Amines

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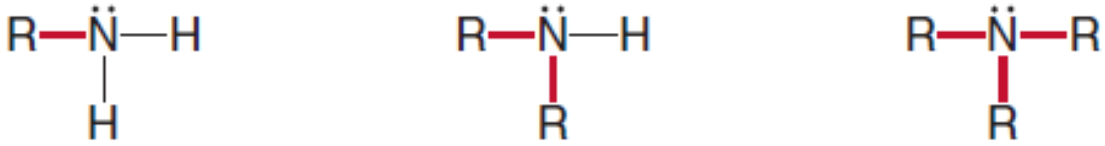
Lecture 14

4. Amines

- **Amines are organic nitrogen compounds**, formed by replacing one or more hydrogen atoms of ammonia (NH_3) with alkyl groups.

Amines are classified as 1°, 2°, or 3° by the number of alkyl groups bonded to the nitrogen atom.



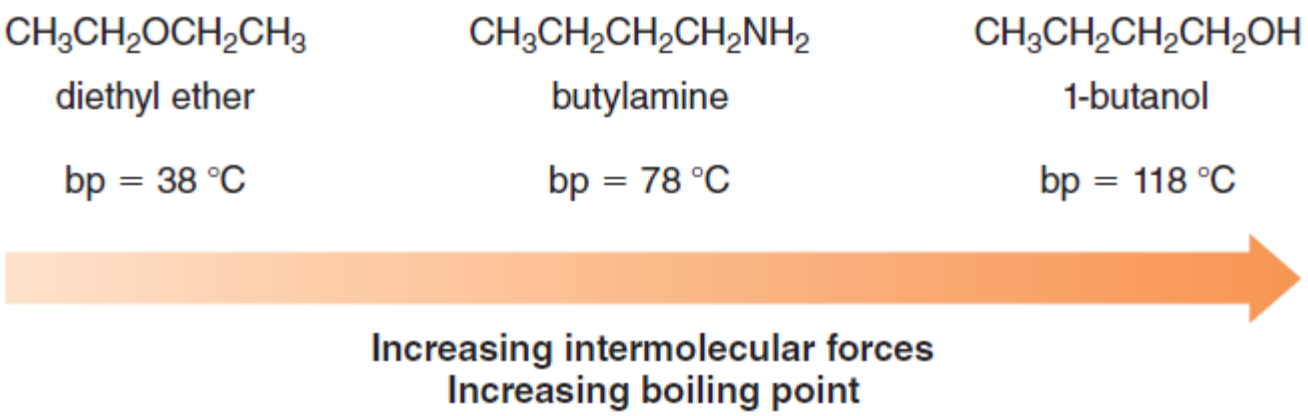
1° amine 2° amine 3° amine

- A **primary (1°) amine** has one C—N bond and the general structure RNH_2.
- A **secondary (2°) amine** has two C—N bonds and the general structure R_2NH.
- A **tertiary (3°) amine** has three C—N bonds and the general structure R_3N.

Like ammonia, the amine nitrogen atom has a lone pair of electrons, which is generally omitted in condensed structures. An amine nitrogen atom is surrounded by three atoms and one non bonded electron pair, making it **trigonal pyramidal in shape**, with bond angles of approximately 109.5°.

4.1. Physical Properties of Amines

1. Many low molecular weight amines have very foul odors.
2. **Cadaverine** ($NH_2CH_2CH_2CH_2CH_2CH_2NH_2$) is a poisonous **diamine** with a putrid odor present in rotting fish, and partly responsible for the odor of semen, urine, and bad breath.
3. **Primary (1°)** and **(2°) amines** are also capable of intermolecular hydrogen bonding, because they contain N-H bonds.
4. **Nitrogen is less electronegative than oxygen**, however, intermolecular hydrogen bonds between N and H are weaker than those between O and H.
5. **Tertiary (3°) amines** have **lower boiling points** than **1° and 2° amines** of comparable size, because they have no N—H bonds.



PROBLEM

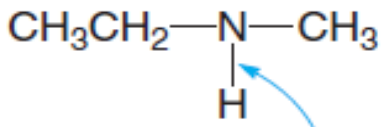
Which compound in each pair has the higher boiling point: (a) $CH_3CH_2NHCH_3$ or $CH_3CH_2OCH_3$; (b) $(CH_3)_3N$ or $CH_3CH_2CH_2NH_2$?

Analysis

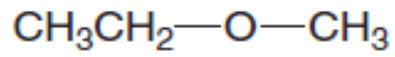
Keep in mind the general rule: For compounds of comparable size, **the stronger the intermolecular forces, the higher the boiling point.** Compounds that can hydrogen bond have higher boiling points than compounds that are polar but cannot hydrogen bond. Polar compounds have higher boiling points than nonpolar compounds.

Solution

a. The 2° amine ($CH_3CH_2NHCH_3$) has an N—H bond, so intermolecular hydrogen bonding is possible. The ether ($CH_3CH_2OCH_3$) has only C—H bonds, so there is no possibility of intermolecular hydrogen bonding. $CH_3CH_2NHCH_3$ has a higher boiling point because it has stronger intermolecular forces.



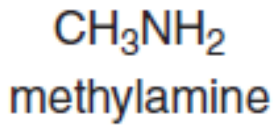
a 2° amine with an N—H bond
intermolecular hydrogen bonding
higher boiling point



an ether with only C—H bonds

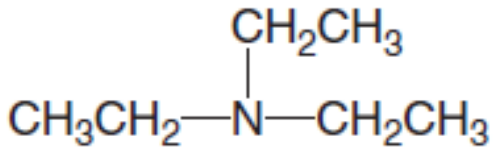
4.2. Nomenclature of Amines

- To name a primary (1°) amine, name the **alkyl group bonded to the nitrogen atom** and add the suffix ***-amine***, forming a single word. For 2° and 3° amines with different alkyl groups, alphabetize the names of the alkyl groups. **Secondary (2°) and 3° amines** having identical alkyl groups are named by using the prefix **di-** or **tri-** with the name of the primary amine.

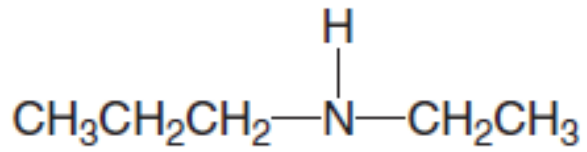


CH_3NH_2

methylamine



triethylamine

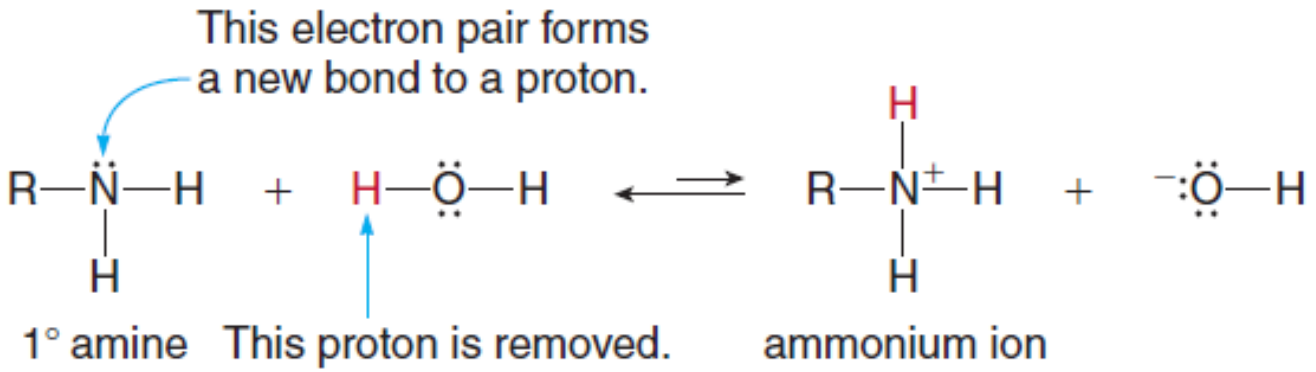


ethylpropylamine

4.3. Reactions of Amines

4.3A. Reaction with water:

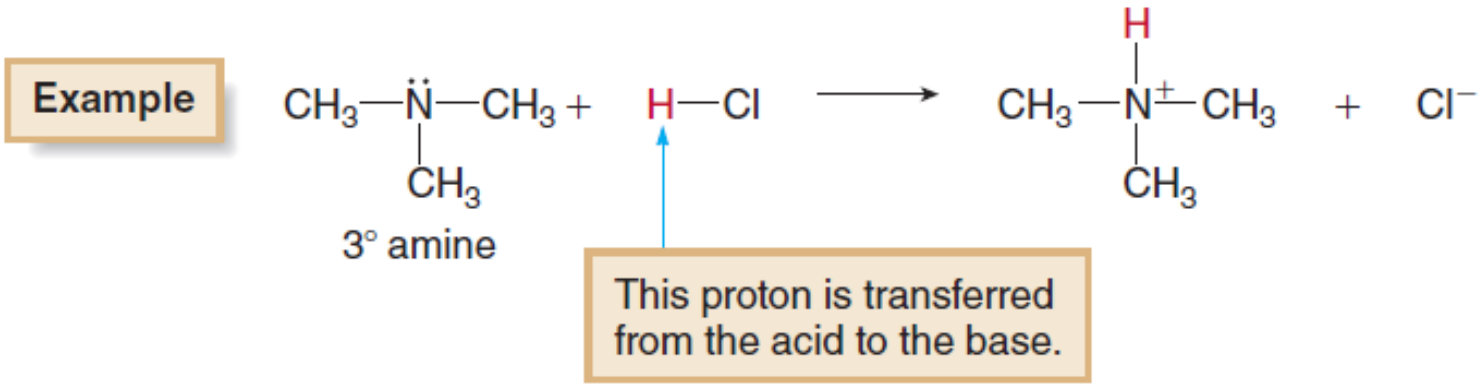
- **Amines are bases; that is, they are proton acceptors.**
- When an amine is dissolved in water, an **acid–base reaction occurs**: **the amine accepts a proton** from H_2O, forming its **conjugate acid**, an **ammonium ion**, and **water loses a proton**, forming hydroxide, $^-$**OH**.



This acid–base reaction occurs with 1°, 2°, and 3° amines. While amines are more basic than other families of organic compounds, they are weak bases compared to inorganic bases like NaOH.

4.3B. Reaction with Bases:

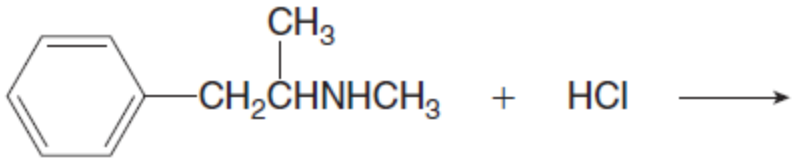
- **Amines** also react with **acids** such as HCl to form **water-soluble salts**. The lone pair of electrons from the amine nitrogen atom is always used to form a new bond to a proton from the acid.



- ✓ The amine [$(CH_3)_3N$] gains a proton to form its conjugate acid, an ammonium cation [$(CH_3)_3NH^+$].
- ✓ A proton is removed from the acid (HCl) to form its conjugate base, the chloride anion (Cl^-).
- ✓ In an **acid–base reaction of an amine**, the amine nitrogen **always forms a new bond** to a proton forming an **ammonium ion**.

PROBLEM

What products are formed when methamphetamine reacts with HCl?



methamphetamine

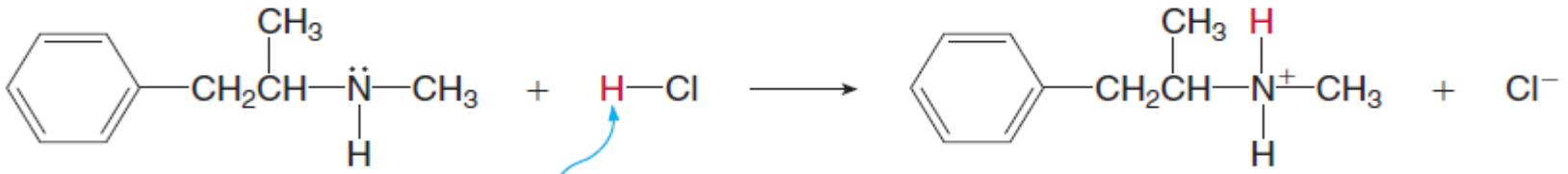
Analysis

In any acid–base reaction with an amine:

- Locate the N atom of the amine and add a proton to it.
- Remove a proton from the acid (HCl) and form its conjugate base (Cl^-).

Solution

Transfer a proton from the acid to the base. Use the lone pair on the N atom to form the new bond to the proton of the acid.



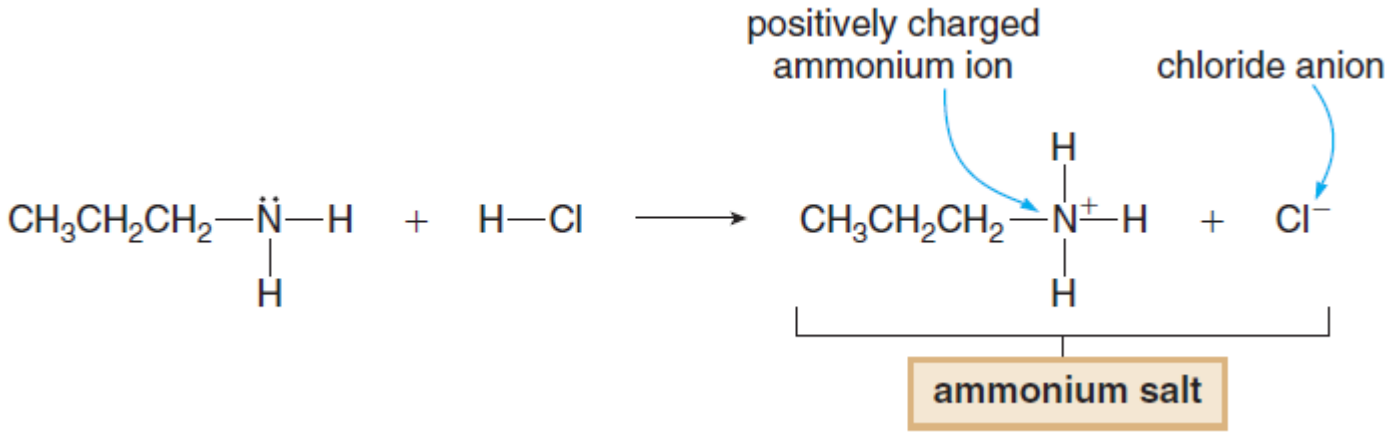
methamphetamine

This proton is transferred from the acid to the amine base.

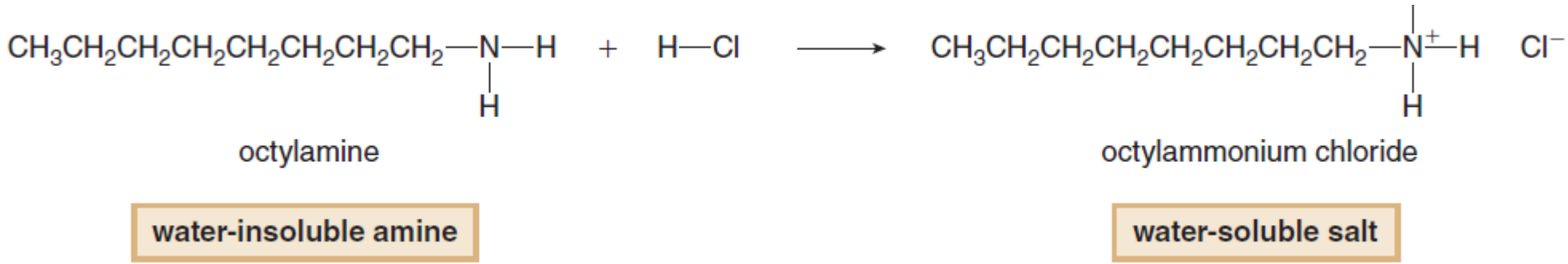
Thus, HCl loses a proton to form Cl^-, and the N atom of methamphetamine gains a proton to form an ammonium cation.

4.3C. Ammonium Salts:

- When an **amine reacts with an acid**, the product is an **ammonium salt**: the amine forms a positively charged ammonium ion and the acid forms an anion.



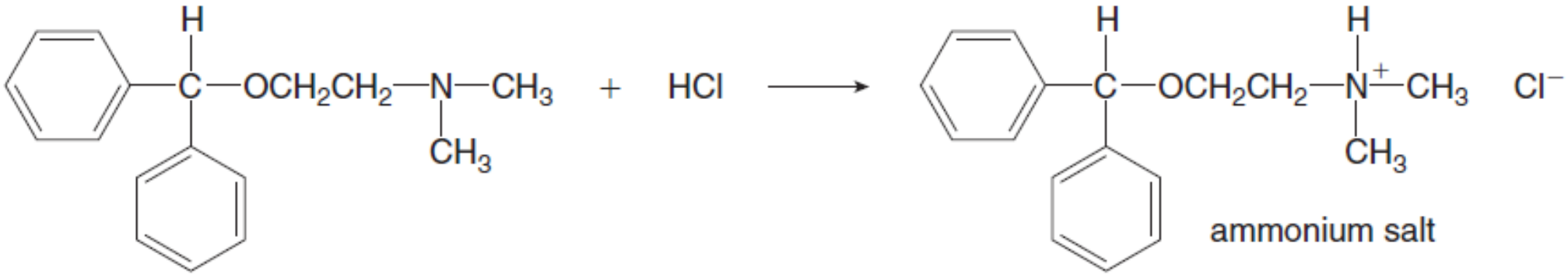
- ✓ Ammonium salts are ionic compounds.
- ✓ Ammonium salts are water-soluble solids.
- ✓ **The solubility properties of an amine can be changed by treatment with acid.**



4.4. Ammonium Salts as Useful Drugs

(FOCUS ON HEALTH & MEDICINE)

- Many amines with useful medicinal properties are sold as their ammonium salts.
- Since the ammonium salts are more water soluble than the parent amine, **they are easily transported through the body in the aqueous medium of the blood.**
- For example, **diphenhydramine** is **a 3° amine** that is sold as its ammonium salt under the name of **Benadryl**.
- **Benadryl**, formed by treating diphenhydramine with HCl, is an over-the-counter **antihistamine** that is used to relieve the **itch and irritation of skin rashes and hives**.



diphenhydramine

Benadryl

End