



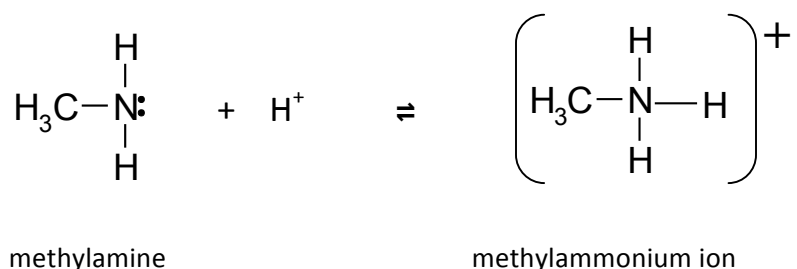
We can also have more than one amine group attached to the chain:

e.g.  $\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$       1,4-diaminobutane      (both amine groups are primary)

### Amines as bases

A base is defined as a **proton acceptor**. The nitrogen atom in an ammonia molecule and similarly in amines can do this since its lone pair can accept a proton forming a dative bond and becoming an  $\text{NH}_4^+$  ammonium ion, or alkylammonium ion respectively.

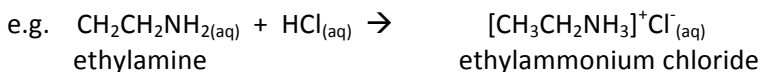
The reaction is reversible, and so ammonia and amines are therefore weak bases.



### Reactions of amines as bases

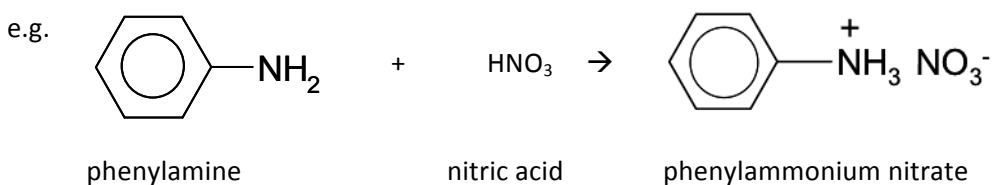
Since amines are weak bases they will react with acids to form salts.

**Notice that the positive charge should to be on the N atom, or the whole ion in square brackets.**



Alkylammonium salts are named based on the acid from which they are formed, just like metal salts and ammonium salts.

Aromatic amines react in exactly the same way:



### Practice:

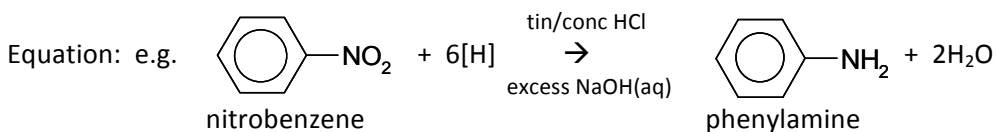
- Write an equation for the formation of ethylammonium sulphate
- Write an equation for the reaction of excess dimethylamine with phosphoric acid
- Write an equation for the reaction of N-ethyl-N-methylamine with ethanoic acid



Similarly a secondary amine can be reacted with a haloalkane to produce a tertiary amine.

**Making aromatic amines (i.e. amine bonded to benzene ring):**

Starting material: Nitroarenes (nitro group on a benzene ring)  
 Conditions: Heat under reflux with mixture of tin and conc. hydrochloric acid.  
 Neutralise the acid with excess NaOH when reaction complete  
 Type of reaction: Reduction. The mixture of tin and HCl acts as a reducing agent which we can show as [H] for simplicity.



Notes:

Remember if there are other groups present e.g. alkyl groups that you are only reducing the nitro- group.

**Extension Material – NOT ON SPECIFICATION**

**The role of amines in dye-making**

The history of synthetic dyes is linked to amines. The first synthetic purple dye, mauveine, was made by Sir W.H. Perkin in 1856. This was the first example of an "aniline dye" since aniline is the trivial name for phenylamine. Another family of dyes are the "azo dyes" and these are also made from aromatic amines.

**Synthesis of azo-dyes**

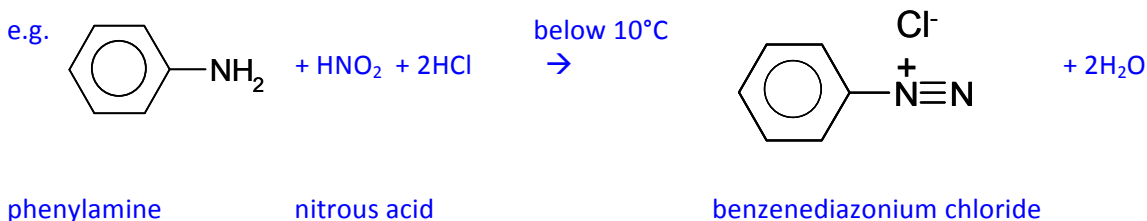
Stage 1: diazotisation

When a mixture of phenylamine and nitrous acid ( $\text{HNO}_2$ ) is reacted below  $10^\circ\text{C}$ , a diazonium salt is formed. The diazonium salt is unstable and decomposes if allowed to warm above  $10^\circ\text{C}$ .

Nitrous acid is generated in-situ by reacting sodium nitrite ( $\text{NaNO}_2$ ) with hydrochloric acid:



The cold nitrous acid then reacts with an aromatic amine such as phenylamine to form a salt containing the diazonium ion:

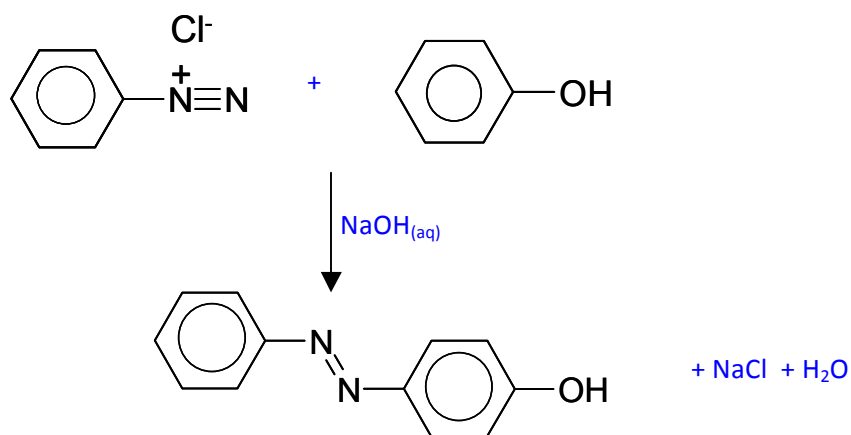


## Stage 2: coupling reaction

A coupling reaction occurs when the diazonium salt, e.g. benzene diazonium chloride is reacted with a phenol, or another aromatic compound such as an amine, under **alkaline conditions**. The temperature must remain below 10°C or the diazonium salt decomposes.

The two benzene rings become linked through an azo functional group, -N=N-  
The azo link is generally formed opposite the -OH or -NH<sub>2</sub> group, although you may see examples where it has been formed elsewhere on the ring.

e.g.



(4-hydroxyphenyl)azobenzene

The product is a brightly coloured compound used as an azo dye. Many different colours can be produced by varying the structure of the azo compound