#### Chapter 24 - Amines and Heterocycles

#### Chapter Outline

- Facts about amines (Section 24.1-24.5).
  - A. Naming amines (Section 24.1).
    - Amines are classified as primary (RNH<sub>2</sub>), secondary (R<sub>2</sub>NH), tertiary (R<sub>2</sub>N) or quaternary ammonium salts (R<sub>4</sub>N<sup>+</sup>).
    - 2. Primary amines are named in several ways:
      - For simple amines, the suffix -amine is added to the name of the alkyl substituent.
      - The suffix, -arraine can replace the final -e of the parent compound.
      - For more complicated amines, the -NH<sub>2</sub> group is an amino substituent on the parent molecule.
    - Secondary and tertiary amines:
      - Symmetrical amines are named by using the prefixes all- and tri- before the name of the alkyl group.
      - b. Unsymmetrical arrines are named as N-substituted primary arrines.
        - i. The largest group is the parent,
    - The simplest arylamine is aniline.
    - Heterocyclic amines (nitrogen is part of a ring) have specific parent names.
       The nitrogens receive the lowest possible numbers.
  - B. Structure and properties of amines (Section 24.2).
    - 1. The three amine bonds and the lone pair occupy the corners of a tetrahedron.
    - 2. An amine with three different substituents is chiral.
      - The two amine enantiomers interconvert by pyramidal inversion.
      - This process is rapid at room temperature.
    - Amines with fewer than 5 carbons are water-soluble and form hydrogen bonds.
    - 4. Amines have higher boiling points than alkanes of similar molecular weight.
    - Amines smell nasty!
  - C. Basicity of amines (Sections 24.3–24.5).
    - The lone pair of electrons makes amines both nucleophilic and basic (Section 24.3).
    - The basicity constant K<sub>8</sub> is the measure of the equilibrium of an amine with water.
      - The larger the value of K<sub>b</sub> (smaller pK<sub>b</sub>), the stronger the base.
    - More often, K<sub>a</sub> is used to describe amine basicity.
      - K<sub>k</sub> is the dissociation constant of the conjugate acid of an amine.
        - b.  $pK_a + pK_b = 14$  (for aqueous media).
        - The smaller the value of K<sub>n</sub> (larger pK<sub>n</sub>), the stronger the base.
    - 4. Base strength.
      - Primary, secondary, and tertiary alkylamines have similar basicities.
      - b. Arylamines and beterocyclic amines are less basic than alkylamines.
        - The xp<sup>2</sup> electrons of the pyridine lone pair are less available for bonding.
        - The pyrrole lone pair electrons are part of the aromatic ring a system.
      - c. Amides are nonbasic.
      - d. Amine busicity can be used as a means of separating amines from a mixture.
         i. An amine can be converted to its salt, extracted from an organic solution with water, neutralized, and re-extracted with an organic solvent.
      - e. Some amines are very weak acids.
        - LDA is formed from disopropylamine and acts as a strong base.

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