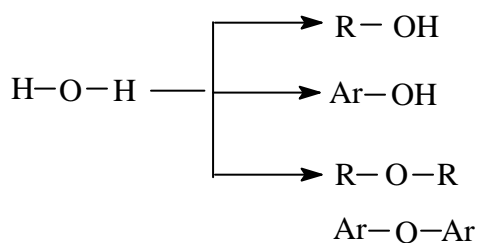
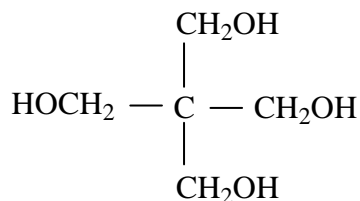
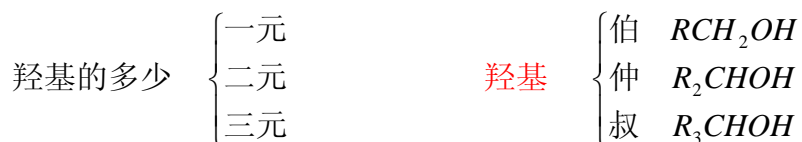


第九章 醇、酚、醚



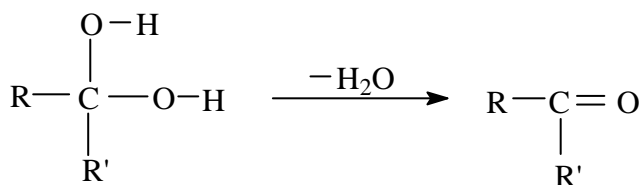
§ 9.1 醇的结构、分类、同分异构和命名

1. 分类



季戊四醇

当同一碳上连有多个羟基时，化合物不稳定，易失水生成醛。



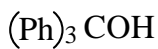
2. 结构:

C 原子 sp^3 杂化, O 原子 sp^3 杂化, $\begin{array}{c} \diagup \\ \diagdown \end{array} \text{C} - \ddot{\text{O}} - \text{H}$ P 轨道中有两对孤对电子。

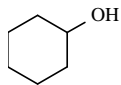
3. 命名:

(1) 普通命名法:

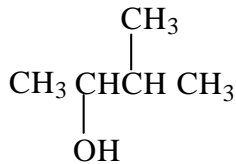
例如: $\text{CH}_3\text{CH}_2\text{OH}$ $(\text{CH}_3)_2\text{CHOH}$ $(\text{CH}_3)_3\text{COH}$



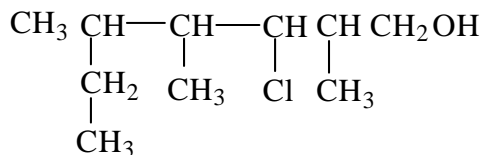
三苯甲醇



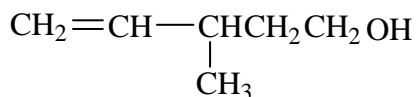
(2) 系统命名：以含羟基的最长链为主链，从羟基端编号。例如：



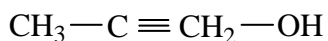
3-甲基-2-丁醇



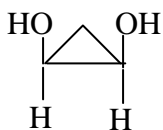
2, 4, 5-三甲基-3-氯-1-庚醇



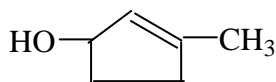
3-甲基-4-戊烯-1-醇



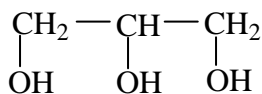
2-丁炔-1-醇



顺-1, 2-环丙二醇



3-甲基-2-环戊烯-1-醇



丙三醇

4. 物性：

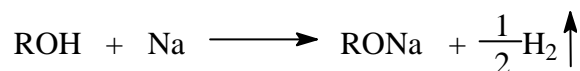
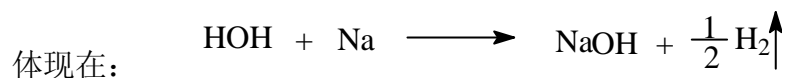
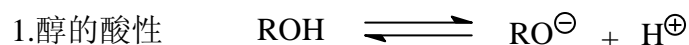
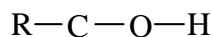
低级醇溶于水，多元醇与水无限混溶。

沸点随分子量增加而升高；直链>支链（同 C 原子数） **P220**

多元醇的沸点高，乙二醇 b.p. 197℃； 丙三醇 290℃。

低级醇与 MgCl_2 ， CaCl_2 形成结晶状的分子化合物（类似水合物），如 $\text{MgCl}_2 \cdot 6\text{CH}_3\text{OH}$ 、 $\text{CaCl}_2 \cdot 3\text{C}_2\text{H}_5\text{OH}$ ，所以醇不能用这些盐干燥，一般用无水 K_2CO_3 、 CaO 等。

5. 化学性质：



pKa = 16, 酸性比水弱, 水的 pKa = 15.7

由于烷基的给电子效应, 使得稳定性 $\text{RCH}_2\text{O}^- > \text{R}_2\text{CHO}^- > \text{R}_3\text{CO}^-$

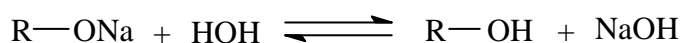
所以与 Na 反应的活性为 伯 > 仲 > 叔; 酸性也为伯 > 仲 > 叔。

当 α -C 上有吸电子基时, pKa 增大。

如 $\text{F}_3\text{CCH}_2\text{OH}$, pKa = 12.2

因为酸性: $\text{H}_2\text{O} > \text{ROH}$,

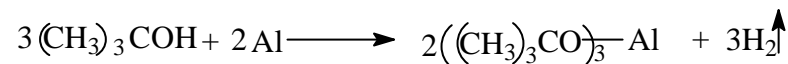
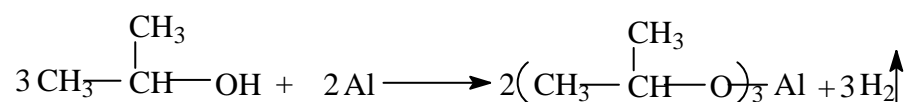
所以其共轭碱: $\text{RO}^{\ominus} > \text{OH}^{\ominus}$



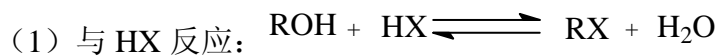
(白色固体)

平衡向右, 但工业上用除去反应中生成水的方式, 使平衡左移, 制备醇钠。(加入苯, 生成三元共沸物, 平衡左移。)

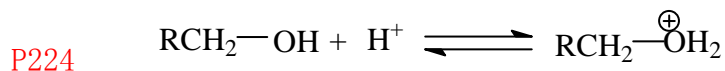
RONa 的亲核性大于 OH^{\ominus}

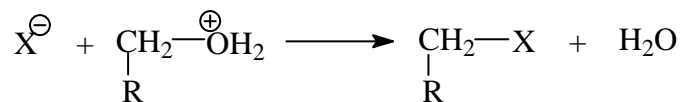


2. 取代反应

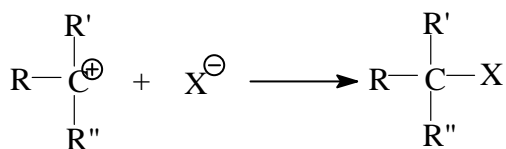
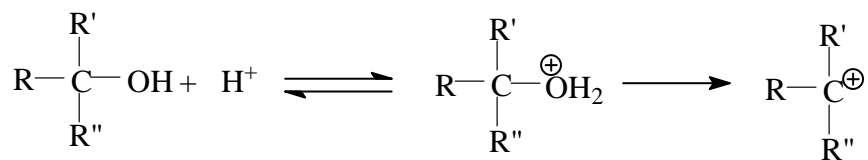


伯醇: $\text{S}_{\text{N}}2$





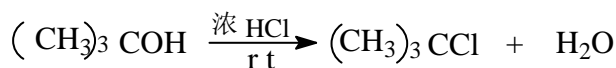
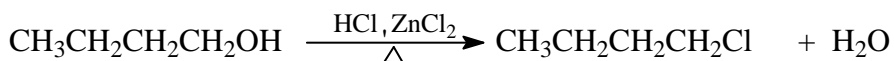
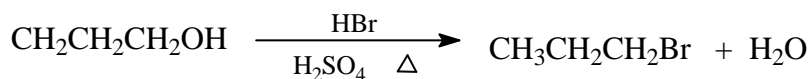
叔醇: S_N1



仲醇可为 S_N1 和 S_N2

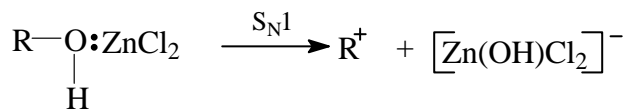
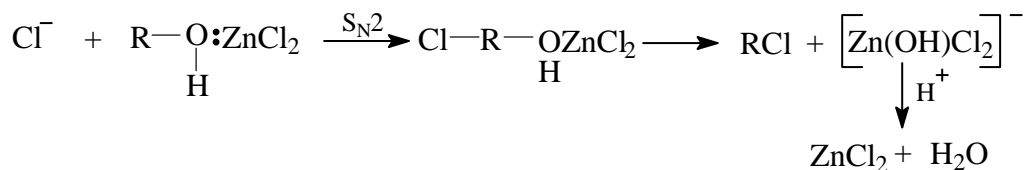
HX 反应活性: HI > HBr > HCl

醇的反应活性: 烯丙基 > 叔 > 仲 > 伯

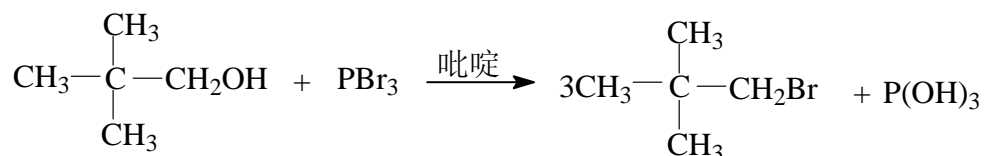


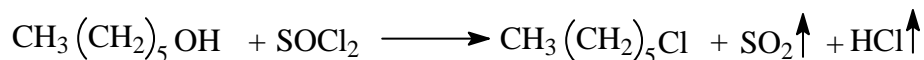
浓 HCl + ZnCl₂ → Lucas 试剂

区别 伯 (Δ)、仲 (放置)、叔 (立即) 醇。

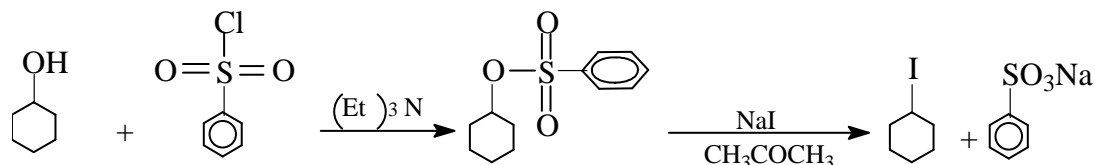


(2) 与 PX₃ 和 SOCl₂ 反应:

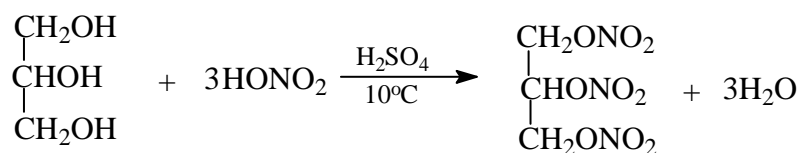
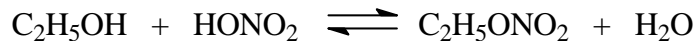
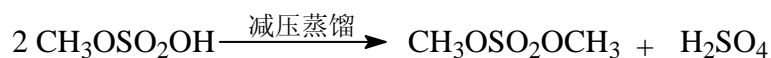
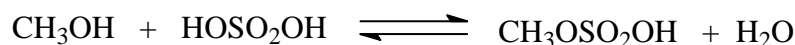




(3) 与磺酸酯的亲核取代反应:

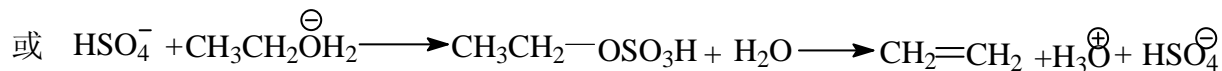
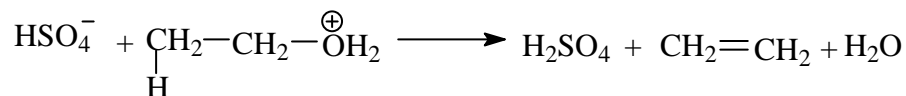
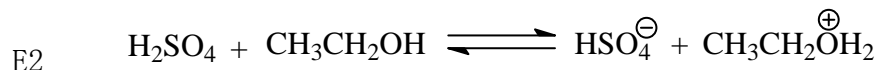


(4) 与无机酸反应:

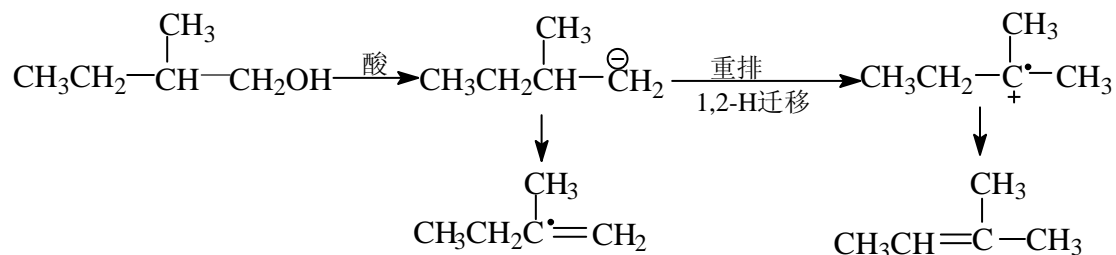


三硝酸甘油酯

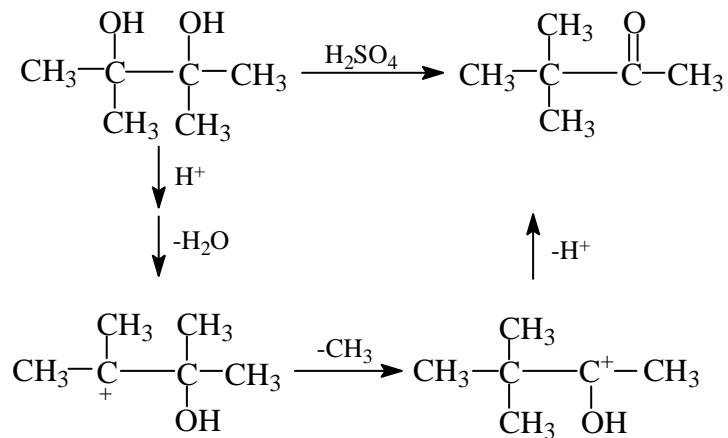
三. 消去反应: 一般为 E1, 也有 E2. 脱水剂: H_2SO_4 、 H_3PO_4 、 Al_2O_3 、 AlCl_3



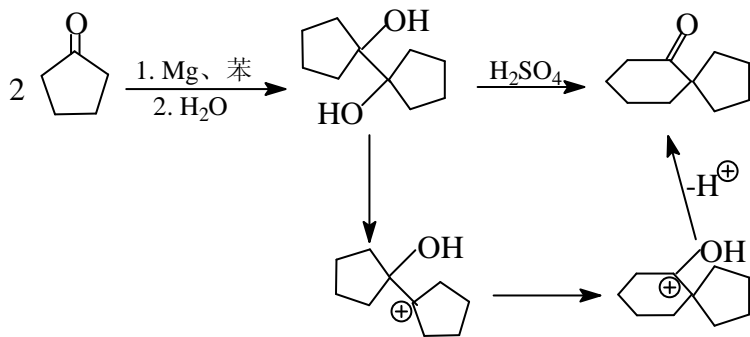
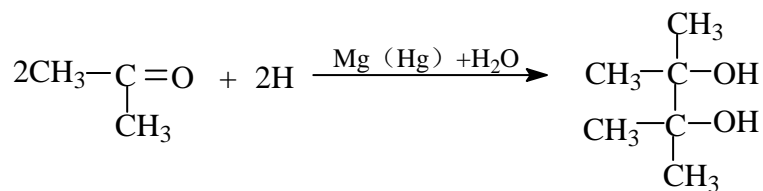
按 E1 历程一般要重排



为避免之, 可用 Al_2O_3 为催化剂。



其中：

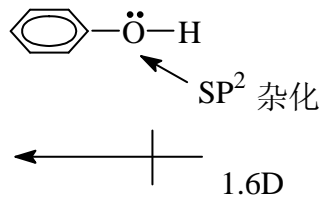


§ 9.4 酚的结构、命名、来源、物性

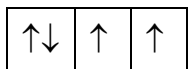
通式： Ar-OH Ar-CH₂-OH 是醇

一. 结构

π-P 共轭



氧原子的两对位共用电子分别占据一个 SP² 杂化轨道和一个 P 轨道

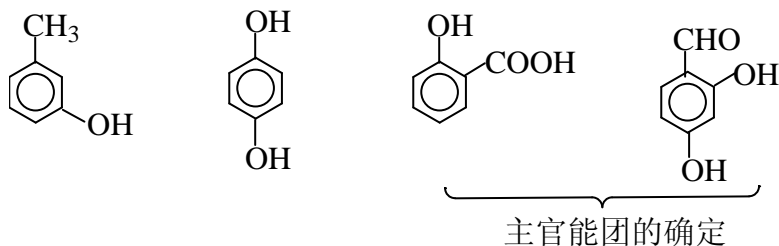


不等性 sp^2 杂化

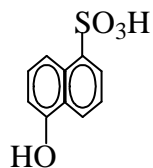
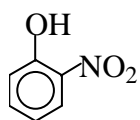
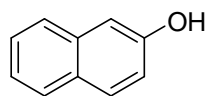
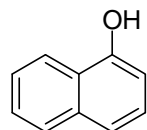
与 R—OH 相反

CH_3 —OH 1.7D

二. 命名: 在酚前面加上芳环的名称



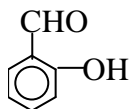
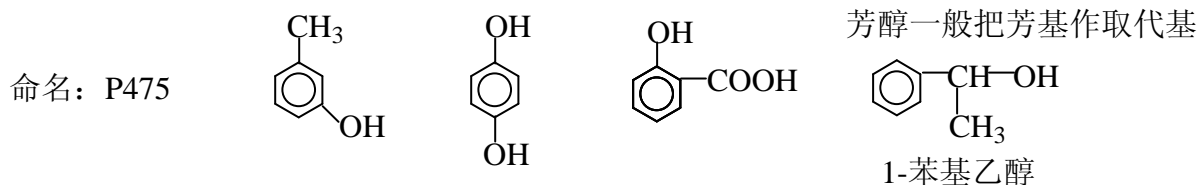
芳醇一般把芳环作取代基



5-羟基-1-萘磺酸

一. 结构和命名:

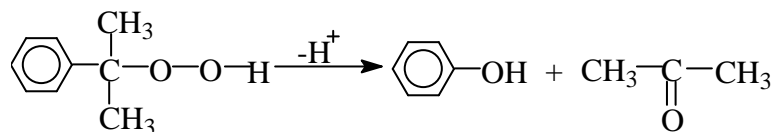
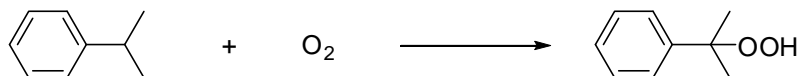
酚的通式: Ar-OH, Ar-CH₂-OH 是醇。



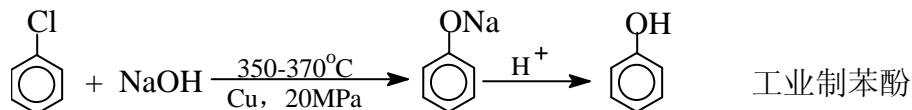
三. 制备:

1. 异丙苯氧化(P247):

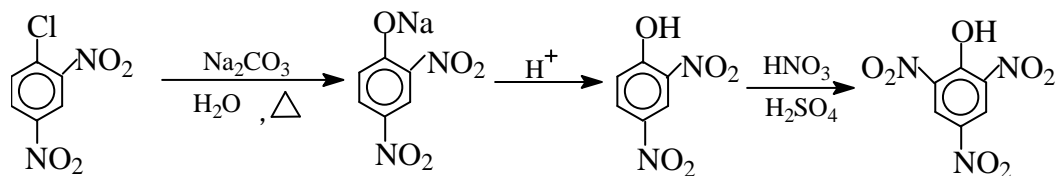




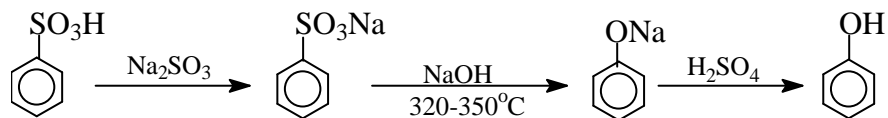
2. $\text{Ar}-\text{Cl} \longrightarrow \text{Ar}-\text{OH}$ (亲核取代)



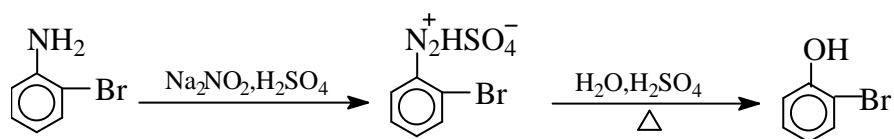
当卤原子邻/对位有强吸电子基时，反应较易进行。



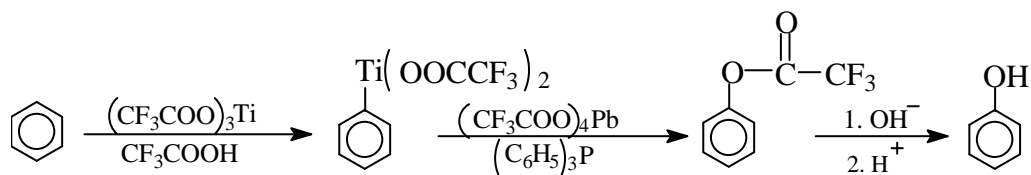
3. $\text{Ar}-\text{SO}_3\text{H} \longrightarrow \text{Ar}-\text{OH}$



4. $\text{Ar}-\text{NH}_2 \longrightarrow \text{Ar}-\text{OH}$



5. 实验室合成:



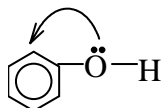
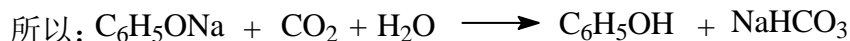
三. 物性 P238

一般为固体，少数烷基酚为液体。苯酚溶于热水，在冷水中 100g 水中可溶解 9g。分子间有氢键，有较高的沸点和熔点。

四. 化性

1. 酚羟基的性质:

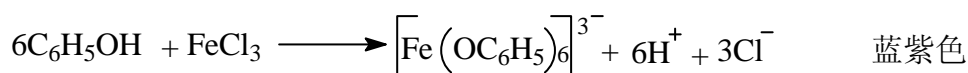
(1). 酸性:



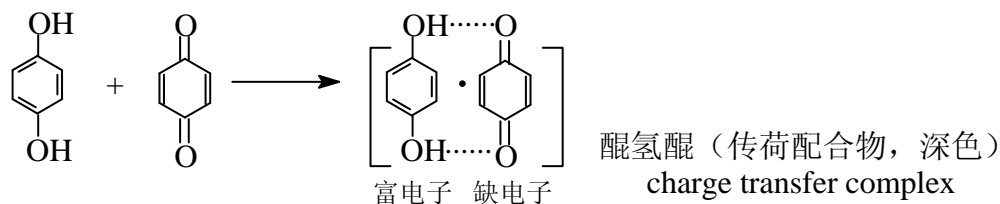
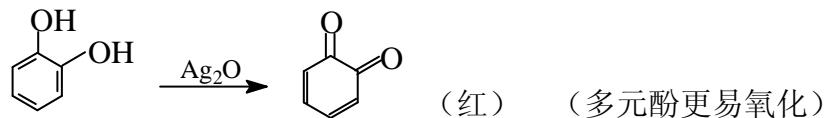
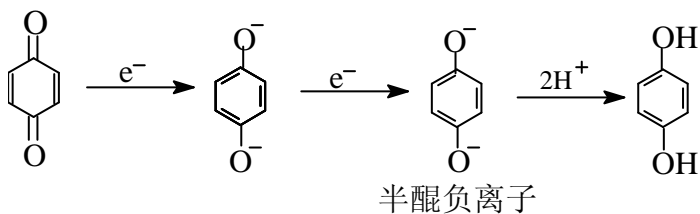
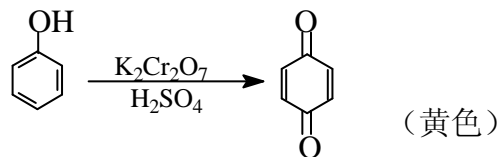
当环上有吸电子基时, 酸性更强, 可用于分离、提纯

(2). 与 FeCl_3 显色:

凡有 $\text{>C}=\overset{\text{O}}{\text{C}}-\text{OH}$ 结构的化合物, 都有颜色反应

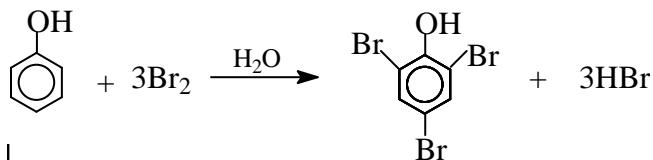


三. 氧化反应:

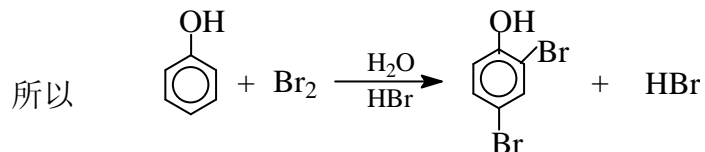


四. 芳环上的反应: ——第一类定位基, 活化苯环

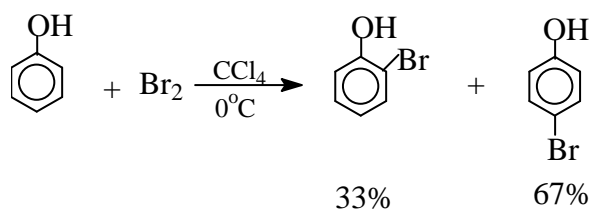
(1) 卤化:



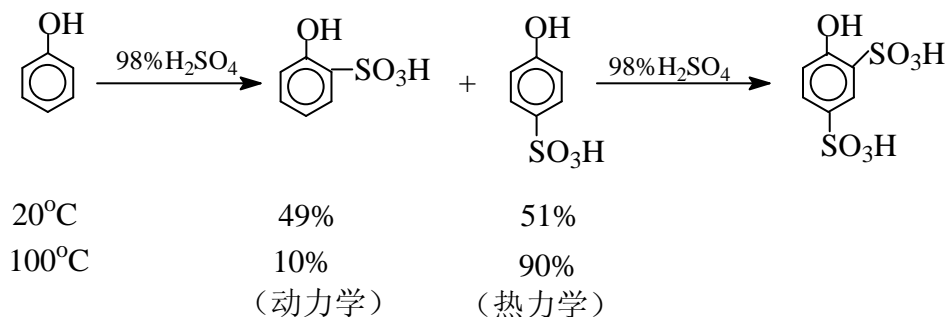
I



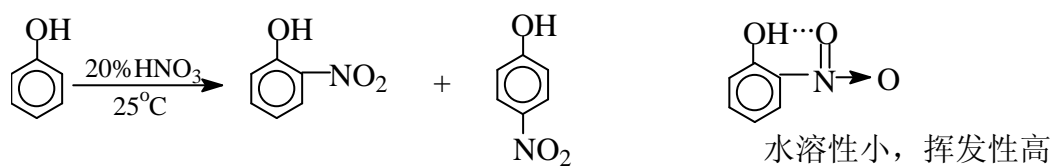
在低极性溶剂中，



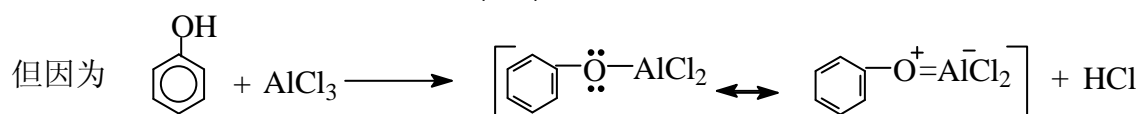
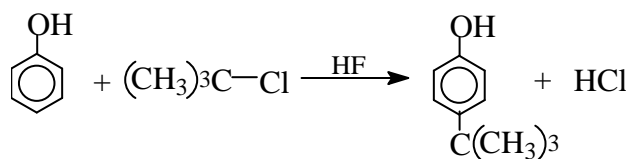
(2) 磺化:



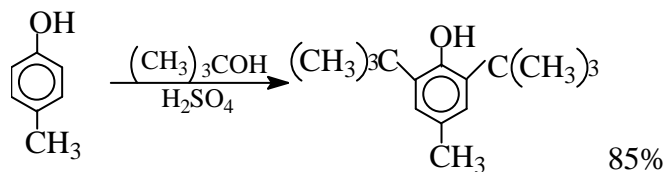
(3) 硝化:



(4) Friedel-Crafts 反应: ——对位优先, 其次邻位。

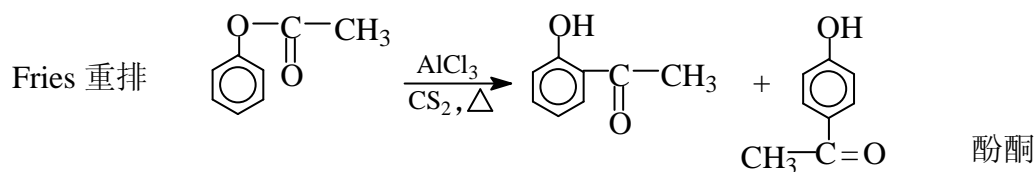
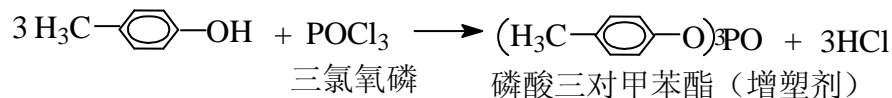
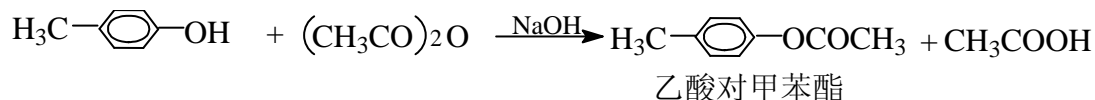


所以反应较难, 需要较多的 AlCl_3 催化剂。

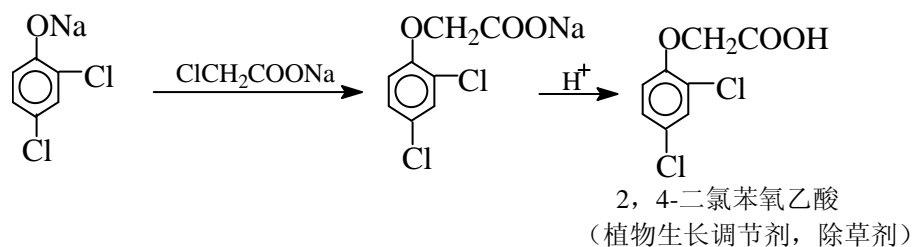
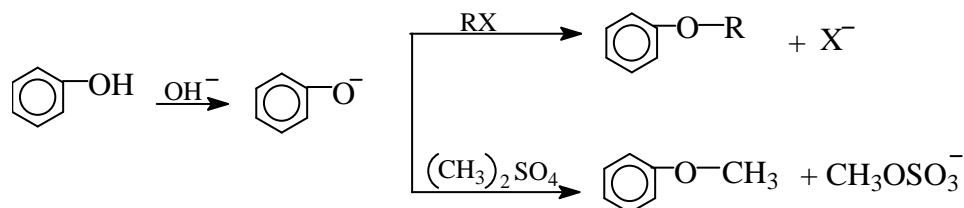


4-甲基-2, 6-二叔丁基苯酚 (抗氧化剂, 防腐剂)

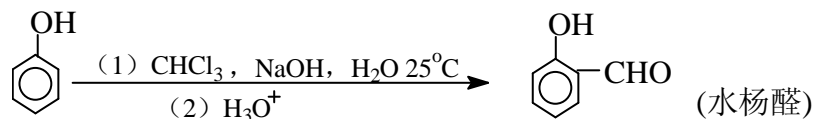
五. 酯的生成:

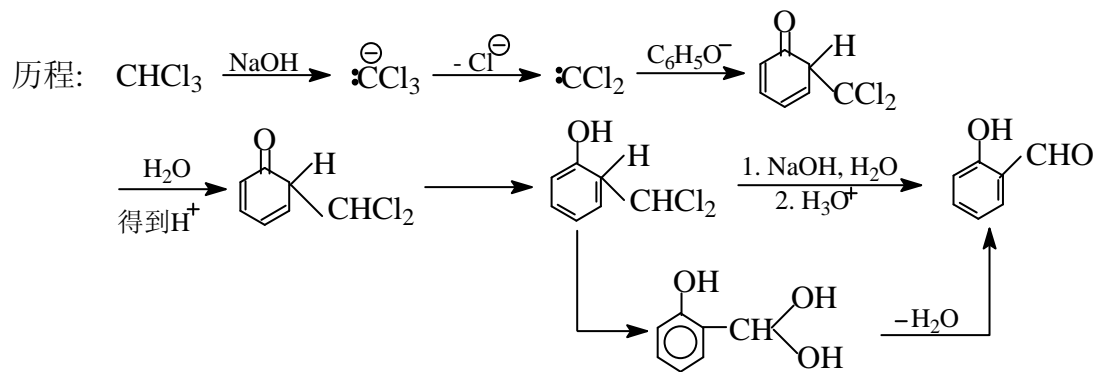


一般, 低温有利于对位, 高温有利于邻位。



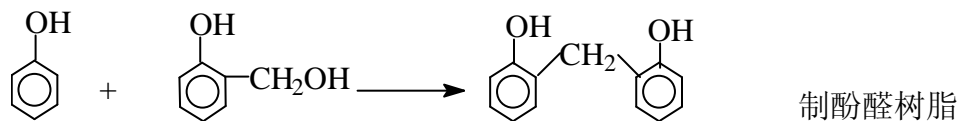
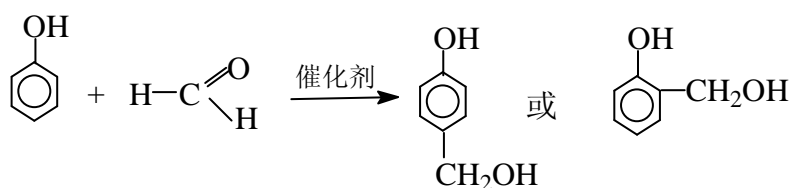
(5). 赖默-梯曼 (Reimer-Tiemann) 反应



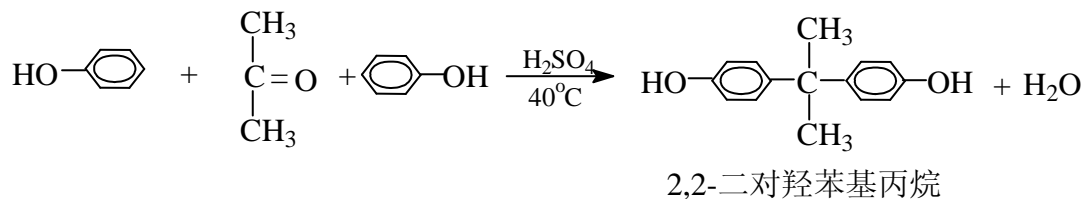


以下略

(6). 与甲醛缩合



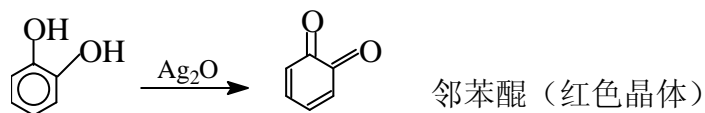
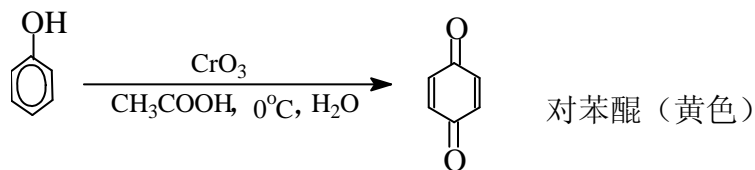
(7). 与丙酮缩合——双酚 A——环氧树脂 (略)

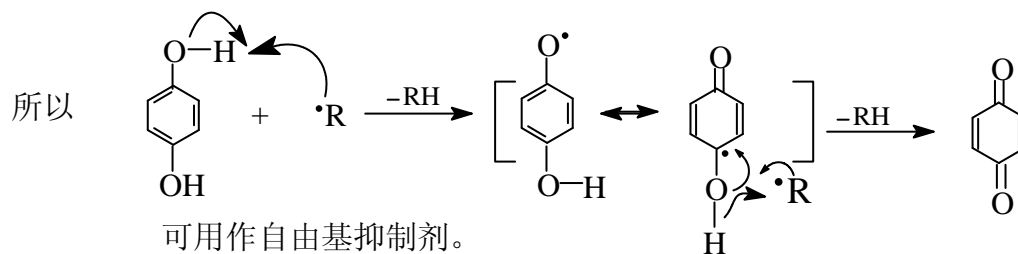
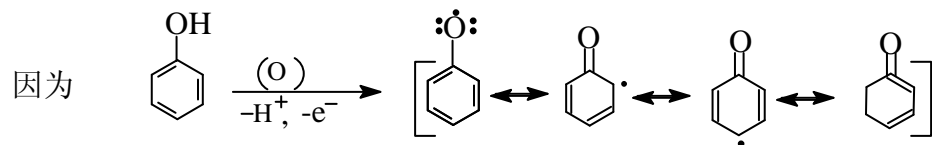
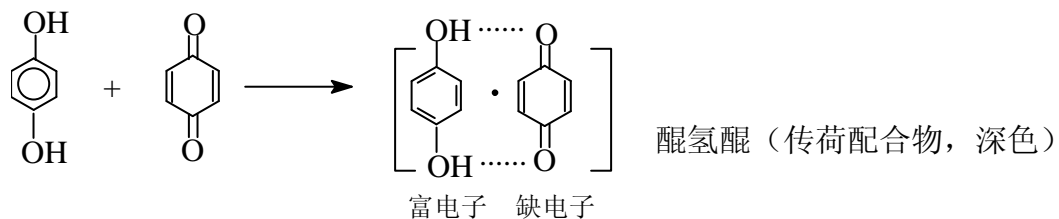


3. 还原:



4. 氧化:



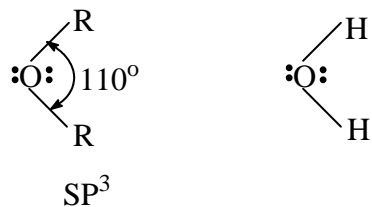


(五) 重要的酚和芳醇举例

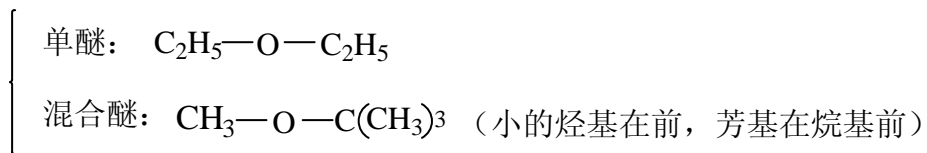
§ 9.6 醚

第二节 醚

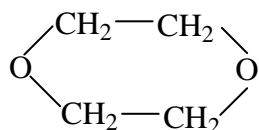
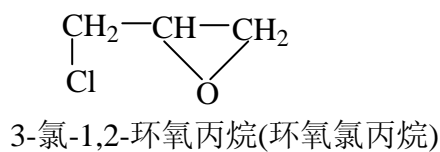
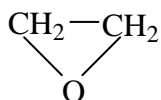
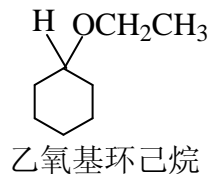
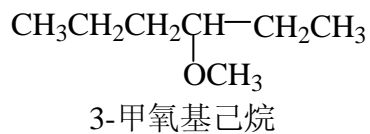
(一) 醚的结构和命名



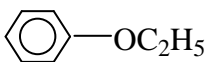
1. 命名:



对于结构复杂的醚, 把烃基作母体, $-OR$ 看作取代基。



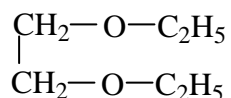
1,4-二氧六环或2-恶烷



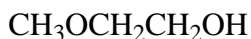
苯乙醚



THF(环氧丁烷)



乙二醇二乙醚



2-甲氧基乙醇

(二) 醚的性质

1. 物性:

沸点低, 高级醚不溶于水, 但 THF 溶于水。化学惰性, 常用作溶剂, 医用麻醉剂。



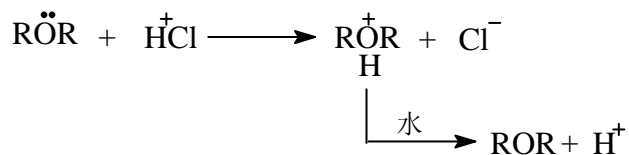
氧原子在外可以于水形成氢键。

溶于水

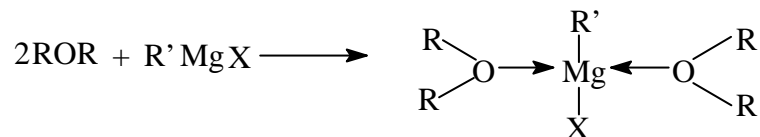
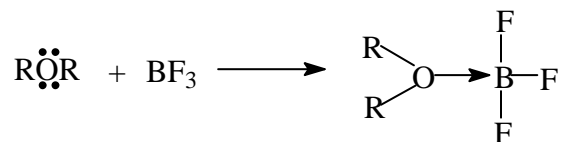
2. 化性:

对碱、氧化剂、还原剂都很稳定, 常温下于 Na 不反应, 可用 Na 干燥乙醚。

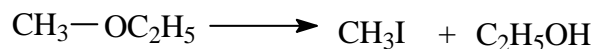
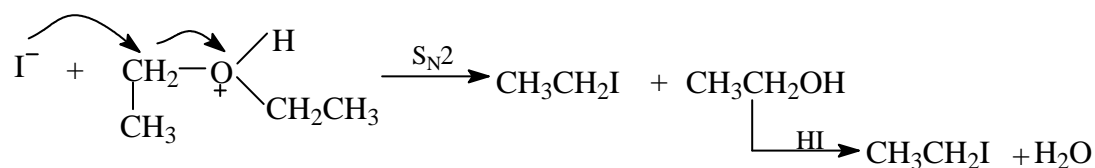
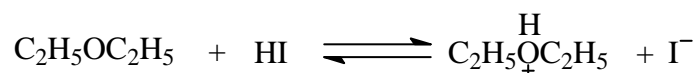
(1) 杨盐的生成——溶于强浓酸中



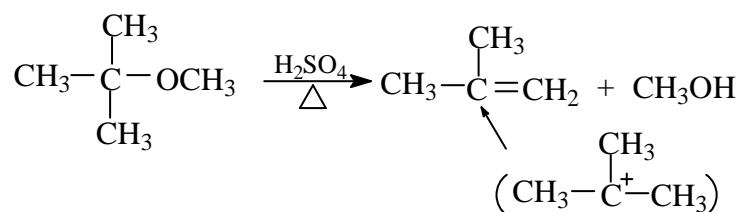
与缺电子体系形成络合物。



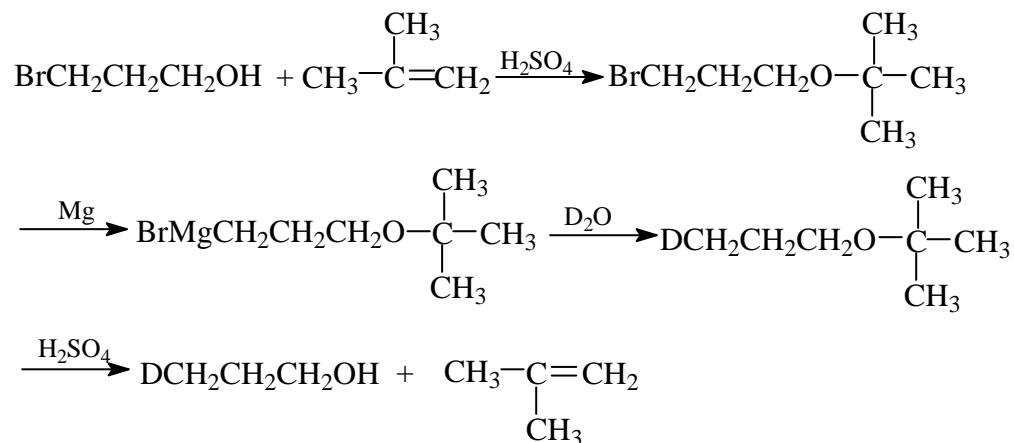
(2) 醚键的断裂: R—O—R (最有效的试剂为氢卤酸, HI 或 HBr)



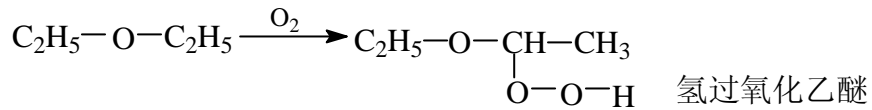
醚键的断裂一般是在含碳原子较少的烷基处断裂, 一般是较小的烷基先生成碘代烷, 生成酚。



叔丁基醚常用来保护醇羟基。

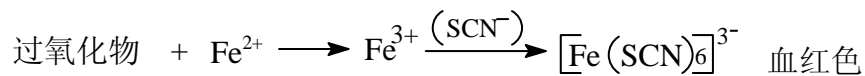


(3) 过氧化物的生成

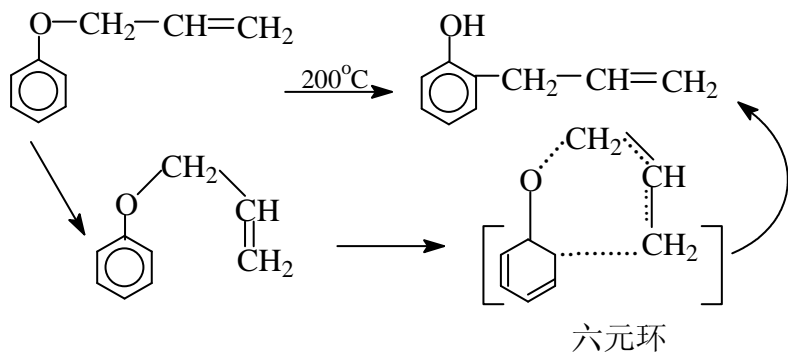


防止：加阻聚剂（对苯二酚等）

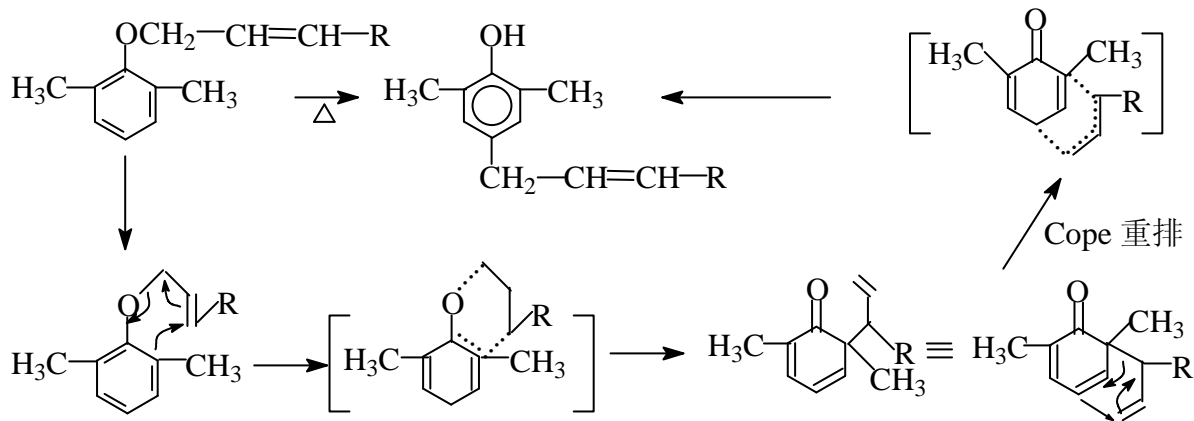
检验：加还原剂



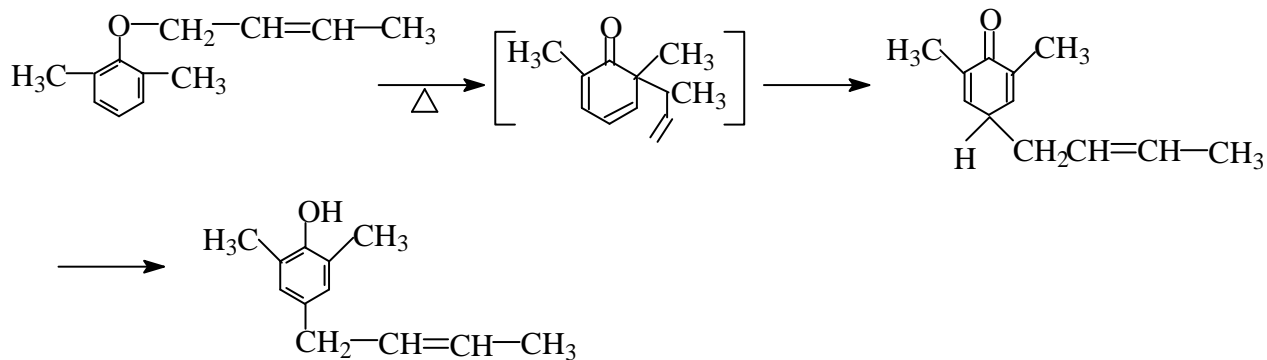
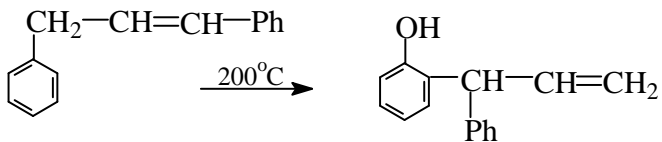
(4) Claisen 重排和 Cope rearrangement



当芳基烯丙基醚的邻位有取代基时，

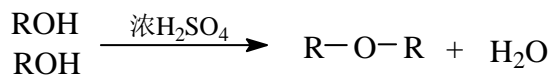


经过两次重排，烯丙基保持原有结构。

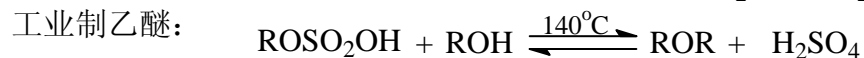
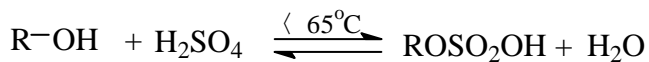


(三) 醚的制备

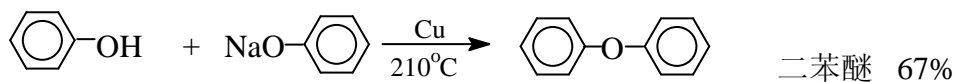
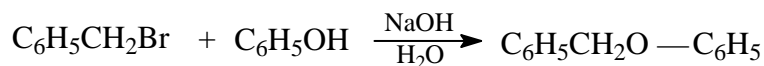
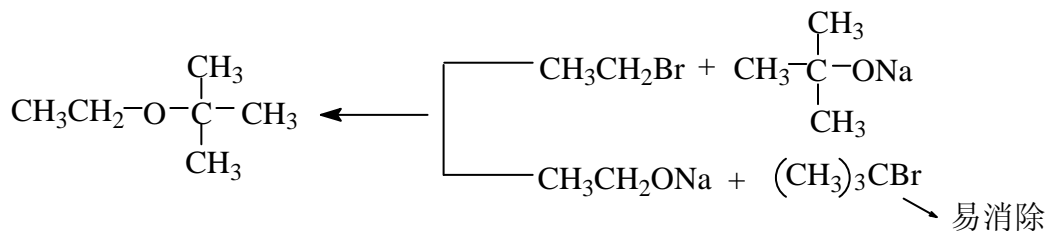
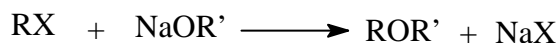
1. 醇脱水—制简单对称醚



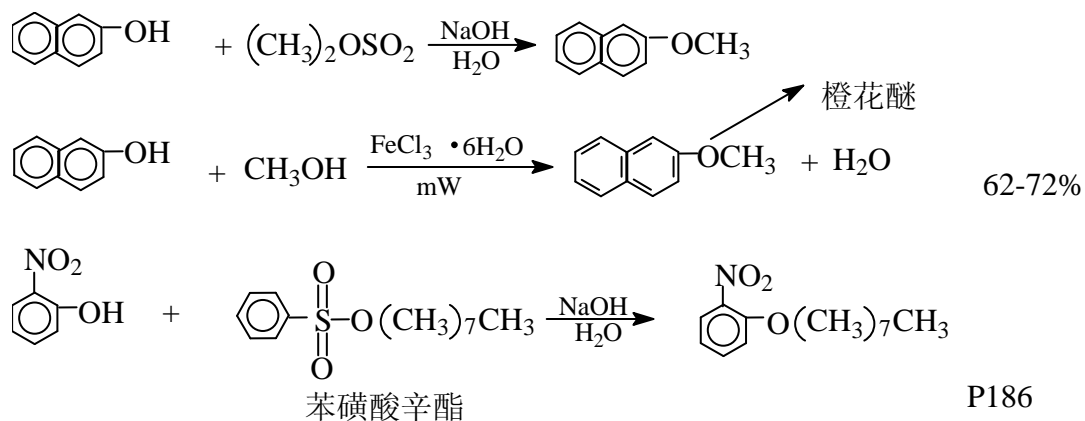
产量 $1^\circ > 2^\circ > 3^\circ$ (3° 醇易生成 烯烃)



2. Williamson 合成—制混合醚（或对称醚）

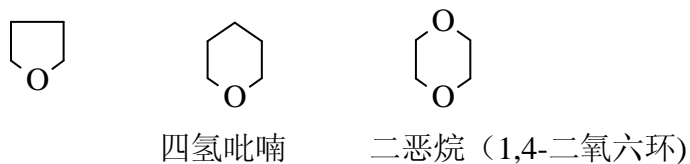


因为卤代芳烃种的卤素不易被取代，



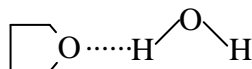
§ 9.7 环醚

一. 五元和六元环醚 P259

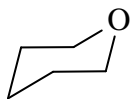


性质:

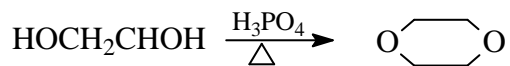
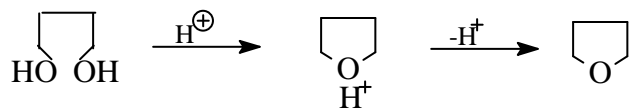
1. 溶于水 (形成氢键)



2. 椅式构象

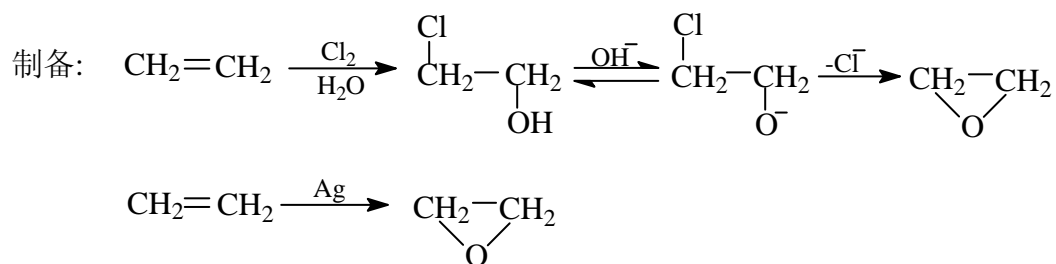


3. 由二元醇脱水制备:



二. 环氧化合物 (epoxide)

环氧乙烷



性质: 与亲核试剂作用开环 P260

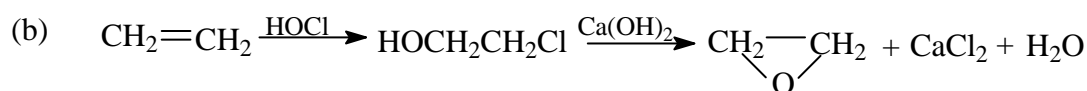
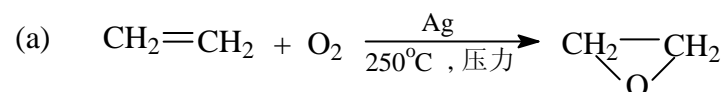
(四) 重要的醚

1. 乙醚:

2. 环氧乙烷: 无色有毒的气体, 沸点: 11°C , 溶于水、醇、醚。

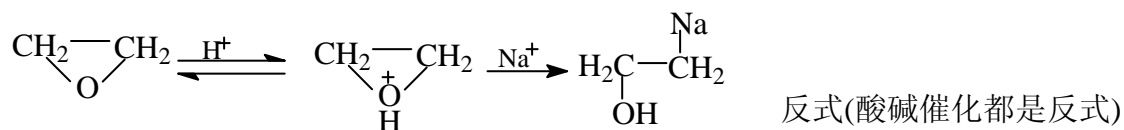
其蒸气与空气混合达到一定的比例时, 会爆炸。

①制备:

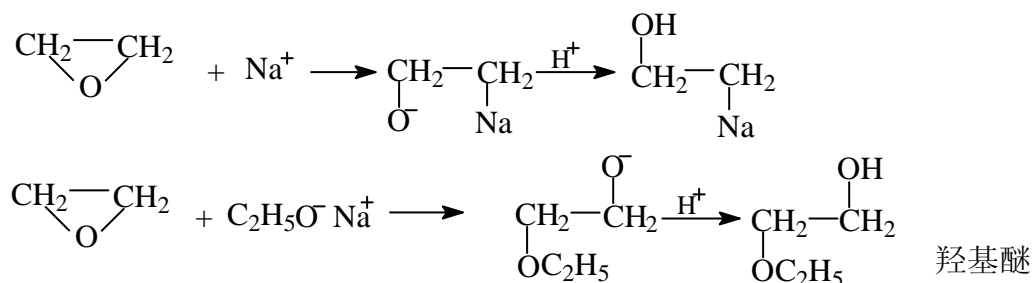


②性质: P259 在酸碱作用下, 与活泼氢试剂作用 (非离子表面活性剂)

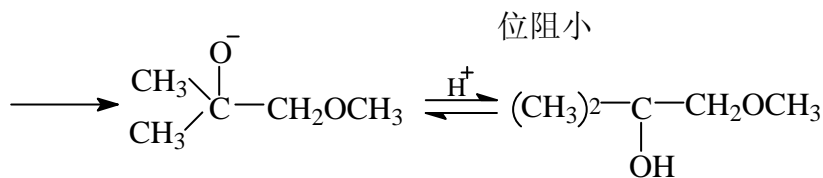
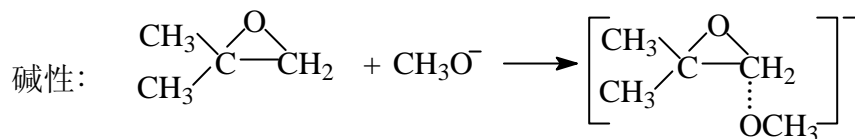
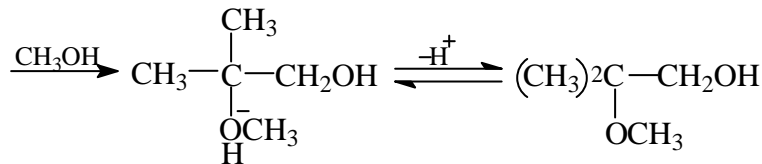
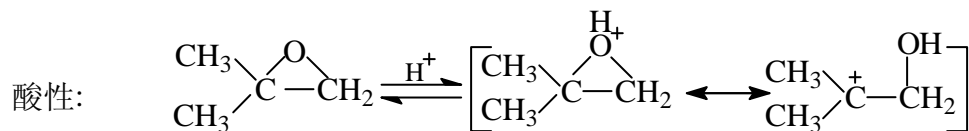
(a) 酸催化:



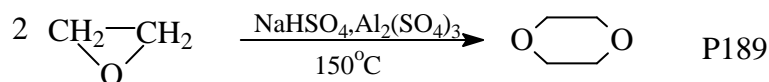
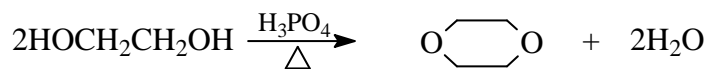
(b) 碱催化:



(c) 不对称环氧乙烷的环方向:



③1, 4-二氧六环(二恶烷) 沸点: 101°C, 有机溶剂

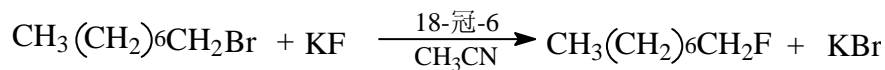
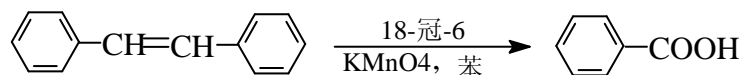


(五) 冠醚

分子中存在 $-(\text{OCH}_2\text{CH}_2\text{O})_n$ 的重要单位

- 命名: X-冠-Y (其中 X 为碳原子数, Y 为氧原子数) P261 (习惯命名)
- 性质: 根据空穴大小不同, 对金属离子的络合有选择性。P262
- 应用: 相转移催化剂 (Phase Transfer Catalysis, PTC)

内圈氧原子亲水, 外圈碳氢原子亲油。

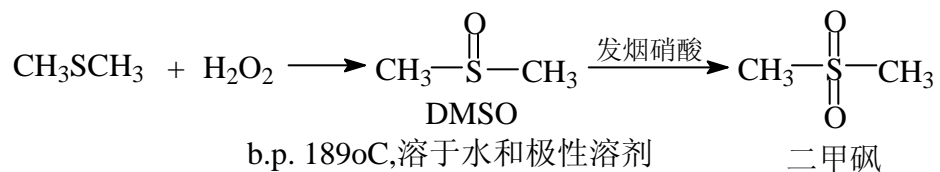


- 制备: Williamson 合成 P263

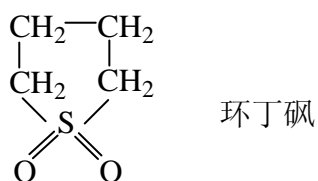
(六) 硫醚

1. 命名:

2. 性质: 沸点>醚, 不溶于水。



此外



3. 制备 P266

§ 9.8 重要的醇、酚、醚 (自阅)

§ 9.9 硫醇、硫酚和硫醚



(thiol) (thiophenol) (sulfide)

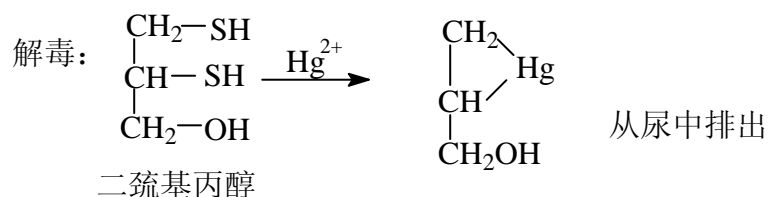
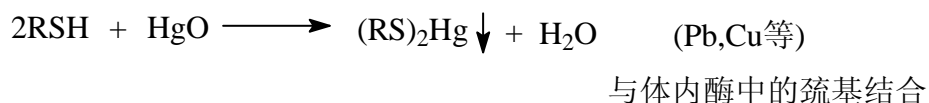
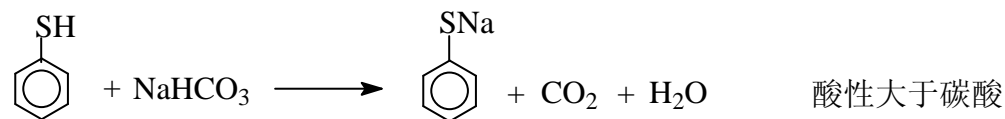
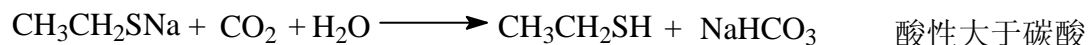
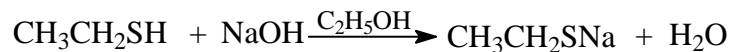
—SH—巯基 (qiu mescapto) 或 (sulfhydryl group)

一. 物性

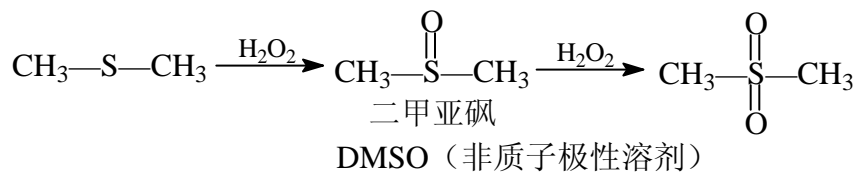
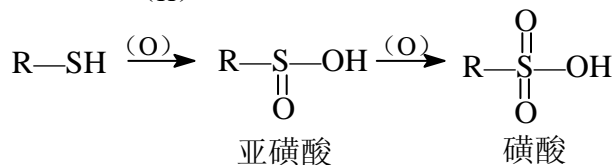
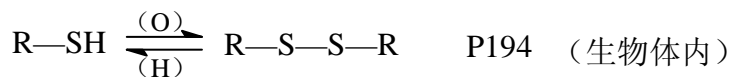
沸点小于相应的醇、酚 (无氢键), 溶解度也小于相应的醇、酚。但硫醚的沸点大于醚, 且不溶于水。

二. 化性:

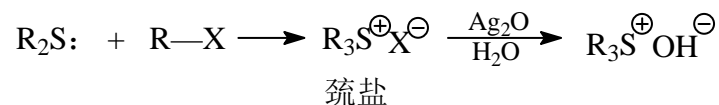
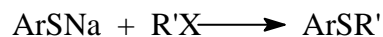
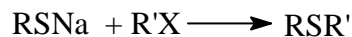
1. 酸性: 大于醇、酚 P264



2. 氧化



3. 硫醇、硫酚和硫作为亲核试剂: 亲核性大于氧



4. 制备: P265