9701 CHEMISTRY · TOPICS 19 & 33 · AS + A LEVEL

Nitrogen Compounds

01 · AMINES — BASICITY

The nitrogen lone pair accepts a proton, so amines are bases: $RNH_2 + HCl \rightarrow RNH_3^+Cl^-$.

Strength order: alkylamine > ammonia > phenylamine. Alkyl groups **release** electrons, making the lone pair more available; in phenylamine the lone pair is delocalised into the ring, so it is far less available.

02 · MAKING AMINES

From a halogenoalkane
RBr + excess NH_3 in ethanol, sealed tube, heat → RNH_2
Excess ammonia limits further substitution.

From a nitrile
$RCN + 4[H] \rightarrow RCH_2NH_2$ · $LiAlH_4$ or H_2/Ni

Phenylamine from nitrobenzene
$C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$
Sn and concentrated HCl, reflux, then NaOH.

03 · REACTIONS OF AMINES

As a **base** with acids to give salts; as a **nucleophile** with halogenoalkanes and with acyl chlorides, giving N-substituted amides.

Phenylamine gives a white precipitate with bromine water without a catalyst — the $-NH_2$ activates the ring.

04 · AMIDES

$RCONH_2$. The nitrogen lone pair is delocalised onto the C=O, so amides are **neutral, not basic** — a favourite exam contrast with amines.

Hydrolysis: with dilute HCl under reflux → carboxylic acid + NH_4^+; with NaOH(aq) → carboxylate salt + NH_3. Reduction with $LiAlH_4$ gives an amine.

05 · NITRILES

$RC{\equiv}N$. Made from a halogenoalkane with KCN in ethanol, or from a carbonyl with HCN — both **add one carbon** to the chain.

Hydrolysis with dilute acid under reflux gives a carboxylic acid; **reduction** with $LiAlH_4$ or H_2/Ni gives a primary amine. That makes nitriles the hinge of most chain-lengthening routes.

06 · AMINO ACIDS

$RCH(NH_2)COOH$ — one basic and one acidic group in the same molecule. All except glycine have a chiral carbon, so they are optically active.

In the solid and at intermediate pH they exist as a **zwitterion**, $^+H_3N–CHR–COO^-$, which is why they have high melting points and dissolve in water rather than in organic solvents.

07 · AMINO ACIDS AND PH

Low pH — the $–COO^-$ takes H^+
$^+H_3N–CHR–COOH$ · a cation, moves to the cathode

Isoelectric point — the zwitterion, no net charge, does not move

High pH — the $^+H_3N–$ loses H^+
$H_2N–CHR–COO^-$ · an anion, moves to the anode

This is the basis of electrophoresis.

08 · PEPTIDES AND PROTEINS

Two amino acids join by **condensation**, losing water and forming a **peptide (amide) link** –CONH–. Two amino acids can give two different dipeptides depending on which $–NH_2$ reacts.

Hydrolysis with 6 mol dm^{-3} HCl under reflux for several hours breaks a protein back into its amino acids, which are then separated by chromatography or electrophoresis.

09 · PROTEIN STRUCTURE

Primary — the sequence of amino acids, held by peptide bonds.

Secondary — α-helix or β-pleated sheet, held by hydrogen bonds between C=O and N–H.

Tertiary — the overall fold, held by hydrogen bonds, ionic attractions between side chains, London forces and disulfide bridges. Heat or extremes of pH break these and denature the protein.

10 · WORKED EXAMPLE — DEDUCE THE ROUTE

Convert bromoethane into propylamine.

The product has one more carbon, so go through a nitrile.

1 · KCN in ethanol, reflux → propanenitrile
2 · $LiAlH_4$ in dry ether (or H_2/Ni) → propylamine

Reacting bromoethane with ammonia directly would give ethylamine — the same number of carbons, so it fails.

11 · EQUATIONS TO KNOW

$C_2H_5Br + 2NH_3 \rightarrow C_2H_5NH_2 + NH_4Br$
$CH_3CN + 4[H] \rightarrow CH_3CH_2NH_2$
$C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$
$C_2H_5NH_2 + HCl \rightarrow C_2H_5NH_3^+Cl^-$

$CH_3CONH_2 + HCl + H_2O \rightarrow CH_3COOH + NH_4Cl$
$CH_3CONH_2 + NaOH \rightarrow CH_3COONa + NH_3$
$CH_3CN + 2H_2O + HCl \rightarrow CH_3COOH + NH_4Cl$

12 · COMPARING THE NITROGEN GROUPS

Group	Lone pair	Behaviour
alkylamine	available	strong base
ammonia	available	base
phenylamine	into the ring	weak base
amide	onto the C=O	neutral

Every one of these follows from a single question: how available is the nitrogen lone pair?

MARKS LOST HERE

— Calling amides basic; the lone pair is delocalised onto the carbonyl.

— Explaining phenylamine's weakness without mentioning delocalisation into the ring.

— Drawing an amino acid as the neutral form when the question asks for the solid or the isoelectric point.

— Forgetting that alkaline hydrolysis of an amide releases ammonia, not the ammonium salt.