WJEC Chemistry A-level

4.6: Amines

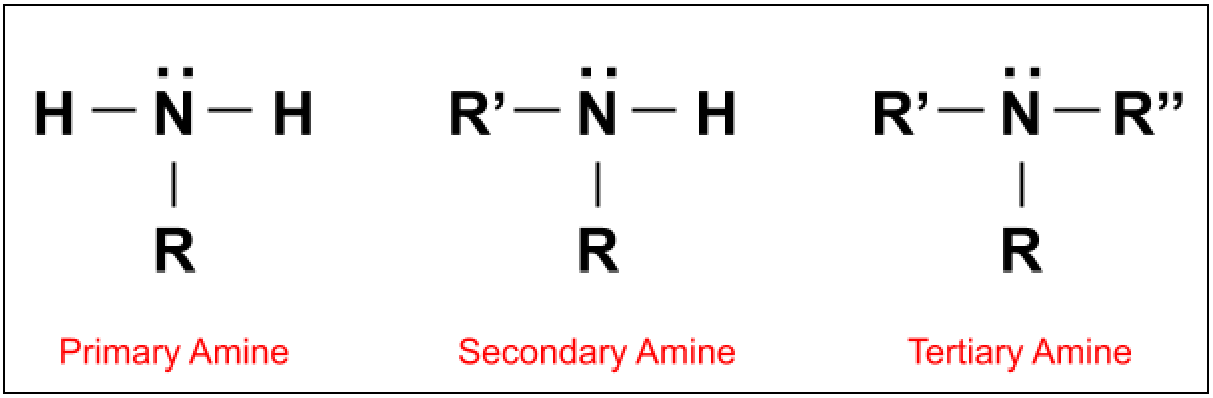
Detailed Notes

Welsh Specification

Preparation of Amines

Amines are formed when one or more of the hydrogen atoms in ammonia is **replaced with an organic group**. They can be **1°, 2° or 3°** depending on how many hydrogen atoms are replaced.

Example:



Primary Amine

Secondary Amine

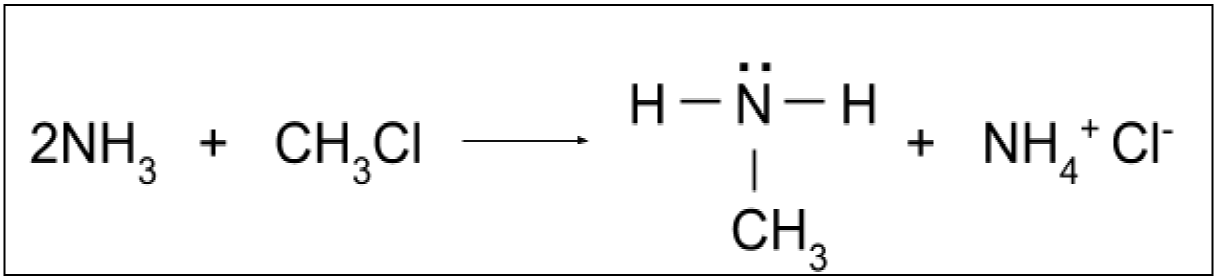
Tertiary Amine

Amines can be produced in two ways either from the **nucleophilic substitution** of **halogenoalkanes** or the **reduction of nitriles**.

Nucleophilic Substitution

This reaction produces amines in the reaction of **halogenoalkanes with ammonia** in a sealed tube. One mole of halogenoalkane reacts with two moles of ammonia producing a **primary amine** and an **ammonium salt**.

Example:

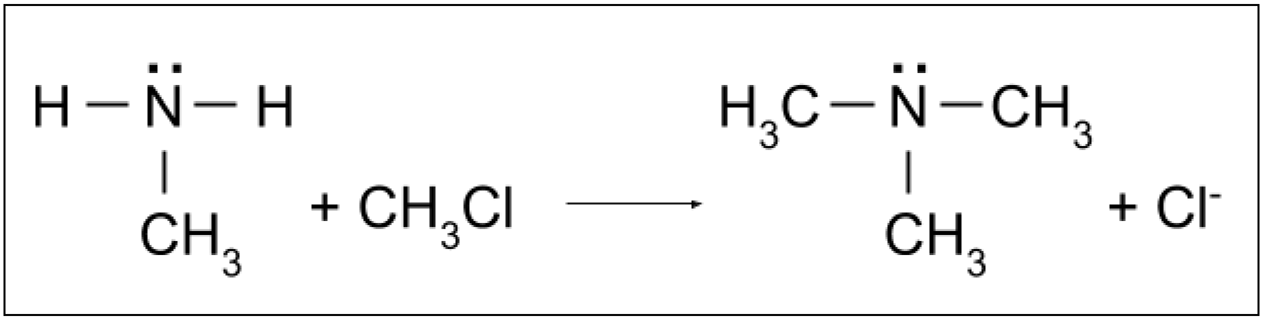


$$2NH_3 + CH_3Cl \longrightarrow \underset{\displaystyle CH_3}{H-\ddot{N}-H} + NH_4^+Cl^-$$

This substitution reaction can continue until all the hydrogen atoms have been **replaced** with organic groups, forming a **tertiary amine**.

Following this, a **further substitution** of an R group can occur, producing a **quaternary ammonium salt**.

Example:



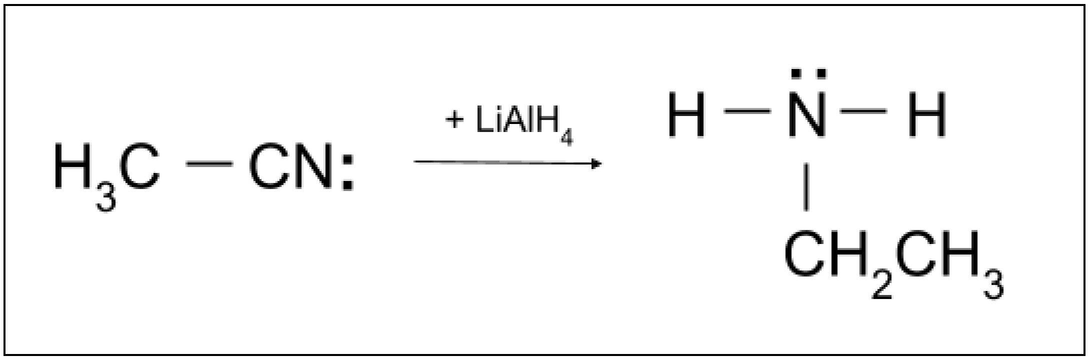
Since multiple substitutions only to the nitrogen atom can occur, a **mixture of products** are produced. Therefore the reaction has **low efficiency**.

The reaction conditions can be changed so that only a **single substitution** occurs. Ammonia can be added **in excess** during the reaction in order to achieve only the **primary amine**, or the final mixture of products can be **separated** using **fractional distillation**.

Reduction of Nitriles

Reducing nitriles via a **hydrogenation** reaction can produce **amines**. This reduction requires either the **$LiAlH_4$** reducing agent and **acidic** conditions, or a combination of **hydrogen and nickel** (catalytic hydrogenation).

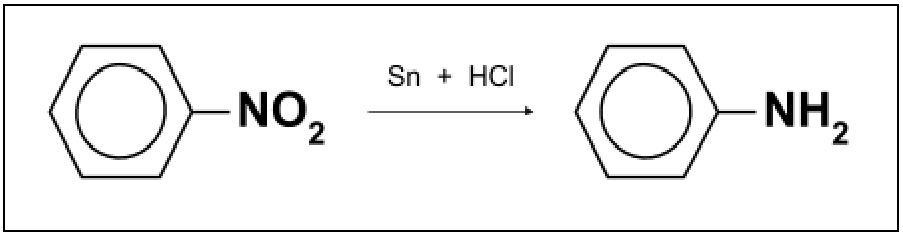
Example:



Preparation of Aromatic Amines

These amines contain a **benzene carbon ring** that has been substituted with an **amine** group. Aromatic amines can be produced from the **reduction of nitrobenzene** using concentrated **hydrochloric acid** (HCl) and a **tin catalyst**.

Example:



Basic Properties of Amines

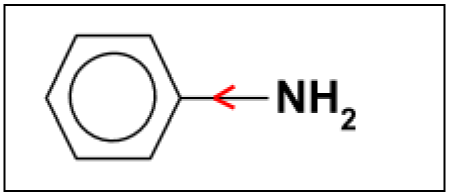
Amines are **weak bases** because the lone electron pair on the nitrogen atom can **accept protons**. The base strength of amines depends on how 'available' the electron pair is on the molecule. The **more available** the electrons, the more likely it is to accept a proton meaning it acts as a **stronger base**.

The Inductive Effect

In an organic molecule, different functional groups can affect how available a lone electron pair is by **changing electron density** around the bond.

1. **Benzene rings** - these draw electron density **away** from the nitrogen atom, towards the ring, making it **'less available'**

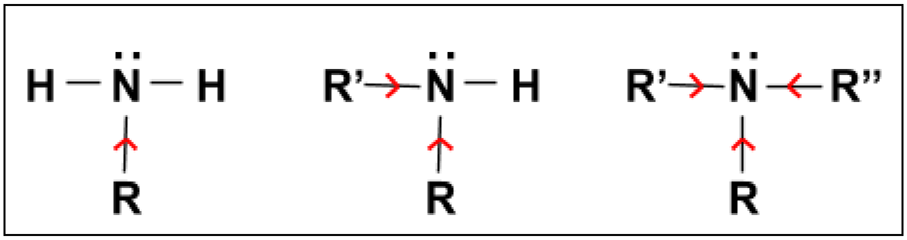
   Example:



The negative inductive effect.

2. **Alkyl groups** - these push electron density **towards** the nitrogen making it **'more available'**. More alkyl groups means more 'pushing'.

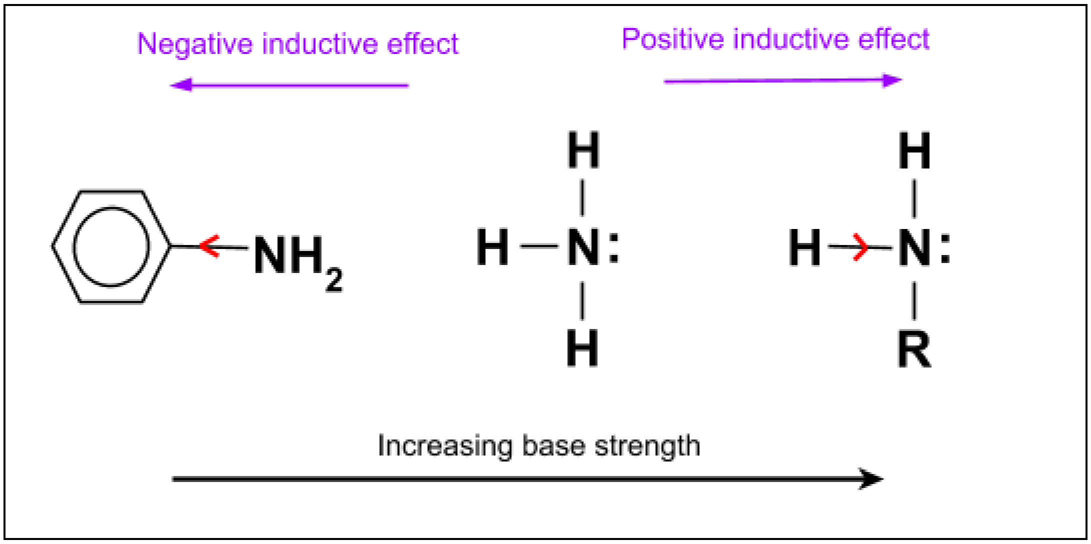
   Example:



Positive inductive effect.

This means **aliphatic amines are stronger** bases and **aromatic amines are weaker** bases.

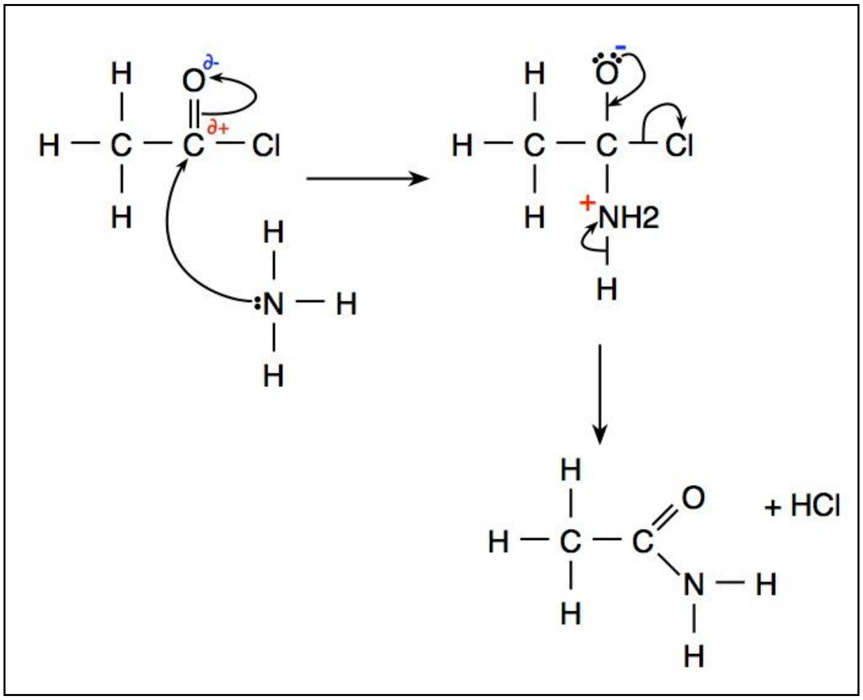
Example:



Ethanoylation of 1° Amines

Primary amines can also undergo **nucleophilic addition-elimination** reactions with **ethanoyl chloride** to produce amides and N-substituted amides. This process is known as **ethanoylation**.

Mechanism - *this shows the addition-elimination of ammonia to ethanoyl chloride but the mechanism is the same format with a primary amine*



This same reaction mechanism can also occur with **acid anhydrides** to produce an **amide** and a **carboxylic acid**.

Testing for Amines

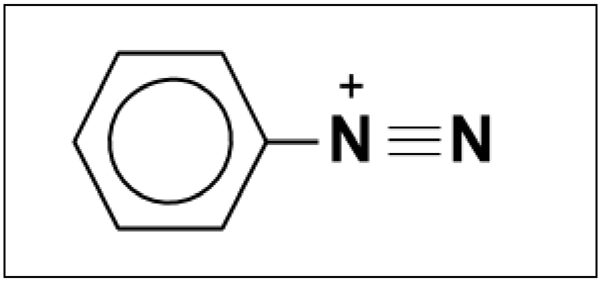
Nitric(III) acid, also known as **nitrous acid** can be used as a test for **primary** amines. When a 1° amine is present, a **burst of nitrogen** which is colourless and odorless is released, confirming the presence of the compound. The nitrogen is produced in a **1:1 ratio** with the primary amine present, meaning the amount of **initial amine can be calculated**.

When a **secondary** amine is present, no gas is produced but instead a **yellow oil**, nitrosamine, forms. These oily compounds are **highly carcinogenic** making them very dangerous. Therefore, this reaction is not carried out in school laboratories.

Diazonium Ions

These ions contain an **N_2^+ group**. One of the most common diazonium ions is the **benzenediazonium ion**, often found with chloride ions forming benzenediazonium chloride solution.

Example:

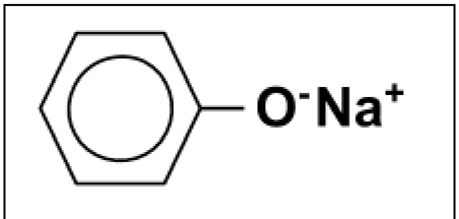


This compound can undergo **coupling reactions** where the nitrogen group forms a **'bridge'** between two different functional groups.

Coupling with Phenol

In this coupling reaction, the nitrogen group bridges together **two benzene rings**. Firstly, phenol is dissolved in sodium hydroxide, forming **sodium phenoxide solution**.

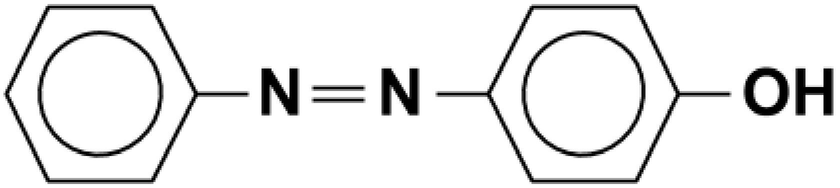
Example:



Sodium Phenoxide

When **benzenediazonium chloride** is then added, the diazonium and phenoxide ions react to form an **orange-yellow precipitate** of an **azo compound**.

Example:

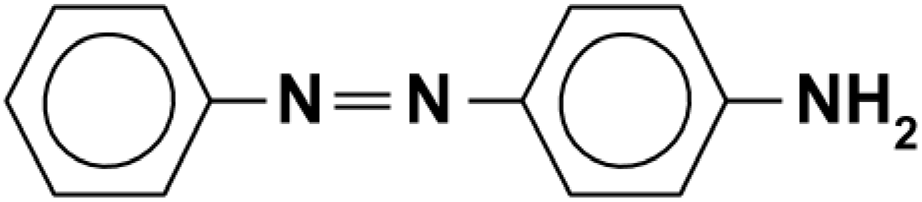


An Azo Compound

Coupling with Aromatic Amines

In this coupling reaction, the nitrogen group **bridges** together a **benzene ring** and an **aromatic amine**. Liquid phenylamine is added to benzenediazonium chloride, forming a **yellow solid**.

Example:



An Azo Dye

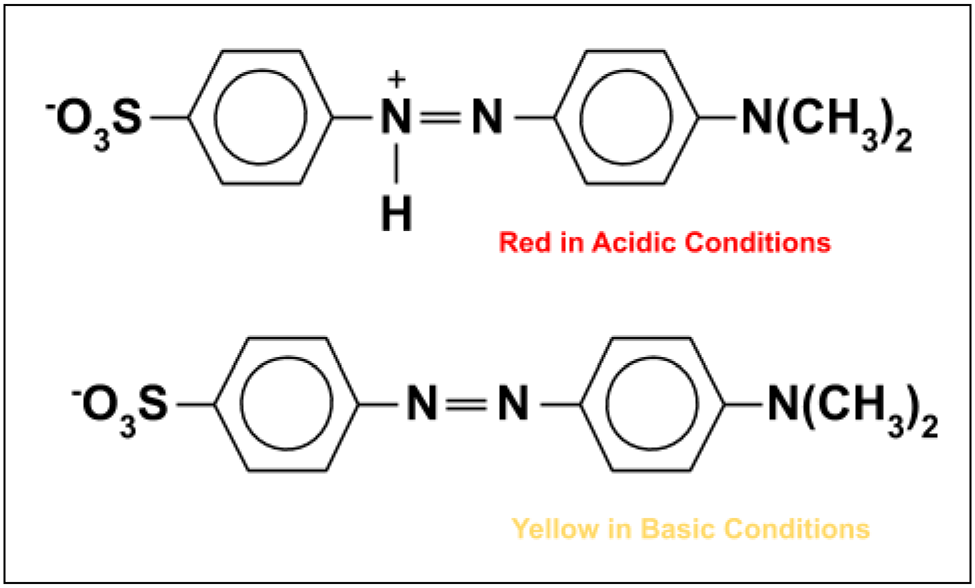
This solid is a **strongly coloured** compound known as an **azo dye**. Such dyes account for over half of modern day dyes.

Chromophores

The nitrogen group in an azo dye has **indicator properties**. It interacts differently with light when in different conditions due to different **wavelengths** of the light being **absorbed or reflected**.

Methyl orange is an azo dye used as an indicator to distinguish between acids and bases. In acidic conditions, the nitrogen group **gains a hydrogen** causing it to interact differently with light, so it appears **red**. In basic conditions, the nitrogen group **reflects yellow wavelengths,** giving it a yellow appearance.

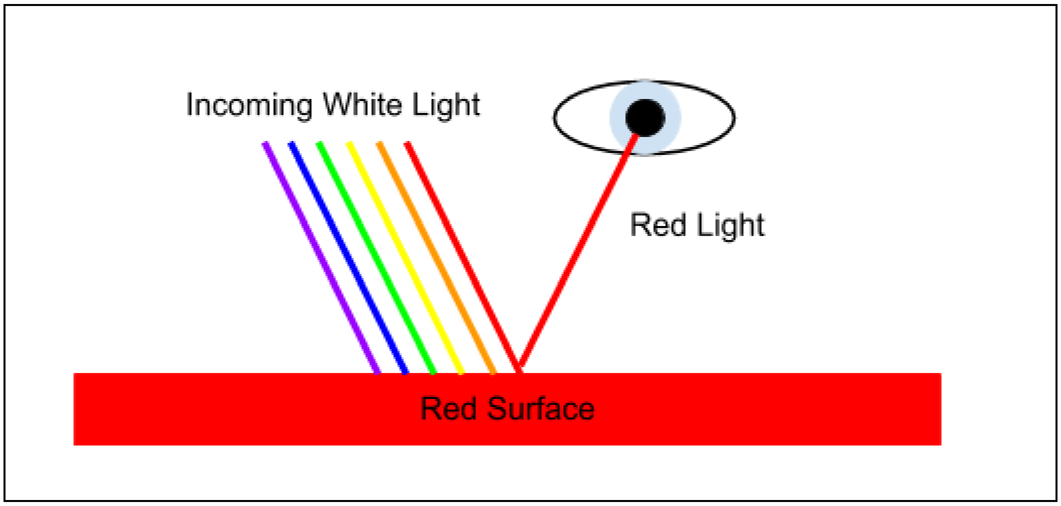
Example: The structure of methyl orange



Observing Coloured Compounds

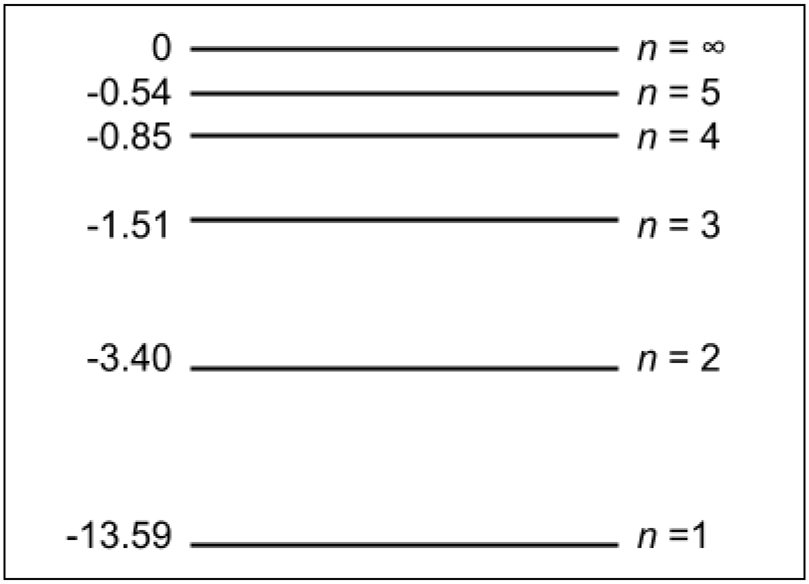
Colour arises because of how substances **absorb and reflect light**. When white light shines on a substance, some of the wavelengths of light are absorbed but the remaining wavelengths are reflected and **transmitted** to the human eye. These **reflected wavelengths correspond to a specific colour** which is then observed by the human eye.

Example:

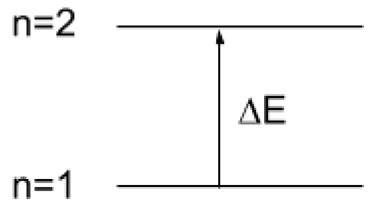


Electrons in the **d-orbital** exist in a series of energy states. When they are **given energy**, they move from the **ground state** (n=0) to a higher energy state called an **'excited state'**.

Example:



The change in energy, **ΔE**, between these states corresponds to a **wavelength and frequency** of light which can be calculated:



$$\boxed{\Delta E = \frac{hc}{\lambda} = h\upsilon}$$

where υ = frequency in hertz, λ = wavelength in meters, h = Planck's constant, 6.63×10^{-34}