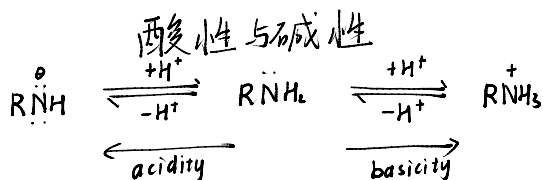


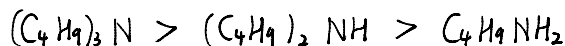
第13章 胺及其衍生物

胺的结构

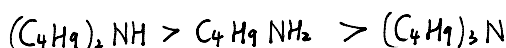


胺的碱性

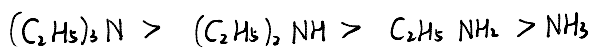
在非质子性溶剂**氯苯**中测定的碱性强弱次序为：



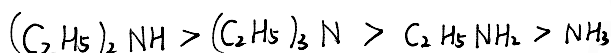
在**水**中测定的碱性强弱次序为：



气相中测定的碱性强弱次序为：

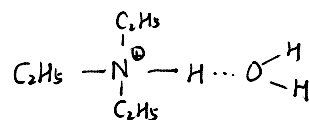
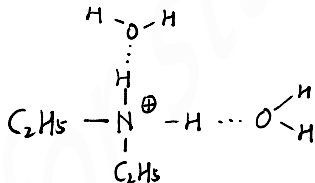
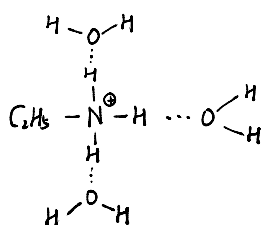


水溶液中测定的碱性强弱次序为：



烷基的给电子作用

氢键的溶剂化作用：氢键使铵离子(共轭酸)更稳定

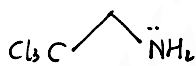


[2122 CX 120] 胺类化合物, 其中碱性最强的氮原子为 b

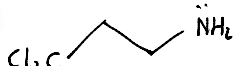


电子效应

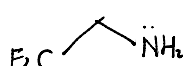
诱导效应



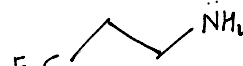
pK_{aH} 5.5



9.65

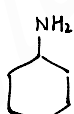


5.7



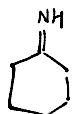
8.7

N原子的杂化类型

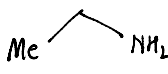


pK_{aH}

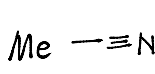
10.7



9.2

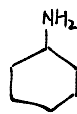


10.8

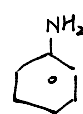


-1.0

共轭效应

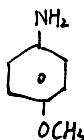


pK_{aH} 10.7



4.6

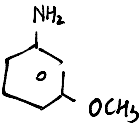
碱性：



>



>

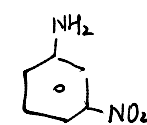


负电荷有利于稳定铵正离子



4.58

>



2.47

>



1.00

影响胺的碱性强弱的因素：

1. 电子效应(氮原子杂化状态)

2. 立体效应

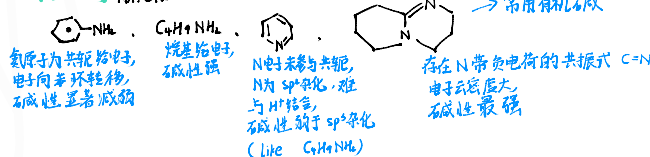
3. 溶剂化效应

脂环仲胺 > 脂肪仲胺 > 脂肪伯、叔胺 > 芳伯胺 > 芳仲胺 > 芳叔胺

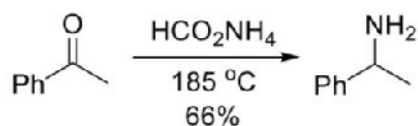
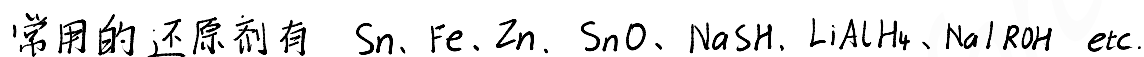


吸电子诱导效应使胺的共轭酸的正电荷更加集中, 从而使胺碱性降低

[21311] 有机胺碱性比较

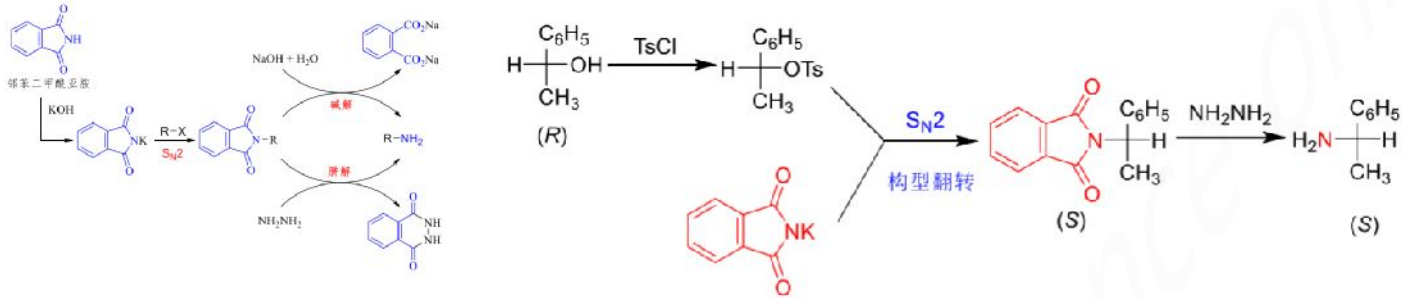


(1) 含氮化合物的还原

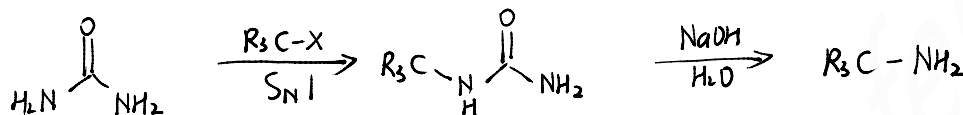


(2) 亲核取代 (N-烷基化反应)

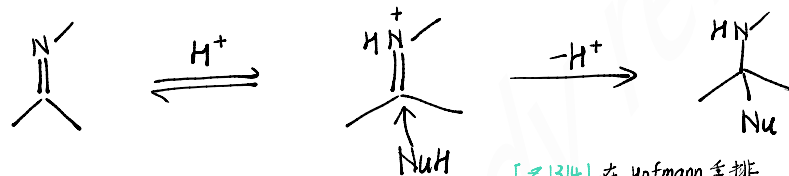
Gabriel 合成法



其他烷基化方法

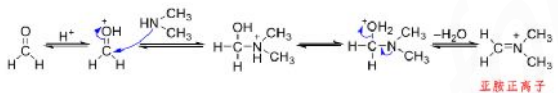
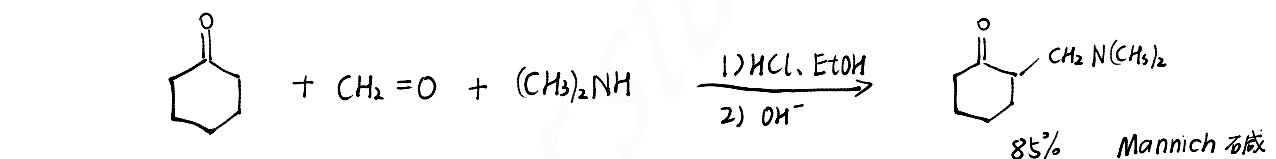


(3) 亲核加成反应 (亚胺的亲核加成)

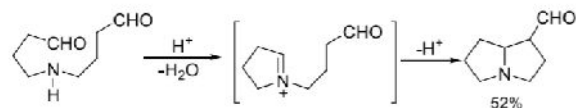


[Z1314] 在 Hofmann 重排、Wolff-Kishner - 黄鸣龙、Cannizzaro、Mannich 反应中, 一定有 C-C 形成的是: Mannich 反应。

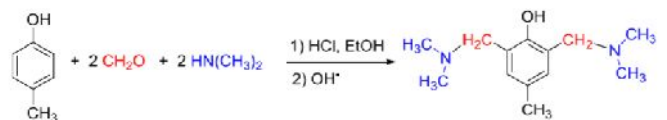
Mannich 反应: 三组分反应, "一锅法"



> 分子内反应更容易发生:

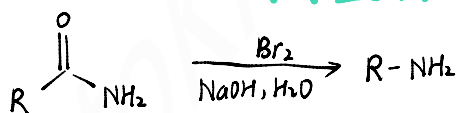


> 酚可代替烯醇:

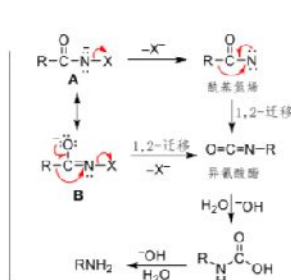
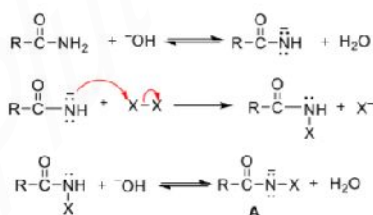


(4) 重排反应 (1,2 迁移到 N 原子)

Hofmann 重排 构型保持



反应机理:

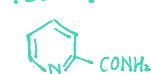


与水发生加成

氨基甲酸, 很不稳定

[Z1313]

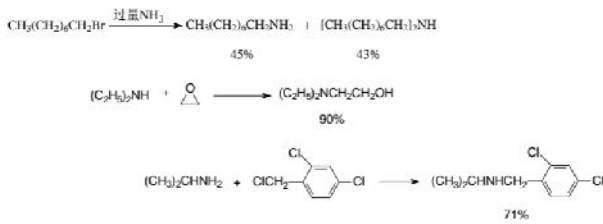
[Z1422]



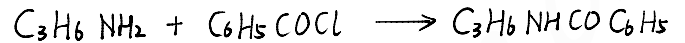
胺的反应

亲核取代反应

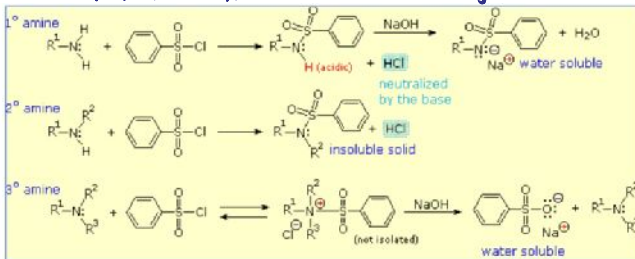
N-烷基化反应：S_N2反应



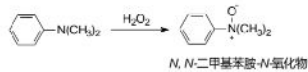
与酰氯/酸酐/酯反应



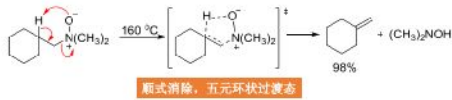
与磺酰氯反应 — Hinsberg test



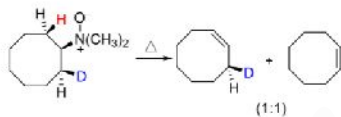
胺的氧化及 Cope 消除反应



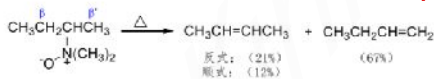
Cope 消除
 — occurs when 3°-amine oxides are heated at temperatures of 150 to 200 °C



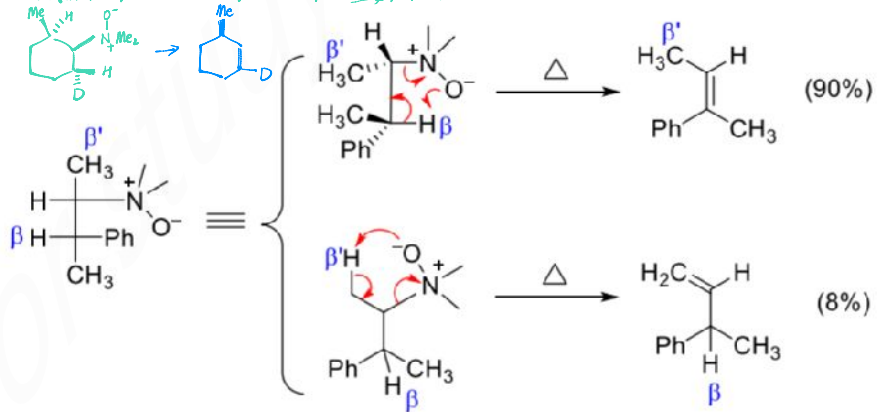
> 立体选择性：顺式消除



> 区域选择性：取决于热力学和动力学因素



[2]22 CXCI5
 下列叔胺氧化物进行 Cope 消除反应，主要产物为

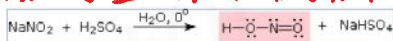


顺式消除 E13220

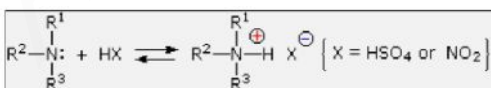
与含更多β-氢位优先消除

生成的烯烃越稳定，其比例越高

胺与亚硝酸的反应

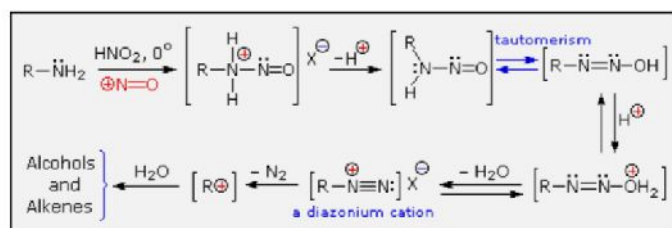


与三级脂肪胺反应



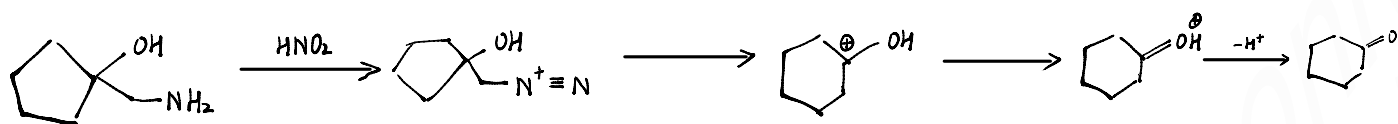
Nitrous acid: HNO₂ or HONO

与一级脂肪胺的反应



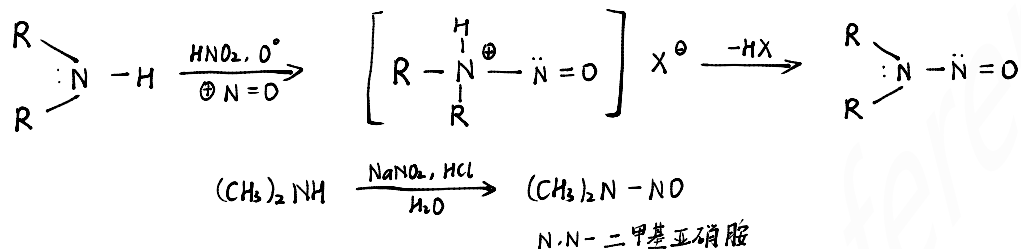
2C. 2.2

Tiffeneau - Demjanov 重排 (TDR): 1,2 - 迁移机理, 半频哪醇重排

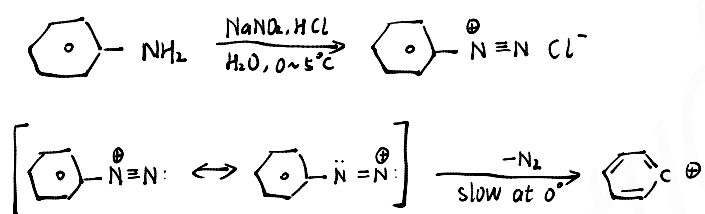


反应的选择性取决于: 立体, 电子, 轨道对称性控制等因素

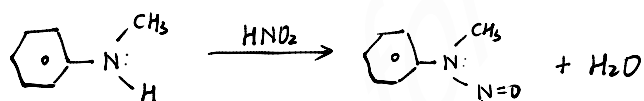
与二级脂胺的反应



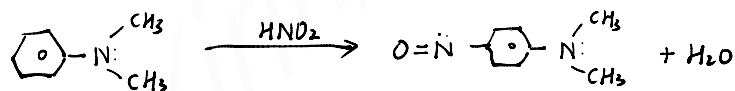
与一级芳胺的反应



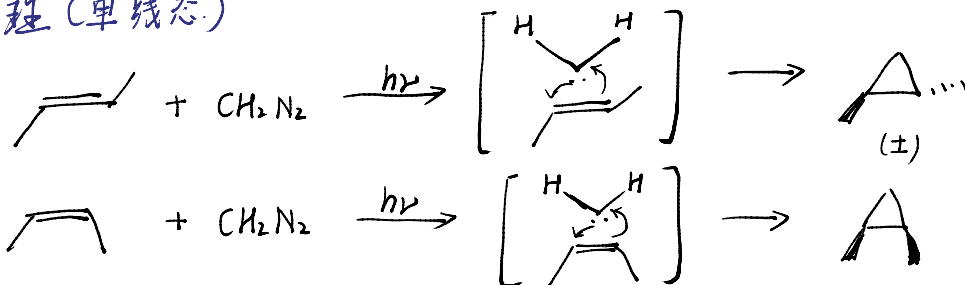
与二级芳胺的反应



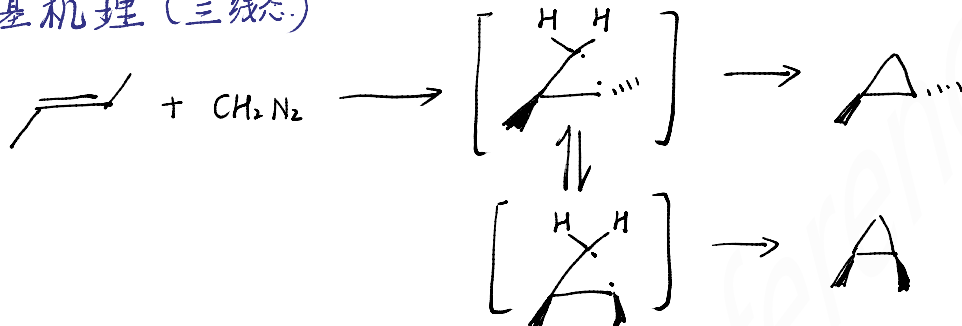
与三级芳胺的反应



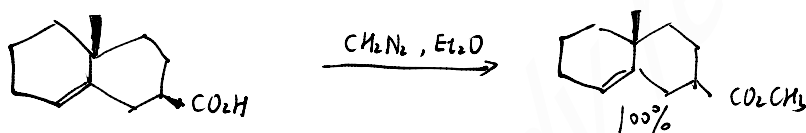
→ 协同机理 (单线态)



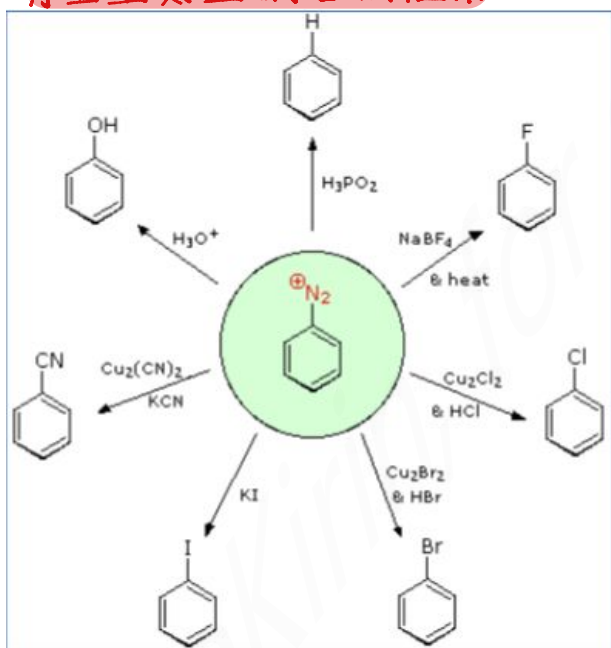
→ 双自由基机理 (三线态)



(*) 2) O-H 插入 - 甲基化成酯或醚

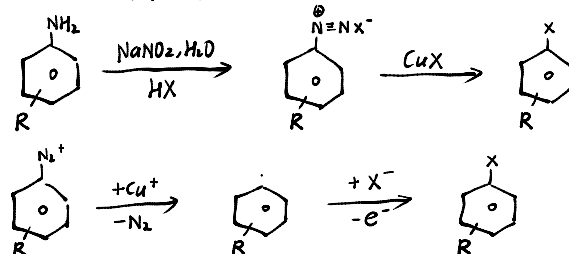


芳基重氮盐的合成应用

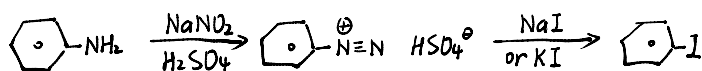


1) 重氮盐基团被 Cl, Br, CN 取代: Sandmeyer 反应

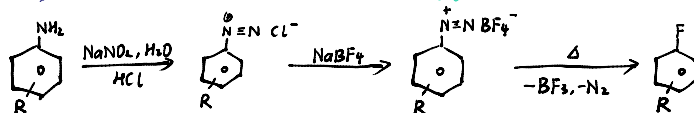
催化剂为相应的 Cu(I) 盐



2) 重氮盐基团被碘取代

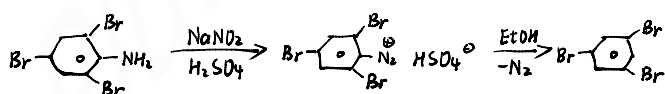


3) 重氮盐基团被氟取代 z 13226

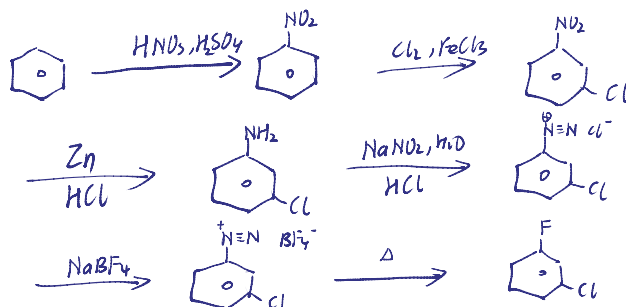
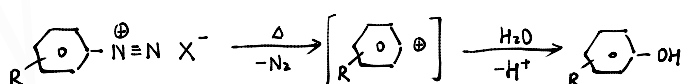


4) 重氮盐基团被 H 取代

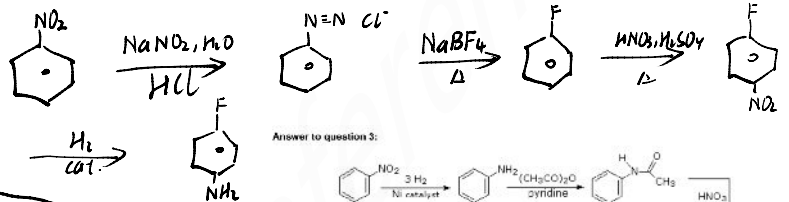
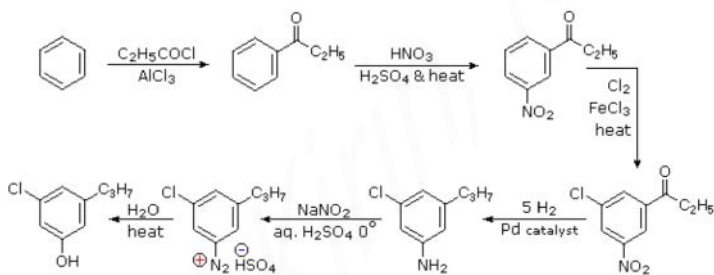
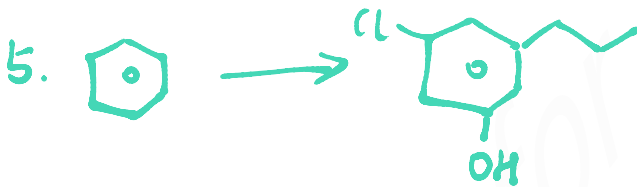
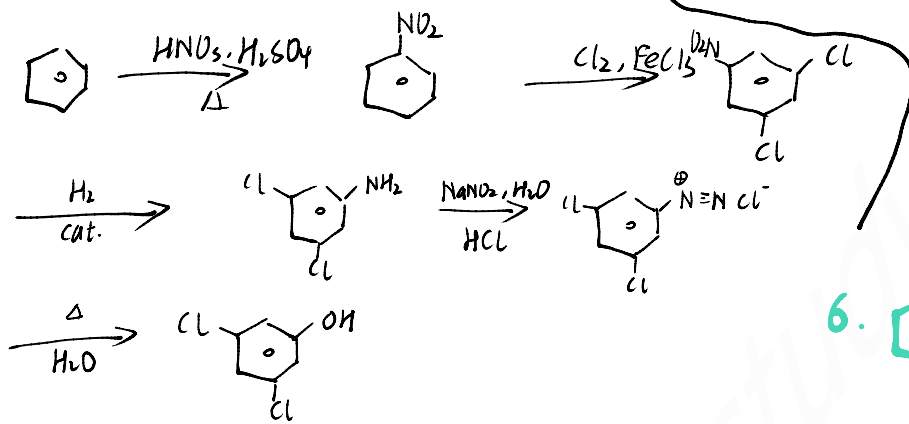
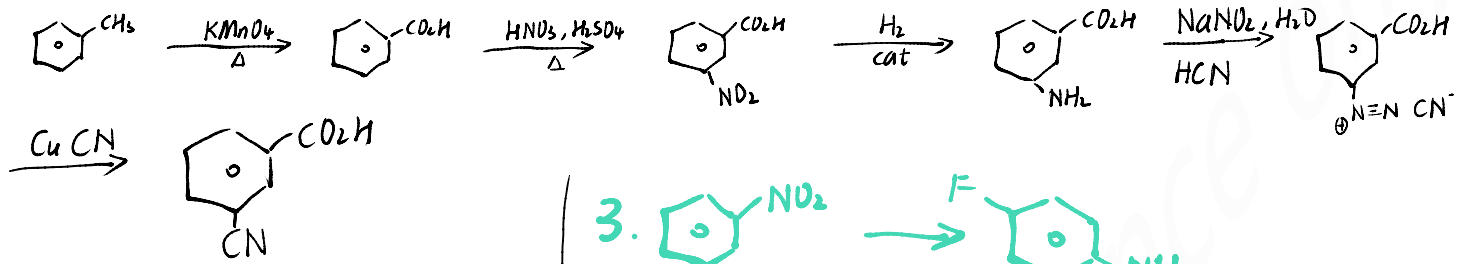
常用还原剂: 次磷酸、乙醇、石肼氢化钠



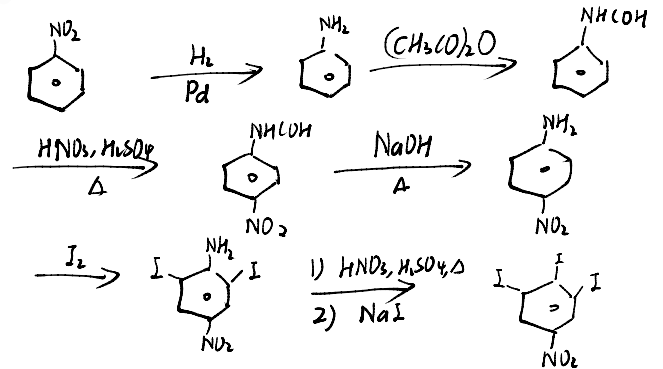
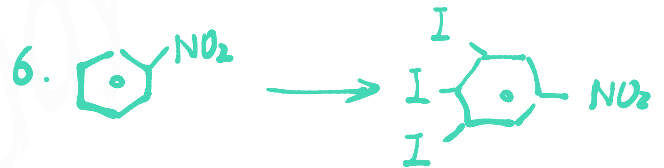
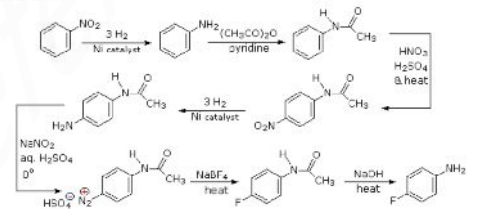
5) 重氮盐基团被 OH 取代 —— 重氮盐的水解



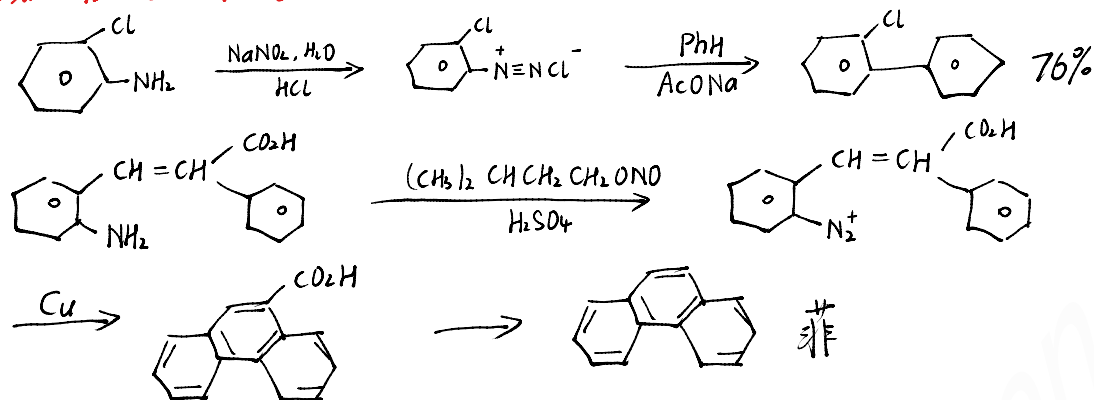
Questions:



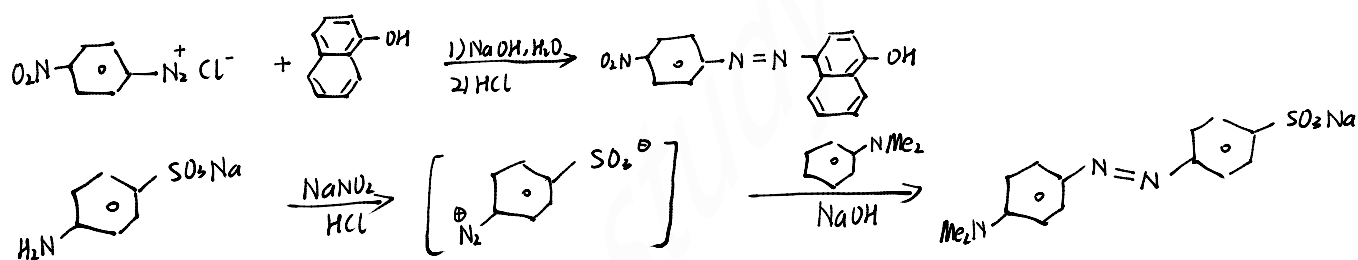
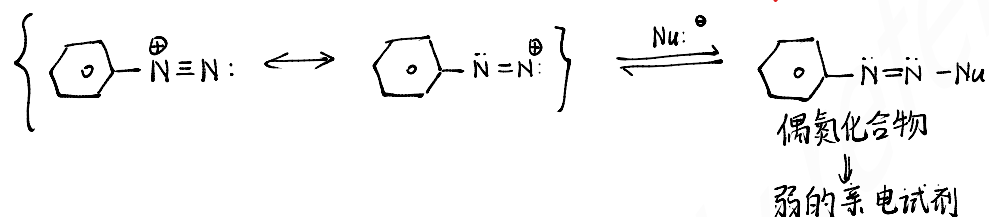
Answer to question 3:



偶联反应 (Coupling Reactions)



亲电取代反应：形成偶氮化合物 (azo compounds)



第13章小结

- 胺的碱性
- 胺的制备方法和反应
- 三级胺氮氧化物和季铵碱的热消除反应
- 重氮化合物的结构与性质
- 重氮盐的合成应用