

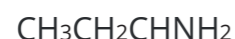
## 4.6 – Amines

### Naming amines

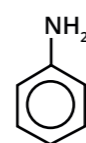
All amines have a nitrogen atom bonded directly to a carbon atom of an alkyl or aryl group. If this nitrogen is bonded to only one carbon atom, the compound is a primary amine. Aromatic amines have the nitrogen atom bonded directly to the benzene ring. The longest carbon chain is used to name the amine with the number of carbon atoms indicated in the usual way, and -amine is used as a suffix.



butylamine



1-methylpropylamine



phenylamine

### Formation of primary aliphatic amines

#### 1. From halogenoalkanes

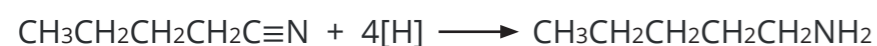
Reacting a halogenoalkane with ammonia using a water/ethanol solvent produces an amine.



This is a simplified picture since ammonia is lost if the mixture is heated. To overcome this, the reactants are heated in a sealed tube and an excess of ammonia is used. The acidic hydrogen bromide reacts with the ammonia to give ammonium bromide. If an excess of halogenoalkane is used, further substitution can occur, giving a secondary amine.

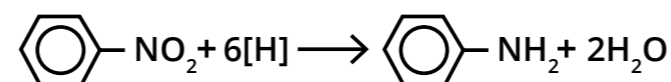
#### 2. From nitriles

Nitriles can be reduced with a suitable reducing agent such as lithium tetrahydridoaluminate(III),  $\text{LiAlH}_4$ , dissolved in ethoxyethane.



### Formation of aromatic amines

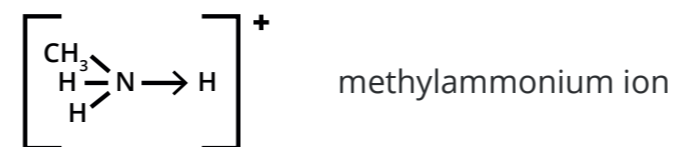
Phenylamine is made by the reduction of nitrobenzene. The general equation is:



In the laboratory, the reducing agent used is tin and concentrated hydrochloric acid. The mixture is heated under reflux in a boiling water bath for about 30 minutes. At this stage you get phenylammonium ions,  $\text{C}_6\text{H}_5\text{NH}_3^+$ , rather than phenylamine. After cooling, aqueous sodium hydroxide is added and phenylamine is formed together with a complex mixture of tin compounds. The mixture is then steam distilled to produce a distillate containing phenylamine and water. The immiscible phenylamine is separated, dried and then redistilled to produce pure phenylamine.

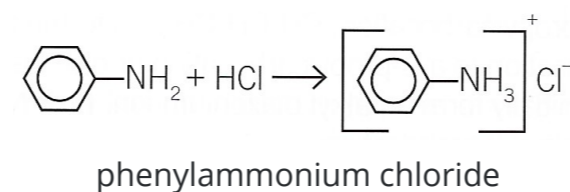
### Basicity of amines

Amines have a lone pair of electrons on the nitrogen atom. These can be used to accept a proton by means of a coordinate bond.



Amines are weak bases. Alkylamines, e.g. ethylamine, are stronger bases than ammonia because the alkyl groups 'push' electrons towards the nitrogen atom, making it more electron-rich than the nitrogen in ammonia.

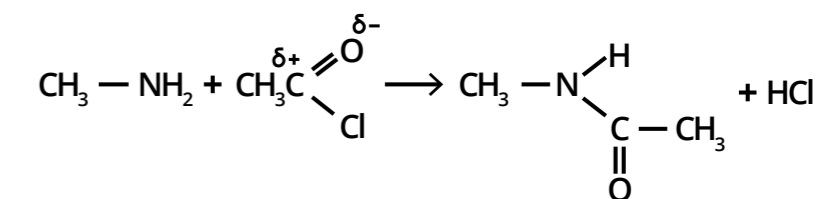
Phenylamine is a much weaker base than ethylamine as the lone pair of electrons becomes, to a certain extent, part of the delocalised  $\pi$  system. Like alkylamines, phenylamine will react with acids forming salts.



### Reactions

#### 1. Ethanoylation

The nitrogen lone pair enables an amine to react as a nucleophile. It attacks the  $\delta^+$  carbon atom of the carbonyl group in ethanoyl chloride to form an amide.



N-methylethanamide

The letter 'N' means that the methyl group is bonded to the nitrogen atom. Phenylamine acts in a similar way to produce N-phenylethanamide.

#### 2. With nitric(III) acid

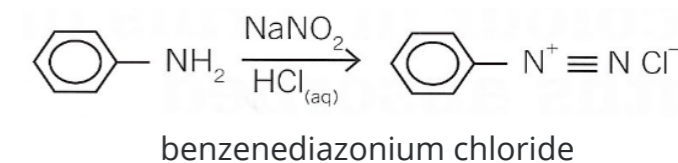
Nitric(III) acid (or nitrous acid),  $\text{HNO}_2$ , is an unstable compound and is made when required by the reaction of a dilute acid, e.g. HCl, on sodium nitrate(III),  $\text{NaNO}_2$ .

A primary aliphatic amine reacts with nitric(III) acid with the evolution of nitrogen, so bubbles are seen. One equation for this reaction is:



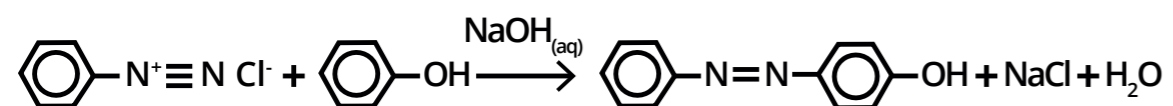
In the corresponding reaction with a primary aromatic amine, e.g. phenylamine, if the temperature is above  $10^\circ\text{C}$ , a similar reaction occurs, giving phenol (and nitrogen).

If the temperature is between  $0^\circ\text{C}$  and  $10^\circ\text{C}$ , a solution containing the stable benzenediazonium ion is formed.

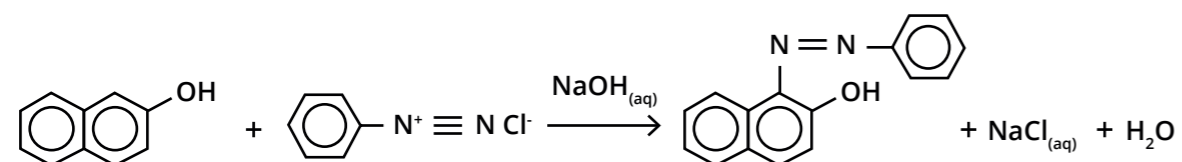


## Coupling reactions of benzenediazonium salts

Below 10°C, benzenediazonium compounds react with phenols and aromatic amines to produce compounds where the -N=N- azo group is retained. The resulting compounds are highly coloured, generally yellow, orange or red, and are called **azo dyes**. These reactions are carried out in alkaline solution. Coupling normally occurs at the 4-position relative to the -OH or -NH<sub>2</sub> group.



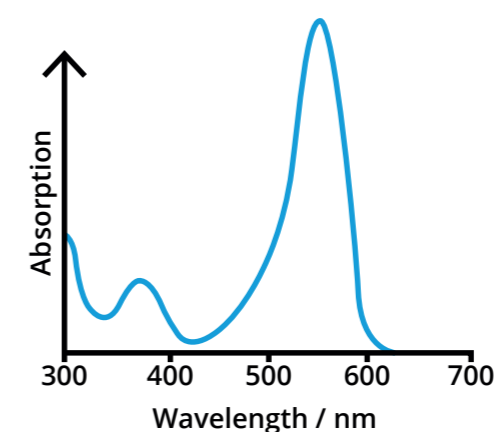
Coupling can also occur with other aromatic systems, e.g. naphthalen-2-ol. Here, the coupling occurs at the 2-position.



## Origin of colour in azo dyes

The -N=N- group in an azo dye is a chromophore, i.e. a group that absorbs colour in the visible (and ultraviolet) region. The wavelength of light absorbed dictates the complementary colour we see. A solution of (1-phenylazo)naphthalen-2-ol has its maximum visible absorption ( $\lambda_{\text{max}}$ ) at 476 nm in the blue-green region. The complementary colour of blue-green is red, which is the colour of (1-phenylazo)naphthalen-2-ol.

The visible spectrum of phenolphthalein in an alkaline solution is:



The spectrum shows that its maximum absorption is at 553 nm, which is in the green region of the spectrum. The red/violet colour of phenolphthalein is the complementary colour of green.