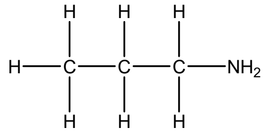
6.10 Amines

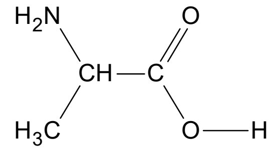
Naming

Amines
These end in **–amine**.
There is, however, rather confusingly two ways of using this suffix.
The exam board tend to use the common version where the name stem ends in **-yl** prop**yl**amine.
Another version of the same chemical is propan-1-amine. (This is used in the same way as naming alcohols)



prop**yl**amine
Or propan-1-amine

If there is another priority functional group as well as the amine group then the prefix amino is used.

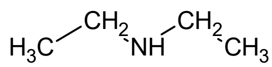


2-aminopropanoic acid.

If the amine is secondary and has two alkyl groups attached to the nitrogen, then each chain is named and the smaller alkyl group is preceded by an –N which plays the same role as a number in positioning a side alkyl chain

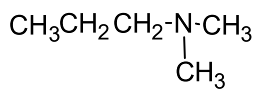
$CH_3CH_2CH_2NHCH_3$
N-methylpropylamine (common name)
N-methylpropan-1-amine (other name)

In the common naming version if the chain lengths are the same an –N is not used.



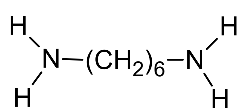
diethylamine (common name- does not use N if chains are same length)
N-ethylethanamine (other name does still use N)

If a tertiary amine similar rules apply, and each alkyl side group is given an N



N,N-dimethylpropylamine (common name)
N,N-dimethylpropan-1-amine (other name)

If there are two amine groups then name as following:

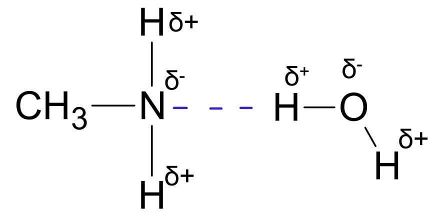


hexane-1,6-diamine

It could also be named 1,6-diaminohexane

Properties of Amines

Amines have a characteristic fishy smell.



Small amines can form hydrogen bonds with water and therefore can dissolve readily in water.

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.

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

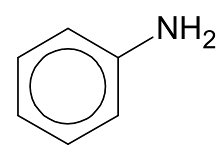
Primary aliphatic amines are stronger bases than ammonia as the alkyl groups are electron releasing and push electrons towards the nitrogen atom and so making the lone pair of electrons on the nitrogen more readily available to accept protons.

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

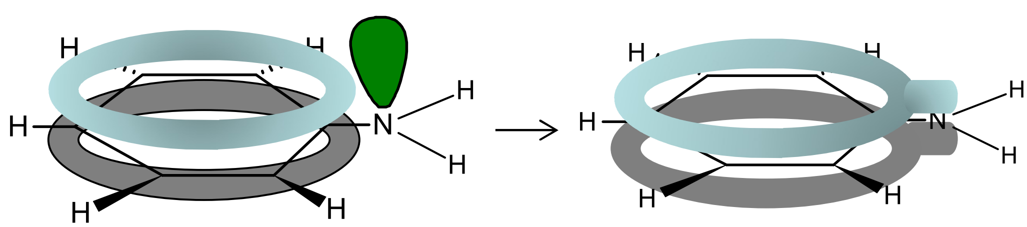
Secondary amines are stronger bases than primary amines because they have more alkyl groups that are substituted onto the N atom in place of H atoms. Therefore more electron density is pushed onto the N atom (as the inductive effect of alkyl groups is greater than that of H atoms), so making the lone 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 nitrogen 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**

Formation of amines

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

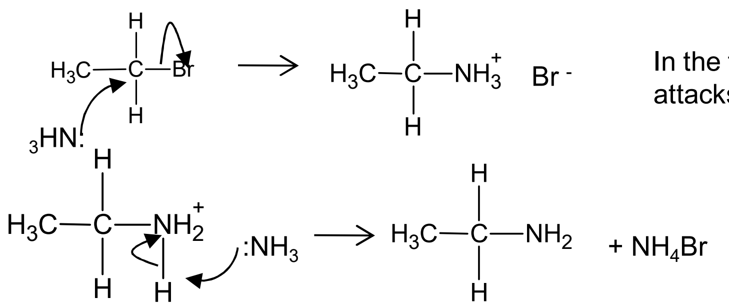
***Change in functional group:* halogenoalkane → amine**
Reagent: NH_3 dissolved in ethanol
Conditions: Heating under pressure in a sealed tube
Mechanism: Nucleophilic Substitution
Type of reagent: Nucleophile, :NH_3

Ammonia dissolved in ethanol is the initial nucleophile

$CH_3CH_2Br + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4Br$

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

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 nitrogen atom 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.



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

2. Preparing amines from nitriles

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 potassium cyanide (KCN) dissolved in aqueous ethanol and heating under reflux.

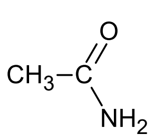
$CH_3CH_2Br + CN^- \rightarrow CH_3CH_2CN + Br^-$

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.

3. Reduction of amides with $LiAlH_4$



$+ 4[H] \rightarrow CH_3CH_2NH_2 + H_2O$

Reduce an amide to amine by using the reducing agent **$LiAlH_4$ in ether**

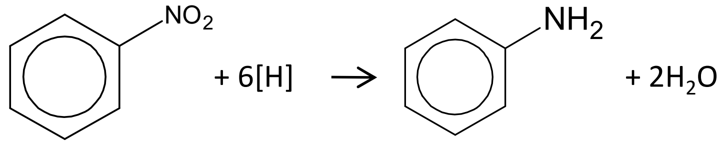
This reaction is then followed by reaction with a dilute acid, such as dilute sulfuric or hydrochloric acid.

4. Reducing nitroarenes to aromatic amines

See the benzene chapter 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.

Ionic ½ equation for reduction: $C_6H_5NO_2 + 6\,e^- + 6\,H^+ \rightarrow C_6H_5NH_2 + 2\,H_2O$

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

Reactions of amines

Reactions with acids

Amines as bases react with acids to form ammonium salts.

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

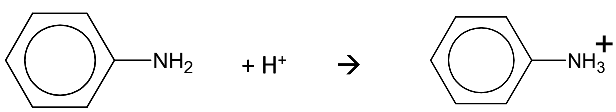
Methylamine methylammonium chloride

$2CH_3NH_{2\,(aq)} + H_2SO_{4\,(aq)} \rightarrow (CH_3NH_3^+)_2\,SO_4^{2-}{}_{(aq)}$

Addition of sodium hydroxide (NaOH) to an ammonium salt will convert it back to the amine

These ionic salts will be solid crystals, if the water is evaporated, because of the strong ionic interactions.

Phenylamines react with acid



phenylammonium ion

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 in water.

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

Formation of complex ions

The lone pair of electrons on the nitrogen enable amines to act as ligands and form dative covalent bonds into transition metal ions to form coloured complex ions.

$$4\,CH_3CH_2NH_2 + Cu(H_2O)_6^{2+} \rightleftharpoons [Cu(CH_3CH_2NH_2)_4(H_2O)_2]^{2+} + 4H_2O$$

This is a similar ligand exchange reaction to the one where ammonia acts as the ligand

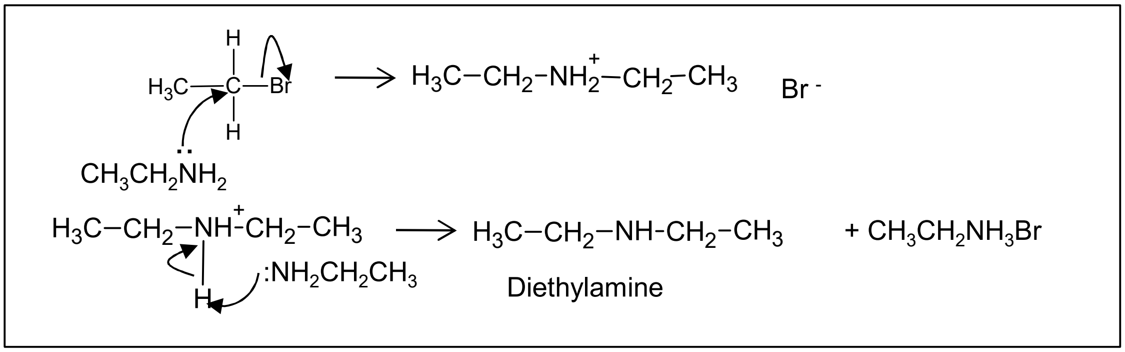
$$4NH_3 + Cu(H_2O)_6^{2+} \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

light blue solution deep blue solution

Reaction of primary amines with halogenoalkanes forming secondary amines

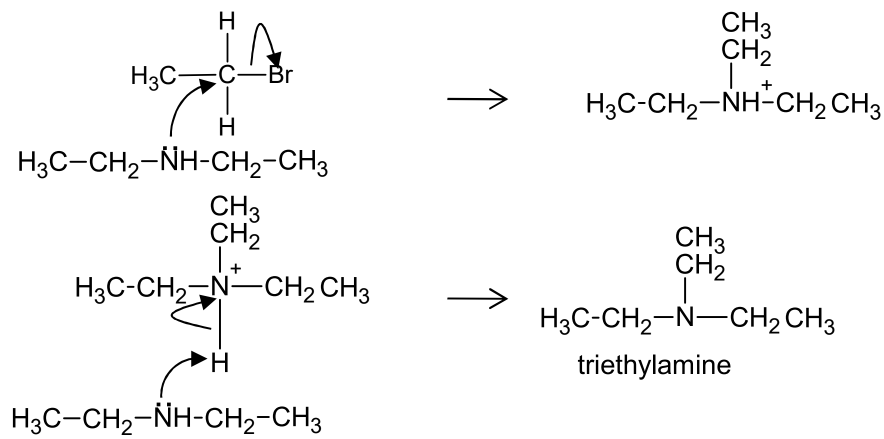
Amines will react with halogenoalkanes in a similar way to the reaction of ammonia with halogenoalkanes via a nucleophilic substitution reaction.

$$2CH_3CH_2NH_2 + CH_3CH_2Br \rightarrow CH_3CH_2NH_2CH_2CH_3 + CH_3CH_2NH_3Br$$

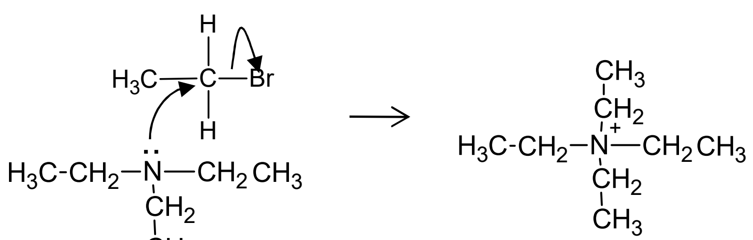


Reaction secondary amines reacting with halogenoalkanes to form a tertiary amine

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



Forming a quaternary ammonium salt



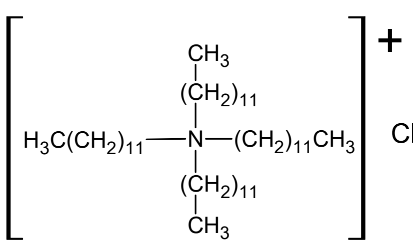
Tetraethylammonium ion

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

quaternary ammonium salt



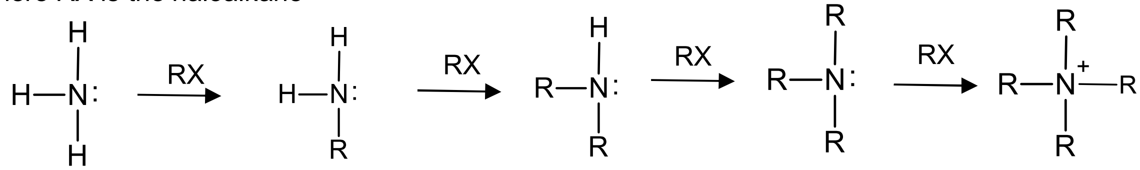
Quaternary salts can be used as **cationic surfactants**

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

Overall scheme of reactions

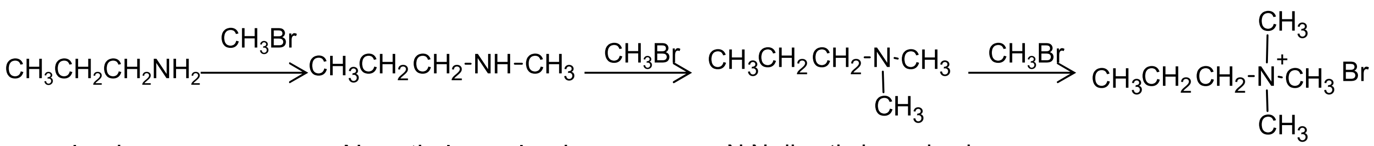
Where RX is the haloalkane



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

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

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

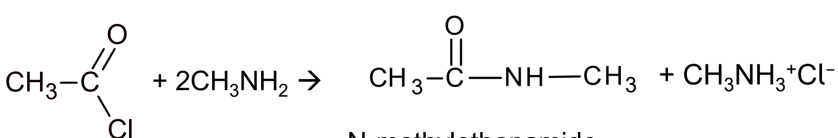
Other reactions of amines

Aliphatic amines and phenylamine can react with acyl chlorides and acid anhydrides to form amides- see chapter on reactions of acyl chlorides for more detail.

Reaction with primary amines with acyl chlorides

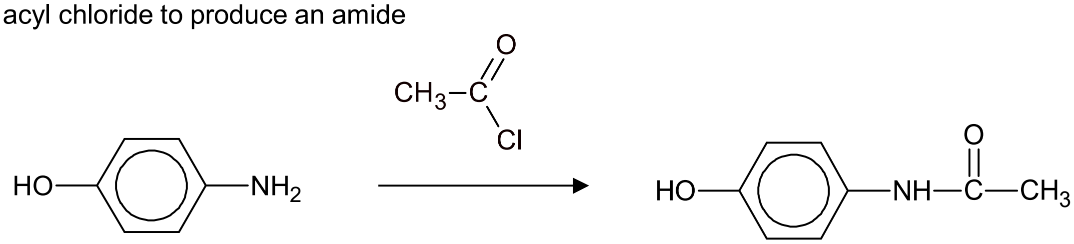
Change in functional group**: acyl chloride → secondary amide**
Reagent: **primary amine**
Conditions: **room temp.**

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



N-methylethanamide

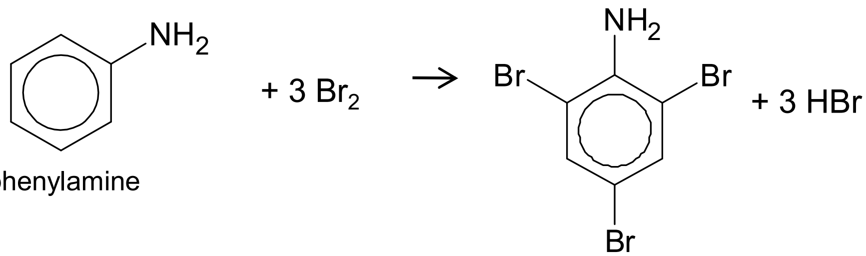
Paracetamol is made by the reaction of an aromatic amine with an acyl chloride to produce an amide



Paracetamol

Reaction of phenylamine with aqueous bromine

The lone pair of electrons on the nitrogen in the amine group delocalise with the ring of electrons in the benzene ring. This makes the benzene ring more reactive. Phenylamine reacts with aqueous bromine at room temperature. (Remember benzene would not do this)



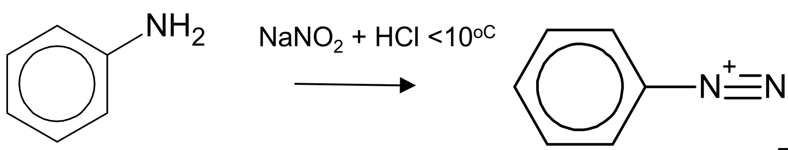
phenylamine

2,4,6-tribromophenylamine

Synthesis of azo dyes

Step 1: reaction of an aromatic amine with nitrous acid at <10 °C, forming a diazonium ion,

Nitrous acid is generated *in situ* from $NaNO_2$/HCl.



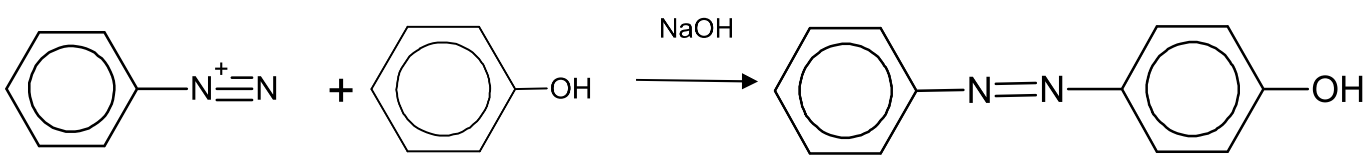
diazonium ion

Below 0^oC the temperature is too low and the reaction would be too slow

$C_6H_5NH_2 + HNO_2 + HCl \rightarrow C_6H_5N_2^+ Cl^- + 2H_2O$

If the diazonium ion is allowed to heat above 10^oC it reacts with water to form phenol and nitrogen (N_2) gas
$C_6H_5N_2^+ + H_2O \rightarrow C_6H_5OH + N_2 + H^+$

Step 2: coupling of diazonium ion with a phenol under alkaline conditions;



4-hydroxyazobenzene

$C_6H_5N_2^+ Cl^- + C_6H_5OH \rightarrow C_6H_5N_2C_6H_4OH + HCl$

Azo dyes are used for dyes, pigments and colourings