CIE A Level Chemistry

Your notes

34.2 Phenylamine & Azo Compounds

Contents

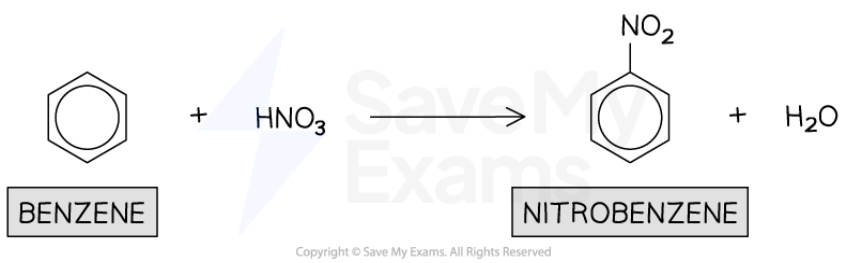
Production & Reactions of Phenylamine

Your notes

Preparation of Phenylamine

- **Phenylamine** is an organic compound consisting of a benzene ring and an **amine** (NH_2) functional group
- It can be produced in a **three-step synthesis** reaction followed by the separation of phenylamine from the reaction mixture
  - **Step 1 – Nitration**
    - Benzene undergoes **nitration** with concentrated nitric acid (HNO_3) and concentrated sulfuric acid (H_2SO_4) at 25 to 60 °C to form **nitrobenzene**

Nitration of benzene



Benzene forms nitrobenzene by reacting with the NO_2^+ electrophile formed by concentrated nitric acid and concentrated sulfuric acid

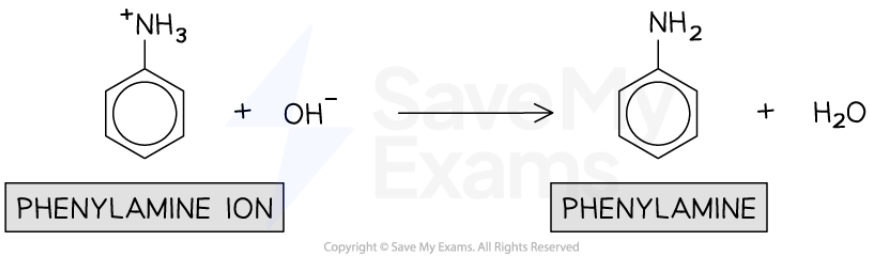
  - **Step 2 – Reduction**
    - Nitrobenzene is **reduced** with **hot tin** (Sn) and **concentrated hydrochloric acid** (HCl) **under reflux** to form an acidic mixture that contains the organic product $C_6H_5N^+H_3$

Reduction of nitrobenzene

Refluxing nitrobenzene with hot tin and concentrated hydrochloric acid forms the phenylamine ion

  - **Step 3 – Deprotonation**
    - Sodium hydroxide (NaOH) is added to the acidic reaction mixture to **deprotonate** the phenylamine ion to **phenylamine**

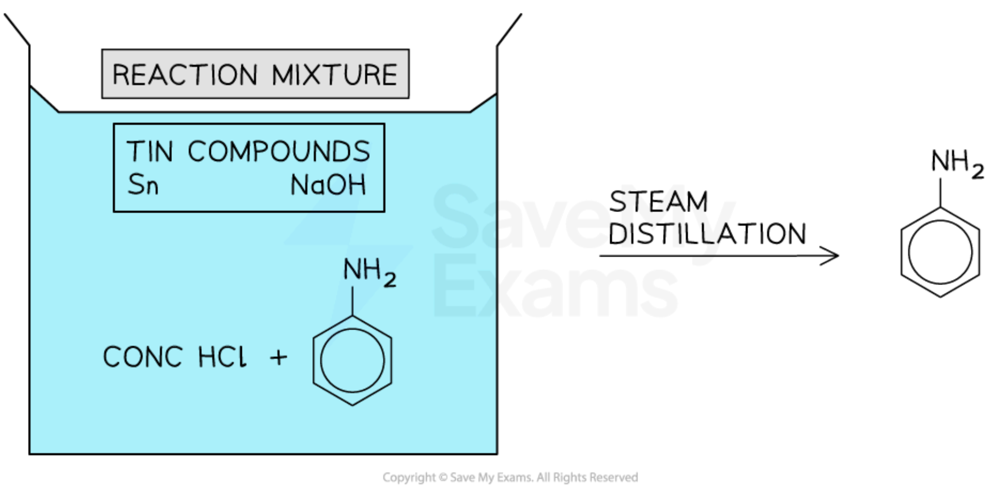
Deprotonation of the phenylamine ion



The hydroxide ion from sodium hydroxide deprotonates the phenylamine ion, forming the desired phenylamine

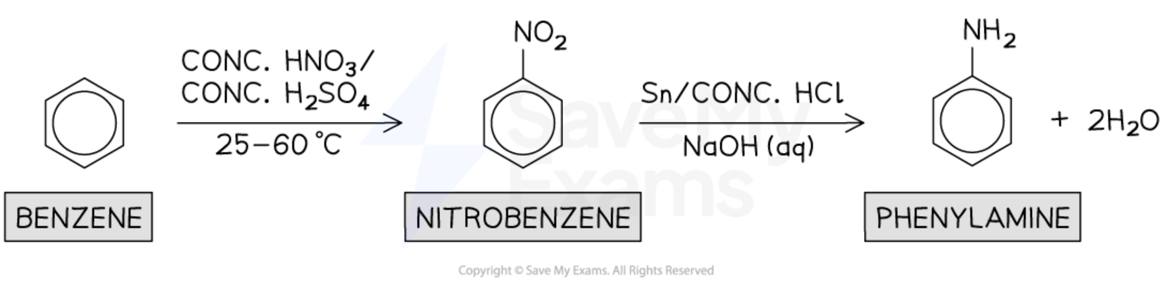
- **Separation / purification**
  - The phenylamine is then separated from the reaction mixture by **steam distillation**

Separation of phenylamine



Steam distillation is used to separate the phenylamine from the reaction mixture

The overall reaction forming phenylamine from benzene



The first reaction step is nitration and the second reaction step is reduction followed by deprotonation

Your notes

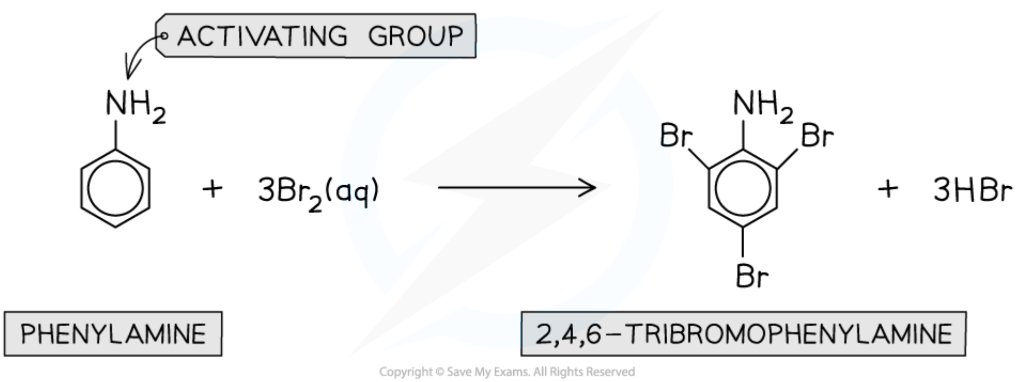
Reactions of Phenylamine

- Both the benzene ring as well as the -NH_2 group in **phenylamine** can take part in chemical reactions
- These reactions include
  - The **bromination** of phenylamine
  - Formation of a **diazonium salt**

Bromination of phenylamine

- Phenylamines react in **electrophilic substitution** reactions in a similar way as **phenols**
- The lone pair of electrons on the nitrogen atom in phenylamines donate electron density into the benzene ring
  - In phenols, the oxygen atom donates its lone pair of electrons instead
- The **delocalisation** of the electrons causes an **increased electron density** in the benzene ring
- The benzene ring, therefore, becomes **activated** and becomes more readily attacked by **electrophiles**
- The incoming electrophiles are directed to the 2,4 and 6 positions
- Phenylamines, therefore, react under milder conditions with **aqueous bromine** at **room temperature** to form 2,4,6–tribromophenylamine

Bromination of phenylamine



The bromination of phenylamine produces 2,4,6–tribromophenylamine

Formation of diazonium salt

- **Diazonium** compounds are very reactive compounds containing an -N_2^+ group
- The amine (-NH_2) group of phenylamines will react with **nitric(III) acid** (HNO_2) at a temperature below 10 °C to form **diazonium salts**
  - Since nitric(III) acid is unstable, it has to be made in the **test-tube** by reacting sodium nitrite ($NaNO_2$) and **dilute acid** (such as HCl)
- These **diazonium salts** are so unstable that they will, upon further warming with water, form **phenol**

Reacting nitrous acid with phenylamine to form a diazonium salt

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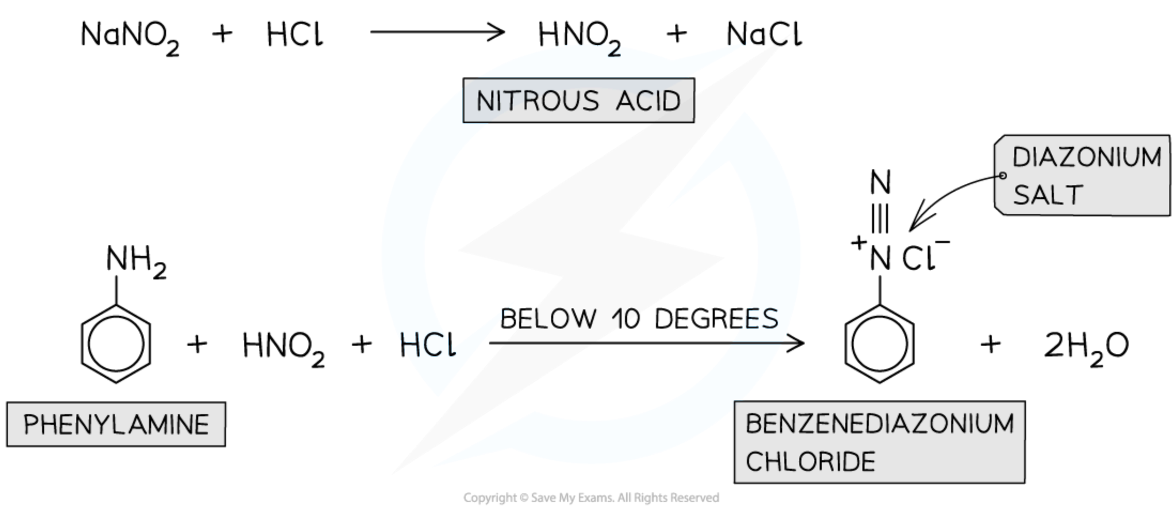

Phenylamine can form an unreactive diazonium salt which thermally decomposes to phenol

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Relative Basicity of Ammonia, Ethylamine & Phenylamine

Relative Basicity of Aqueous Ammonia, Ethylamine & Phenylamine

- Ammonia and amines act as **bases** as they can donate their lone pair of electrons to form a dative covalent bond with a proton
- The **basicity** of the amines depends on how readily available their lone pair of electrons is
- **Electron-donating** groups (such as alkyl groups) increase the electron density on the nitrogen atom and cause the lone pair of electrons to become **more** available for dative covalent bonding
  - The amine becomes **more** basic
- **Delocalisation** of the lone pair of electrons into an aromatic ring (such as a benzene ring) causes the lone pair of electrons to become **less** available for dative covalent bonding
  - The amine becomes **less** basic

Comparing basicity of ammonia, ethylamine & phenylamine

- The order of basicity of ammonia, ethylamine and phenylamine is as follows:

Ethylamine > **ammonia** **> phenylamine**

STRONGEST BASE WEAKEST BASE

- This trend can be explained by looking at the groups attached to the amine (-NH_2) group
- In ethylamine, the electron-donating alkyl group donates electron density to the nitrogen atom causing its lone pair to become more available to form a dative covalent bond with a proton
- Ammonia lacks an electron-donating group
  - Hence, it is less basic than ethylamine
  - However, it is more basic than phenylamine as the lone pair on the nitrogen is **not delocalised**
- In phenylamine, the lone pair of electrons overlap with the conjugated system on the benzene ring and become delocalised
  - As a result, the lone pair of electrons become less readily available to form a bond with a proton

Trends in the basicity of ammonia, ethylamine, and phenylamine

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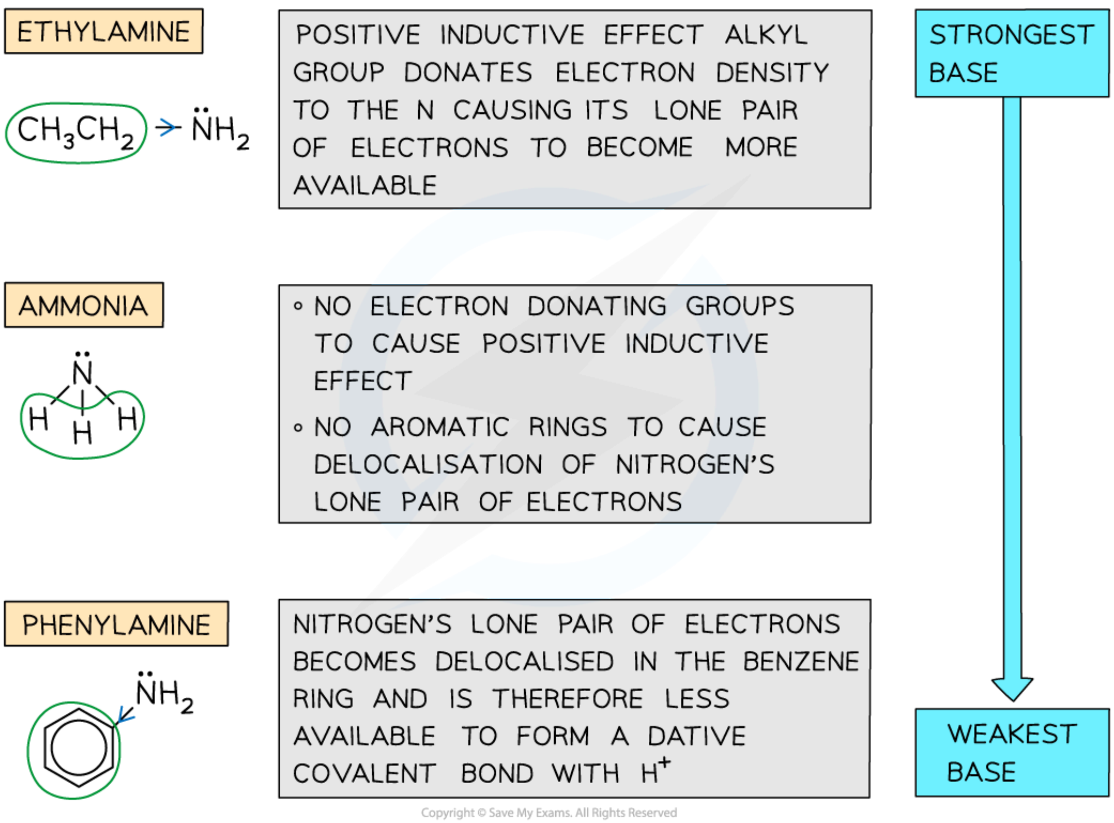

The positive inductive effect of electron donating groups increases the basicity of an amine, while the negative inductive effect of electron withdrawing groups decreases the basicity of an amine

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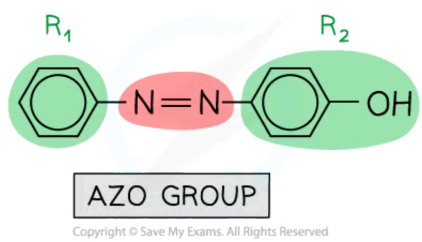
Azo Compounds

Azo Compounds

- **Azo** (or **diazonium**) **compounds** are organic compounds that have an R_1-N=N-R_2 group
- They are often used as **dyes** and are formed in a **coupling reaction** between the **diazonium ion** and an **alkaline solution** of **phenol**

Example compound containing an azo group

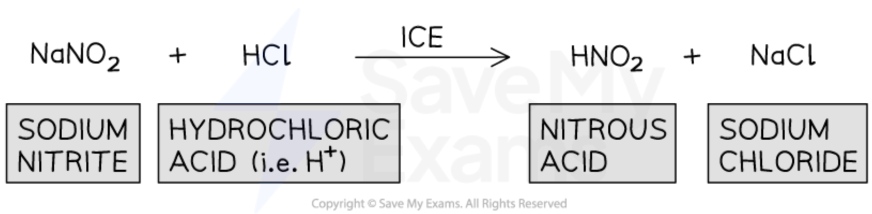


Azo compounds are characterized by the presence of an R_1-N=N-R_2 group

Coupling of benzenediazonium chloride with phenol in NaOH

- Azo compounds can be formed from the coupling reaction of a **benzenediazonium chloride salt** with **alkaline phenol**
- Making an azo dye is a **multi-step process**:
  - **Step 1 – Formation of nitrous acid**
    - The nitrous acid, HNO_2, is so unstable that it needs to be prepared in a test-tube by reacting sodium nitrite ($NaNO_2$) and dilute hydrochloric acid (HCl) while keeping the temperature below 10 °C using **ice**

Forming nitrous acid, HNO_2



Nitrous acid can be prepared in a test-tube by reacting sodium nitrate with dilute hydrochloric acid

- **Step 2 – Diazotisation**
  - This is the reaction between nitrous acid and phenylamine to form a diazonium ion
  - Dilute acid is used for this step, e.g. HCl
  - The reaction mixture must be kept < 10 °C using ice to prevent the diazonium ion from **thermally decomposing** to benzene and nitrogen

Forming benzenediazonium chloride

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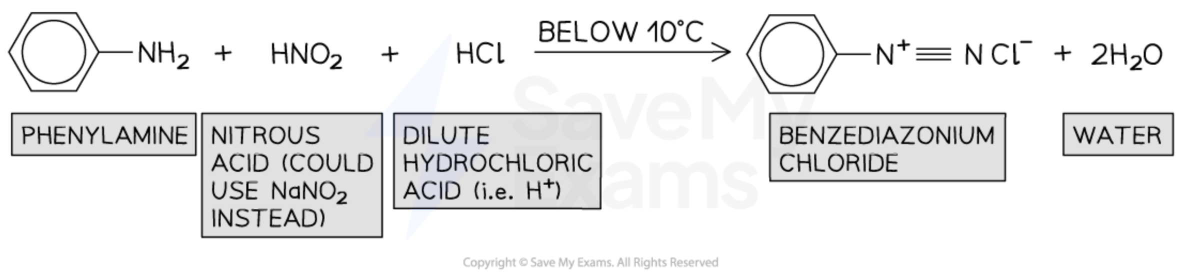
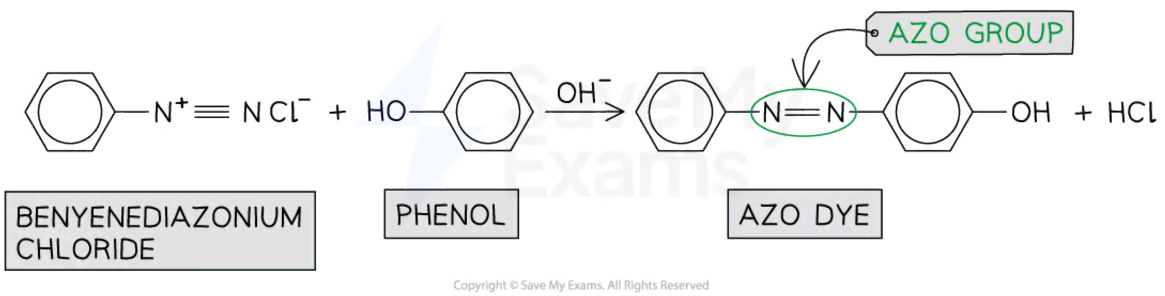


Benzenediazonium chloride is an unstable diazonium salt

- **Step 3 - Coupling reaction**
  - The diazonium ion acts as an **electrophile** and substitutes into the benzene ring of the **phenol**, at the 4th position
  - Alkaline conditions are required to deprotonate the organic product and form the **azo compound**

Forming the azo compound



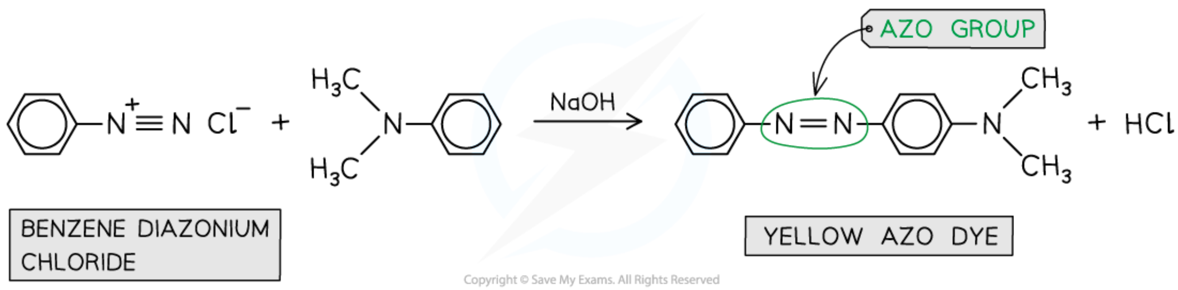
The azo compound is formed by the electrophilic substitution reaction of benzenediazonium chloride and phenol

- The **delocalised** electrons in the π bonding systems of the two benzene rings are **extended** through the -N=N- which acts as a **bridge** between the two rings
- As a result of the delocalisation of electrons throughout the compound, azo compounds are **very stable**

Making other azo dyes

- Other dyes can be formed via a **similar route** as described above
- For example, the **yellow dye** can be formed from the **coupling reaction** between **benzenediazonium chloride** and $\mathbf{C_6H_5N(CH_3)_2}$ instead of phenol (C_6H_5OH)

Making yellow azo dye



The yellow azo dye is formed via a coupling reaction between benzenediazonium chloride and $C_6H_5N(CH_3)_2$

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