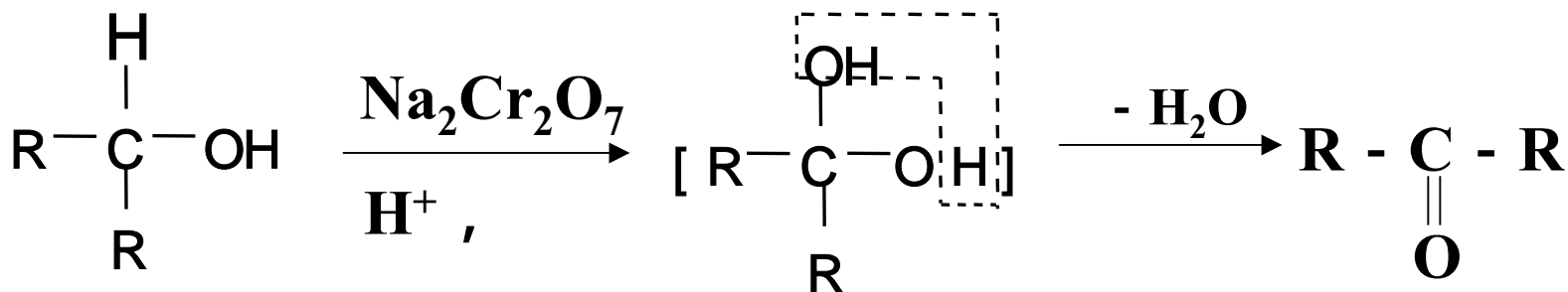
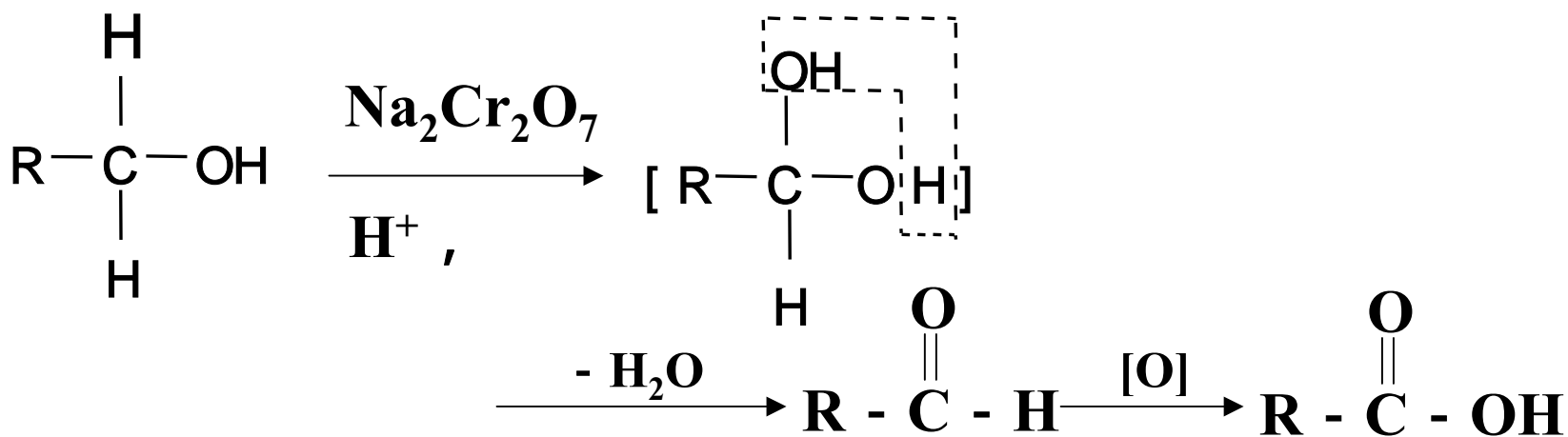
## (2) 分子间脱水成醚 (取代反应)

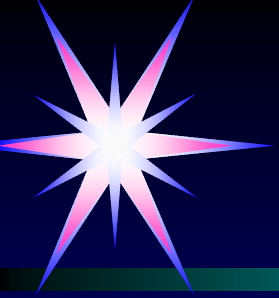




# 5. 氧化反应

## (1) 加氧方式





# 讨论：

叔醇不氧化（无  $\alpha$ -H）

用途： 制备酮、酸

鉴别伯仲醇：桔红色 亮绿色

制醛：沙瑞特试剂  $\text{CrO}_3 \cdot (\text{C}_5\text{H}_5\text{N})_2$

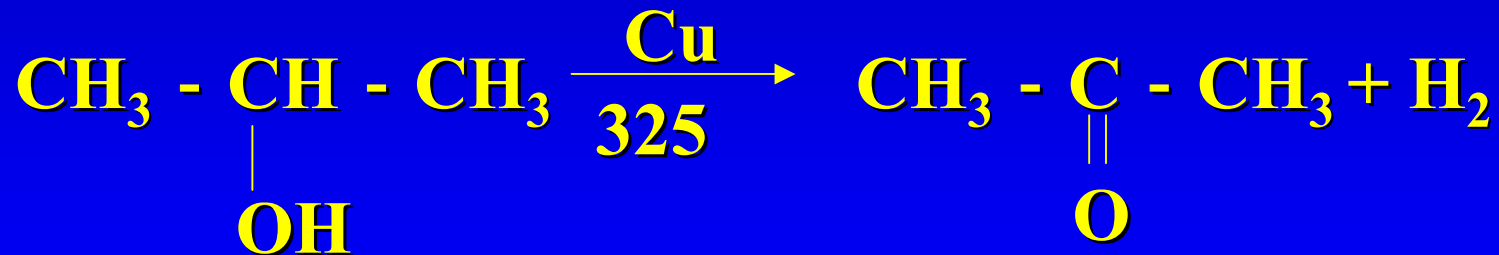
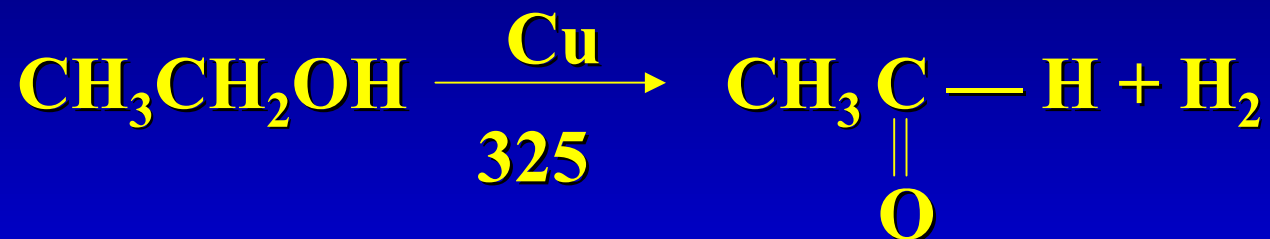


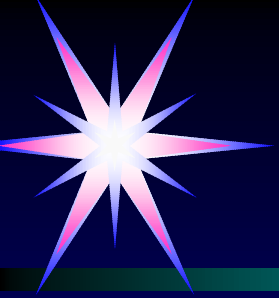
重键不被氧化保留。



# 氧化反应

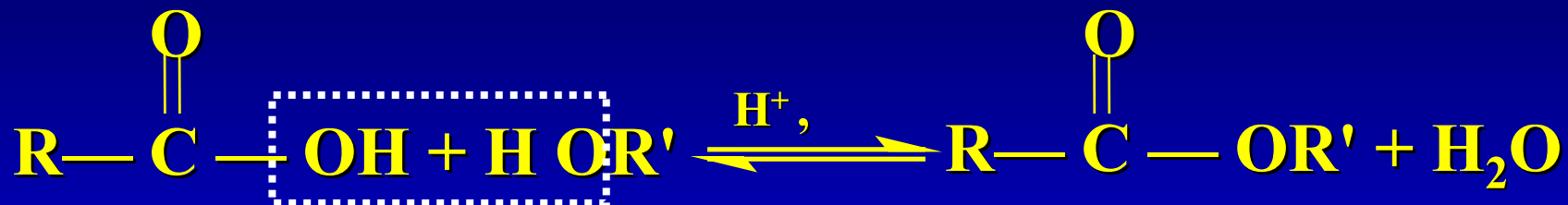
(2) 脱氢 用pt、Cu、pd催化完成





## 6. 酯化反应：

酸与醇失水成酯的反应

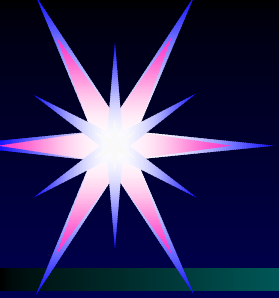


讨论：(1)可逆反应：提高产率

加 $\text{H}_2\text{SO}_4$ （催化剂，脱水）

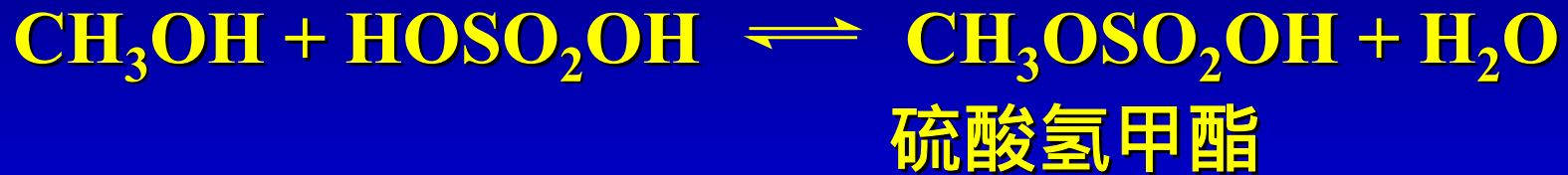
原料过量

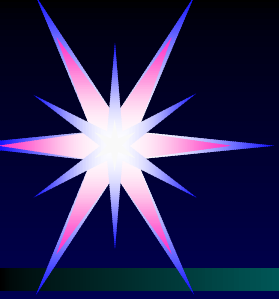
移走产物（蒸出酯和水）



## 讨论：

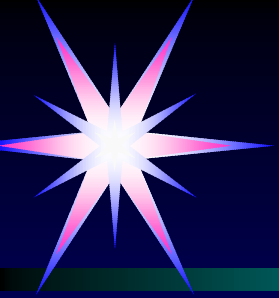
(2) 醇与 $\text{H}_2\text{SO}_4$ 、 $\text{HNO}_3$ 、 $\text{H}_3\text{PO}_4$ 成无机酸酯





## 第二节 酚 ( Phenols )

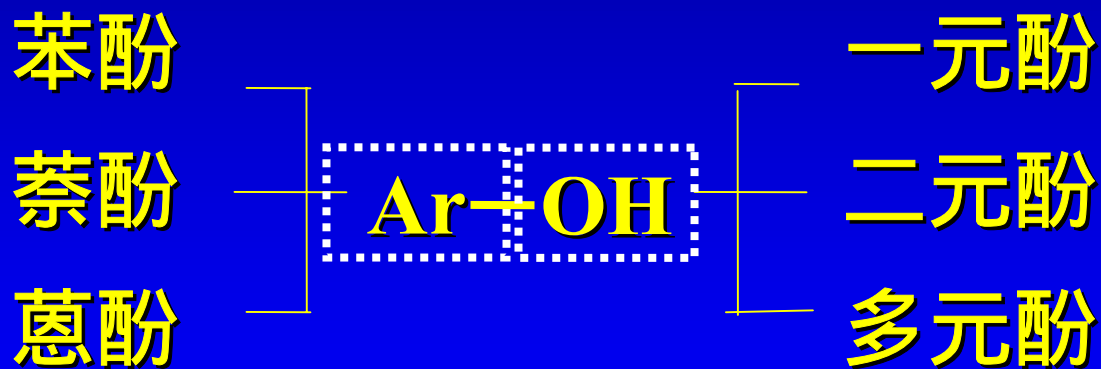
- 一、酚的分类和命名  
( Classification and nomenclature )
- 二、酚的物理性质  
( Properties of phenols )
- 三、酚的化学性质  
( Reactions of phenols )



# 一、酚的分类与命名

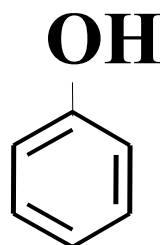
## ( Classification and nomenclature )

### 1. 分类 ( Classification )

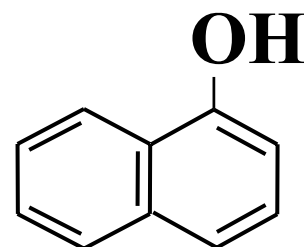


## 2. 命名 (Nomenclature)

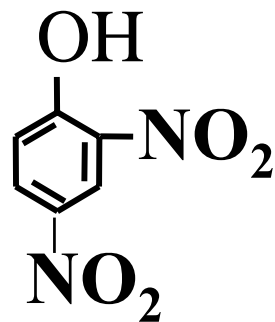
只有 -OH，酚为母体，指明 -OH 的位置



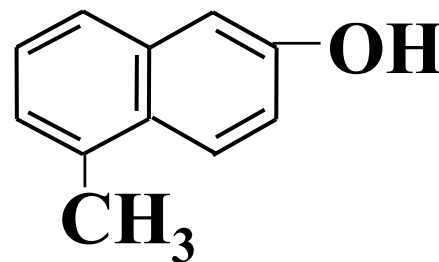
苯酚  
phenol



-萘酚  
-naphthol

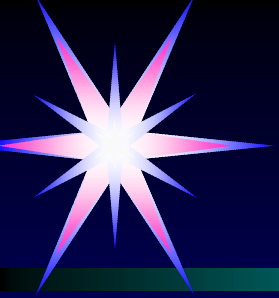


2,4-二硝基苯酚  
2,4-dinitrophenol



5-甲基-2-萘酚  
5-methyl-2-naphthol

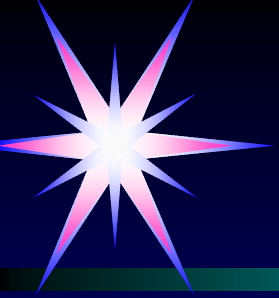




## 二、酚的物理性质

### ( Properties of phenols)

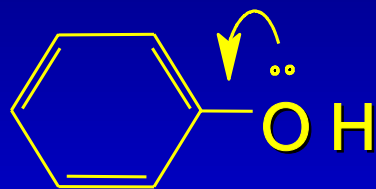
1. 为什么 **苯** 和 **苯酚** 的沸点相比差距较大？  
**b.p. 80.1 181**
2. 邻氯苯酚的沸点为什么比对、间位低的多？
3. 苯酚一般为无色，打开瓶盖后常常呈微红 暗红，为什么？



# 三、酚的化学性质

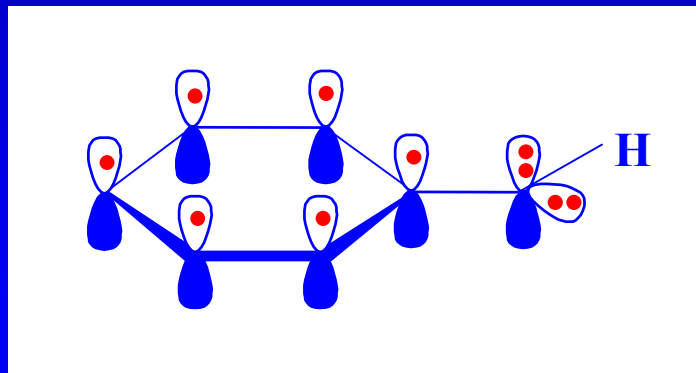
## (Reactions of phenols)

结构分析：



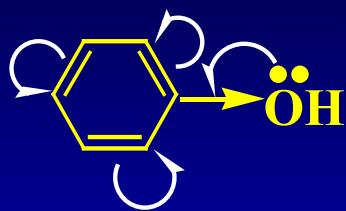
C,O均为 $sp^2$ 杂化, p- 共轭体系

- \*1. 增强了苯环上的电子云密度
- \*2. 增加了羟基上的解离能力

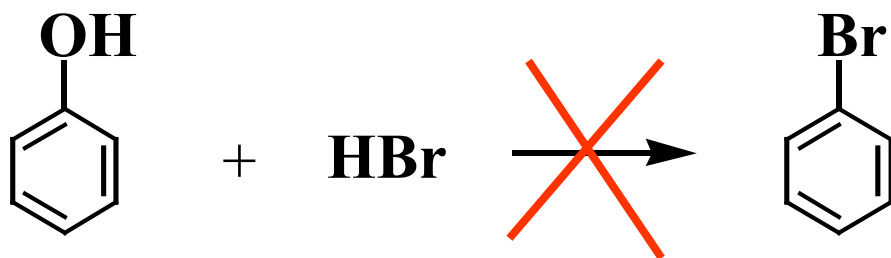


酸性                      显色  
亲电取代                氧化

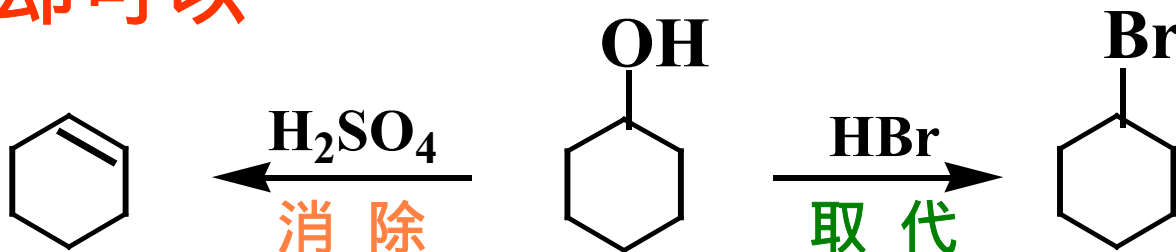
# 酚与醇的不同之处：



C O键结合较为牢固，所以苯酚不易进行亲核取代反应。



而醇却可以



# 1. 酸性

比醇强，但仍然为弱酸性。

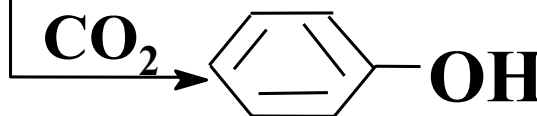
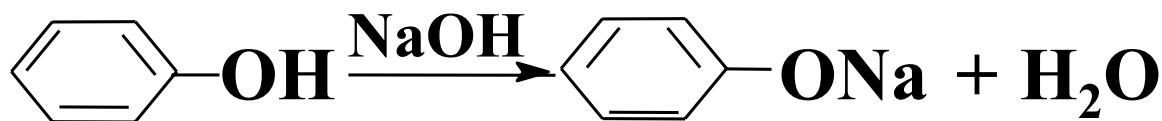
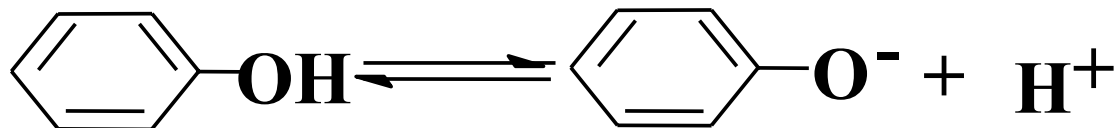


pKa

10

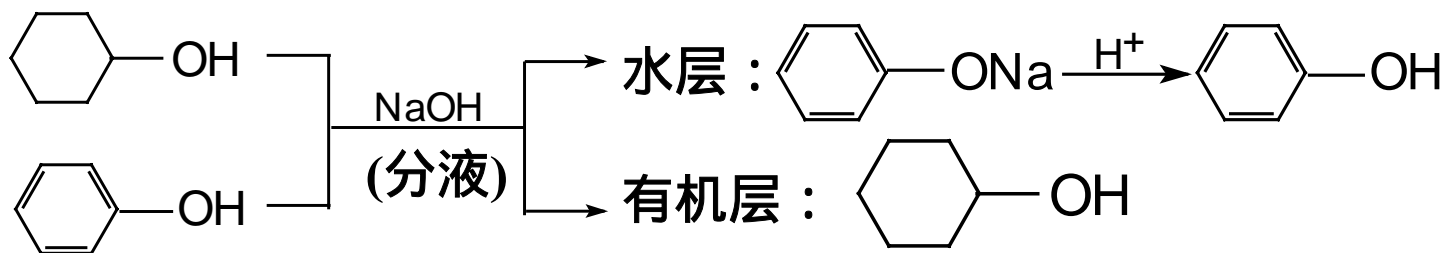
17

18



# 讨论：

## (1) 用途：提高水溶性和用于酚的分离



## (2) 电子效应对酚酸性的影响

环上： $+I$  越大， $\text{H}^+$  越小；

$-I$  越大， $\text{H}^+$  越大。



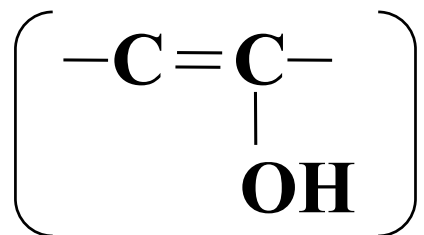
## 2. 与FeCl<sub>3</sub>反应



酚铁络离子（紫色）

用途：鉴别苯酚

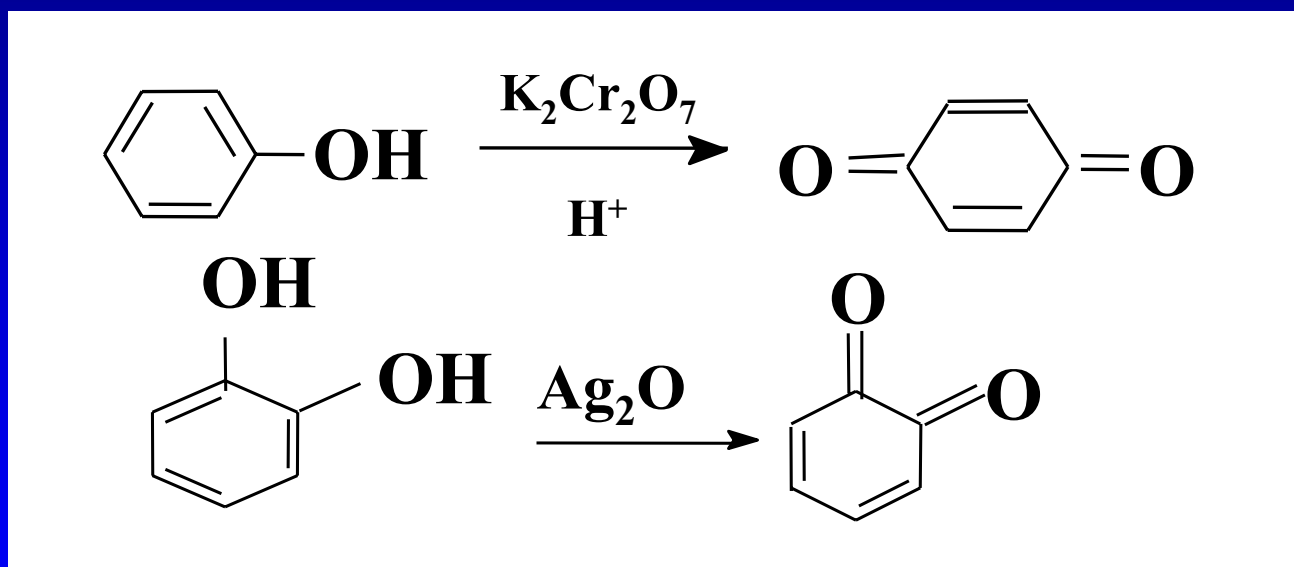
注意：烯醇式结构也能与FeCl<sub>3</sub>显色



### 3. 氧化反应

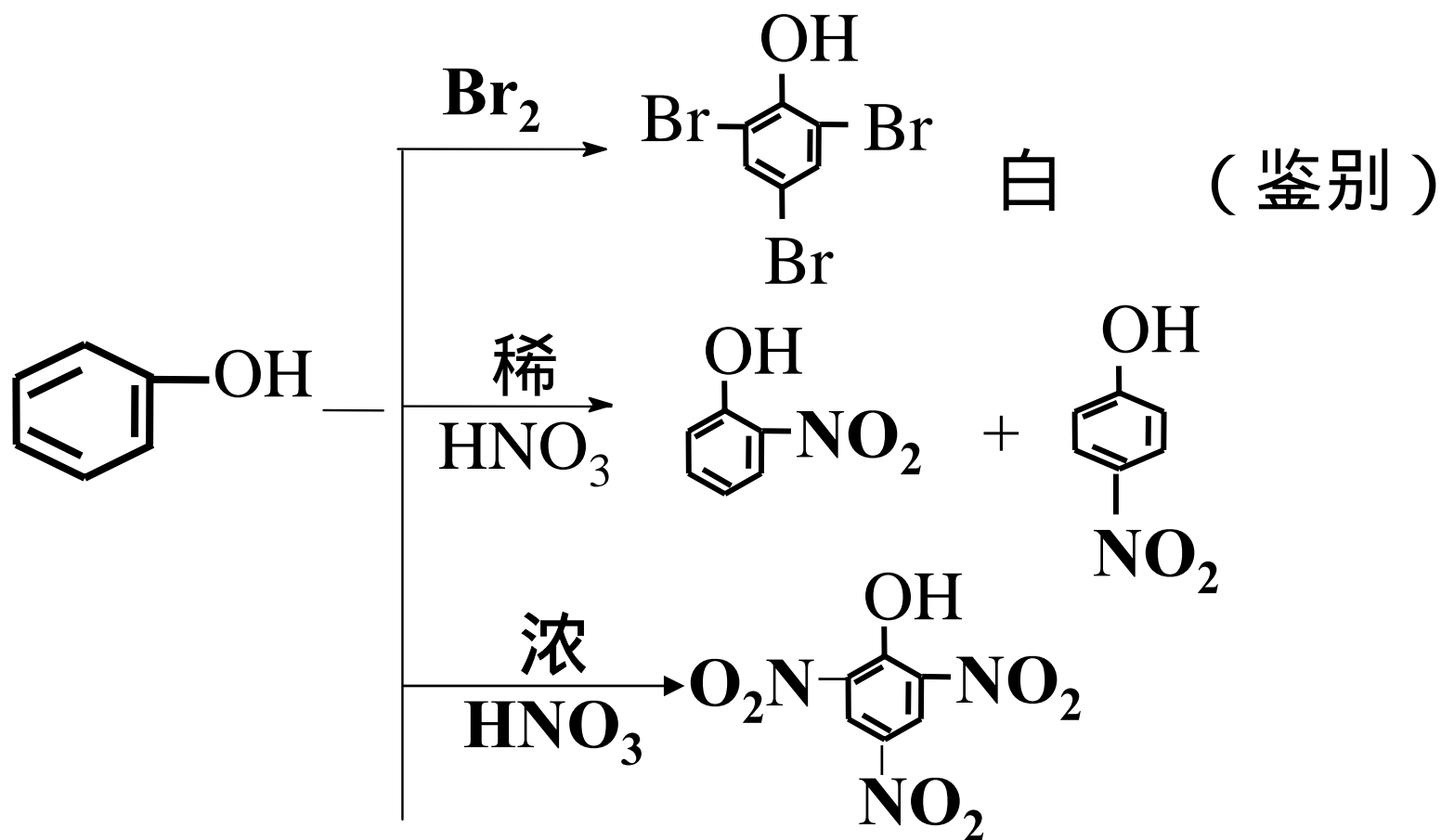
(过程复杂, 历程不详)

空气中: 无色 粉红 红 暗红色



多元酚更易氧化。

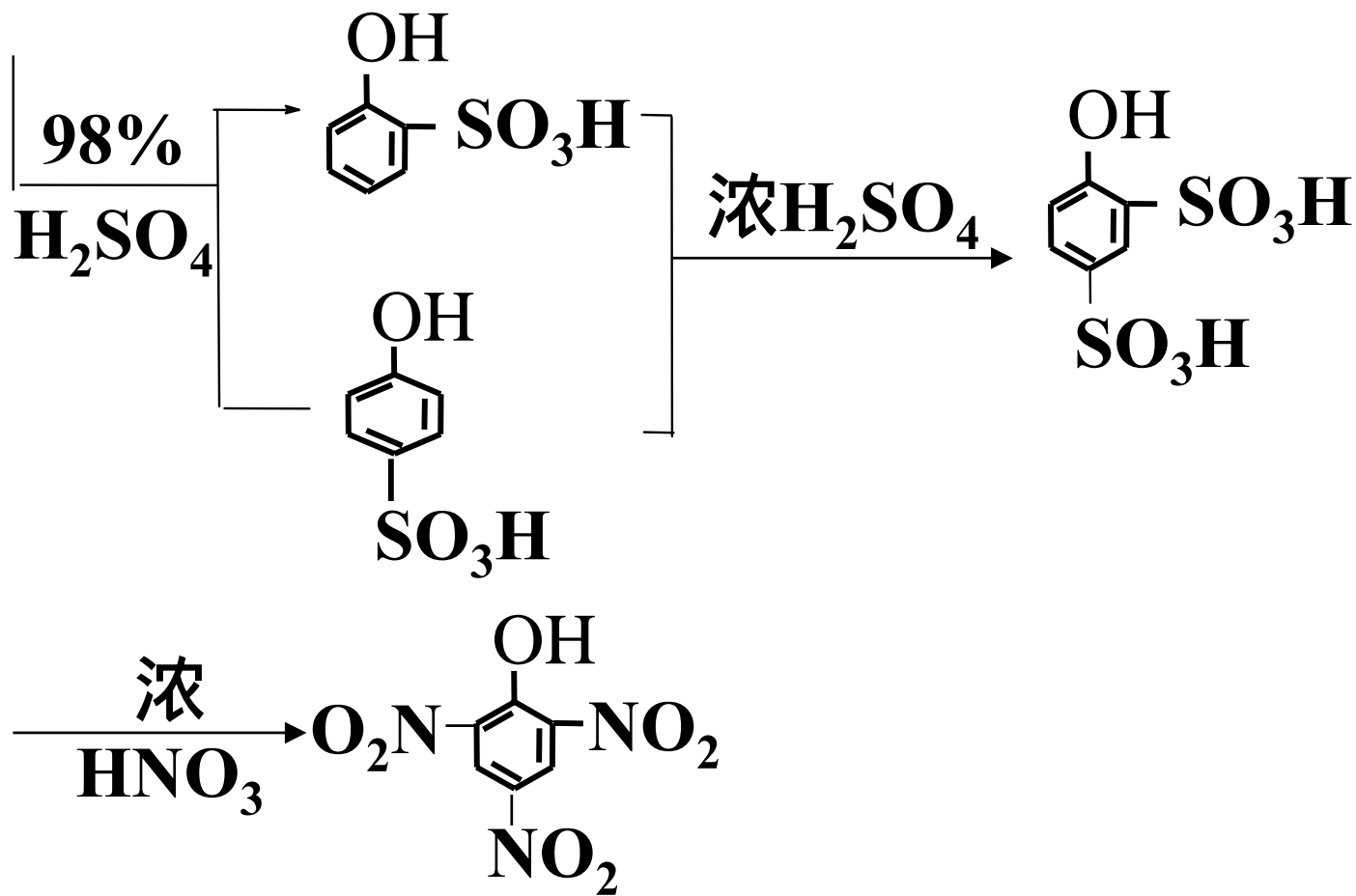
# 4. 取代反应

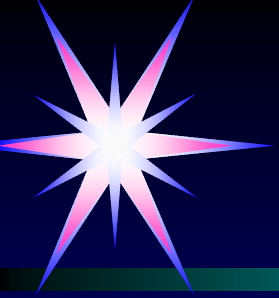


(炸药, 易氧化, 产率低, 一般不用)



# 取代反应



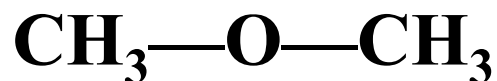


# 一、醚的分类与命名

## ( Classification and nomenclature )

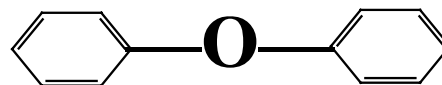
### 1. 分类 ( Classification )

**单纯醚**



**甲醚**

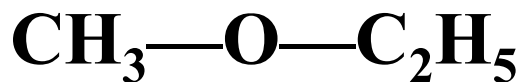
**dimethyl ether**



**二苯醚**

**diphenyl ether**

**混合醚**



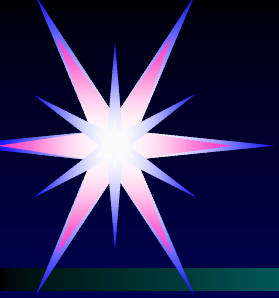
**甲乙醚**

**ethyl methyl ether**



**苯甲醚**

**methyl phenyl ether**

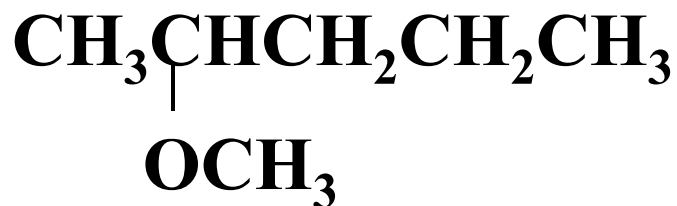


## 2. 命名 ( Nomenclature)

普通法：“××（先小后大，先芳后脂）醚”

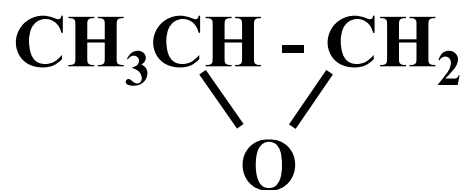
系统法：RO - (ArO - )为取代基

环 醚：“环氧×烷”



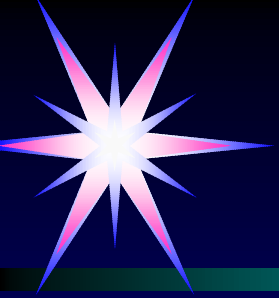
2-甲氧基戊烷

2- methoxypentane



1,2-环氧丙烷

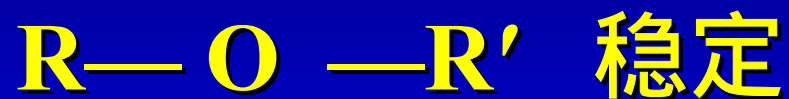
1,2- epoxypropane



## 二、醚的化学性质

### (Reactions of ethers)

结构分析：



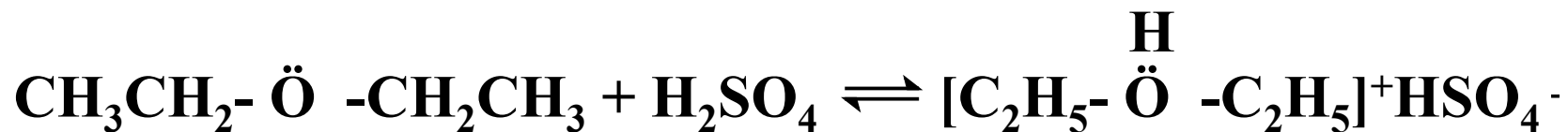
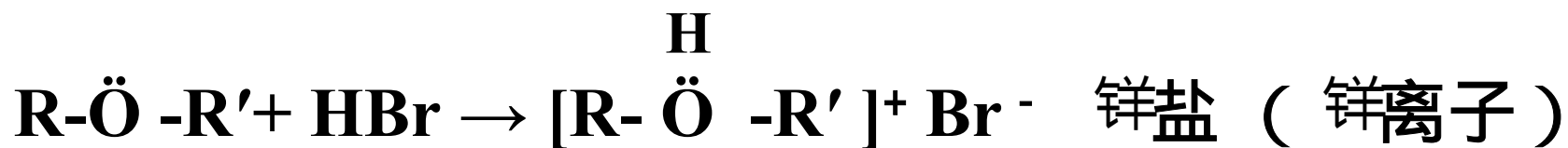
钡盐

醚键断裂

过氧化物

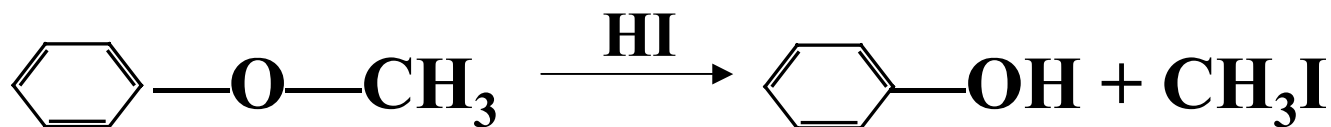


# 1. 生成 铵盐：



用途：分离提纯

## 2. 醚键断裂

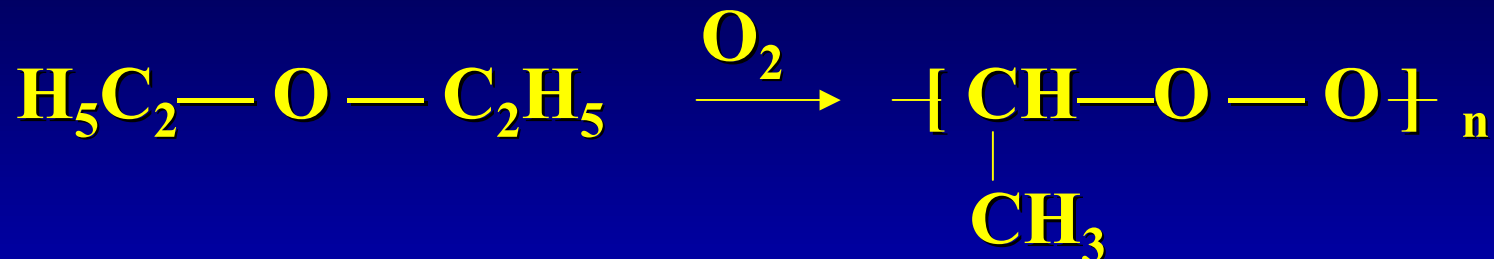


规律：混合脂肪醚较小烷基变成碘代烃

芳脂醚中芳环部分变成酚（p- 共轭）

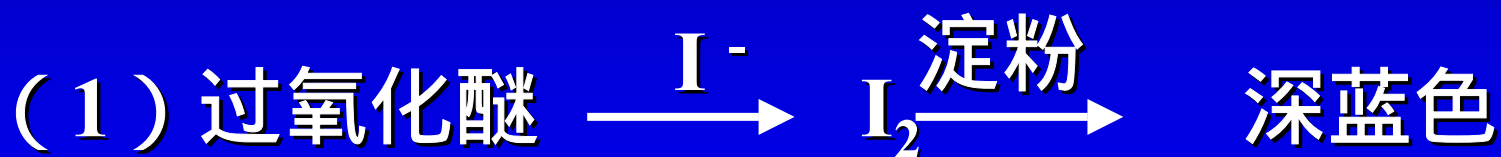


### 3. 生成过氧化物

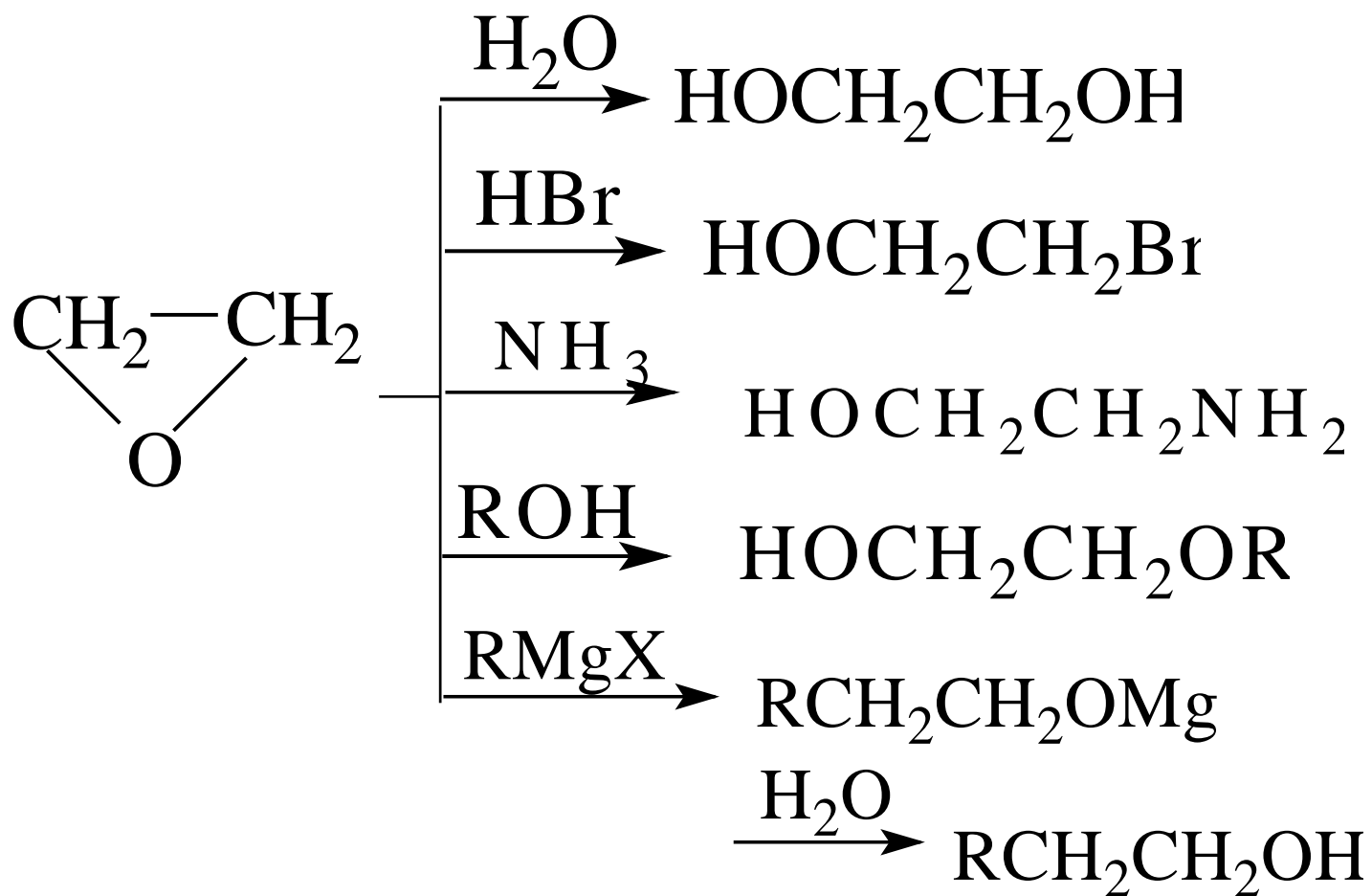


过氧化物（易炸）

检查：



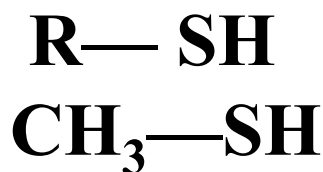
### 三、重要的醚(环氧乙烷)



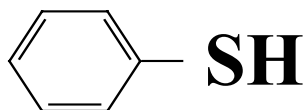


# 一、硫醇、硫酚、硫醚的命名

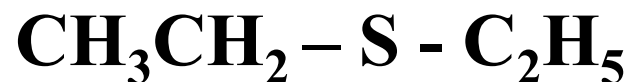
在相应含氧物前加“硫”字，  
—SH 巯基或氢硫基



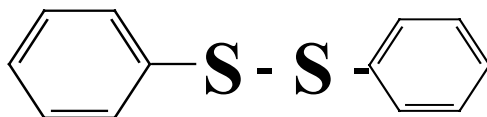
甲硫醇



苯硫酚



乙硫醚



二苯基二硫

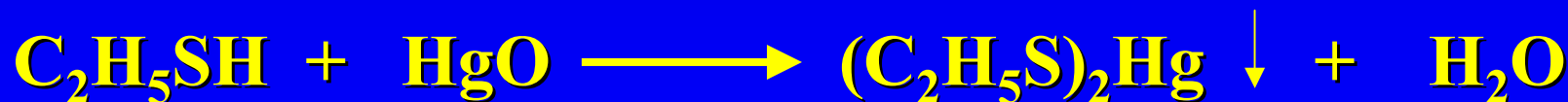
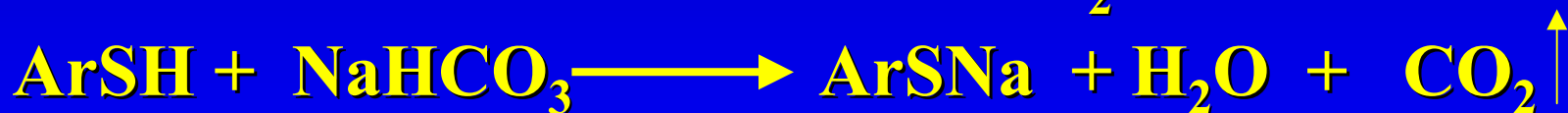
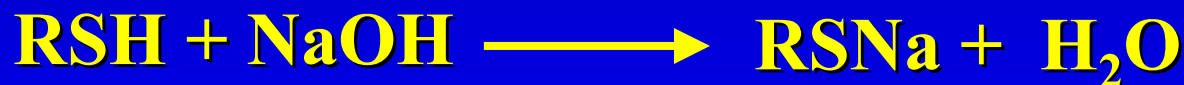


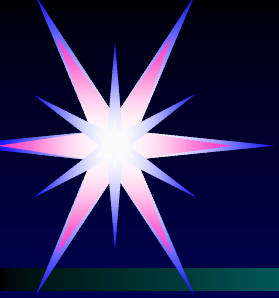
## 二、化学性质

### 1. 硫醇和硫酚的酸性比相应的醇和酚强

	$C_2H_5SH$	$C_6H_5SH$	$C_2H_5OH$	$C_6H_5OH$
$pK_a$	10.5	7.8	17	9.98

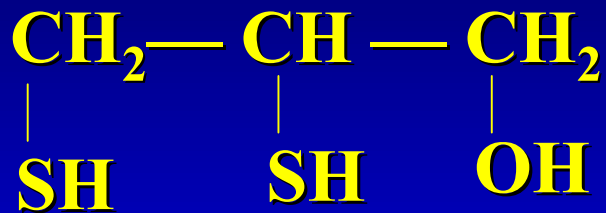
成盐：



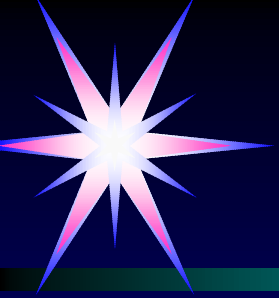


解毒：

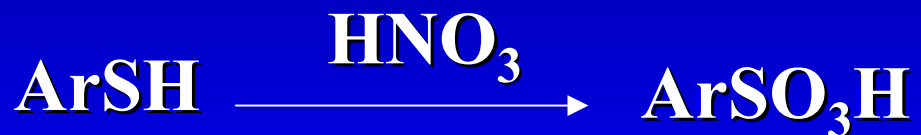
巴尔

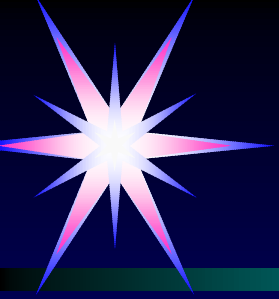


2,3-二巯基-1-丙醇



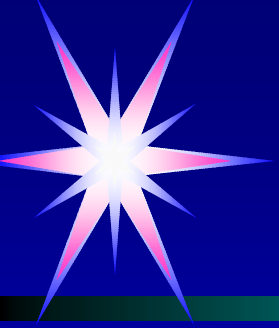
## 2. 氧化反应





# 第八章 重点讲解问题

1. 醇、酚、醚的命名
2. 醇、酚、醚的物理性质
3. 醇、酚、醚的化学性质
4. 硫醇、硫酚、硫醚的命名和性质



再见  
Good-bye

