Topic 18: Organic Chemistry III

Edexcel A Level Chemistry • Paper 1 (9CH0/01)

18.1

Understand that benzene bonding has been represented using Kekulé and delocalised models.

Kekulé model: benzene represented as cyclohexatriene with alternating C=C and C–C bonds. This model is incorrect because it predicts benzene should readily undergo electrophilic addition (like alkenes) and have two different C–C bond lengths — neither is observed.

Delocalised model: each carbon is sp^2 hybridised with one p-orbital perpendicular to the ring. The six p-orbitals overlap sideways to form a delocalised π-system above and below the plane of the ring. Electrons are shared equally around all six carbons, giving benzene extra thermodynamic stability.

18.2

Understand that evidence for delocalisation comes from enthalpy of hydrogenation data and bond length data.

Enthalpy of hydrogenation evidence: if benzene were cyclohexatriene (Kekulé), its ΔH of hydrogenation would be approximately 3 × (ΔH for cyclohexene) = 3 × (–120) = –360 kJ mol^{-1}. The actual measured value is only –208 kJ mol^{-1}. The difference (152 kJ mol^{-1}) is the delocalisation energy — benzene is this much more stable than predicted by the Kekulé structure.

Bond length evidence: all C–C bonds in benzene are equal length at 140 pm, intermediate between a C–C single bond (154 pm) and a C=C double bond (134 pm). The Kekulé model would predict alternating short (double) and long (single) bonds.

18.3

Understand why benzene is resistant to bromination compared to alkenes.

In alkenes: the π-bond is localised between two carbons — high electron density at one point → readily attacked by electrophiles → electrophilic addition occurs easily.

In benzene: the π-electrons are delocalised over all six carbons — electron density is spread out and less concentrated → weaker attraction for electrophiles. Also, addition would destroy the stable delocalised ring (losing 152 kJ mol^{-1} of stabilisation), which is thermodynamically unfavourable. Therefore benzene undergoes electrophilic substitution (preserving the ring) rather than addition, and requires a catalyst (halogen carrier) to generate a strong enough electrophile.

© Chemistry with Chloe | chemistrywithchloe.com
For personal educational use only. Not for redistribution.

18.4 Understand reactions of benzene with: (i) O_2, (ii) Br_2/catalyst, (iii) conc. HNO_3/H_2SO_4, (iv) halogenoalkanes and acyl chlorides with $AlCl_3$.

(i) Combustion with O_2: benzene burns with a smoky, sooty flame (high C:H ratio — incomplete combustion).

(ii) Bromination: $C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$. Catalyst: $AlBr_3$ or $FeBr_3$ (halogen carrier). Electrophilic substitution.

(iii) Nitration: $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$. Catalyst: conc. H_2SO_4. Temperature: ~50°C (above 55°C gives dinitration). Electrophile = NO_2^+ (nitronium ion), generated by: $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$.

(iv) Friedel-Crafts alkylation: $C_6H_6 + RCl \rightarrow C_6H_5R + HCl$. Catalyst: $AlCl_3$. Friedel-Crafts acylation: $C_6H_6 + RCOCl \rightarrow C_6H_5COR + HCl$. Catalyst: $AlCl_3$.

18.5 Understand the mechanism of electrophilic substitution of benzene (halogenation, nitration, Friedel-Crafts).

General mechanism (4 steps):

1. Generate the electrophile (E^+).
2. Electrophile attacks the delocalised π-system: curly arrow from ring to E^+ → forms a positively charged intermediate (arenium ion) with E and H both bonded to the ring. The ring is temporarily non-aromatic.
3. Intermediate loses H^+: curly arrow from C–H bond back into the ring, restoring aromaticity.
4. E is now substituted into the ring; HX (or $H^+ + X^-$) is eliminated.

Electrophile generation:

- Halogenation: $Br_2 + AlBr_3 \rightarrow Br^+ + AlBr_4^-$
- Nitration: $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$
- Friedel-Crafts: $RCl + AlCl_3 \rightarrow R^+ + AlCl_4^-$ (or RCO^+ for acylation)

18.6 Understand the reaction of phenol with bromine water.

Phenol reacts with bromine water (no catalyst needed) to give 2,4,6-tribromophenol (white precipitate) + 3HBr. The bromine water is decolourised. Three positions on the ring are substituted simultaneously. This is in stark contrast to benzene, which requires a catalyst and only monosubstitutes under normal conditions.

18.7 Understand reasons for the relative ease of bromination of phenol compared to benzene.

The –OH group on phenol donates a lone pair of electrons from the oxygen into the benzene ring via p-orbital overlap. This increases the electron density of the ring, particularly at the 2, 4 and 6 positions (ortho and para). The ring becomes much more attractive to electrophiles and the activation energy for attack is lowered. Therefore no catalyst is needed, and three substitutions occur readily with bromine water alone.

© Chemistry with Chloe | chemistrywithchloe.com
For personal educational use only. Not for redistribution.

18.8 Be able to identify: (i) amine and amide functional groups, (ii) amino acids.

Amine: contains $–NH_2$ (primary), –NHR (secondary), or $–NR_2$ (tertiary). Suffix –amine or prefix amino-. Acts as a base (lone pair on N accepts H^+).

Amide: contains $–CONH_2$ (primary amide), –CONHR, or $–CONR_2$. A C=O bonded directly to N. Suffix –amide.

Amino acid: contains both an $–NH_2$ group AND a –COOH group on the same molecule. In α-amino acids, both groups are on the carbon adjacent to the COOH (the α-carbon).

18.9 Understand reactions of primary aliphatic amines with: (i) water, (ii) acids, (iii) ethanoyl chloride, (iv) halogenoalkanes, (v) Cu^{2+} ions.

(i) + Water: $RNH_2 + H_2O \quad RNH_3^+ + OH^-$. Weakly alkaline solution; the lone pair on N accepts H^+ from water.

(ii) + Acids: $RNH_2 + HCl \rightarrow RNH_3^+Cl^-$ (salt formation; amine acts as a base).

(iii) + Ethanoyl chloride: $RNH_2 + CH_3COCl \rightarrow CH_3CONHR + HCl$. N-substituted amide formed.

(iv) + Halogenoalkanes: $RNH_2 + R'X \rightarrow R'NHR + HX$ (secondary amine formed; further substitution can give tertiary amines and quaternary ammonium salts).

(v) + Cu^{2+} ions: the amine acts as a ligand, donating its lone pair on N to Cu^{2+} to form a deep blue complex ion.

18.10 Understand reasons for the difference in basicity of ammonia, primary aliphatic and primary aromatic amines.

Basicity order: aliphatic amine > ammonia > aromatic amine.

Aliphatic amines (e.g. CH_3NH_2): the alkyl group is electron-donating (positive inductive effect), increasing the electron density on the N lone pair → better proton acceptor → stronger base than NH_3.

Aromatic amines (e.g. $C_6H_5NH_2$, phenylamine): the N lone pair is delocalised into the benzene ring (p-orbital overlap) → less available to accept a proton → much weaker base than NH_3.

18.11 Understand the preparation of primary aliphatic amines: (i) from halogenoalkanes, (ii) by reduction of nitriles.

(i) From halogenoalkanes: $RX + 2NH_3 \rightarrow RNH_2 + NH_4X$. Heat with excess concentrated ammonia in a sealed tube. Excess NH_3 minimises further substitution to secondary/tertiary amines.

(ii) Reduction of nitriles: $RCN + 4[H] \rightarrow RCH_2NH_2$. Reduce using $LiAlH_4$ in dry ether or H_2/Ni catalyst. Gives a primary amine with one more carbon than the nitrile (chain extension by one C).

18.12 Know that aromatic nitro-compounds can be reduced to form amines using tin and concentrated HCl.

$ArNO_2 + 6[H] \rightarrow ArNH_2 + 2H_2O$

Reagents: tin (Sn) and concentrated hydrochloric acid (HCl). Heat under reflux. The Sn/HCl acts as the reducing agent. Produces the aromatic amine (e.g. nitrobenzene → phenylamine, $C_6H_5NH_2$). The product is initially formed as a salt; treat with excess NaOH to liberate the free amine.

© Chemistry with Chloe | chemistrywithchloe.com
For personal educational use only. Not for redistribution.

18.13 Understand that amides can be prepared from acyl chlorides.

$RCOCl + NH_3 \rightarrow RCONH_2 + HCl$ (primary amide).

$RCOCl + RNH_2 \rightarrow RCONHR + HCl$ (N-substituted/secondary amide).

Reactions are vigorous at room temperature with no catalyst needed. The HCl produced gives steamy white fumes.

18.14 Know that polyamide formation is a condensation polymerisation reaction.

A polyamide (e.g. nylon-6,6) forms by condensation polymerisation between a dicarboxylic acid (or diacyl chloride) and a diamine. An amide bond (–CONH–) forms at each link with loss of H_2O (or HCl if using acyl chloride). Proteins are natural polyamides — amino acids linked by peptide bonds (–CONH–).

18.15 Be able to draw repeat units of condensation polymers formed by: (i) dicarboxylic acids + diols, (ii) dicarboxylic acids + diamines, (iii) amino acids.

(i) Polyester: repeat unit shows –COO– ester link with continuation bonds extending from each end. Loss of H_2O at each link.

(ii) Polyamide: repeat unit shows –CONH– amide link with continuation bonds. Loss of H_2O at each link.

(iii) From amino acids: each amino acid has both $–NH_2$ and –COOH, so condenses with the next to form a peptide bond (–CONH–). The repeat unit contains one amino acid residue. Loss of H_2O at each peptide bond.

Always show the bonds extending from the repeat unit and indicate loss of nH_2O.

18.16 Understand properties of 2-amino acids: (i) zwitterion formation, (ii) effect on plane-polarised light.

(i) Zwitterion: at neutral pH, the $–NH_2$ group is protonated ($–NH_3^+$) and the –COOH is deprotonated ($–COO^-$), forming an internal salt (zwitterion). This explains the high melting points (ionic interactions) and water solubility of amino acids. In acid solution: NH_3^+ and COOH (overall positive ion). In alkaline solution: NH_2 and COO^- (overall negative ion). Amino acids are amphoteric.

(ii) All amino acids except glycine have a chiral α-carbon (four different groups) → optically active → rotate plane-polarised light.

18.17 Understand that the peptide bond in proteins: (i) is formed by condensation, (ii) can be hydrolysed and products separated by chromatography.

(i) Amino acids join by condensation: the –COOH of one amino acid reacts with the $–NH_2$ of another, forming a peptide bond (–CONH–) with loss of H_2O. Proteins are polypeptides (long chains).

(ii) Hydrolysis of proteins: heat with 6 mol dm^{-3} HCl under reflux → breaks all peptide bonds → mixture of individual amino acids. Separate and identify the amino acids by chromatography (e.g. TLC or paper chromatography) by comparing Rf values with known amino acid standards.

© Chemistry with Chloe | chemistrywithchloe.com
For personal educational use only. Not for redistribution.

18.18 Be able to deduce empirical, molecular and structural formulae from combustion analysis, elemental composition, functional group tests, IR, mass spec and NMR data.

Combine analytical techniques systematically:

- Mass spectrum: Mr from M^+ peak; fragmentation identifies groups present.
- IR spectrum: identifies functional groups (broad O–H, sharp C=O, N–H, etc.).
- Combustion analysis / elemental %: divide each % by Ar → mole ratio → empirical formula. Use Mr to find molecular formula.
- NMR: number of environments, integration ratios, splitting patterns → connectivity.
- Chemical tests: confirm functional groups (2,4-DNPH for C=O, bromine water for C=C, Tollens' for aldehyde, etc.).

Always state your reasoning at each step and build the structure systematically.

18.19 Be able to plan reaction schemes, of up to four steps, to form familiar and unfamiliar compounds.

Key synthetic routes to know for multi-step syntheses:

- Alkene → alcohol (steam/H_3PO_4) → halogenoalkane (PCl_5 or HBr) → nitrile (KCN) → carboxylic acid (acid hydrolysis) or amine ($LiAlH_4$)
- Alcohol → aldehyde ($K_2Cr_2O_7$, distil) → carboxylic acid ($K_2Cr_2O_7$, reflux)
- Halogenoalkane → amine (excess NH_3) or alcohol (aq KOH) or alkene (ethanolic KOH)
- Carboxylic acid → ester (alcohol + H_2SO_4) or acyl chloride (PCl_5) or primary alcohol ($LiAlH_4$)
- Halogenoalkane → Grignard (Mg/dry ether) → carboxylic acid (CO_2 then H^+) or alcohol (carbonyl compound then H^+)

Always state: reagents, conditions, and intermediate products for each step.

18.20 Understand methods of increasing carbon chain length using Grignard reagents and their reactions with CO_2 and carbonyl compounds.

Grignard reagent formation: RX + Mg → RMgX (in dry ether). The Grignard reagent is destroyed by water — dry ether solvent is essential throughout.

Reactions:

- RMgX + CO_2 → $RCOO^-MgX^+$, then acid hydrolysis → RCOOH. Carboxylic acid with one extra carbon.
- RMgX + HCHO → primary alcohol (after acid hydrolysis).
- RMgX + R'CHO → secondary alcohol (after acid hydrolysis).
- RMgX + R'COR'' → tertiary alcohol (after acid hydrolysis).

All Grignard reactions extend the carbon chain and are followed by acid hydrolysis to give the final product.

© Chemistry with Chloe | chemistrywithchloe.com
For personal educational use only. Not for redistribution.

18.21 Be able to select and justify practical procedures for reactions, including identifying control measures to reduce risk.

Choose appropriate techniques for each synthetic step and justify them:

- Flammable solvents (e.g. ether, ethanol): no naked flames; use water bath or electric heating.
- Toxic/corrosive chemicals (e.g. conc. HCl, acyl chlorides, HCN): use fume cupboard; wear gloves and goggles.
- Volatile products: work in fume cupboard; use ice bath to collect distillate.
- Exothermic reactions: add reagents slowly; cool if necessary.
- Grignard: must use rigorously dry apparatus and solvents; moisture destroys the Grignard reagent.

Always link each hazard to a specific risk and a specific precaution.

18.22 Understand techniques for preparation and purification: reflux, washing, extraction, recrystallisation, drying, distillation (including steam), melting and boiling point determination.

(i) Reflux: heating in a flask with a vertical condenser. Vapour condenses and returns. Allows prolonged heating without loss of volatile substances.

(ii) Washing (separating funnel): removes water-soluble impurities (e.g. wash with $NaHCO_3$ to remove acid, then water).

(iii) Solvent extraction: dissolve product in an immiscible organic solvent; separate layers.

(iv) Recrystallisation: dissolve impure solid in minimum hot solvent; filter hot to remove insoluble impurities; cool slowly to crystallise pure product; filter and dry.

(v) Drying: add anhydrous drying agent (e.g. $MgSO_4$, $CaCl_2$) to organic liquid; filter off before distillation.

(vi) Distillation/steam distillation: separate by boiling point; steam distillation for heat-sensitive products.

(vii) Melting/boiling point: compare with literature value to confirm identity and assess purity. Pure substances have sharp, reproducible m.p. values.

Analysis of Some Inorganic and Organic Unknowns (A2 Level)

The Preparation of Aspirin

ABOUT THESE NOTES

Notes written by Chloe Archard (MSc Biochemistry, Oxford-trained chemist, 20+ years teaching experience at top UK independent schools). For 1-1 tuition, revision courses, and more free resources: chemistrywithchloe.com

© Chemistry with Chloe | chemistrywithchloe.com
For personal educational use only. Not for redistribution.