

Chapter 18



Other Nitrogen Compounds

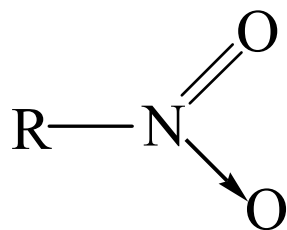
其他含氮化合物

§ 18.1 硝基化合物

Nitro compounds

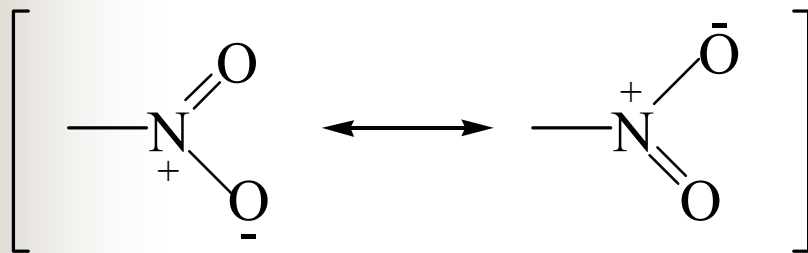
硝基化合物：烃分子中的氢原子被硝基(-NO₂)取代后形成的化合物

硝基的结构



两个N-O键的键长相等

共振式



偶极矩为3.5D。因此，硝基是一个强烈的吸电子取代基。

1. 芳香族硝基化合物的物理性质

无色或淡黄色高沸点液体或低熔点固体，常可随水蒸气蒸馏蒸出，不溶于水，常有剧毒

多硝基混合物为固体，有爆炸性

三硝基甲苯 (TNT): 炸药

UV: 250-300nm处强而宽的吸收峰。

IR: $-\text{NO}_2$ 1555-1487和1357-1318 cm^{-1}

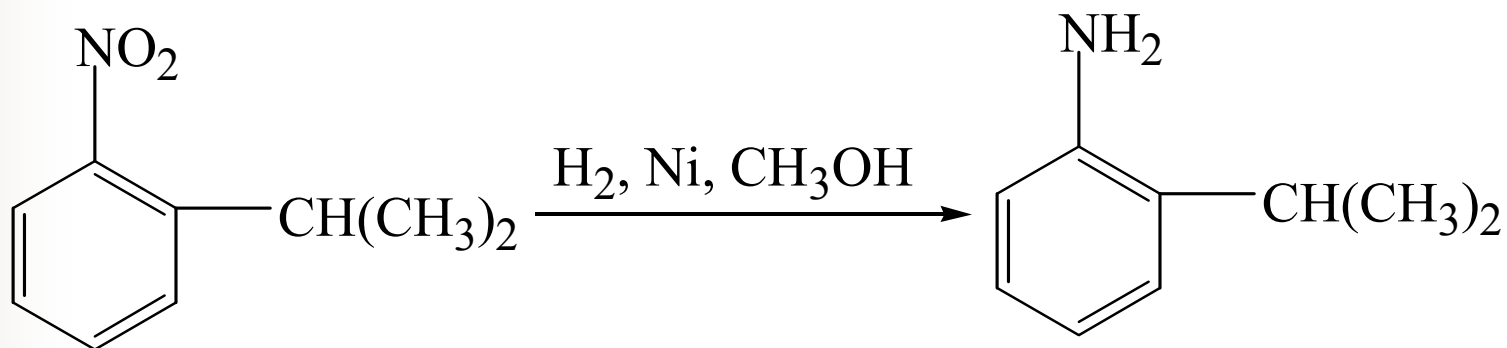
^1H NMR: $-\text{NO}_2$ 使苯环上质子的化学位移向低场移动

MS: 常有分子离子峰

2. 芳香族硝基化合物的反应

(1) 还原

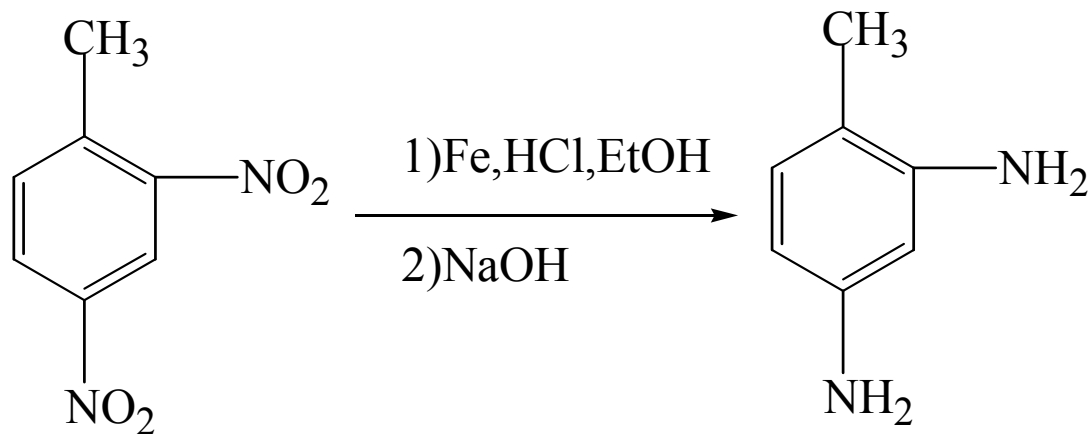
I. 催化氢化



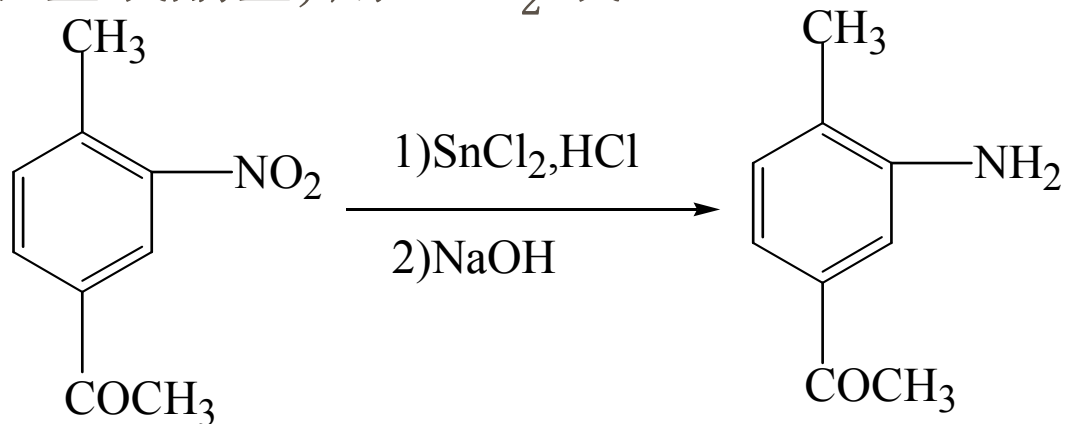
II. 化学试剂还原

A. 酸性介质

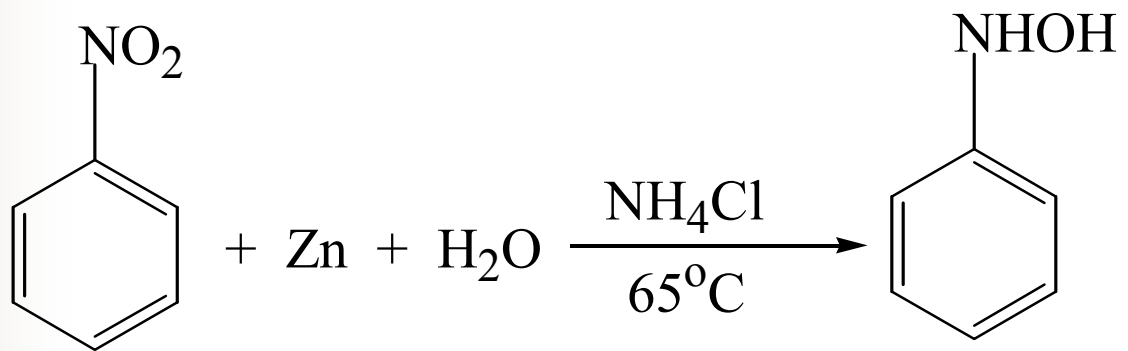
金属+强酸(金属: Fe、Zn、Sn、 SnCl_2)



含醛基或酮基, 用 SnCl_2 或 Sn

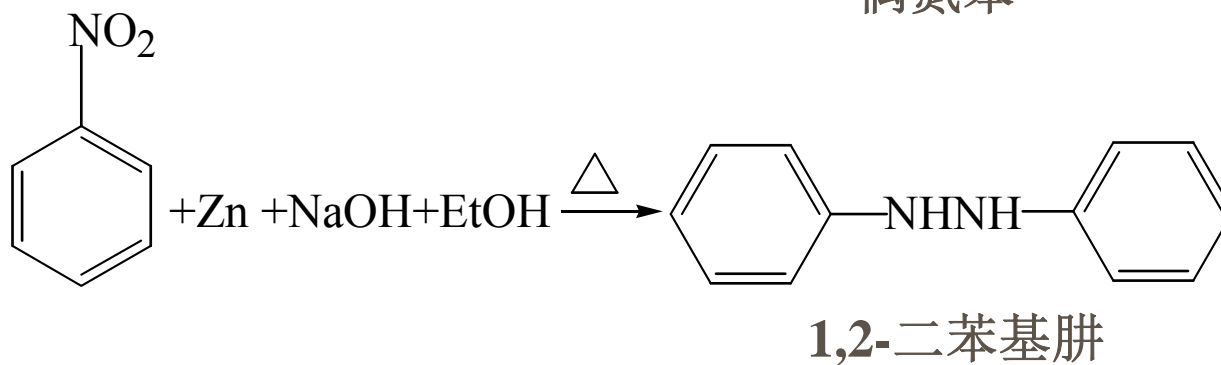
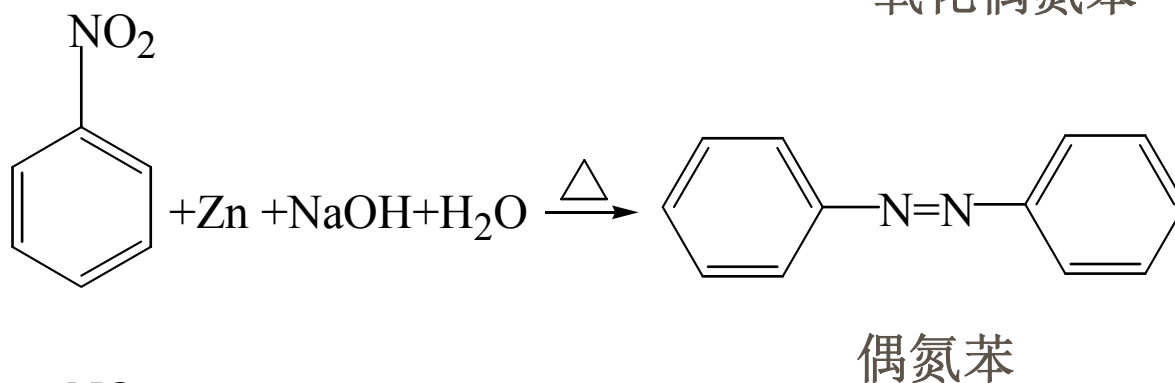
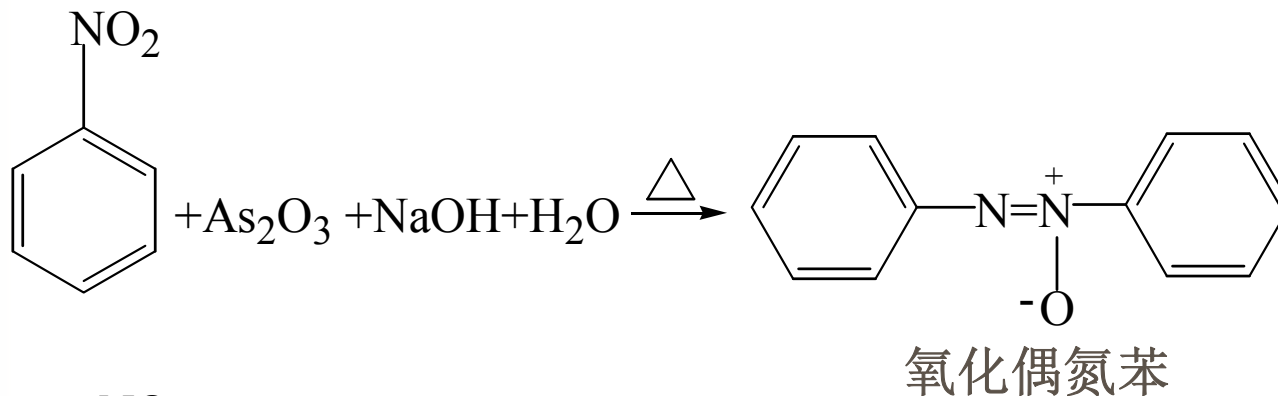


B. 中性或弱酸性

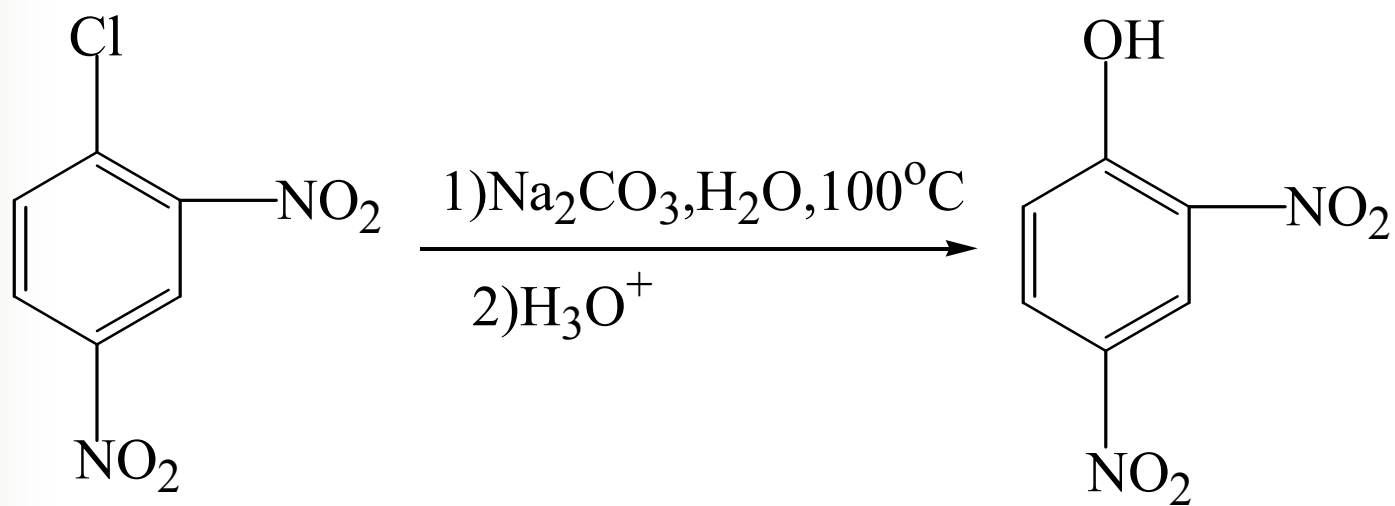
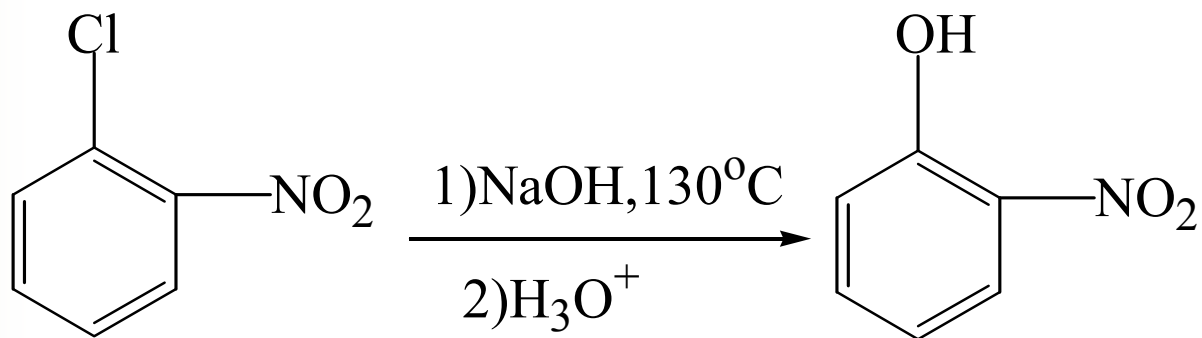


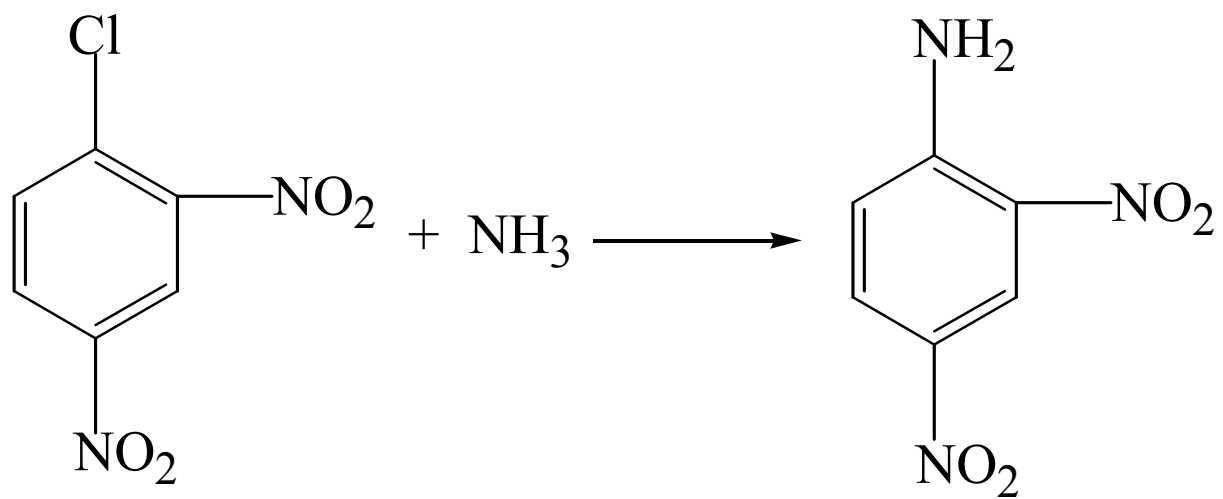
N-苯基羟胺

C. 碱性介质



(2) 芳环上的亲核取代反应

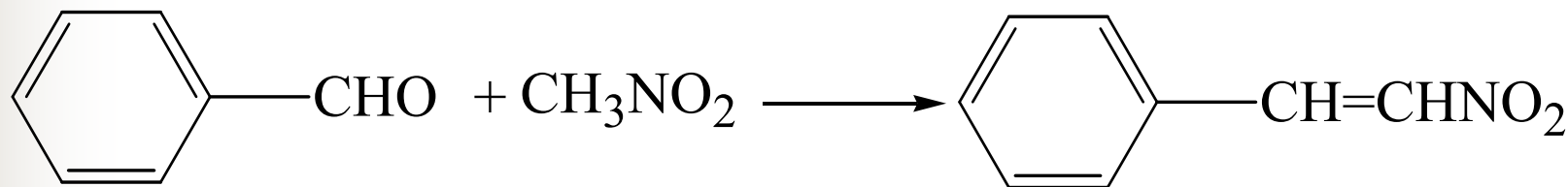
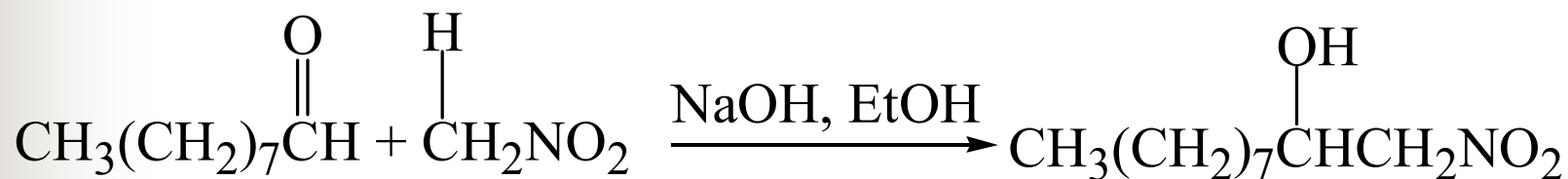




3. 脂肪族硝基化合物

硝基是吸电子的取代基, 其 α - 位的氢有明显的酸性,
 \therefore 有 α - 氢的硝基化合物能溶于碱。

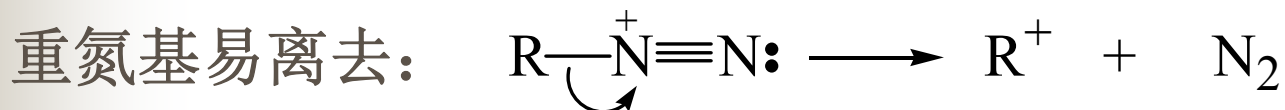
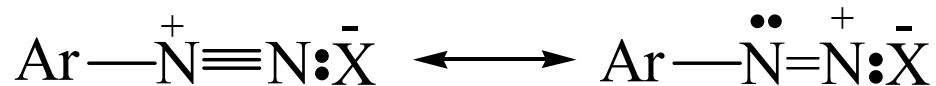
亨利(Henry)反应:



§ 18.2 芳基重氮盐

Aryl diazonium salts

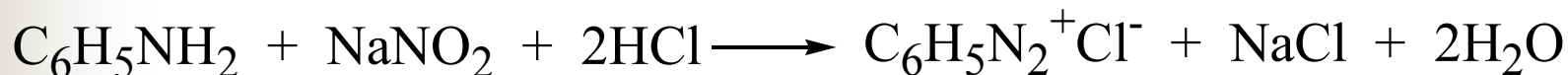
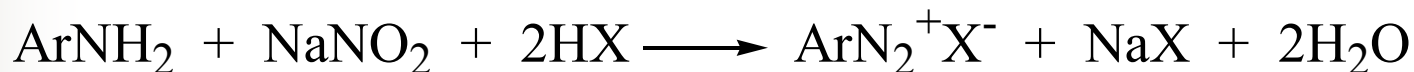
一、重氮盐的结构



碳正离子

二、重氮盐的制法 —— 重氮化反应

芳香族伯胺在强酸存在下与亚硝酸反应，生成重氮盐



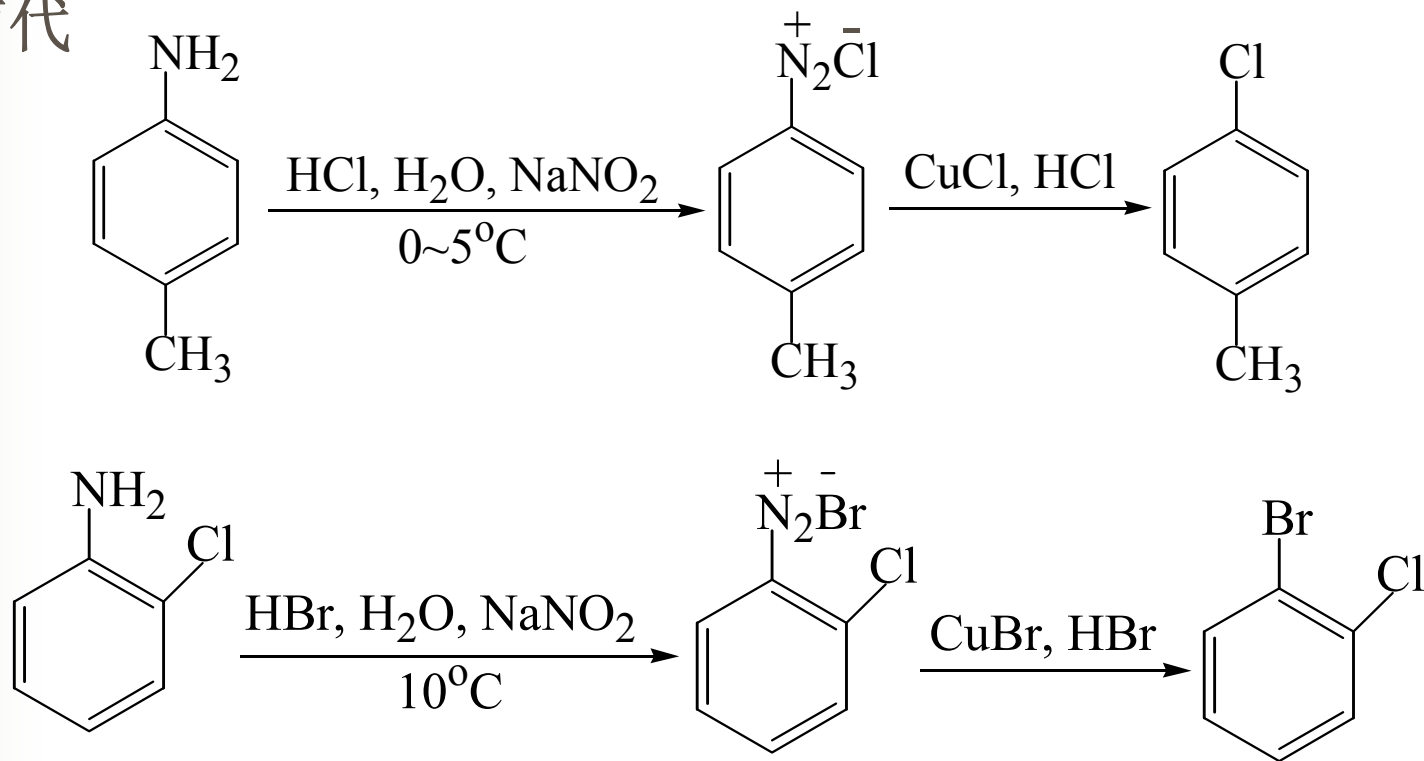
氯化重氮苯

三、芳基重氮盐的反应

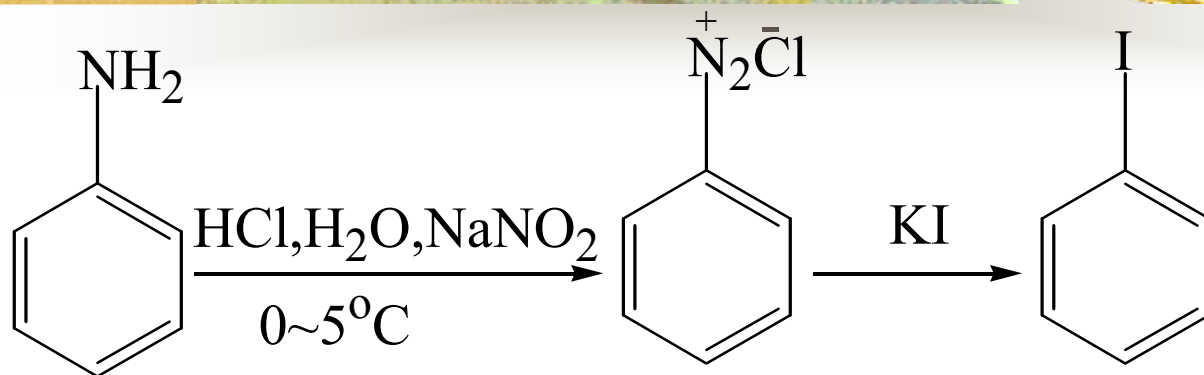
I. 放出N₂ 的反应---取代反应



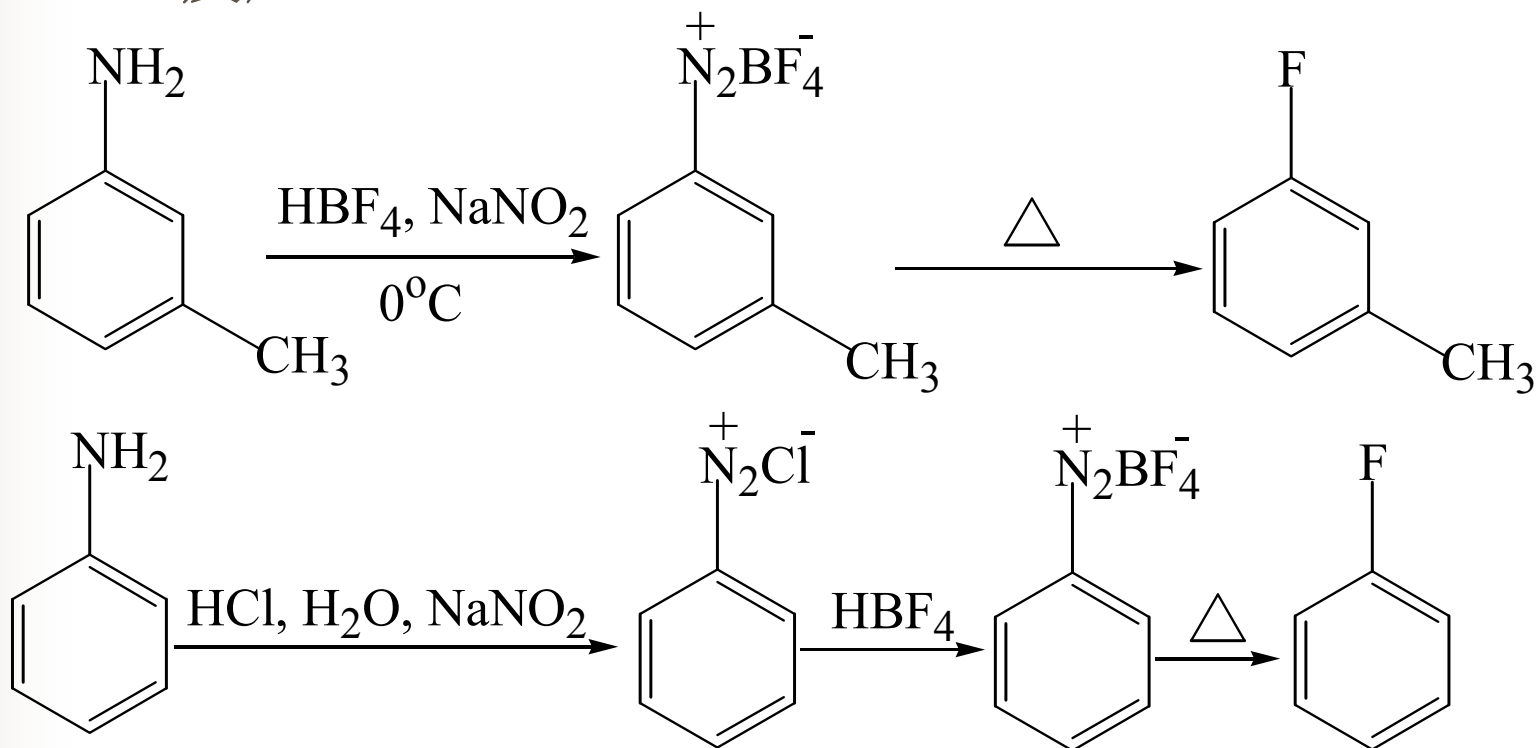
1. 卤代



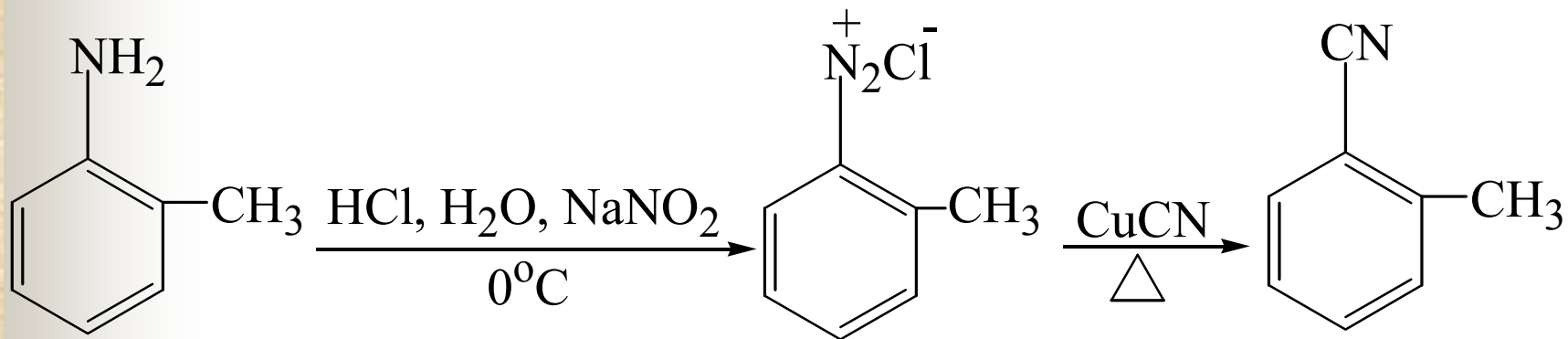
Sandmeyer反应



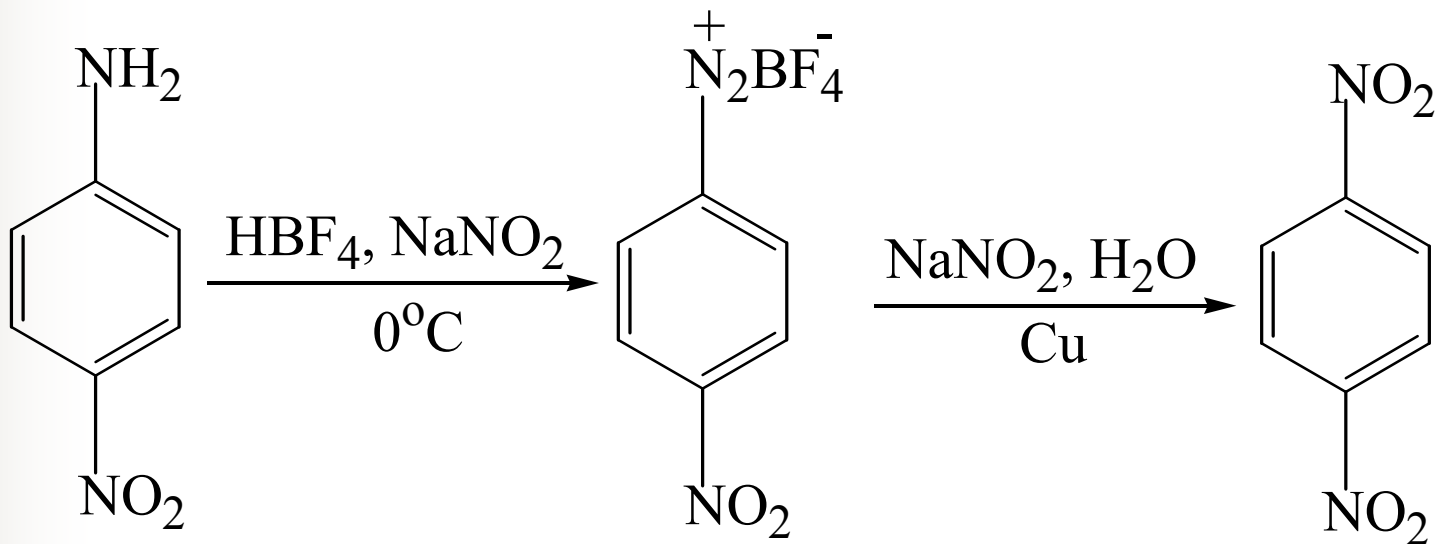
Schiemann反应:



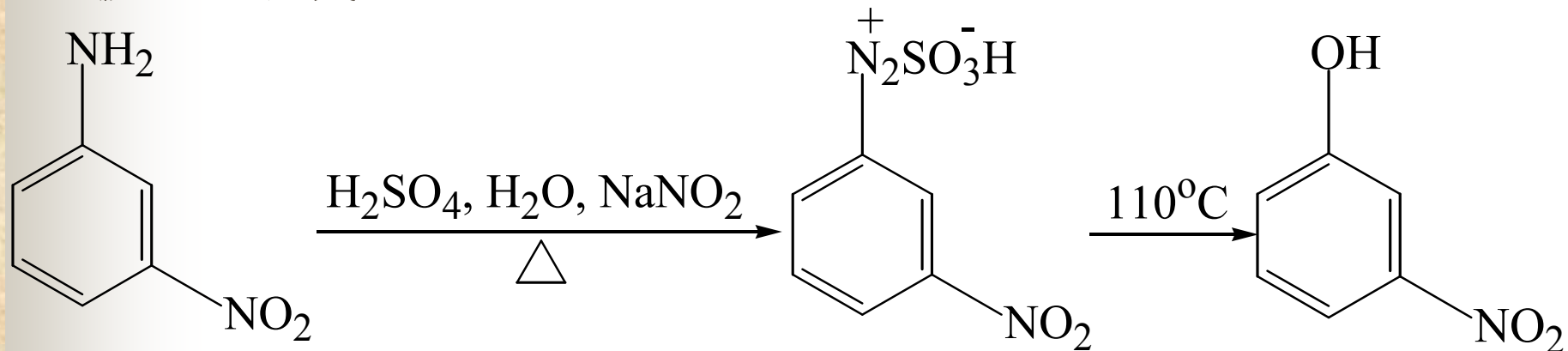
2. 氰代(Sandmeyer反应)



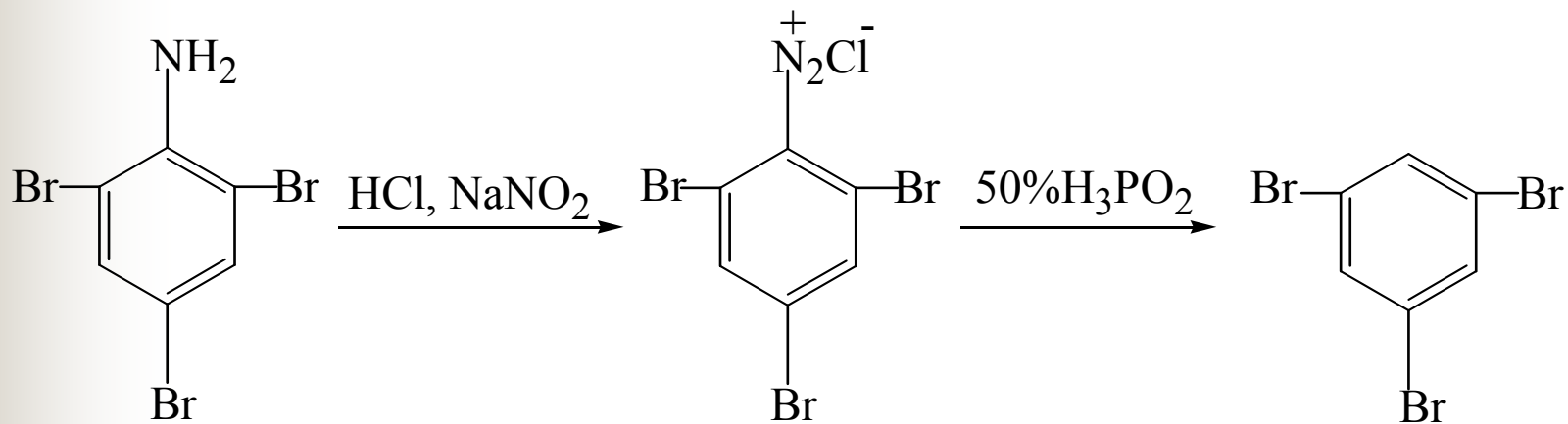
3. 被-NO₂取代(Gatterman反应)



4. 被-OH取代

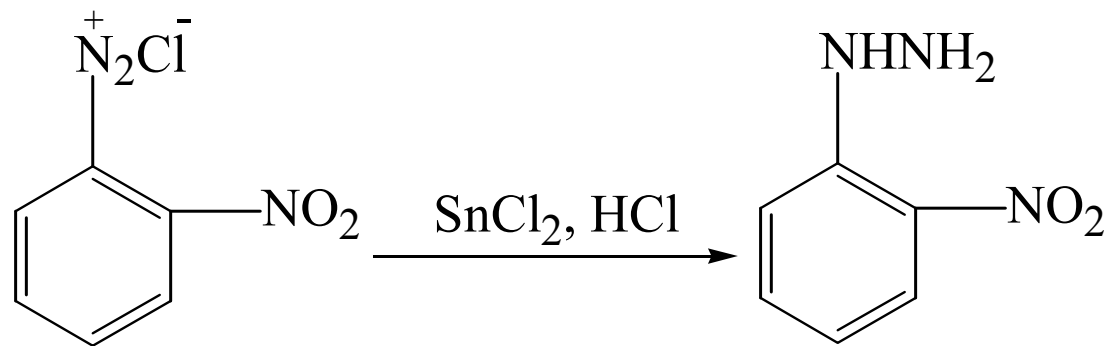


5. 被H取代



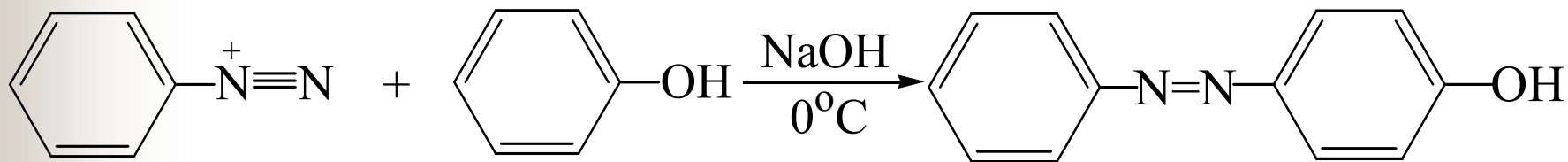
II. 不放N₂ 的反应

1. 还原成肼 用锌和盐酸、氯化亚锡和盐酸还原



邻硝基苯肼

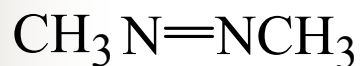
2. 偶联



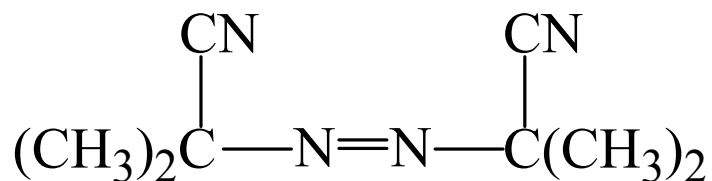
对羟基偶氮苯

§ 18.3 偶氮化合物

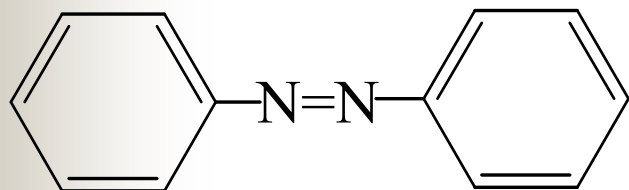
Azo compounds



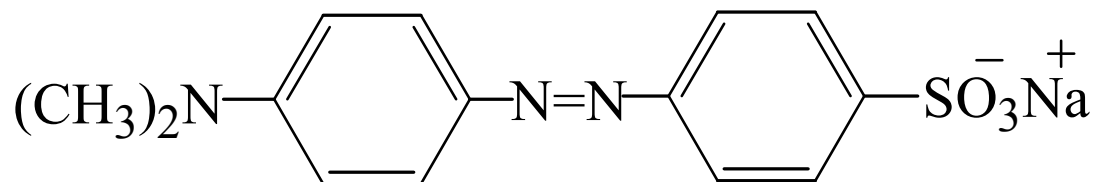
偶氮甲烷



偶氮二异丁腈



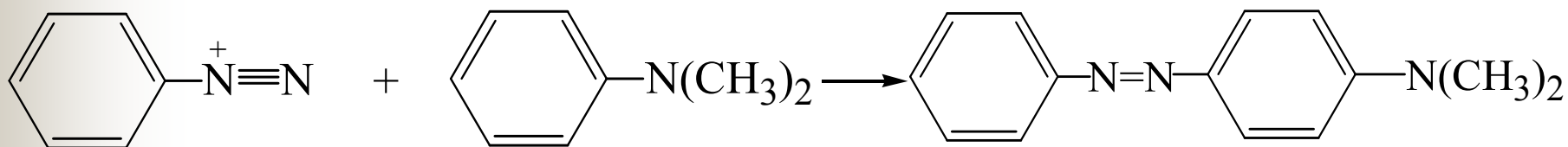
偶氮苯



4[4-(二甲氨基)苯基]偶氮苯磺酸钠
(甲基橙)

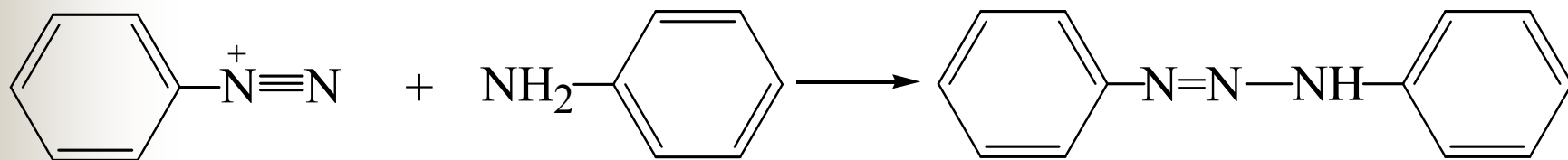
1. 芳香族偶氮化合物的制法

芳基重氮盐与N,N-二烷基芳胺的偶联在弱酸性溶液（pH=4-7）中进行：

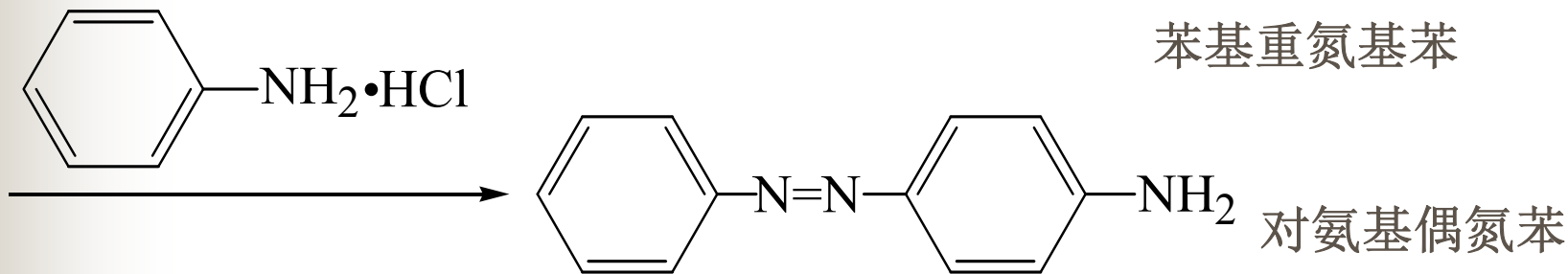


对二甲氨基偶氮苯

芳基重氮盐与芳香族伯胺或仲胺的偶联：



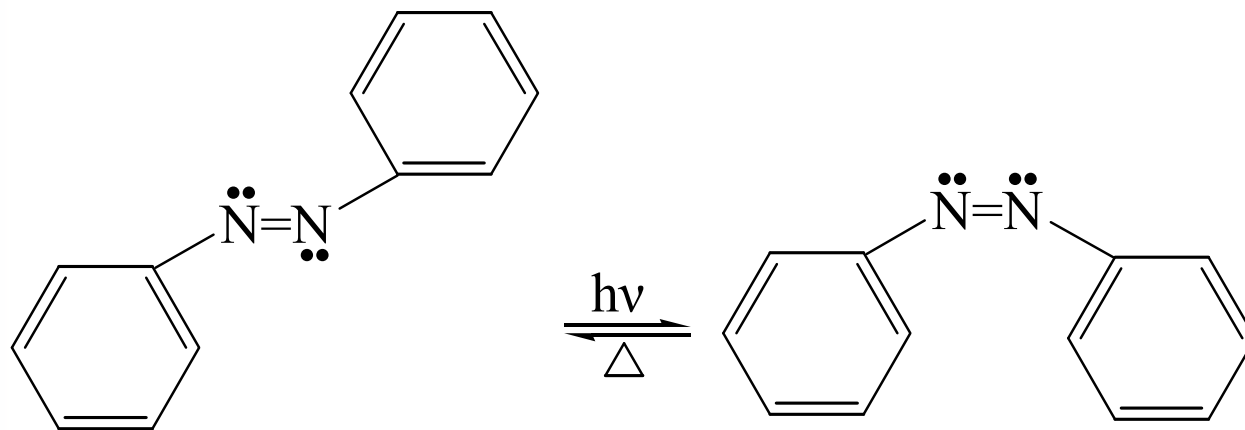
苯基重氮基苯



对氨基偶氮苯

2. 芳香族偶氮化合物的性质和反应

芳香族偶氮化合物具有高度的热稳定性,有颜色,可用作指示剂或染料。



(E)-偶氮苯

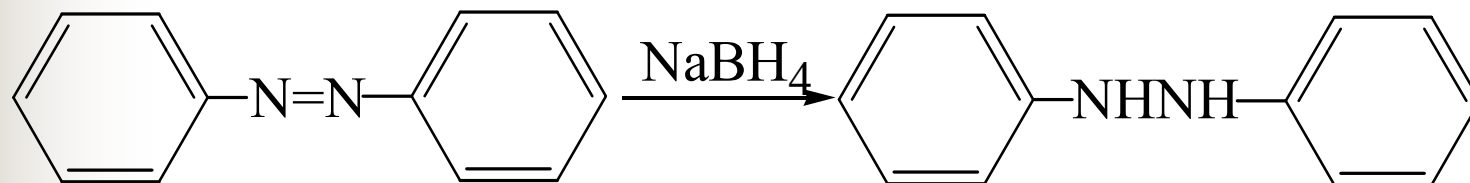
m.p.68°C

(Z)-偶氮苯

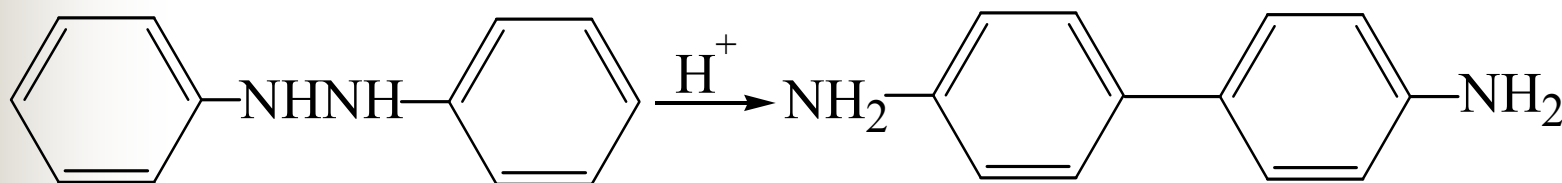
m.p.71-74°C

室温下可相互转化

(1) 联苯胺的重排

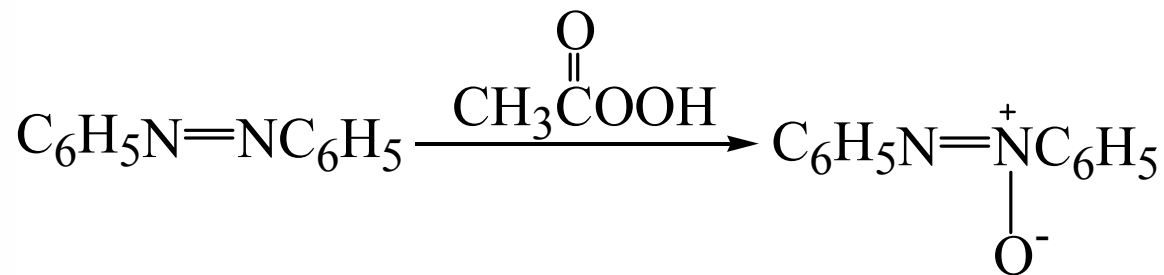


二苯肼



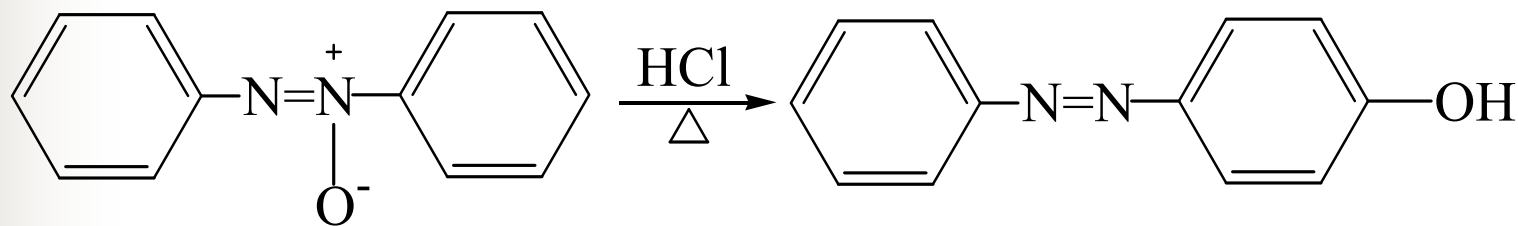
联苯胺

(2) 氧化偶氮苯

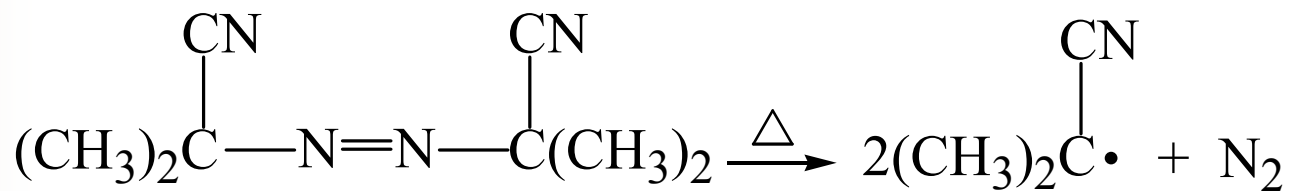


氧化偶氮苯

氧化偶氮苯在浓酸中重排为对羟基偶氮苯：



3. 脂肪族偶氮化合物



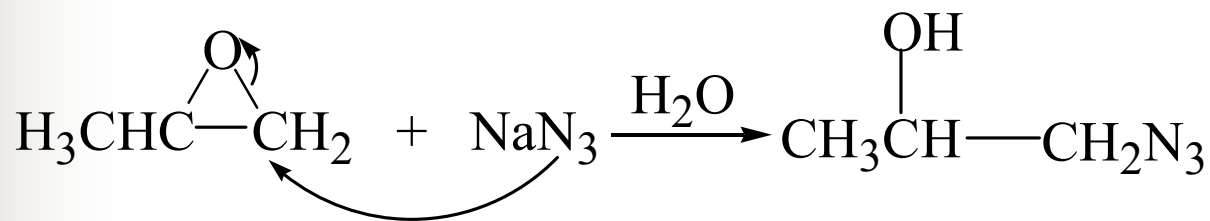
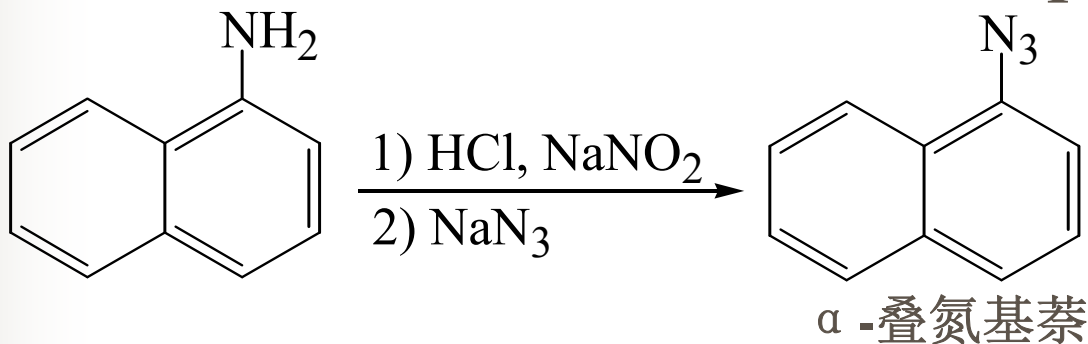
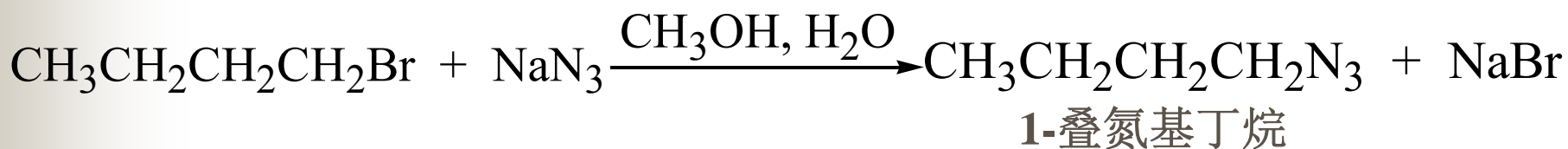
可作为自由基引发剂

§ 18.4 叠氮化合物 (Azides)

通式: RN_3 是有用的合成中间体

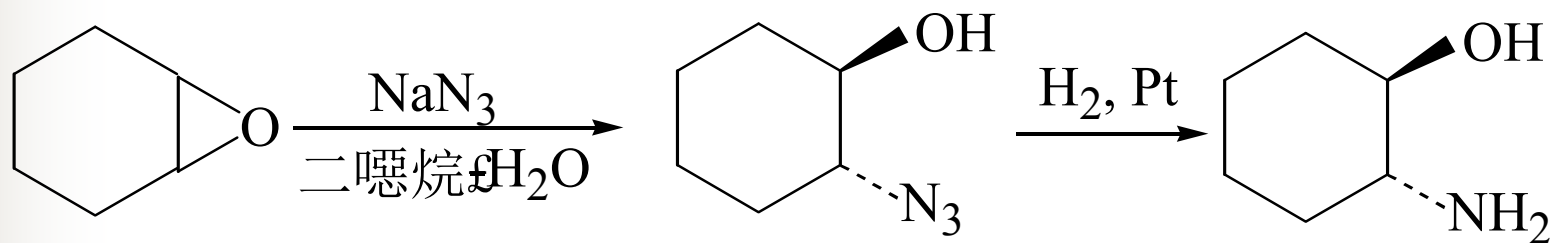
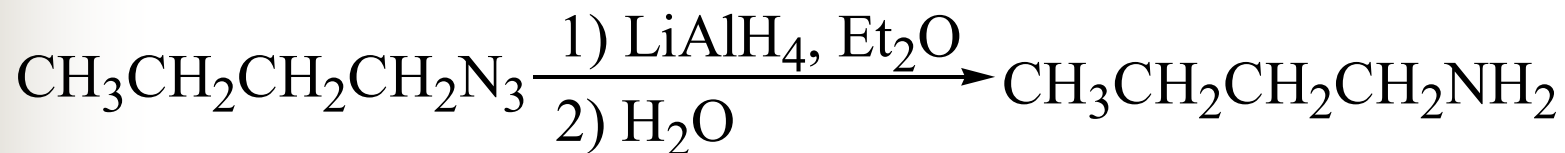
一、叠氮化合物的制法

叠氮酸(HN_3)是一弱酸($\text{pK}_a = 11$), 其负离子有很强的亲核性:



二、叠氮化化合物的反应

用氢化铝锂还原或催化加氢生成胺：

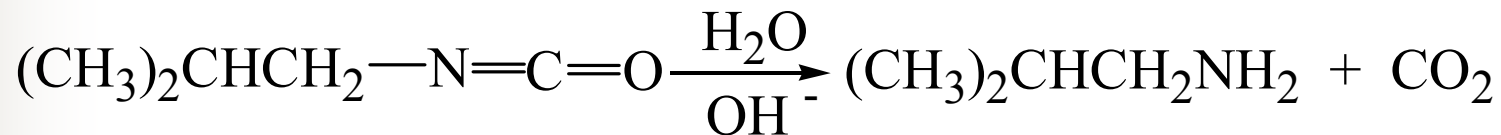
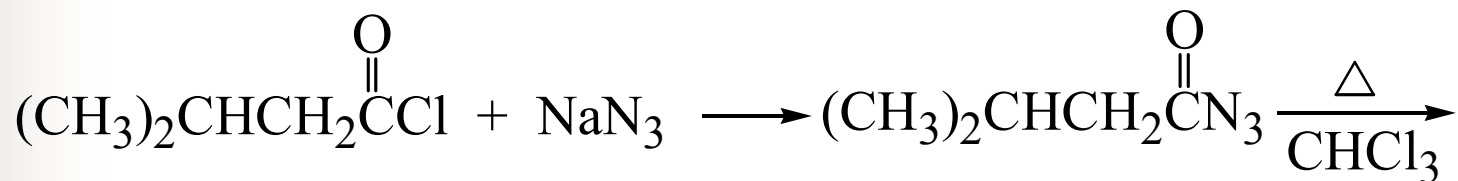
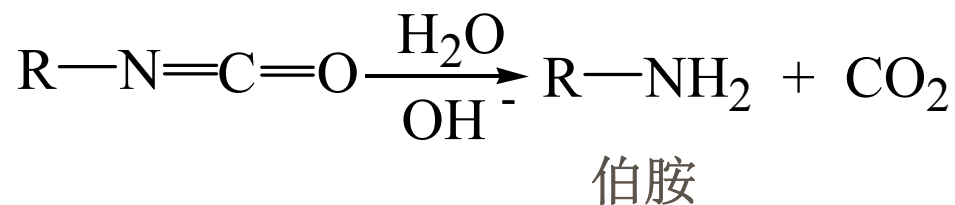
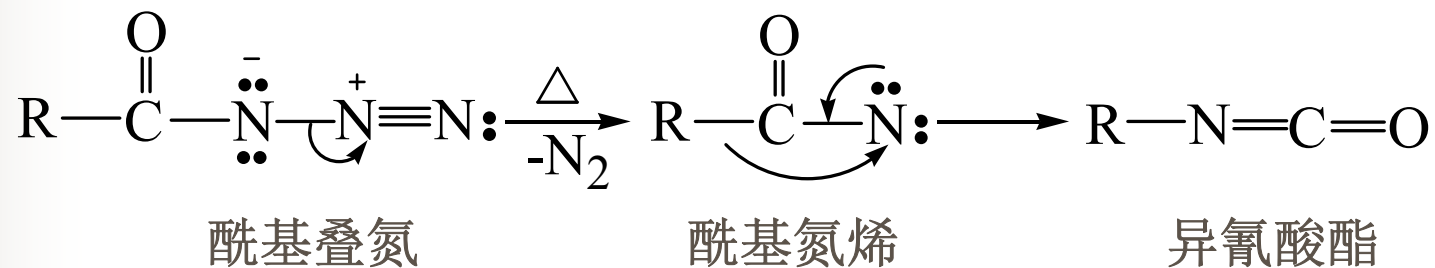


1,2-环氧环己烷

反-2-叠氮基环己醇

反-2-氨基环己醇

库尔提斯重排(Curtius rearrangement)



施密特(Schmidt)重排

