

## 6.10 Amines

### Naming

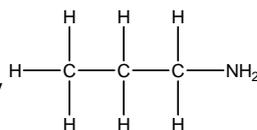
#### Amines

These end in **-amine**.

There is, however, rather confusingly two ways of using this suffix.

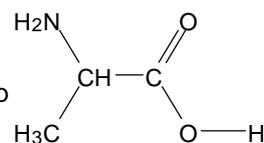
The exam board tend to use the common version where the name stem ends in **-yl** propylamine.

The IUPAC version of the same chemical is propan-1-amine. (This is used in the same way as naming alcohols)



propylamine  
Or propan-1-amine

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



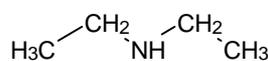
2-aminopropanoic acid.

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



N-methylpropylamine (common name)

N-methylpropan-1-amine (IUPAC name)

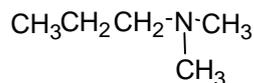


In the common naming version if the chain lengths are the same an **-N** is not used

Diethylamine (common name- does not use N if chains are same length)

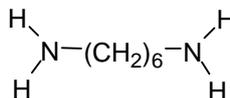
N-ethylethanamine (IUPAC name does still use N)

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 (IUPAC name)



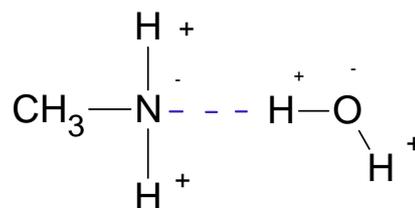
hexane-1,6-diamine

It could also be named  
1,6-diaminohexane

## Properties of Amines

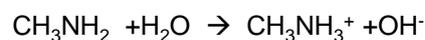
Amines have a characteristic fishy smell

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

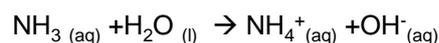


### Base Properties

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  $\text{H}^+$  and so accepting a proton.



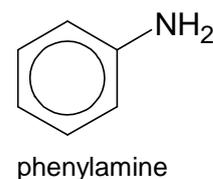
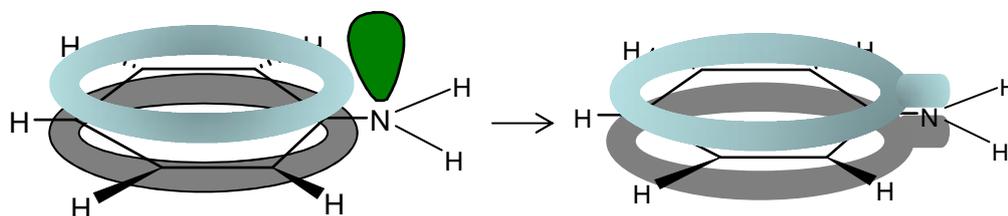
Primary aliphatic amines are stronger bases than ammonia as the alkyl groups are electron releasing and push electrons towards the nitrogen atom and so make it a stronger base.



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

### 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 nitrogen is less able to accept protons.



### 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

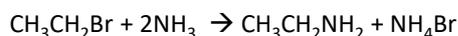
**Reagent:** NH<sub>3</sub> dissolved in ethanol

**Conditions:** Heating under pressure in a sealed tube

**Mechanism:** Nucleophilic Substitution

**Type of reagent:** Nucleophile, :NH<sub>3</sub>

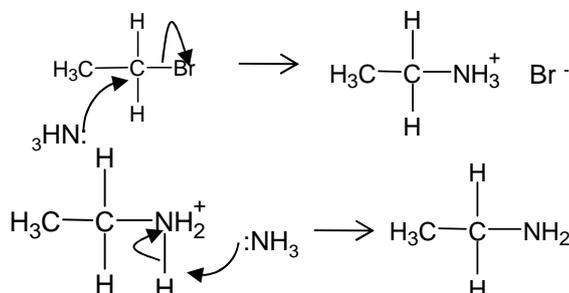
Ammonia dissolved in ethanol is the initial nucleophile



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 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.



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

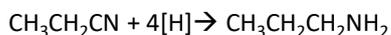
Using the method above of reacting halogenoalkanes and ammonia is not an efficient method for preparing a high yield of the primary amine because of the further substitution reactions that occur.

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

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

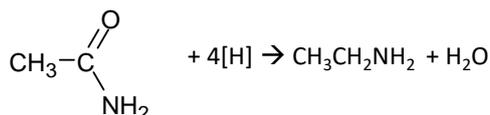


Step 2. reduce **nitrile to amine** by using **LiAlH<sub>4</sub> in ether** or by reducing with H<sub>2</sub> using a Ni catalyst



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<sub>4</sub>



Reduce an amide to amine by using the reducing agent **LiAlH<sub>4</sub> in ether**

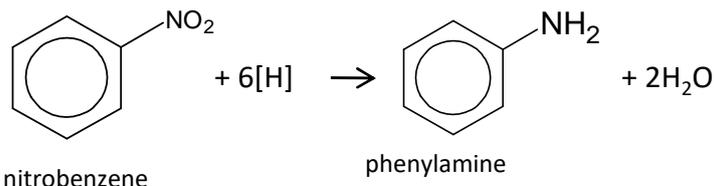
This reaction is then followed by reaction with a dilute acid, such as dilute sulfuric or hydrochloric acid.

#### 4. Reducing nitroarenes to aromatic amines

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

See the benzene chapter for how to form nitrobenzene from benzene.

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



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.

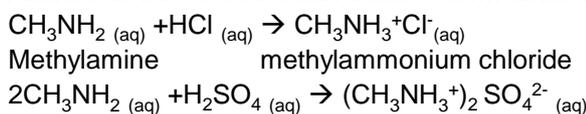


This reduction reaction can also be done with catalytic hydrogenation ( $H_2$  using a Ni catalyst).

### Reactions of amines

#### Reactions with acids

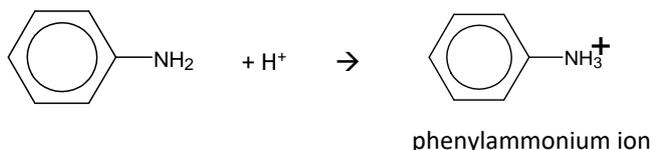
Amines as bases react with acids to form ammonium salts.



Addition of 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



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

#### Making a basic buffer from an amine

Basic buffers can be made from combining a weak base with a salt of that weak base

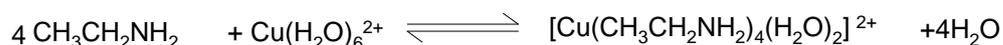
e.g. Ammonia and ammonium chloride

Methylamine and methylammonium chloride

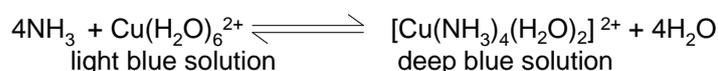
Ethylamine and ethylammonium chloride

#### 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.

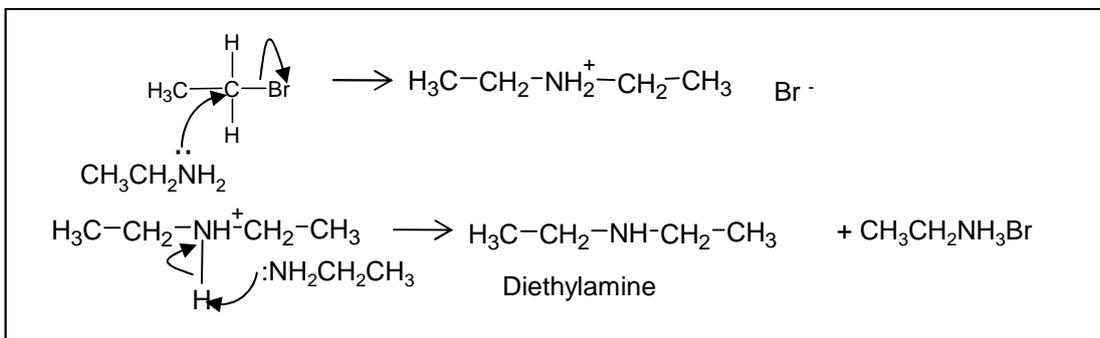
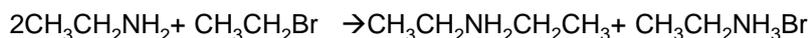


This is a similar ligand exchange reaction to the one where ammonia acts as the ligand



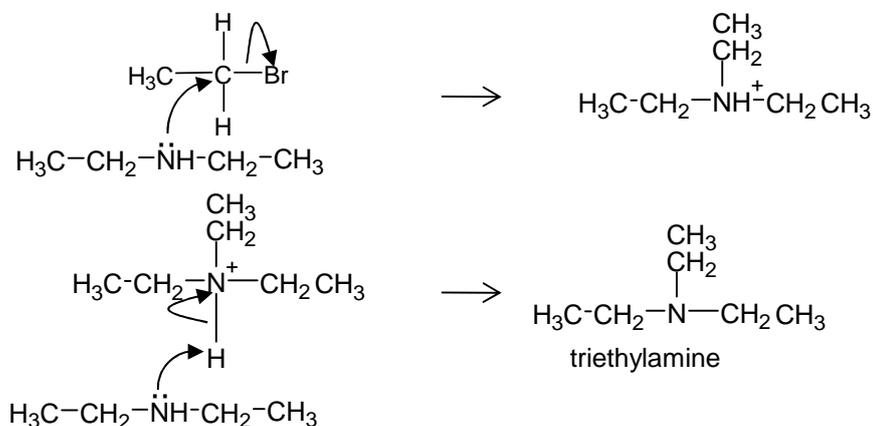
## Reaction of primary Amines with halogenoalkanes forming secondary amines

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

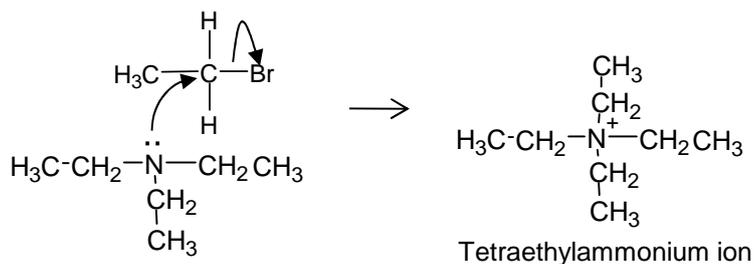


## Reaction secondary amines reacting with halogenoalkanes to form a tertiary amine

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



## Forming a quaternary ammonium salt

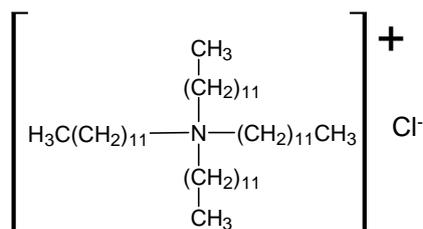


Using an **excess of the halogenoalkane** will promote the formation of **the quaternary salt**

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

Quaternary ammonium salts are not amines

### quaternary ammonium salt



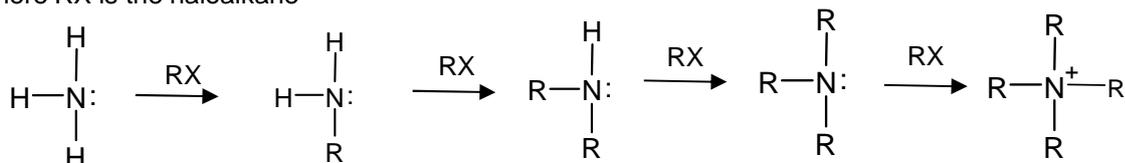
### Quaternary Salts can be used as cationic surfactants

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

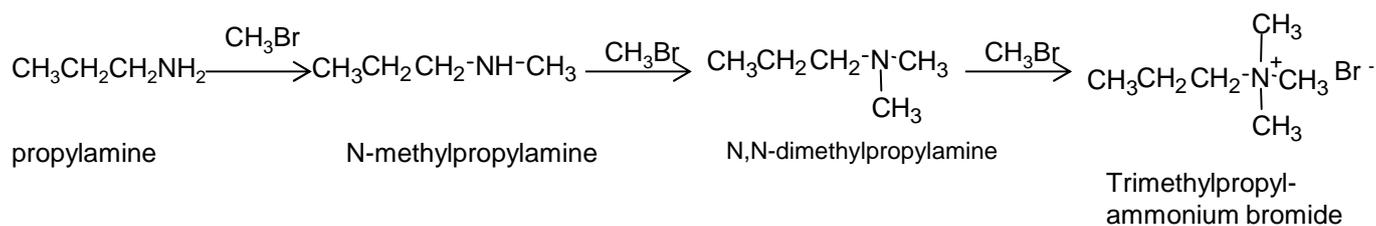
Where RX is the haloalkane



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



Using excess bromomethane would promote the final quaternary salt

## Other reactions of amines

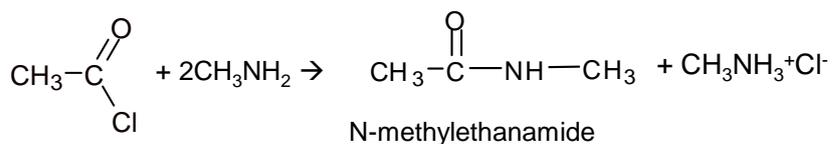
Aliphatic amines and phenylamine can react with acyl chlorides and acid anhydrides to form amides- see chapter on reactions of acyl chlorides for more detail.

### Reaction with primary amines with acyl chlorides

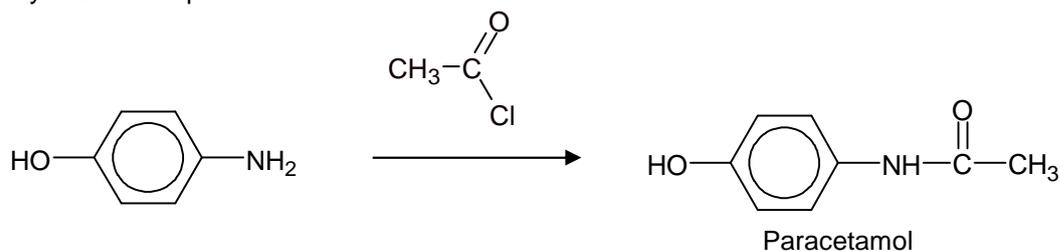
Change in functional group: **acyl chloride** → **secondary amide**

Reagent: **primary amine**

Conditions: **room temp.**

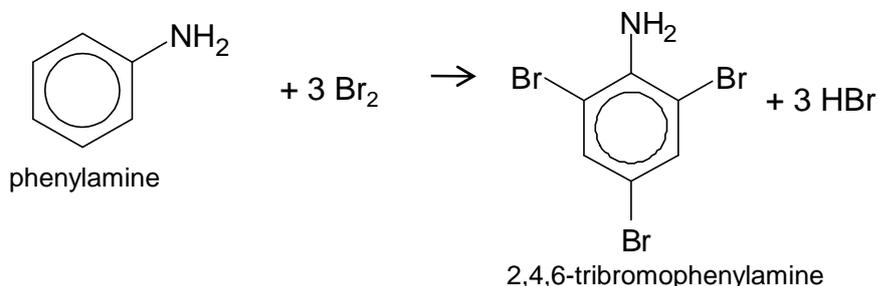


Paracetamol is made by the reaction of an aromatic amine with an acyl chloride to produce an amide



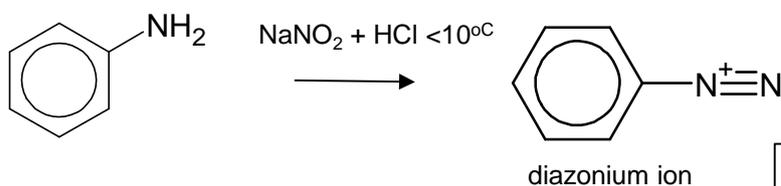
### Reaction of phenylamine with aqueous bromine

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)



### Synthesis of azo dyes

Step 1: reaction of an aromatic amine with nitrous acid at  $<10^{\circ}\text{C}$ , forming a diazonium ion,

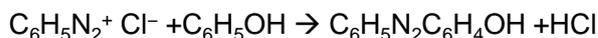
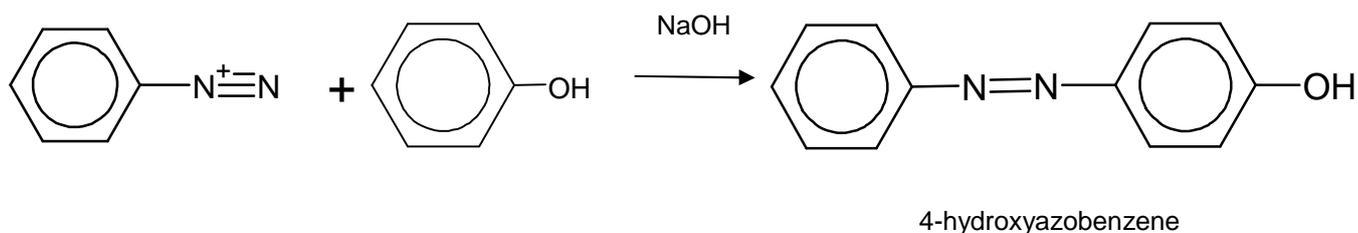


Nitrous acid is generated *in situ* from  $\text{NaNO}_2/\text{HCl}$ .

Below  $0^{\circ}\text{C}$  the temperature is too low and the reaction would be too slow

If the diazonium ion is allowed to heat above  $10^{\circ}\text{C}$  it reacts with water to form phenol and  $\text{N}_2$  gas  
 $\text{C}_6\text{H}_5\text{N}_2^+ + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{N}_2 + \text{H}^+$

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



Azo dyes are used for dyes, pigments and colourings