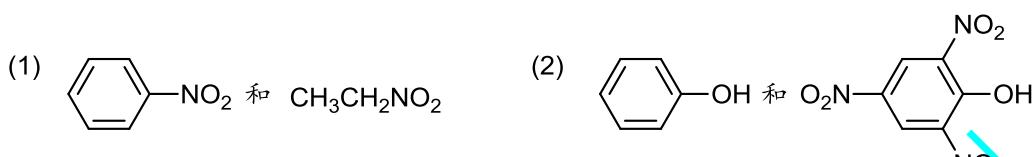


## 第十四章 含氮有机化合物

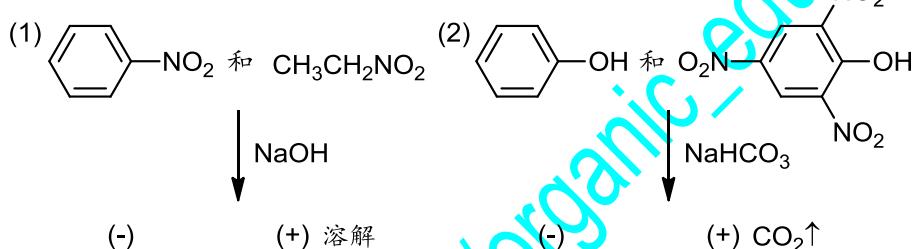
课本插题:

问题 14-1 用化学方法区别下列各组化合物:

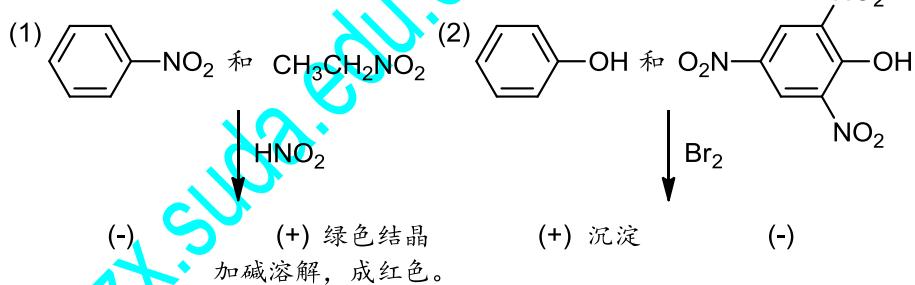


解答:

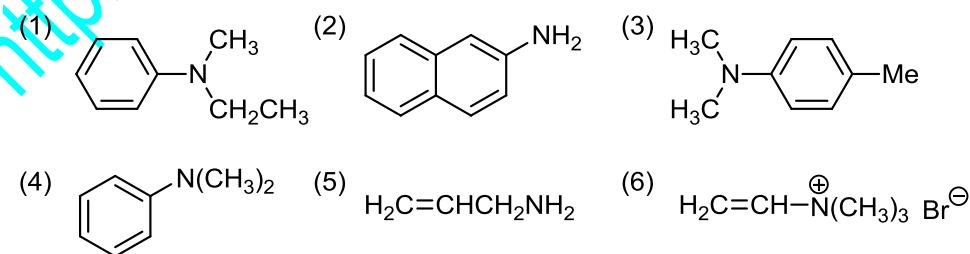
方法一:



方法二:



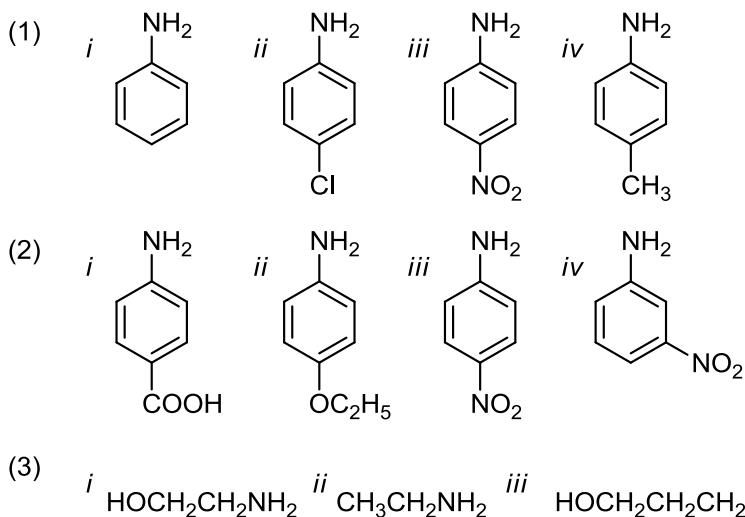
问题 14-2 命名下列化合物:



解答:

- (1). N-甲基-N-乙基苯胺; (2).  $\beta$ -萘胺; (3). 对二甲氨基苯胺;  
 (4). N,N-二甲基苯胺; (5). 烯丙胺; (6). 溴化三甲基乙烯基铵.

**问题 14-3** 比较下列化合物的碱性强弱:



解答: 碱性由强到弱为:

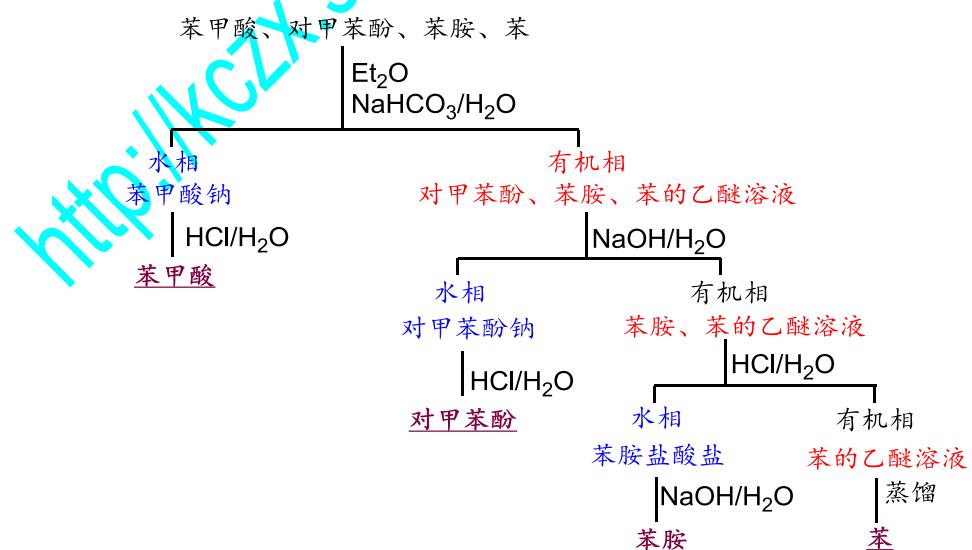
(1). *iv* > *i* > *ii* > *iii*; (2). *ii* > *iv* > *iii* > *i*; (3). *ii* > *iii* > *i*.

**问题 14-4** 用化学方法鉴别: 乙胺、二乙胺和三乙胺。

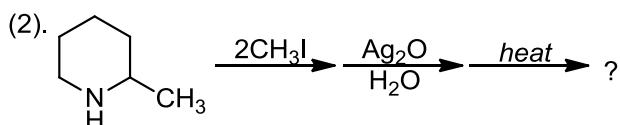
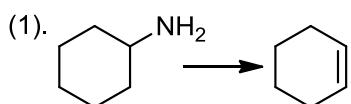
解答: 略, 见课件胺的通性, 磺酰化反应: Hinsberg 反应.

**问题 14-5** 简要写出用酸、碱和有机溶剂分离提纯苯甲酸、对甲苯酚、苯胺和苯等混合物的方法.

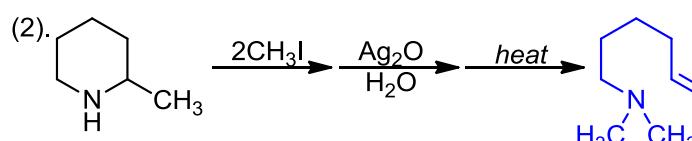
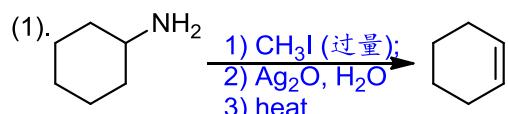
解答:



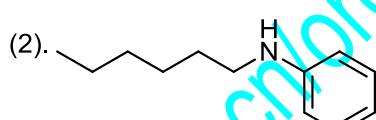
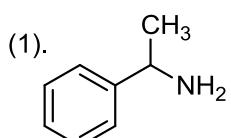
**问题 14-6** 完成下列反应式:



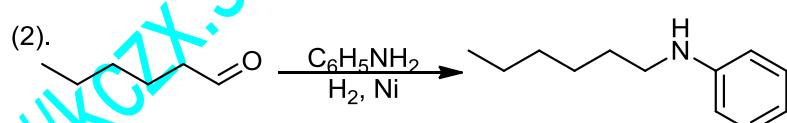
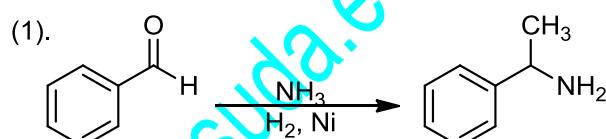
解答:



**问题 14-7** 如何通过还原氨化的方法制备下列胺:

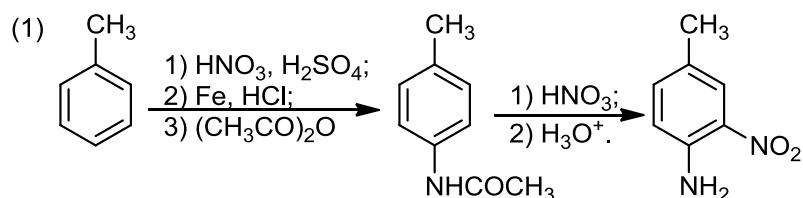


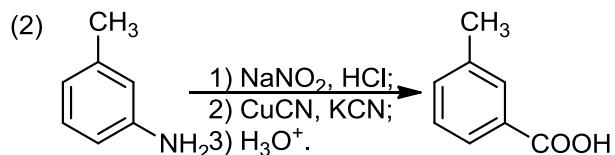
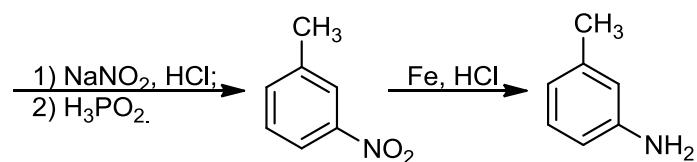
解答:



**问题 14-8** 以甲苯为主要原料合成下列化合物: 间甲苯胺、间甲苯甲酸。

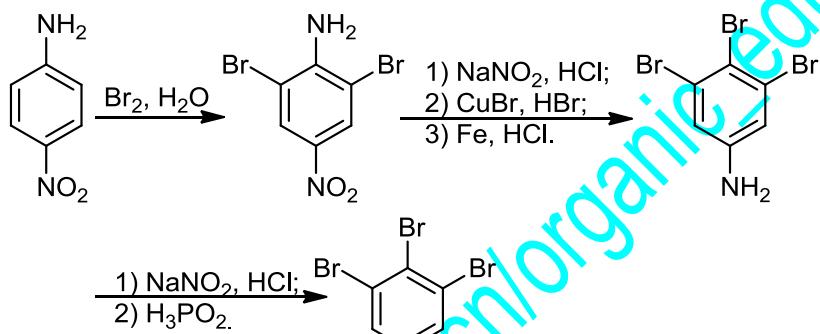
解答:





**问题 14-9** 以硝基苯胺为起始原料合成 1,2,3-三溴苯。

解答:



课后习题:

1. 给出下列化合物名称或写出结构式。

(1). 对硝基氯化苄

(2). 1,4,6-三硝基苯

(3). 苦味酸

(4). 1,4-环己基二胺

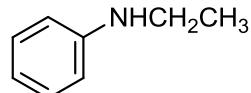
(5). N,N-二甲基乙胺

(6). CH<sub>3</sub>CH<sub>2</sub>CH(NH<sub>2</sub>)CH<sub>2</sub>CH<sub>3</sub>

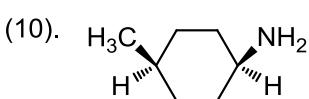
(7). (CH<sub>3</sub>)<sub>2</sub>CHNH<sub>2</sub>

(8). (CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>3</sub>

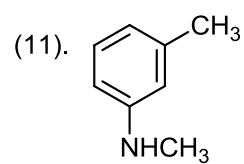
(9).



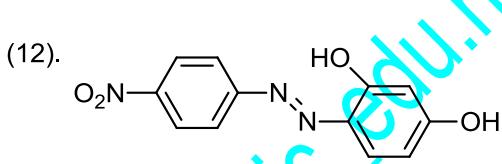
(10).



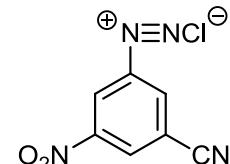
(11).



(12).

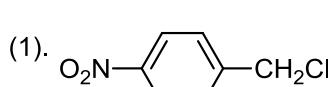


(13).

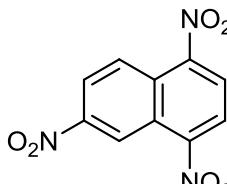


解答:

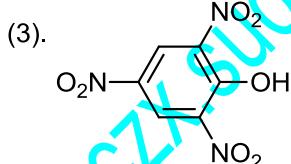
(1).



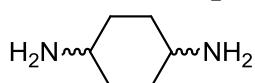
(2).



(3).



(4).



(5). (CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>3</sub>

(6). 3-氨基戊烷

(7). 异丙胺

(8). 二甲基乙基胺

(9). N-乙基苯胺

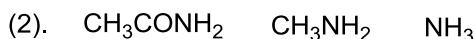
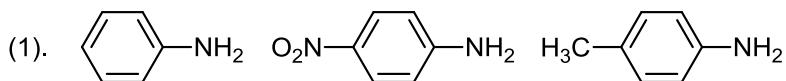
(10). 顺-4-氨基-1-甲基环己烷

(11). N-甲基间甲苯胺

(12). 2,4-二羟基-4'-硝基偶氮苯

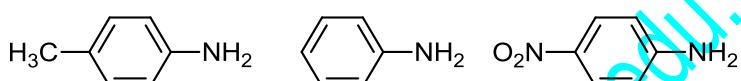
(13). 氯化 3-氰基-5-硝基重氮苯

2. 按其碱性的强弱排列下列各组化合物，并说明理由。

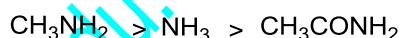


解答:

(1). 苯胺分子中存在苯环的 $\pi$ 键与 N 原子上的含孤对电子(p 电子)的 p 轨道间的 p- $\pi$ 共轭作用。苯环上连接拉电子取代基, 如硝基时, p- $\pi$ 共轭的结果会使 N 上的电子云密度进一步下降, 因而碱性减弱; 与之相反, 苯环上连接给电子取代基时, 苯环上电子云密度的增高会降低因 p- $\pi$ 共轭作用引起的 N 上的电子云密度的降低程度, 因而碱性增强:



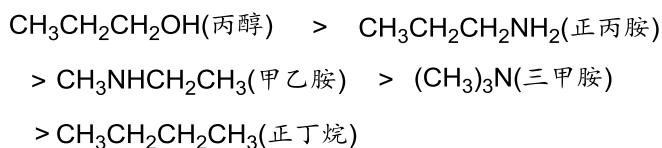
(2). 甲基具有给电子诱导效应, 氨分子一个氢原子被甲基取代后, 氮原子接受质子或提供电子对的能力提高, 碱性增强。而氨分子一个氢被乙酰基取代后, 氮原子的 p 轨道与羰基的 $\pi$ 键之间存在 p- $\pi$ 共轭, 结果导致氮上的电子密度明显降低, 氧原子上的电子云密度升高, 因此碱性增强:



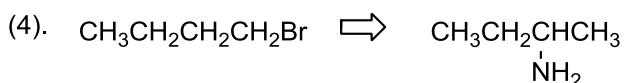
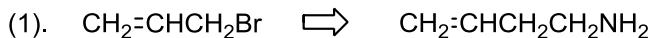
3. 比较正丙醇、正丙胺、甲乙胺、三甲胺和正丁烷的沸点高低并简明说明理由。

解答:

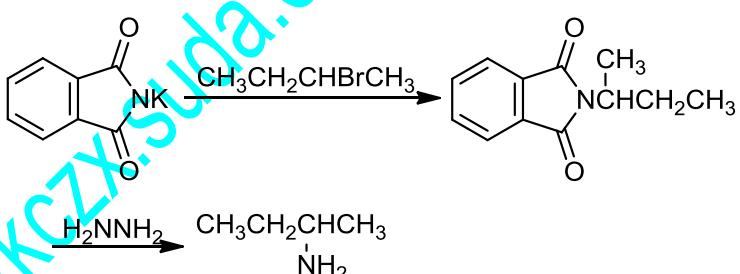
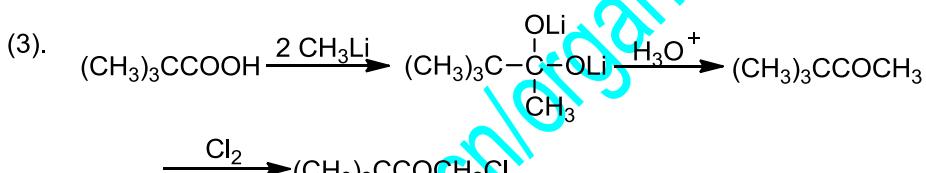
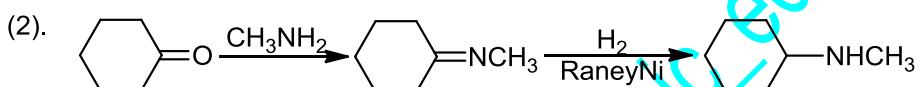
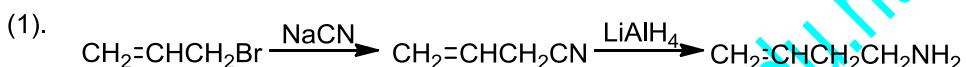
醇羟基的极性比氨基的极性大, 因此形成的分子间氢键较强, 所以丙醇的沸点比丙胺的高。正丙胺分子 N 上含有两个能形成氢键的氢原子, 甲乙胺只含有一个, 而三甲胺则无。因此, 正丙胺分子间已形成较强的氢键, 甲乙胺次之, 而三甲胺不能形成分子间氢键, 这是引起三种胺沸点不同的主要原因。三甲胺 C—N 的键属于极性键, 分子间存在偶极相互作用, 而正丁烷分子间只存在范德华色散力作用, 因此三甲胺的沸点要高于正丁烷的沸点。



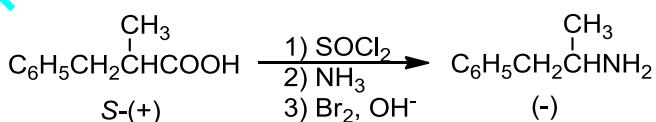
4. 如何完成下列的转变:



解答:



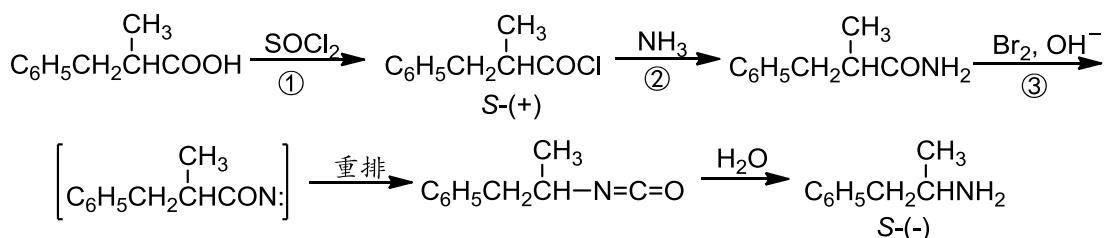
5. 完成下列各步反应，并指出最后产物的构型是(R)或(S)。



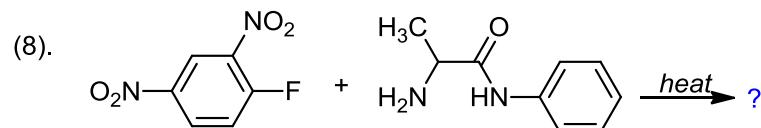
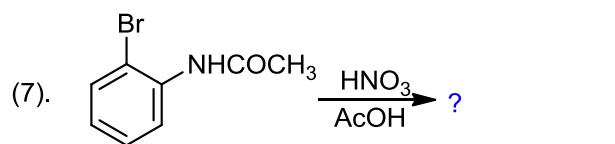
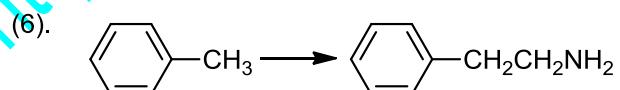
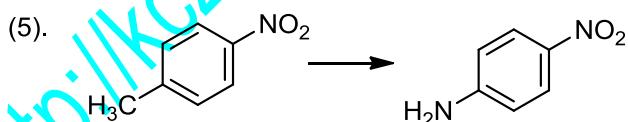
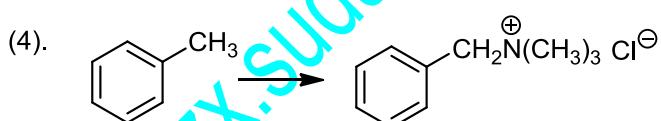
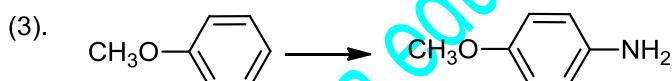
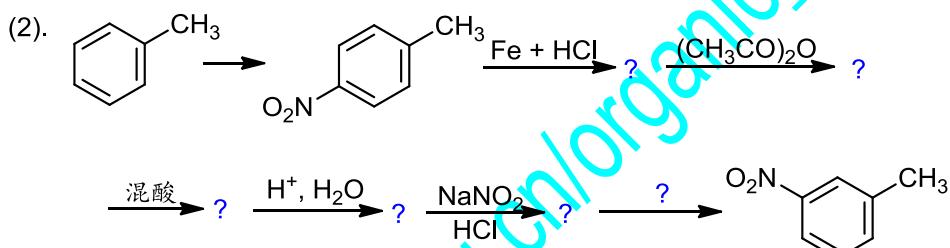
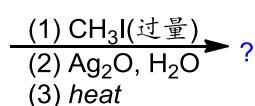
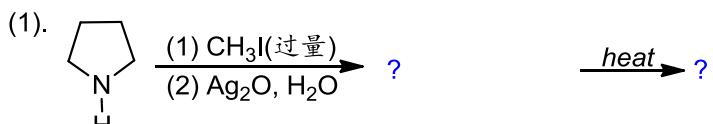
解答:

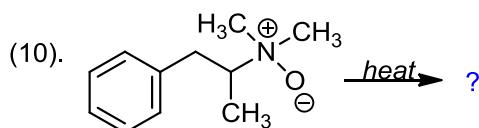
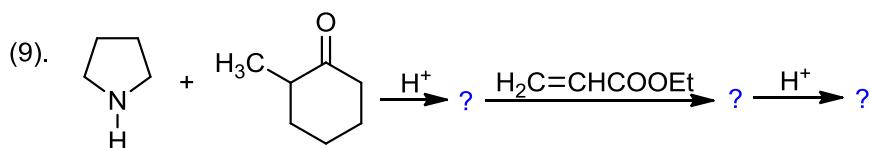
在步骤①中，未涉及手性碳相连的四个σ键的断裂。步骤②也未涉及。

步骤③中虽然涉及手性碳相连的一个σ键，但重排过程中手性碳的构型并未发生翻转。因此，可以确定最后产物的构型仍然是(S)-型。

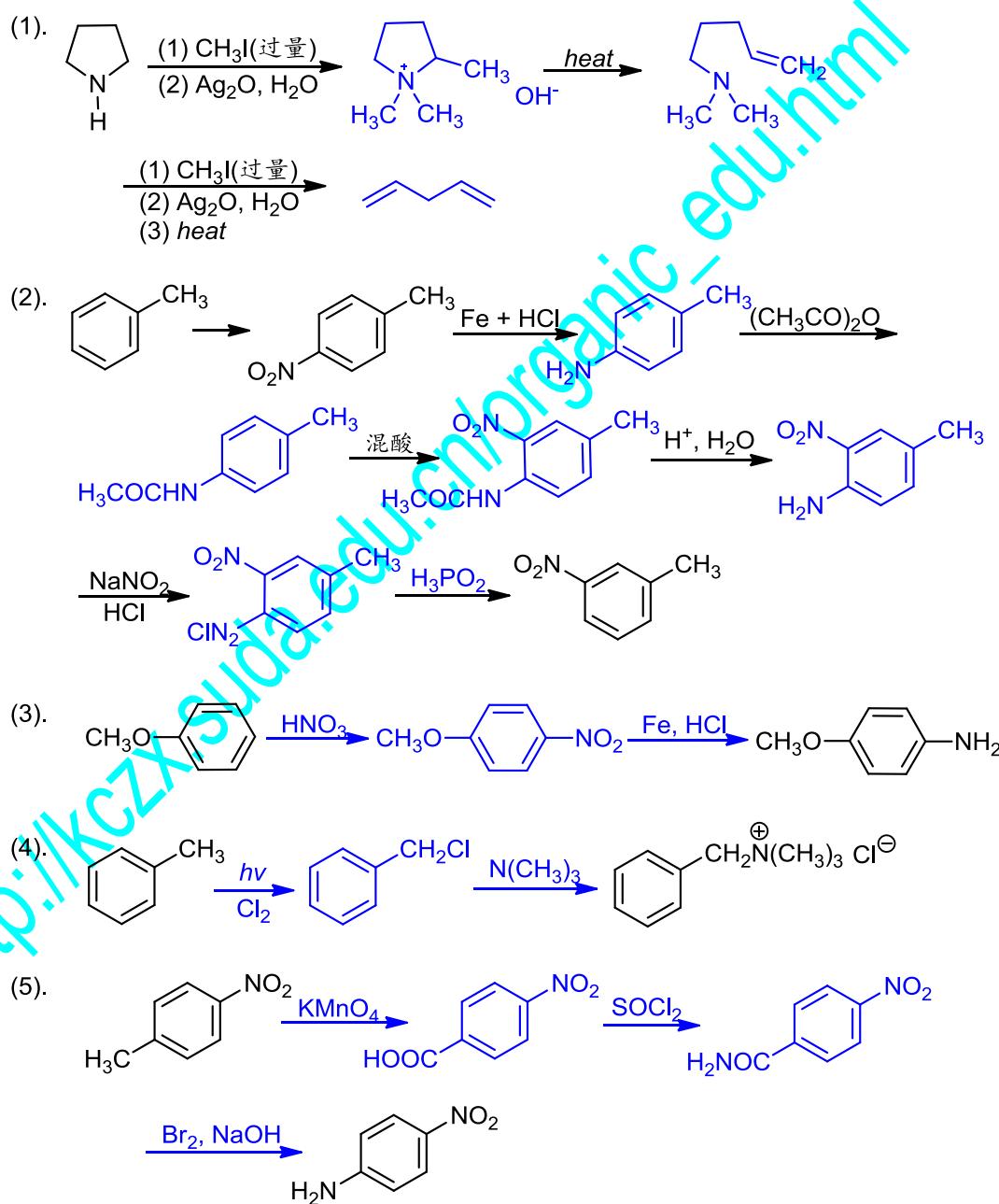


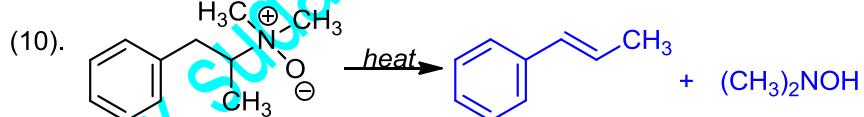
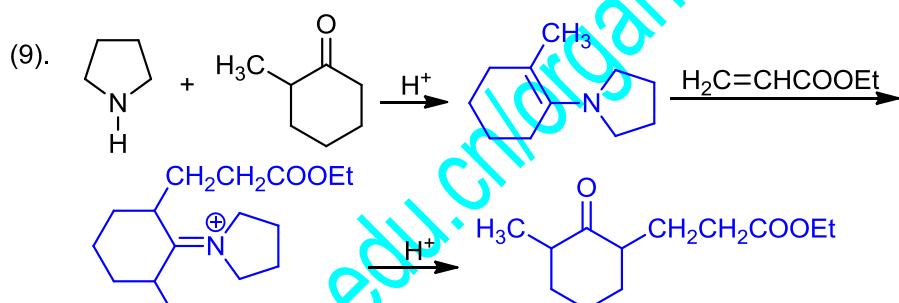
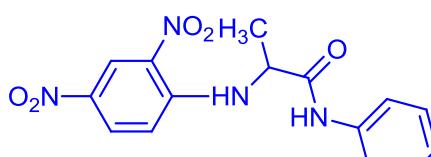
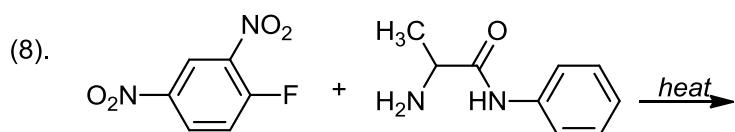
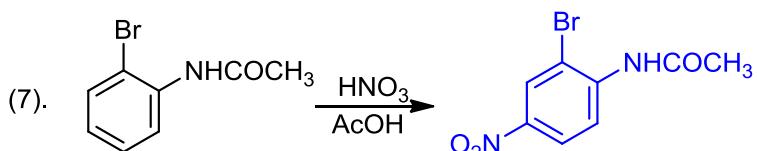
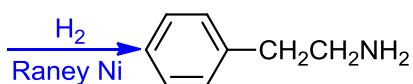
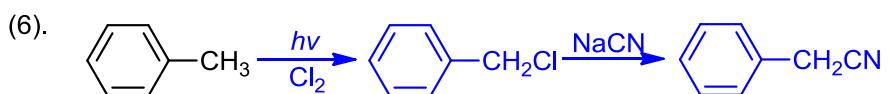
6. 完成下列反应:



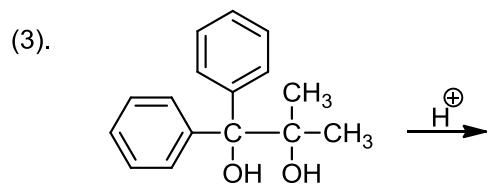
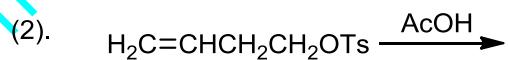
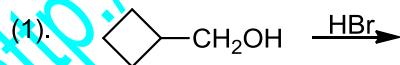


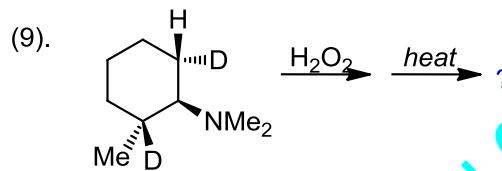
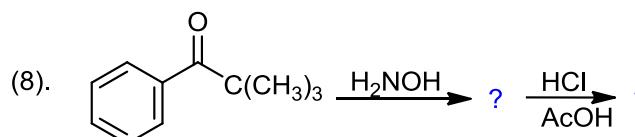
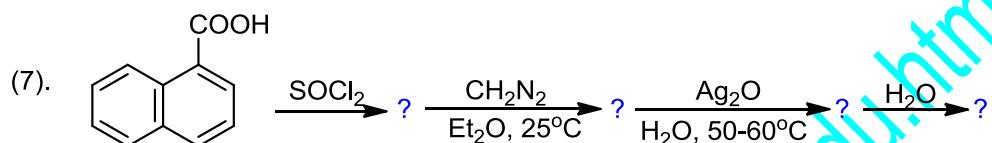
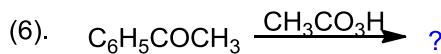
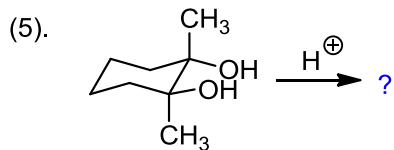
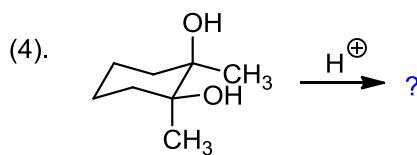
解答:



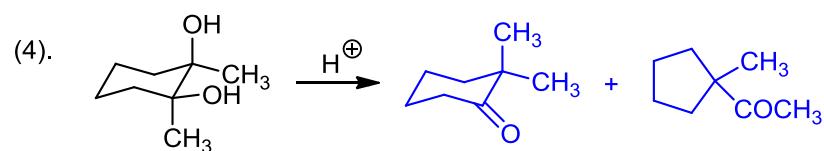
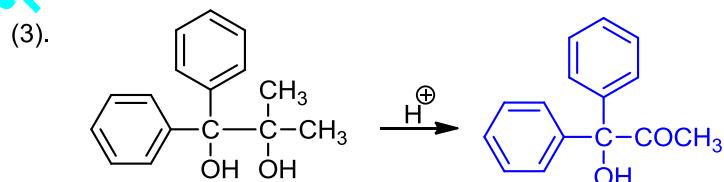
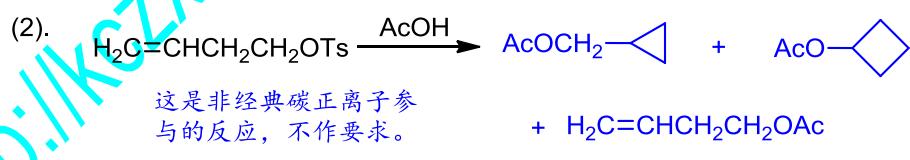


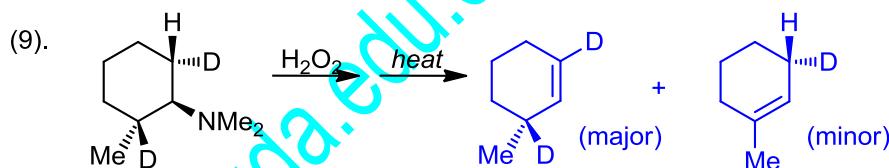
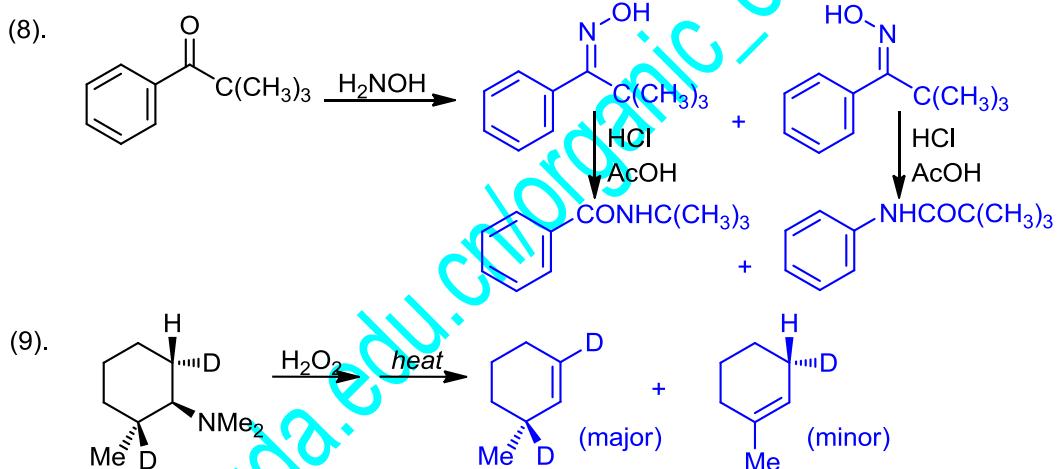
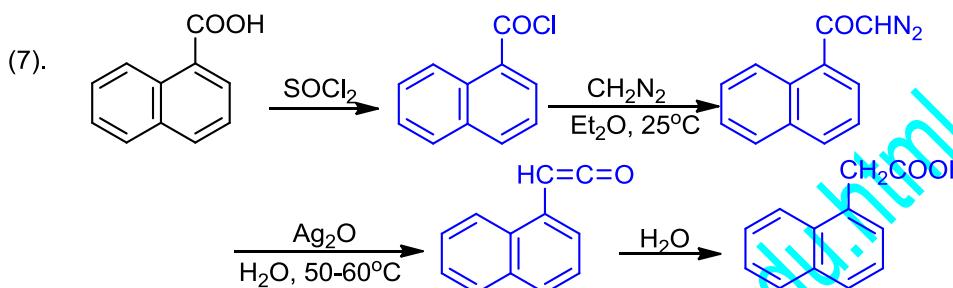
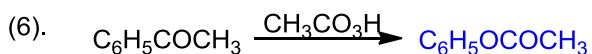
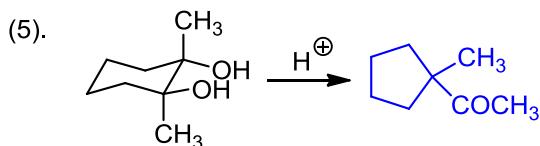
7. 指出下列重排反应的产物:





解答:





8. 解释下述实验现象:

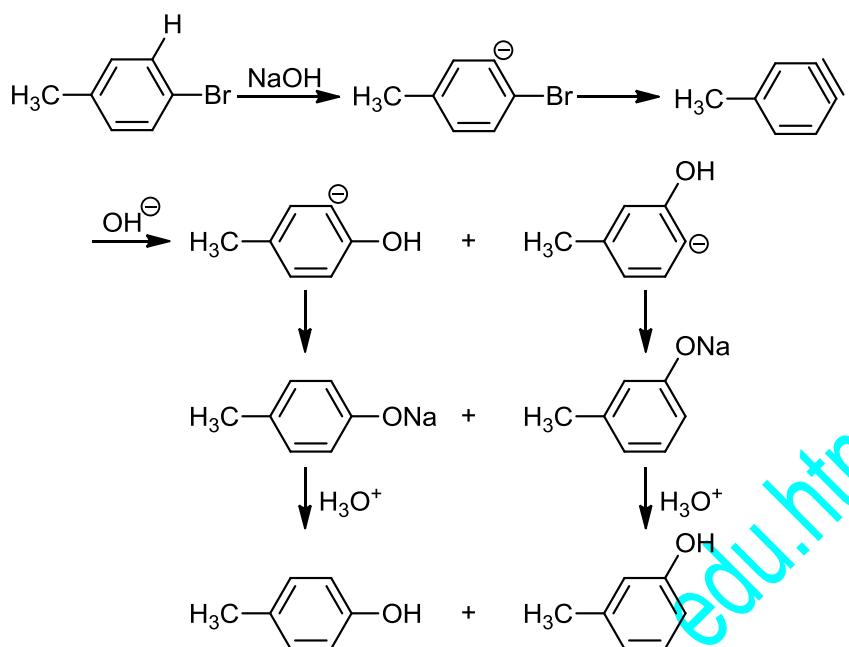
(1). 对溴甲苯与氢氧化钠在高温下反应,生成几乎等量的对甲基苯酚和间甲基苯酚。

(2). 2,4-二硝基氯苯可由氯苯硝化而得,但是如果反应用碳酸氢钠水溶液洗涤除酸,则得不到产品。

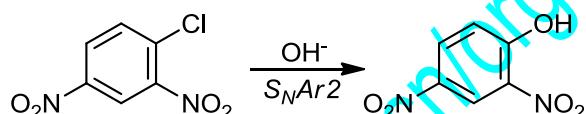
解答:

(1). 在高温下,作为强碱可以攫取芳环上的质子,然后形成苯炔中间体。

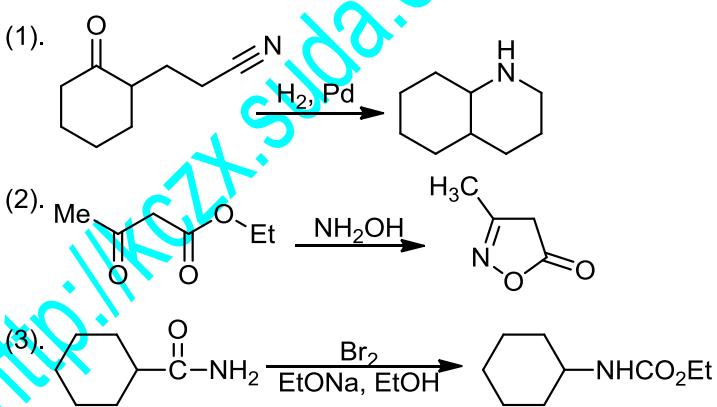
具体过程为:



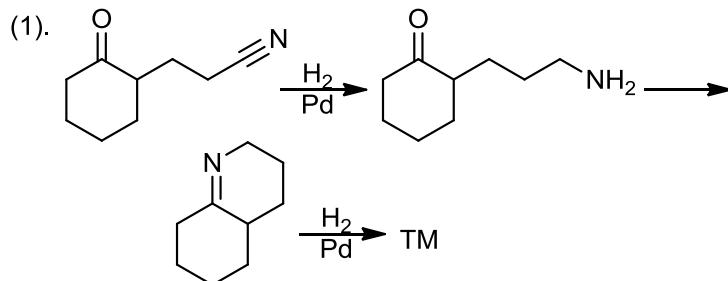
(2). 这是因为 2,4-二硝基氯苯可以在碱性条件下发生取代反应，形成 2,4-二硝基苯酚。



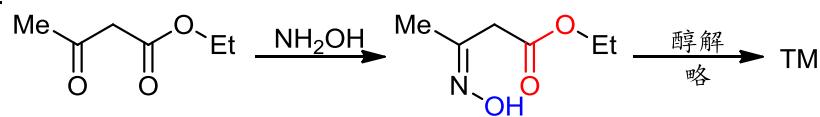
9. 写出下列反应的反应历程。



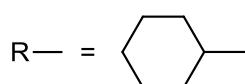
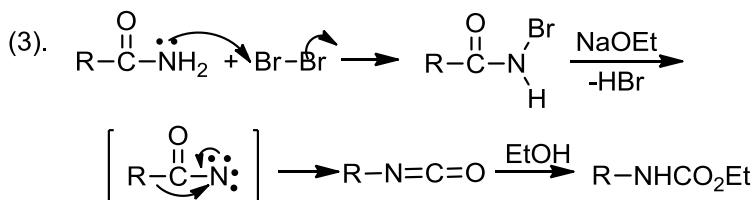
解答：



(2).



(3).

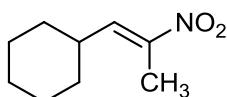


10. 从指定的原料合成:

- (1). 从环己酮和 HCN 合成环己酮;
- (2). 从 1,3-丁二烯合成制备尼龙-66 的两个单体: 己二酸和己二胺;
- (3). 从乙醇、甲苯及其他无机原料合成普鲁卡因:

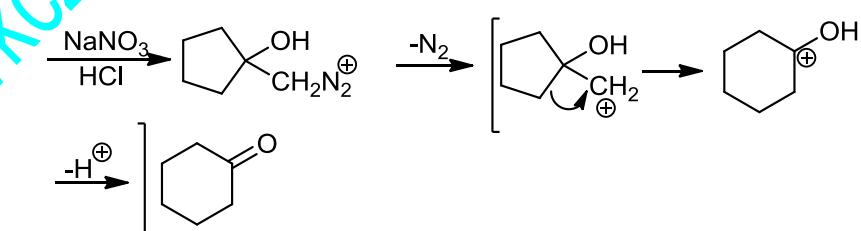
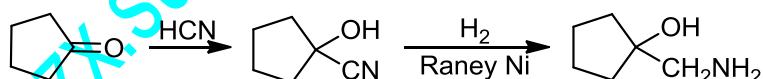


- (4). 从简单的开链化合物合成:

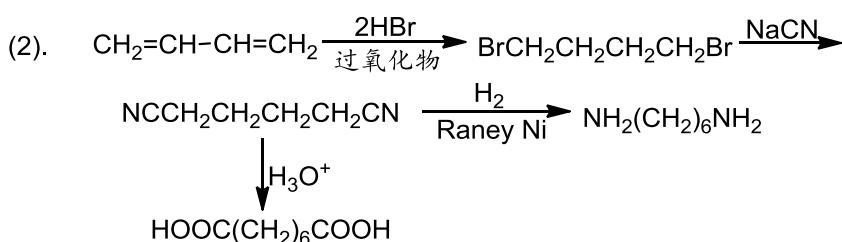


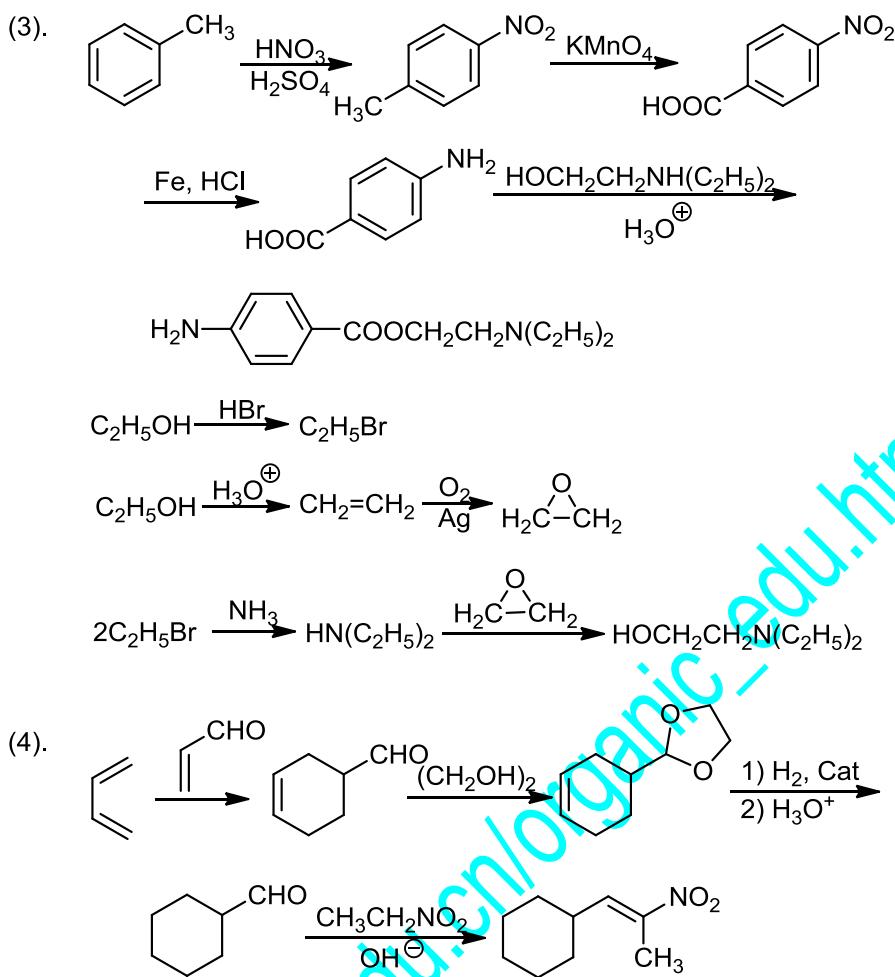
解答:

(1).



(2).

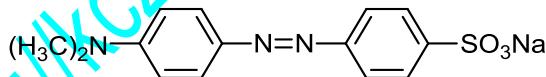




11. 选择适当的原料经偶联反应合成:

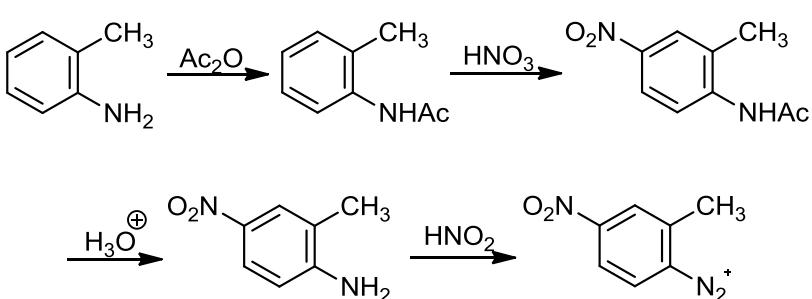
(1). 2,2'-二甲基-4-硝基-4'-氨基偶氮苯;

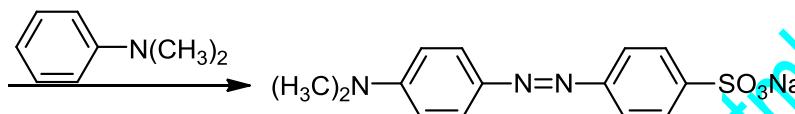
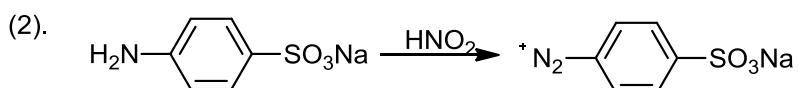
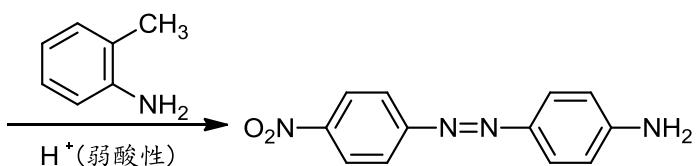
(2). 甲基橙:



解答:

(1).





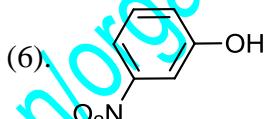
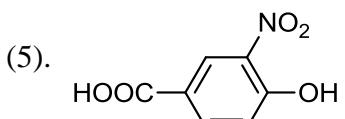
12. 从甲苯或苯为原料合成下列化合物:

(1). 间氨基苯乙酮;

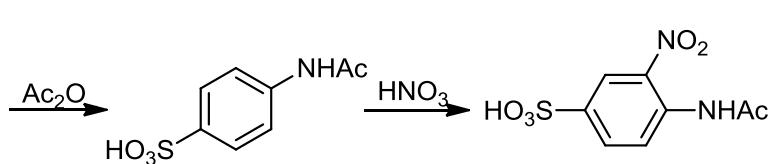
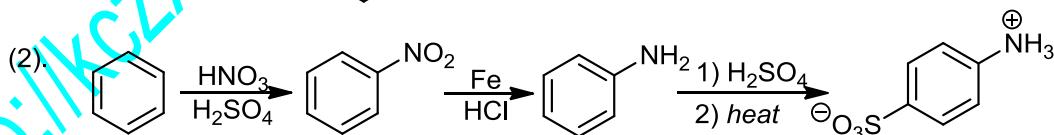
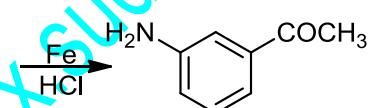
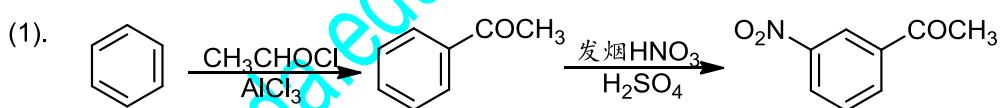
(2). 邻硝基苯胺;

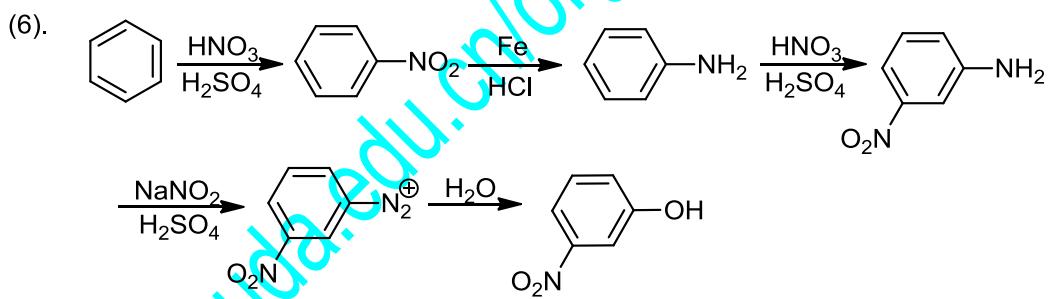
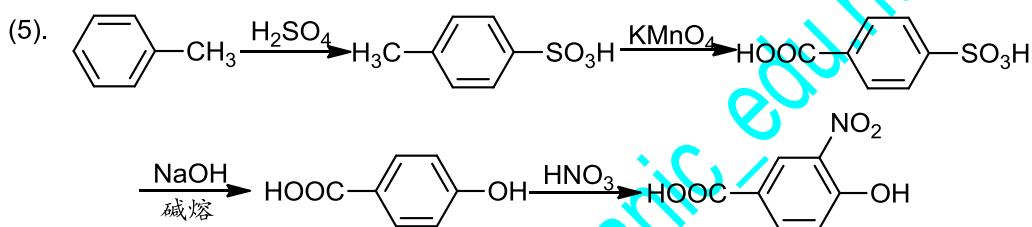
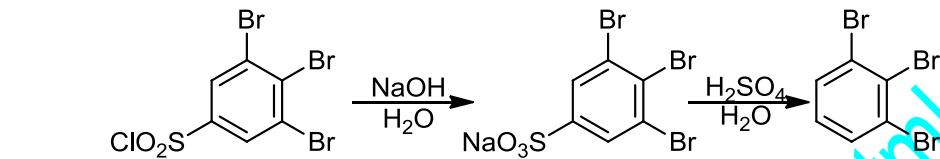
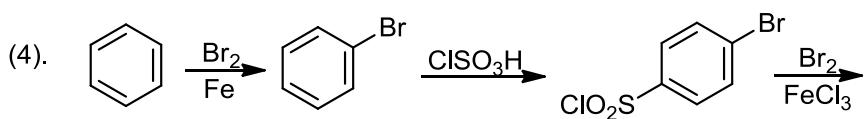
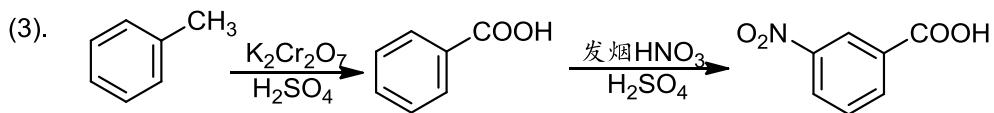
(3). 间硝基苯甲酸;

(4). 1,2,3-三溴苯



解答:





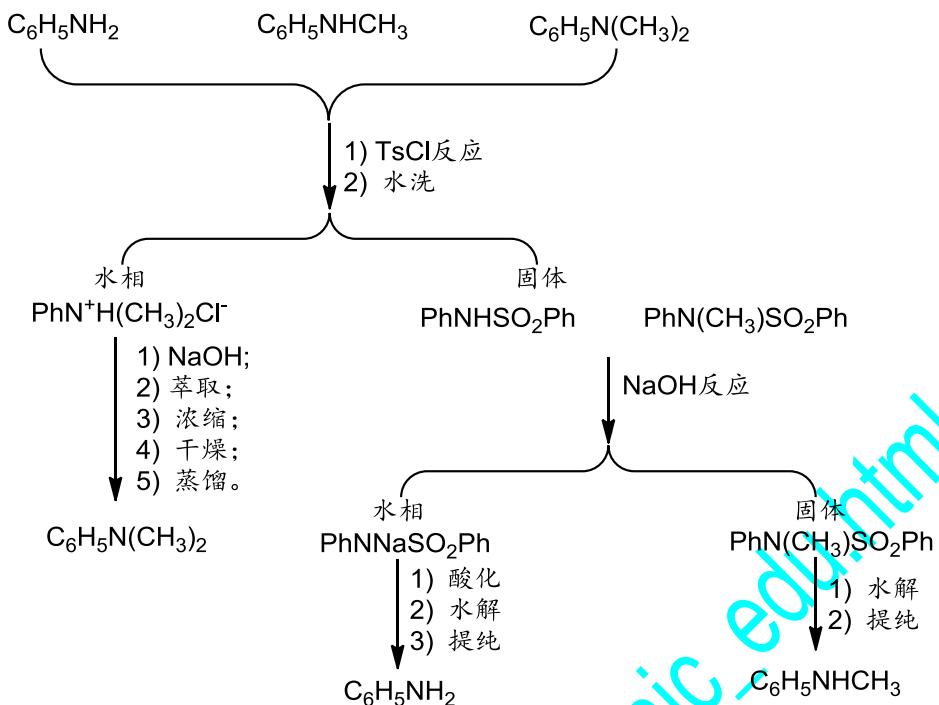
13. 试分离提纯下列各组化合物:

(1). 苯胺, N-甲基苯胺, N,N-二甲基苯胺.

(2). 苯甲酸, 对甲苯酚, 对甲苯胺.

解答:

(1). 苯胺, N-甲基苯胺, N,N-二甲基苯胺的分离与提纯:



(2). 苯甲酸, 对甲苯酚, 对甲苯胺分离与提纯参见课本插题 14-5.

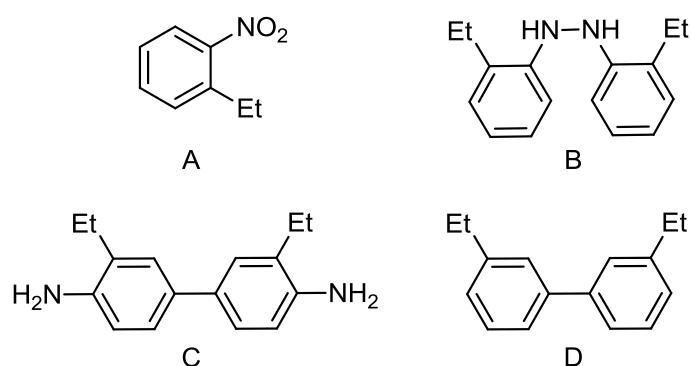
14. 利用简便的化学试剂鉴别: 丙胺, 甲基乙基胺, 三甲胺.

解答: 参加课本插题 14-4.

15. 某化合物  $\text{C}_8\text{H}_9\text{NO}_3$ (A)在  $\text{NaOH}$  中被  $\text{Zn}$  还原生成(B), 强酸性下(B)重排生成芳香胺(C), (C)用亚硝酸处理, 再用  $\text{H}_3\text{PO}_2$  处理生成 3,3'-二乙基联苯(D)。写出 A/B/C/D 的结构式。

解答:

化合物 A( $\text{C}_8\text{H}_9\text{NO}_3$ )不饱和度为 5。从产物 D 可以推测 A 含有一个苯环和一个乙基。另一个为硝基。另外, 硝基与乙基互相处于邻位。故 A 的结构式为:

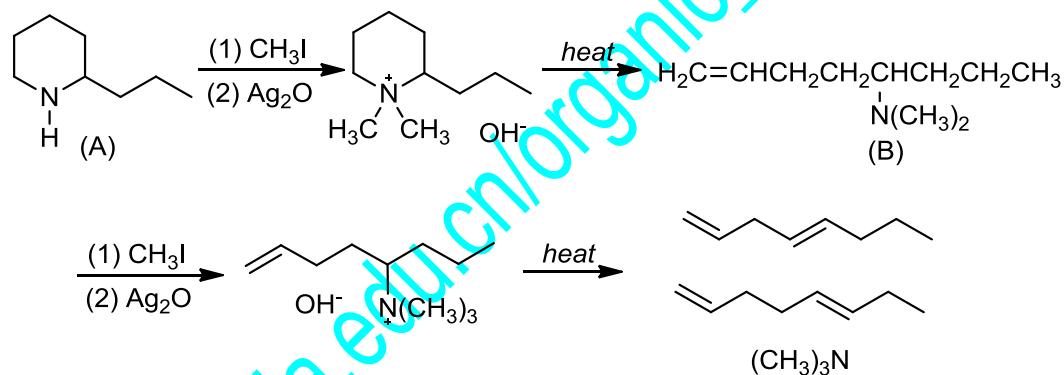


16. 某化合物 A, 分子式为 C<sub>8</sub>H<sub>17</sub>N, 其核磁共振谱无双重峰, 它与 2mol 碘甲烷反应, 然后与 Ag<sub>2</sub>O(湿). 作用, 接着加热, 则生成一个中间体 B, 其分子式为 C<sub>10</sub>H<sub>21</sub>N。B 进一步甲基化后与湿的 Ag<sub>2</sub>O 作用, 转变为氢氧化物, 加热则生成三甲胺, 5-辛二烯和 1, 4-辛二烯混合物。写出 A 和 B 的结构式。

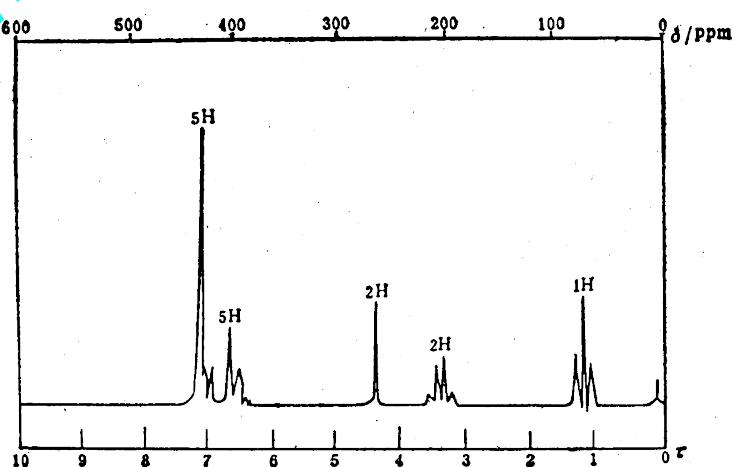
解答:

分子式为 C<sub>8</sub>H<sub>17</sub>N 的化合物 A 含有一个不饱和度。由于该化合物的 NMR 谱无双重峰, 说明分子内无 CHCH<sub>3</sub> 结构单元。由 A 可以与 2mol 碘甲烷反应, 在经与 Ag<sub>2</sub>O 反应, 加热分解后得到的化合物 B 的碳原子数比 A 的碳原子数多 2 个这些事实, 可以断定该化合物为环状仲胺。

由最终热解产物的结构, 可以推测化合物 A、B 及相应的反应为:



17. 化合物 A 分子式为 C<sub>15</sub>H<sub>17</sub>N 用苯磺酰氯和 KOH 溶液处理它没有作用, 酸化该化合物得到一清晰的溶液, 化合物 A 的核磁共振谱如下图所示, 是推导出化合物 A 的结构式。

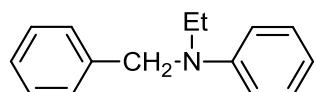


解答：

由分子式  $C_{15}H_{17}N$  可以算出化合物 A 的不饱和度为 8(两个苯环)。

用苯磺酰氯和 KOH 溶液处理它没有使用，说明 A 为叔胺化合物。

由  $^1H$ NMR 谱可以看出，化学位移  $\delta$  值 6-8 处含两个苯环，每个苯环上有 5 个氢原子。 $\delta$  值 ~4.3 处 2H 为单峰，说明分子内含有一个孤立的  $CH_2$  结构单元。 $\delta$  值 3.3 和  $\delta$  值 1.1 处的三重峰和四重峰，表明分子内含有一个  $CH_2CH_3$  结构单元。综合上述分析，可以推测化合物 A 的结构式：



18. 请用概念图或者思维导图的形式总结芳香烃衍生物的合成方法。

解答：从重氮盐法合成的方法有：

