3.11 Amines

Naming Amines

See 3.7 revision guide :naming and isomerism for discussion of naming 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. They are weak bases as only a low concentration of hydroxide ions is produced.

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

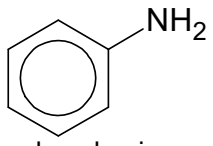
Primary aliphatic amines are stronger bases than ammonia as the alkyl groups are electron releasing and push electrons towards the nitrogen atom and **so making the lone pair of electrons on the nitrogen more readily available to accept protons.**

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

Secondary amines are stronger bases than primary amines because they have more alkyl groups that are substituted onto the N atom in place of H atoms. Therefore more electron density is pushed onto the N atom (as the inductive effect of alkyl groups is greater than that of H atoms), so making the lone pair of electrons on the nitrogen more readily available.
One might expect using the same trend that tertiary amine would be the strongest amine base but the trend does not hold. The tertiary amines and corresponding ammonium salts are less soluble in water and this makes them less strong bases than the secondary amines. (This point will not be examined)

Base strength of aromatic amines

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 **lone pair on the N** is **less able to accept protons**.



phenylamine

Overall order of base strength
Aromatic amines < ammonia< primary amines< tertiary amines< secondary amines
Weaker bases **Stronger bases**

Reactions with acids

All amines will react with acids to become ammonium salts

$CH_3NH_{2\,(aq)} + H^+_{\,(aq)} \rightarrow CH_3NH_3^+{}_{(aq)}$
$(CH_3CH_2)_2NH_{\,(aq)} + H^+_{\,(aq)} \rightarrow (CH_3CH_2)_2NH_2^+{}_{(aq)}$
$(CH_3CH_2)_3N_{\,(aq)} + H^+_{\,(aq)} \rightarrow (CH_3CH_2)_3NH^+_{(aq)}$

Amines as bases react with acids to form ammonium salts.
$CH_3NH_{2\,(aq)} + HCl_{\,(aq)} \rightarrow CH_3NH_3^+Cl^-_{(aq)}$
Methylamine 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 will be solid crystals, if the water is evaporated, because of the strong ionic interactions.

Making a basic buffer from an amine

Basic buffers can be made from combining a weak base with a salt of that weak base
e.g. Ammonia and ammonium chloride
Methylamine and methylammonium chloride
Ethylamine and ethylammonium chloride

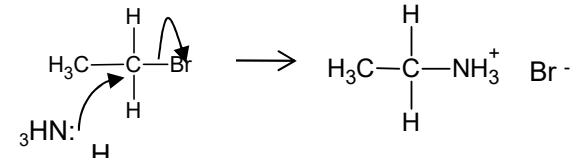
Nucleophilic properties

Forming a primary amine in a one step reaction of halogenoalkanes with ammonia

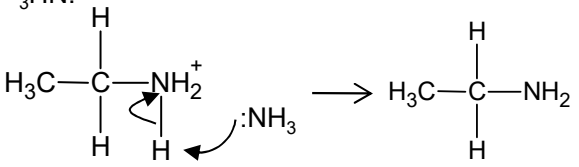
Primary amines can be formed by the **nucleophilic substitution** reaction between halogenoalkanes and ammonia in a **one step reaction**. However, as the lone pair of electrons is still available on the N in the amine formed, the primary amine can react in the same nucleophilic way in a successive series of reactions forming secondary, tertiary amines and quaternary ammonium salts.
This is therefore not a good method for making a primary amine because of the further reactions. It would mean the desired product would have to be separated from the other products.

$CH_3CH_2Br + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4Br$

Ammonia dissolved in ethanol is the initial nucleophile



In the first step of the mechanism the nucleophile attacks the halogenoalkane 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

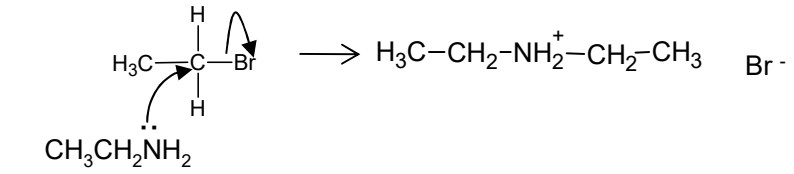
Using an **excess of ammonia** can limit the further subsequent reactions and will **maximise the amount of primary amine** formed

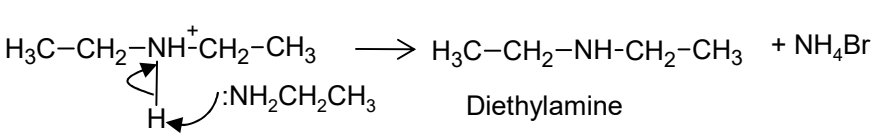
Further reactions

Reaction forming secondary amine

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

$2CH_3CH_2NH_2 + CH_3CH_2Br \rightarrow CH_3CH_2NH_2CH_2CH_3 + CH_3CH_2NH_3Br$

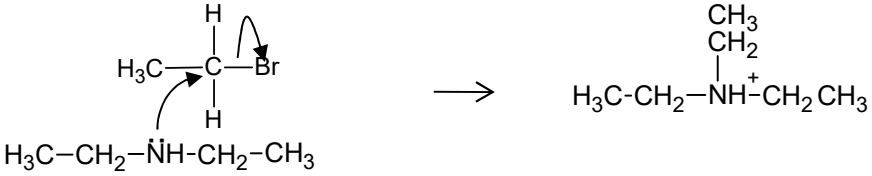


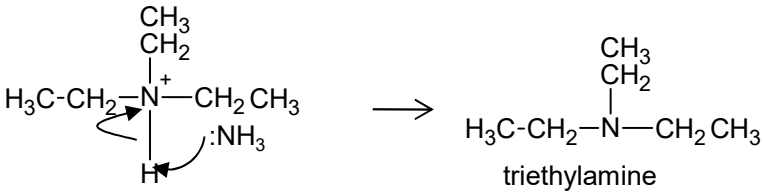


In this second step of the mechanism either ammonia or the amine can remove a proton from the intermediate (acts as base) to form the amine.

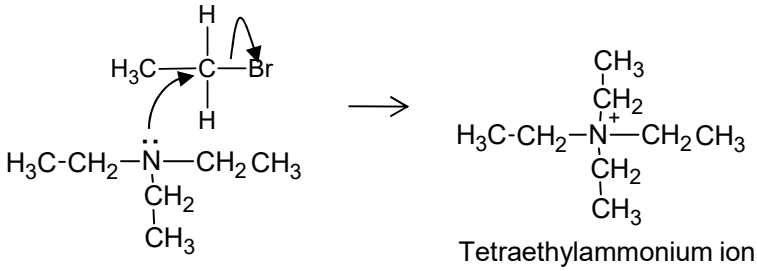
Reaction forming a tertiary amine

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





Reaction forming a quaternary ammonium salt



Tetraethylammonium ion

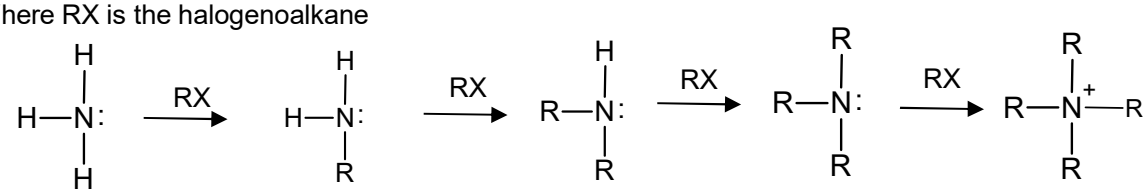
Using an **excess of the halogenoalkane** will promote the formation of **the quaternary salt**

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

Quaternary ammonium salts are not amines

Overall scheme of reactions

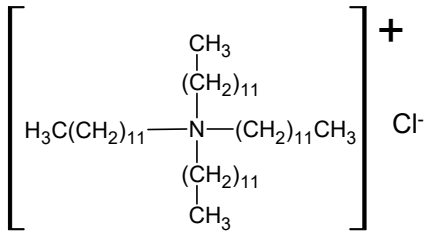
Where RX is the halogenoalkane



Using a large **excess of ammonia** will **maximise the amount of primary amine** formed.

Using an **excess of the halogenoalkane** will promote the formation of **the quaternary salt.**

Quaternary ammonium salt

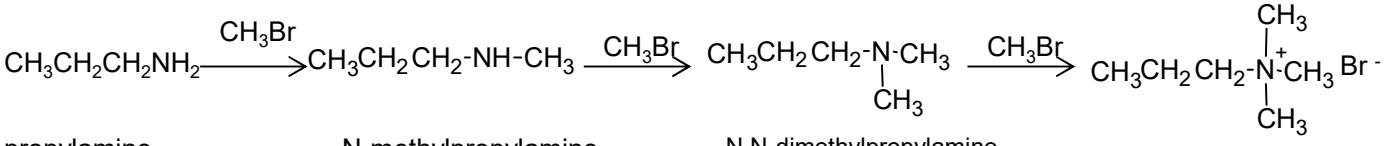


Quaternary salts can be used as **cationic surfactants**

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.

Some questions will involve substituting an amine onto a halogenoalkane which has a different length of carbon chain from the amine.



propylamine

N-methylpropylamine

N,N-dimethylpropylamine

Trimethylpropyl-ammonium bromide

Using excess bromomethane would promote the final quaternary salt

Preparing amines from nitriles in a 2 step reaction

Using the method above of reacting halogenoalkanes and ammonia is not an efficient method for preparing a high yield of the primary amine because of the further substitution reactions that occur.

A better method is to use the following 2 step reaction scheme.

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

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

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

$CH_3CH_2CN + 4[H] \rightarrow CH_3CH_2CH_2NH_2$

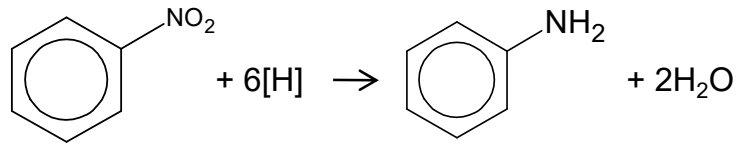
A disadvantage of this method is that it is a two step reaction that may therefore have a low yield. Also KCN is toxic.

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 ionic salt $C_6H_5NH_3^+Cl^-$ will be formed. Reacting this salt with NaOH will give phenylamine.

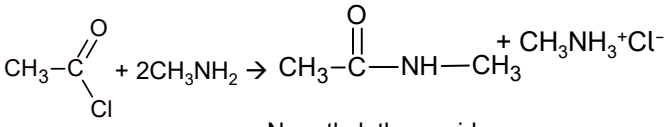
This reduction reaction can also be done with catalytic hydrogenation (H_2 using a Ni catalyst).

Other reactions of amines

Aliphatic amines and phenylamine can react with acyl chlorides and acid anhydrides to form amides in a nucleophilic addition-elimination reaction- see chapter on reactions of C=O bond for more details.

Change in functional group**: acyl chloride → secondary amide**
Reagent: **primary amine**
Conditions: **room temp.**

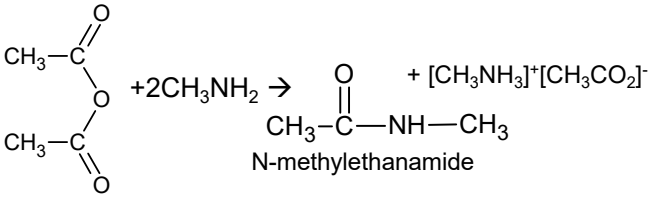
$RCOCl + 2CH_3NH_2 \rightarrow RCONHCH_3 + CH_3NH_3^+Cl^-$



N-methylethanamide

Change in functional group**: acid anhydride → secondary amide**
Reagent: **primary amine**
Conditions: **room temp.**

$(RCO)_2O + 2CH_3NH_2 \rightarrow RCONHCH_3 + [CH_3NH_3]^+[RCO_2]^-$



N-methylethanamide