

Chemistry 204: Amines

Classification

Shape of Amines (aliphatic)

- sp^3 -hybridized nitrogen atom is trigonal pyramidal
- however, not configurationally stable
 - rapid, reversible inversion at nitrogen takes place

Even though **A** and **B** are non-superimposable mirror images, they cannot be resolved into isolable enantiomers, since they are in rapid equilibrium with each other.

Acidity and Basicity of Amines

a) acidity => very weakly acidic

alkyl amines (alkanamines):

Amide ions can be prepared and used as bases in organic chemistry.

- used to deprotonate weak organic C-H acids like ketones, esters, amides, nitriles etc.

b) basicity

A measure of basicity is the acidity constant of the base's conjugate acid. Strong bases have weak conjugate acids.

Amines are weak bases – more basic than H_2O or ROH , but less basic than HO^- (hydroxide). (Simple amines cannot deprotonate water.)

Ammonia is slightly less basic than substituted amines.

The alkyl groups attached to the nitrogen atom stabilize the alkylammonium ion (electron-donating effect).

Basicity of Aryl Amines

Aryl amines are considerably less basic than alkyl amines.

Aniline is ~6 orders of magnitude less basic than methylamines.

Why?

Electron-donating groups increase the basicity; electron-withdrawing groups decrease the basicity. These effects are due to both inductive and resonance effects.

Basicity of Heterocycles

Why is pyridine a weaker base than piperidine?

Why is pyrrole a weaker base than pyridine?

Why is imidazole more basic than pyridine?

Basicity of Guanidine

Synthesis of Amines

Alkylation of Ammonia and Amines

Three solutions:

1° Amines by Preparation and Reduction of Alkyl Azides

In general:

Preparation of Amines by Reduction of Nitriles or Amides using LiAlH_4

Reductive Amination of Aldehydes and Ketones (Section 16.11D)

problem:

solution, in general:

an example, with mechanism:

Preparation of Arylamines by Reduction of Nitro Compounds

- a number of reagents can be used to carry out this reaction

Diazotization of Aniline and its Derivatives. Replacement of the -NH_2 group by -H , -Cl , -Br , -I , -CN and -OH .

Aniline (and aniline derivatives) react with nitrous acid (HNO_2) to form diazonium salts. This process is called diazotization.

Note: temperature is important—diazonium salts are unstable above $\sim 10^\circ\text{C}$

mechanism:

Replacement of Diazonium Salts by Various Groups

- replacement by $-\text{Cl}$, $-\text{Br}$, $-\text{CN}$ (Sandmeyer reaction)
 - the decomposition of diazonium salts is catalyzed by copper (I) (cuprous) salts
- replacement by $-\text{I}$
 - this does not require the use of CuI , but can be accomplished simply by warming the diazonium salt with KI or NaI
- replacement by $-\text{H}$
 - very important and useful
 - the diazonium salt is reduced by hypophosphorous acid (H_3PO_2)

- replacement by -OH
- this is accomplished by adding a diazonium sulfate to hot water

Construction of Substituted Benzenes