3.3.11 Amines

★ A-LEVEL ONLY — not examined at AS level

3.3.11.1 *Amine preparation: from halogenoalkanes, nitriles, and reduction of nitro compounds.*

From halogenoalkanes (excess NH3, sealed tube, heat): RX + 2NH3 → RNH2 + NH4X. Further substitution gives 2°, 3° amines and quaternary ammonium salts.

From nitriles (LiAlH4 in dry ether, or H2/Ni): RCN + 4[H] → RCH2NH2. Carbon chain extended by 1.

Aromatic amines from nitro compounds: ArNO2 + 6[H] → ArNH2 + 2H2O (Sn + conc. HCl, reflux). Used in manufacture of dyes and pharmaceuticals.

3.3.11.2 *Amines as weak bases. Basicity order: aliphatic > NH3 > aromatic.*

Amines are weak bases — the lone pair on N accepts H■.

Basicity order: aliphatic amine > NH3 > aromatic amine.

Aliphatic amines: alkyl group is electron-donating (+I effect) → increases electron density on N → lone pair more available for protonation → stronger base.

Aromatic amines: N lone pair delocalised into the benzene ring → less available → weaker base than NH3.

3.3.11.3 *Amines as nucleophiles: with halogenoalkanes, acyl chlorides and acid anhydrides. Mechanisms.*

With halogenoalkanes: nucleophilic substitution → 2°, 3° amines and quaternary ammonium salts.

Quaternary ammonium salts (R4N■X■): cationic surfactants — positively charged head attracts negatively charged surfaces (fabric conditioners, disinfectants).

With acyl chlorides/acid anhydrides: nucleophilic addition–elimination → amides (RCONHR' + HCl).

Mechanism: lone pair on N attacks δ+C of C=O. Curly arrows from lone pair → C=O π-bond breaks → leaving group departs.