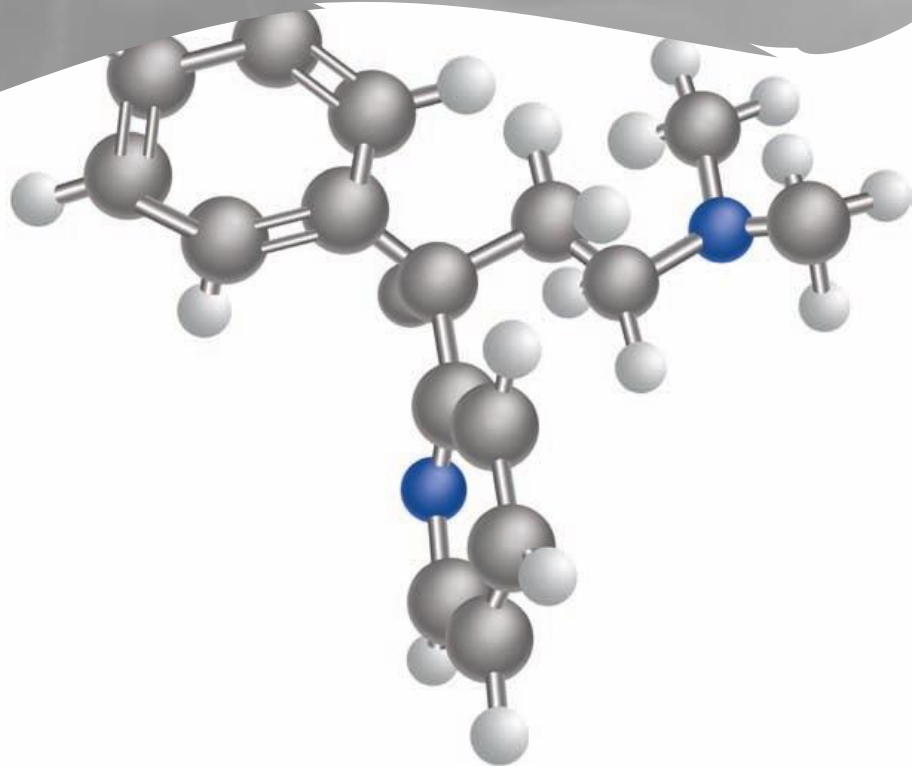
西安交通大学化学学院
XI'AN JIAOTONG UNIVERSITY SCHOOL OF CHEMISTRY

Organic Chemistry

西安交通大学化学学院
XI'AN JIAOTONG UNIVERSITY SCHOOL OF CHEMISTRY

Chapter 10

Amines



10.1 What Are Amines?

10.2 How Are Amines Named?

10.3 What Are the Characteristic Physical Properties of Amines?

10.4 What Are the Acid–Base Properties of Amines?

10.5 What Are the Reactions of Amines with Acids?

10.6 How Are Arylamines Synthesized?

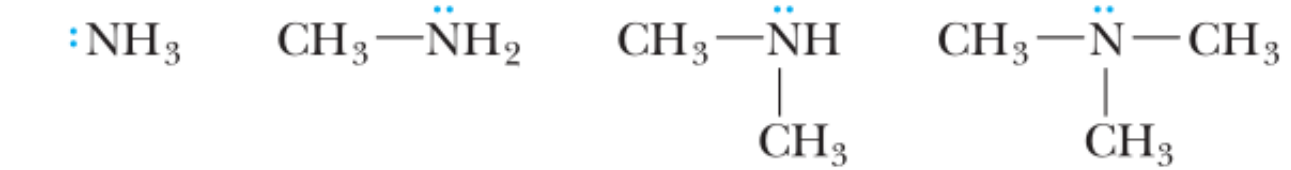
10.7 How Do Amines Act as Nucleophiles?

10.1 What Are Amines?

Aliphatic amine(脂肪族胺) An amine in which nitrogen is bonded only to alkyl groups.

Aromatic amine（芳胺） An amine in which nitrogen is bonded to one or more aryl groups.

脂肪族胺



Ammonia

Methylamine (a 1° amine)

伯胺

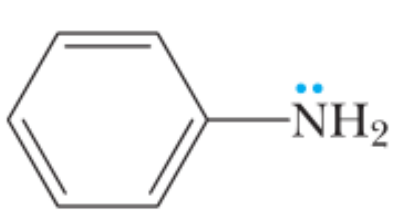
Dimethylamine (a 2° amine)

仲胺

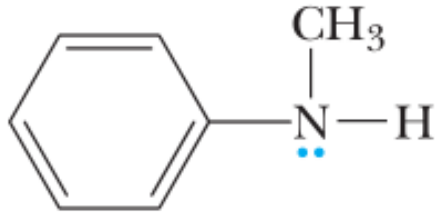
Trimethylamine (a 3° amine)

叔胺

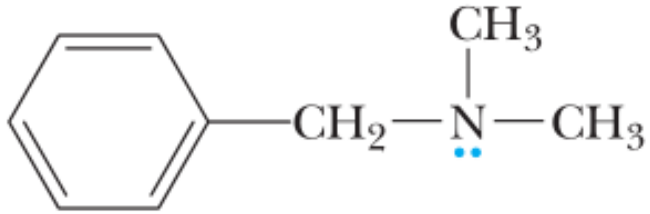
芳胺



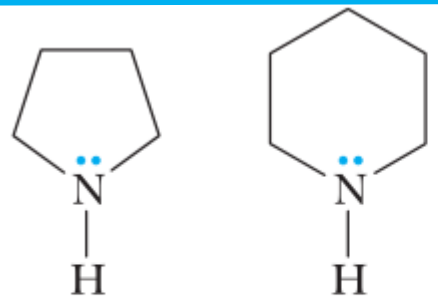
Aniline (a 1° aromatic amine)



N-Methylaniline (a 2° aromatic amine)



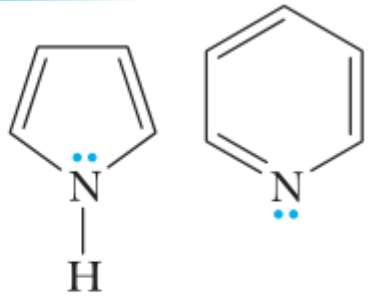
Benzyldimethylamine (a 3° aliphatic amine)



Pyrrolidine Piperidine

(heterocyclic aliphatic amines)

杂环胺



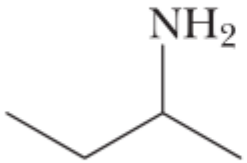
Pyrrole Pyridine

(heterocyclic aromatic amines)

芳杂环胺

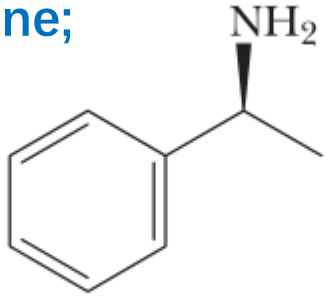
10.2 How Are Amines Named?

A. Systematic Names： Just as they are for alcohols， The suffix -e of the parent alkane is dropped and is replaced by -amine;



2-Butanamine

2-丁胺



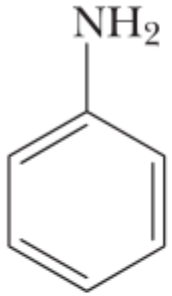
(*S*)-1-Phenylethanamine

(s) -1-苯基乙胺

$H_2N(CH_2)_6NH_2$

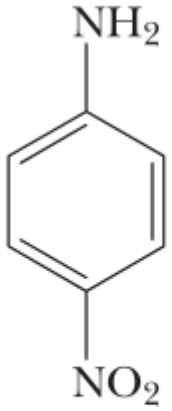
1,6-Hexanediamine

1，6-己二胺



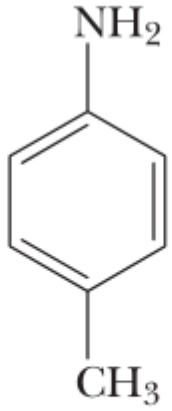
Aniline

苯胺



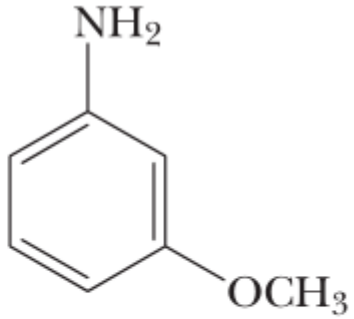
4-Nitroaniline
(*p*-Nitroaniline)

(4-）对硝基苯胺



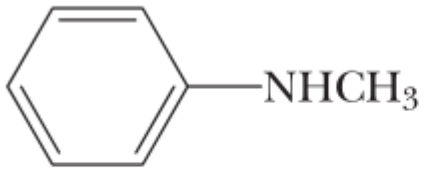
4-Methylaniline
(*p*-Toluidine)

(4-）对甲苯胺



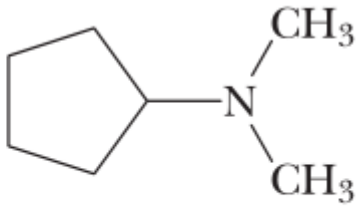
3-Methoxyaniline
(*m*-Anisidine)

3-甲氧基苯胺/间茴香胺



N-Methylaniline

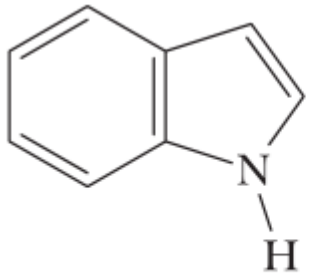
N-甲基苯胺



N,*N*-Dimethyl-
cyclopentanamine

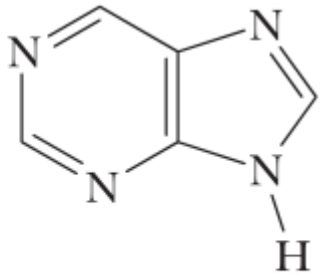
N,N-二甲基环戊胺

芳杂环胺



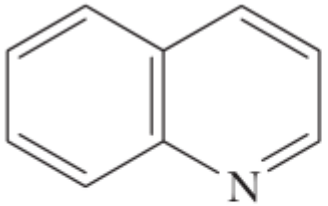
Indole

吲哚



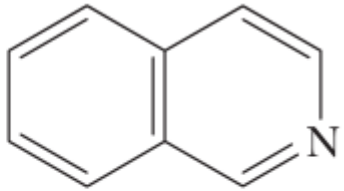
Purine

嘌呤



Quinoline

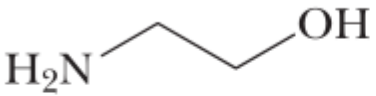
喹啉



Isoquinoline

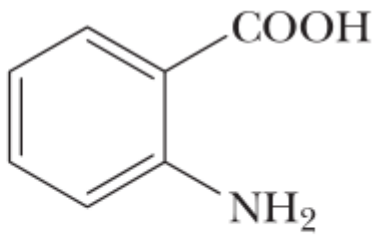
异喹啉

-NH_2优先次序较低



2-Aminoethanol
(Ethanolamine)

2-氨基乙醇



2-Aminobenzoic acid
(Anthranilic acid)

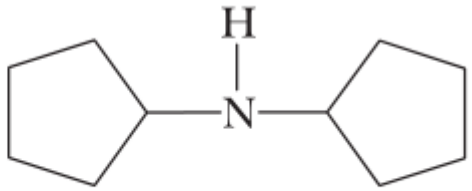
2-氨基苯甲酸

B. Common Names

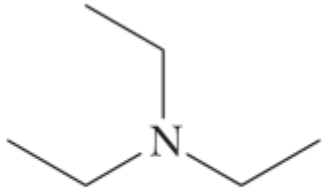
Alkyl+amines 烃基+胺

Methylamine
甲胺

tert-Butylamine
叔丁胺

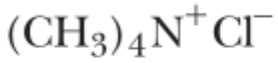


Dicyclopentylamine
二环戊胺

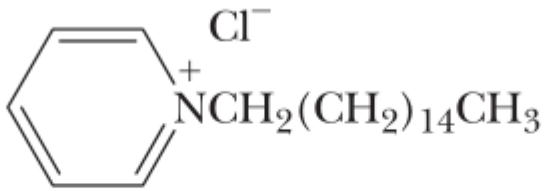


Triethylamine
三乙胺

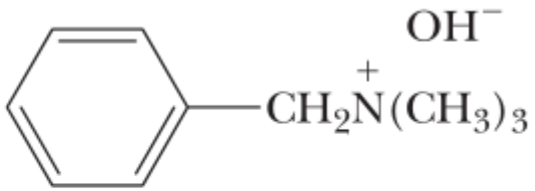
季铵盐



Tetramethylammonium chloride
氯化四甲基铵



Hexadecylpyridinium chloride
(Cetylpyridinium chloride)
氯化十六烷基吡啶

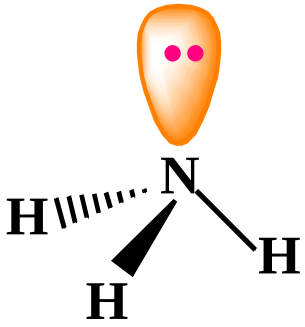


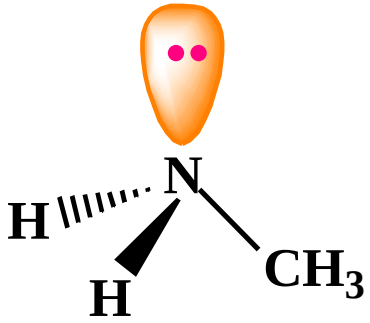
Benzyltrimethylammonium hydroxide
氢氧化苄基三甲基铵

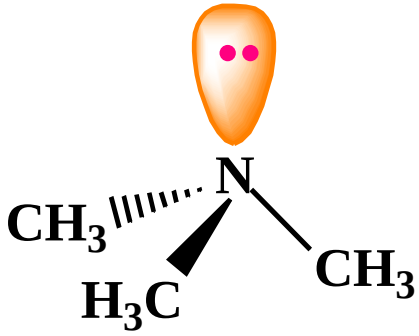
胺的结构

氮原子的电子结构：$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$

氮原子是sp^3杂化，　胺具有锥形体结构。







碱　性

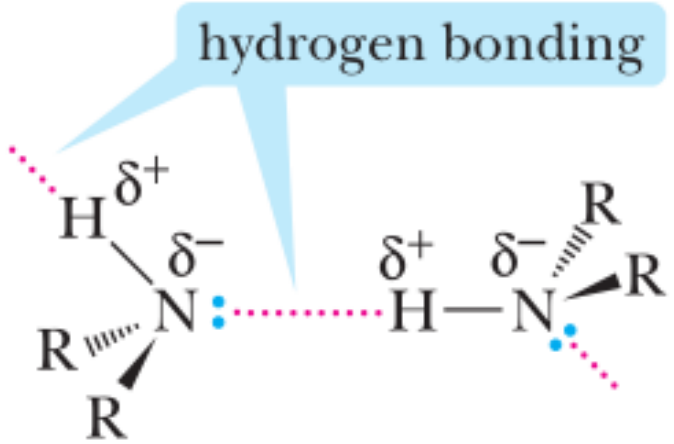
特征结构：$-\ddot{N}H_2$

对烃基的影响

亲核性

10.3 What Are the Characteristic Physical Properties of Amines?

伯胺和仲胺分子间可形成氢键

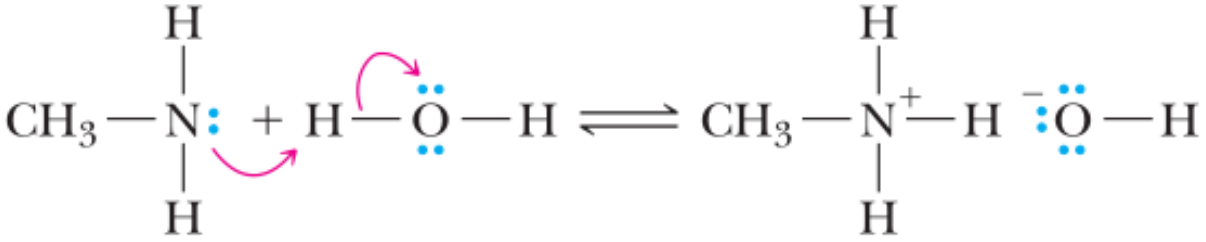


伯胺和仲胺分子间氢键比醇分子间氢键弱

	CH_3NH_2	CH_3OH
molecular weight (g/mol)	31.1	32.0
boiling point (°C)	−6.3	65.0

10.4 What Are the Acid–Base Properties of Amines?

Like ammonia, all amines are weak bases, and aqueous solutions of amines are basic.



Methylamine

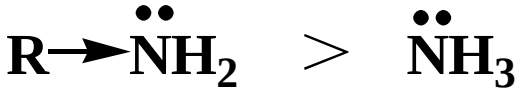
Methylammonium hydroxide

$$K_b = K_{eq}[H_2O] = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = 4.37 \times 10^{-4} \quad pK_b = 3.36$$

$$CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$$

$$K_a = \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3^+]} = 2.29 \times 10^{-11} \quad pK_a = 10.64$$

脂肪胺的碱性：



芳香族胺的碱性

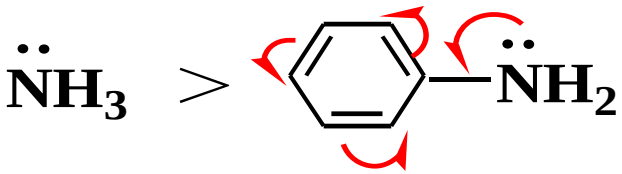
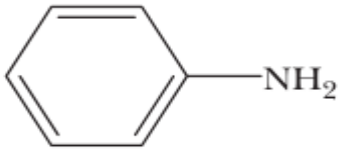
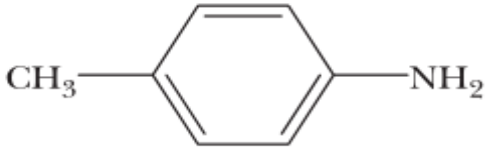
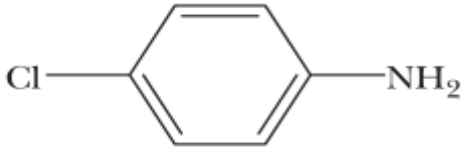


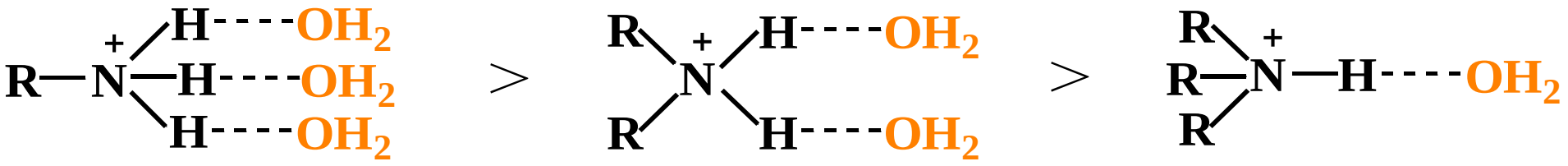
TABLE 10.2 Base Strengths (pK_b) of Selected Amines and Acid Strengths (pK_a) of Their Conjugate Acids*

Amine	Structure	pK_b	pK_a
Ammonia	NH_3	4.74	9.26
Primary Amines			
methylamine	CH_3NH_2	3.36	10.64
ethylamine	$CH_3CH_2NH_2$	3.19	10.81
cyclohexylamine	$C_6H_{11}NH_2$	3.34	10.66
Secondary Amines			
dimethylamine	$(CH_3)_2NH$	3.27	10.73
diethylamine	$(CH_3CH_2)_2NH$	3.02	10.98
Tertiary Amines			
trimethylamine	$(CH_3)_3N$	4.19	9.81
triethylamine	$(CH_3CH_2)_3N$	3.25	10.75
Aromatic Amines			
aniline		9.37	4.63
4-methylaniline (*p*-toluidine)		8.92	5.08
4-chloroaniline		9.85	4.15

脂肪族胺水溶液中碱性：　NH_3 < $(CH_3)_3N$ < CH_3NH_2 < $(CH_3)_2NH$

pKb　4.74　　4.19　　3.36　　3.27

$$R\ddot{N}H_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$



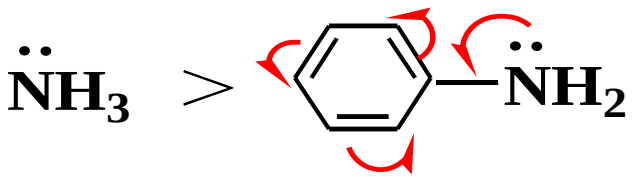
共轭酸稳定性好，酸性弱，碱性强。

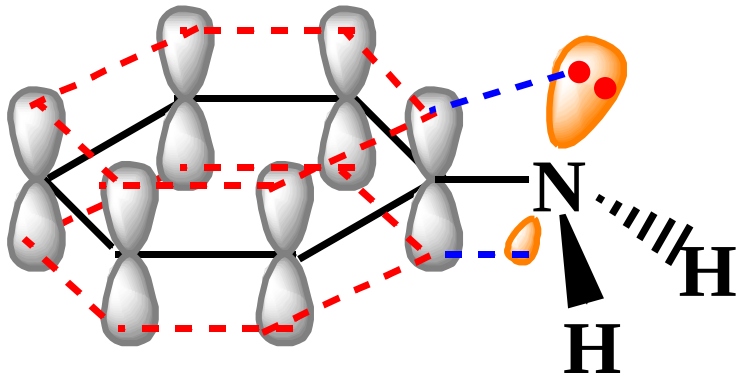
电子效应：　3°胺＞2°胺＞1°胺

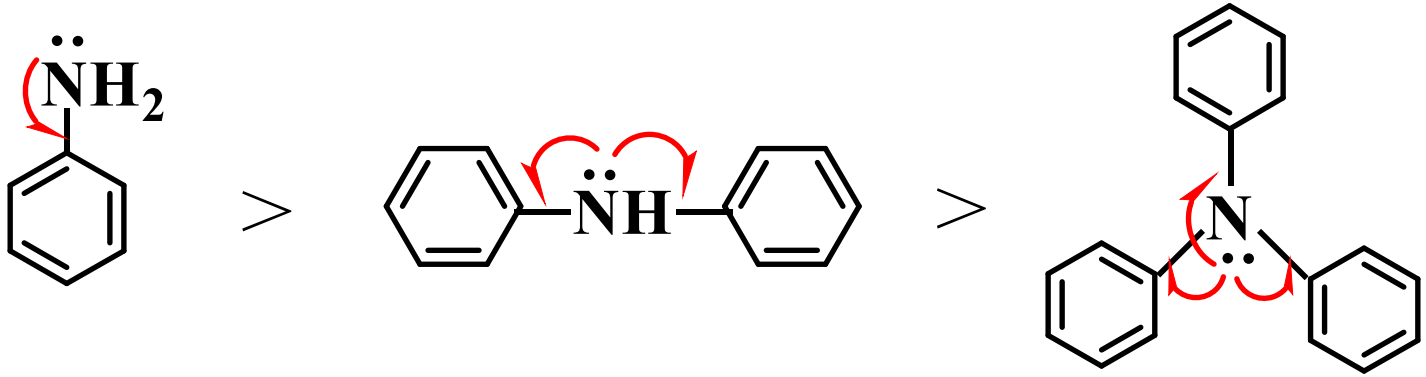
溶剂化效应：1°胺＞2°胺＞3°胺

电子效应和溶剂化等效应的综合作用：　2°胺＞1°胺＞3°胺

芳香族胺的碱性







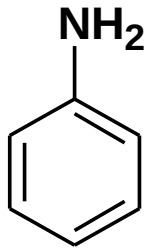
pk_b 9.37 13.21

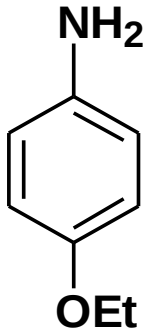
结论：① 脂肪胺 ＞ NH_3 ＞ 芳香胺

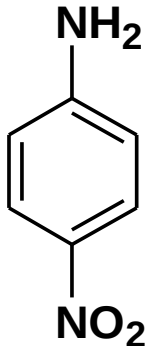
② 脂肪胺：$R_2NH > RNH_2 > R_3N$

③ 芳香胺：$PhNH_2$ ＞ $(Ph)_2NH$ ＞ $(Ph)_3N$

练习：



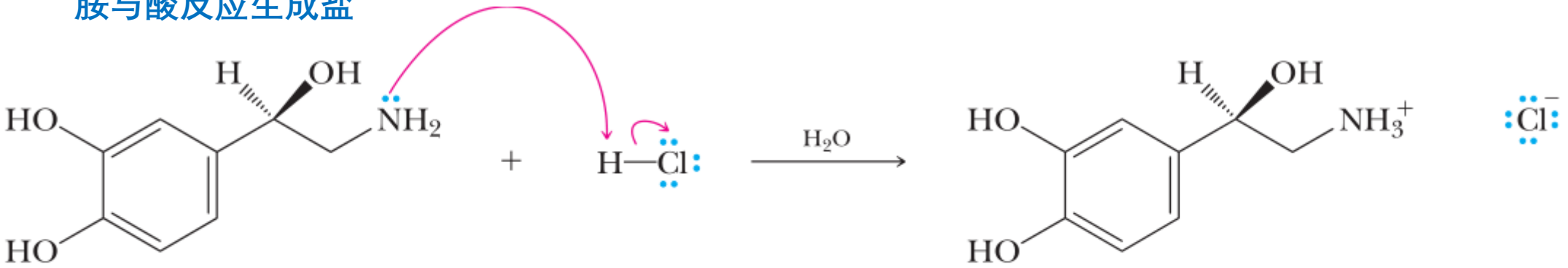




pK_b 9.40 8.82 12.0

10.5 What Are the Reactions of Amines with Acids?

胺与酸反应生成盐

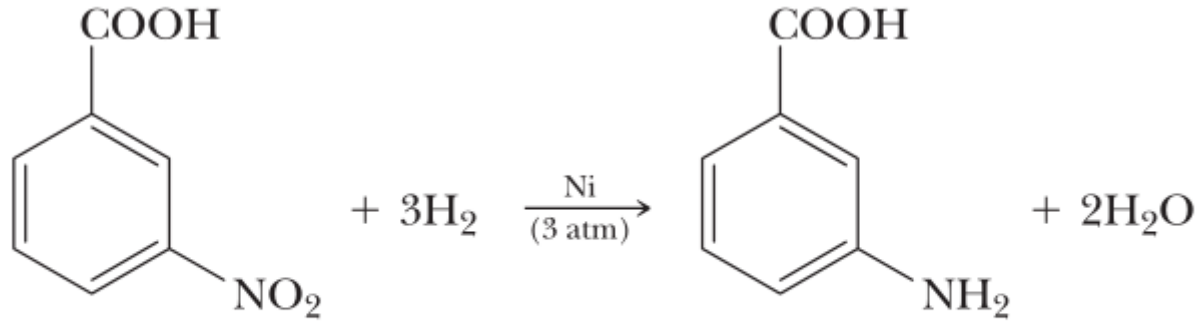


(*R*)-Norepinephrine 去甲肾上腺素
(only slightly soluble in water)

(*R*)-Norepinephrine hydrochloride
(a water-soluble salt)

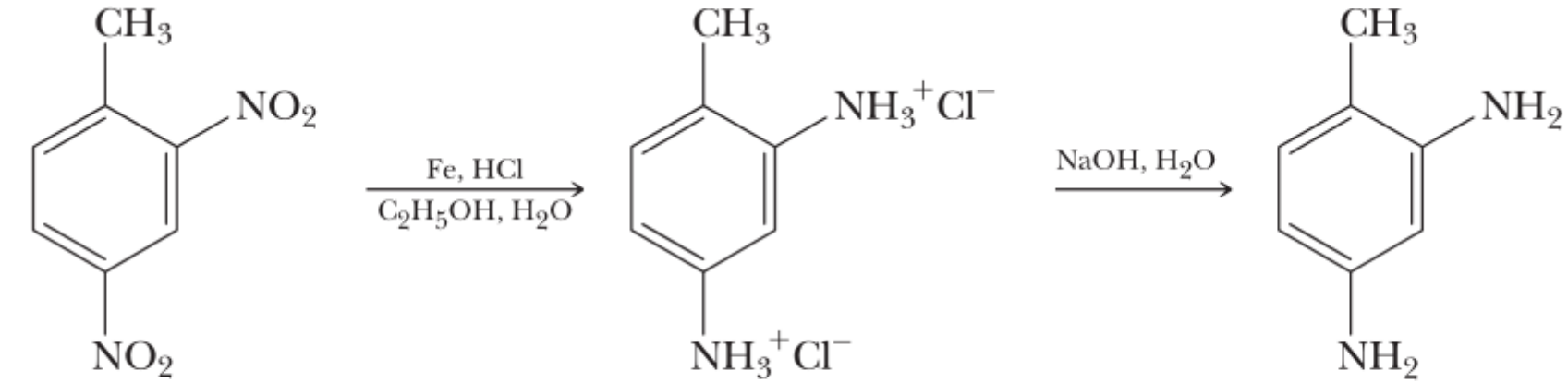
10.6 How Are Arylamines Synthesized?

还原硝基



3-Nitrobenzoic acid

3-Aminobenzoic acid



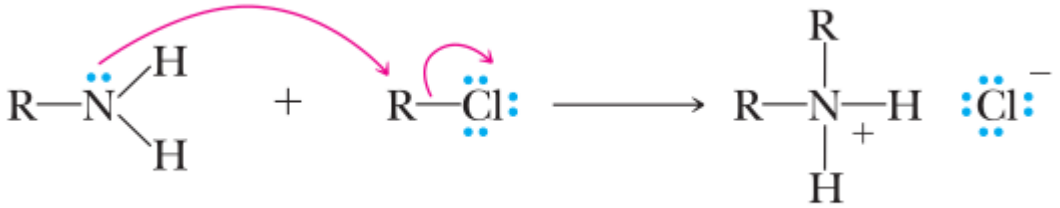
2,4-Dinitrotoluene

2,4-Diaminotoluene

10.7 How Do Amines Act as Nucleophiles?

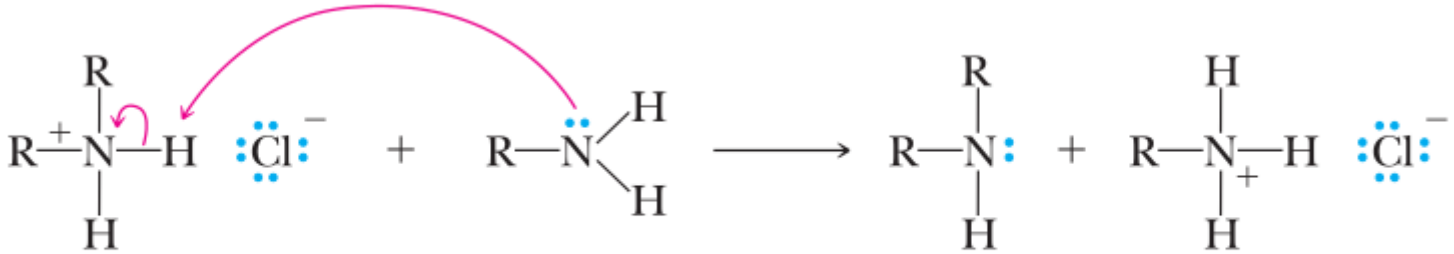
胺与氯代烷的亲核取代：中等强度亲核试剂

Step 1: Reaction of an electrophile and a nucleophile to form a new covalent bond.



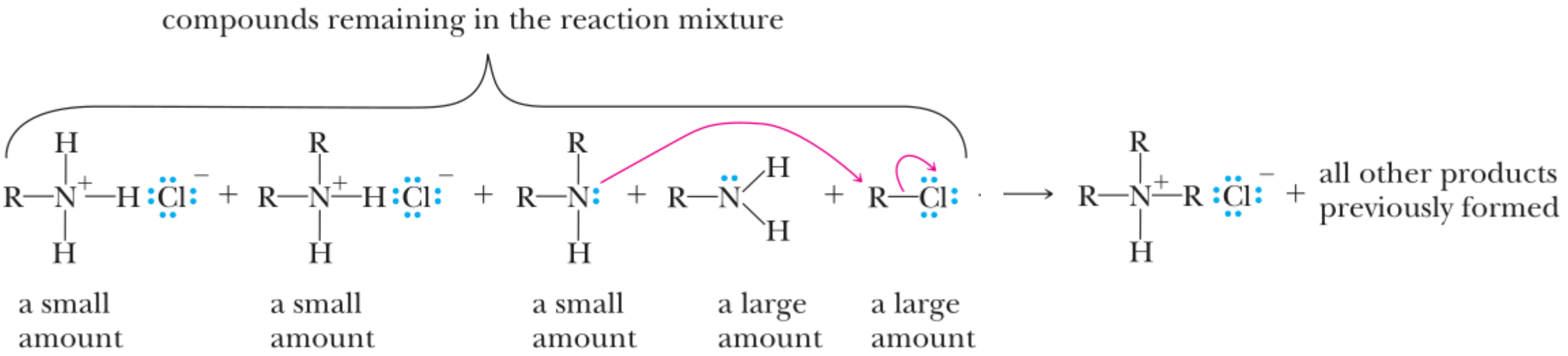
(a nucleophile) (an electrophile)

Step 2: Take a proton away.



unreacted
starting material

Step 3: Reaction of an electrophile and a nucleophile to form a new covalent bond.



产物是混合物，应用范围有限

作 业

10.11 （a、c、e、g）、10.12（a、b、c）

10.22、10.41、10.44 （a、b、c、d、f、g）