This page looks at the preparation of amines from halogenoalkanes (also known as haloalkanes or alkyl halides) and from nitriles.

Making amines from halogenoalkanes

The halogenoalkane is heated with a concentrated solution of ammonia in ethanol. The reaction is carried out in a sealed tube. You couldn't heat this mixture under reflux, because the ammonia would simply escape up the condenser as a gas. We'll talk about the reaction using 1-bromoethane as a typical halogenoalkane. You get a mixture of amines formed together with their salts. The reactions happen one after another.

Making a primary amine

The reaction happens in two stages. In the first stage, a salt is formed - in this case, ethylammonium bromide. This is just like ammonium bromide, except that one of the hydrogens in the ammonium ion is replaced by an ethyl group.

\[
CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_3^+Br^-
\]

There is then the possibility of a reversible reaction between this salt and excess ammonia in the mixture.

\[
CH_3CH_2NH_3^+Br^- + NH_3 \rightleftharpoons CH_3CH_2NH_2 + NH_4^+ Br^-\]

The ammonia removes a hydrogen ion from the ethylammonium ion to leave a primary amine - ethylamine. The more ammonia there is in the mixture, the more the forward reaction is favored.

Making a secondary amine

The reaction doesn't stop at a primary amine. The ethylamine also reacts with bromoethane - in the same two stages as before. In the first stage, you get a salt formed - this time, diethylammonium bromide. Think of this as ammonium bromide with two hydrogens replaced by ethyl groups.

\[
CH_3CH_2Br + CH_3CH_2NH_2 \rightarrow CH_3CH_2NH_2 + CH_3CH_2NH_3^+Br^-
\]

There is again the possibility of a reversible reaction between this salt and excess ammonia in the mixture.

\[
CH_3CH_2NH_3^+Br^- + NH_3 \rightleftharpoons CH_3CH_2NH_2 + NH_4^+ Br^-\]

The ammonia removes a hydrogen ion from the diethylammonium ion to leave a secondary amine - diethylamine. A
secondary amine is one which has two alkyl groups attached to the nitrogen.

Making a tertiary amine

The reaction does not stop! The diethylamine also reacts with bromoethane - in the same two stages as before. In the first stage, you get triethylammonium bromide.

\[
\text{CH}_3\text{CH}_2\text{Br} + \text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{NH}^+\text{Br}^- + \text{H}_2\text{O}
\]

There is again the possibility of a reversible reaction between this salt and excess ammonia in the mixture.

\[
\text{CH}_3\text{CH}_2\text{NH}^+\text{Br}^- + \text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 + \text{NH}_4^+\text{Br}^{-}
\]

The ammonia removes a hydrogen ion from the triethylammonium ion to leave a tertiary amine - triethylamine. A tertiary amine is one which has three alkyl groups attached to the nitrogen.

Making a quaternary ammonium salt

The final stage! The triethylamine reacts with bromoethane to give tetraethylammonium bromide - a quaternary ammonium salt (one in which all four hydrogens have been replaced by alkyl groups).

\[
\text{CH}_3\text{CH}_2\text{NH}_2 + \text{CH}_3\text{CH}_2\text{Br} \rightarrow \text{CH}_3\text{CH}_2\text{N}^+\text{CH}_3\text{CH}_2\text{CH}_3\text{CH}_3\text{Br}^- + \text{H}_2\text{O}
\]

This time there isn't any hydrogen left on the nitrogen to be removed. The reaction stops here.

Reacting bromoethane with ammonia

Whatever you do, you get a mixture of all of the products (including the various amines and their salts) shown on this page. To get mainly the quaternary ammonium salt, you can use a large excess of bromoethane. If you look at the reactions going on, each one needs additional bromoethane. If you provide enough, then the chances are that the reaction will go to completion, given enough time.

On the other hand, if you use a very large excess of ammonia, the chances are always greatest that a bromoethane molecule will hit an ammonia molecule rather than one of the amines being formed. That will help to prevent the formation of secondary (etc) amines - although it won't stop it entirely.
Making primary amines from nitriles

Nitriles are compounds containing the -CN group, and can be reduced in various ways. Two possible methods are described here.

1. Reducing nitriles using LiAlH₄. One possible reducing agent is lithium tetrahydridoaluminate(III) - often just called lithium tetrahydridoaluminate or lithium aluminum hydride. The nitrile reacts with the lithium tetrahydridoaluminate in solution in ethoxyethane (diethyl ether, or just "ether") followed by treatment of the product of that reaction with a dilute acid. Overall, the carbon-nitrogen triple bond is reduced to give a primary amine. For example, with ethanenitrile you get ethylamine: \[ CH_3CN + 4[H] \rightarrow CH_3CH_2NH_2 \]

2. The reduction of nitriles using hydrogen and a metal catalyst. The carbon-nitrogen triple bond in a nitrile can also be reduced by reaction with hydrogen gas in the presence of a variety of metal catalysts. Commonly quoted catalysts are palladium, platinum or nickel. The reaction will take place at a raised temperature and pressure. It is impossible to give exact details because it will vary from catalyst to catalyst. For example, ethanenitrile can be reduced to ethylamine by reaction with hydrogen in the presence of a palladium catalyst.

\[ \text{CH}_3\text{C}≡\text{N} + 2\text{H}_2 \xrightarrow{\text{Pd}} \text{CH}_3\text{CH}_2\text{NH}_2 \]

Contributors

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