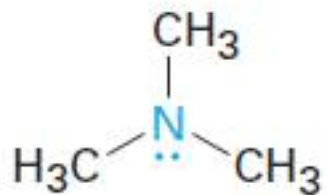


Organic Chemistry

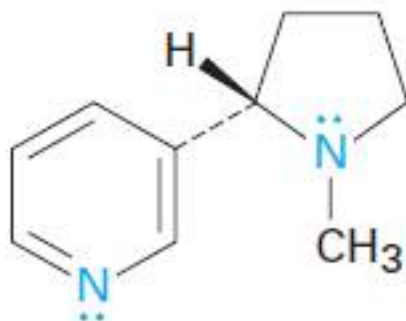
Amines

Amines are organic derivatives of ammonia in the same way that alcohols and ethers are organic derivatives of water. Like ammonia, amines contain a nitrogen atom with a lone pair of electrons, making amines both basic and nucleophilic. Most of the chemistry of amines depends on the presence of this lone pair of electrons.

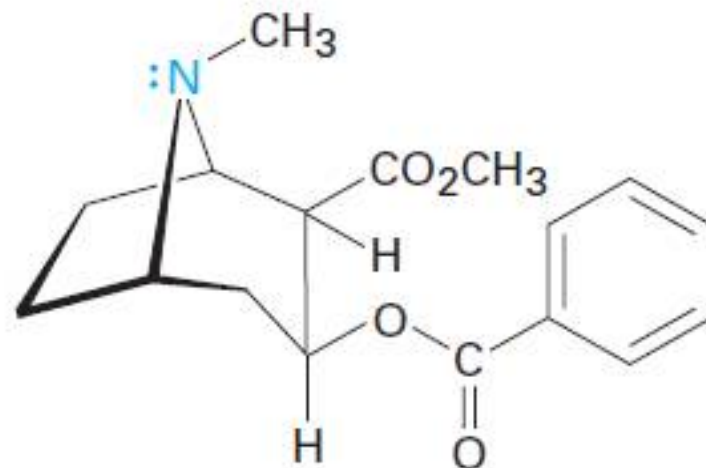
Amines occur widely in all living organisms. Trimethylamine, for instance, occurs in animal tissues and is partially responsible for the distinctive odor of fish; nicotine is found in tobacco; and cocaine is a stimulant found in the leaves of the South American coca bush. In addition, amino acids are the building blocks from which all proteins are made, and cyclic amine bases are constituents of nucleic acids.



Trimethylamine



Nicotine

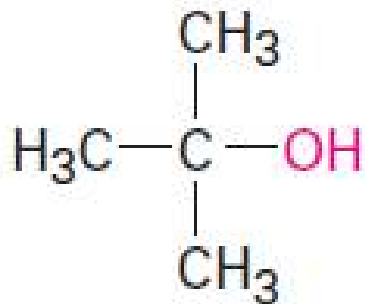


Cocaine

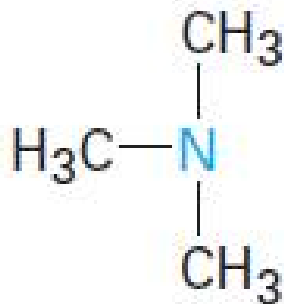
Naming Amines

Amines can be either alkyl-substituted (alkylamines) or aryl-substituted (arylamines). Although much of the chemistry of the two classes is similar, there are also substantial differences. Amines are classified as primary (RNH_2), secondary (R_2NH), or tertiary (R_3N), depending on the number of organic substituents attached to nitrogen. Thus, methylamine (CH_3NH_2) is a primary amine

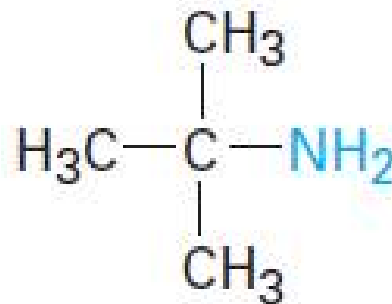
dimethylamine $[(\text{CH}_3)_2\text{NH}]$ is a secondary amine, and trimethylamine $[(\text{CH}_3)_3\text{N}]$ is a tertiary amine. Note that this usage of the terms *primary*, *secondary*, and *tertiary* is different from our previous usage.



***tert*-Butyl alcohol**
(a tertiary alcohol)

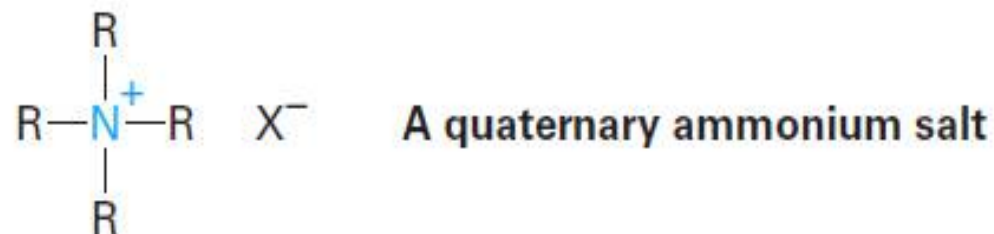


Trimethylamine
(a tertiary amine)

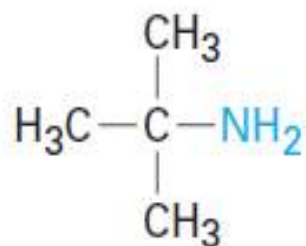


***tert*-Butylamine**
(a primary amine)

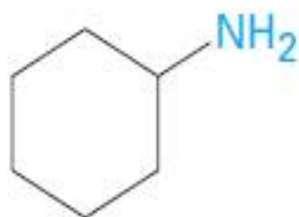
Compounds containing a nitrogen atom with four attached groups also exist, but the nitrogen atom must carry a formal positive charge. Such compounds are called quaternary ammonium salts.



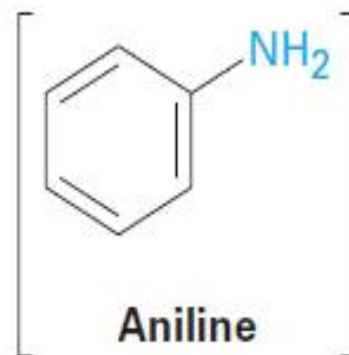
Primary amines are named in the IUPAC system in several ways. For simple amines, the suffix *-amine* is added to the name of the alkyl substituent. You might also recall from Chapter 15 that phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, has the common name *aniline*.



tert-Butylamine

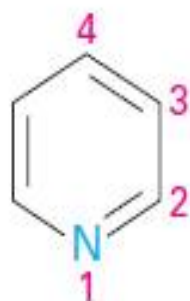


Cyclohexylamine

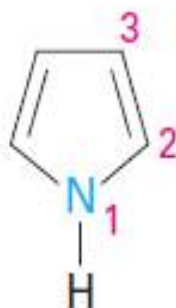


Aniline

Heterocyclic amines—compounds in which the nitrogen atom occurs as part of a ring—are also common, and each different heterocyclic ring system has its own parent name. The heterocyclic nitrogen atom is always numbered as position 1.



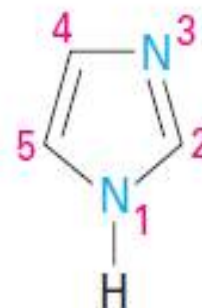
Pyridine



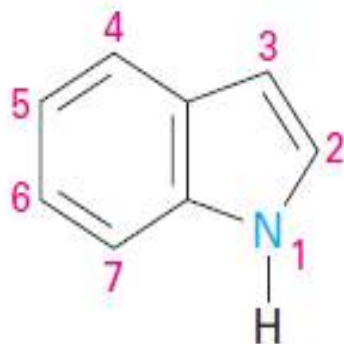
Pyrrole



Quinoline



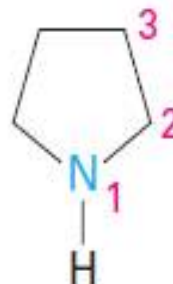
Imidazole



Indole



Pyrimidine



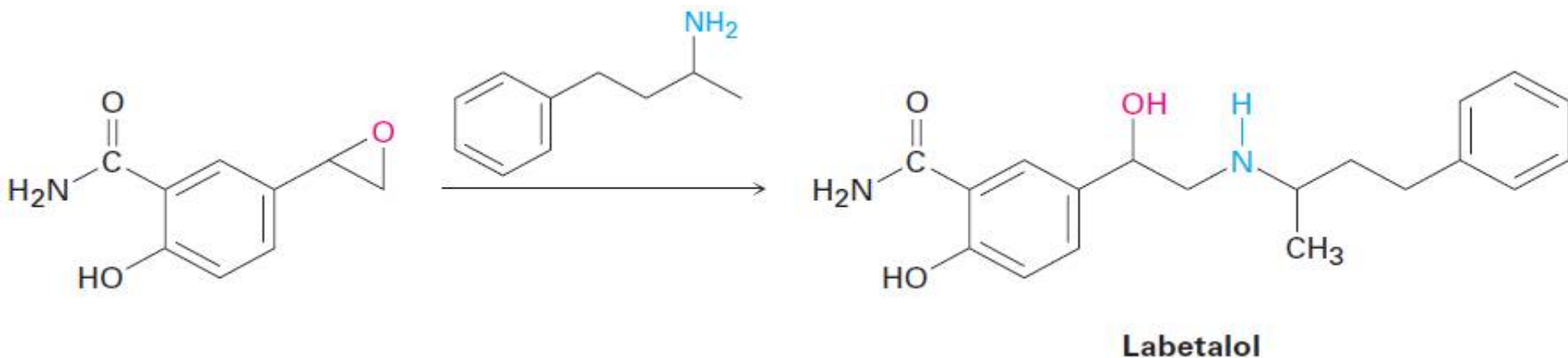
Pyrrolidine



Piperidine

Properties of Amines

Alkylamines have a variety of applications in the chemical industry as starting materials for the preparation of insecticides and pharmaceuticals. Labetalol, for instance, a so-called *b*-blocker used for the treatment of high blood pressure.

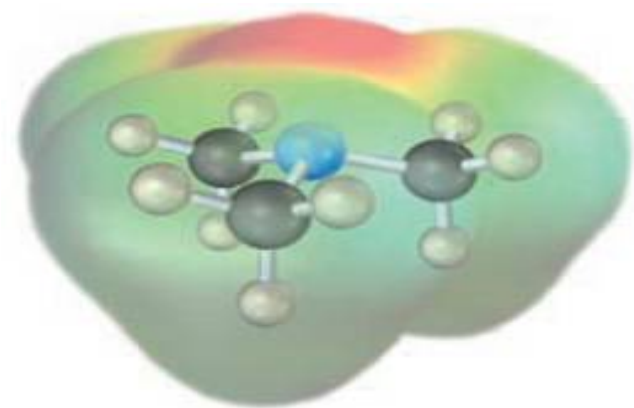


Like alcohols, amines with fewer than five carbon atoms are generally water soluble. Also like alcohols, primary and secondary amines form hydrogen bonds and are highly associated. As a result, amines have higher boiling points than alkanes of similar molecular weight. Diethylamine (MW 73) boils at 56.3 °C, for instance, while pentane (MW 72) boils at 36.1 °C.

One other characteristic of amines is their odor. Low-molecular-weight amines such as trimethylamine have a distinctive fishlike aroma, while diamines such as cadaverine (1,5-pentanediamine) and putrescine (1,4-butanediamine) have the appalling odors you might expect from their common names. Both these diamines arise from the composition of proteins.

Basicity of Amines

The chemistry of amines is dominated by the lone pair of electrons on nitrogen, which makes amines both basic and nucleophilic. They react with acids to form acid–base salts, and they react with electrophiles in many of the polar reactions. Note in the following electrostatic potential map of trimethylamine how the negative (red) region corresponds to the lone pair of electrons on nitrogen.



It's often possible to take advantage of their basicity to purify amines. For example, if a mixture of a basic amine and a neutral compound such as a ketone or alcohol is dissolved in an organic solvent and aqueous acid is added, the basic amine dissolves in the water layer as its protonated salt, while the neutral compound remains in the organic solvent layer. Separation of the water layer and neutralization of the ammonium ion by addition of NaOH then provides the pure amine (**Figure 24.2**).

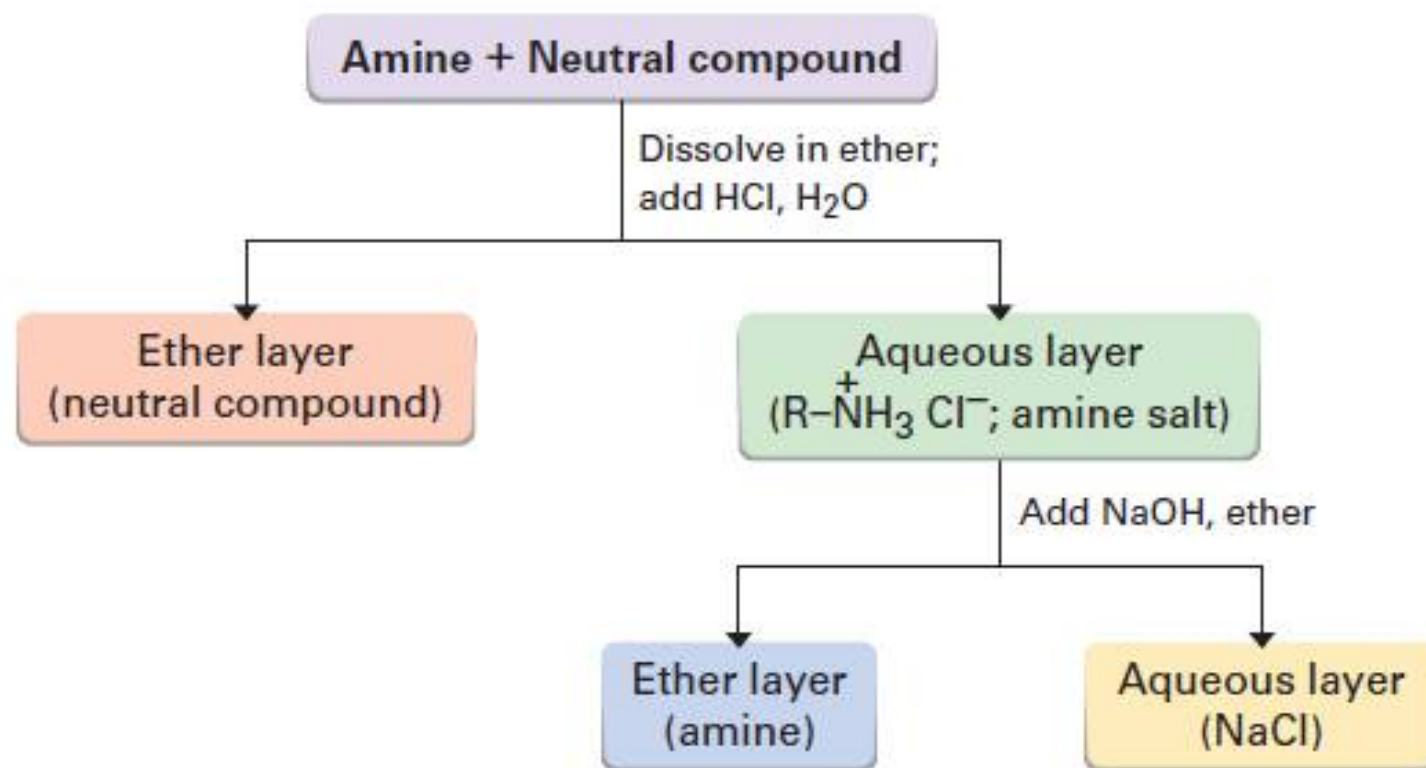


Figure 24.2 Separation and purification of an amine component from a mixture by extraction of its ammonium salt into water.