Amines

Base Properties

Primary aliphatic amines act as Bronsted Lowry Bases because the lone pair of electrons on the nitrogen is readily available for forming a dative covalent bond with a H^+ and so accepting a proton

$$CH_3NH_2 + H_2O \rightarrow CH_3NH_3^+ + OH^-$$

Primary aliphatic amines are stronger bases than ammonia as the alkyl groups are electron releasing and push electrons towards the nitrogen atom and so make it a stronger base.

$$NH_{3\,(aq)} + H_2O_{(l)} \rightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

Primary aromatic amines such as Phenylamine do not form basic solutions because the lone pair of electrons on the nitrogen delocalise with the ring of electrons in the benzene ring. This means the N is less able to accept protons.

Amines as bases react with acids to form ammonium salts.

$$CH_3NH_{2\,(aq)} + HCl_{(aq)} \rightarrow CH_3NH_3^+Cl^-{}_{(aq)}$$

methylammonium chloride

Addition of NaOH to an ammonium salt will convert it back to the amine

The ionic salts formed in this reaction means that the compounds are soluble in the acid.
e.g. Phenylamine is not very soluble in water but phenylammonium chloride is soluble

These ionic salts formed will be solid crystals if the water is evaporated

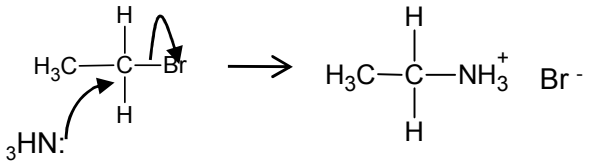
Nucleophilic properties

Primary amines can be formed by the **nucleophilic substitution** reaction between haloalkanes and ammonia. However, as the lone pair of electrons is still available on the N in the amine formed, the primary amine can react in the same nucleophilic way in a successive series of reactions forming secondary, tertiary amines and quaternary ammonium salts

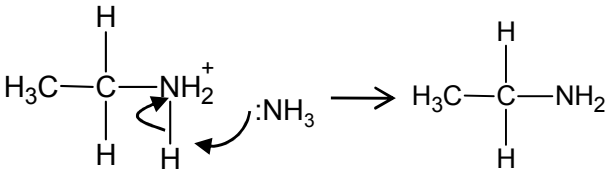
reaction 1 with ammonia forming primary amine

$$CH_3CH_2Br + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4Br$$

Ammonia dissolved in ethanol is the initial nucleophile



In the first step of the mechanism the nucleophile attacks the haloalkane to form an intermediate

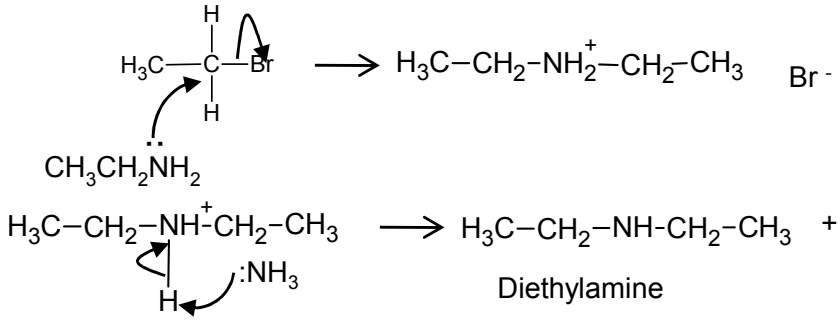


In the second step of the mechanism a second ammonia removes a proton from the intermediate (acts as base) to form the amine

reaction 2 forming secondary amine

The amine formed in the first reaction has a lone pair of electrons on the nitrogen and will react further with the haloalkane.

Using an **excess of Ammonia** can limit this second reaction and will **maximise the amount of primary amine** formed



In this second step of the mechanism either ammonia or the amine can remove a proton from the intermediate (acts as base) to form the amine

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Reaction 3 forming a tertiary amine

The same reaction mechanism occurs with the secondary amine reacting to form a tertiary amine

$R_2NH + RX \rightarrow [R_3NH]^+X^-$

$[R_3NH]^+X^- + NH_3 \rightarrow R_3N + NH_4^+X^-$

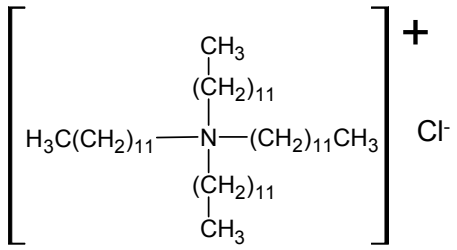
Reaction 4 forming a quaternary ammonium salt

$R_3N + RX \rightarrow [R_4N]^+X^-$

Only the first step of the mechanism occurs when forming the quaternary salt

Using an **excess of the haloalkane** will promote the formation of **the quaternary salt**

quaternary ammonium salt



Quaternary Salts can be used as **cationic surfactants**

Surfactants reduce the surface tension of liquids

The positive nitrogen is attracted toward negatively charged surfaces such as glass, hair, fibres and plastics. This helps in their uses as fabric softeners, hair conditioners and sewage flocculants

Preparing Amines from Nitriles

Using the method above of haloalkanes and ammonia is not an efficient method for preparing primary amines because of the further substitution that occurs.

A better method is to use the following reactions

Step 1. convert **haloalkane to nitrile** by using KCN in ethanol (heat under reflux)

$CH_3CH_2Br + CN^- \rightarrow CH_3CH_2CN + Br^-$

Step 2. reduce **nitrile to amine** by using $LiAlH_4$ in ethanol or by reducing with H_2 using a Ni catalyst

$CH_3CH_2CN + 4[H] \rightarrow CH_3CH_2CH_2NH_2$

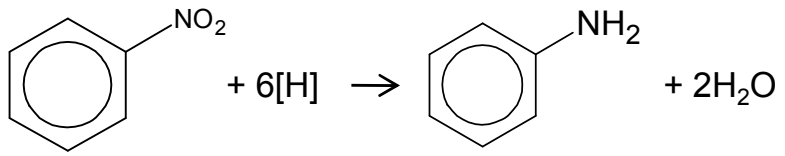
A disadvantage of this method is that it is a two step reaction that may therefore have a low yield. Also KCN is toxic

Reducing nitroarenes to aromatic amines

See the last topic for how to form nitrobenzene from benzene

The nitro group on an arene can be reduced an amine group as follows

Reagent: Sn and HCl or Fe and HCl
Conditions: Heating
Mechanism:reduction



nitrobenzene phenylamine

As the reaction is carried out in HCl the salt $C_6H_5NH_3^+Cl^-$ will be formed. Reacting this salt with NaOH will give phenylamine

This reduction reaction can also be done with catalytic hydrogenation (H_2 using a Ni catalyst)

Other reactions of amines

Aliphatic amines and phenylamine can react with acyl chlorides and acid anhydrides to form amides- see previous chapter on reactions of C=O bond.

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