2.11 Chemistry: Aromatic Chemistry, Carbonyls and Amines

AQA 7405 · Calculator allowed · about 140 minutes · Write-in edition

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 Phenol reacts rapidly with bromine water at room temperature, without the need for a halogen-carrier catalyst, to give an immediate white precipitate. Benzene does not react with bromine water under these conditions.

(a) Explain, in terms of the interaction between the oxygen lone pair and the ring, why phenol is far more reactive than benzene towards electrophilic substitution. **(3)**

(b) Identify the organic product formed when phenol reacts with excess bromine water, and give its molecular formula. **(2)**

(c) State the electrophile involved in the reaction between phenol and bromine water, and explain why this electrophile does not need to be generated using a halogen-carrier catalyst (unlike the bromination of benzene). **(2)**

(Total for Question 1 is 7 marks)

2 Propanal, CH_3CH_2CHO, and propanone, CH_3COCH_3, are both reduced by aqueous sodium tetrahydridoborate(III), $NaBH_4$, to alcohols.

(a) Describe the mechanism for the reduction of propanal by $NaBH_4$, including the role of the hydride ion. **(4)**

(b) State a reagent, and the conditions needed, that would distinguish propanal from propanone using a simple test-tube test, and state what would be observed with propanal. **(3)**

(c) 2,4-dinitrophenylhydrazine (Brady's reagent) reacts with propanal (and with propanone) to give an orange precipitate, confirming the presence of a carbonyl group but not distinguishing between the two compounds. Explain how this orange precipitate could then be used to identify which specific carbonyl compound (e.g. propanal or propanone) was originally present. **(2)**

(d) Calculate the atom economy for the conversion of propanone, C_3H_6O (Mr = 58), into propan-2-ol, C_3H_8O (Mr = 60), by reduction, treating the overall reaction as simple addition of H_2 (Mr = 2) across the C=O bond, with propan-2-ol as the only product. **(2)**

(Total for Question 2 is 11 marks)

---

3 Glycine (aminoethanoic acid), H_2NCH_2COOH, is the simplest naturally occurring amino acid.

(a) Define the term 'zwitterion' and state the type of ion glycine forms at its isoelectric point. **(2)**

(b) Explain why glycine exists mainly as a cation in strongly acidic solution, but mainly as an anion in strongly alkaline solution. **(3)**

(c) Glycine and alanine can react together to form a dipeptide. State the type of reaction that occurs and name the type of linkage formed between the two amino acid residues. **(2)**

(Total for Question 3 is 7 marks)

4 Poly(ethylene terephthalate), PET, is a polyester formed from benzene-1,4-dicarboxylic acid (terephthalic acid) and ethane-1,2-diol. Nylon-6,6 is a polyamide formed from hexanedioic acid and 1,6-diaminohexane.

(a) Identify the type of polymerisation that forms PET, and state the small molecule released during its formation. **(3)**

(b) Write an equation to show the formation of one amide (peptide-type) linkage between one molecule of hexanedioic acid and one molecule of 1,6-diaminohexane, identifying the small molecule by-product. **(3)**

(c) Evaluate the environmental impact of using condensation polymers such as PET and nylon in packaging and clothing, compared with using naturally occurring materials, and discuss strategies that could be used to reduce this impact. **(6)**

(Total for Question 4 is 12 marks)

5 Compound Q is an amine used as a precursor in a pharmaceutical synthesis route. Compound Q contains only carbon, hydrogen and nitrogen. Complete combustion of 12.1 g of Q produces 35.2 g of carbon dioxide and 9.9 g of water. On combustion analysis, all of the nitrogen in Q is converted to gaseous nitrogen, N_2, and 1.40 g of N_2 is also collected.

(a) Calculate the empirical formula of compound Q. **(4)**

(b) Given that the relative molecular mass, Mr, of compound Q is 121, determine its molecular formula. **(1)**

(c) Compound Q reacts with dilute hydrochloric acid to form a soluble salt. Suggest the class of organic compound to which Q belongs. **(1)**

(Total for Question 5 is 6 marks)

6 A four-step synthetic route converts benzene into 1-phenylethylamine, $C_6H_5CH(NH_2)CH_3$, as follows. Step 1: benzene -> phenylethanone ($C_6H_5COCH_3$), using ethanoyl chloride and a catalyst. Step 2: phenylethanone -> 1-phenylethanol, $C_6H_5CH(OH)CH_3$, using $NaBH_4$. Step 3: 1-phenylethanol -> (1-chloroethyl)benzene, $C_6H_5CHClCH_3$, using a suitable chlorinating reagent. Step 4: (1-chloroethyl)benzene -> 1-phenylethylamine, using excess ethanolic ammonia.

(a) Name the catalyst used in Step 1, state the type of mechanism, and describe the catalyst's role in generating the electrophile. **(3)**

(b) State the type of reaction occurring in Step 2, and identify the nucleophile involved in its mechanism. **(2)**

(c) Name a suitable reagent for Step 3, and state one observation that might be made during this reaction. **(2)**

(d) Explain why, in Step 4, the ammonia used must be (i) in excess and (ii) dissolved in ethanol rather than water. **(2)**

(e) Calculate the atom economy of Step 4, given Mr[(1-chloroethyl)benzene] = 140.5, Mr(NH_3) = 17.0, Mr(1-phenylethylamine) = 121, and Mr(HCl) = 36.5, if only 1-phenylethylamine is considered the desired product. **(3)**

(Total for Question 6 is 12 marks)

7 Benzene reacts with a mixture of concentrated nitric acid and concentrated sulfuric acid to form nitrobenzene.

(a) State the conditions used for this nitration reaction. **(2)**

(b) Write an equation to show how the electrophile is generated from nitric acid in the presence of sulfuric acid. **(2)**

(c) Describe the mechanism for the nitration of benzene by the electrophile NO_2^+, including the structure of the intermediate formed. **(4)**

(d) Nitration of methylbenzene occurs faster than nitration of benzene, and gives mainly a mixture of 2-nitromethylbenzene and 4-nitromethylbenzene (with very little of the 3-isomer). Explain, in terms of the effect of the methyl group on the ring, (i) why methylbenzene reacts faster than benzene and (ii) why substitution occurs mainly at the 2- and 4-positions. **(4)**

(Total for Question 7 is 12 marks)

8 Ethanoic acid reacts with phosphorus(V) chloride, PCl_5, to form ethanoyl chloride, CH_3COCl.

(a) Write a balanced equation for this reaction and state what would be observed. **(3)**

(b) Ethanoyl chloride reacts with water far more readily (violently) than an ester such as ethyl ethanoate does. Explain, in terms of the bonding and leaving group involved, why acyl chlorides are much more reactive towards nucleophiles such as water than esters. **(3)**

(c) A 2.50 g sample of ethyl butanoate, $C_6H_{12}O_2$ (Mr = 116), is completely hydrolysed by refluxing with an excess of water in the presence of a dilute acid catalyst. Calculate the maximum mass of butanoic acid, $C_4H_8O_2$ (Mr = 88), that could be formed. **(3)**

(d) State the other organic product formed in this hydrolysis. **(1)**

(Total for Question 8 is 10 marks)

9 Ethylamine, ammonia and phenylamine differ considerably in their base strength.

(a) Explain, in terms of the availability of the nitrogen lone pair, why ethylamine is a stronger base than ammonia, and why phenylamine is a weaker base than ammonia. **(4)**

(b) State the type of mechanism occurring when bromoethane reacts with excess ethanolic ammonia to form ethylamine. **(1)**

(c) Explain why an excess of ammonia (rather than an excess of bromoethane) is used in this reaction. **(2)**

(d) Chloromethane can be converted into ethylamine by a two-step route. In step 1, chloromethane reacts with potassium cyanide dissolved in ethanol, under reflux. State the type of mechanism for this step and name the organic product formed. **(2)**

(e) State a suitable reagent and condition for step 2, the reduction of this nitrile to ethylamine. **(1)**

(Total for Question 9 is 10 marks)

10 Triethylamine, $(C_2H_5)_3N$, reacts with excess chloromethane, CH_3Cl, to form a quaternary ammonium salt.

(a) Write an equation for this reaction, and state the type of bond formed between the nitrogen atom and the new methyl group. **(3)**

(b) Quaternary ammonium salts with one long hydrocarbon chain and three short alkyl/methyl groups are used industrially as cationic surfactants (e.g. in fabric conditioners). Suggest, in terms of its structure, why such a compound can act as a surfactant. **(2)**

(c) Nitrobenzene can be converted into phenylamine (aniline) in the laboratory. Outline the two steps of a suitable synthetic route, including the reagents and conditions for the reduction step. **(2)**

(d) State one safety hazard of this reduction and one precaution that should be taken. **(2)**

(Total for Question 10 is 9 marks)

Mark scheme · 2.11 Chemistry: Aromatic Chemistry, Carbonyls and Amines

Question 1

(a) one of the lone pairs on the oxygen atom of the -OH group overlaps with (is delocalised into) the ring π system **B1**

(a) this increases the electron density of the delocalised ring, particularly at the 2-, 4- and 6- positions **B1**

(a) so the ring more strongly polarises/attracts electrophiles such as Br_2, so no halogen-carrier catalyst is needed and reaction occurs readily at room temperature **B1**

(a) Answer: The oxygen lone pair delocalises into the ring, increasing electron density (especially at 2/4/6 positions), so phenol reacts with electrophiles such as Br_2 far more readily than benzene, without a catalyst.

(b) 2,4,6-tribromophenol **B1**

(b) $C_6H_3Br_3O$ **B1**

(b) Answer: 2,4,6-tribromophenol, $C_6H_3Br_3O$

(c) electrophile is Br+ (a bromine atom carrying a partial/full positive charge) **B1**

(c) the electron-rich ring of phenol polarises the Br-Br bond sufficiently on its own (induces a dipole in Br_2) for heterolytic fission to occur, so a catalyst (e.g. $FeBr_3$/$AlBr_3$) is not required **B1**

(c) Answer: Br+ (from polarisation of Br_2 by the electron-rich ring); phenol's ring is electron-rich enough to induce the necessary polarisation of Br-Br itself, without a halogen-carrier catalyst.

Question 2

(a) $NaBH_4$ provides a hydride ion, H-, which acts as a nucleophile **B1**

(a) the carbon atom of the C=O group is delta-positive (polarised, due to oxygen being more electronegative), so it is attacked by the hydride ion **B1**

(a) a new C-H bond forms as the hydride ion's electron pair moves to carbon, while the electron pair in the C=O π bond moves onto the oxygen, forming an alkoxide ion intermediate **B1**

(a) the alkoxide ion is then protonated (by water or on addition of dilute acid) to give the alcohol product, propan-1-ol **B1**

(a) Answer: H- (nucleophile) attacks the delta+ carbonyl carbon; the C=O π electrons move onto O forming an alkoxide intermediate, which is then protonated to give propan-1-ol.

(b) Tollens' reagent (ammoniacal silver nitrate) **B1**

(b) warmed (in a water bath) **B1**

(b) propanal gives a silver mirror (Ag^+ reduced to Ag), while propanone gives no visible change/no silver mirror **B1**

(b) Answer: Tollens' reagent, warmed: propanal (an aldehyde) forms a silver mirror; propanone (a ketone) gives no reaction.

(c) the orange precipitate (2,4-dinitrophenylhydrazone derivative) is recrystallised to purify it, and its melting point is measured **B1**

(c) the measured melting point is compared with data book (literature) values of melting points of known 2,4-dinitrophenylhydrazone derivatives, to identify which specific aldehyde/ketone was present **B1**

(c) Answer: Purify (recrystallise) the derivative, measure its melting point, and match this against data book values for known derivatives to identify the specific carbonyl compound.

(d) atom economy = (Mr of desired product / sum of Mr of all reactants) x 100 = 60 / (58 + 2) x 100 **M1**

(d) = 100% **A1**

(d) Answer: Atom economy = 100%

Question 3

(a) a zwitterion is a species (molecule) that carries both a positive and a negative charge (on different atoms within the same species), with an overall net charge of zero **B1**

(a) at its isoelectric point, glycine exists predominantly as the zwitterion, $+H_3NCH_2COO-$ **B1**

(a) Answer: A zwitterion carries both a positive and a negative charge but has zero overall net charge; at its isoelectric point glycine exists mainly as the zwitterion $+H_3NCH_2COO-$.

(b) in strongly acidic solution, there is a high concentration of H^+ ions, which protonates the $-NH_2$ (or -COO-) group, giving the fully protonated cation, $+H_3NCH_2COOH$ **B1**

(b) in strongly alkaline solution, there is a high concentration of OH^- ions, which removes/accepts a proton from the -COOH (or $-NH_3^+$) group, giving the fully deprotonated anion, H_2NCH_2COO- **B1**

(b) the position of these acid-base equilibria shifts depending on the pH (H^+ concentration) of the solution, so the dominant species present changes with pH **B1**

(b) Answer: In strongly acidic solution, excess H^+ protonates the amine/carboxylate group to give the cation $+H_3NCH_2COOH$; in strongly alkaline solution, OH^- removes a proton from the ammonium/acid group to give the anion H_2NCH_2COO-.

(c) condensation reaction (with loss of a molecule of water) **B1**

(c) peptide bond (amide linkage) **B1**

(c) Answer: Condensation reaction (loss of H_2O); a peptide (amide) bond is formed.

Question 4

(a) condensation polymerisation **B1**

(a) water, H_2O, is released (at each ester linkage formed) **B1**

(a) the polymer chain contains repeating ester linkages (-C(=O)-O-) formed between the -COOH groups of the diacid and the -OH groups of the diol **B1**

(a) Answer: Condensation polymerisation; water is released at each ester linkage formed between the diacid and the diol.

(b) $HOOC-(CH_2)_4-COOH + H_2N-(CH_2)_6-NH_2 \rightarrow HOOC-(CH_2)_4-CONH-(CH_2)_6-NH_2 + H_2O$ **M1**

(b) structure correctly shows one new amide (-CONH-) linkage formed, with one -COOH and one $-NH_2$ group remaining unreacted at the ends **A1**

(b) water, H_2O, identified as the by-product **B1**

(b) Answer: $HOOC-(CH_2)_4-COOH + H_2N-(CH_2)_6-NH_2 \rightarrow HOOC-(CH_2)_4-CONH-(CH_2)_6-NH_2 + H_2O$

(c) **L3** A well-developed, balanced evaluation is given, covering both environmental drawbacks and possible benefits/counterpoints, together with at least two distinct, relevant strategies to reduce impact, supported by chemical reasoning (e.g. reference to bond types/structure). The answer is coherent and logically structured throughout. **5-6**

(c) **L2** A reasonably clear discussion is given, covering some environmental drawbacks and at least one relevant strategy to reduce impact, with some supporting reasoning. The answer shows some structure but may lack balance or full development. **3-4**

(c) **L1** Basic, isolated relevant points are made (e.g. a simple statement that polymers do not biodegrade, or one disposal method named), with little or no supporting reasoning or structure. **1-2**

(c) **L0** No relevant content, or the response does not address the question. **0**

(c) Indicative content:

- Condensation polymers such as PET and nylon are generally not readily biodegradable, as microorganisms lack enzymes able to break the ester/amide linkages quickly, unlike many naturally occurring polymers such as cellulose or proteins, which are broken down by natural enzymes/organisms, so they persist in landfill or the environment for a very long time
- Most condensation polymers are made from non-renewable, fossil-fuel-derived monomers (crude oil feedstocks), depleting finite resources and contributing to carbon dioxide emissions during their manufacture
- However, condensation polymers such as PET are strong, lightweight and durable, which can reduce material use, food waste (via effective packaging/preservation) and transport emissions compared with heavier or less durable natural-material alternatives, so a straightforward comparison is not always fair
- Strategy: mechanical recycling - used PET/nylon items can be collected, cleaned, melted and reformed into new products, reducing the demand for virgin monomers/crude oil and reducing landfill waste
- Strategy: chemical recycling (hydrolysis) - the ester/amide linkages in used PET or nylon can be hydrolysed back into their original monomers (the diacid and diol/diamine), which can then be re-polymerised, in principle allowing indefinite reuse of the same atoms
- Strategy: development and use of biodegradable polyesters (e.g. those containing more easily hydrolysed linkages, or blends with natural biodegradable polymers) as substitutes in single-use applications
- Strategy: incineration with energy recovery, as an alternative to landfill, though this releases CO_2 and requires careful control of emissions
- A balanced evaluation should weigh the durability/resource benefits of these polymers against their persistence and fossil-fuel origin, and recognise that no single disposal strategy solves the whole problem

(c) Answer: Awarded via levels of response (0-6) against the indicative content: a full-mark answer balances drawbacks (non-biodegradability, fossil-fuel origin) against benefits (durability, reduced waste elsewhere), and gives at least two well-explained reduction strategies (e.g. mechanical recycling, chemical hydrolysis/re-polymerisation, biodegradable alternatives, energy recovery).

Question 5

(a) moles CO_2 = 35.2 / 44 = 0.800 mol, so moles C = 0.800 mol **M1**

(a) moles H_2O = 9.9 / 18 = 0.550 mol, so moles H = 2 x 0.550 = 1.10 mol **M1**

(a) moles N_2 = 1.40 / 28 = 0.0500 mol, so moles N = 2 x 0.0500 = 0.100 mol **M1**

(a) ratio C : H : N = 0.800 : 1.10 : 0.100 = 8 : 11 : 1, so empirical formula = $C_8H_{11}N$ **A1**

(a) Answer: Empirical formula = $C_8H_{11}N$

(b) empirical formula mass of $C_8H_{11}N$ = (8x12)+(11x1)+14 = 121, which equals the given Mr, so the molecular formula is the same as the empirical formula, $C_8H_{11}N$; ft their empirical formula from (a) if the mass matches **B1**

(b) Answer: Molecular formula = $C_8H_{11}N$

(c) an amine (the nitrogen lone pair accepts a proton from HCl to form an ammonium/aminium salt, characteristic of amines) **B1**

(c) Answer: Q is an amine.

Question 6

(a) aluminium chloride, $AlCl_3$ (a halogen carrier) **B1**

(a) electrophilic substitution (Friedel-Crafts acylation) **B1**

(a) $AlCl_3$ accepts a lone pair of electrons from the chlorine atom of ethanoyl chloride (CH_3COCl), polarising and breaking the C-Cl bond to generate the acylium ion, CH_3CO+, as the electrophile (and $[AlCl_4]^-$) **B1**

(a) Answer: $AlCl_3$ (halogen carrier catalyst); Friedel-Crafts acylation (electrophilic substitution); $AlCl_3$ accepts a lone pair from Cl in CH_3COCl, generating the electrophile CH_3CO+ and $[AlCl_4]^-$.

(b) reduction (nucleophilic addition) **B1**

(b) hydride ion, H- (from $NaBH_4$) **B1**

(b) Answer: Reduction, by nucleophilic addition; the nucleophile is the hydride ion, H-.

(c) phosphorus(V) chloride, PCl_5 (accept $SOCl_2$ or PCl_3) **B1**

(c) steamy white fumes (of HCl) are seen (if using PCl_5 or $SOCl_2$) **B1**

(c) Answer: PCl_5 (or $SOCl_2$); steamy white fumes of HCl are observed.

(d) (i) excess ammonia favours reaction of the haloalkane with NH_3 rather than with the primary amine product formed, minimising further substitution to secondary/tertiary amines or a quaternary ammonium salt **B1**

(d) (ii) an aqueous solvent would allow water (a nucleophile) to compete with ammonia in a hydrolysis side reaction with the haloalkane (substitution by OH^-, giving the alcohol back); ethanol dissolves both the organic haloalkane and ammonia without this competing reaction **B1**

(d) Answer: (i) Excess NH_3 minimises further nucleophilic substitution to secondary/tertiary amines or a quaternary salt. (ii) Ethanol (rather than water) avoids competing hydrolysis of the haloalkane by water and dissolves both reactants.

(e) sum of Mr of reactants = 140.5 + 17.0 = 157.5 **M1**

(e) atom economy = (Mr desired product / sum Mr reactants) x 100 = (121 / 157.5) x 100 **M1**

(e) = 76.8% (awrt 76.8-76.9%) **A1**

(e) Answer: Atom economy = 76.8%

Question 7

(a) concentrated nitric acid and concentrated sulfuric acid (as a catalyst) used together **B1**

(a) temperature kept at or below about 50°C (reflux); higher temperatures/prolonged heating cause further substitution to give dinitrobenzene products oe **B1**

(a) Answer: Conc. HNO_3 + conc. H_2SO_4 (catalyst), maintained at around 50°C.

(b) $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$ (state symbols not required) **M1**

(b) correctly balanced with NO_2^+ identified as the electrophile (nitronium ion) **A1**

(b) Answer: $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

(c) NO_2^+ is attracted to/attacks the delocalised π electron ring (electrophilic attack) **B1**

(c) a pair of electrons from the ring forms a new C-N bond to the nitrogen of NO_2^+ **B1**

(c) this generates a positively charged intermediate (arenium/Wheland ion) in which the delocalised ring system now extends over only five carbon atoms (the ring is no longer fully aromatic; positive charge delocalised over the remaining five carbons) **B1**

(c) a proton, H^+, is lost from the carbon bearing both the H and the NO_2 group, which restores the full delocalised aromatic ring, regenerating a catalytic H^+ that reforms H_2SO_4 with HSO_4^- **B1**

(c) Answer: NO_2^+ attacks the ring; a C-N bond forms, breaking full delocalisation and giving a positively charged arenium intermediate (delocalised over 5 C); loss of H^+ restores the aromatic ring, regenerating the H_2SO_4 catalyst.

(d) the methyl group is electron-donating (positive inductive/hyperconjugative effect), which increases the electron density of the delocalised ring π system **B1**

(d) this makes the ring more strongly attract (more strongly polarise) the electrophile NO_2^+, so the reaction is faster than with benzene **B1**

(d) the increase in electron density is greatest at the carbon atoms ortho (2-) and para (4-) to the methyl group oe **B1**

(d) so the arenium (Wheland) intermediates formed by attack at the 2- and 4- positions are more stabilised/lower in energy than attack at the 3-position, so 2- and 4- substitution predominate **B1**

(d) Answer: The methyl group donates electron density into the ring (activating it, so reaction is faster than benzene) and increases electron density most at the 2- and 4- positions, favouring attack (and forming more stable intermediates) there rather than at the 3-position.

Question 8

(a) $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$ **M1**

(a) correctly balanced (all species; state symbols not required) **A1**

(a) steamy white fumes (of HCl gas) are observed **B1**

(a) Answer: $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$; steamy white fumes of HCl are seen.

(b) in both compounds, water (a nucleophile) attacks the delta-positive carbonyl carbon (nucleophilic addition-elimination) **B1**

(b) chlorine is more electronegative than oxygen, so it withdraws electron density more strongly from the carbonyl carbon in the acyl chloride, making that carbon more delta-positive/more strongly attacked by the nucleophile than in an ester **B1**

(b) chloride ion, Cl^-, is also a much better/more stable leaving group than the alkoxide/RO- group that would have to leave in the corresponding step for an ester, so elimination occurs much more readily for the acyl chloride **B1**

(b) Answer: The more electronegative Cl makes the carbonyl carbon of an acyl chloride more strongly delta+ than in an ester, and Cl^- is a far better leaving group than RO-, so acyl chlorides react with nucleophiles like water much faster than esters do.

(c) moles of ethyl butanoate = 2.50 / 116 = 0.02155 mol **M1**

(c) since the ratio of ester : acid is 1:1, mass of butanoic acid = 0.02155 x 88 **M1**

(c) = 1.90 g (3 sf) **A1**

(c) Answer: Maximum mass of butanoic acid = 1.90 g

(d) ethanol **B1**

(d) Answer: Ethanol

Question 9

(a) ethylamine: the ethyl group is electron-donating (positive inductive effect), pushing electron density onto the nitrogen atom **B1**

(a) this increases the electron density (availability) of the nitrogen lone pair in ethylamine, making it more able to accept (form a dative bond with) a proton, H^+, than the lone pair in ammonia **B1**

(a) phenylamine: the nitrogen lone pair overlaps with (is partially delocalised into) the aromatic ring's π system **B1**

(a) this reduces the electron density/availability of the lone pair on nitrogen in phenylamine, making it much less able to accept a proton than the lone pair in ammonia **B1**

(a) Answer: Ethylamine's alkyl group donates electron density onto N, making its lone pair more available (stronger base than ammonia); phenylamine's N lone pair delocalises into the ring, making it far less available (weaker base than ammonia).

(b) nucleophilic substitution **B1**

(b) Answer: Nucleophilic substitution

(c) ethylamine formed is itself a nucleophile and could go on to react further with remaining bromoethane, giving secondary/tertiary amines and eventually a quaternary ammonium salt **B1**

(c) using excess ammonia makes it far more likely that a molecule of bromoethane reacts with an ammonia molecule than with an ethylamine molecule, so further substitution is minimised and the primary amine is favoured as the major product **B1**

(c) Answer: Ethylamine can itself act as a nucleophile towards unreacted bromoethane; a large excess of ammonia makes it much more likely a bromoethane molecule reacts with ammonia rather than with product amine, minimising further substitution to secondary/tertiary amines or quaternary salts.

(d) nucleophilic substitution **B1**

(d) ethanenitrile, CH_3CN (accept: a nitrile) **B1**

(d) Answer: Nucleophilic substitution; the product is ethanenitrile, CH_3CN.

(e) $LiAlH_4$ (lithium tetrahydridoaluminate) in dry ether (or: H_2 gas with a Ni catalyst, heat/pressure); either accepted **B1**

(e) Answer: $LiAlH_4$ in dry ether (or H_2/Ni catalyst).

Question 10

(a) $(C_2H_5)_3N + CH_3Cl \rightarrow (C_2H_5)_3(CH_3)N^+ Cl^-$ **M1**

(a) correctly balanced, with the ionic product shown as a salt (cation and Cl^- anion) **A1**

(a) dative covalent (coordinate) bond **B1**

(a) Answer: $(C_2H_5)_3N + CH_3Cl \rightarrow (C_2H_5)_3(CH_3)N^+ Cl^-$; the N-$CH_3$ bond formed is a dative covalent (coordinate) bond.

(b) the molecule has an ionic, charged (hydrophilic) 'head' at the nitrogen, which can interact with/dissolve in water **B1**

(b) and a long, non-polar hydrocarbon (hydrophobic) 'tail', which can interact with/dissolve in oils, grease or the surface of fabric fibres, allowing the molecule to bridge between polar and non-polar environments **B1**

(b) Answer: It has a charged, hydrophilic 'head' (the N+ centre) that associates with water, and a long, hydrophobic hydrocarbon 'tail' that associates with grease/fabric, so the molecule can bridge water and non-polar surfaces like a surfactant.

(c) Step 1: nitrobenzene is heated under reflux with tin (or another suitable reducing metal) and excess concentrated hydrochloric acid, reducing the nitro group to give a salt of phenylamine (the anilinium/phenylammonium salt) **B1**

(c) Step 2: excess concentrated sodium hydroxide solution is then added, to liberate the free phenylamine base (which may be separated by steam distillation) **B1**

(c) Answer: Reflux nitrobenzene with tin and excess conc. HCl (reduction, forming the anilinium salt); then add excess NaOH(aq) to release free phenylamine.

(d) hazard: concentrated hydrochloric acid is corrosive (heated under reflux, so hot corrosive vapours/liquid are present); nitrobenzene and phenylamine are both toxic/harmful **B1**

(d) precaution: carry out the procedure in a fume cupboard and wear eye protection/gloves, any sensible matching precaution **B1**

(d) Answer: Concentrated HCl is corrosive and nitrobenzene/phenylamine are toxic; the reduction should be carried out in a fume cupboard with eye protection and gloves.