

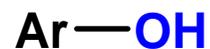
第十章 酚和醌

主要内容

- 酚羟基的性质：酸性，醚化和酯化
- 酚类芳环上的亲电取代（重点介绍几个新反应）
- 间苯二酚的**Houben-Hoesch**反应

第一节 酚

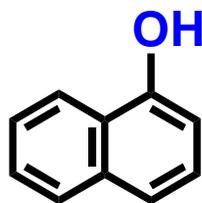
■ 酚类结构通式



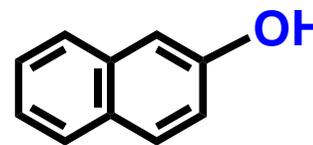
羟基直接与
芳环相连



苯酚



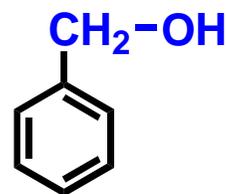
α -萘酚



β -萘酚

比较:

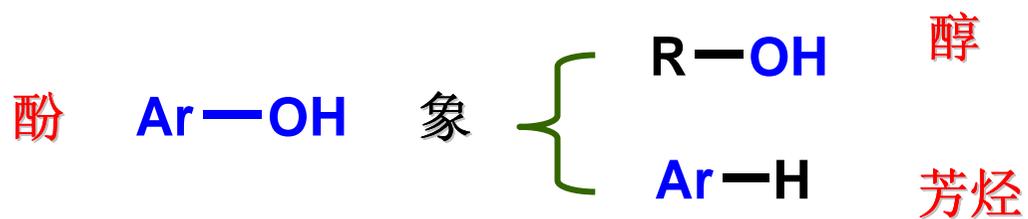
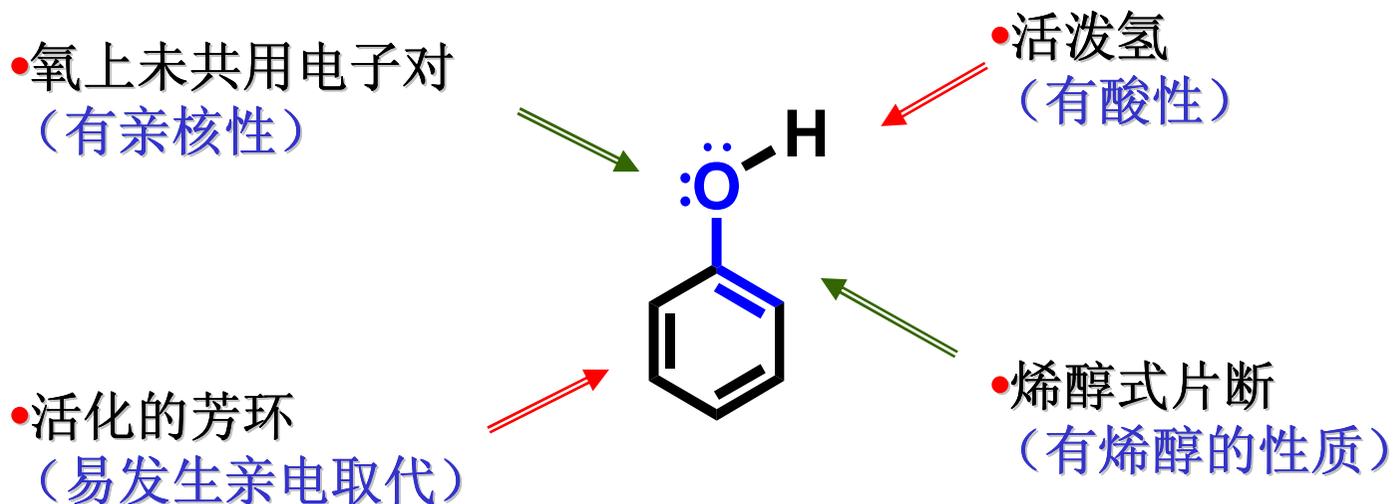
芳香醇（带有芳基
的醇类化合物）



苯甲醇，苄醇

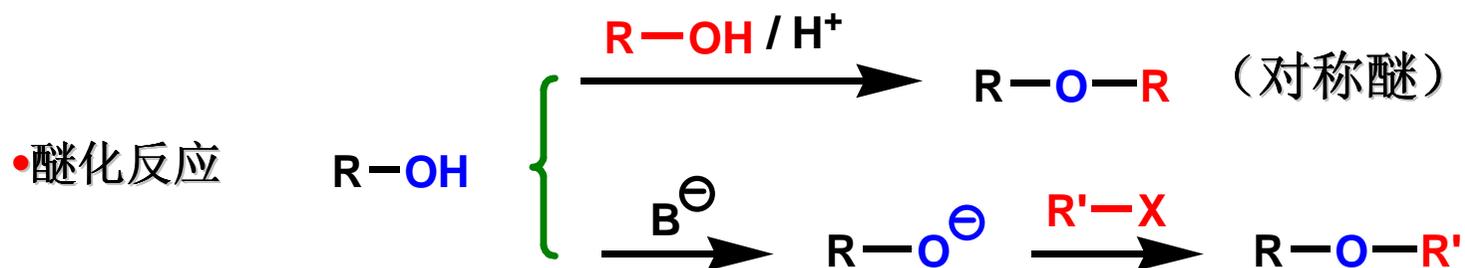
一.分类和命名

二. 化学性质

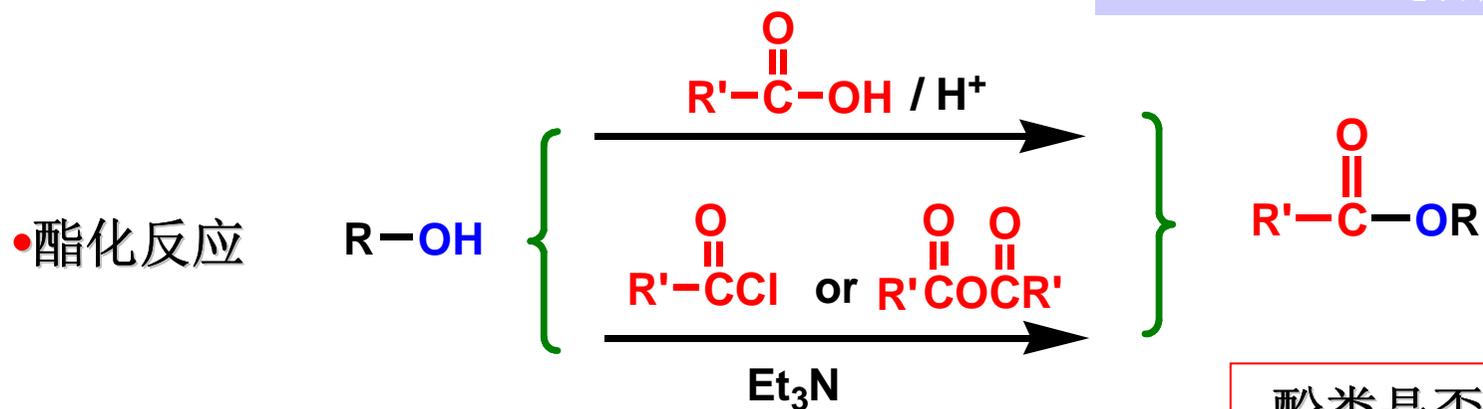


■ 复习：醇类羟基的典型的化学性质

- 羟基H有酸性
- 羟基O有亲核性



Williamson 醚合成法



酚类是否有类似反应？

1. 酚羟基的性质

■ 酚羟基的酸性

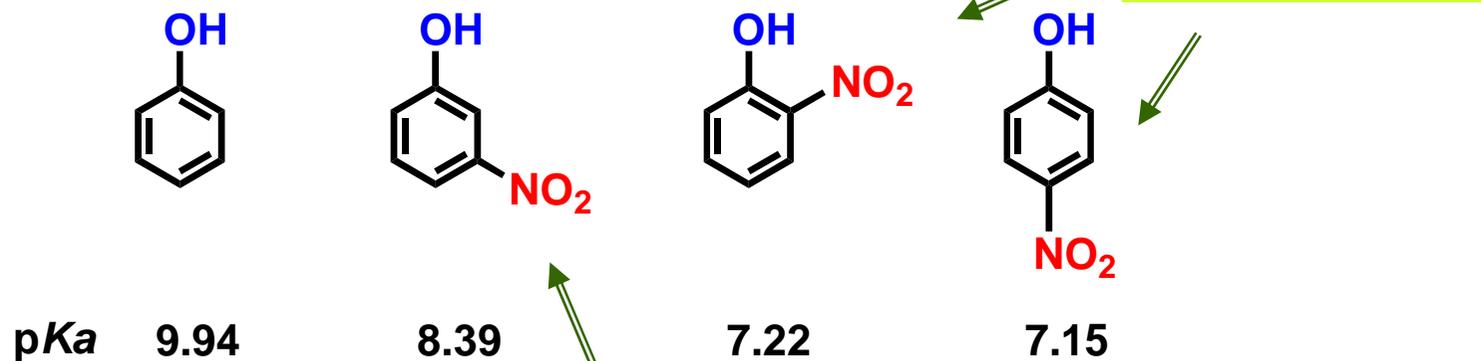
	R-COOH	Ar-OH	R-OH
pKa	~ 5	~ 10	~ 18
NaOH	溶	溶	不溶
NaHCO ₃	溶	不溶	不溶

应用：有机物的纯化和分离



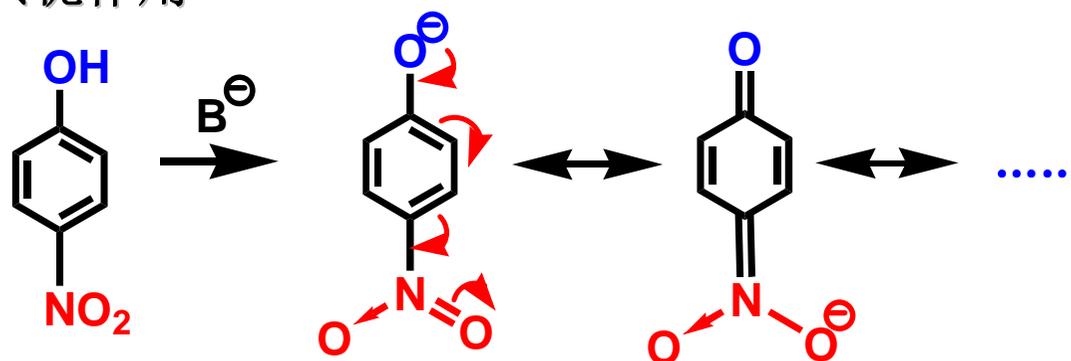
■ 环上取代基对酚羟基酸性的影响

• 吸电子基的影响（使酸性增强）

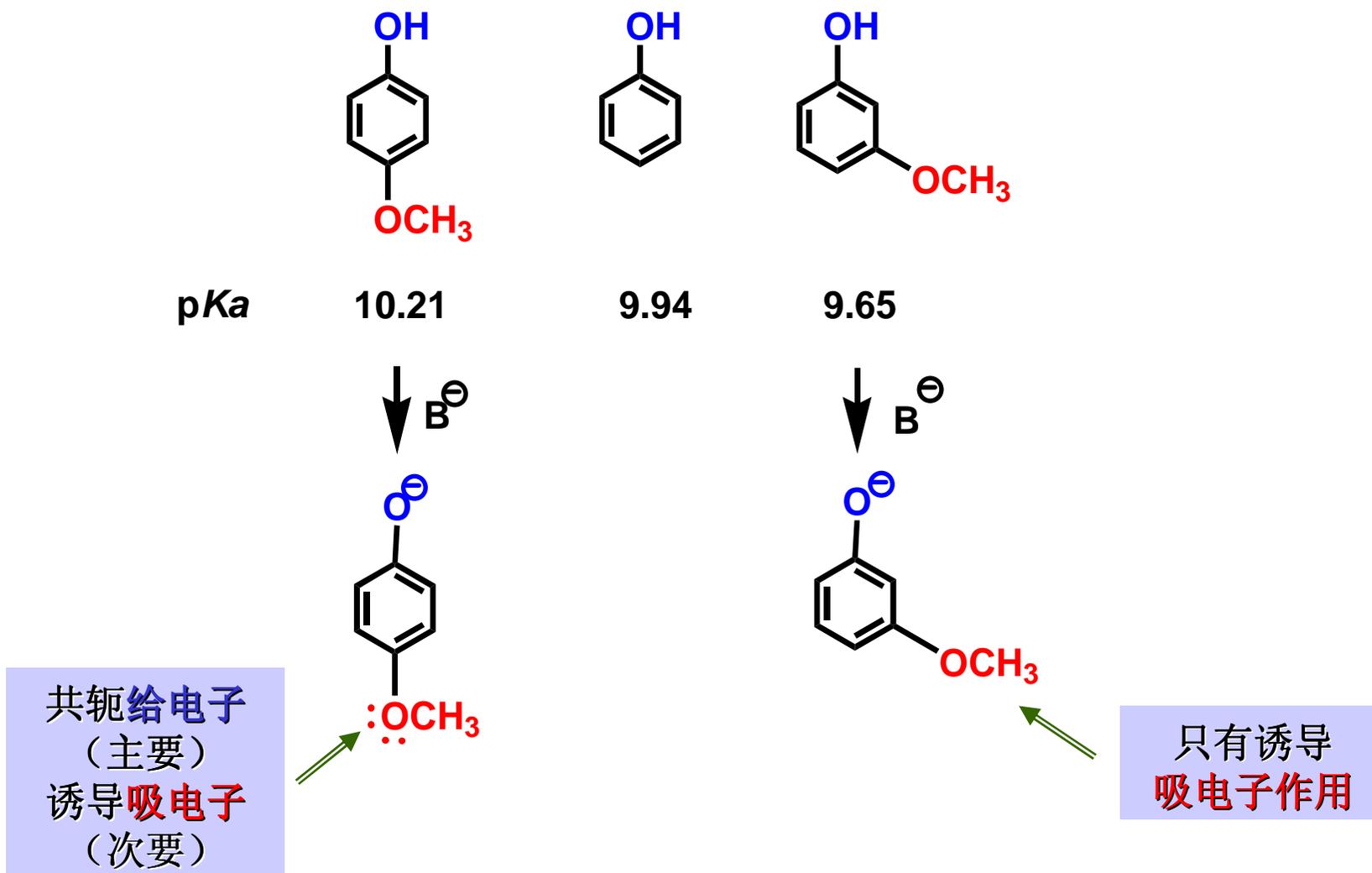


只有诱导吸电子作用

• 硝基的共轭作用

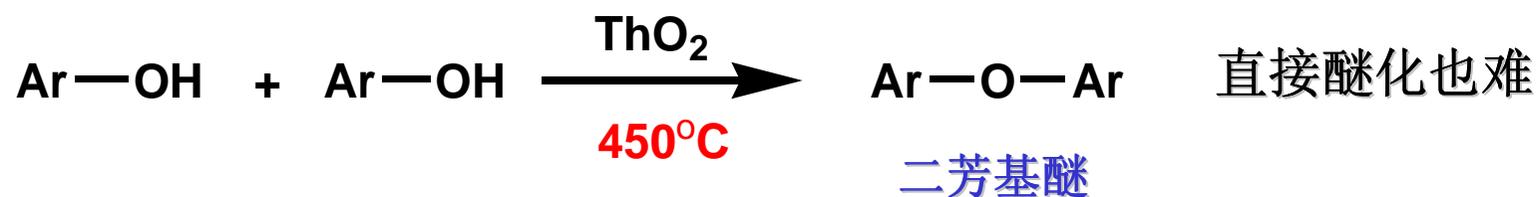
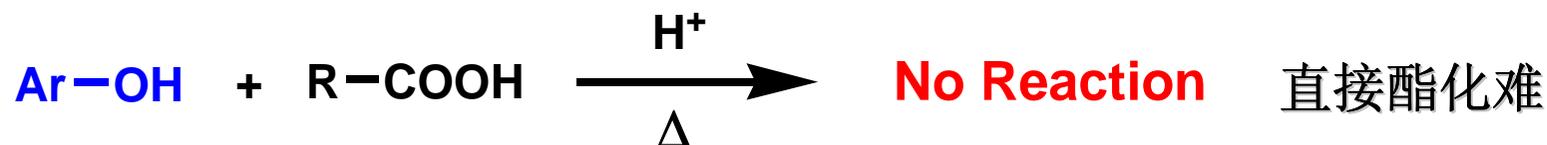


• 给电子基的影响（使酸性减弱）

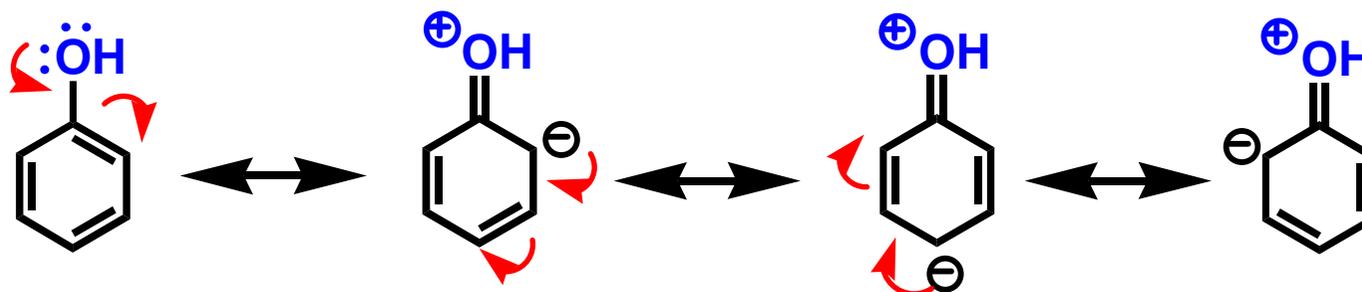


■ 酚羟基的亲核性（比醇弱）

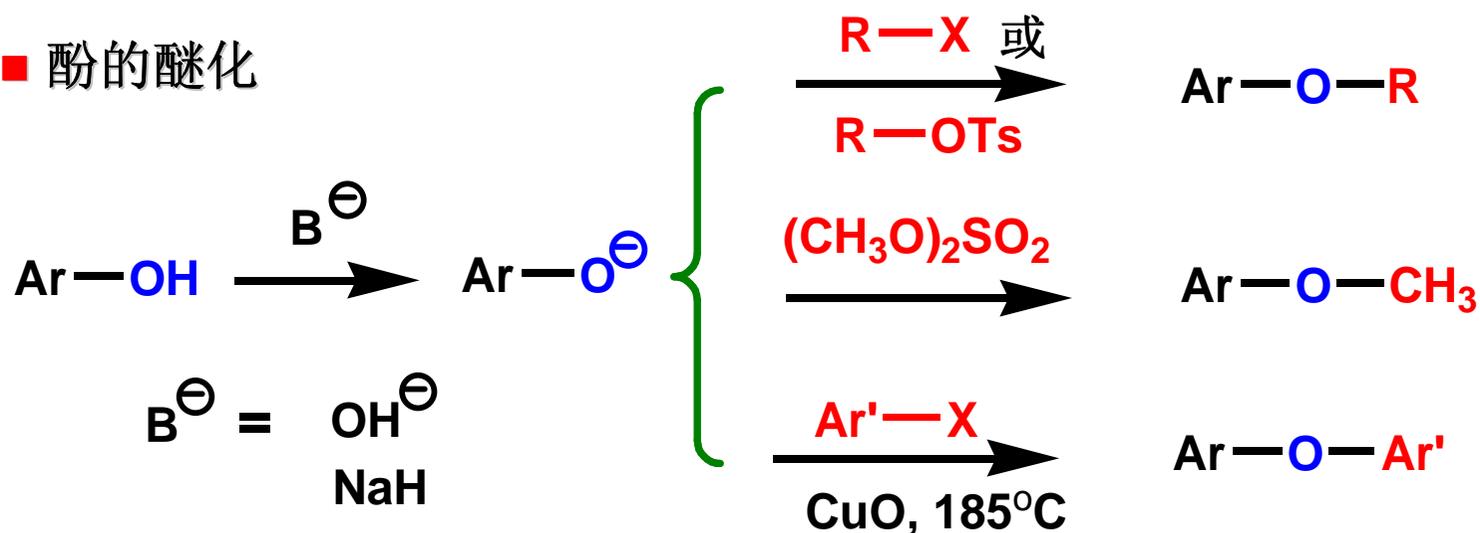
如：酚类化合物直接醚化和酯化较难



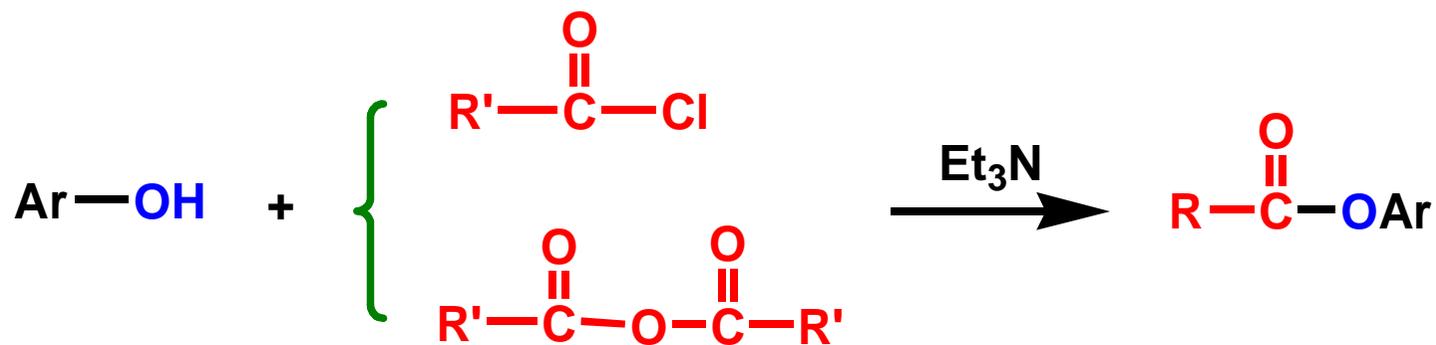
• 原因：酚羟基氧与苯环有共轭作用，使亲核性减弱



■ 酚的醚化



■ 酚的酯化

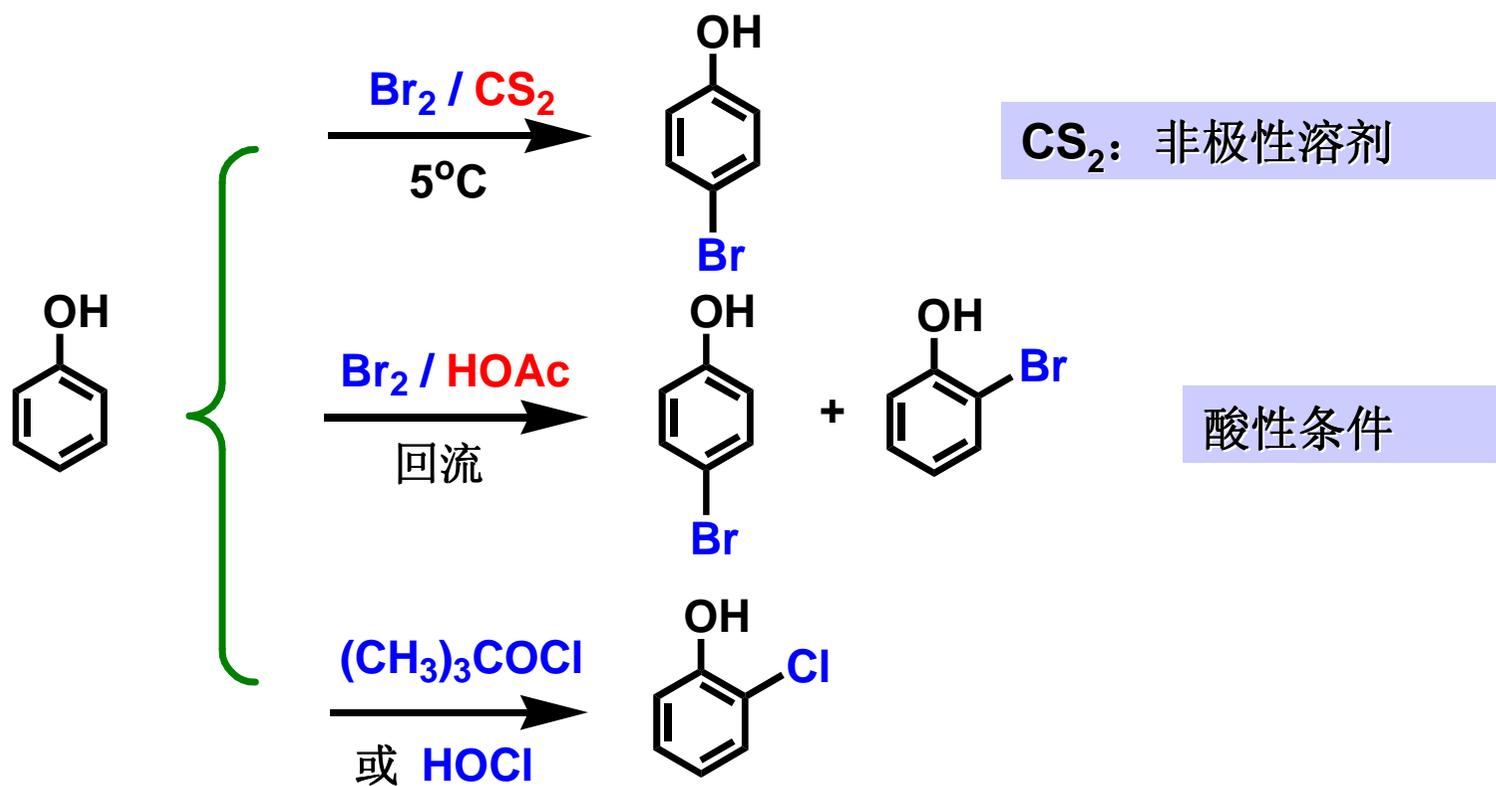


通过羧酸衍生物的亲核取代制备酚酯

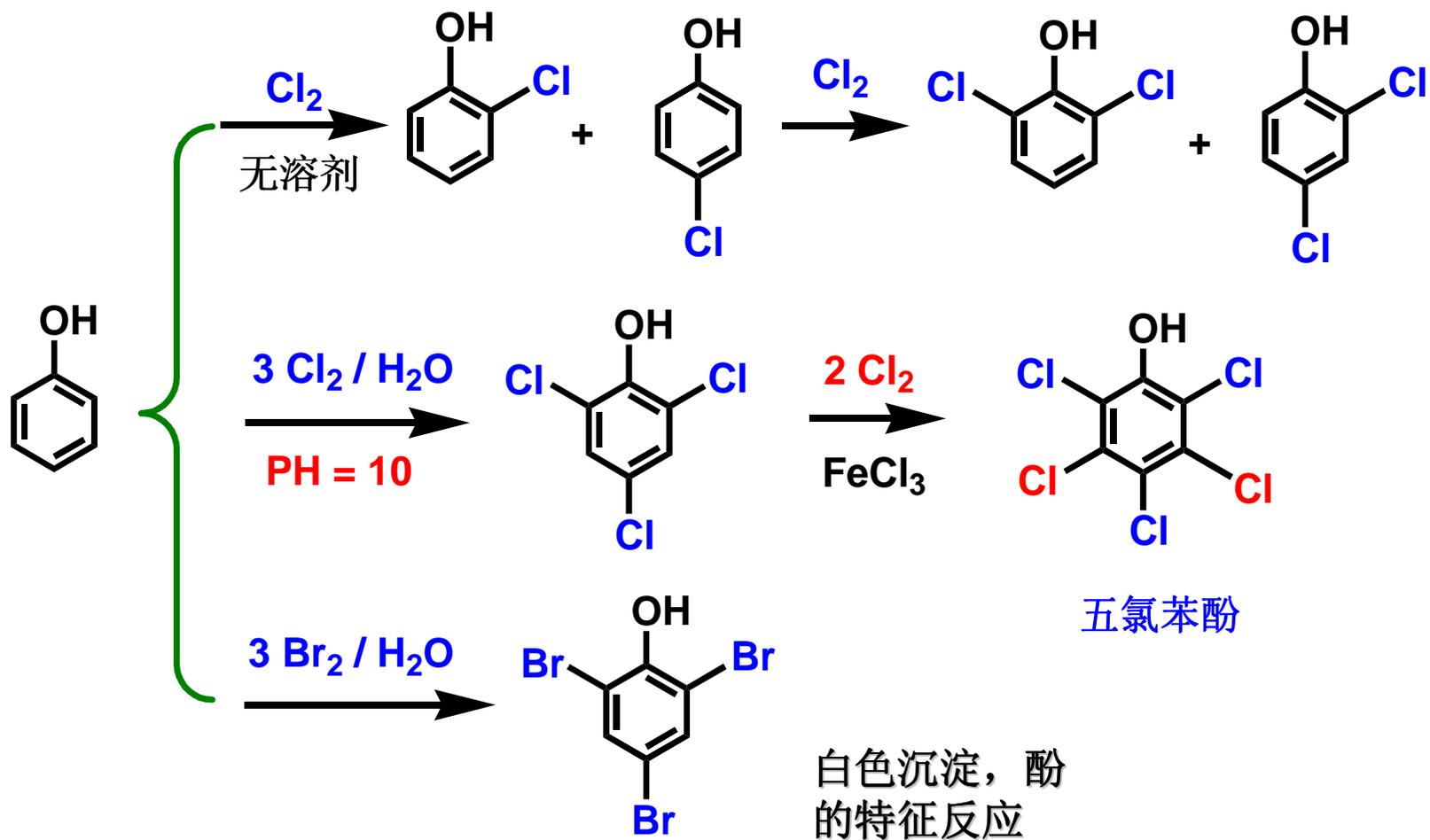
2. 酚类化合物苯环上的亲电取代

■ 卤代

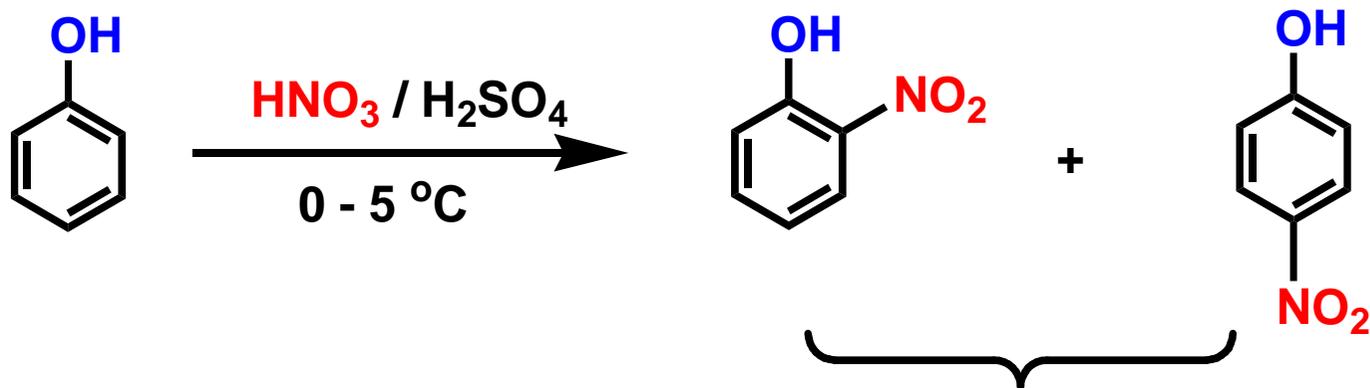
- 一卤代：反应条件——非极性溶剂或酸性体系



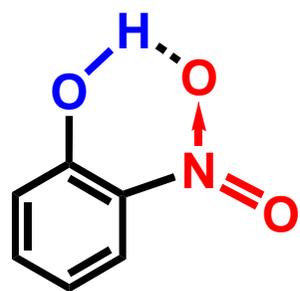
- 多卤代：反应条件——中性及碱性体系



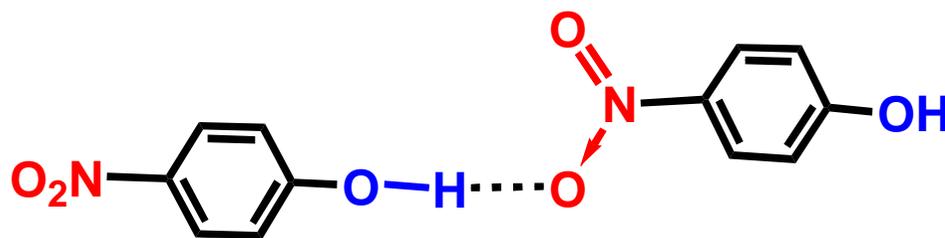
■ 硝化



用水蒸气蒸馏法分离

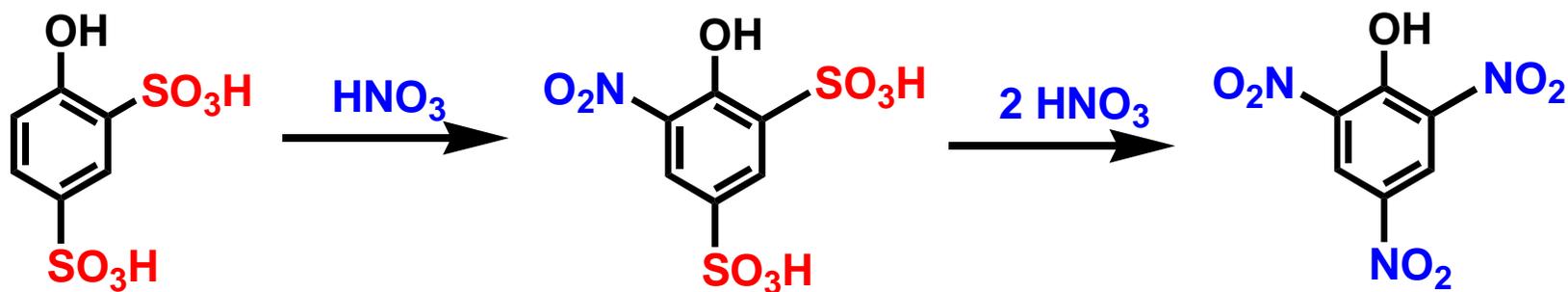
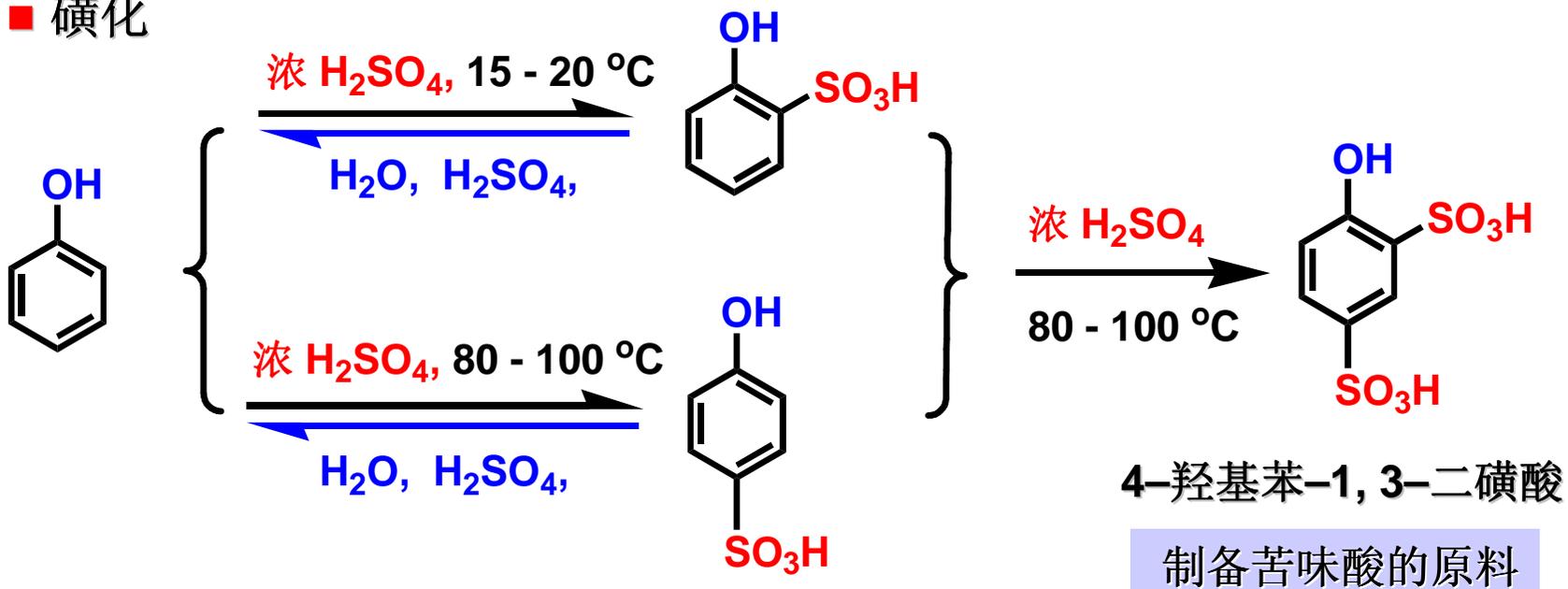


可形成分子内氢键，挥发性较大



只形成分子间氢键，挥发性较小

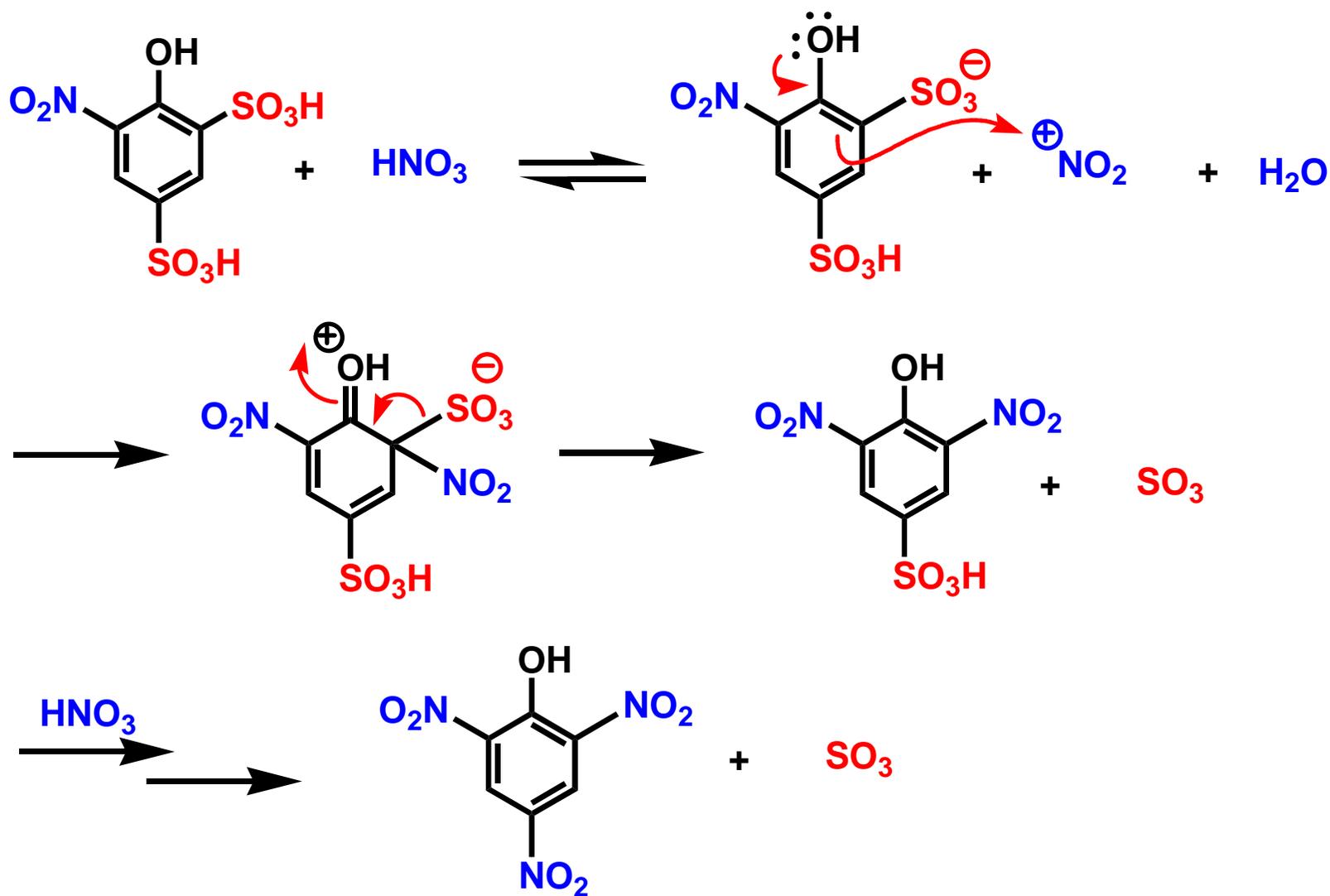
■ 磺化



发生了什么反应?

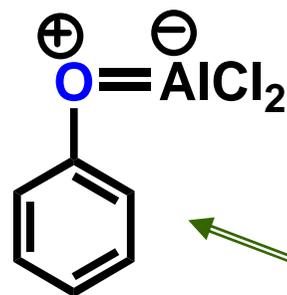
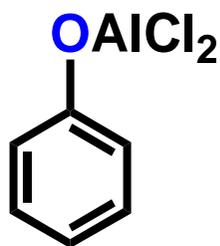
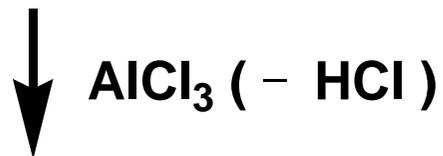
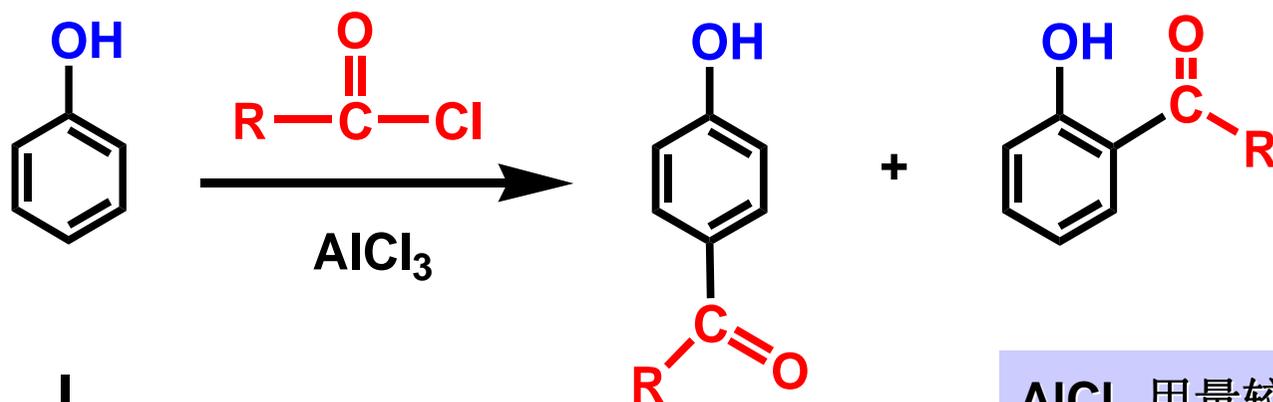
苦味酸
(2,4,6-三羟基苯酚)

- 硝基取代磺酸基的机理



■ Friedel-Crafts 反应

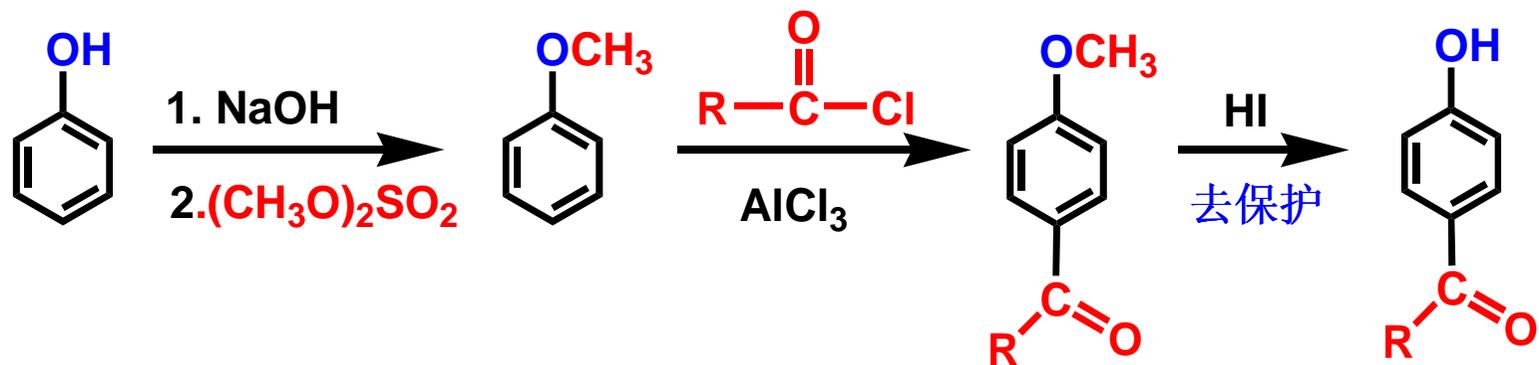
➤ 酰基化



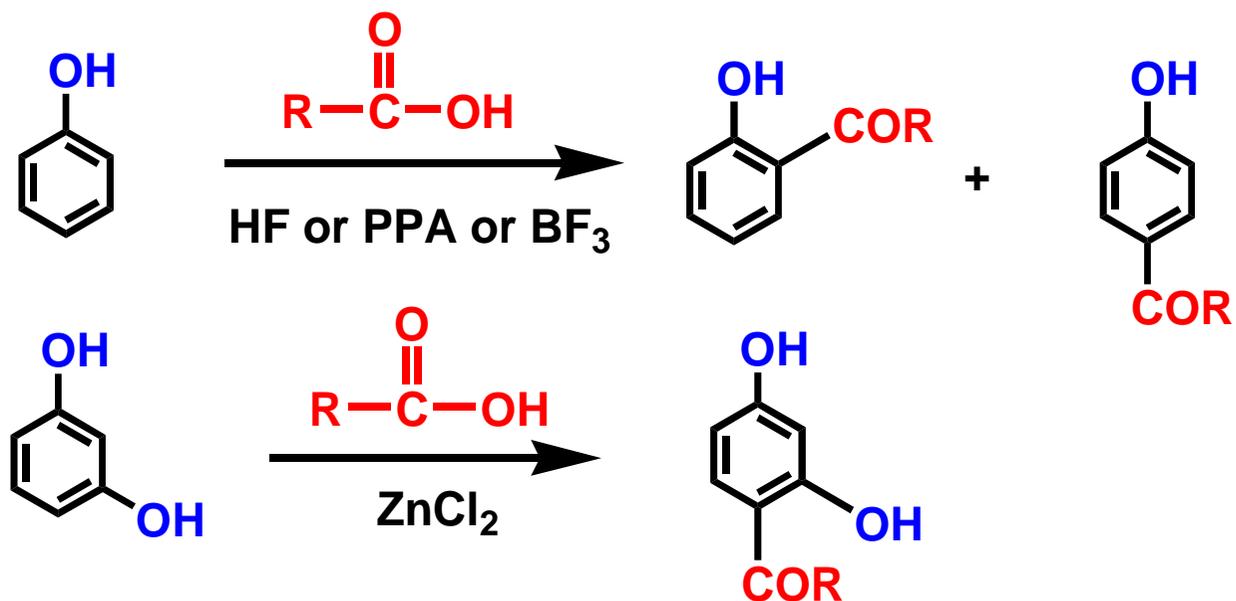
苯环活性减弱

$AlCl_3$ 用量较大,
产率不高

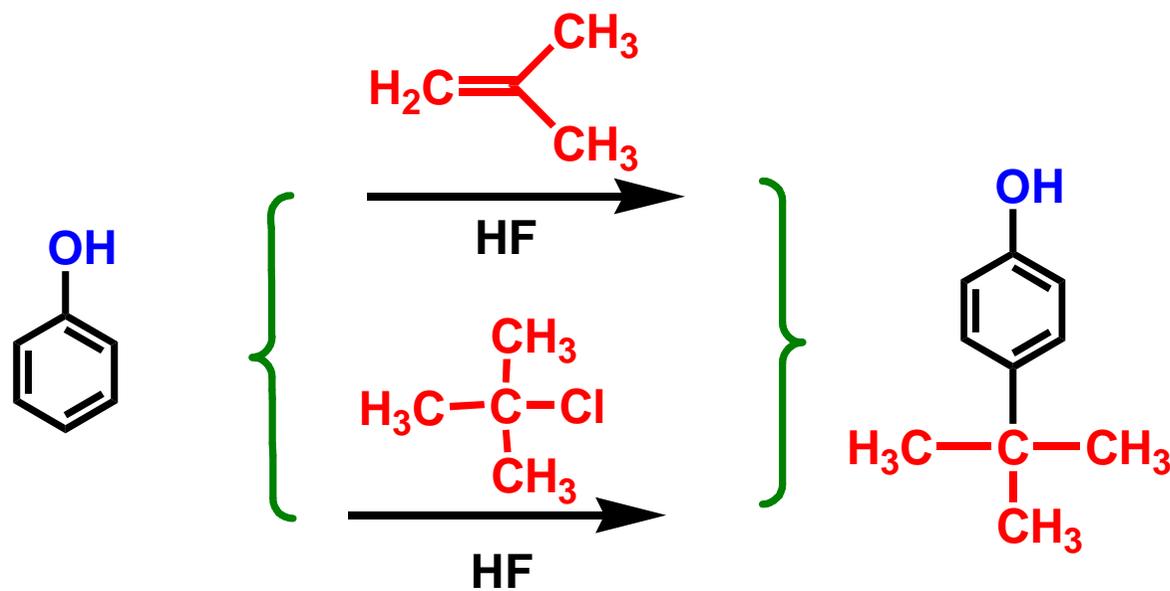
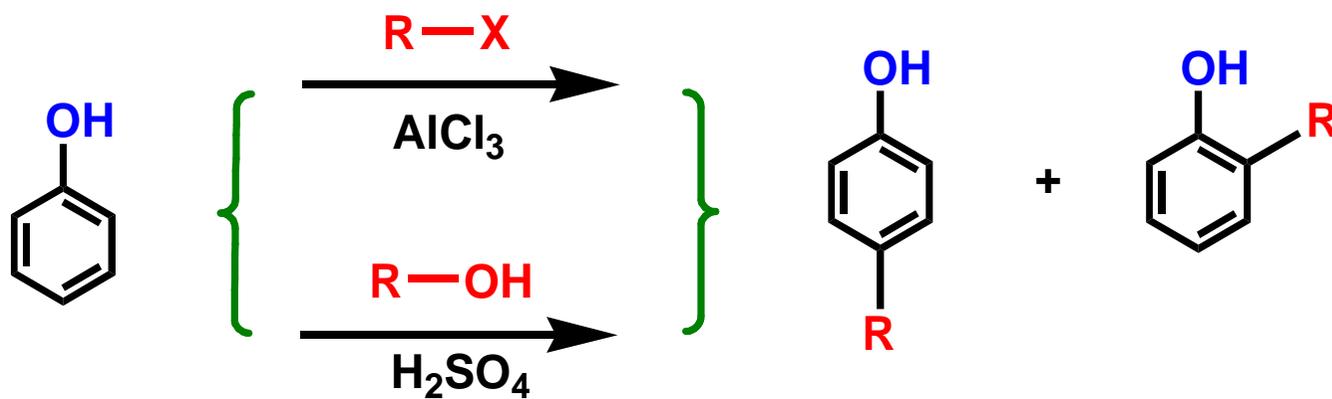
- 保护OH，再酰基化



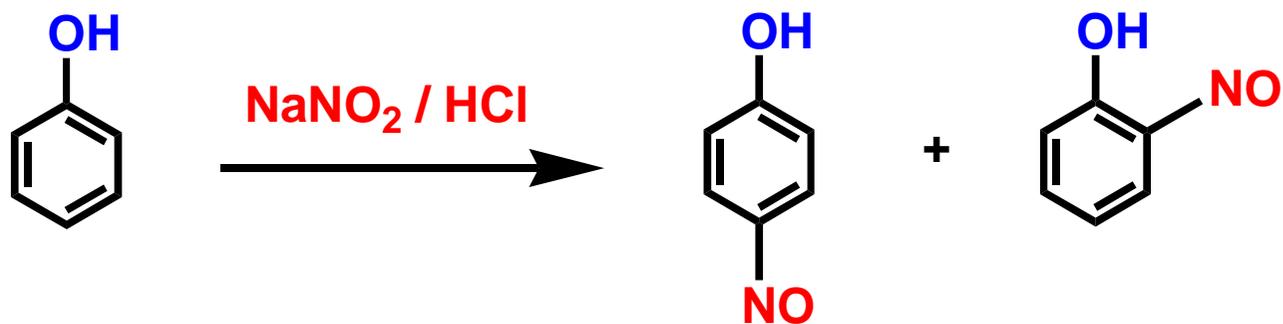
- 通过羧酸酰基化



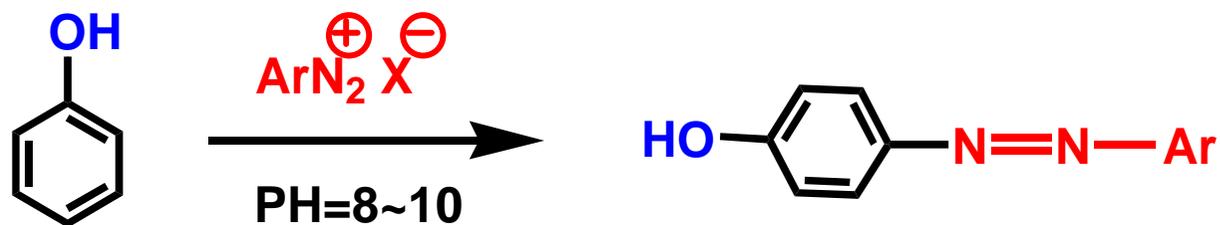
➤ 烷基化



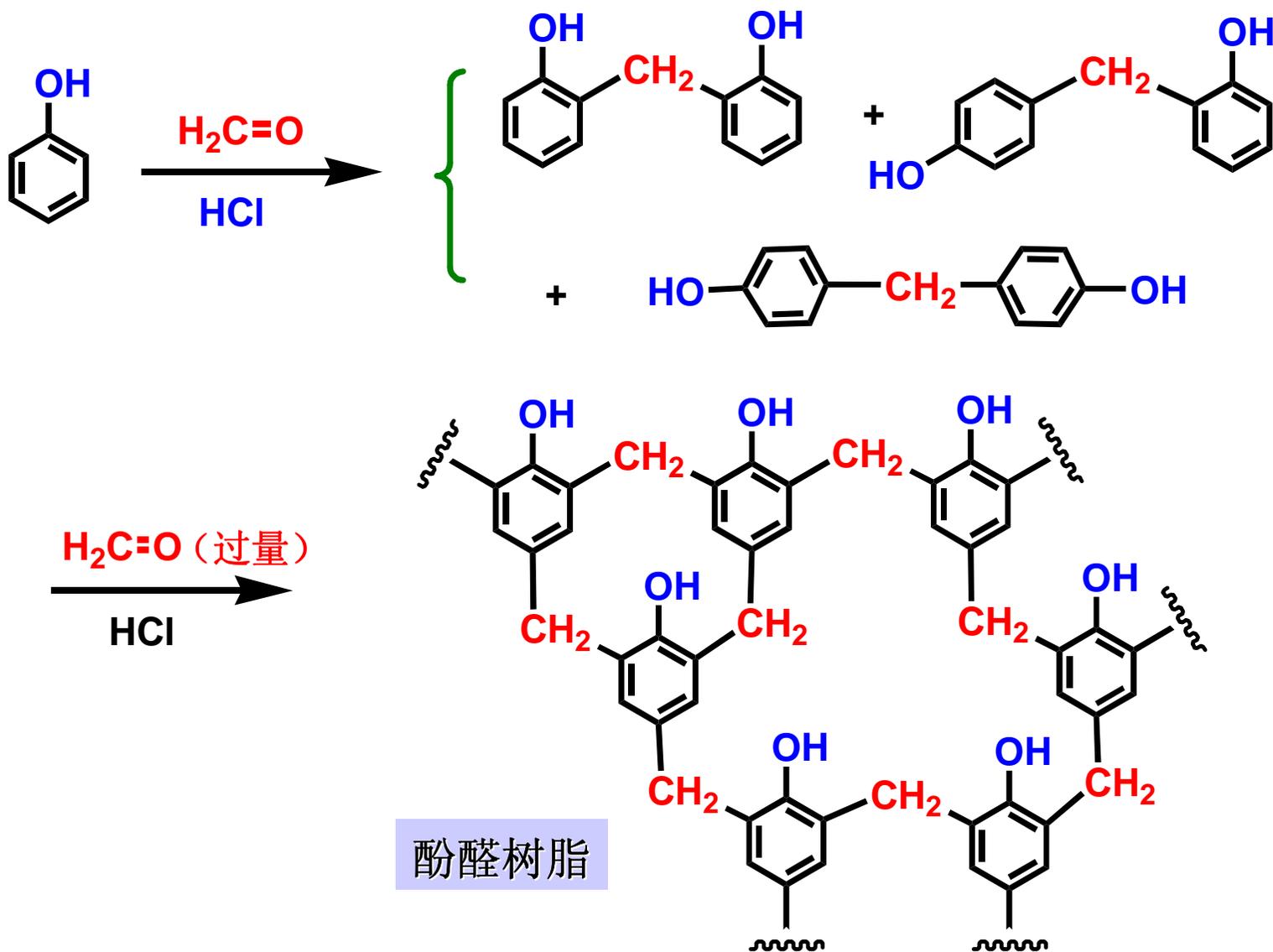
■ 与亚硝酸的反应

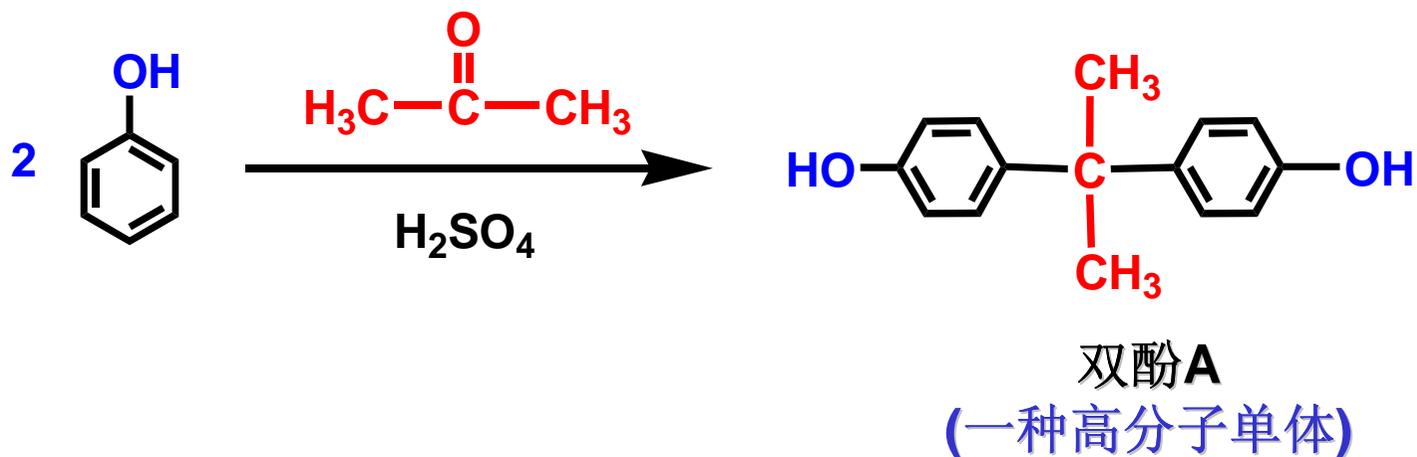


■ 与重氮盐的偶联反应

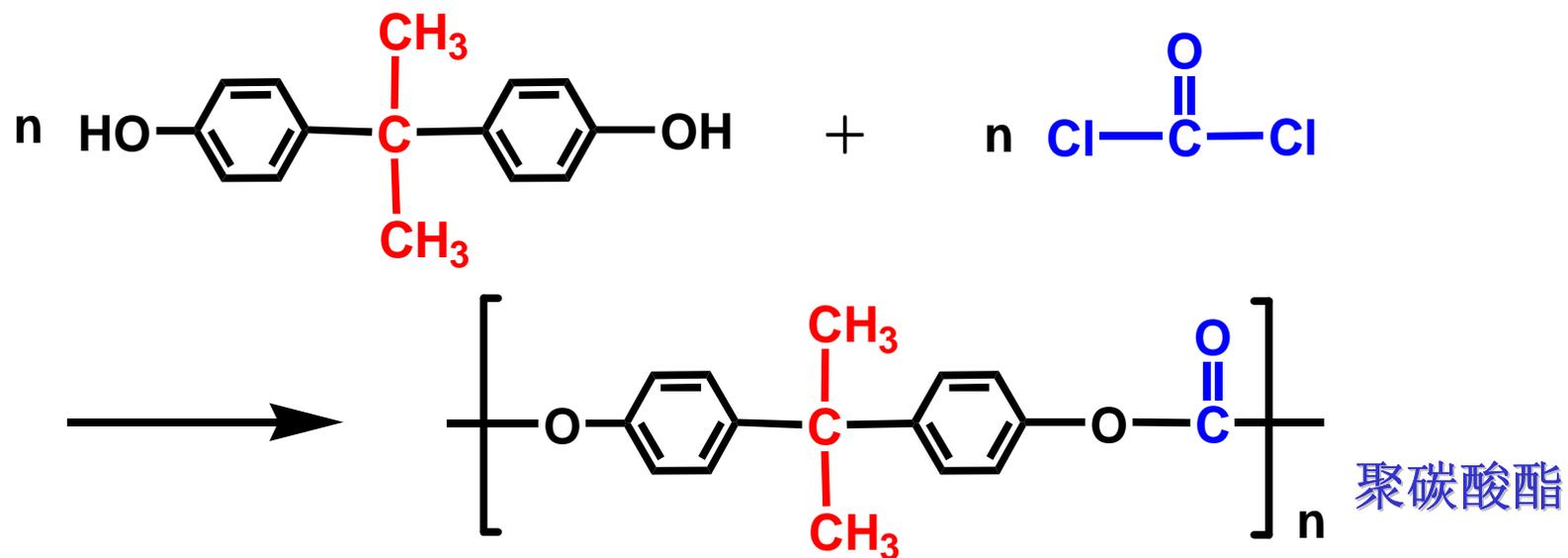


■ 酚醛（酮）缩合（一类亲电取代和烷基化反应）

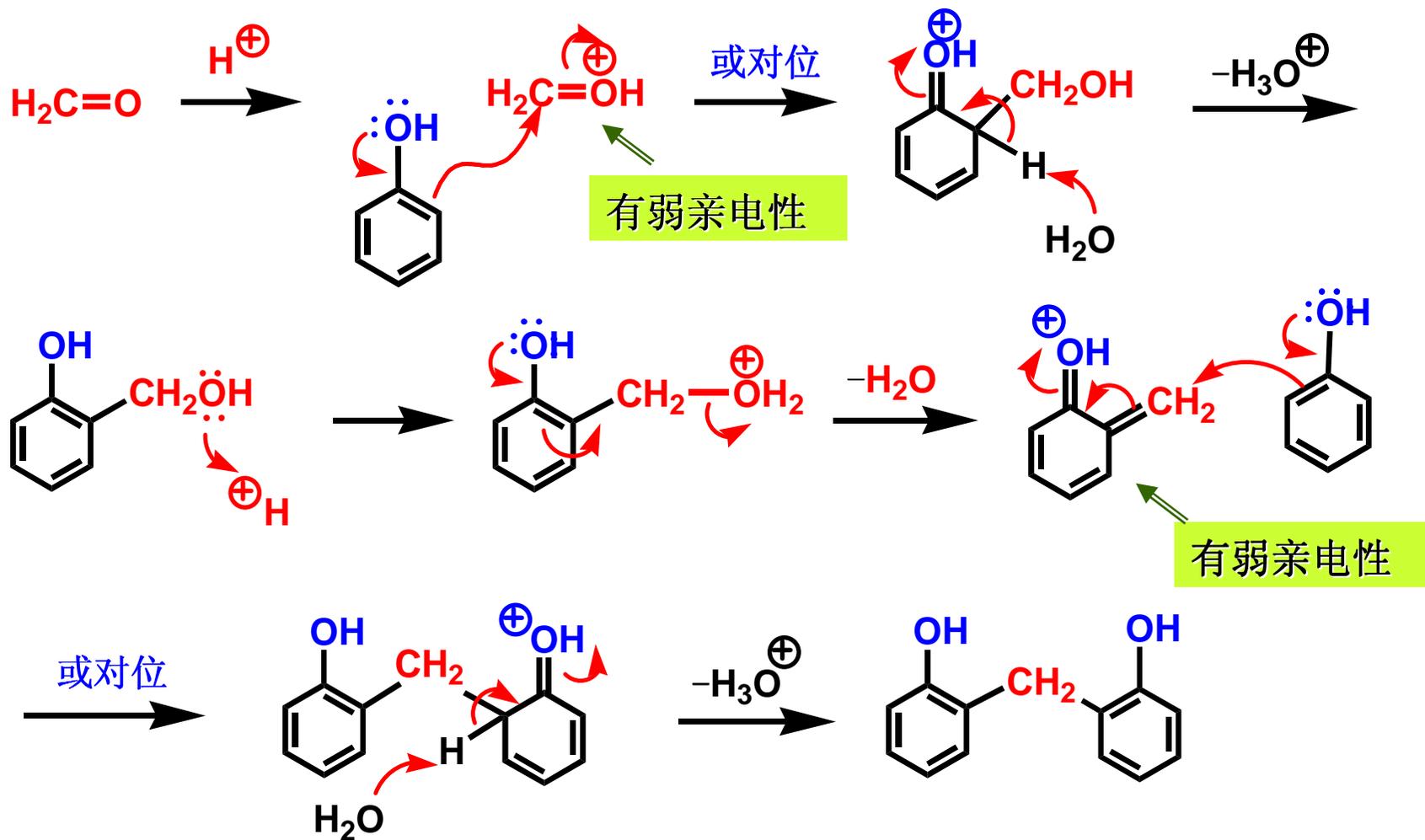




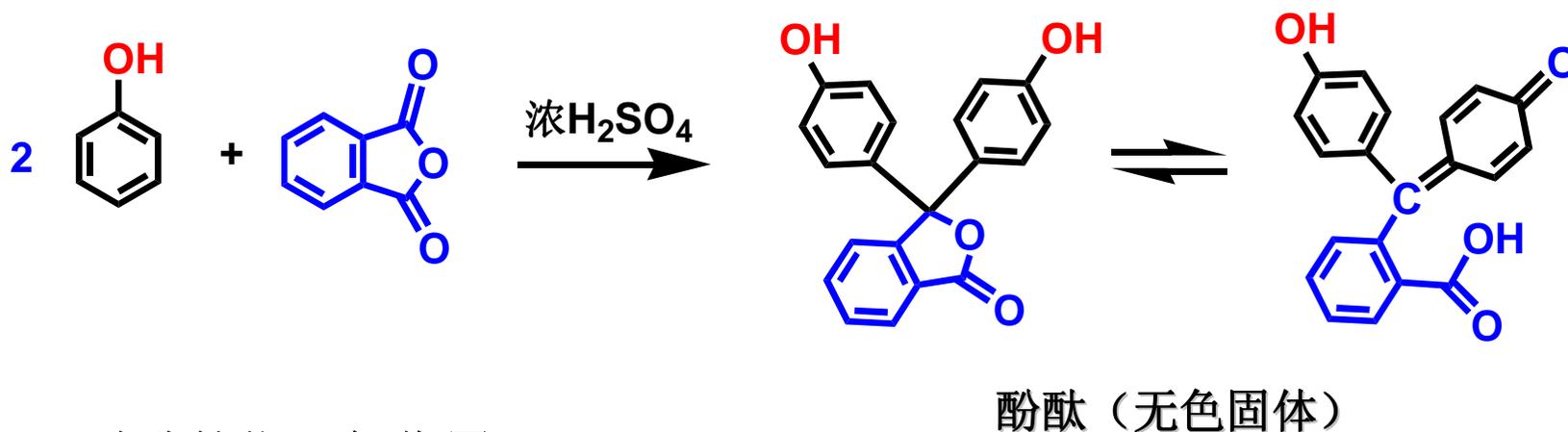
例：双酚A的聚合



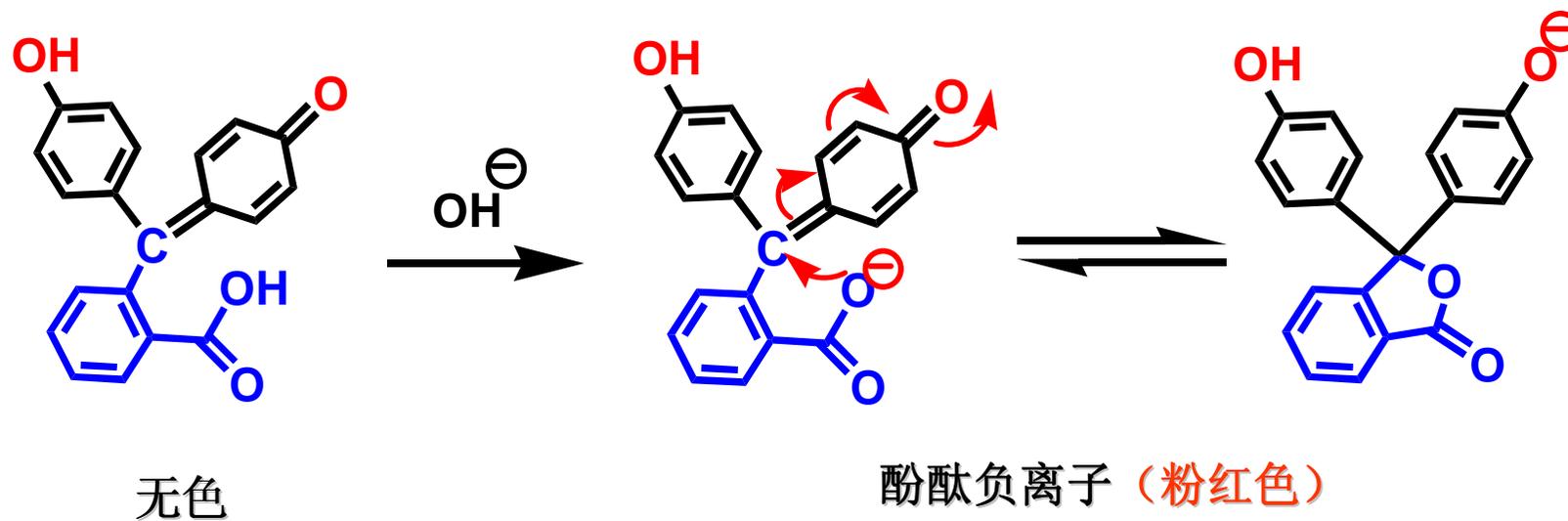
➤ 酚与醛酮缩合机理（以甲醛的反应为例）



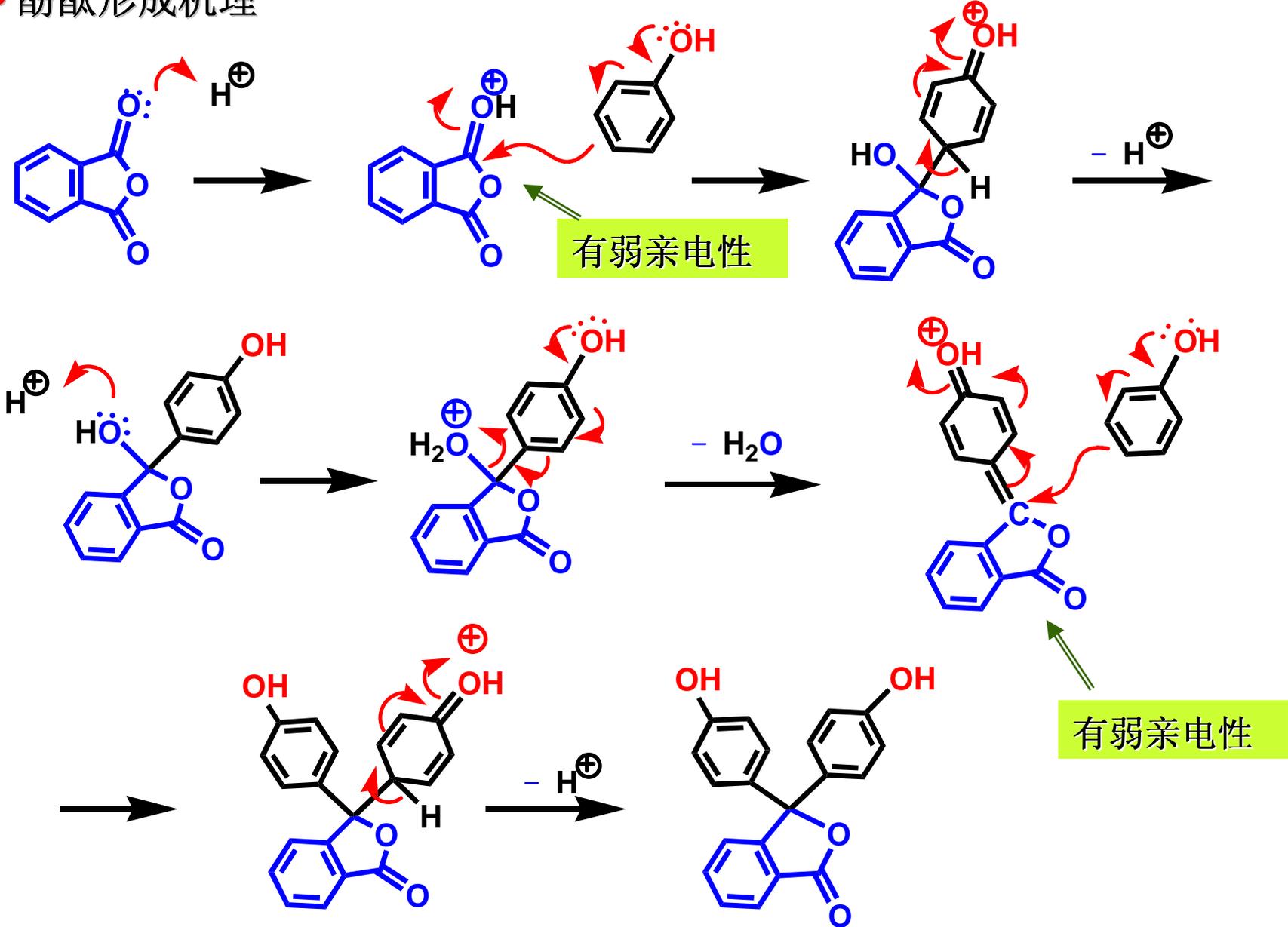
■ 与邻苯二甲酸酐的缩合——酚酞的制备



● 酚酞的指示剂作用

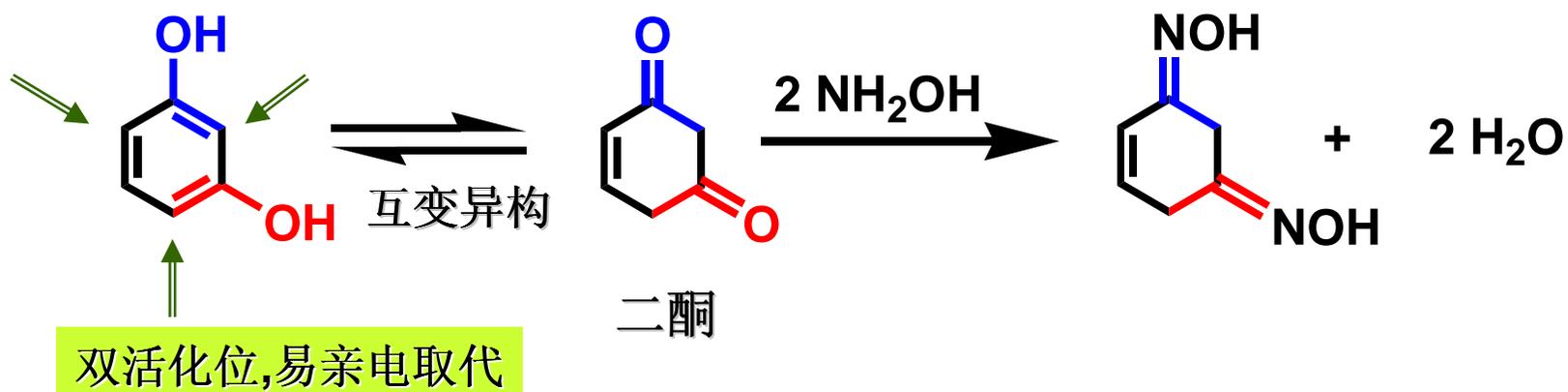


• 酚酞形成机理

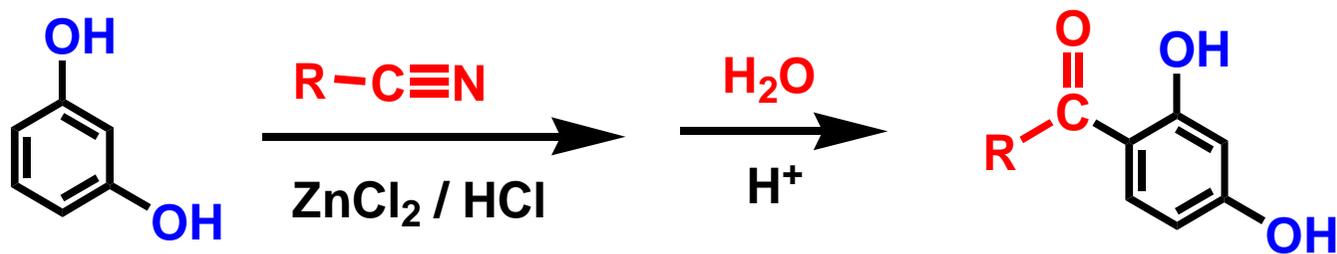


■ 间苯二酚和 Houben-Hoesch 反应 (p788)

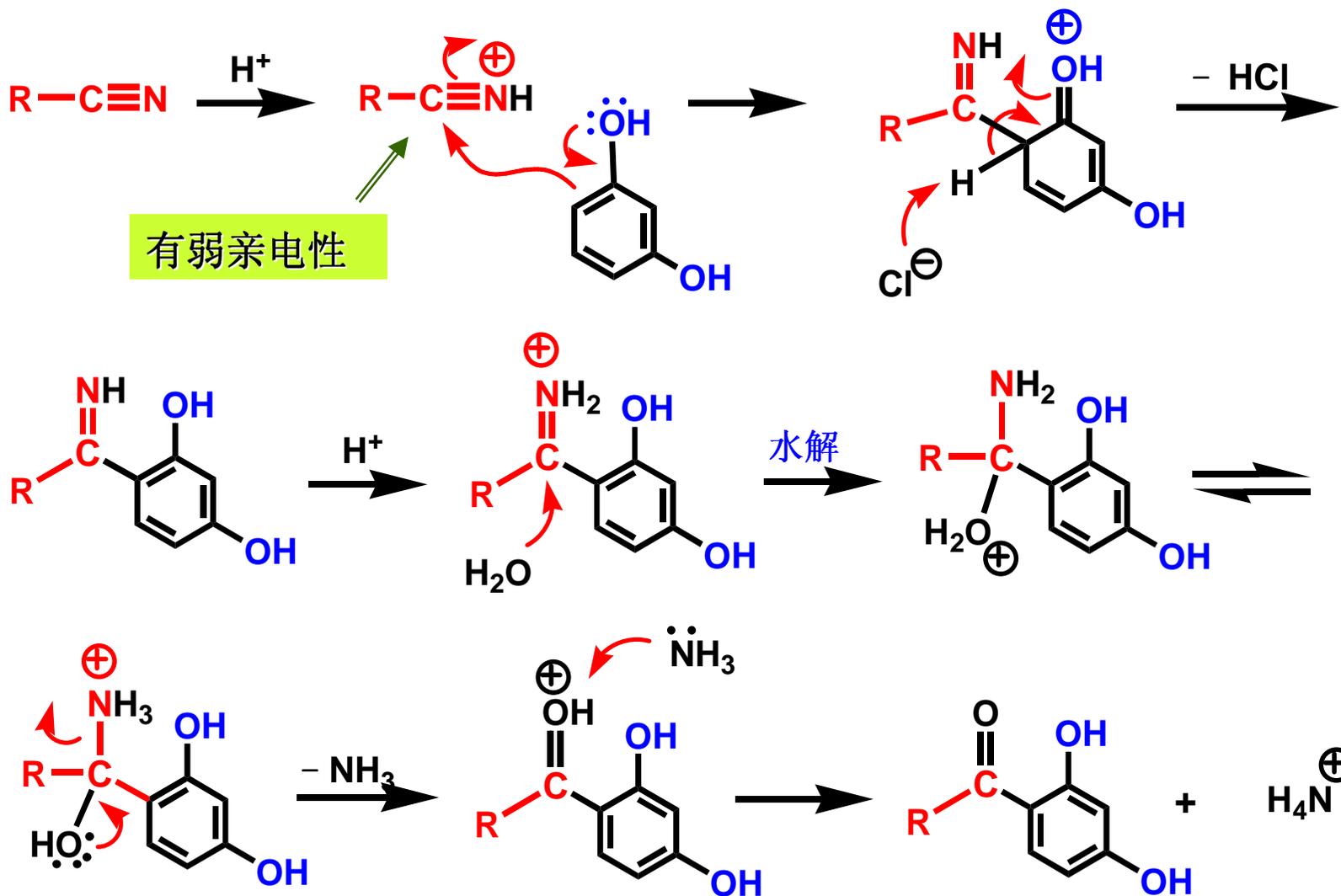
➤ 间苯二酚的互变异构



➤ Houben-Hoesch 反应 (间苯二酚与腈的反应)



• Houben-Hoesch反应机理:

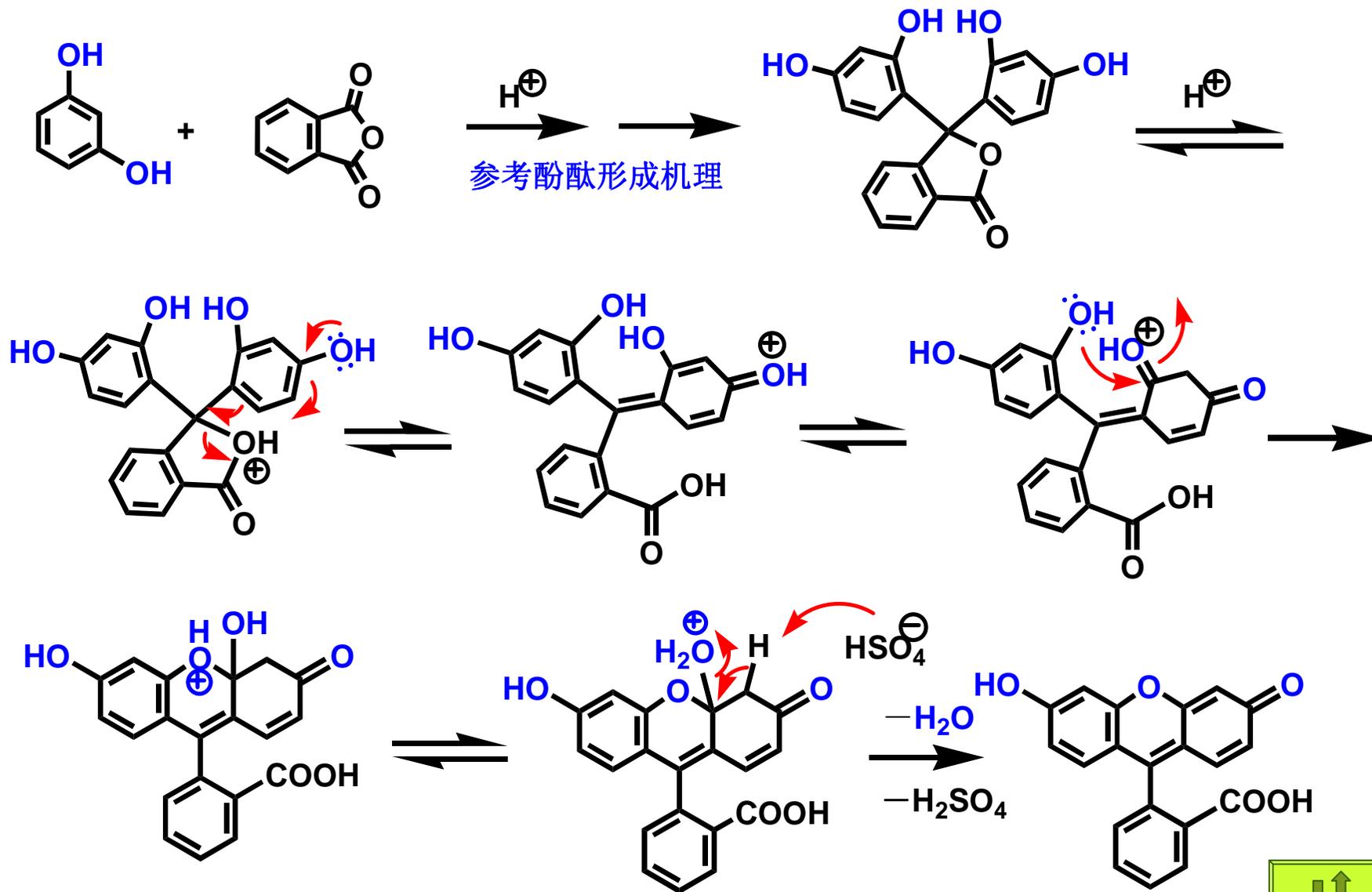


本次课小结:

- 酚类化合物的一般制备方法
- 酚羟基的酸性
- 酚羟基的醚化和酯化
- 酚类芳环上的亲电取代（新内容：酚醛缩合，与邻苯二甲酸酐的缩合）
- 间苯二酚的**Houben-Hoesch**反应

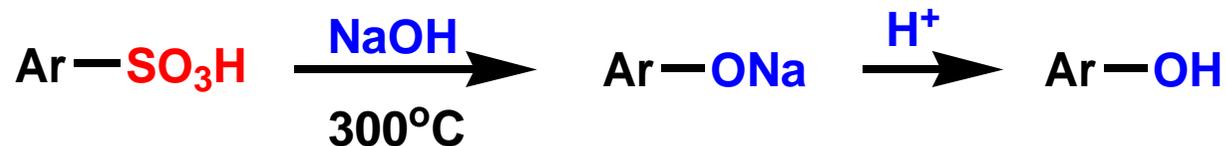
习题：17-12; 17-16

思考题参考答案

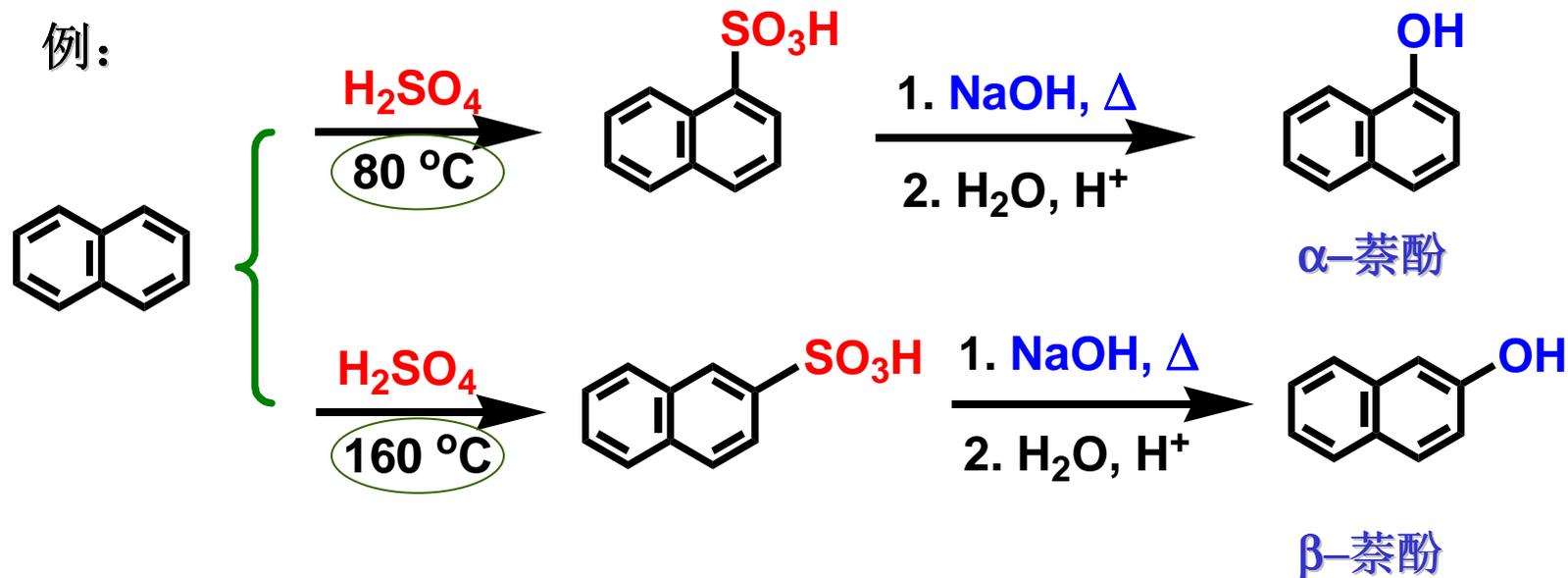


一. 酚类化合物的一般制备方法

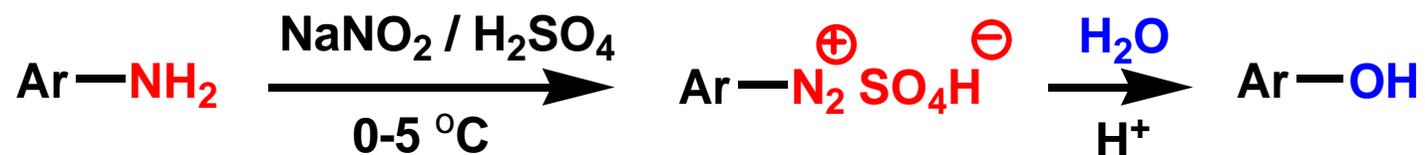
■ 通过苯磺酸衍生物的碱熔制备酚



注意：芳环上 $-\text{X}$, $-\text{NO}_2$, $-\text{COOH}$ 等基团将受影响。

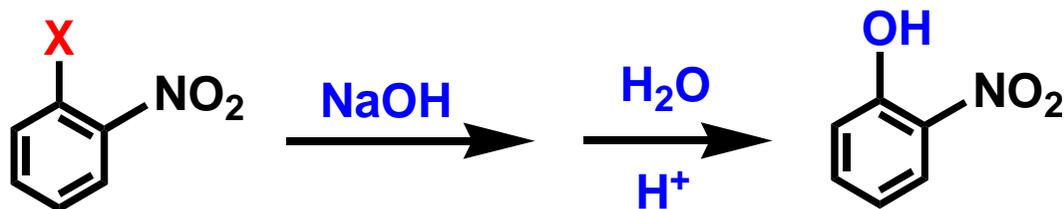
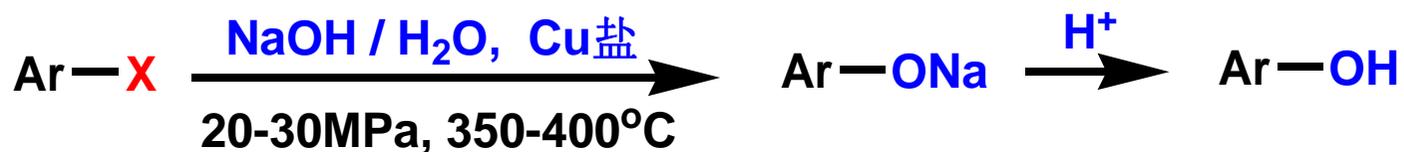


■ 通过重氮盐的水解制备酚



一般产率不高，有偶联副产物

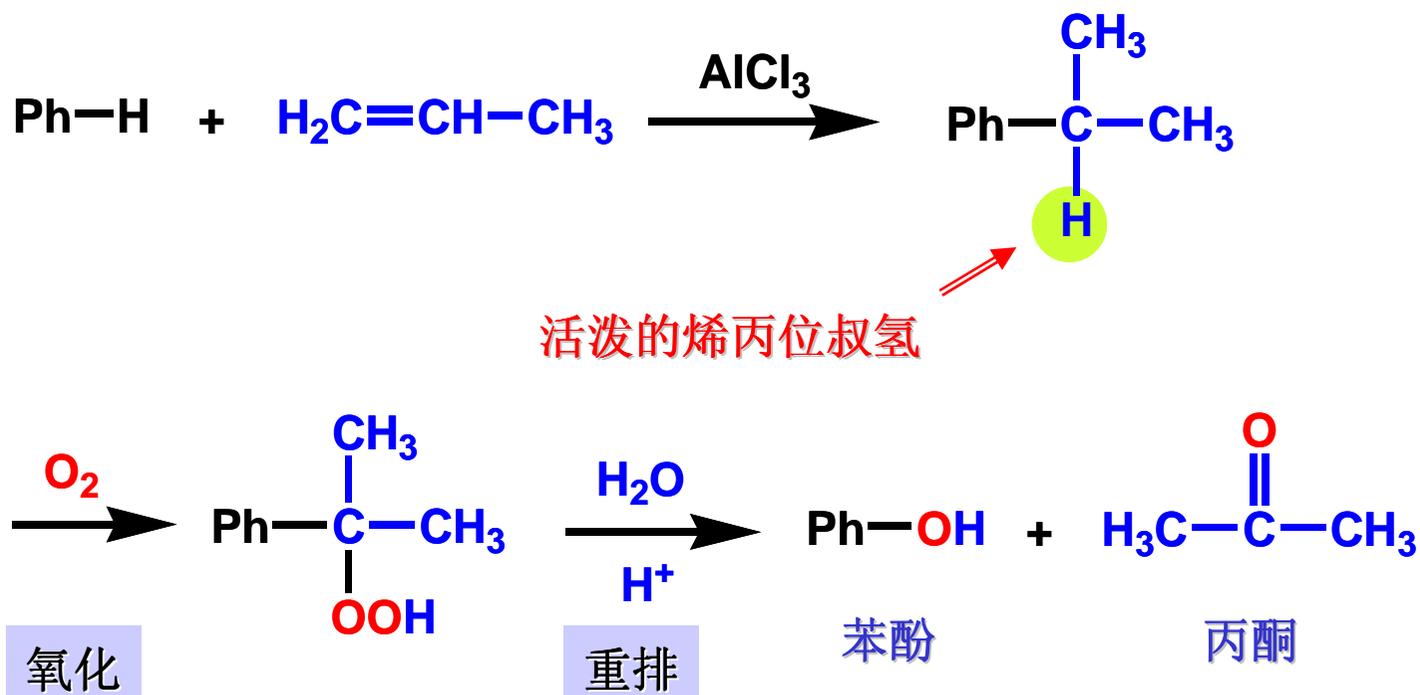
■ 通过卤代芳烃的取代



加成-消除
机理

■ 苯酚的特殊制法：异丙基苯氧化—重排反应

(上册, p444, 10.10.3节)



工业制备苯酚和丙酮的方法