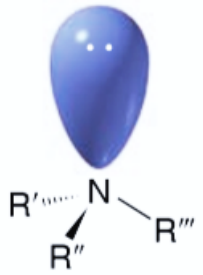
108 Chem

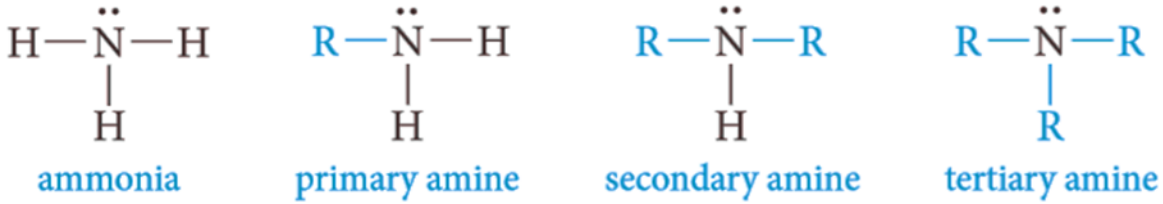
Chapter 8

Amines

Structure and Classification of Amines

- Amines are organic derivatives of ammonia in which one or more hydrogens are replaced with alkyl or aryl groups.
- It has high degree of biological activity, many amines are used as drugs and medicines.
- Amines are classified as primary, secondary, or tertiary, depending on the number of carbon atoms bonded directly to nitrogen.





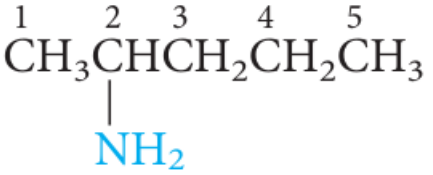
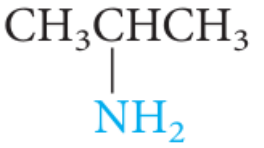
$CH_3CH_2NH_2$
ethylamine
(primary)

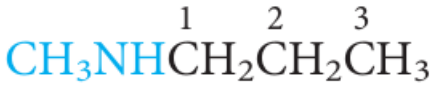
$(CH_3CH_2)_2NH$
diethylamine
(secondary)

$(CH_3CH_2)_3N$
triethylamine
(tertiary)

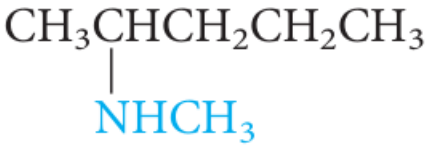
Nomenclature of Amines

- Common names are formed from the names of the alkyl groups bonded to nitrogen, followed by the suffix *-amine*.
- The prefixes *di-*, *tri-*, and *tetra-* are used to describe two, three, or four identical substituents.
- The IUPAC system, the *amino* group, $-NH_2$, is named as a substituent.
- In this system, secondary or tertiary amines are named by using a prefix that includes all but the longest carbon chain.
- Recently, Chemical Abstracts (CA) introduced a system for naming amines that is rational and easy to use. In this system, amines are named as *alkanamines*, the *-e* ending in the alkane name is changed to *-amine*, and a number shows the position of the amino group along the chain.
- Other substituents on the carbon chain are given numbers, and the prefix *N-* is used for each substituent on nitrogen.

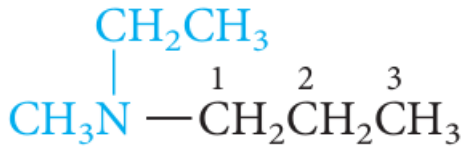
				
IUPAC name:	aminoethane	aminopropane	2-aminopentane	2-aminopropane
	ethanamine	propanamine	2-pentanamine	2-propanamine
Common name:	ethylamine	propylamine	*sec*-butylamine	isopropylamine



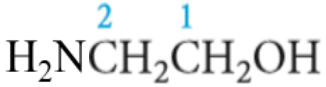
1-(methylamino)propane
N-methyl-1-propanamine
methylpropylamine



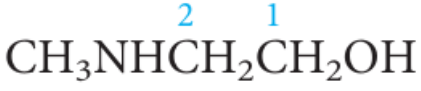
2-(methylamino)pentane
N-methyl-2-pentanamine
methylpentylamine



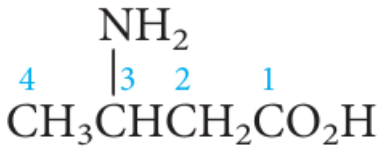
1-(ethylmethylamino)propane
N-ethyl-*N*-methyl-1-propanamine
ethylmethylpropylamine



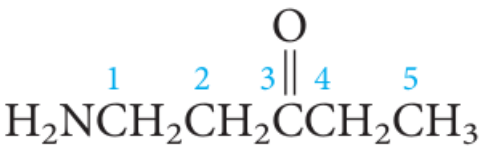
2-aminoethanol



2-methylaminoethanol



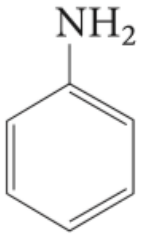
3-aminobutanoic acid



1-amino-3-pentanone

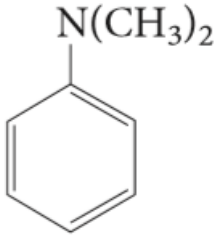
Nomenclature of Amines

- Aromatic amines are named as derivatives of aniline. In the CA system, aniline is called benzenamine.

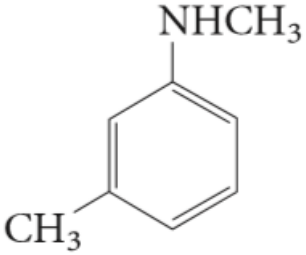


Aniline
benzenamine

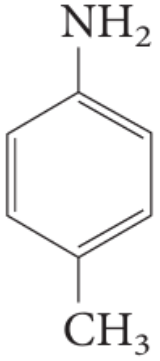
4-bromoaniline
p-bromoaniline



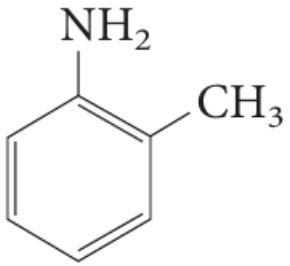
N,*N*-dimethylaniline
N,*N*-dimethylbenzenamine



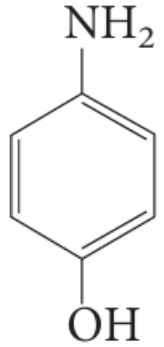
N-methyl-3-methylaniline
N-methyl-*m*-toluidine



4-methylaniline
p-Toluidine



2-methylaniline
o-Toluidine



p-hydroxyaniline
p-aminophenol

Physical Properties of Amines

Solubility

- 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. Thus, most simple amines with up to five or six carbon atoms are either completely or appreciably soluble in water.

Boiling point

- Amines are moderately polar substances; they boil well above alkanes with comparable molecular weights, but below comparable alcohols.
- 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. The reason for this is that nitrogen is not as electronegative as oxygen.
- Molecules of tertiary amines cannot form hydrogen bonds to each other, as a result, tertiary amines generally boil at lower temperatures than primary and secondary amines of comparable molecular weight.

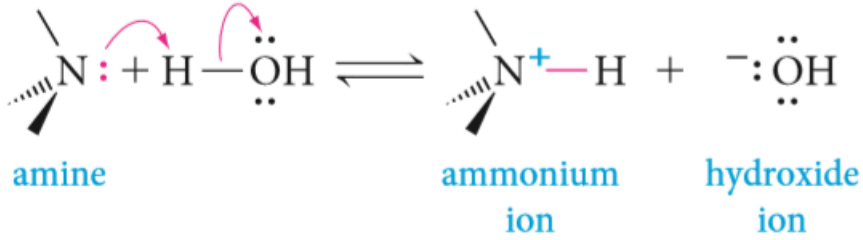
$CH_3CH_2CH_3$	$CH_3CH_2NH_2$	CH_3CH_2OH
Propane	Ethylamine	Ethanol
bp −42°C	bp 17°C	bp 78°C

$CH_3CH_2CH_2NH_2$	$CH_3CH_2NHCH_3$	$(CH_3)_3N$
Propylamine (a primary amine)	*N*-Methylethylamine (a secondary amine)	Trimethylamine (a tertiary amine)
bp 50°C	bp 34°C	bp 3°C

Physical Properties of Amines

Basicity of Amines: Amine Salts

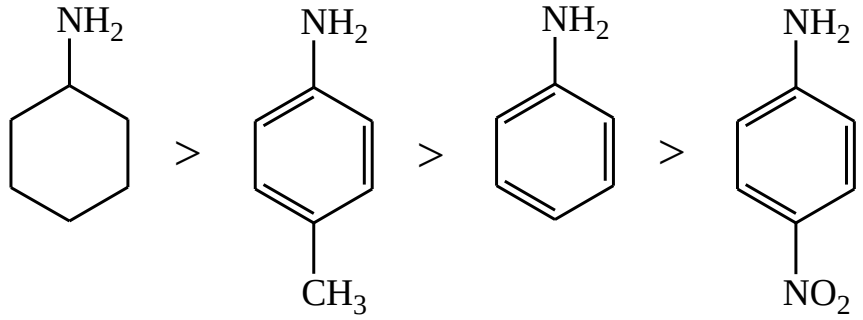
- The unshared pair of electrons on the nitrogen atom dominates the chemistry of amines. Because of this electron pair, amines are both basic and nucleophilic. Aqueous solutions of amines are basic because of the following equilibrium:



- Amines are relatively weak bases. Most are stronger bases than water but are far weaker bases than hydroxide ions.
- Alkylamines are approximately 10 times as basic as ammonia. Recall that alkyl groups are electron-donating relative to hydrogen.

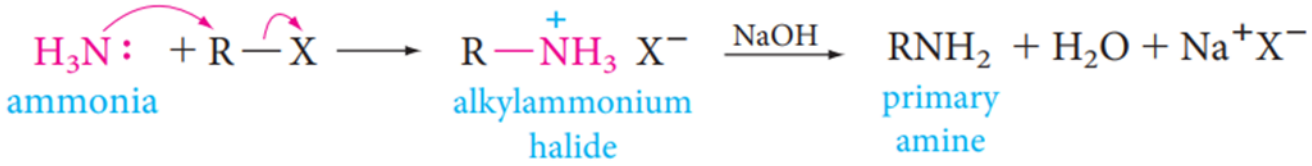
$$CH_3\text{-}NH\text{-}CH_3 > NH_2\text{-}CH_3 > NH_3$$

- Aromatic amines less basic than aliphatic amines.
- Electron-donating groups increase the basicity of amines, and electron-withdrawing groups decrease their basicity.

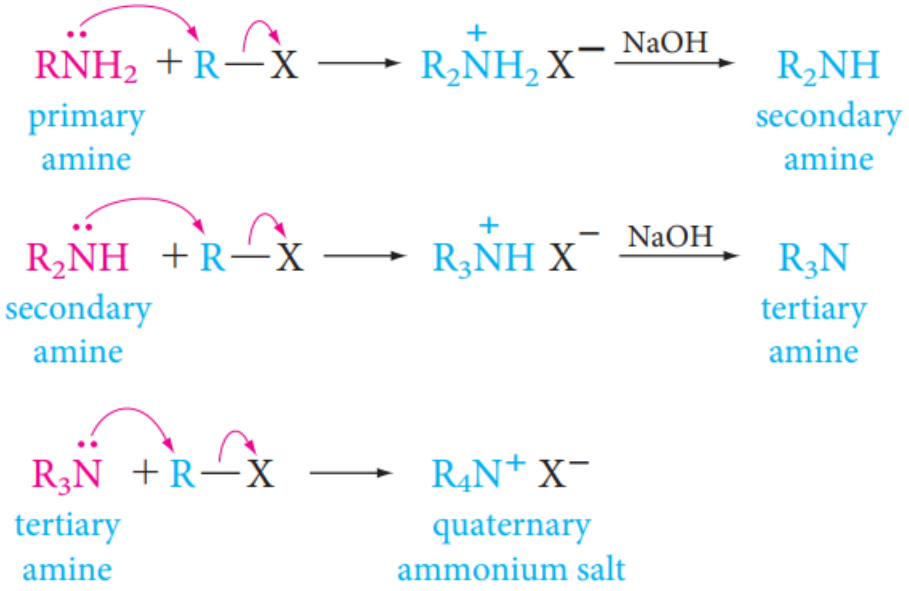


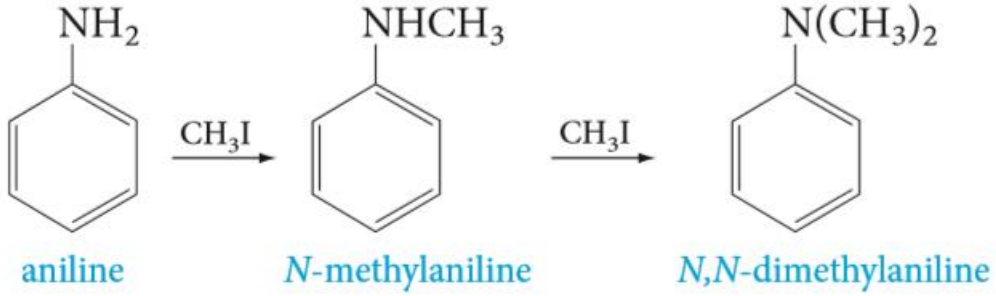
Preparation of Amines

1- Alkylation of Ammonia and amines : Nucleophilic Substitution Reaction (S_N2)



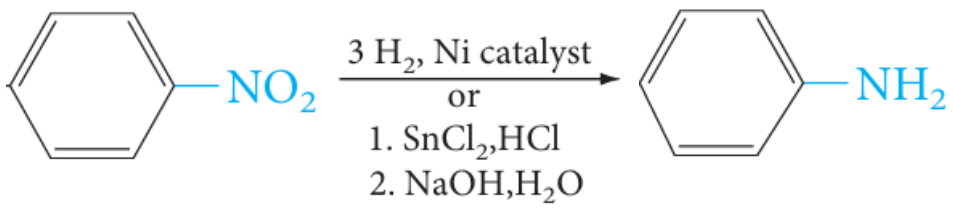
Primary, secondary, and tertiary amines can be similarly alkylated.

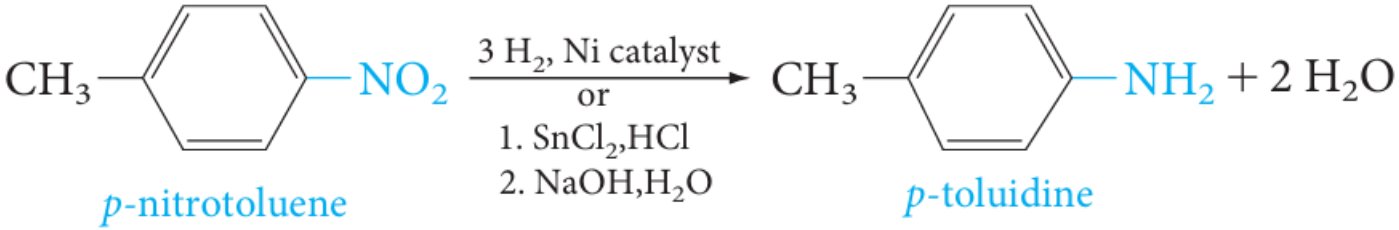




Preparation of Amines

2- Reduction of nitro compounds

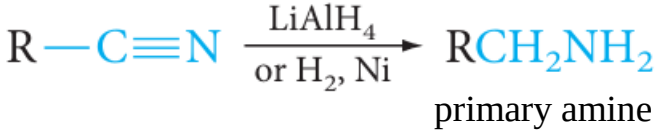




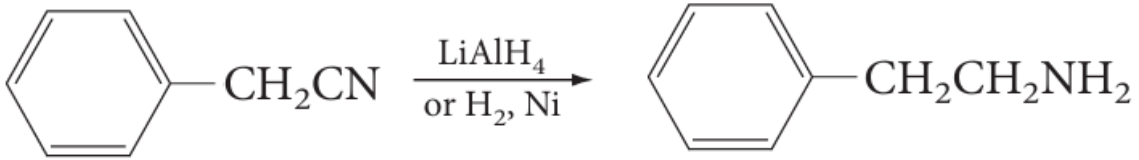
p-nitrotoluene

p-toluidine

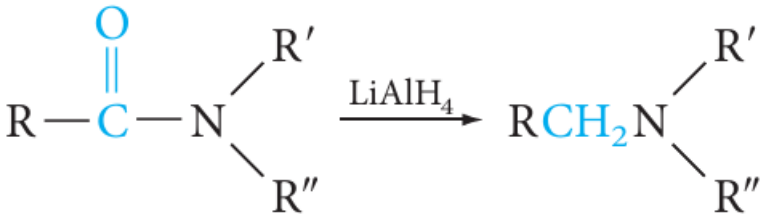
3- Reduction of Nitriles

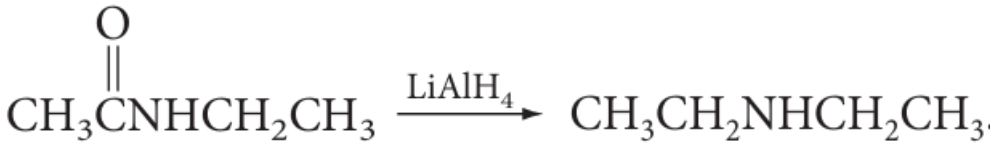


primary amine



4- Reduction of Amides

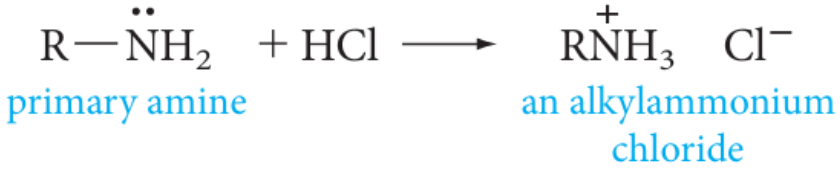


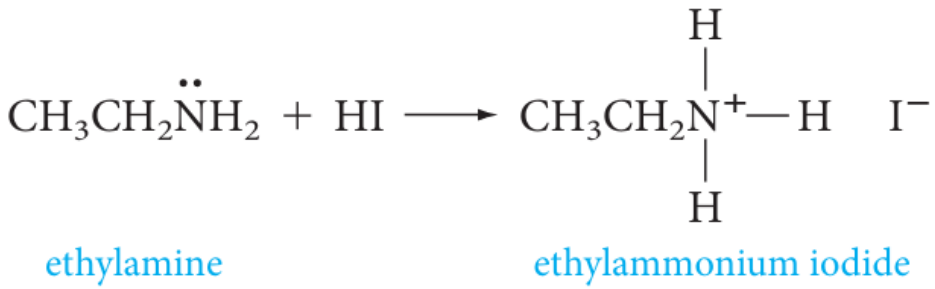


Reactions of Amines

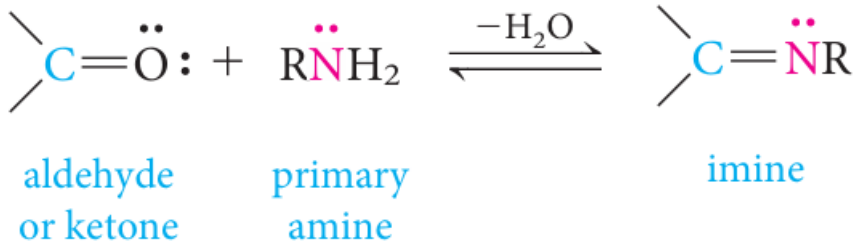
1- Reaction of Amines with Strong Acids; Amine Salts

Amines react with strong acids to form alkylammonium salts



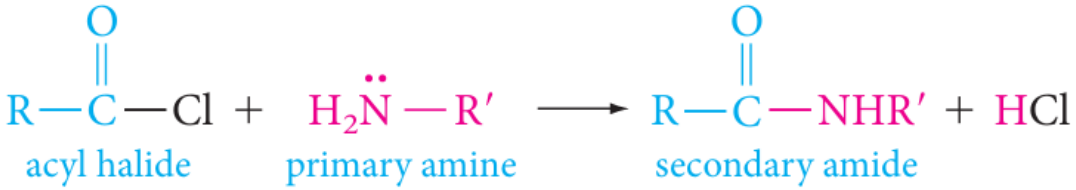


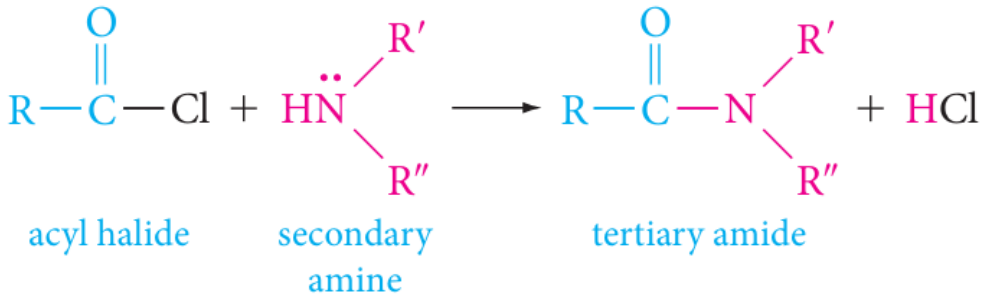
2- Imines Formation

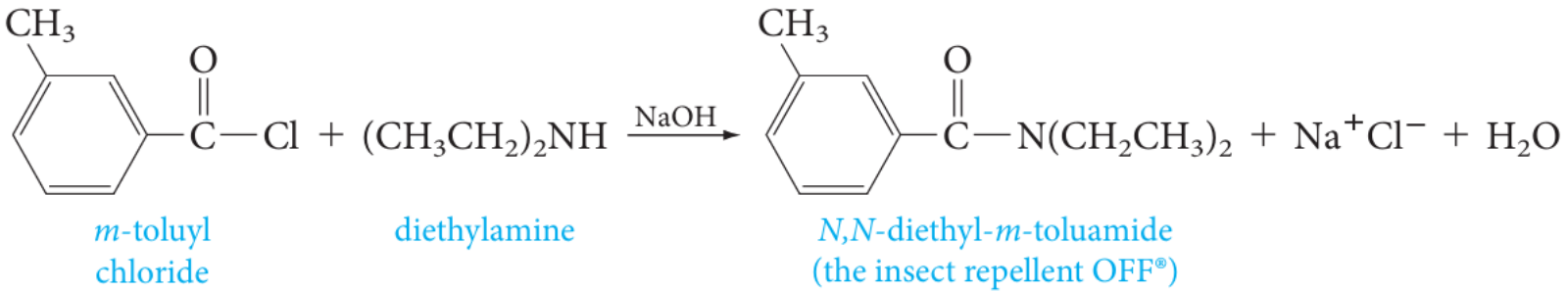


Reactions of Amines

3- Acylation of Amines : Amide formation







Reactions of Amines

4- Syntheses Using Diazonium Salts