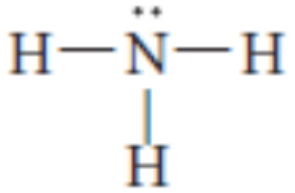
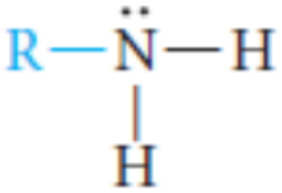
Organic chemistry for nonmajor students
Chem 233

11 Amines

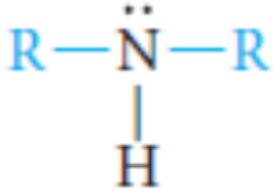
11.1 Classification and Structure of Amines



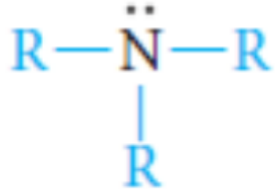
ammonia



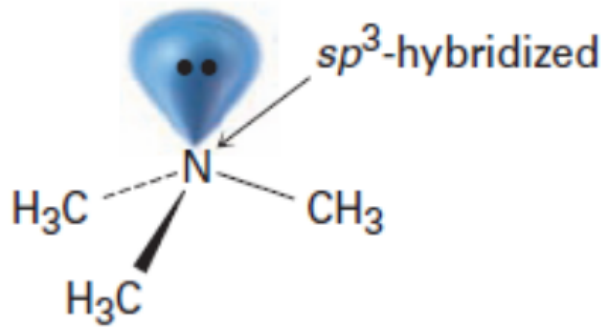
primary amine



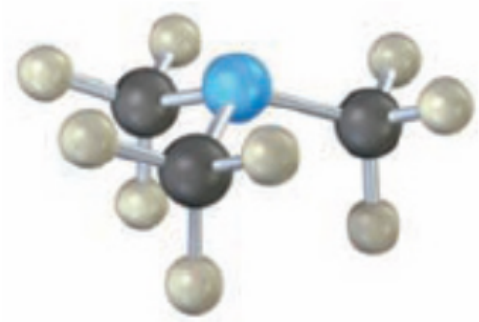
secondary amine



tertiary amine



Trimethylamine



11.2 Nomenclature of Amines

$CH_3CH_2NH_2$
ethylamine
(primary)

$(CH_3CH_2)_2NH$
diethylamine
(secondary)

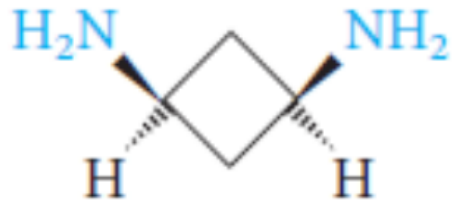
$(CH_3CH_2)_3N$
triethylamine
(tertiary)

$CH_3CH_2NH_2$

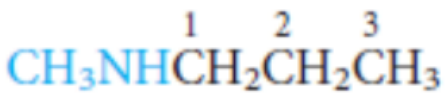
aminoethane

$CH_3\overset{1}{C}H(NH_2)\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3$

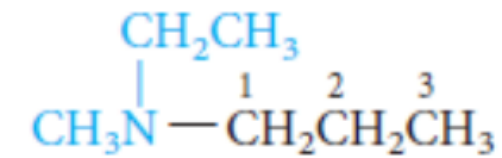
2-aminopentane



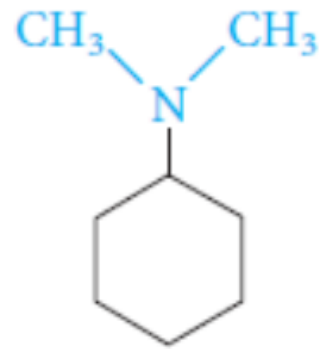
cis-1,3-diaminocyclobutane



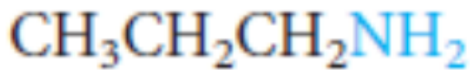
1-methylaminopropane



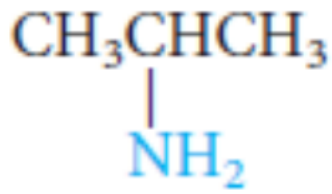
1-(ethylmethylamino)propane



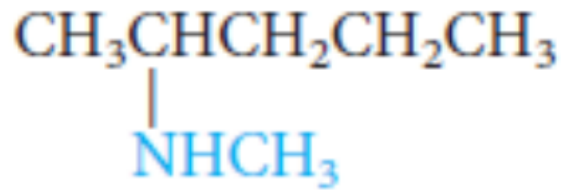
dimethylaminocyclohexane



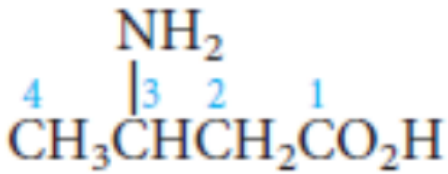
propanamine



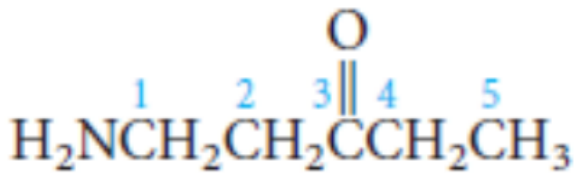
2-propanamine



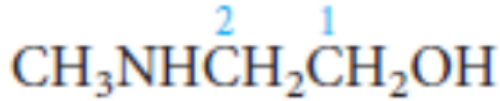
N-methyl-2-pentanamine



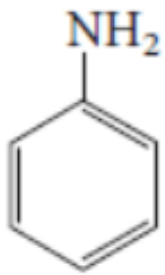
3-aminobutanoic acid



1-amino-3-pentanone

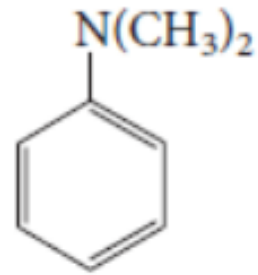


2-methylaminoethanol

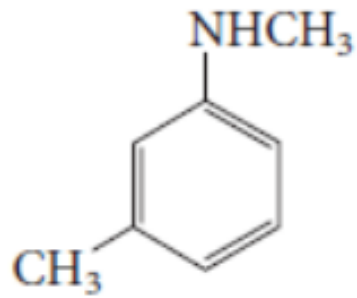


aniline
(benzenamine)

p-bromoaniline
(4-bromobenzenamine)



N,*N*-dimethylaniline
(*N*,*N*-dimethylbenzenamine)



m-methyl-*N*-methylaniline, or
N-methyl-*m*-toluidine
(*N*-methyl-3-methylbenzenamine)

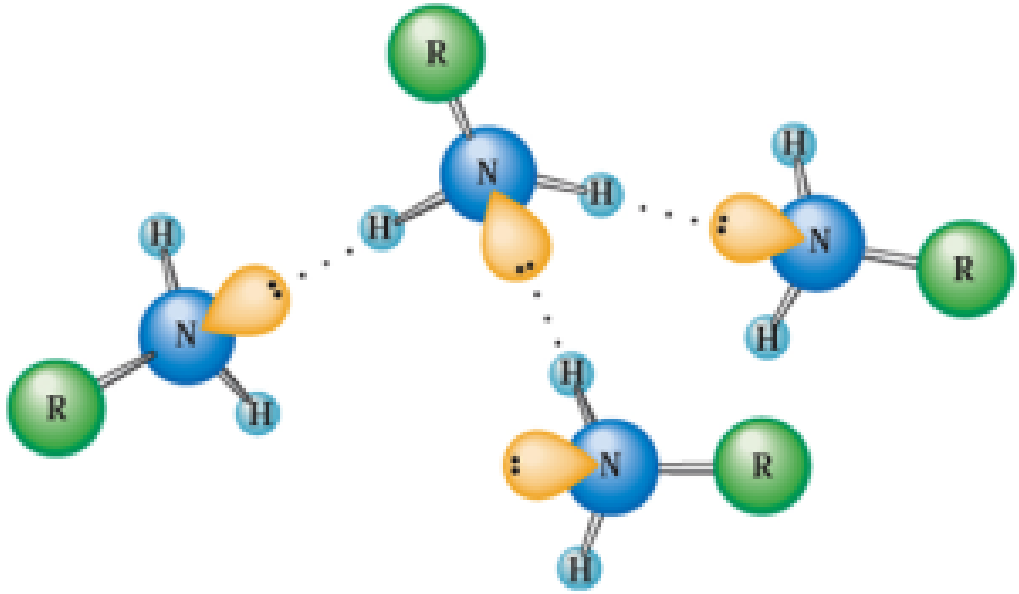
Physical properties of amines

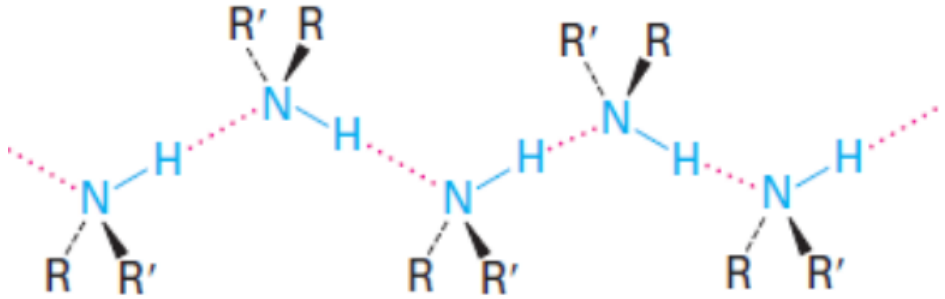
Primary amines boil well above alkanes with comparable molecular weights, but below comparable alcohols

alkane	CH_3CH_3 (30) bp −88.6°C	$CH_3CH_2CH_3$ (44) bp −42.1°C
amine	CH_3NH_2 (31) bp −6.3°C	$CH_3CH_2NH_2$ (45) bp +16.6°C
alcohol	CH_3OH (32) bp +65.0°C	CH_3CH_2OH (46) bp +78.5°C

H-bonding in amines

Intermolecular N-H···N hydrogen bonds are important and raise the boiling points of primary and secondary amines but are not as strong as the O-H···O bonds of alcohols

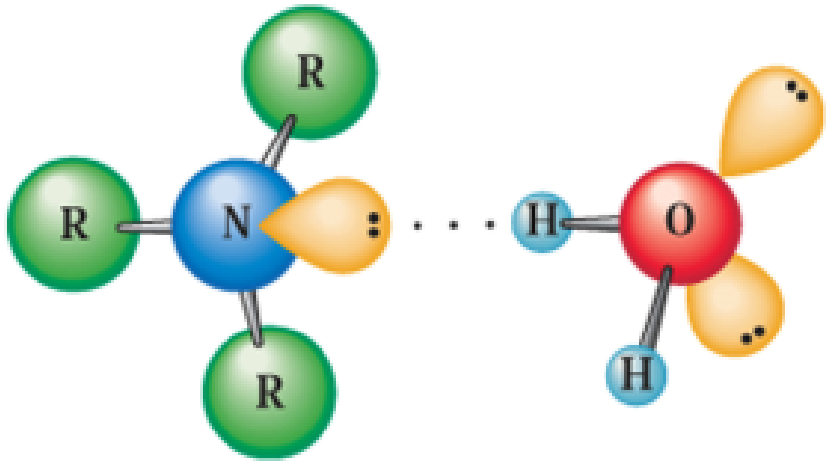




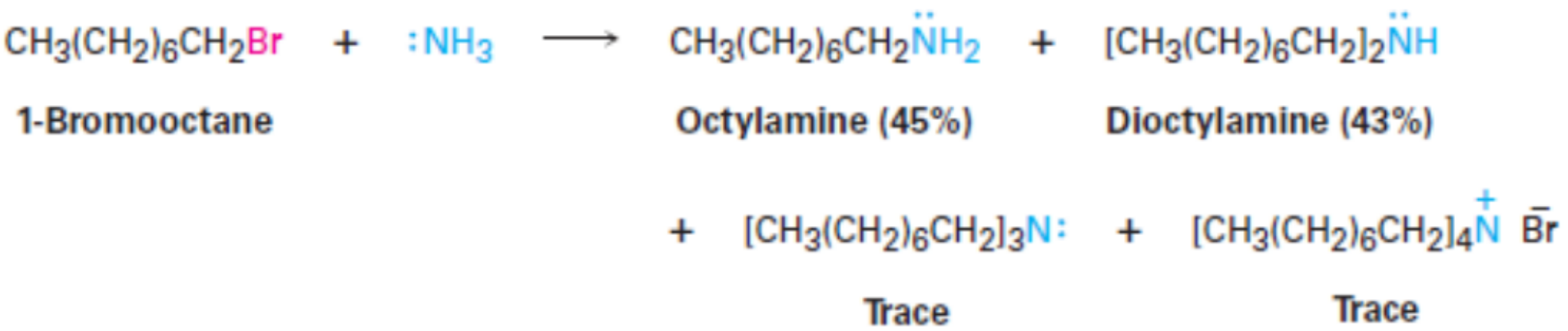
Name	Formula	bp, °C
ammonia	NH_3	–33.4
methylamine	CH_3NH_2	–6.3
dimethylamine	$(CH_3)_2NH$	7.4
trimethylamine	$(CH_3)_3N$	2.9
ethylamine	$CH_3CH_2NH_2$	16.6
propylamine	$CH_3CH_2CH_2NH_2$	48.7
butylamine	$CH_3CH_2CH_2CH_2NH_2$	77.8
aniline	$C_6H_5NH_2$	184.0

Solubility of amines in water

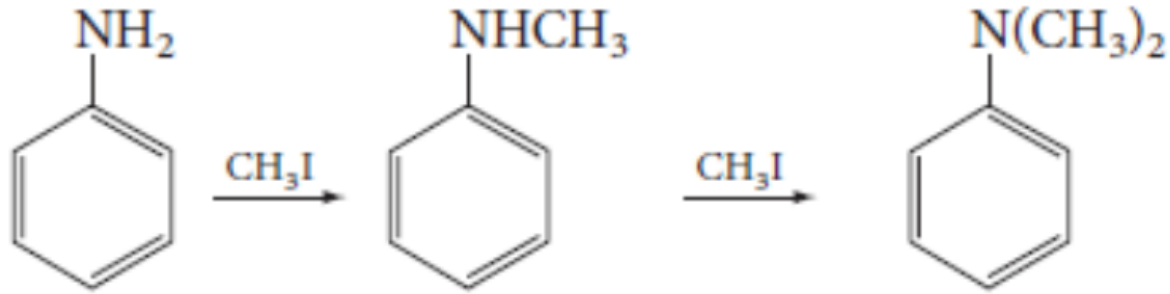
All three classes of amines can form hydrogen bonds with the -OH group of water (that is, O-H· · ·N). Primary and secondary amines can also form hydrogen bonds with the oxygen atom in water:. N-H· · ·O



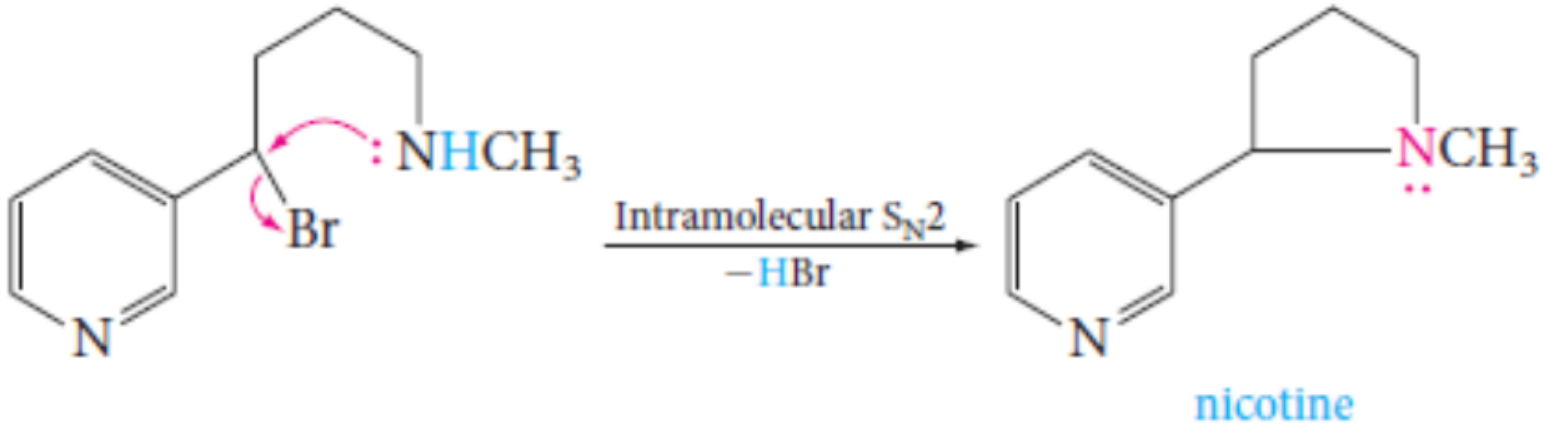
11.4 Preparation of Amines; Alkylation of Ammonia and Amines



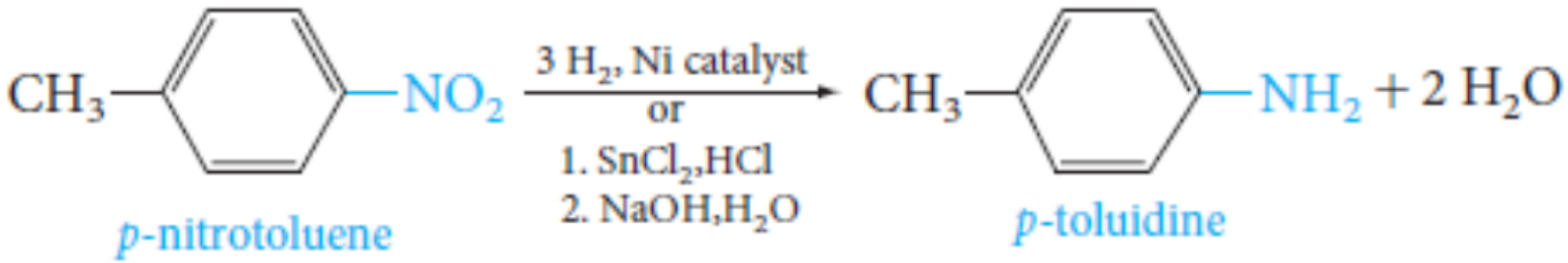
Aromatic amines can often be alkylated selectively



The alkylation can be intramolecular



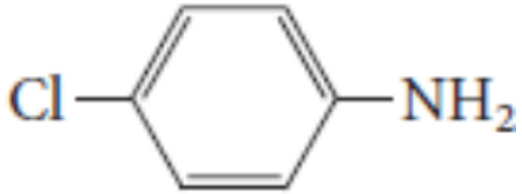
11.5 Preparation of Amines; Reduction of Nitrogen Compounds

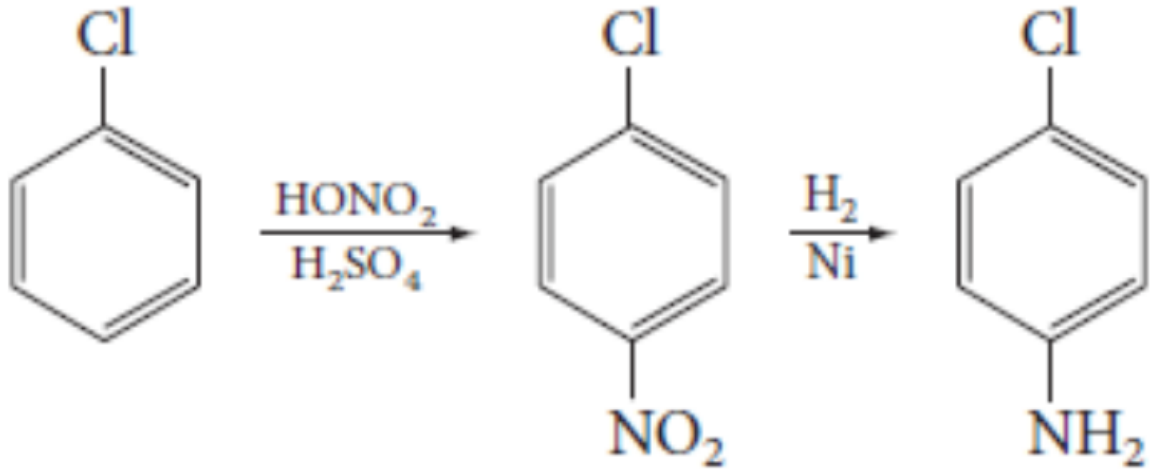


p-nitrotoluene

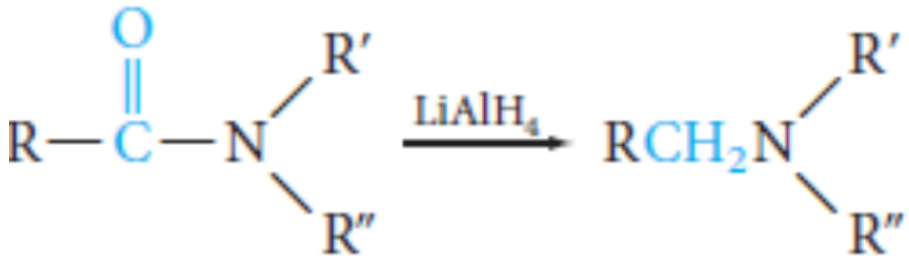
p-toluidine

Devise a synthesis of *p*-chloroaniline, from chlorobenzene

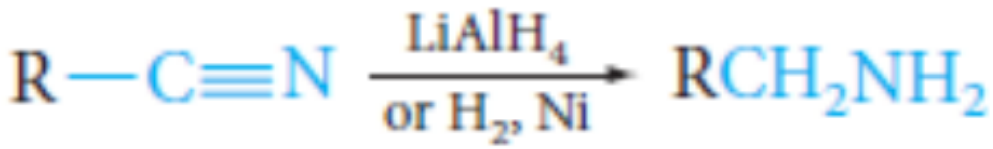




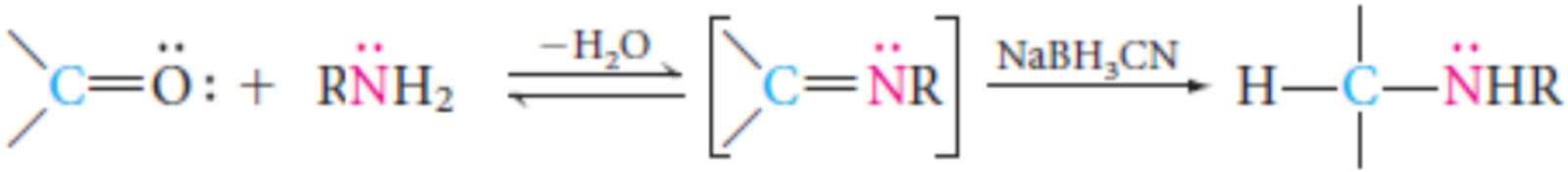
Reduction of amides to amines with lithium aluminum hydride.



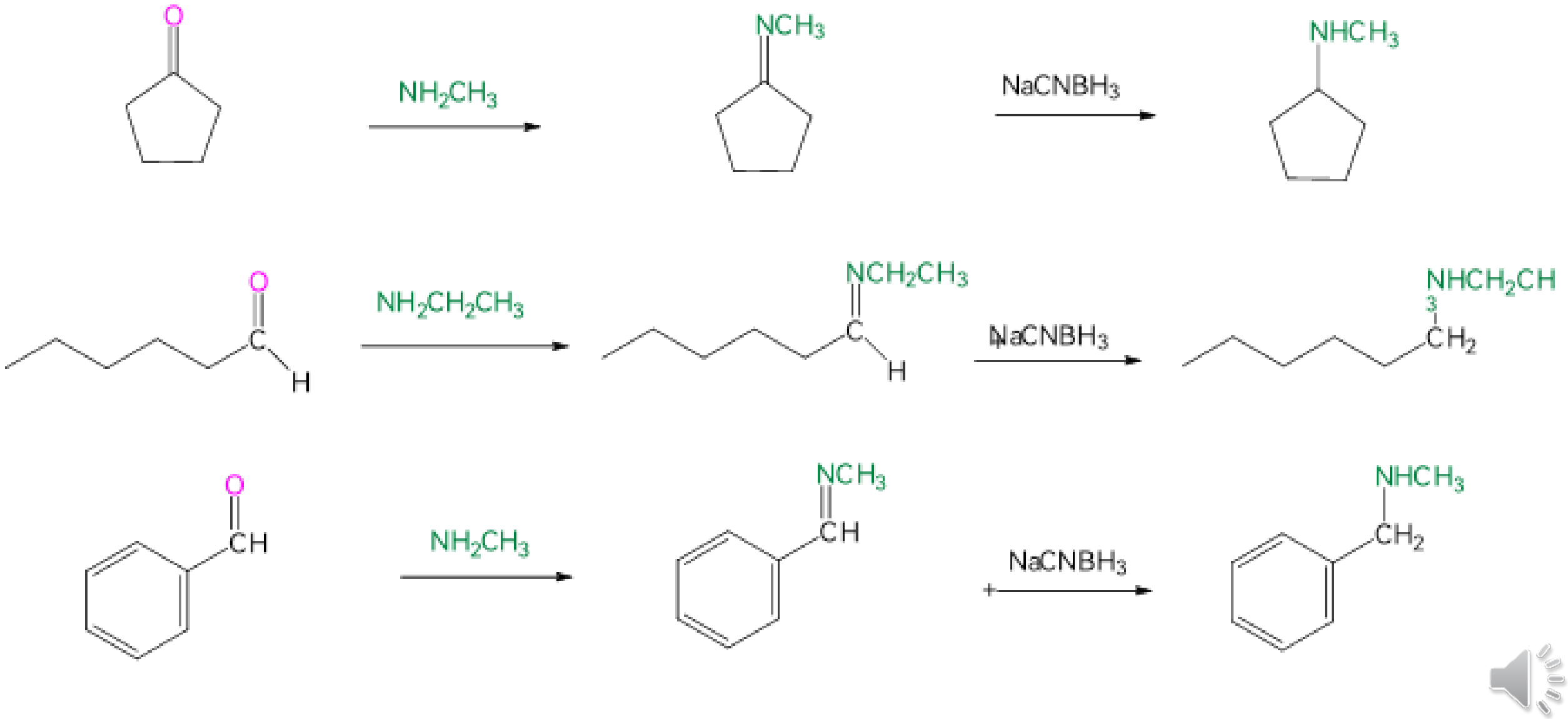
Reduction of nitriles (cyanides) gives **primary amines**



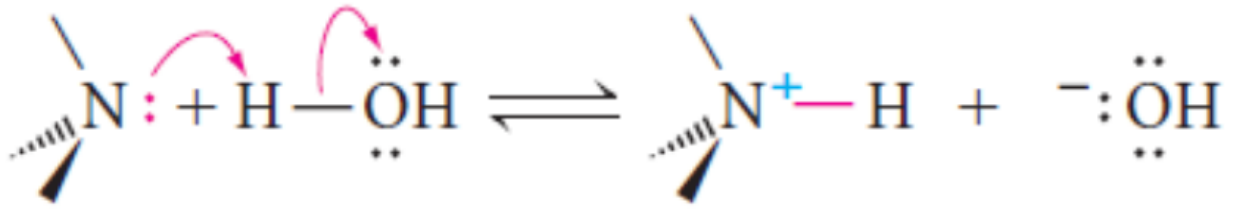
Preparation of Amines from Imines



Reduction of Imines



11.6 The Basicity of Amines

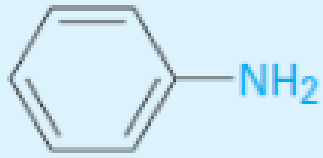


amine — ammonium ion — hydroxide ion

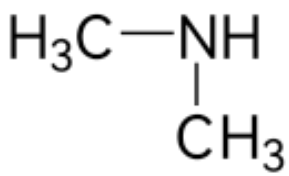
$$RNH_3^+ + H_2O \rightleftharpoons RNH_2 + H_3O^+$$

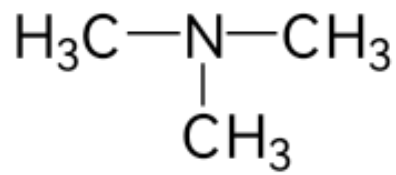
conjugate acid — base

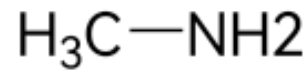
Table 24.1 Basicity of Some Common Amines

Name	Structure	pK_a of ammonium ion
Ammonia	NH_3	9.26
Primary alkylamine		
Methylamine	CH_3NH_2	10.64
Ethylamine	$CH_3CH_2NH_2$	10.75
Secondary alkylamine		
Diethylamine	$(CH_3CH_2)_2NH$	10.98
Pyrrolidine		11.27
Tertiary alkylamine		
Triethylamine	$(CH_3CH_2)_3N$	10.76
Arylamine		
Aniline		4.63

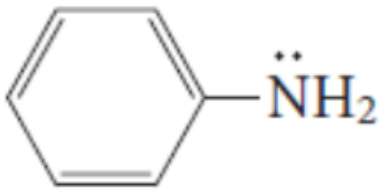
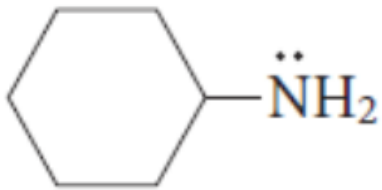
Basicity

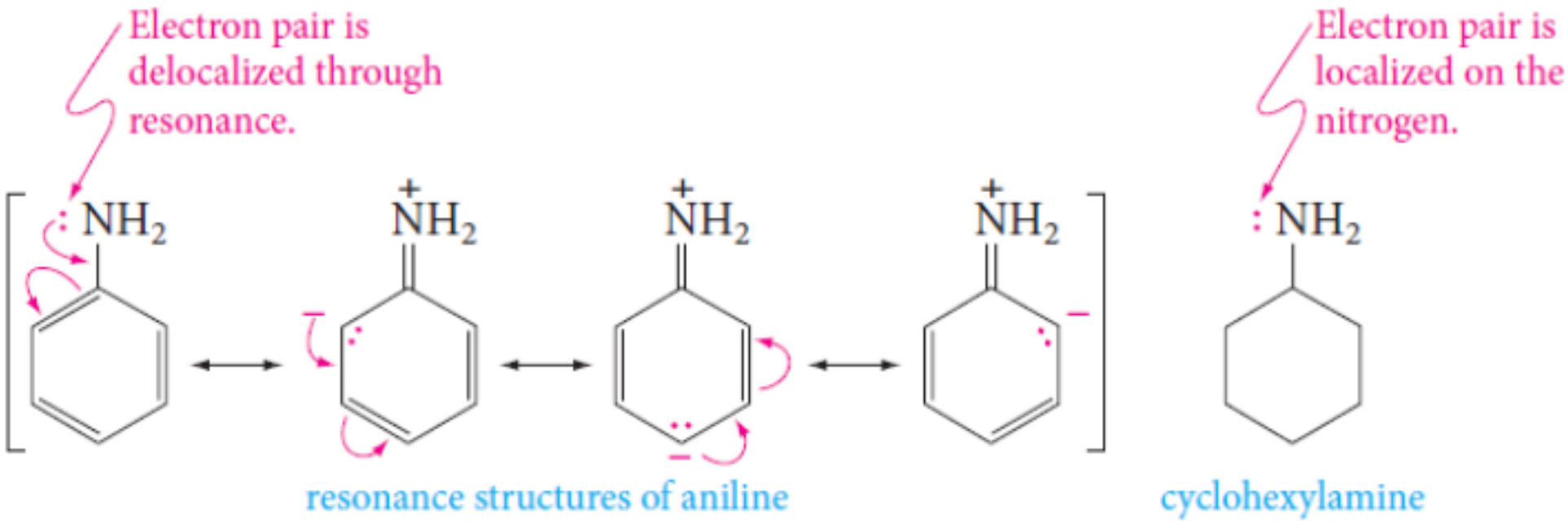


2^{O} > 

3^{O} > 

1^{O}

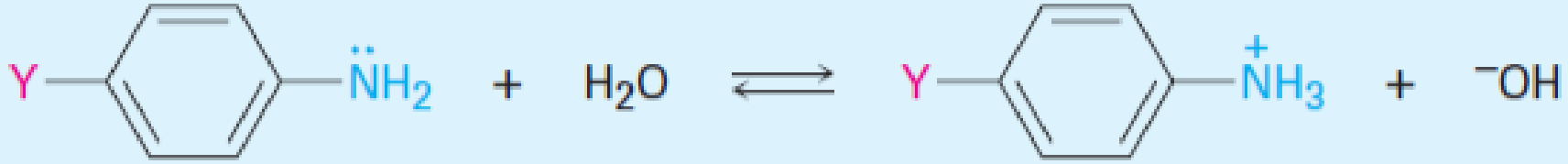
		
	aniline	cyclohexylamine
pK_a of ammonium ion	4.62	9.8



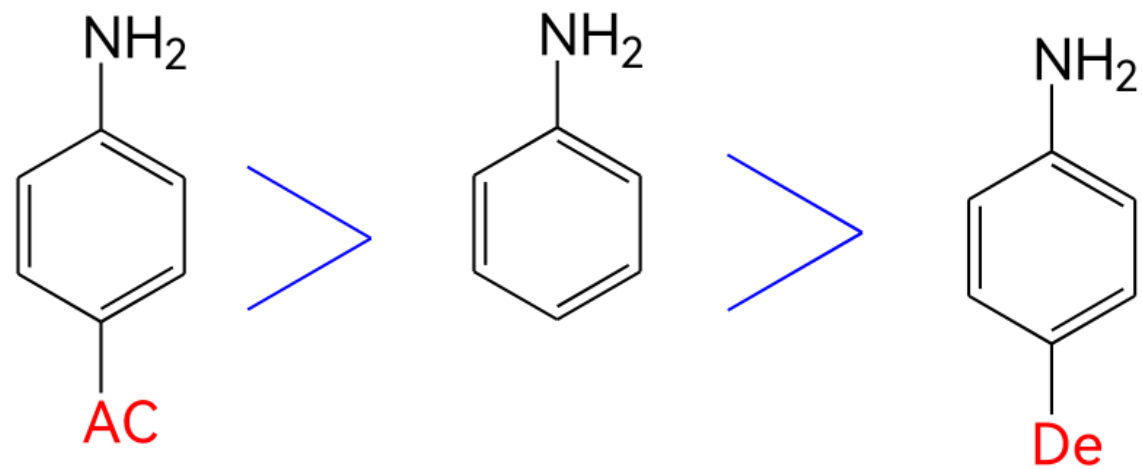
resonance structures of aniline

cyclohexylamine

Table 24.2 Base Strength of Some *p*-Substituted Anilines

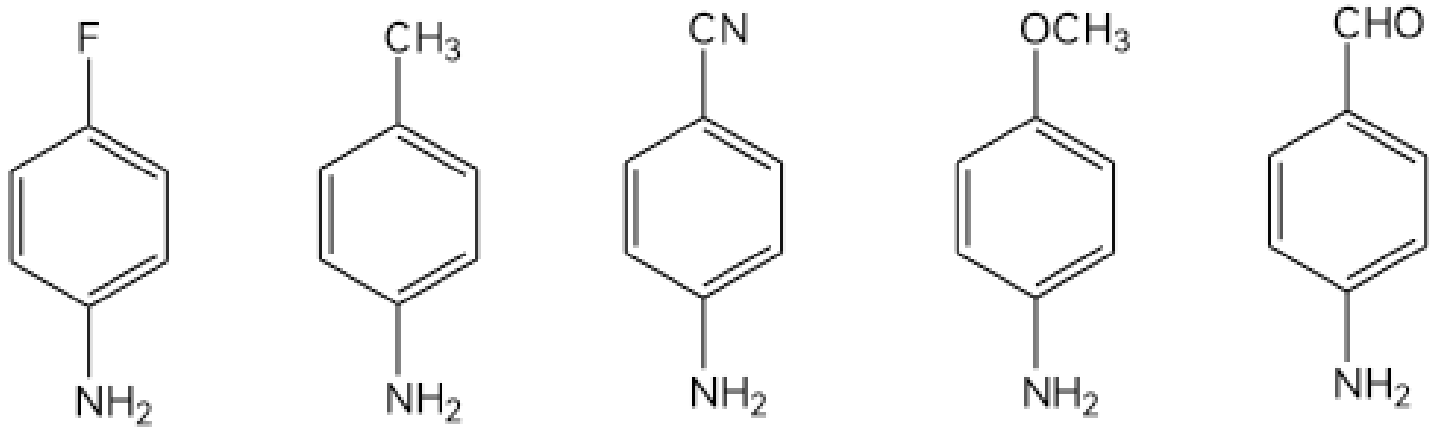


	Substituent, Y	pK_a	
Stronger base			
	–NH_2	6.15	Activating groups
	–OCH_3	5.34	
	–CH_3	5.08	
	–H	4.63	
	–Cl	3.98	Deactivating groups
	–Br	3.86	
	–CN	1.74	
Weaker base	–NO_2	1.00	


NH2
AC
NH2
NH2
De

Basicity of different substituted Amines

Rank the following compounds according to their basicity

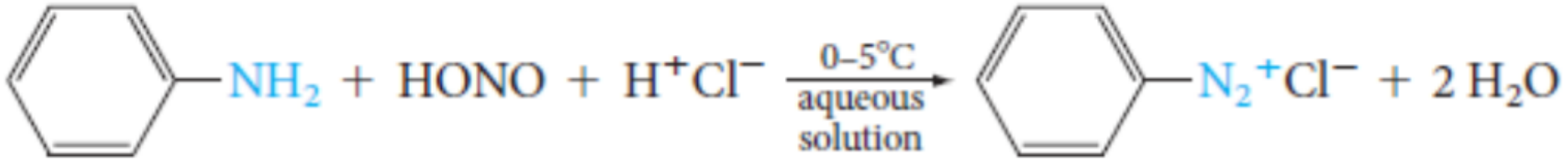


I II III IV V

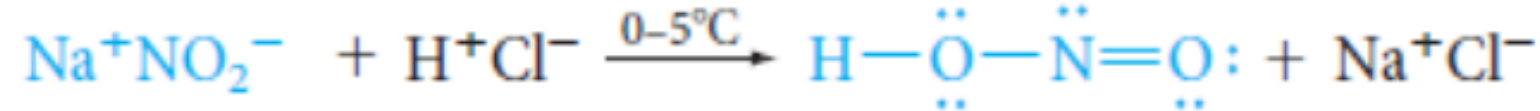
De Ac De Ac De

IV > II > I > V > III

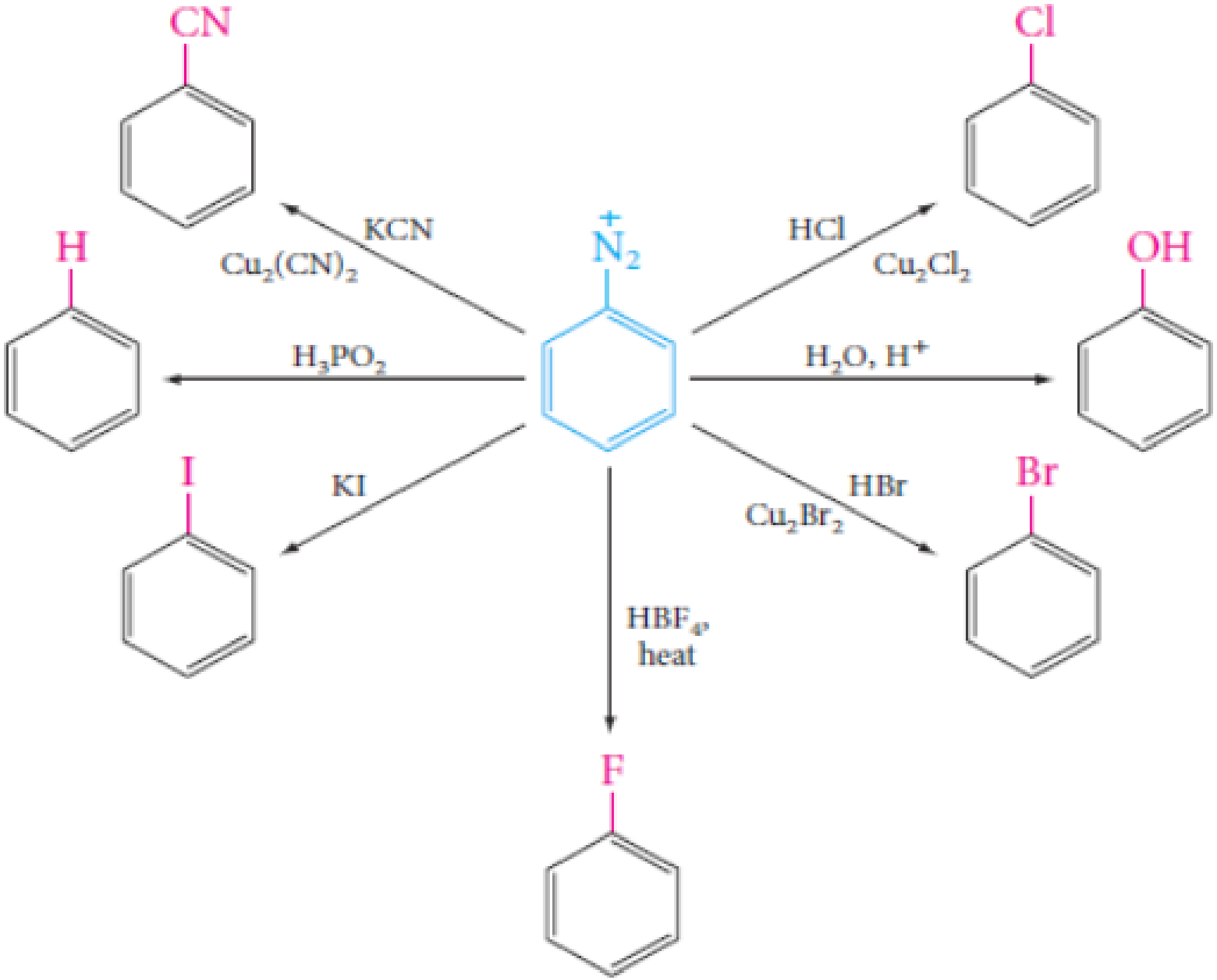
11.12 Aromatic Diazonium Compounds



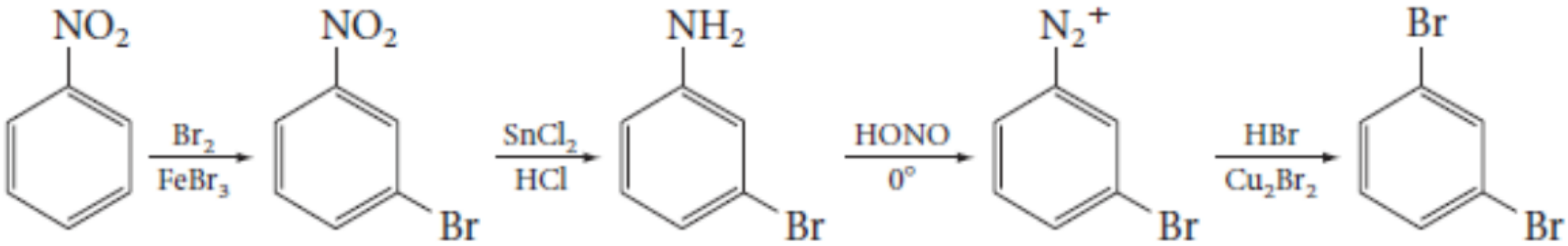
aniline — nitrous acid — benzenediazonium chloride



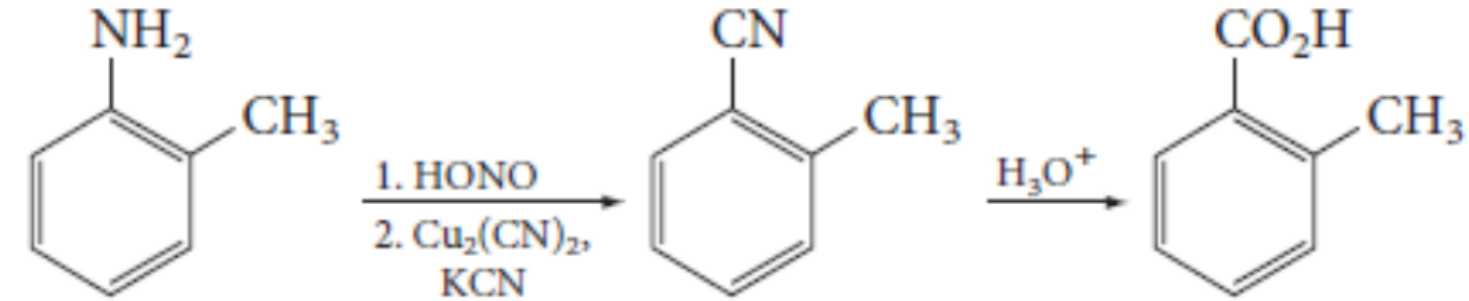
sodium nitrite — nitrous acid


CN
KCN
$Cu_2(CN)_2$
Cl
HCl
Cu_2Cl_2
H
H_3PO_2
N_2^+
OH
H_2O, H^+
I
KI
HBr
Cu_2Br_2
Br
HBF_4,
heat
F

How can *m*-dibromobenzene be prepared



How can [redacted]-toluic ([redacted]-methylbenzoic) acid be prepared from [redacted]-toluidine

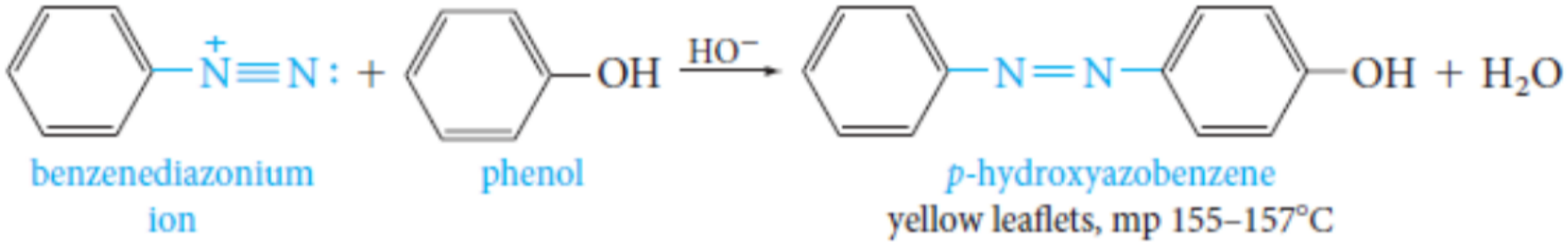


o-toluidine

o-toluic acid

11.13 Diazo Coupling; Azo Dyes

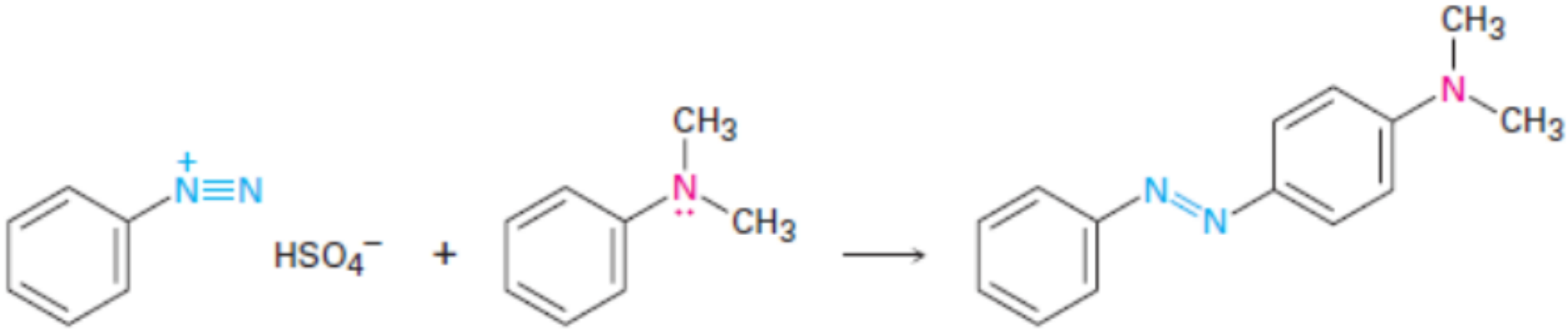
Aryldiazonium ions react with strongly activated aromatic rings (phenols and aromatic amines) to give **azo compounds**



benzenediazonium ion

phenol

p-hydroxyazobenzene
yellow leaflets, mp 155–157°C



Benzenediazonium bisulfate

***N,N*-Dimethylaniline**

***p*-(Dimethylamino)azobenzene**
(yellow crystals, mp 127 °C)

Researchers Inc.

Methyl orange indicator in basic solution (right) and in acidic