

Chapter 17



Amines (胺)

胺: organic derivatives of ammonia (氨的烷基取代物)



Ammonia Primary amine Secondary amine Tertiary amine

氨

伯胺

仲胺

叔胺



氨基



亚氨基



叔氮原子



铵盐



季铵盐



氢氧化四烷基铵

(季铵碱)

§ 17.1 胺的分类和命名

§ 17.1 Classification and Nomenclature of Amines

一、分类 (Classification of Amines)

按氨基数目分：一元胺、二元胺、三元胺、多元胺

按烃基性质分：脂肪胺 芳香胺



一元胺

脂肪胺



二元胺

脂肪胺



一元胺

芳香胺



二、命名 (Nomenclature of Amines) 烃基+胺

Amines are named in two main ways, in the IUPAC system: either as *alkylamines* or as *alkanamines*.

When primary amines are named as alkylamines, the ending *-amine* is added to the name of the alkyl group that bears the nitrogen. When named as alkanamines, the alkyl group is named as an alkane and the *-e* ending replaced by *-amine*.



甲胺

Methylamine

Methanamine



乙胺

Ethylamine

Ethanamine



乙二胺

Ethylenediamine



苯胺

Aniline

Benzenamine



二乙胺

Diethylamine



Symmetrical secondary and tertiary amines are named by adding the prefix *di-* or *tri-* to the alkyl group.

Unsymmetrical substituted secondary and tertiary amines are named as *N*-substituted derivatives of primary amines. The parent primary amine is taken to be the one with the longest carbon chain. The prefix *N-* is added as a locant to identify substituents on the amino nitrogen as needed.



甲乙胺

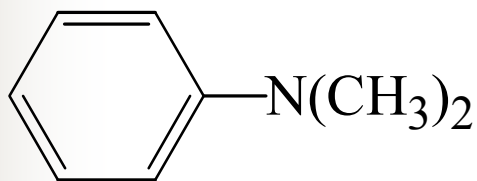
N-Methylethylamine

Ethyl methylamine



三甲胺

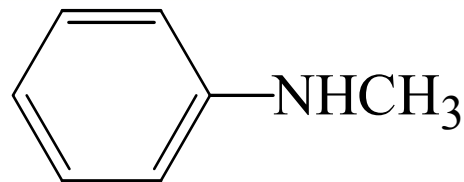
Trimethylamine



N,N-二甲基苯胺

N,N-Dimethylaniline

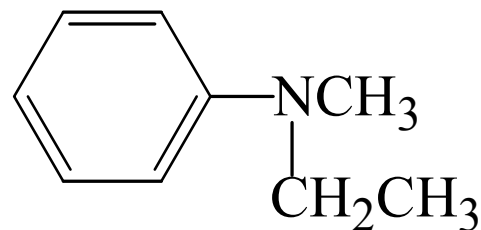
N,N-Dimethylbenzenamine



N-甲基苯胺

N-Methylaniline

N-Methylbenzenamine

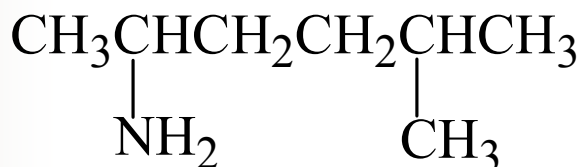


N-甲基-*N*-乙基苯胺

N-Ethyl-*N*-methylaniline

N-Ethyl-*N*-methylbenzenamine

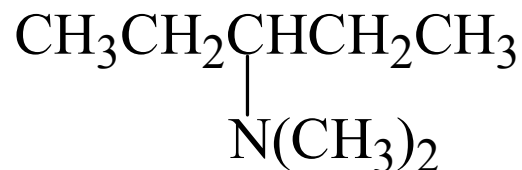
复杂的胺以氨基为取代基，烃基为母体



2-氨基-5-甲基己烷

2-Amino-5-methylhexane

季铵盐的命名与铵盐相似



3-(N,N-二甲氨基)戊烷

3-(N,N-Dimethylamino)pentane



氯化四乙铵

Tetraethylammonium chloride



氢氧化甲基三乙基铵

Triethylmethyl hydroxide

胺——氨(NH₃)的烃基衍生物

氨——氨基(-NH₂)或烃基取代的氨基

铵——季铵化合物或铵盐

§ 17.2 一元胺的物理性质

Physical Properties of Amines

一、熔点、沸点和溶解度

极化程度： $\text{N-H键} < \text{O-H键}$

氢键强弱： $\text{N-H...N} < \text{O-H...O}$

∴沸点：分子量相近时，烷烃 $<$ 伯胺 $<$ 醇
碳数相同时，伯胺 $>$ 仲胺 $>$ 叔胺

含6~7个碳原子的低级胺能溶于水，高级胺不溶于水

熔点、沸点：邻硝基苯胺 $<$ 间、对硝基苯胺

芳香胺的毒性很大

二、偶极矩

脂肪胺 < 醇



$\mu = 1.2\text{D}$

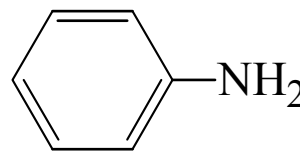


$\mu = 1.7\text{D}$

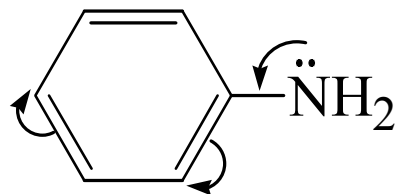
芳胺的偶极矩与脂肪胺相近，但方向相反



$\mu = 1.2\text{D}$



$\mu = 1.3\text{D}$



p-π 共轭

三、红外光谱

脂肪族伯胺: N—H 3400~3300cm⁻¹ 3300~3200 cm⁻¹

芳香族伯胺: N—H 3500~3390cm⁻¹ 3420~3300 cm⁻¹

仲胺: N—H 3500~3300cm⁻¹

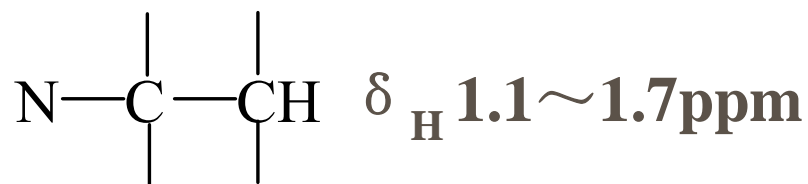
四、核磁共振谱

N—CH₃ δ_H 2.2ppm

N—CH₂— δ_H 2.4ppm

N—CH< δ_H 2.8ppm

-NH₂, -NHR δ_H 0.5~5ppm



价值不大



五、质谱

脂肪族胺的分子离子峰很弱，

环胺和芳胺的分子离子峰很强

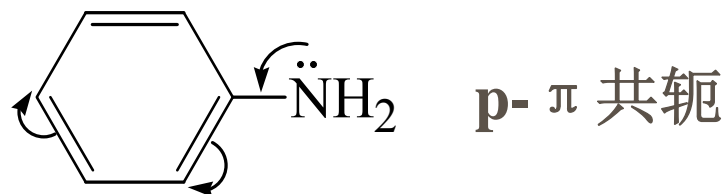
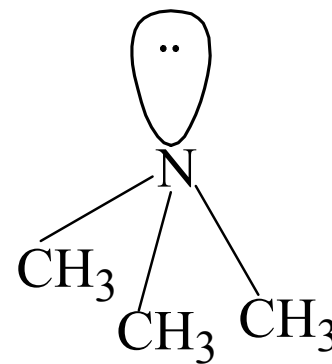
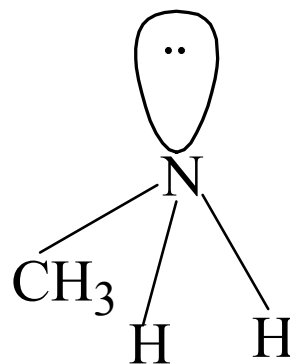
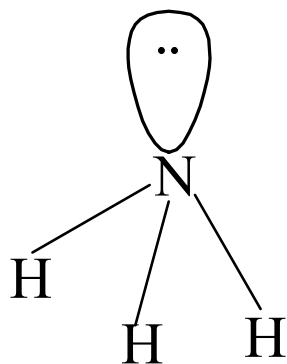
含奇数氮原子的化合物，其分子量为奇数

§ 17.3 胺的结构和化学性质

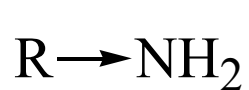
Structure and Chemical Properties of Amines

一、胺的结构

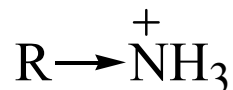
N: sp^3 杂化



1. 脂肪胺



R具有+I效应

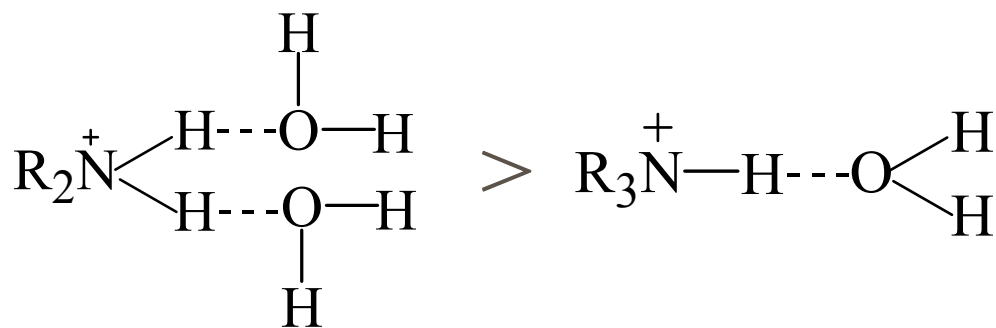


电荷能得到分散，稳定

气相和非质子性溶剂（如：氯仿、乙腈等）中，

碱性：叔胺 > 仲胺 > 伯胺

水溶液中，碱性：叔胺 < 仲胺 > 伯胺

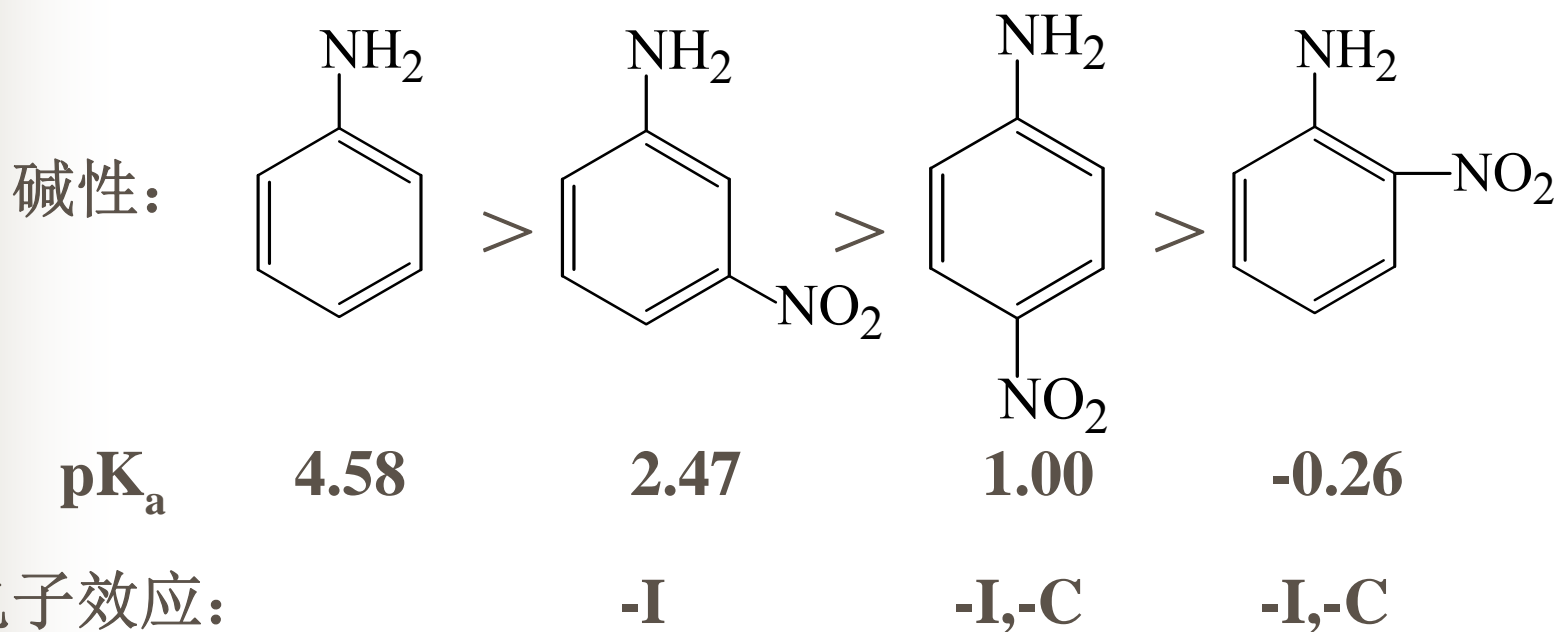


吸电子取代基使胺的碱性减弱

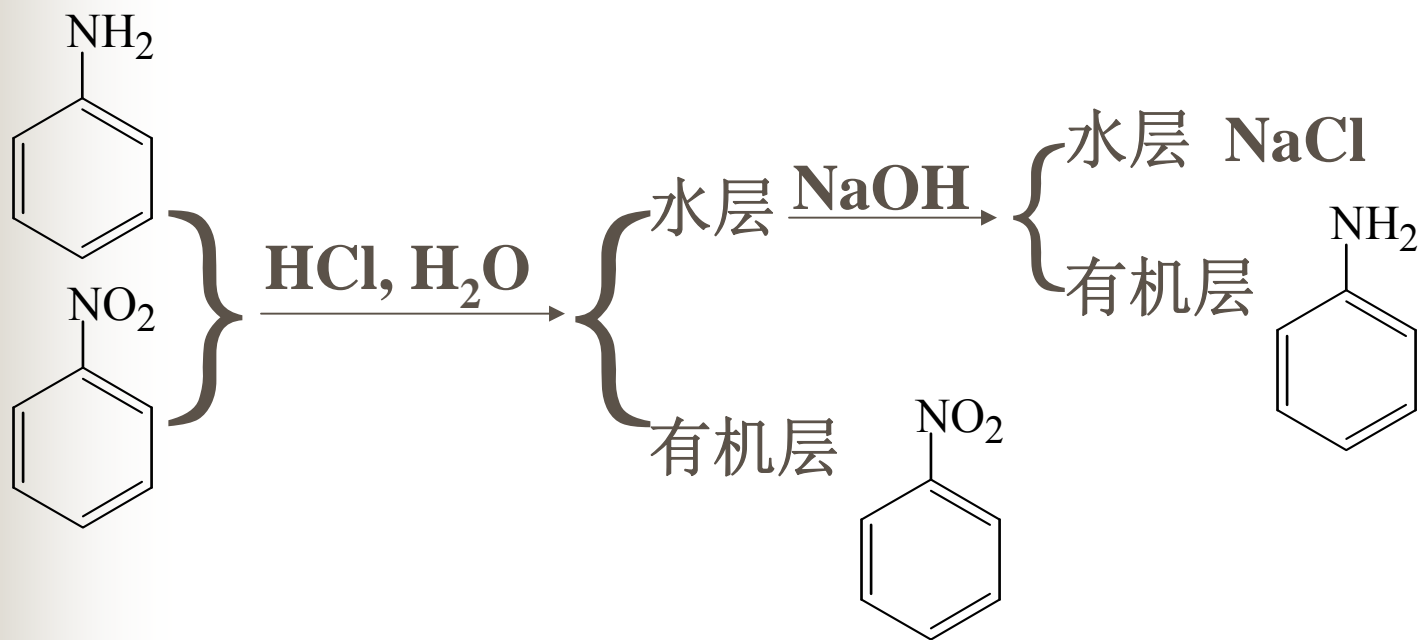
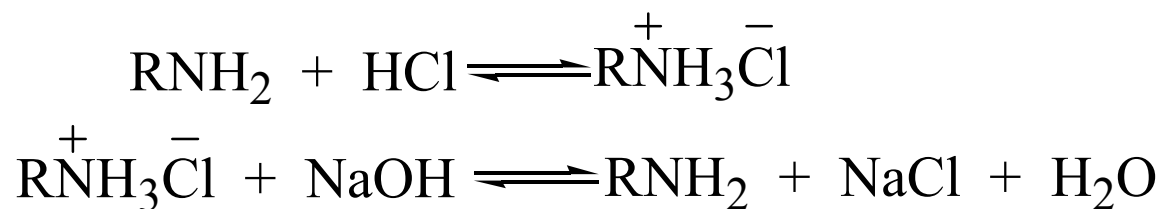
2. 芳香族胺

碱性: $\text{NH}_3 > \text{C}_6\text{H}_5\text{NH}_2 > (\text{C}_6\text{H}_5)_2\text{NH} > (\text{C}_6\text{H}_5)_3\text{N}$

苯环上有吸电子取代基使芳胺的碱性减弱

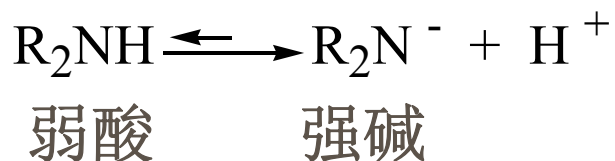


3. 胺的分离

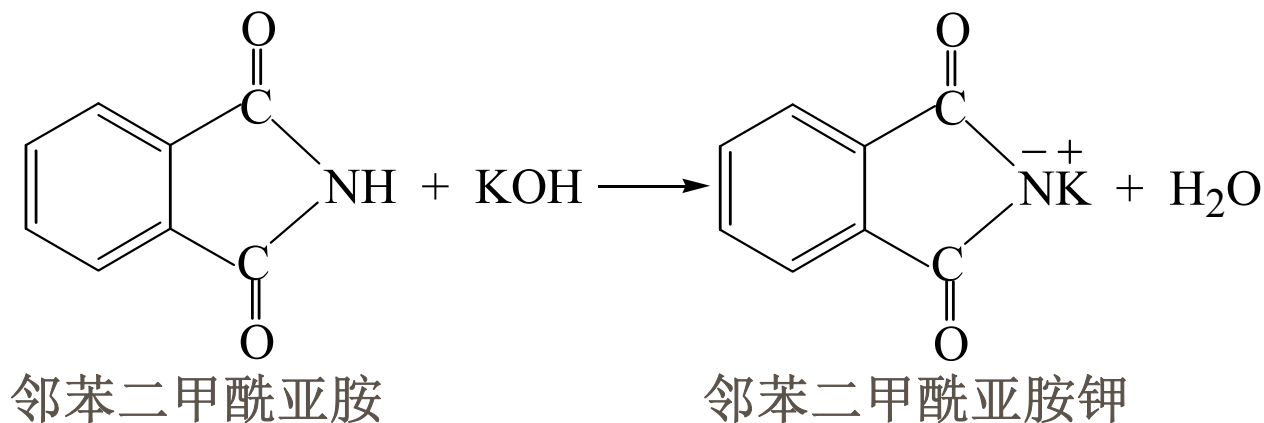


4. 胺的酸性

氨、伯胺和仲胺分子中N—H键可电离，具有弱酸性，其共轭碱 NH_2^- 、 RNH^- 、 R_2N^- 是很强的碱



酰胺的酸性比胺强，酰亚胺的酸性比酰胺更强

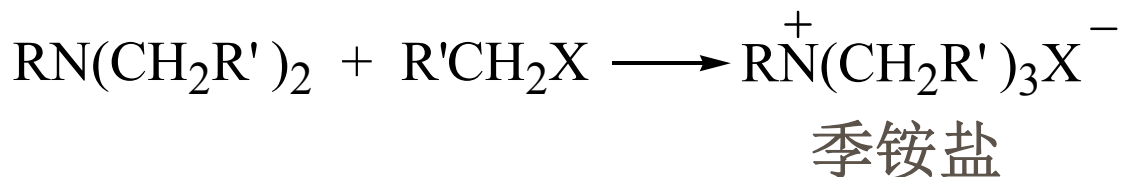
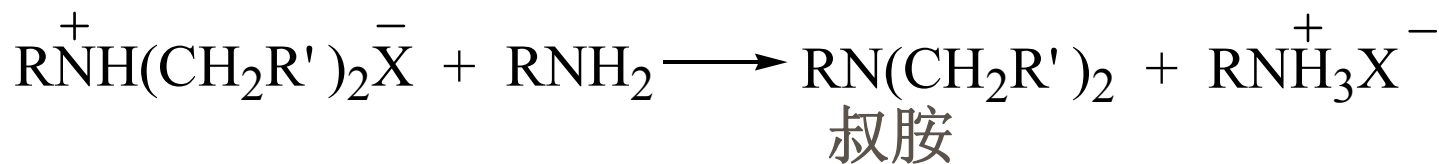
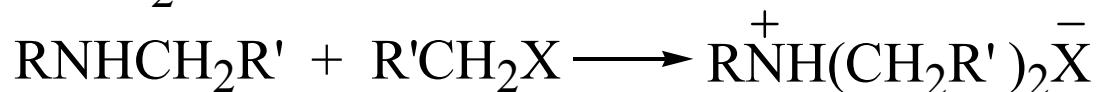
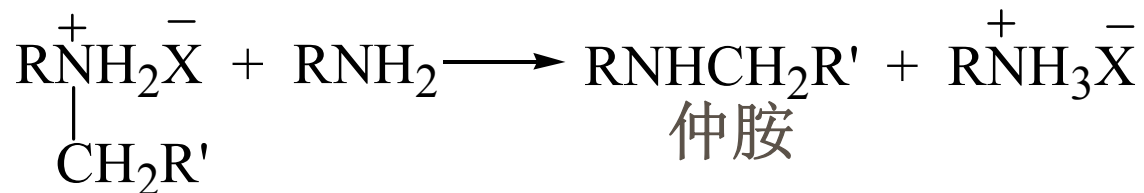
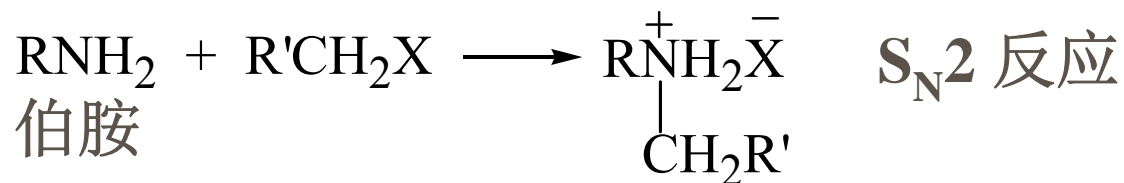


pK_a

8.3

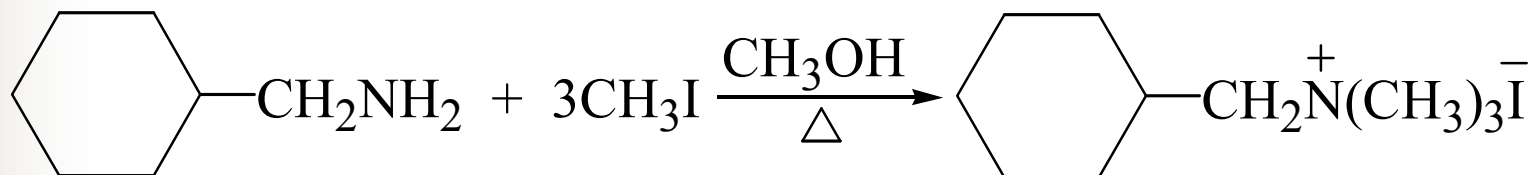
17.15

(二) 胺的烃化

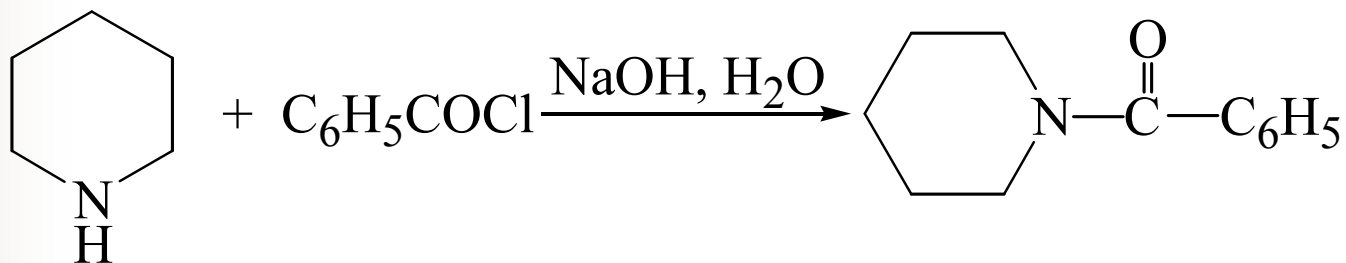


反应难以停留在只生成仲胺或叔胺的一步

如用过量的伯卤代烷，可以得到季铵盐

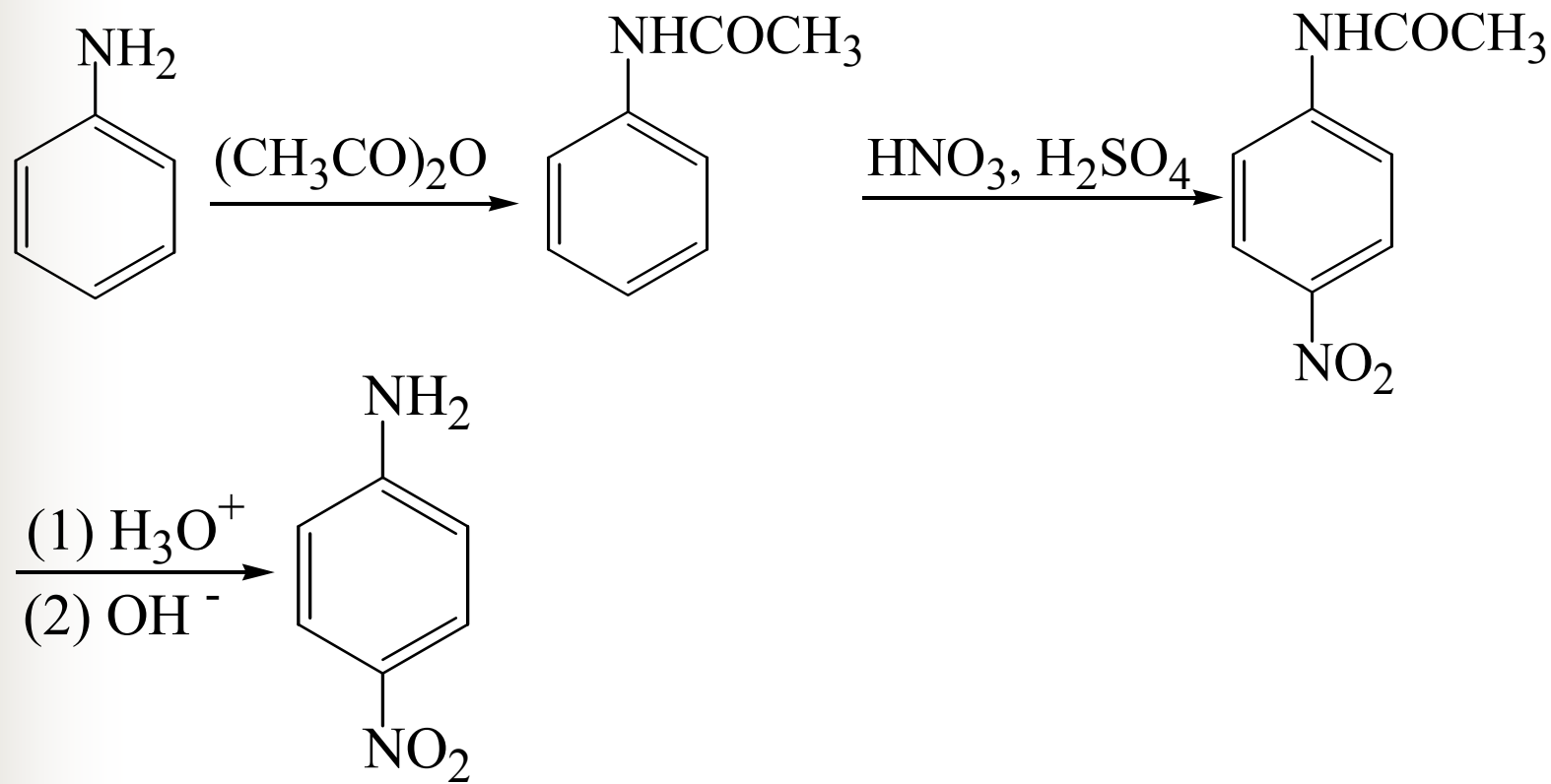


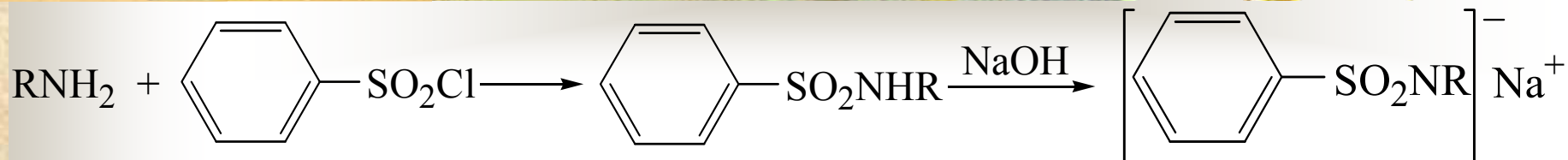
(三) 胺的酰化和磺酰化



叔胺不反应

酰化反应的应用：有机合成上保护氨基



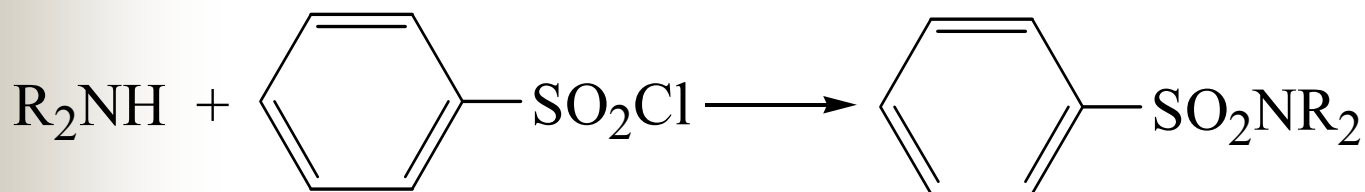


伯胺

苯磺酰氯

N-烃基苯磺酰胺
(固体)

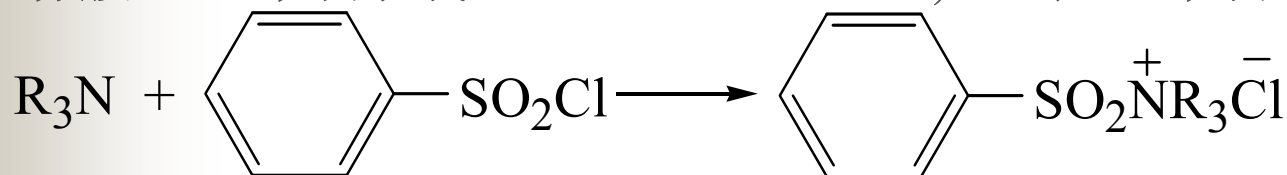
(溶解)



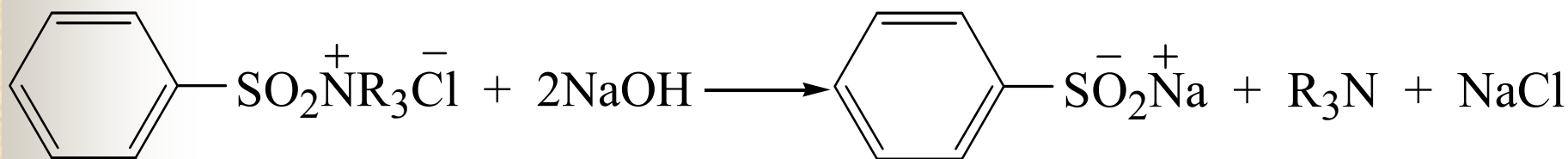
仲胺

苯磺酰氯

N,N-二烃基苯磺酰胺 (固体)



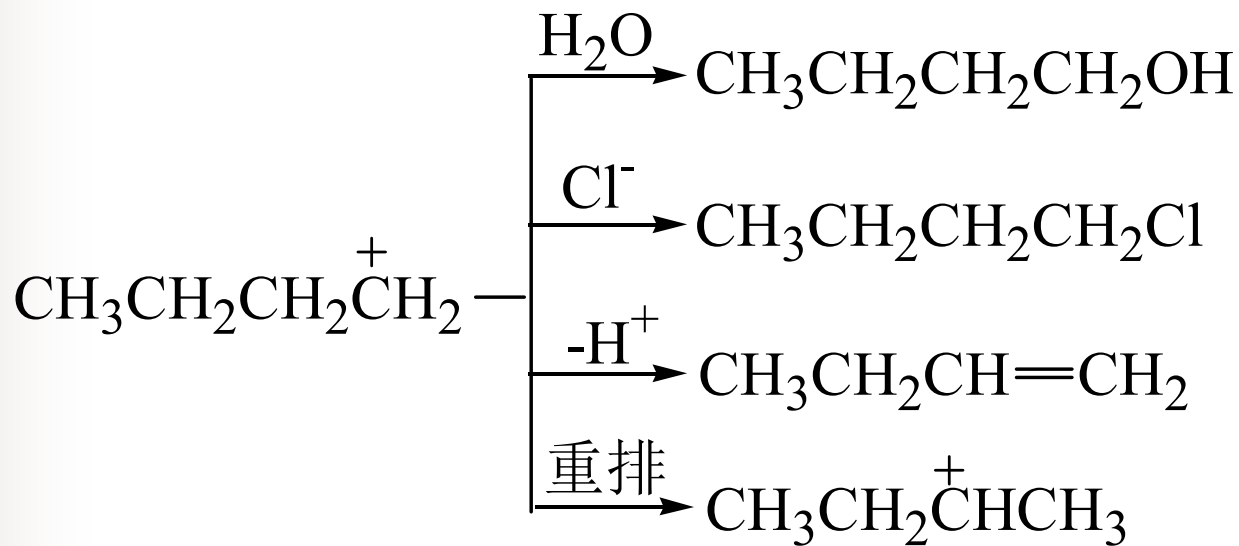
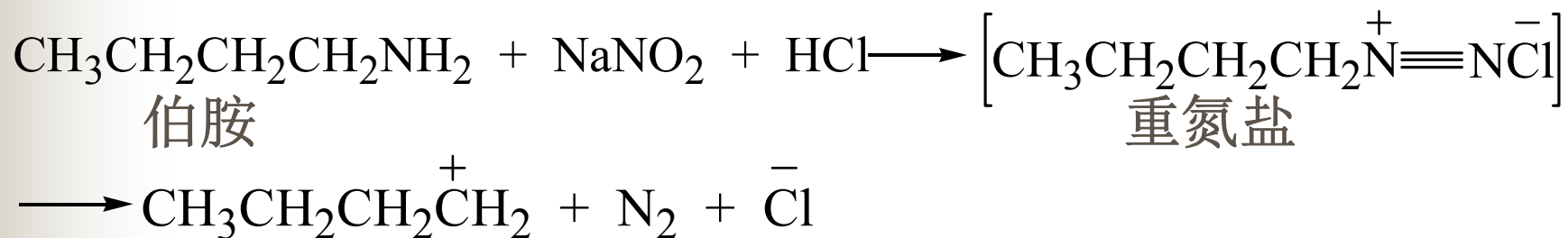
叔胺



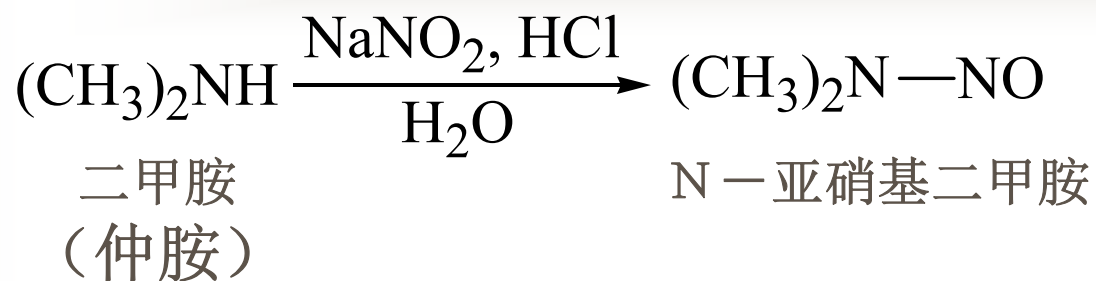
用于区别伯、仲、叔胺

(四) 胺的亚硝化

1. 脂肪胺与亚硝酸的作用

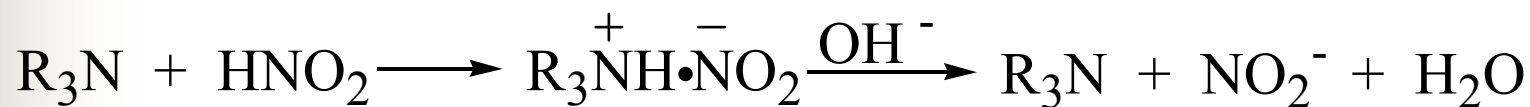


生成复杂的混合物，在有机合成上没有实际意义

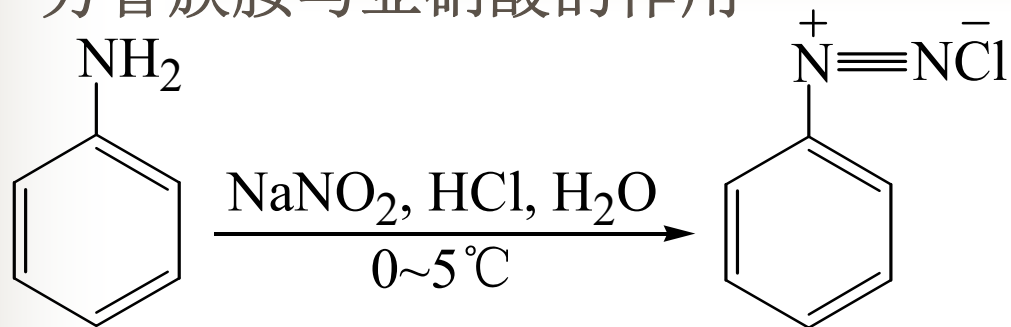


N-亚硝基胺有强致癌作用

脂肪族叔胺不能发生亚硝化反应

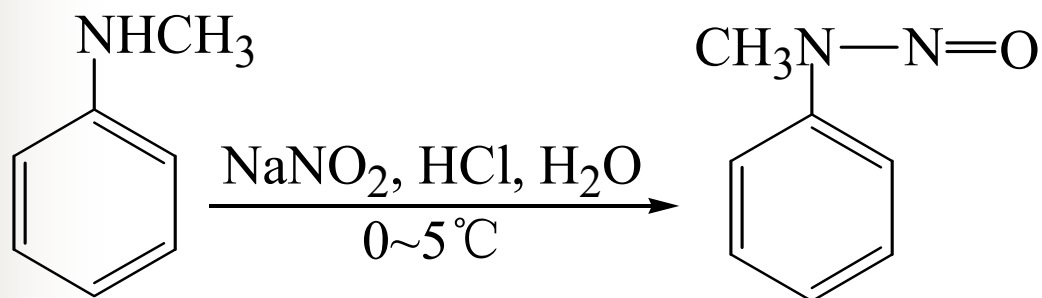


2. 芳香族胺与亚硝酸的作用

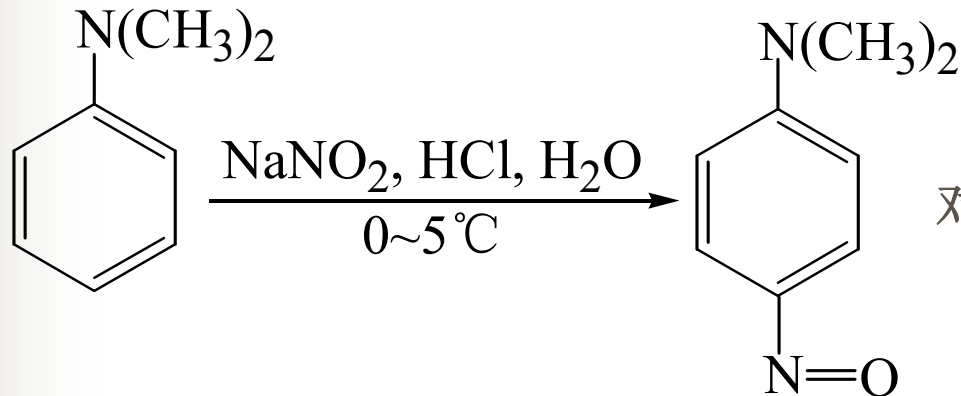


芳基重氮盐用于合成
多种芳香族化合物

氯化重氮苯



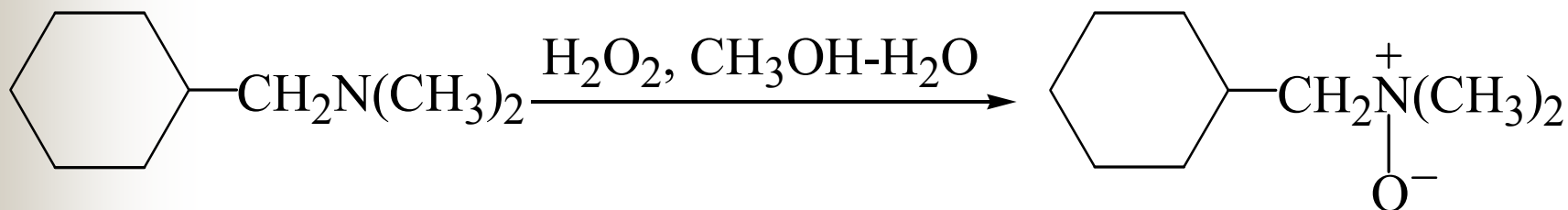
N-甲基-N-亚硝基苯胺



对亚硝基-N,N-二甲基苯胺

(五) 胺的氧化

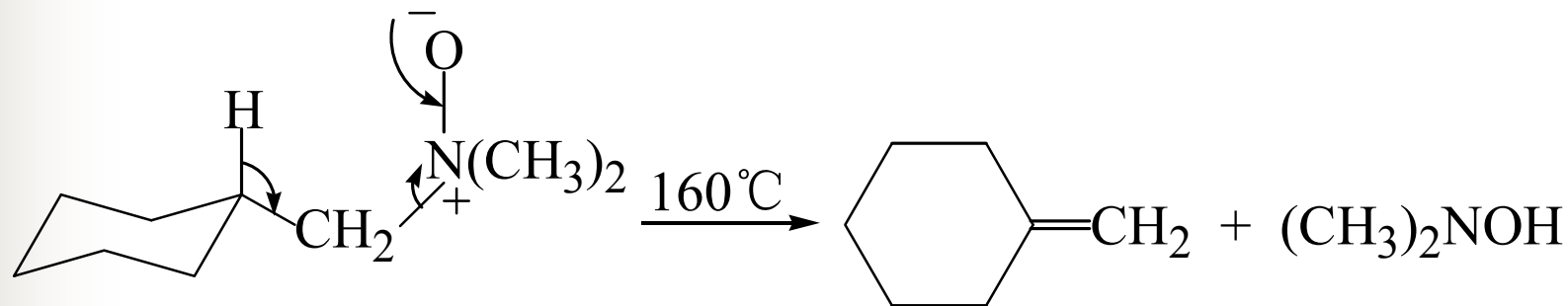
1. 叔胺的氧化



N,N=二甲基环己基甲胺

N,N=二甲基环己基甲胺-N-氧化物

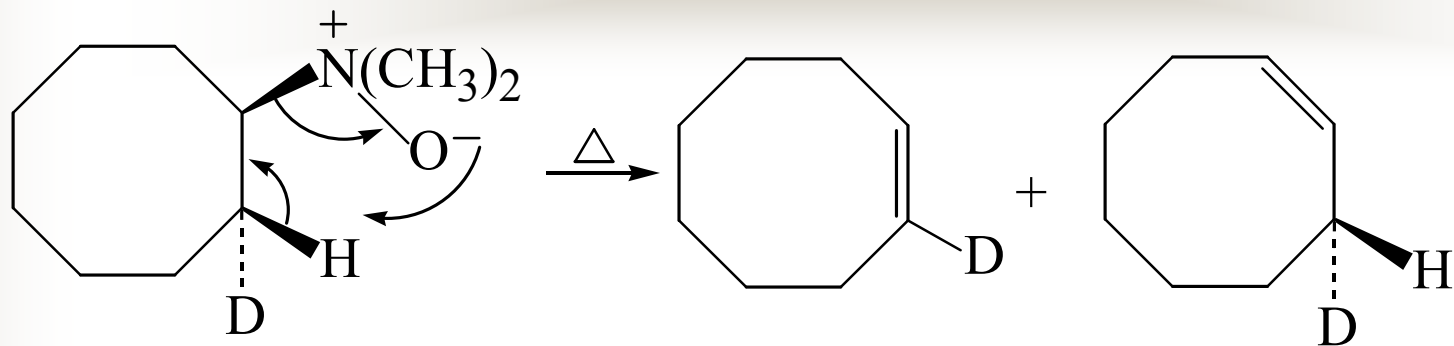
2. Cope消去



亚甲基环己烷

N,N-二甲基羟胺

如有两种不同的 β -氢，则生成烯烃的混合物

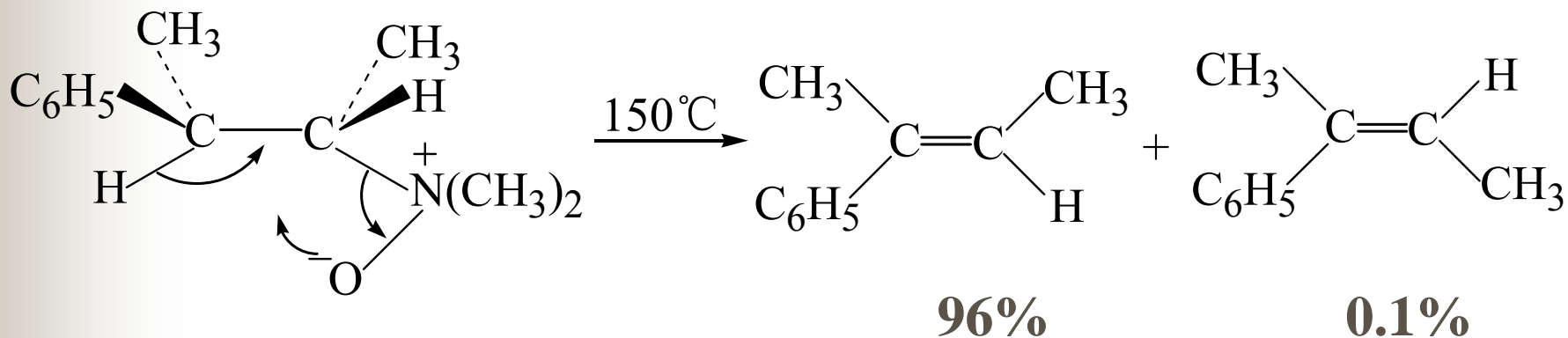


N,N-二甲基环辛胺-N-氧化物

环辛烯-1-d

环辛烯-3-d

是顺式消去反应

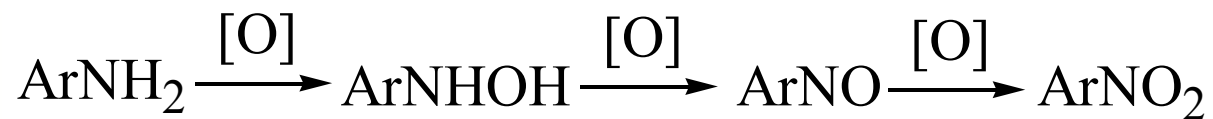


96%

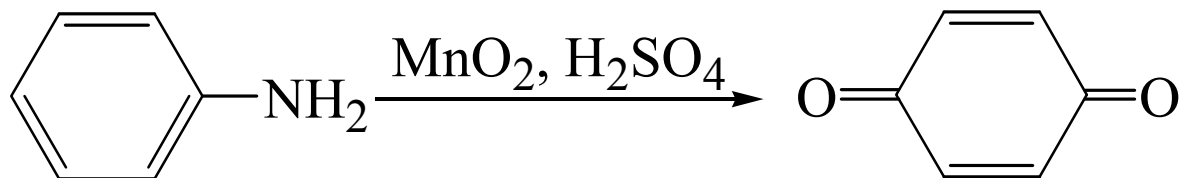
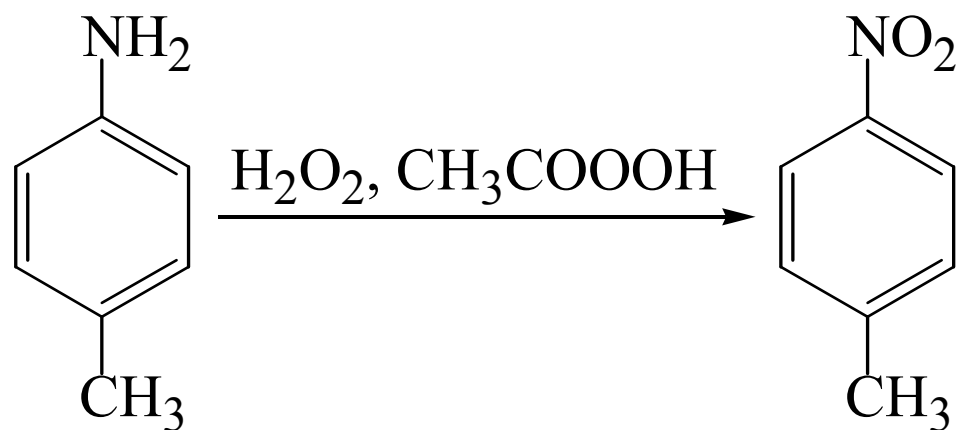
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用于合成烯烃

3. 芳胺的氧化



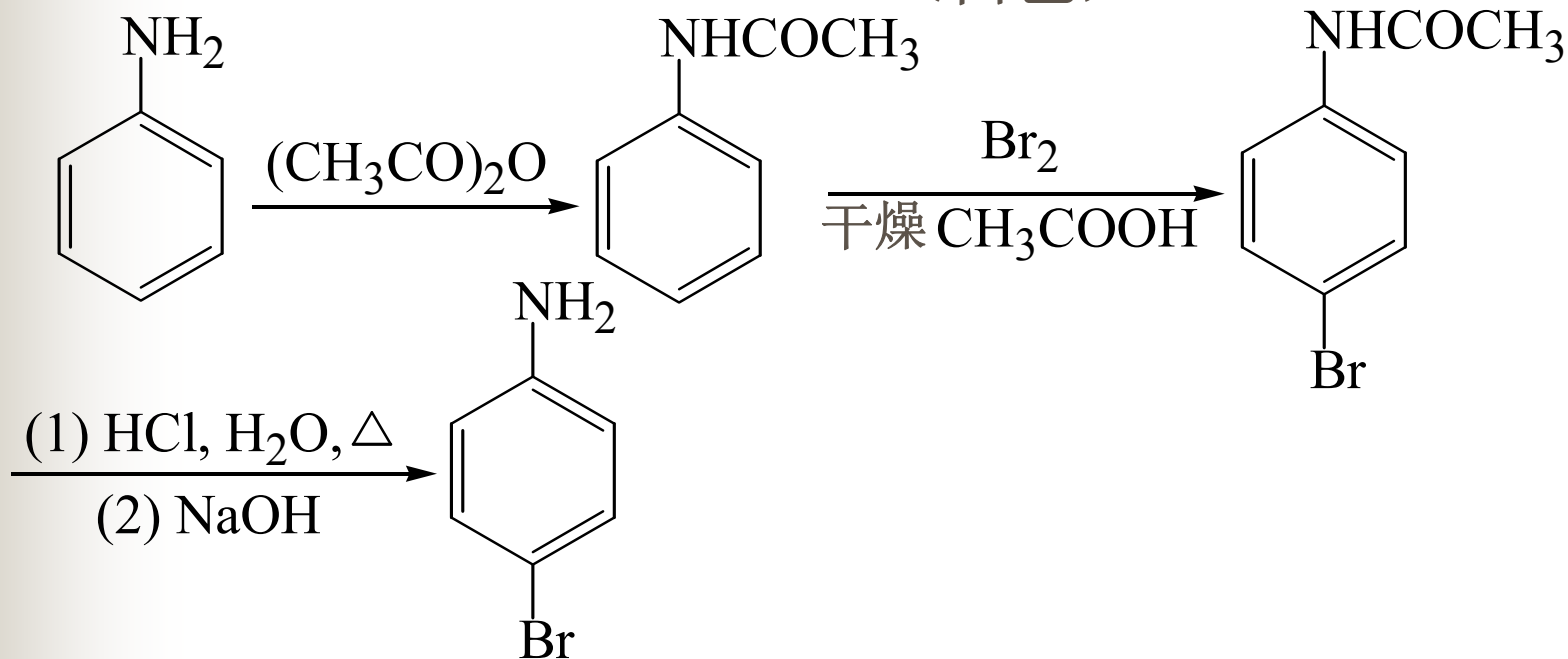
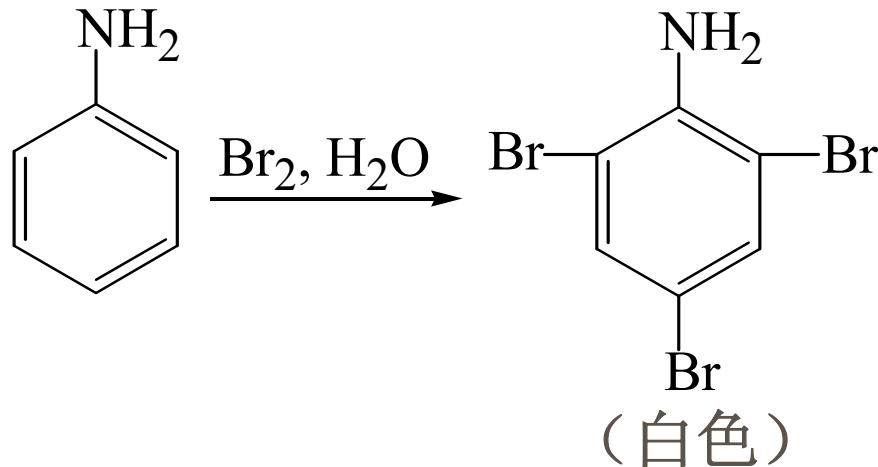
伯胺

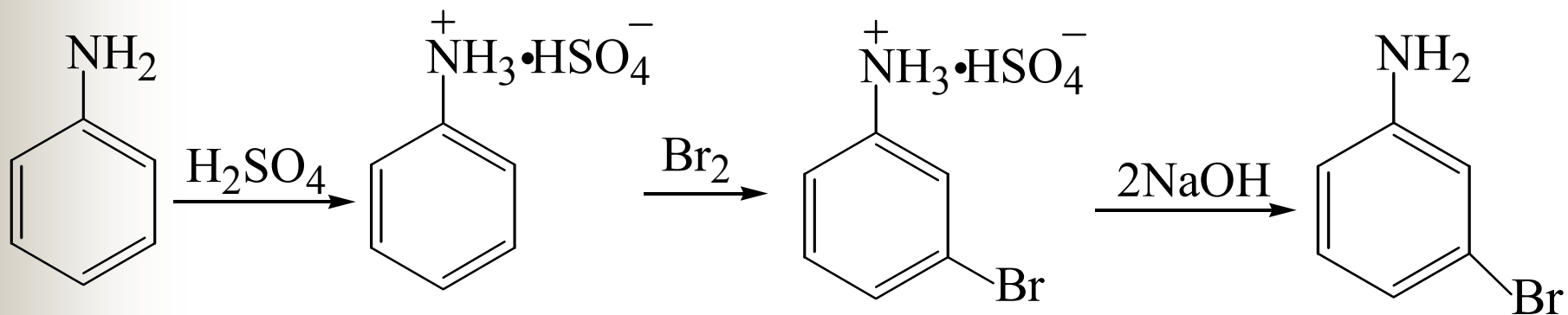


对苯醌

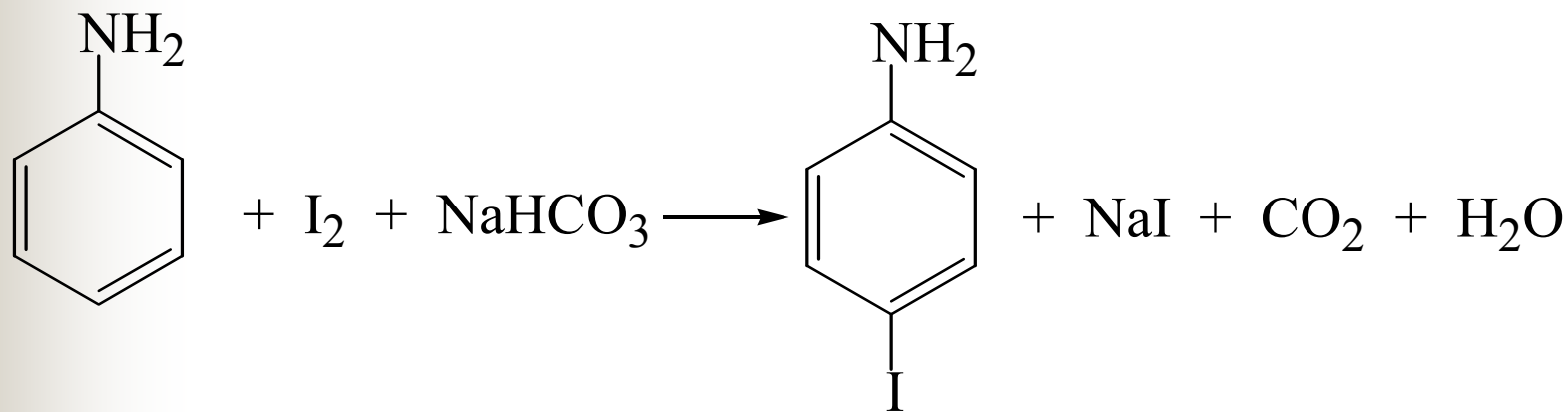
(六) 芳胺的亲电取代反应

1. 卤化

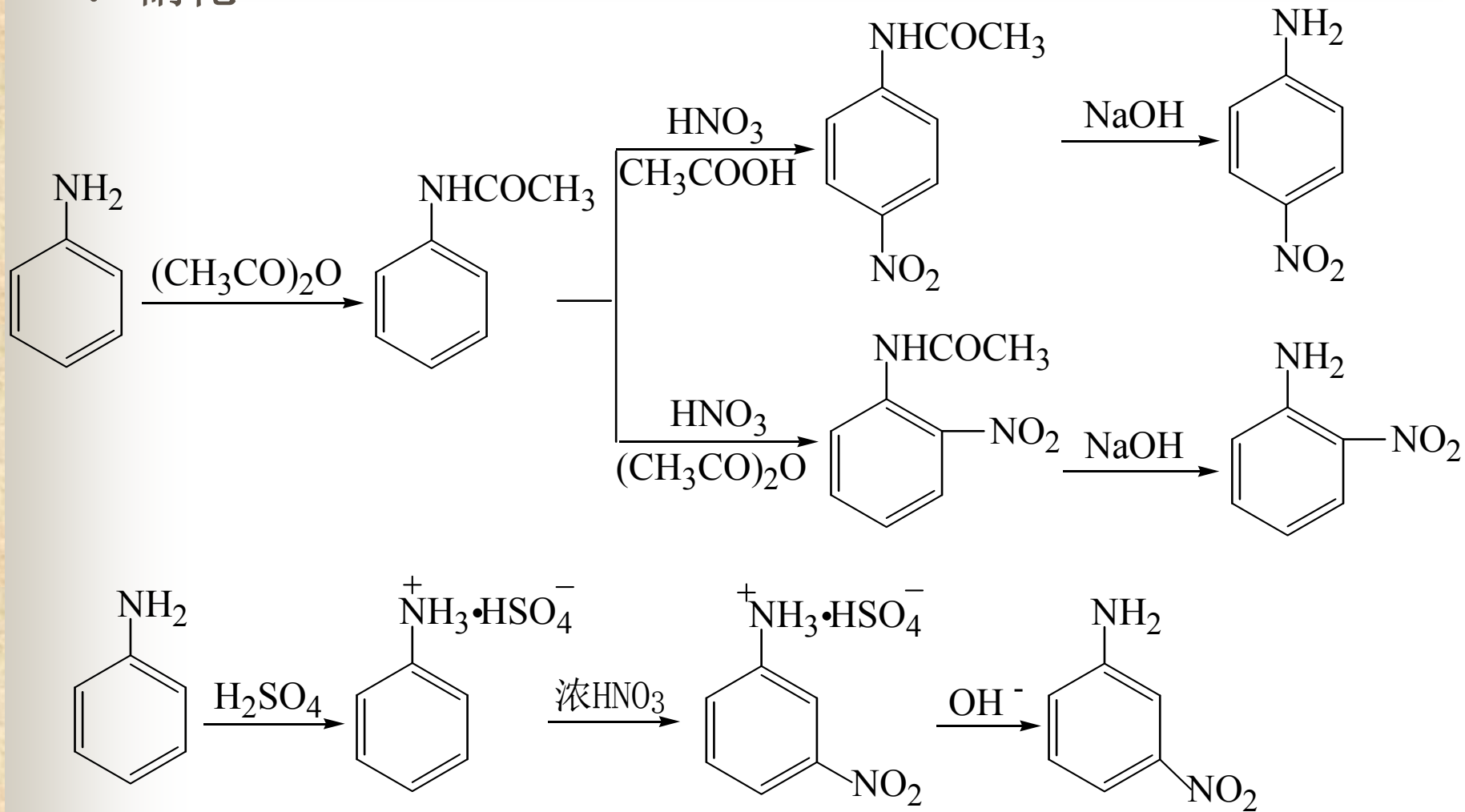




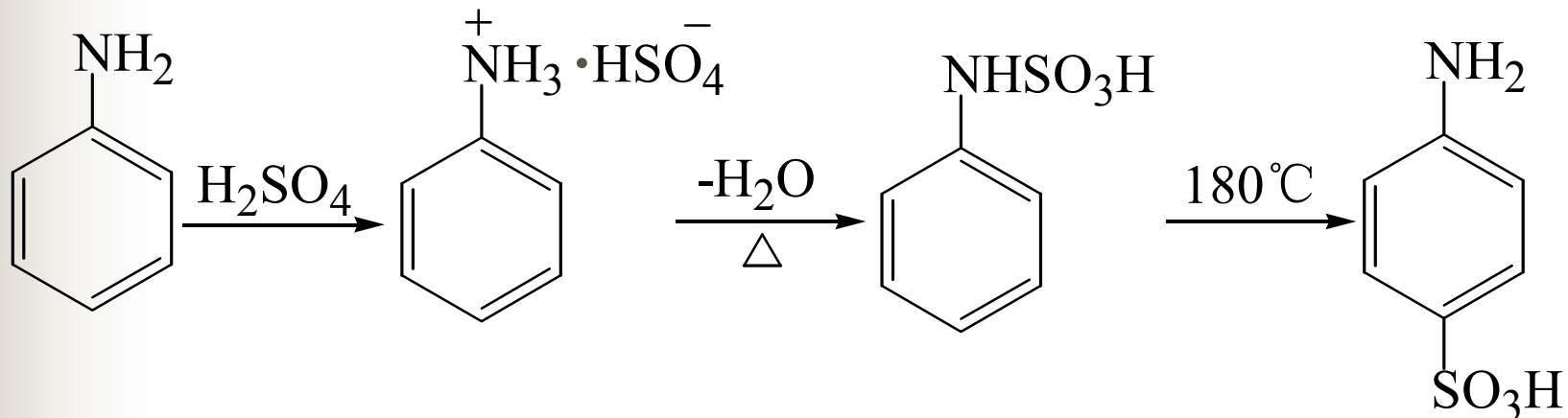
芳胺与碘反应，可得到一碘化物



2. 硝化

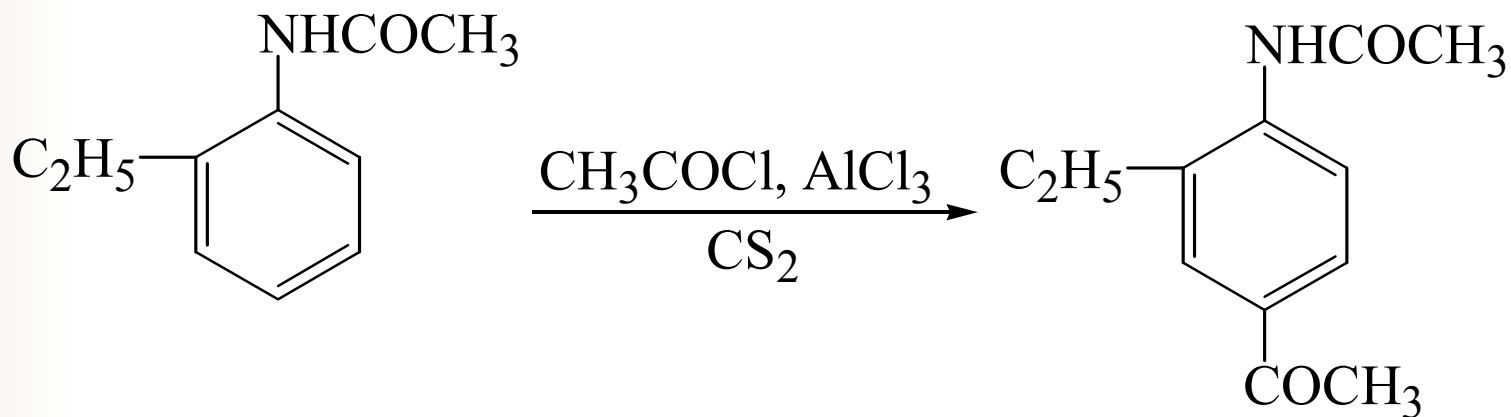


3. 磺化



对氨基苯磺酸

4. 弗瑞德-克莱福特反应



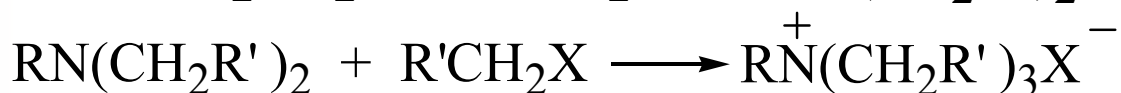
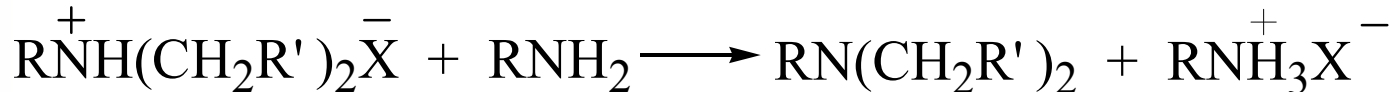
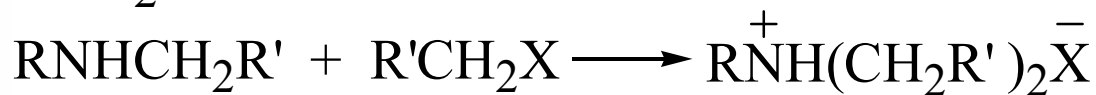
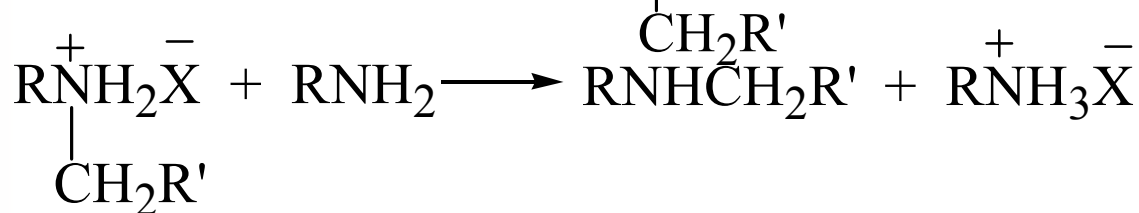
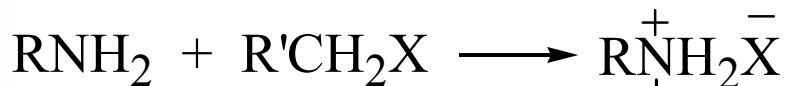
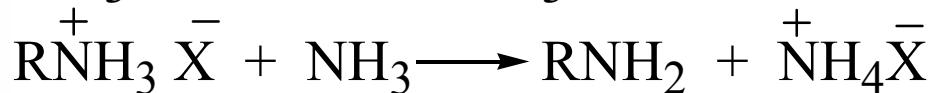
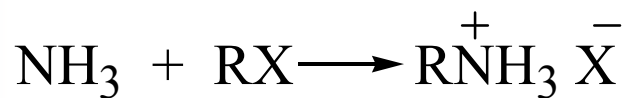
邻乙基乙酰苯胺

4-乙酰氨基-3-乙基苯乙酮

§ 17.3 胺的制法

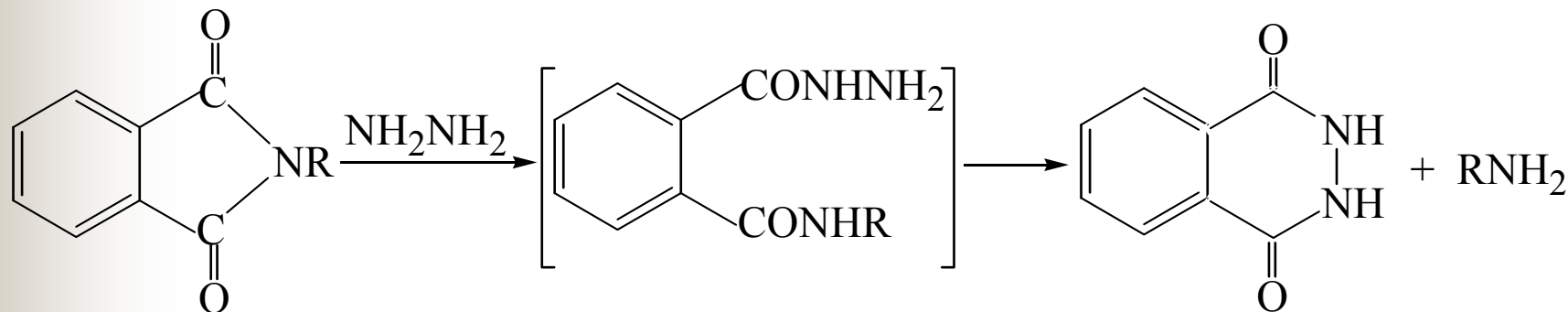
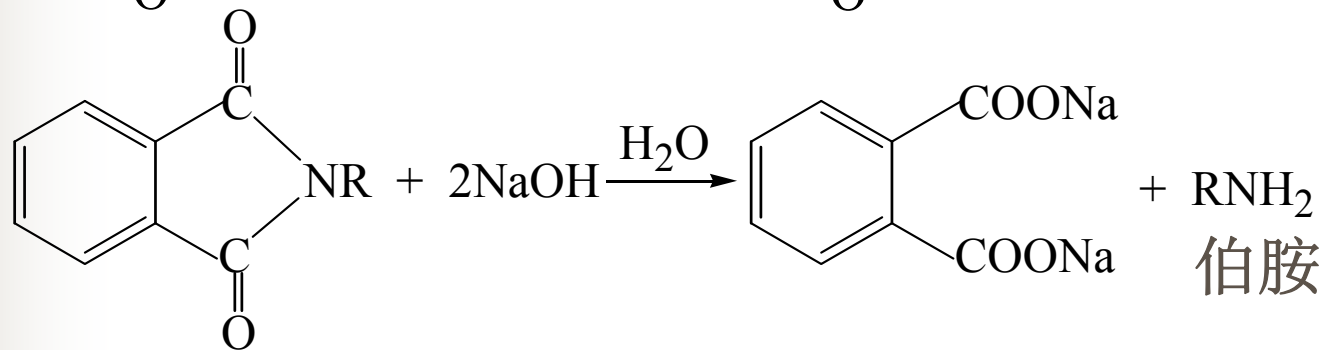
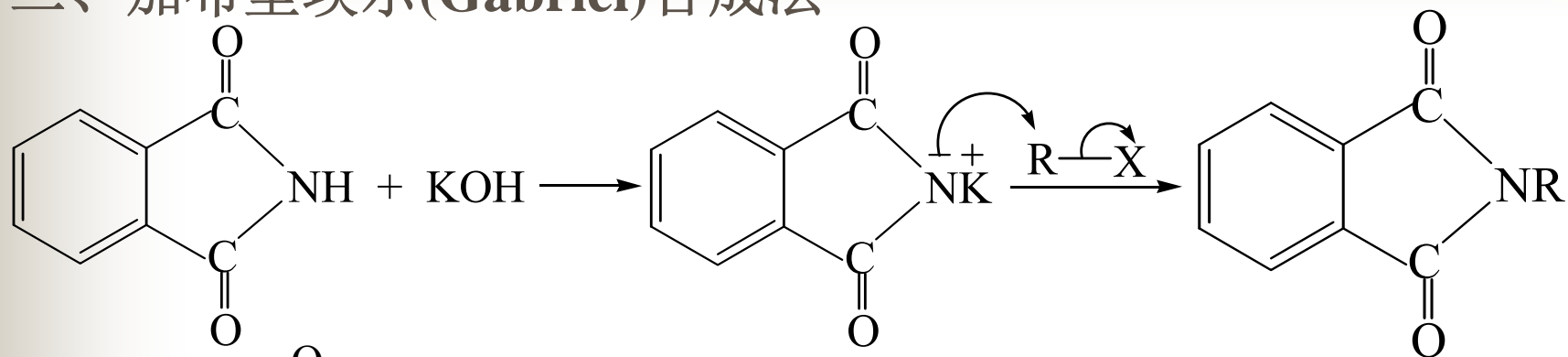
Preparation of Amines

一、氨或胺的直接烃化

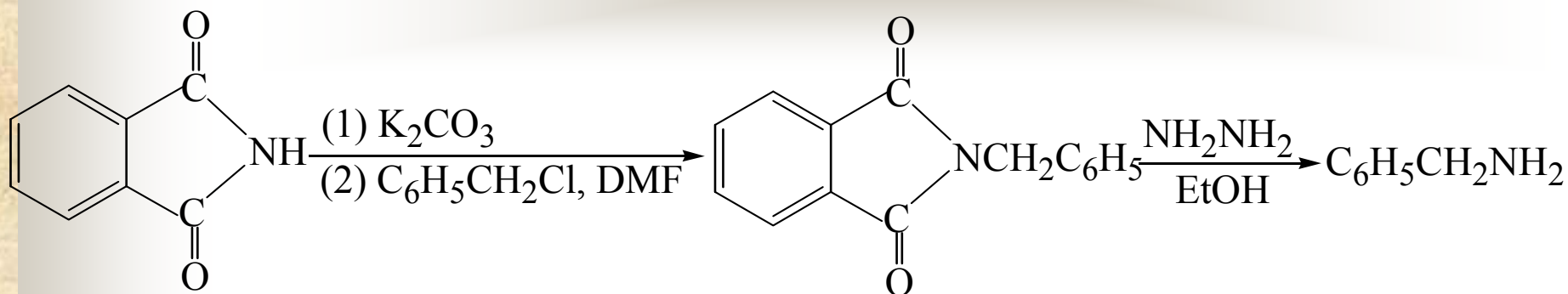


适用于工业上胺的大量制备

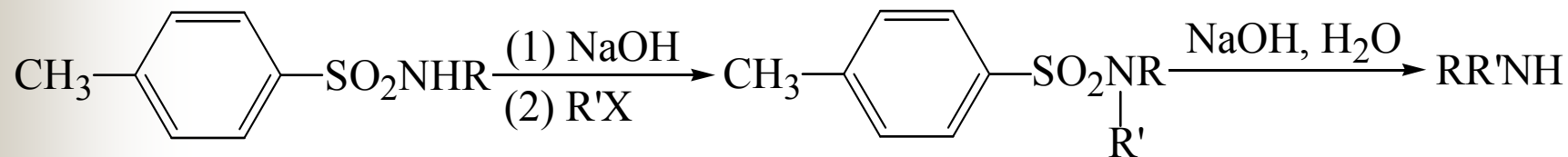
二、加布里埃尔(Gabriel)合成法



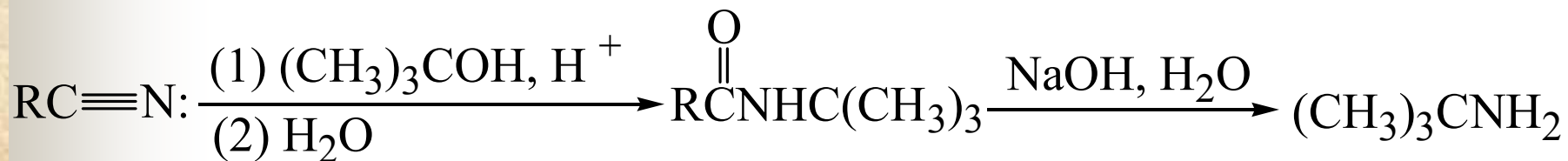
用于合成伯胺



用对甲苯磺酰基把伯胺中氮原子上的一个价占据，只剩下一个可供取代的氢，烃化和水解后可得仲胺



里特反应:



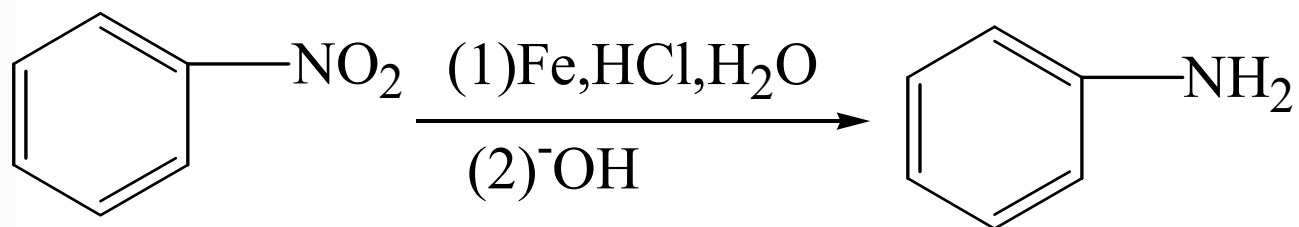
三、还原法

1. 硝基化合物的还原

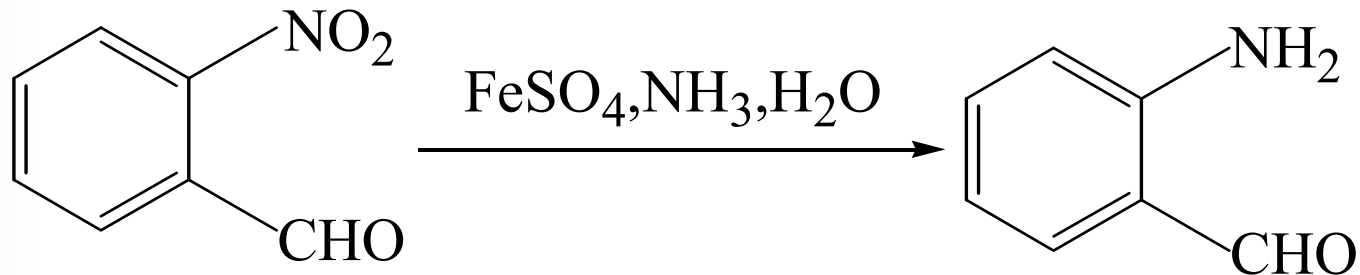
制备芳香族伯胺的常用方法

a. 化学还原

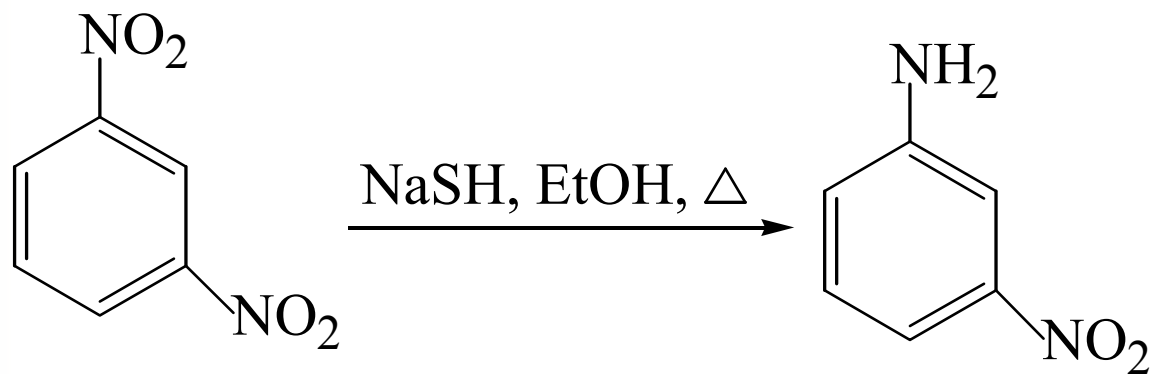
硝基化合物常用锡、铁和锌等金属和盐酸还原



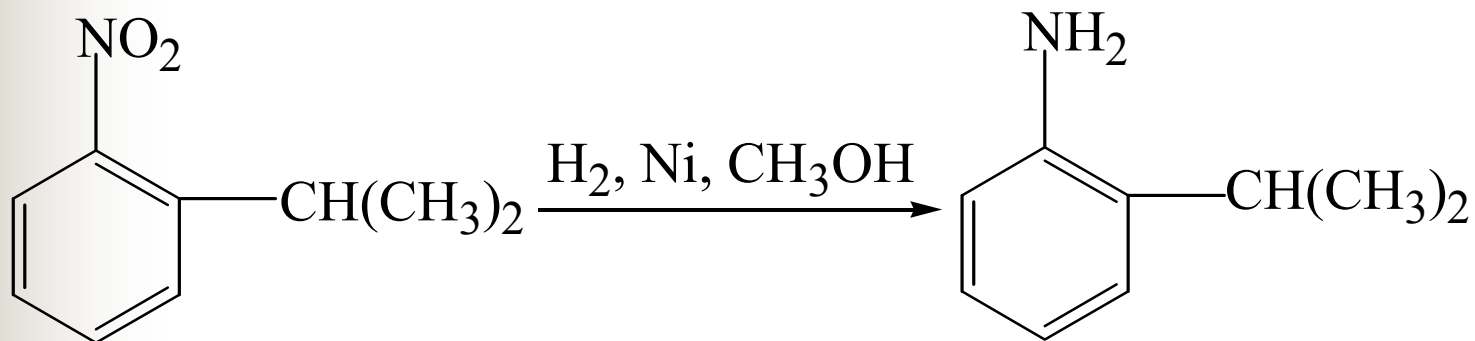
如硝基化合物中含有醛基或酮基,则要用较温和的还原剂



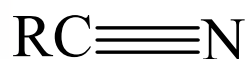
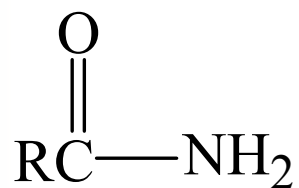
氢硫化钠、硫化钠、硫化铵可以只还原一个硝基



b. 催化氢化 常用的催化剂有镍、铂、钯等

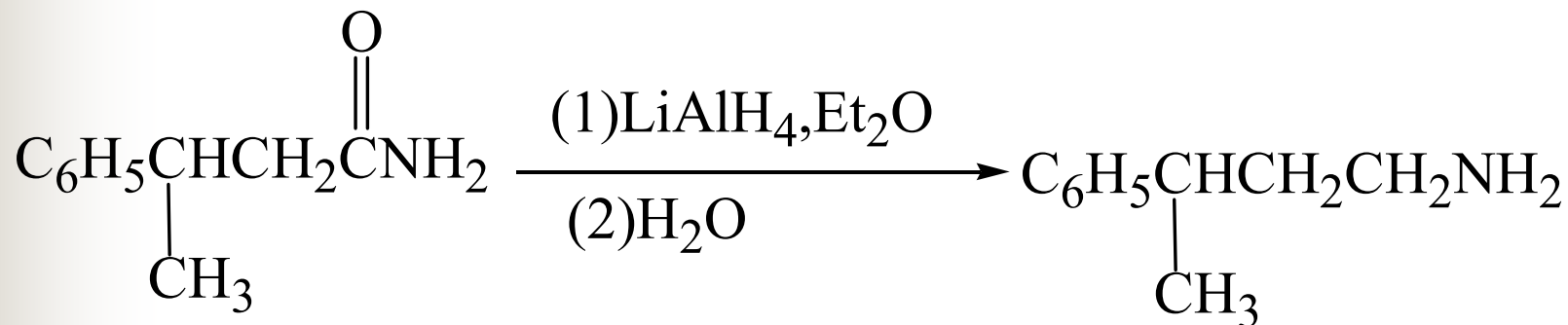


2. 酰胺,肟和腈的还原

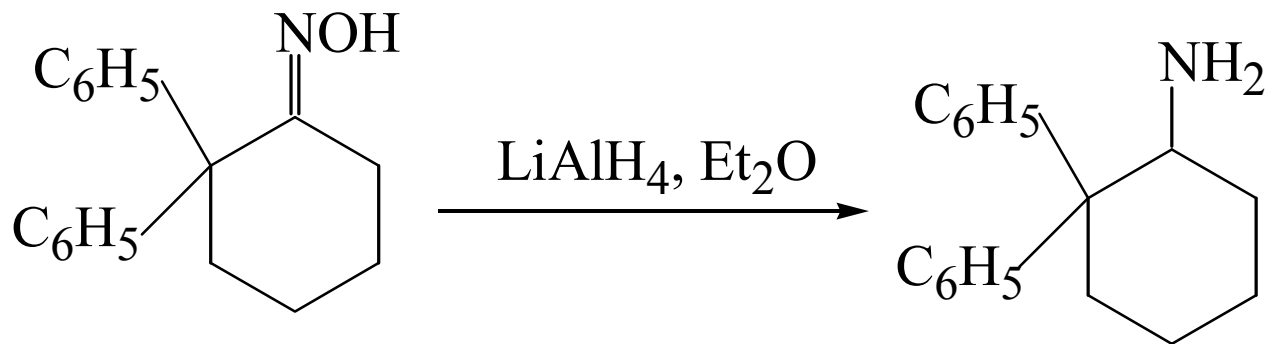
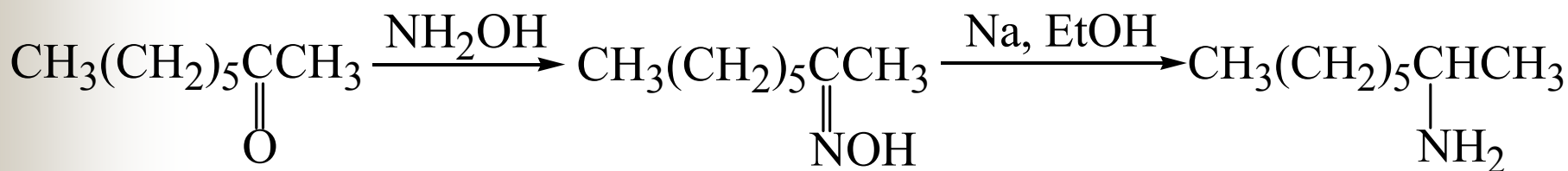
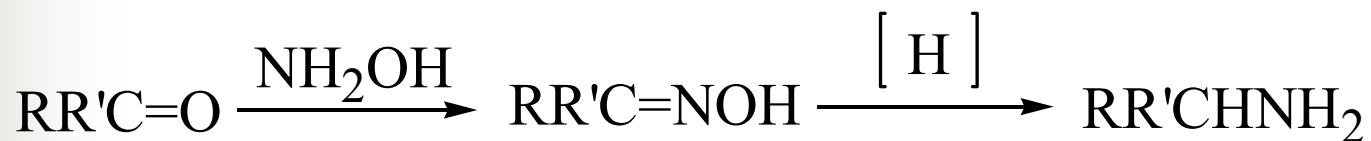


催化氢化法

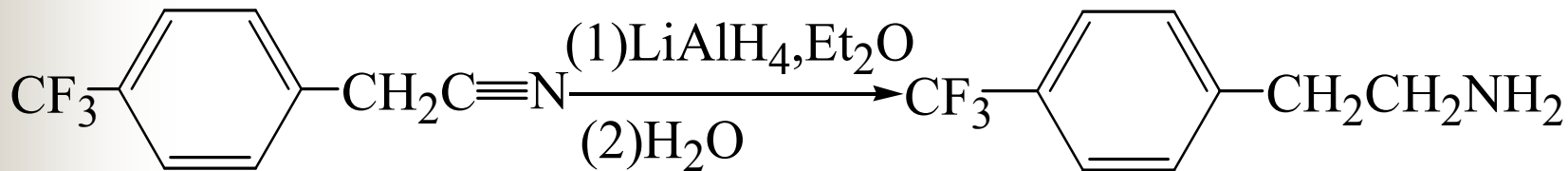
或化学还原法



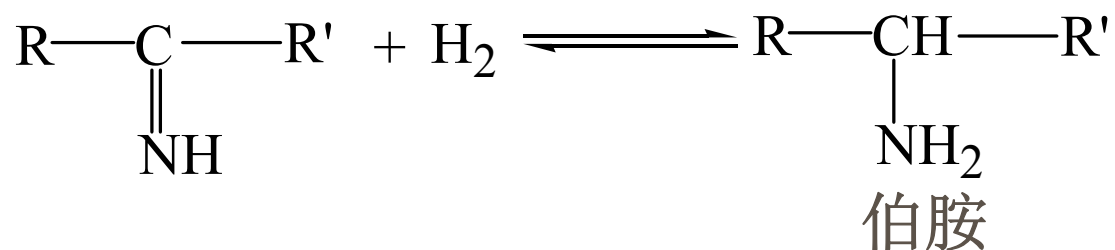
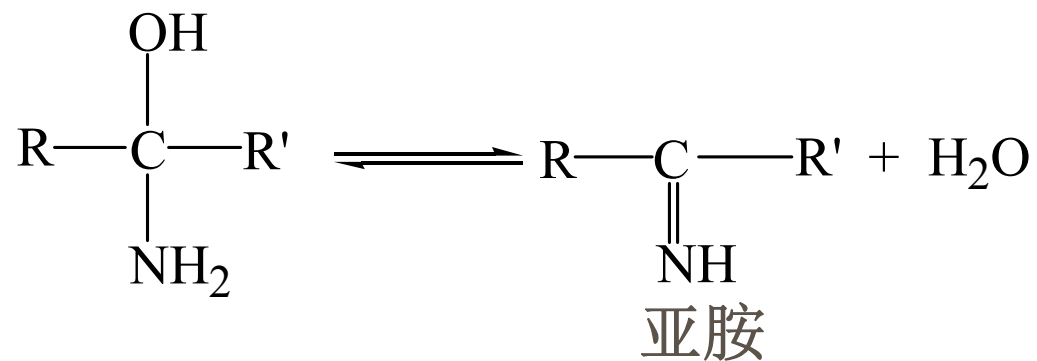
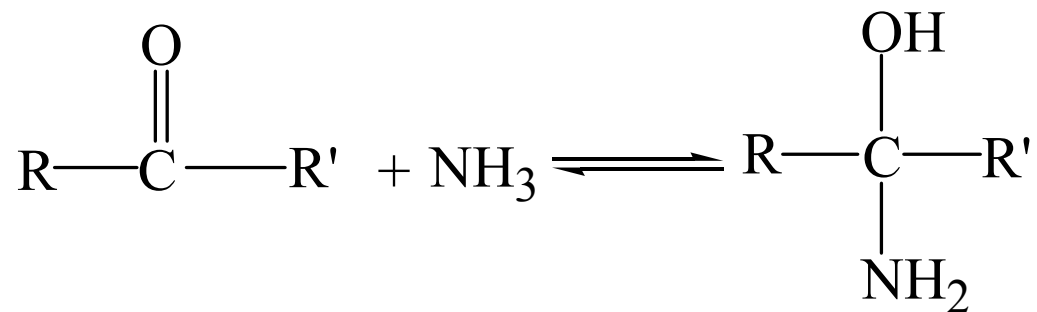
肟容易还原成伯胺, 这是由醛酮制备伯胺的方便方法

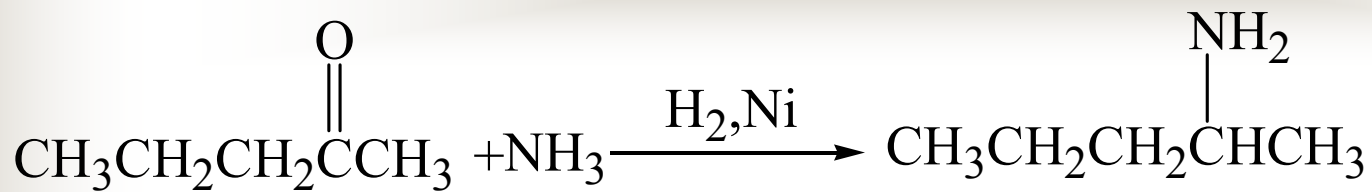


腈可以用氢化铝锂还原成伯胺

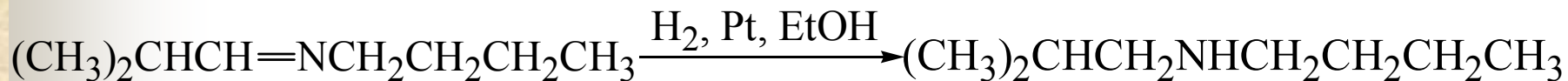
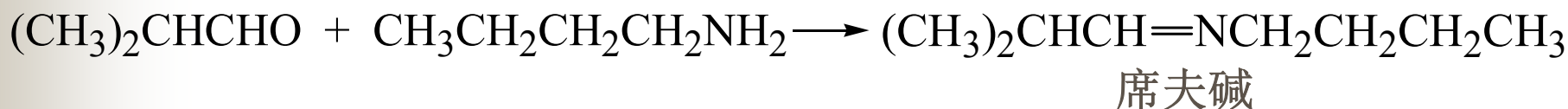


3. 醛酮的还原胺化

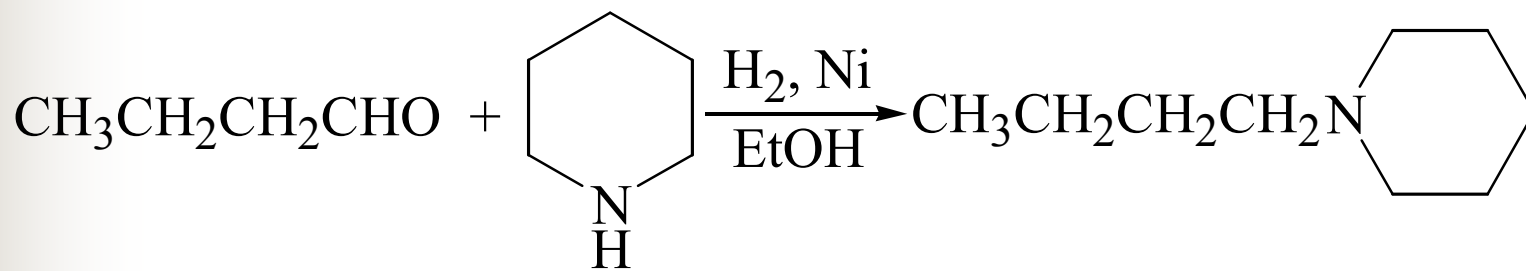




醛酮与伯胺一起催化加氢得到仲胺, 中间产物是席夫碱



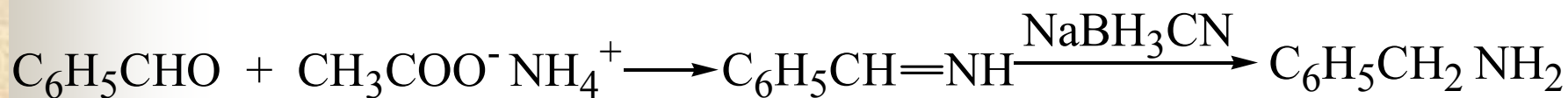
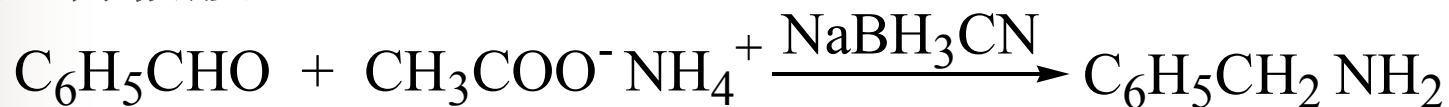
醛酮与仲胺一起催化加氢得到叔胺



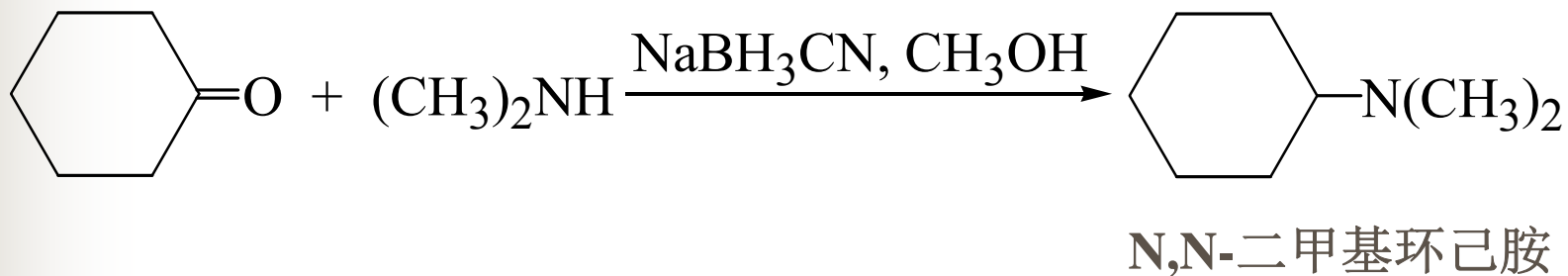
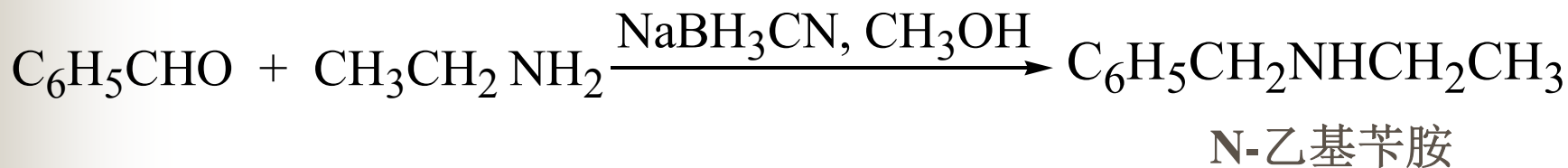
六氢吡啶

N-丁基六氢吡啶

醛酮和乙酸铵在醇溶液中用氰基氢硼化钠 (NaBH_3CN) 还原得伯胺

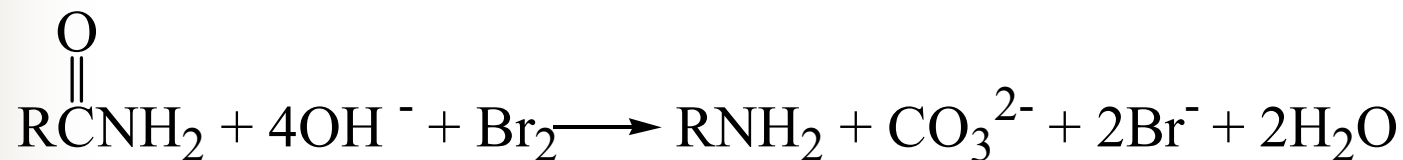


用类似的方法可合成仲胺和叔胺

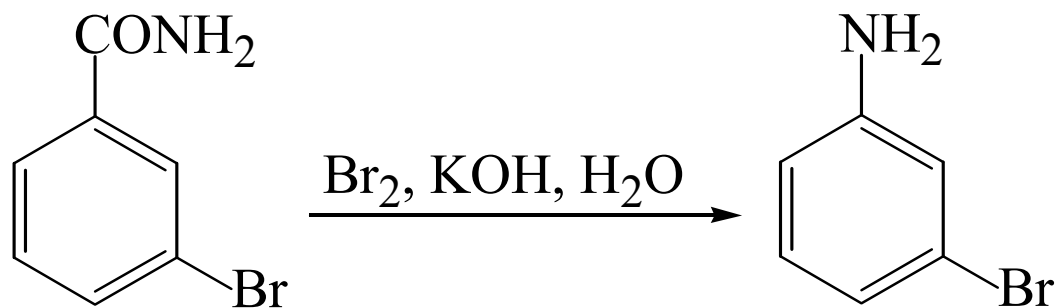
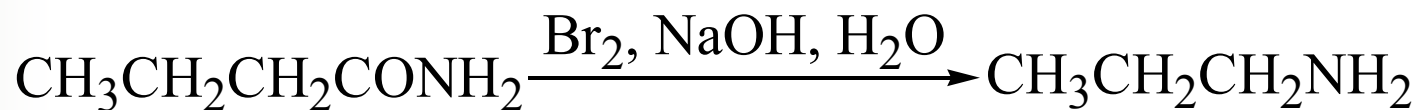


用此法合成胺操作方便

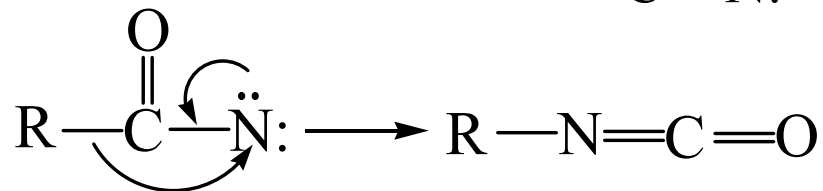
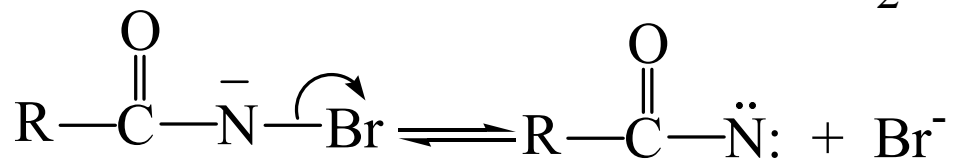
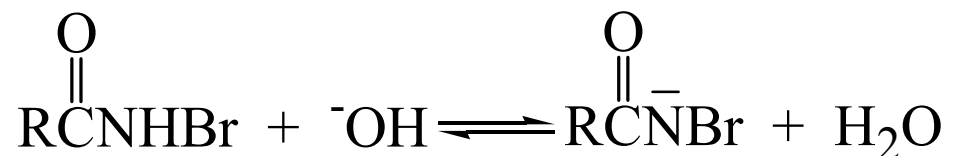
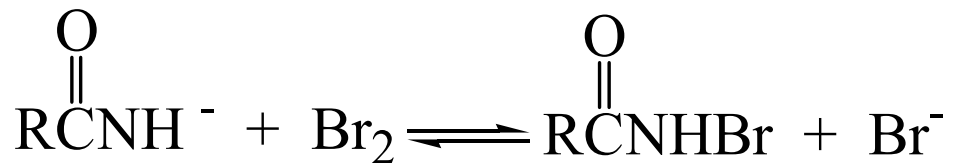
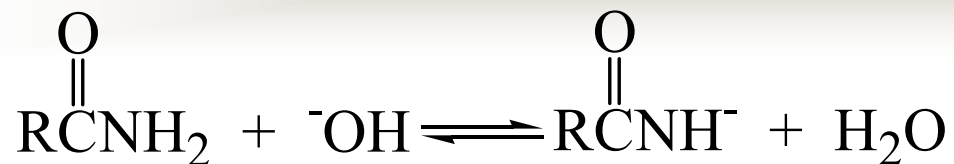
4. 酰胺的霍夫曼重排



制少一个碳的伯胺

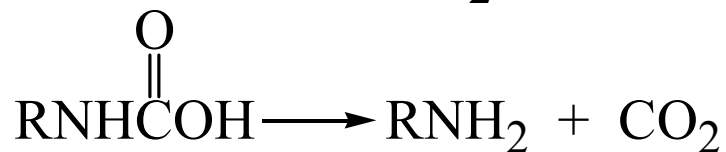
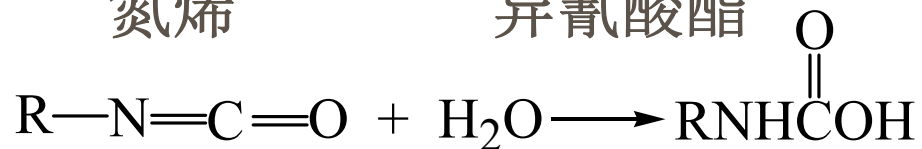


机理:



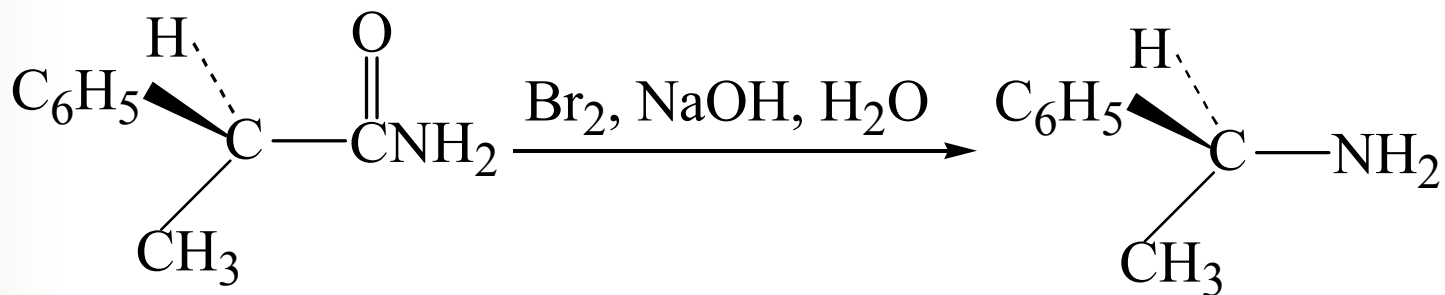
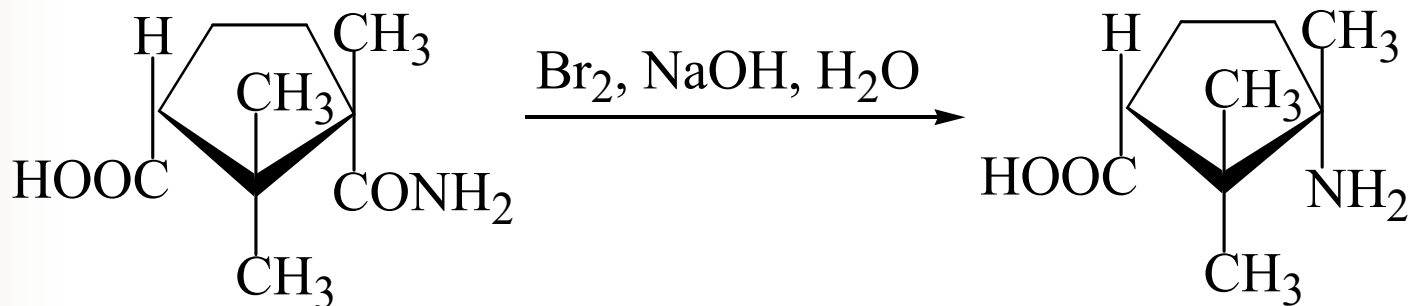
氮烯

异氰酸酯



立体化学

霍夫曼重排中，**迁移的烃基的构型保持不变**



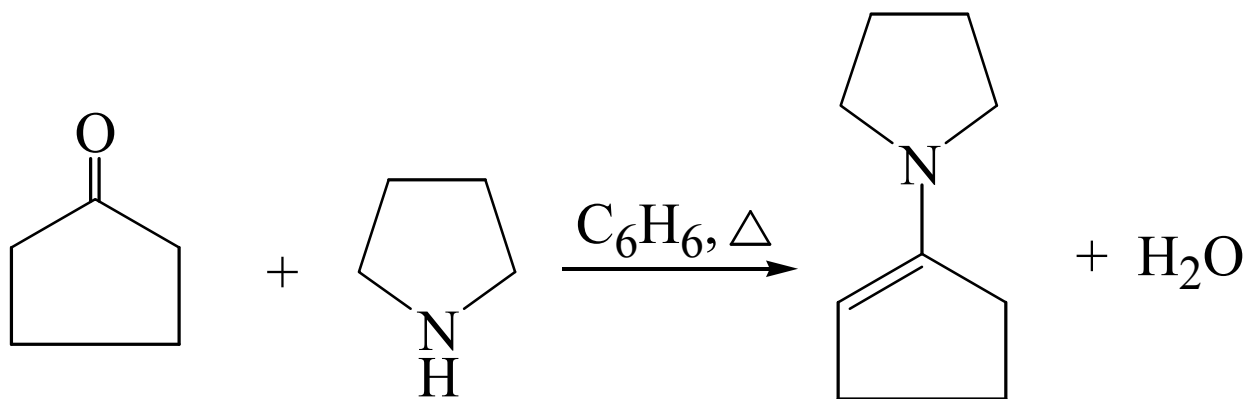
(S)-(+)-2-甲基-3-苯基丙酰胺

(S)-(+)-2-氨基-1-苯丙烷

§ 17.4 烯 胺

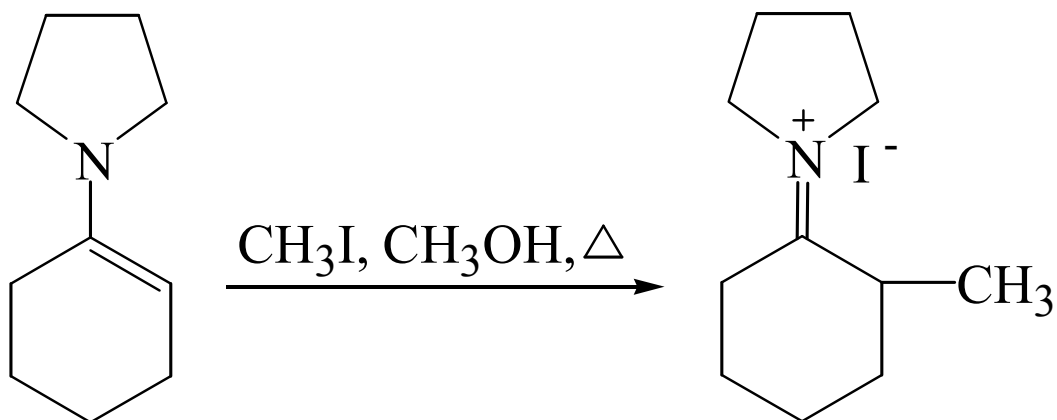
烯胺：氨基直接与双键碳原子相连

一、烯胺的制法 醛酮与仲氨缩合

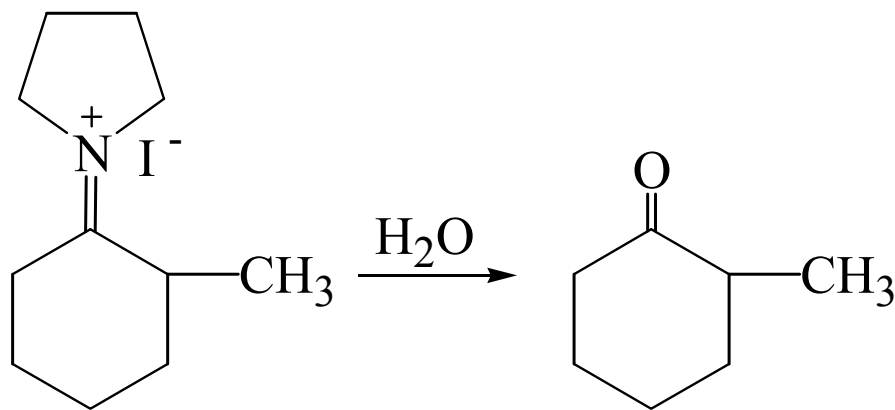


二、烯胺的反应

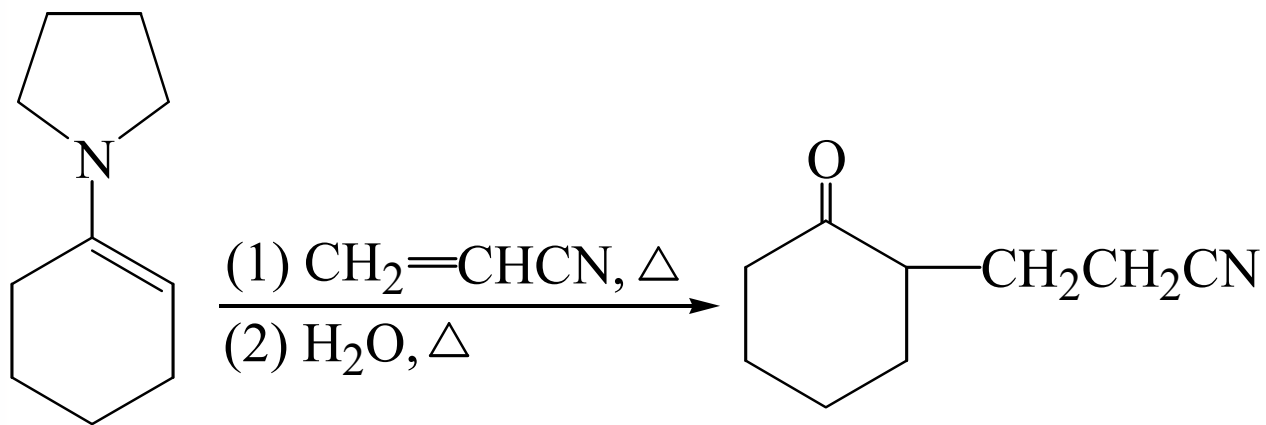
1. 烯胺与卤代烃的亲核取代反应



N-(1-环己烯基) 四氢吡咯

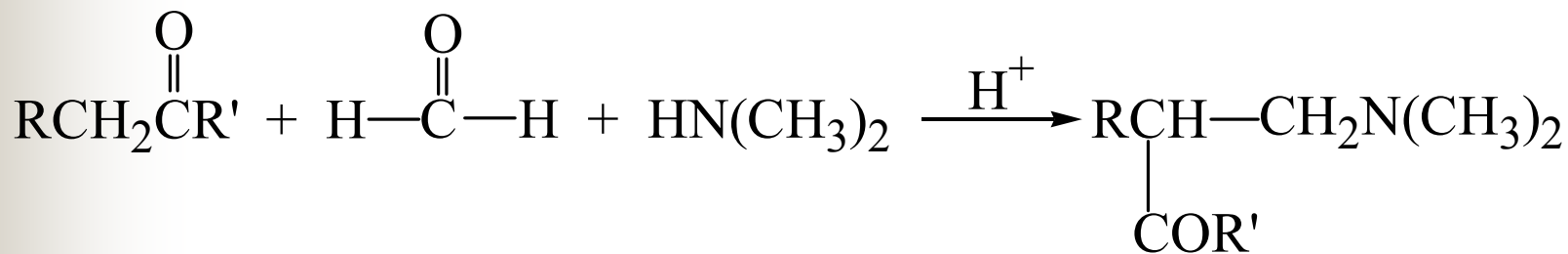


2. 烯胺与活性双键的迈克尔加成反应

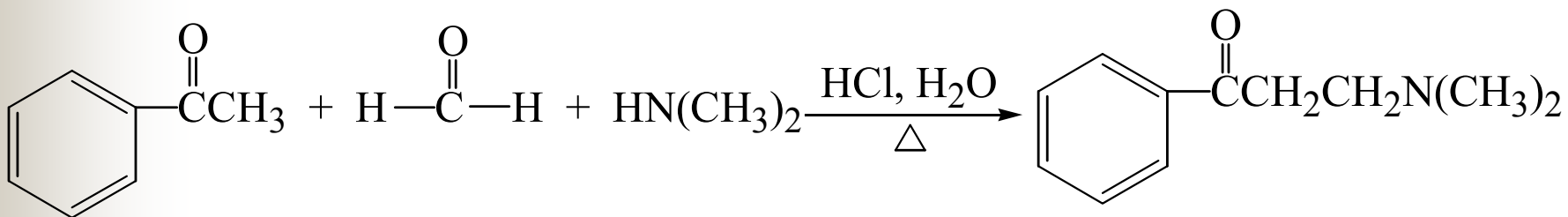


3. Mannich反应

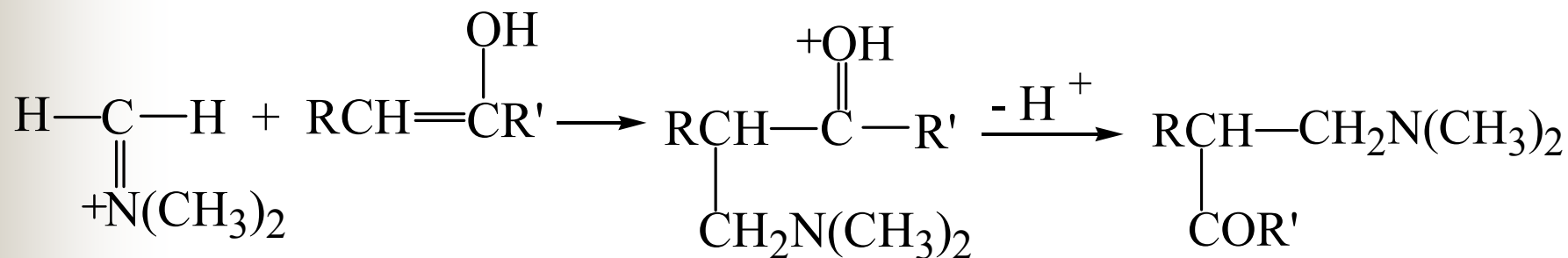
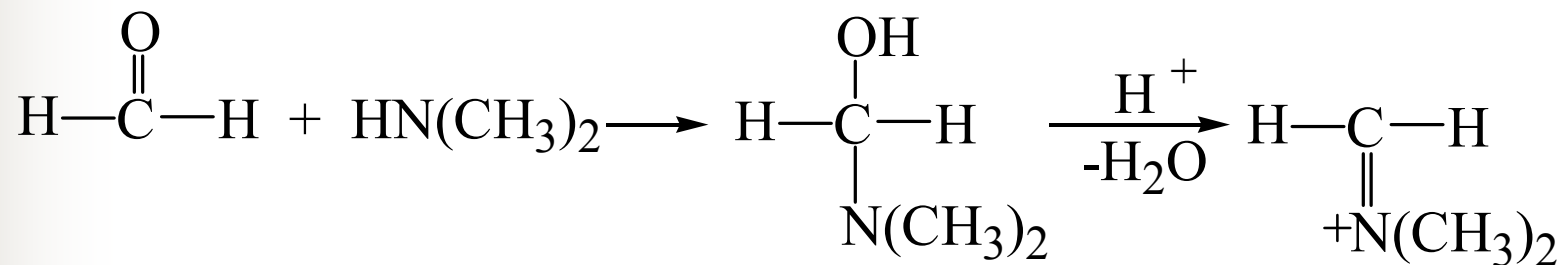
含有活泼氢的化合物和甲醛（有时采用其它醛）及胺类缩合，得到β-氨基（或取代氨基）的羰基化合物的反应，产物常称为Mannich碱。



含有活泼氢的化合物都能发生Mannich反应



Mannich反应的机理:



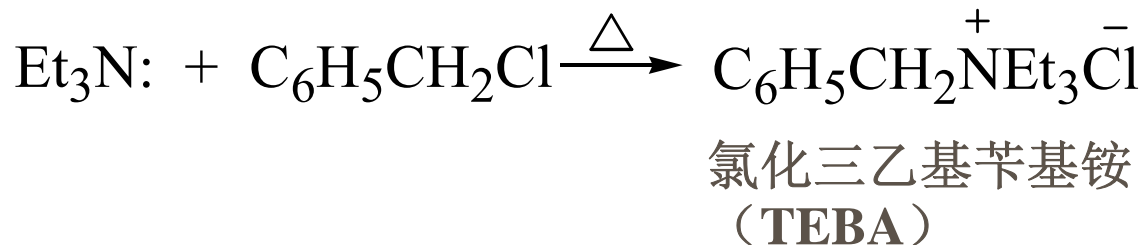
§ 17.5 季铵盐和氢氧化四烷基铵

Quaternary ammonium salts and quaternary ammonium hydroxide

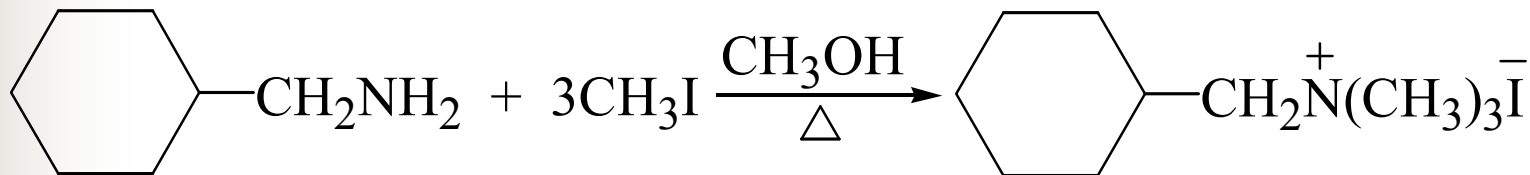
一、季铵盐

1. 制法

由叔胺与烷基化试剂（卤代烷、硫酸酯、磺酸酯等）发生 S_N2 反应制取：



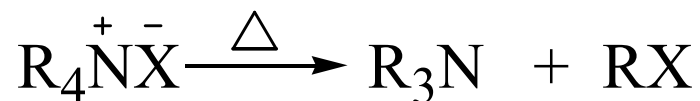
由伯胺的烃化制取：



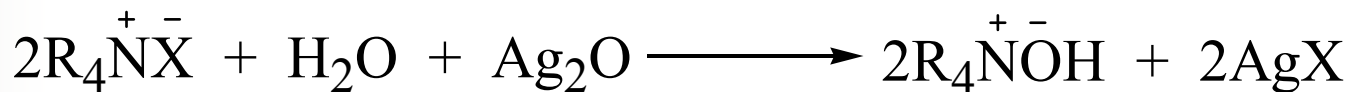
2. 季铵盐的性质

季铵盐易溶于水，并具有较高的熔点

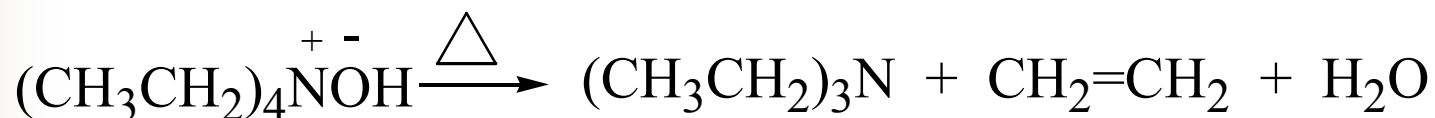
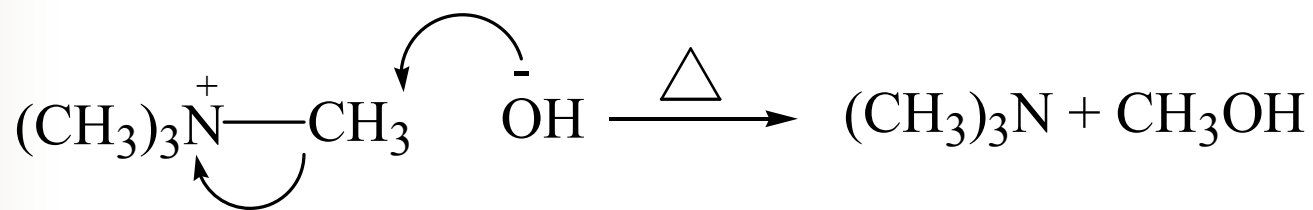
季铵盐在加热时分解为叔胺和卤代烷：



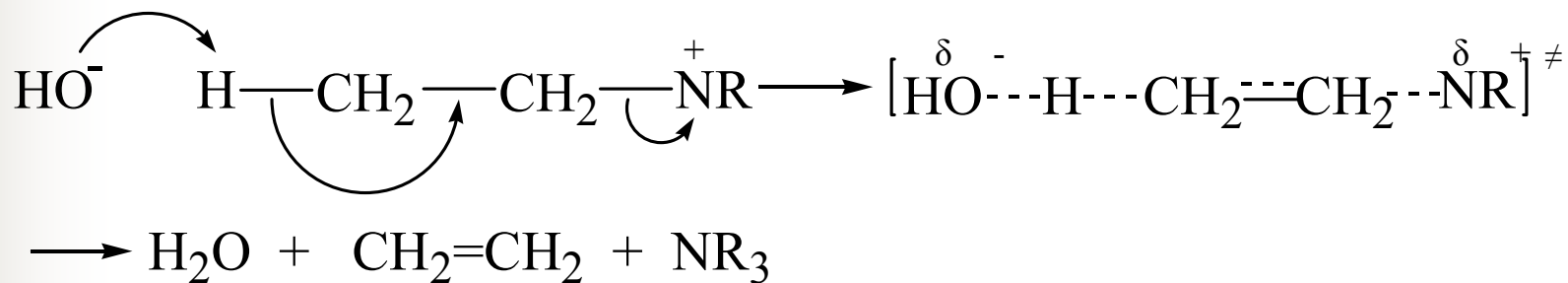
季铵盐不与氢氧化钠反应，但用水和氧化银处理，可转变为氢氧化四烷基铵



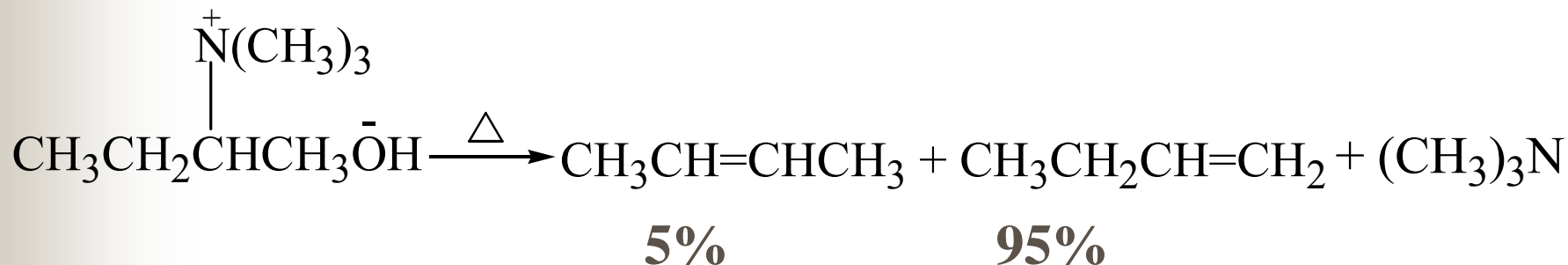
二、氢氧化四烷基铵的霍夫曼消去反应



霍夫曼消去是E2消去

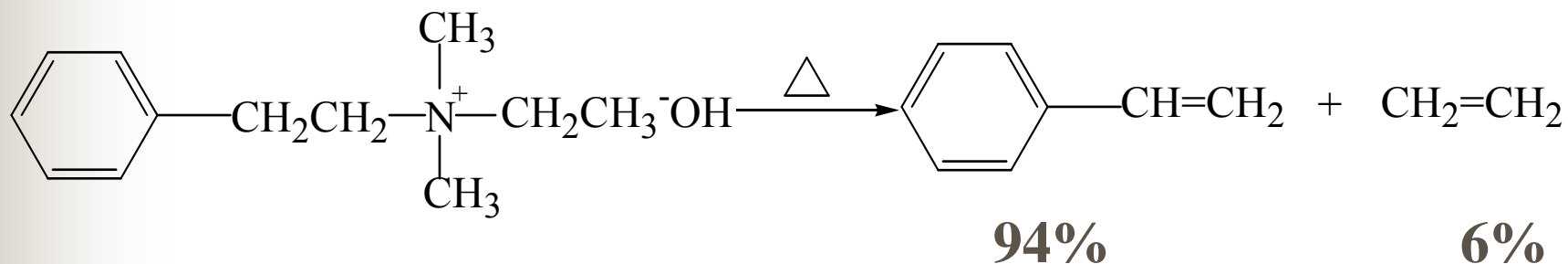


(1) 霍夫曼消去的区域选择性

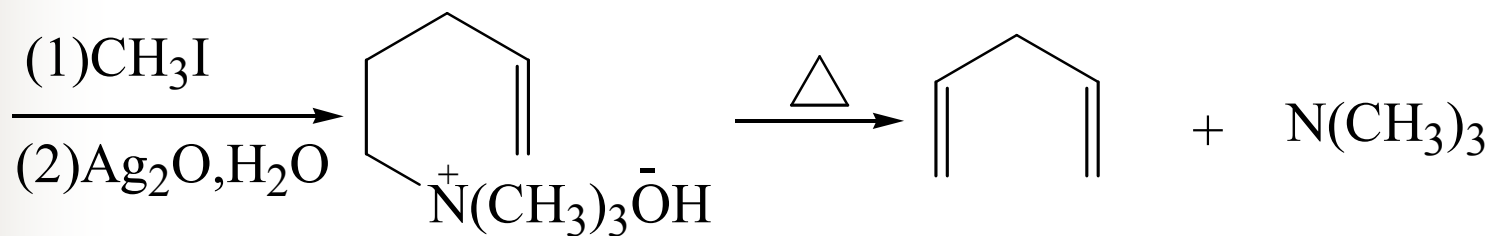
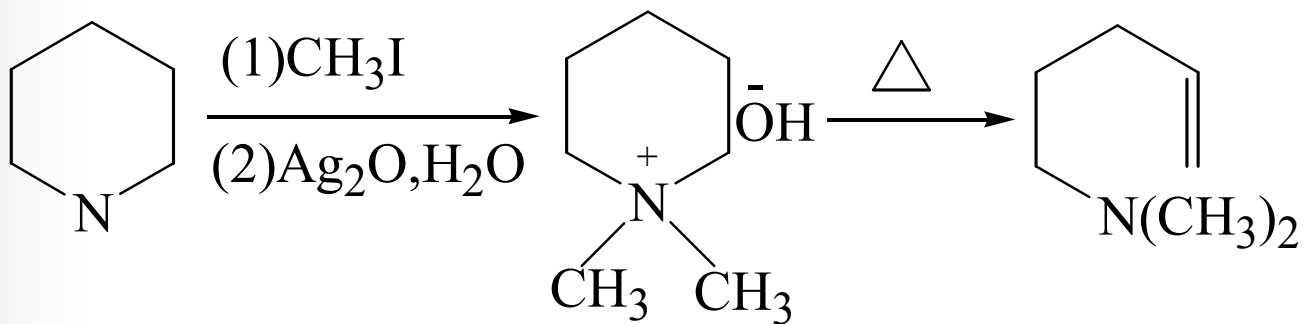


霍夫曼规律： 只含简单烷烃的氢氧化四烷基铵热分解时，最容易从 CH_3 (β -碳)上脱去氢,其次是 RCH_2 ,而最难从 R_2CH 上脱氢。

β -碳原子上有芳基时，霍夫曼规则不适用。



霍夫曼消去用于测定结构



(2) 霍夫曼消去的立体化学

多为反式消去

