3.11 AMINES

Preparation

Formation of aromatic amines

- Reduction of a nitro aromatic compound
  - React with tin metal and concentrated hydrochloric acid followed by an alkali
    - Obtains the aromatic amine from the salt

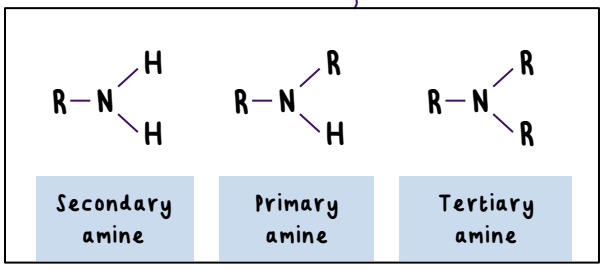
Formation of aliphatic amines

- Heat a halogenoalkane with ammonia
  - Nucleophilic substitution reaction
  - Produces a mix of primary, secondary and tertiary amines and quaternary ammonium salts
    - Excess ammonia favours primary amine
- Reduction of a nitrile
  - React with $LiAlH_4$ in a non-aqueous solvent
    - Followed by dilute acid
  - React with hydrogen and a nickel catalyst
    - Industrially, this method is generally chosen over $LiAlH_4$
      - This is because it is more affordable

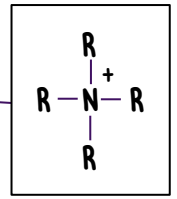
Structure

Organic derivatives of ammonia

- Amines are categorised as being primary, secondary or tertiary
  - Depends on how many of the H atoms are replaced by alkyl groups



- Quaternary ammonium salts are formed when the nitrogen atom forms four covalent bonds
  - Forms a positive ion



  - Quaternary ammonium salts are used as cationic surfactants
    - Used in fabric cleaners and hair products

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Base Properties

- Amines have a lone pair of electrons on the nitrogen atom
  - Lone pair can form a dative covalent bond with an H^+ ion
- Base strength depends on the availability of the lone pair of electrons
  - Ammonia is a stronger base than aromatic amines
    - On aromatic amines the nitrogen lone pair is delocalised into the benzene ring
      - Makes it less available to accept a proton
  - Primary aliphatic amines are stronger bases than ammonia
    - Alkyl groups push electrons towards the nitrogen atom
      - Positive inductive effect
        - Makes the lone pair more available to accept a proton

Nucleophilic Properties

- Amines are nucleophiles due to the lone pair of electrons on the nitrogen atom
  - Nucleophilic substitution reactions with halogenoalkanes
  - Nucleophilic addition–elimination reactions
    - Primary amines and ammonia with acyl chlorides and acid anhydrides

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