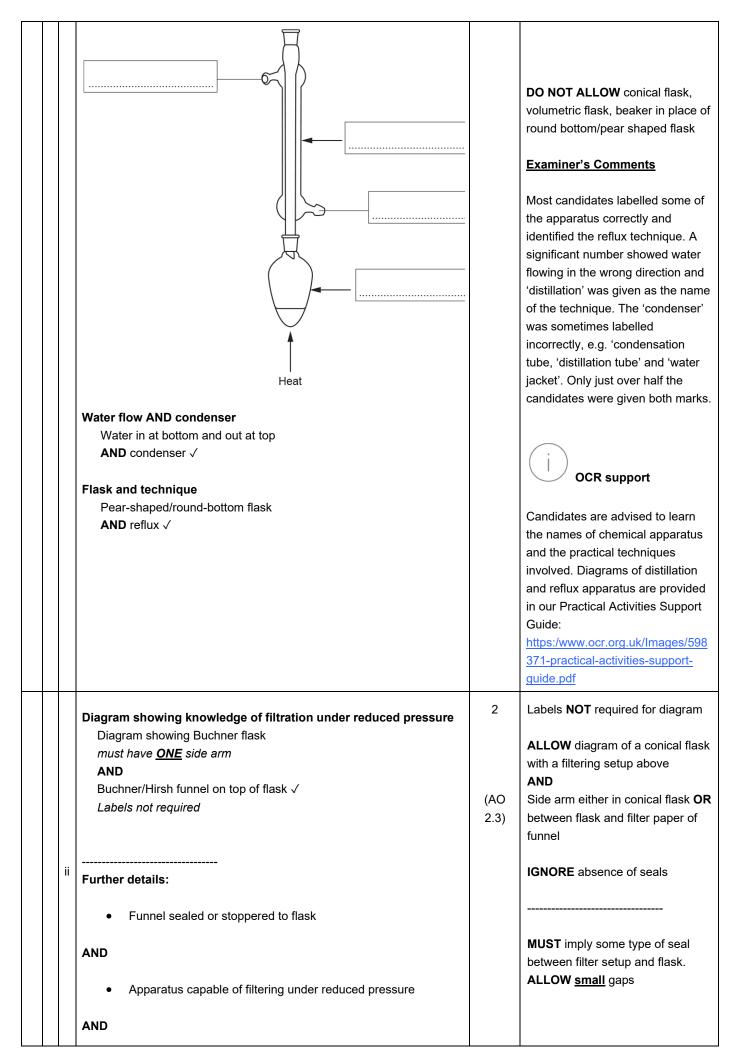
Mark scheme - Synthesis

	Questi on		Answer/Indicative content	Marks	Guidance
1	а		$ \begin{array}{c} $	5 (AO2.5 ×5)	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous
			$ \begin{array}{c} $		ALLOW for the bottom left structure NH ₃ Br CH H ₃ C CH ₃
	b	i	Ester Amide Amine Carboxylic acid 4 groups correct ✓ ✓ ✓ 3 groups correct ✓ ✓ 2 groups correct ✓	3 (AO1.2 ×3)	IGNORE amino acid ALLOW carboxyl IGNORE attempt to classify amide, e.g. secondary IGNORE formulae (question asks for names) IF > 4 functional groups are shown, • Count 4 groups max but incorrect groups first IGNORE aryl OR alkyl group e.g. benzene, phenyl, aryl, arene, methyl
		ii	Methanol 1 mark $H_3C - OH \checkmark$ $H_{OOC} + NH_2 + HOOC + NH_3$ $OR + OOC + NH_3 + V + V + V + V + V + V + V + V + V + $	4 (AO2.5 ×4)	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW + charge on H of NH ₃ group, i.e.NH ₃ ⁺

		HOOC COOH OR HOOC COOH $$ Both amino acids shown with NH ₃ ⁺ \checkmark		If BOTH amino acids are shown with NH ₃ groups (without the + charge) OR as NH ₂ ⁺ groups, award 2 of the 3 marks for the amino acids If BOTH amino acids are shown as correctly balanced salts, e.g NH ₃ Cl, all marks can be awarded.
	ii i	FIRST CHECK ANSWER ON THE ANSWER LINE If answer = 22.4 OR 22 OR 23 award 3 marks n(aspartame) in 1 can = $0.167 / 294 = 5.68 \times 10^{-4} \pmod{\sqrt{10}} \sqrt{10}$ n(aspartame) limit per day = $1.7 \times 10^{-4} \times 75 = 0.01275 \pmod{\sqrt{10}} \sqrt{10}$ number of cans = $0.01275 / 5.68 \times 10^{-4} = 22.4 \sqrt{10}$	3 (AO2.2 ×3)	If there is an alternative answer, apply ECF and look for alternative methods Alternative methods n(aspartame) in 1 can = 0.167 / 294 = 5.68 x 10 ⁻⁴ (mol) \checkmark n(aspartame) per kg = 5.68 x 10 ⁻⁴ / 75 = 7.57 x 10 ⁻⁶ (mol) \checkmark number of cans = 1.7 x 10 ⁻⁴ / 7.57 x 10 ⁻⁶ = 22.4 \checkmark OR n(aspartame) limit per day = $1.7x10^{-4} x 75$ =0.01275 (mol) \checkmark mass(aspartame) limit per day =0.01275 x 294 = 3.7485 (g) \checkmark number of cans = 3.7485 / 0.167 = 22.4 \checkmark
		Total	15	
2	i		2 (AO 1.2x2)	



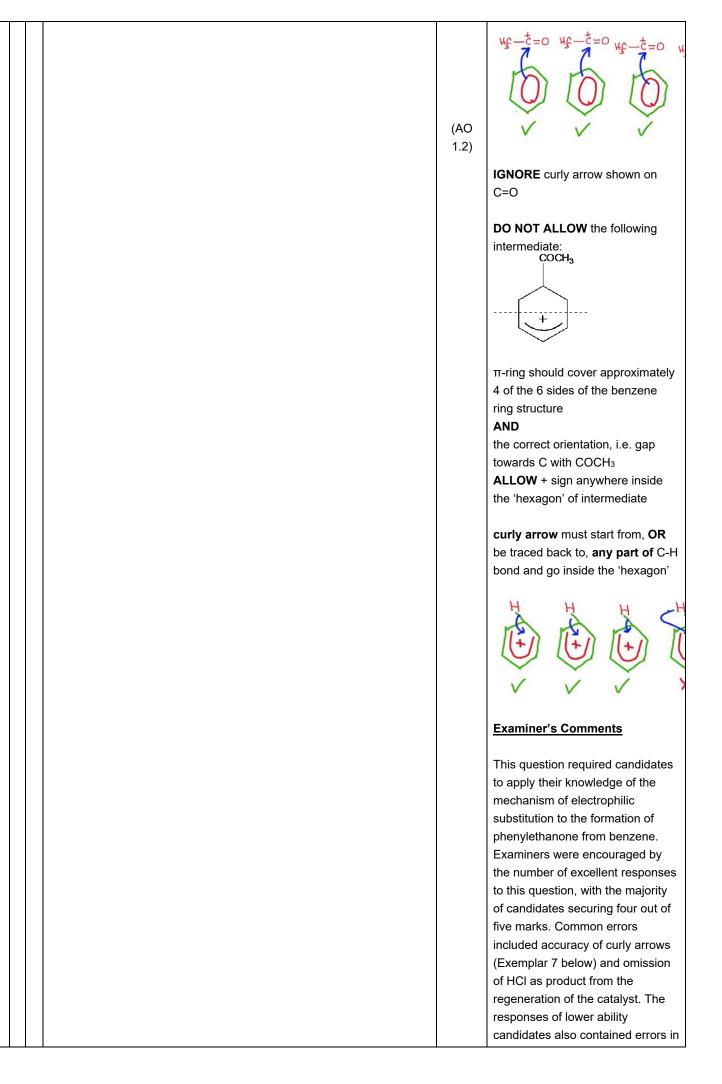
		• Label for setup from side arm to indicate reduced pressure AND • Label for Buchner flask OR Buchner/Hirsh funnel √ <i>ALOW slips in spelling of 'Buchner'</i>	(AO 2.7)	Examples of suitable labels (may have arrow from side arm or tube attached) • to pump • to vacuum • air out • suction • reduced pressure • etc. For Buchner flask and Buchner funnel DO NOT ALLOW just 'flask OR 'funnel' <i>Flask and funnel used in normal</i> <i>filtration</i> Examiner's Comments Many diagrams were incomplete and it was comparatively rare for both of the two available marks to be given. Important labels were often missing. Some candidates drew diagrams of other techniques, such as distillation. Many responses were not credited with marks and this question was often omitted. Candidates need practice in recognising practical techniques and in drawing acceptable diagrams.
		Total	4	
3	i	К С Н	1 AO 2.5	DO NOT ALLOW more than one * ALLOW a circle for * Examiner's Comments Most candidates showed one asterisk at the base of the cyclic part of the structure. The most common error was to show two asterisks, the second being on *C(CH ₃) ₂ OH, despite this carbon not being connected to four different groups.

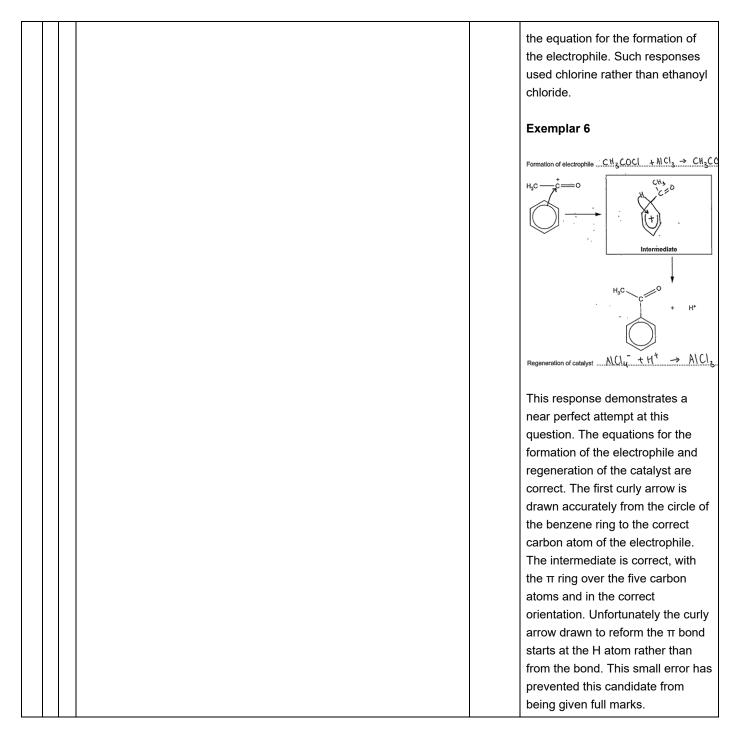
				IGNORE no H attached to C=C
				IGNORE functional',
				i.e. ALLOW different functional groups
				gioups
				ALLOW in context of groups with
				largest atomic number ORA
				Award BOTH identification
				marks for:
	MAXIMUM OF 4 MARKS FROM 5 MARKING POINTS			Z- isomer AND (high) priority
				groups on same side
	Requirement for <i>E/Z</i> isomerism 2	marks		Mark independently of previous
				part
	C=C/double bond \checkmark		4	
		ha	·	Response MUST be linked to the
	Each C (in C=C) is attached to (two) different groups/at	toms √		ring/cyclic structure
			AO1.2	IGNORE just 'E isomer is
	Identification as <i>E</i> - or <i>Z</i> - isomer 2	marks	x2	impossible'
ii	<i>E/</i> Z isomerism linked to (high) priority groups \checkmark			IGNORE C=C bond cannot rotate
				IGNORE Groups can't swap side
	Z- isomer AND groups are on same side			
	OR the ring carbons \checkmark		AO2.5	Examiner's Comments
	Descent when the first is such as the second state of the second		x2	Ore didates disulated a second
	Reason why other <i>E/Z</i> isomer does not exist 1 mark ring would be strained			Candidates displayed a good knowledge of the requirements for
	OR ring would break/deform			E/Z isomerism in terms of a C=C
	OR Cannot form ring if high priority groups are on op	posite		double bond and different groups
	sides			on the carbon atoms of the C=C
	OR ring locks groups on one side of C=C bond \checkmark			bond. Many assigned terpineol a
				the Z isomer explained in terms of the priority groups being on the
				same side of the C=C bond.
				Candidates found it difficult to
				explain why terpineol has only or
				<i>E</i> / <i>Z</i> isomer. Many candidates
				thought that the C=C bond could not rotate because it was part of
				the ring. however, a C=C bond
				cannot rotate whether it is in a rir
				or not. Few candidates considered
				the strain put on the ring if the
				priority groups (being part of the
				ring) were to be placed in an <i>E</i> conformation.

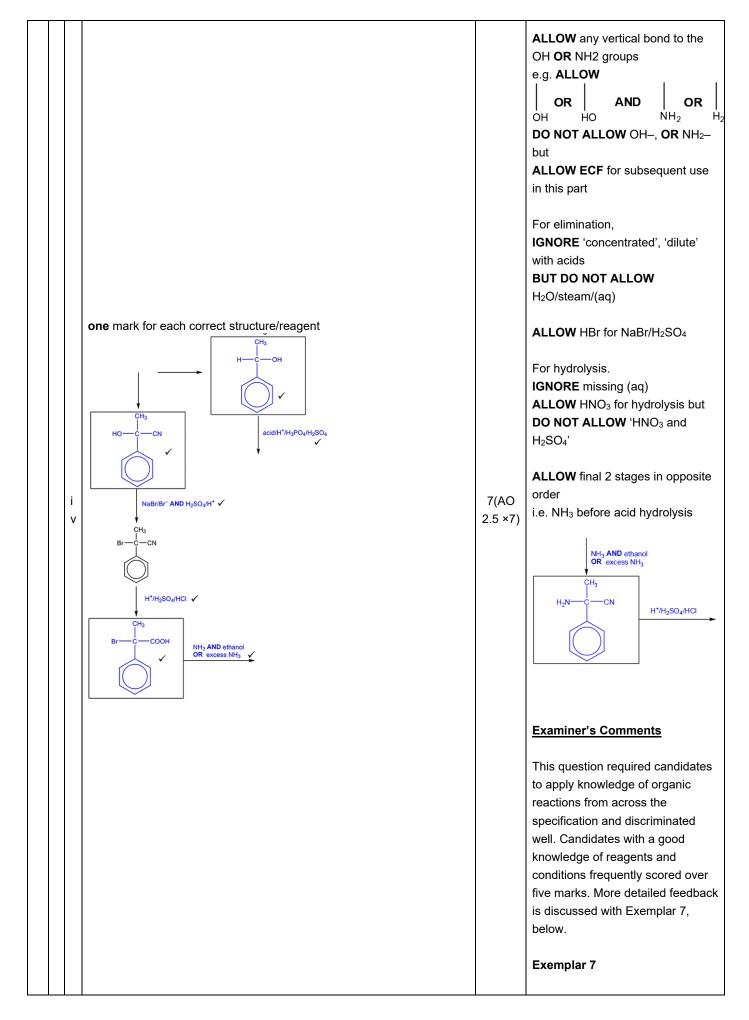
				CONTACT TEAM LEADER FO
				ALLOW GROUPS EITHER WA
				Functional group MUST be nam
First	group: Reagent AND Functional group: Alkene OR c	ycloalkene √		DO NOT ALLOW UV with halogens ALLOW H ₂ SO ₄ /H ₃ PO ₄ /acid for H ALLOW addition of HBr/ H ₂ O either way across C=C
	<i>Examples of reagents</i> Br₂ or other halogen, HBr, H₂ AN H₂O(g)/steam AND H⁺ (catalyst)			
ALLO	nic product for reagent with C=C i DW product from H_2 or H_2O if H^+ can t.	in α-terpineol √		ALLOW ANY HALIDE, i.e. CI [−] , F , I [−] ALLOW H ₂ SO ₄ /H ₃ PO ₄ /acid for F ALLOW HBr for H ⁺ and Br [−]
-	nd group Reagent AND Functional group: (Tertiary) alco	ohol 🗸	4 AO3.2	ALLOW name or formula of any carboxylic acid or acyl chloride for esterification
i Exam	ples of reagents		×4	
	/KBr/Br⁻ AND acid/H⁺	(substitution),		ALLOW Na \rightarrow product with $-ON$ OR $-O^-$ DO NOT ALLOW Cr ₂ O ₇ ²⁻ /H ⁺
Acid/I	H⁺ (catalyst)	(elimination),		(tertiary alcohol)
CH₃C	COOH AND acid/H ⁺ (catalyst)	(esterification)		Examiner's Comments
CH₃C	:OOCOCH₃ :OCI nic product for reagent with OH in	(esterification) (esterification)		In this question, candidates were given the opportunity to demonstrate some knowledge of organic reaction in a new contex The choice of reaction was up to the candidate.
-	W product if catalyst omitted fro			Most candidates were able to identify the alkene group in terpineol and to suggest a reage that would react with this functior group. A correct structure for the organic product then usually followed.
				Although most candidates identified the alcohol group, man struggled with a reagent and resulting product. Although the

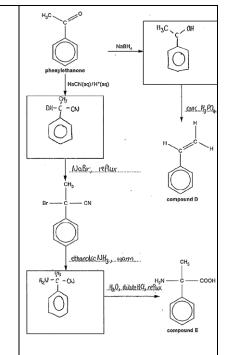
			alcohol –OH group has many reactions, (e.g. elimination, substitution, esterification) many candidates were fixated on oxidation with acidified dichromate despite a tertiary alcohol not being capable of oxidation with this reagent. Some candidates quoted acidified dichromate but then copied the structure of terpineol, stating that there was no reaction, despite the question directing them to select a reagent that would react with their chosen group.
	Total	9	
4 i	Polymer from D H H H H H C C C C C C C C C C C C C C C C C C	3 (AO 2.5) (AO 2.5) (AO 2.5)	For BOTH structures, ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous 'End bonds' MUST be shown BUT ALLOW ECF IF end bonds omitted in both structures DO NOT ALLOW more than 2 repeat units BUT ALLOW ECF in subsequent structure IGNORE connectivity of C ₆ H ₅

	D Addition / polyalkene		able to draw two repeats units of the polymer formed from D and scored at least one mark. While most candidates drew the polymer from E correctly, securing full marks, some candidates were unable to show the amide link correctly. This common error is demonstrated in Exemplar 6. Exemplar 5 $\left(-\frac{\mu}{k_{o}} - \frac{\lambda}{k_{o}} - \frac{\mu}{k_{o}} $
ii	AND E: Condensation / polyamide √	1(AO 1.1)	DO NOT ALLOW 'additional'
ii i	Formation of electrophile $CH_3COCI + AICI_3 \rightarrow CH_3-C^+=O + AICI_4 - \checkmark$ Mechanism Curly arrow from π -bond to $CH_3C^+=O \checkmark$ $H_3C - C = O \land$ $H_3C - C = O \land$ $H_3C - C = O \land$ $H_3C - C = O \land$ Correct intermediate \checkmark Curly arrow from C-H bond to reform π -ring \checkmark $H \rightarrow COCH_3 \rightarrow$	5 (AO 2.5) (AO 2.5) (AO 3.1) (AO 2.5)	ANNOTATE ANSWER WITH TICKS AND CROSSES ALLOW '+' charge anywhere on CH ₃ C+O i.e. CH ₃ CO ⁺ NOTE: curly arrows can be straight, snake-like, etc. but NOT double headed or half headed arrows 1st curly arrow must • go to the C of C=O AND • start from, OR close to circle of benzene ring









Phenylethanone is the starting point of this flowchart which shows the synthesis of compounds **D** and **E**.

Synthesis of ${\bf D}$

The first step in the synthesis of D is the reduction of the ketone group. This response demonstrates a common error seen by examiners. The candidate has correctly deduced that than alcohol is formed but has omitted a hydrogen atom. Candidates are advised to take care when drawing structures. If a carbon atom is displayed it should be shown to be making four bonds. The final step of the synthesis is the dehydration of the alcohol with an acid. This candidate has used H₃PO₄. H₂SO₄ was also frequently seen. Lower ability responses included reference to water or steam and this was not credited.

Synthesis of E

The first step of the synthesis of **E** from phenylethanone is the reaction with NaCN(aq)/H⁺(aq). This candidate identifies that the product of the reaction is a hydroxynitrile but unfortunately this cannot be credited due to the incorrect linking of the OH group

			0	
				via the H atom. Candidates should be aware that, when drawing structures, groups must be bonded via the correct atoms. The next step of the synthesis is the substitution of the OH group. The candidate correctly recognises that NaBr is a suitable reagent but omits an acid, e.g. H ₂ SO ₄ , which is also required for this reaction. This error was seen frequently by examiners.
				The final two steps involve the substitution of the Br atom and acid hydrolysis of the nitrile group. In this case the candidate chooses the reaction with excess NH ₃ . The structure of the correct product of this reaction is shown and the synthesis is completed by identifying a suitable reagent for the final step. Other candidates opted to perform these steps in the reverse order and the mark scheme allowed full credit for either approach.
				Common errors in the final steps were omissions. Some candidates simply stated NH ₃ without mentioning ethanol. Others identified water as important for the hydrolysis but did not include reference to an acid.
		Total	16	
				ALLOW 3-hydroxybutan-1-al IGNORE lack of hyphens or addition of commas ALLOW 4-oxobutan-2-ol OR 1- oxobutan-3-ol
5	i	3-hydroxybutanal √	1	DO NOT ALLOW 3-hydroxybutal 3-hydroxylbutanal Examiner's Comments Most candidates made good
				Most candidates made good

ii						carboxylic acid).
	Addition √				1	IGNORE nucleophilic OR electrophilic OR radical DO NOT ALLOW addition- elimination, condensation, polymerisation Examiner's Comments This part was answered well with most choosing nucleophilic addition. Credit was given just for 'addition'.
11	charge are co e.g. For CH ₃ (Step 1: • Correct e One corr • i.e. A1 ar	CHO, ALLOW CH₃(COH, C2H4O, et / 2 2CHO + H2O		3	Throughout, IGNORE 'connectivity in any formula or structures shown. Examples in Answer column and in 6a(iv) guidance below
	CH₃CH For ⁻ CH₂CH(B2 B1 + ⁻ CH ₂ CHO + H ₂ O HOHCH ₂ CHO + OH D: ALLOW CH ₂ CHO	⁻ √ D ⁻ ; CH₃CO ⁻ ; C₂ł	A2 A1 H₃O⁻		B2 A1 A2 B1 OR B1 A2 A1 B2 Step 2: CH ₃ CHO + CH ₃ CH ₂ O ⁺ + O ²⁻ \rightarrow CH ₃ CHOHCH ₂ CHO + OH ⁻ \checkmark For CH ₃ CH ₂ O ⁺ : ALLOW CH ₃ CHOH ⁺ , C ₂ H ₅ O ⁺ Examiner's Comments

				acid–base equilibria with a multi- step process. Many candidates completed an equation to generate acid–base pairs, which were then usually assigned correctly. The final equation was challenging but the highest ability candidates were able to combine together all the information with their earlier responses to arrive at the correct equation. See Exemplar 15. Exemplar 15 $CH_{3}CHO + OH \Rightarrow CH_{3}CO^{-} + H_{4}O$ acidbase 1 acid Suggest the equation for step 2. $CH_{3}CHO + \frac{4}{3}CO^{-} + H_{2}O \Rightarrow H - \frac{H}{c} - \frac{OH}{c} - \frac{H}{c} - \frac{OH}{c} - \frac{H}{c} - \frac{CH}{c} - \frac{CH}$
				ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous For connectivity, ALL CH ₃ - C ₃ H- OH CH ₃
	i v		1	(Connectivity not being assessed) Examiner's Comments This part was one of the most challenging on the paper. Candidates needed to link the earlier information for combining two ethanal molecules to derive the product for combining two propanone molecules. Despite the challenge, the highest ability candidates were able to come up with the correct structure.
		Total	6	
6	i	Phenol √ Amide √	2	IF > 2 functional groups are shown,

IGNORE attempt to classify amide, e.g. secondary	Mark 2 groups ONLY Mark incorrect groups first
	Treat carbonyl with aldehyde OR with ketone as one functional
	group,
	i.e.
	1.0.
	carbonyl, aldehyde
	carbonyl, ketone
	• carbonyl
	IGNORE aryl OR alkyl group
	e.g. benzene, phenyl, aryl, arene,
	methyl
	IGNORE hydroxyl/hydroxy
	Examiner's Comments
	This part assessed knowledge of
	functional groups and proved to be
	a very good discriminator. Able
	candidates usually identified the
	phenol and amide functional
	groups, with 'secondary amide'
	also seen.
	In Exemplar 9, the candidate has
	identified the correct functional
	groups. The candidate's working
	by circling the functional groups in
	the structure shows good
	examination technique, helping the
	candidate to arrive at the correct
	conclusion.
	The phenol group was often
	incorrectly identified as an alcohol
	and the amide group as a
	combination of 'amine', 'ketone',
	'keytone' or 'carbonyl'. Neutral
	responses such as 'hydroxyl' and
	'benzene' were ignored.
	Candidates need to be careful that
	they do not present an extensive
	list of many functional groups in
	the hope that the correct groups
	are amongst them, as shown in
	Exemplar 10. Incorrect groups are
	marked first.
	Exemplar 9

			(i) Name the functional groups present in paracetamol.
	Refer to marking instructions on page 5 of mark scheme for guidance on marking this question.		Indicative scientific points may include: <u>Calculation of mass of 4-</u> <u>nitrophenol</u> Using moles
	Level 3 (5-6 marks) A correct calculation of the mass of 4-nitrophenol. AND Identifies the reagents AND intermediate. AND A detailed description of most purification steps.		• $n(\text{paracetamol}) = \frac{5.00}{151} = 0.0331 \text{ (mol)}$ • $n(4\text{-nitrophenol}) = 0.0331 \times \frac{100}{40} = 0.082$ • Mass of 4-nitrophenol = 139 × 0.0828 = 11.5 g ALLOW 11.4-11.6 for small slip/rounding
	There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.		Using mass
	Level 2 (3-4 marks) Calculates the mass of 4-nitrophenol with some errors AND suggests reagents and intermediate with some omissions. OR		• Theoretical mass paracetamol = $5.00 \times -$ Theoretical <i>n</i> (4-nitrophenol) = $\frac{12.5}{151} = 0.($
ii	Calculates the mass of 4-nitrophenol with some errors AND describes some purification steps, with some detail. OR Suggests reagents and intermediate with some omissions AND	6	Mass of 4-nitrophenol = 139 × 0.0828 = 11.5 g NOTE : Incorrect inverse 100 ratio of 40
	describes some purification steps, with some detail. There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.		gives:
	Level 1 (1-2 marks) Attempts to calculate the mass of 4-nitrophenol OR		 0.0331 × ⁴⁰/₁₀₀ = 0.0132 (mol) Mass = 139 × 0.0132 = 1.84 g <u>Reagents and intermediate</u>
	Suggests reagents OR intermediate but may be incomplete OR Describes few purification steps.		 Reagents: Sn + (conc) HCl (then NaOH) Intermediate: 4-aminophenol or structure
	There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.		Purification
	0 marks No response or no response worthy of credit.		 Dissolve impure solid in minimum volume of hot solvent Cool solution and filter solid Scratch with glass rod Wash with cold solvent/solvent and dry

Examples of detail in **bold (NOT** INCLUSIVE)

NOTE: 'Recrystallisation' on its own is **NOT** a detailed description

Examiner's Comments

This part assessed practical aspects of a two-stage organic synthesis. Overall, candidates responded well, and this part was discriminating. Many candidates produced well-structured responses although lower ability candidates do have problems with constructing a cohesive response.

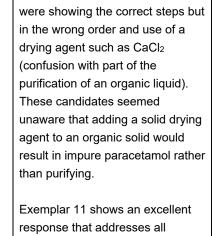
Most candidates identified the correct reagents (Sn and concentrated HCI) and the intermediate (4-aminophenol), which was usually shown as its structure.

Able candidates usually showed that 11.5 g of 4-nitrophenol is needed for the synthesis. A common error used the 'inverse percentage' ratio of 40/100, resulting in an incorrect mass of 1.84 g. Candidates are recommended to check whether a calculated answer looks sensible. Looking at the structures and with a percentage yield of 40%, 1.84 g does not look to be enough of the starting chemical.

Some lower ability candidate responses assumed that 5.00 g was 40% of the required mass and responded with $5.00 \times 100/40 = 12.5 \text{ g}.$

There were some good descriptions of purification, although finer details such as using a minimum volume of hot solvent, washing with cold solvent, and drying) were often omitted. Candidates needed to respond with more than just 'recrystallisation'.

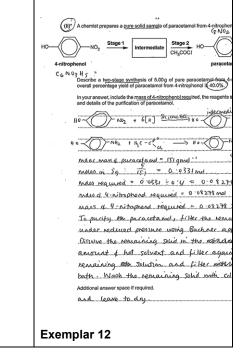
In the purification, common errors



aspects of the problem.

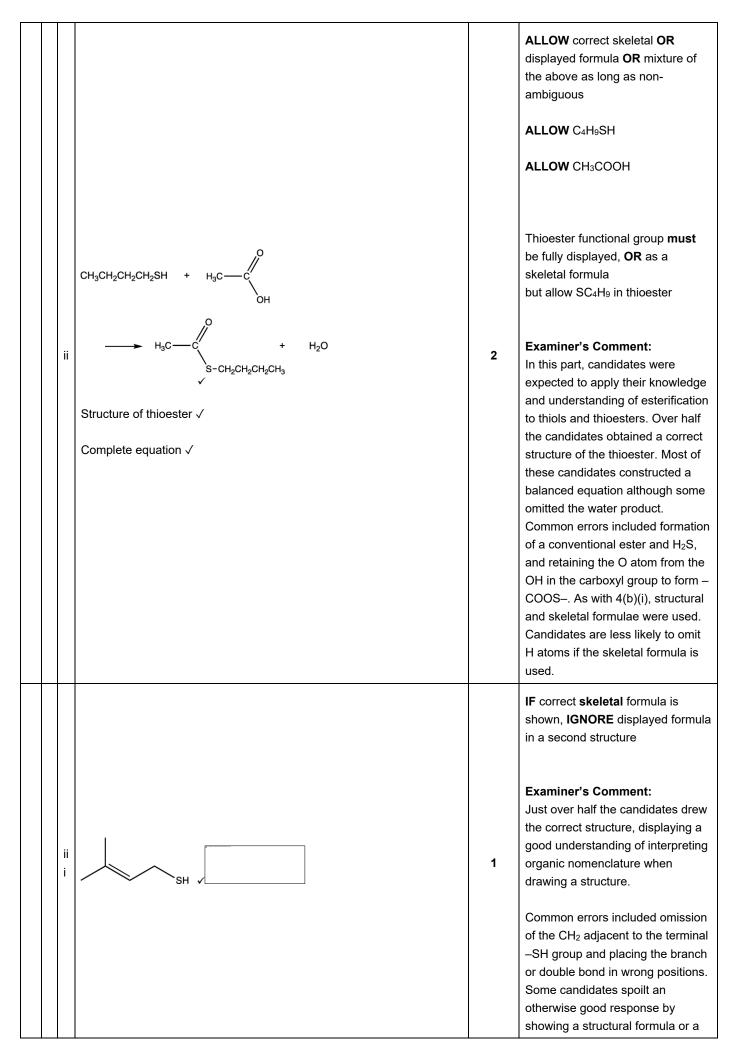
In comparison, Exemplar 12 is much less detailed: concentrated HCl has not been shown as a reagent for step 1, the candidate has not shown that they know how to carry out a percentage yield calculation, and the purification is confused, and lacks detail.

Exemplar 11

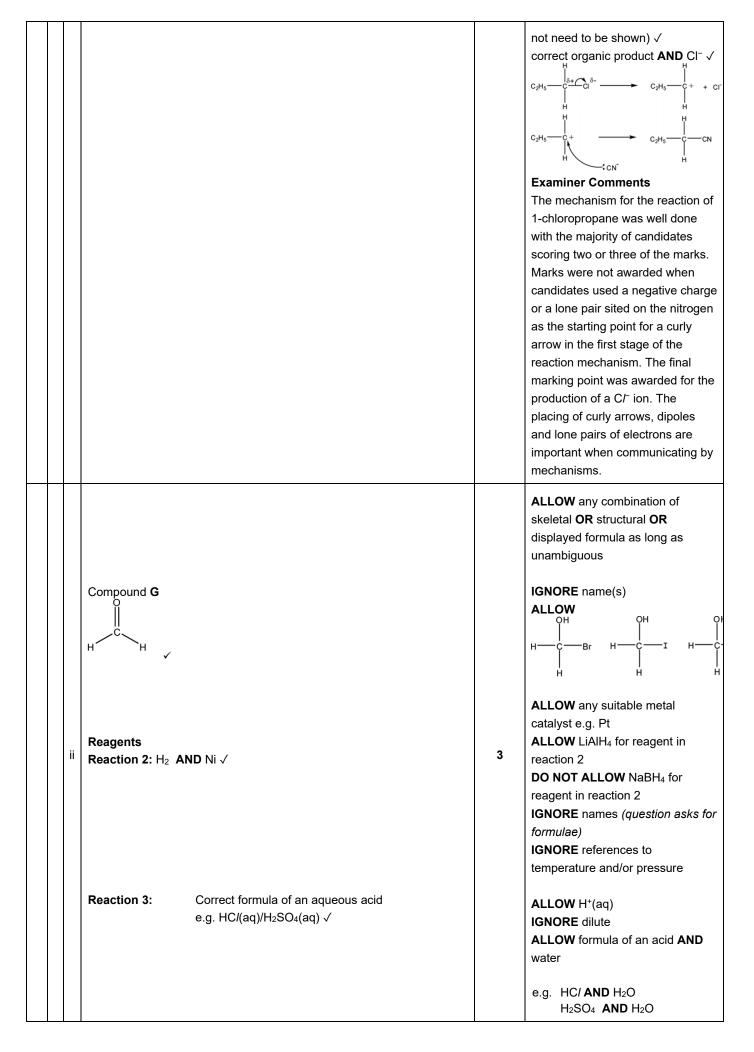


	Total	8	In your answer, include the mass of 4-nitrophenol required, the reagents and and details of the purification of paracetamic. A -nitrophenol is reserved with reduced (Sn) tim in presence of and acid and f tophy t-phenolylamide under high HO
7	One mark for each correct structure/reagent as shown below $\begin{split} & = & \left(\begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	4	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW PCI5 OR PCI3 for reagent mark. IGNORE references to temperature for reagent mark IGNORE additional reagents shown with SOCI2/PCI5/PCI3 e.g. H2O, AICI3, HCI etc. IGNORE names (question asks for structures of organic compounds and formula of reagent) DO NOT ALLOW more than two repeat units ALLOW 1 mark for one correct repeat unit e.g.

				H but only some identified SOC/ ₂ as the correct reagent. Common incorrect reagents included HCI and AIC/ ₃ . Most candidates recognised that polymer I was a polyester but only some were able to draw two repeat units correctly. Candidates are advised to practice drawing different polymers, taking care to ensure the correct number of repeat units are present when a specific number is required.
		Total	4	
8	i	Reflux	1	
	ii	Nucleophilic substitution (1) <i>Mechanism</i> Curly arrow from lone pair on OH ⁻ to δ+ carbon atom (1) Curly arrow and dipole on C–I bond (1) Correct products (1)	4	The curly arrow must start from the oxygen atom of the OH ⁻ and must start from either the lone pair or the negative charge
		Total	5	
9	i	$K_{a} = \frac{[H^{+}][C_{4}H_{9}S^{-}]}{[C_{4}H_{9}SH]} \checkmark$ Square brackets required	1	ALLOW correct structural OR skeletal OR displayed formula OR mixture of the above as long as non- ambiguous Examiner's Comment: This part was very well answered. Candidates responded with either near molecular formulae, such as C4H9SH, structural formulae or with skeletal formulae. Some candidates made careless errors such as omitting the negative charge or showing [H ⁺] ² as numerator rather than [C4H9S ⁻] [H ⁺].

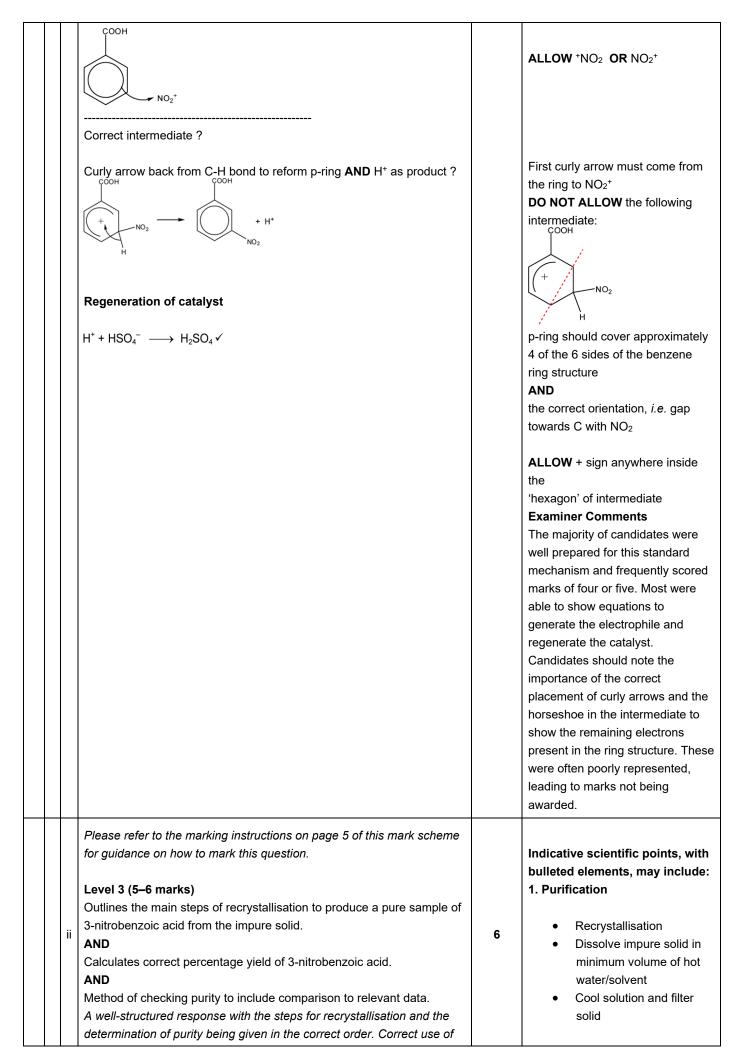


				mixture of skeletal and structural formulae.
				ALLOW correct structural OR skeletal OR displayed formula OR mixture of the above as long as non- ambiguous
	i v		2	Examiner's Comment: In this part, candidates were expected to apply their knowledge and understanding of condensation to an entirely new context. One mark was allocated for the reactants and this was usually scored. The second mark for the novel cyclic compound and water was much more difficult, aimed at stretch and challenge. A significant number of candidates interpreted the information to obtain a correct cyclic structure but this mark was the domain of the most able candidates.
		Total	6	
1	i	curly arrow from ⁻ CN to carbon atom of C–C/ bond \checkmark Dipole shown on C–C/ bond, C ⁵⁺ and C/ ^{5–} , AND curly arrow from C–C/ bond to C/ atom \checkmark $c_2H_5 - c_1^{\delta+} - c_1^{\delta-} - c_$	2	ANNOTATE ANSWER WITH TICKS AND CROSSES Curly arrow must come from lone pair on C of \neg CN OR CN \neg OR from minus sign on C of \neg CN ion (then lone pair on CN \neg does not need to be shown) IGNORE NaCl ALLOW S _N 1 mechanism: Dipole shown on C–Cl bond, C ⁵⁺ and Cl ⁵⁻ , AND curly arrow from C–Cl bond to Cl atom \checkmark Correct carbocation AND curly arrow from \neg CN to carbocation. Curly arrow must come from lone pair on C of \neg CN OR CN \neg OR from minus sign on C of \neg CN



		Examiner Comments Although many candidates were able to provide the structure of methanal as the starting material for this synthesis, the structures of chloromethanol, bromomethanol and iodomethanol were accepted as suitable alternatives. It should be noted that hydrolysis is carried out using aqueous acid and that dilute acid is not a suitable alternative.
Explanation Nitrogen electron pair OR nitrogen lone pair AND accepts a proton / $H^+ \checkmark$ Structure of salt $H^ H^ H^-$ <td>2</td> <td>IGNORE NH₂ group donates electron pair ALLOW nitrogen donates an electron pair to H⁺ DO NOT ALLOW nitrogen donates lone pair to acid IGNORE comments about the O in the –OH group Compound H is a base is not sufficient (role of lone pair required) DO NOT ALLOW nitrogen/N lone pair accepts hydrogen (proton/H⁺ required) ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW H H H <i>i.e.</i> charges not sunambiguous ALLOW OH H H H <i>i.e.</i> charges not sunambiguous ALLOW OH H H H <i>i.e.</i> charges not sunambiguous ALLOW OH H H H H <i>i.e.</i> charges not sunambiguous ALLOW OH H H H H H H H H H H H</td>	2	IGNORE NH ₂ group donates electron pair ALLOW nitrogen donates an electron pair to H ⁺ DO NOT ALLOW nitrogen donates lone pair to acid IGNORE comments about the O in the –OH group Compound H is a base is not sufficient (role of lone pair required) DO NOT ALLOW nitrogen/N lone pair accepts hydrogen (proton/H ⁺ required) ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW H H H <i>i.e.</i> charges not sunambiguous ALLOW OH H H H <i>i.e.</i> charges not sunambiguous ALLOW OH H H H <i>i.e.</i> charges not sunambiguous ALLOW OH H H H H <i>i.e.</i> charges not sunambiguous ALLOW OH H H H H H H H H H H H

					stating that amines accept protons or that a salt is produced when an acid reacts with a base were not credited. Where a full displayed structure is given the positive charge must be shown on the nitrogen atom, although $-NH_3^+$ is acceptable. As the question required the formula of the salt, the $C\Gamma$ had to be included.
					ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous
					DO NOT ALLOW more than two repeat units for second marking point.
			o		'End bonds' MUST be shown (do not have to be dotted)
					IGNORE brackets
		i			IGNORE n
		v	Ester link √ Rest of structure√ (polymer J is biodegradable because) the ester / ester bond / ester group / polyester can be hydrolysed√	3	Broken down by water is not sufficient
					IGNORE references to photodegradable
					Examiner Comments The most common mark for this question was two out of the three marks available, with candidates giving a correct structure of the polymer but failing to express that the polymer was biodegradable due the ability of the ester functional group to undergo hydrolysis.
			Total	11	
1			Generation of electrophile HNO ₃ + H ₂ SO ₄ \longrightarrow H ₂ O + HSO ₄ ⁻ + NO ₂ ⁺ \checkmark		ANNOTATE ANSWER WITH TICKS AND CROSSES ALLOW HNO ₃ + 2H ₂ SO ₄ ? H ₃ O ⁺ + 2HSO ₄ ⁻ + NO ₂ ⁺
1	а	i	Electrophilic substitution	5	
			Curly arrow from p-bond to NO_2^+ ?		ALLOW HNO ₃ + H ₂ SO ₄ ?H ₂ NO ₃ ⁺ + HSO ₄ ⁻ Then H ₂ NO ₃ ⁺ ? H ₂ O + NO ₂ ⁺



terminology throughout.	Wash with cold
	water/solvent and dry
Level 2 (3–4 marks) Attempts all three scientific points but explanations may be incomplete. OR	2. Percentage yield
Explains two scientific points thoroughly with very few omissions.	n(benzoic acid) used = $\frac{4.97}{122}$ = 0.0 n(3-nitrobenzoic acid) made = $\frac{4.85}{167}$ =
The description of checking for purity or recrystallisation is clear and any calculations structured. Key terminology used appropriately.	• percentage yield = $\frac{0.0290}{0.0407} \times 100 = 71.3$
Level 1 (1–2 marks) A simple explanation based on at least two of the main scientific points.	ALLOW 71 to calculator value of 71.29001554 correctly rounded.
OR Explains one scientific point thoroughly with few omissions. There is an attempt at a logical structure. The description of the	CHECK for extent of errors by ECF
 practical techniques provides some detail but may not be in the correct order. Purification step is unclear with few scientific terms and little detail, e.g. just 'recrystallise'. Calculation is difficult to follow, may just include a calculation of moles of reactants and/or products. Purity check specifies a method but this is unclear with little detail, e.g. take melting point. 0 marks No response or no response worthy of credit. 	Alternative correct calculation may calculate theoretical mass of 3- nitrobenzoic acid that can be produced as $0.0407 \times 167 = 6.80$ (g) followed by: percentage yield $= \frac{4.85}{6.80} \times 100 = 71$ Calculation must attempt to calculate <i>n</i> (benzoic acid) in mol. 3. Checking purity • Obtain melting point • Compare to known value • Pure sample will have a
	(sharp) melting point very close to data book value ALLOW alternative approach based on spectroscopy or TLC Spectroscopy
	 Run an NMR/IR spectrum Compare to (spectral) database Spectrum of pure sample will contain same peaks and not others
	 TLC Run a TLC Compare (<i>R</i>_f value) to

• Pure sample will have a very similar R_f

Examiner Comments

This question tested some of the practical techniques covered as part of the practical endorsement as well as requiring candidates to calculate a percentage yield for the reaction. This proved to be quite a challenging question with some candidates giving little detail of how to carry out a recrystallisation. Common answers included a statement that the solid should be allowed to dissolve in a solvent and then filtered to obtain crystals. This did not gain credit for the scientific content as there was no indication of the solid dissolving in a hot solvent and then being allowed to cool before carrying out filtration. High quality answers often went above and beyond the requirements of the marking scheme with some candidates discussing the importance of dissolving in the minimum amount of hot solvent to obtain a saturated solution, the need to wash and dry the crystals and provided detail of the apparatus and or method required.

Most candidates discussed that purity could be determined by taking the melting point of the product and comparing this to a value obtained from data book. The most comprehensive answers gave an indicated of the apparatus required to carry out the melting point determination and discussed how the melting point becomes higher and sharper as impurities are removed. Common errors included comments about carrying out a boiling point determination.

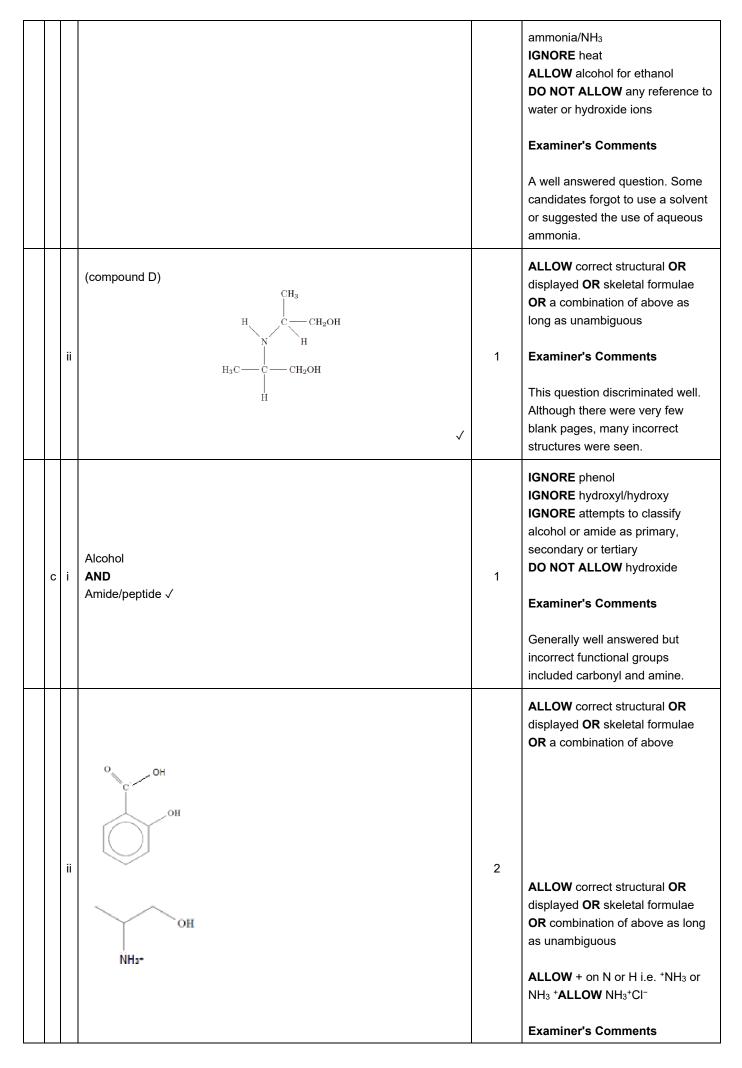
When carrying out a percentage yield calculation, it is important to round answers only at the last stage of the calculation. Early rounding frequently led candidates to obtain answers, which did not

				gain credit. Weaker Candidates divided the mass of 3-nitrobenzoic acid by the mass of benzoic acid and obtained an answer of 97.6%. Answer = 71.3%
				ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW any suitable halogen carrier catalyst ALLOW Kekulé structure IGNORE names (question asks for formulae)
		Bromination: Br₂ AND A/Br₃/FeBr₃/Fe √		IGNORE reaction conditions even if incorrect
Ь	Ĩ	Intermediate	3	IGNORE 'dilute' for HC/ IGNORE H ₂ IGNORE NaOH if seen as a reagent to convert nitro group into amine e.g 'Sn/(concentrated) HC/ then NaOH' scores the mark Examiner Comments Candidates were able, in the main, to provide the reagents for bromination and reduction. The structure of the intermediate compound in the preparation of 3- bromophenylamine proved to be straightforward, however common errors involved the omission of the halogen carrier catalyst for bromination or stating names rather than formulae as indicated in the question.
	ii	NH ₂ is 2,4 directing \checkmark Products (1 mark for each):	3	IGNORE references to electron donating/withdrawing groups ALLOW –NH ₂ activates the ring causing the new group to join at positions 2 and 4.
		→ Br		ALLOW ortho and para directing for 2,4 directing IGNORE 6-directing
				ALLOW Kekulé structure IGNORE names

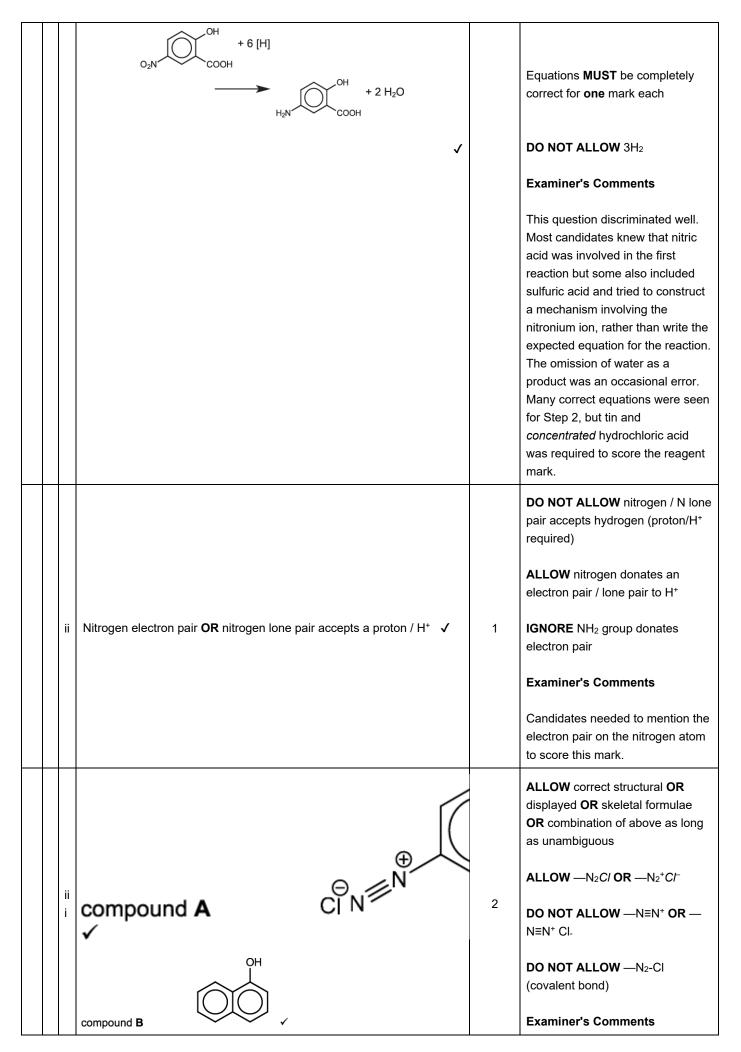
			Examiner Comments The most able candidates completed this question with a clear statement that the NH ₂ group was 2,4 directing and provided two clearly drawn structures of 2-bromophenylamine and 4-bromophenylamine. The most common errors observed included drawing two structures that were identical and explaining the two structures in terms of electron donation from theNH ₂ without any indication of positioning. Candidates using the terms ortho and para directing were awarded full marks for their answers.
	Total	17	
1 a	One mark for each correct structure/reagent/condition as shown below $ \underbrace{ \bigoplus_{\substack{i \in I_1 - Cr_i \leftarrow i}}_{\substack{i \in I_2 \leftarrow i}} \bigoplus_{\substack{i \in I_2 \leftarrow i} \bigoplus_{\substack{i \in I_2 \leftarrow i}} \bigoplus_{\substack{i \in I_2 \leftarrow i}} \bigoplus_{\substack{i \in I_2 \leftarrow i} \bigoplus_{\substack{i \in I_2 \leftarrow i}} \bigoplus_{\substack{i \in I_2 \leftarrow i} \bigoplus_{\substack{i \in I_2 \leftarrow i}} \bigoplus_{\substack{i \in I_2 \leftarrow i} \bigoplus_{i$	6	ANNOTATE ANSWER WITH TICKS AND CROSSES ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous IGNORE names of organic compounds (question asks for structures) ALLOW aluminium(III) chloride OR aluminium trichloride ALLOW FeC/3 OR Fe as halogen carrier in first step. ALLOW sodium borohydride OR sodium tetrahydridoborate IGNORE [H] for reducing agent in second step

			Use as an organic feedstock \checkmark		ALLOW the production of plastics or monomers
	b		OR	1	or new polymers
			Combustion for energy production \checkmark		Combustion alone is not sufficient
			Total	7	
1 3		i	\mathbf{AND} Acid (catalyst) \checkmark	1	Note: both the structure and condition are required for the mark ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW H ⁺ / H ₂ SO ₄ / H ₃ PO ₄ / named mineral acid
		ii	Diagram Diagram showing correct apparatus for distillation √ <i>i.e.</i> • Round-bottom/pear-shaped flask • Condenser (correctly orientated) • Stopper/thermometer • Delivery tube and suitable collection vessel • Very tube and suitable collection vessel • Very tube and suitable collection vessel • Delivery tube a	2	DO NOT ALLOW conical flask, volumetric flask, beaker in place of round bottomed/pear shaped flask DO NOT ALLOW diagram mark if top of distillation head not closed Note: suitable collection vessels include: conical flask, boiling tube, test-tube, beaker etc.
			Total	3	

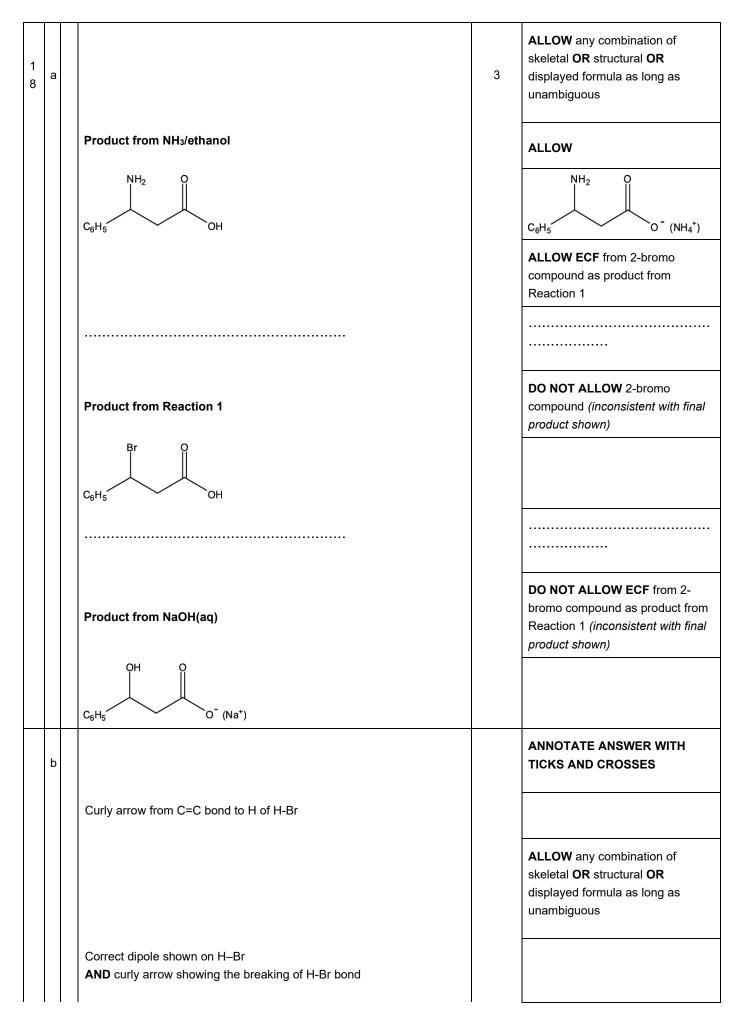
1 4	ß	i	¹ H NMR spectro Chemical shift, <u>8/ppm</u> 0.8 - 2.0 2.3 - 3.0 3.3 - 4.2	um for 2-aminopro Relative peak area 3 1 2	opan-1-ol Splitting pattern doublet multiplet doublet	$\sqrt{\sqrt{2}}$	3	One mark for each correct row ALLOW δ values as a range or a value within the specified range. ALLOW δ values +/- 0.2 ppm. ALLOW a response that implies a splitting into two for a doublet etc. ALLOW sextet/hextet/six (or more than 5) as alternative to multiplet Relative peak area = CH /3H etc. penalise once Examiner's Comments Although it could be argued that this question tested the same skill three times, the full range of marks was awarded and errors were seen in the chemical shift, relative peak area and splitting pattern. Fully correct responses included either a chemical shift value within the range specified on the data sheet or a range that matched the one given on the data sheet.
		ii	M ⁺ peak at 75 (peak 1) CH ₃ CH(NH ₂)CH ₂ OH ⁺ /C ₃ H ₉ NO ⁺ <u>Fragment peak at 44</u> (peak 2) CH ₃ CH(NH ₂) ⁺ /C ₂ H ₆ N ⁺			√	2	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous Positive charge is essential but ALLOW maximum of one mark if both formulae are correct AND neither species has a positive charge Examiner's Comments Although peak 2 was often correct, the species responsible for the M+ peak was often missing a positive charge. Possibly students have learned that the particles become charged as part of the fragmentation process and don't realise that only charged particles can be detected by a mass spectrometer.
	b	i	Ethanolic ammonia OR ammonia/NH ₃ AND ethan	ol √			1	ALLOW ammonia in a sealed tube ALLOW dilute ethanolic



				Many candidates were able to score one mark for this question but the amine group was often not protonated and it was surprisingly common to see the amine group as NH ₂ ⁺ .
		Total	10	
1 5	i	• pent-2-ene $H_{3}C = 0 \qquad 0 = 0 \qquad (H_{2}CH_{3} \qquad)$ • hexa-2,4-diene $H_{3}C = 0 \qquad 0 = C - C = 0 \qquad (H_{1}H_{1}H_{2} \qquad)$	3	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous ALLOW C ₂ H ₅ CHO and CH ₃ CHO Examiner's Comments Many candidates responded well when asked to apply information in a unfamiliar situation. The question discriminated well but a high proportion scored all three marks. Some candidates lost marks in the second part by providing a list of three or more different structures, some of them being incorrect.
	ï		1	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous Examiner's Comments This was a challenging question. Only more able candidates predicted the correct cyclic structure.
		Total	4	
1	i	Step 1 Add HNO ₃ \checkmark $\qquad \qquad $	4	ALLOW reagent mark if HNO ₃ in equation IGNORE H ₂ SO ₄ (NOTE: H ₂ SO ₄ not required with phenols) IGNORE concentrations of acids / temperature ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous



			The vast majority of candidates gave the correct structure for compound B, but common errors were the omission of the chloride ion in the formulae of the diazonium salt, or placing the positive charge on the wrong nitrogen atom.
	Total	7	
	 Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question. Level 3 (5–6 marks) Correctly calculates mass of 2-hydroxybenzoic acid. AND Outlines full details of the two steps to obtain a pure sample of aspirin from the hot reaction mixture Calculation shows all relevant steps. Purification steps are detailed and clear, in the correct order, using appropriate scientific terms, e.g. filter under reduced pressure / using a Buchner flask; dissolve in the minimum volume of solvent. 		Indicative scientific points, with bulleted elements, may include: 1. Mass of 2-hydroxybenzoic acid • $n(aspin) needed = \frac{8.10}{100} = 0.0450 (mol)$ • $n(2-hydroxybenzoic acid)$ needed $= 0.0450 \times \frac{100}{90} = 0.0500 (mol)$
1 7	 Level 2 (3–4 marks) Attempts a calculation which is mostly correct AND Some details of steps to obtain impure aspirin from the hot reaction mixture and recrystallisation Calculation can be followed but lacks clarity. Purification steps lack detail, e.g. filter without reduced pressure; dissolve without minimum volume of solvent. 	6	 Mass = 0.0500 × 138 = 6.9(0) g 2. Purification Impure aspirin from hot reaction mixture Cool reaction mixture Filter product under reduced pressure Recrystallisation of impure aspirin:
	 Level 1 (1–2 marks) Attempts to calculate the mass of B using mole approach but makes little progress with only 1 step correct. AND Few or imprecise details about steps to obtain impure aspirin from hot reaction mixture and recrystallisation Calculation is difficult to follow and lacks clarity Purification steps are unclear with few scientific terms and little detail, e.g. just 'filter and crystallise'. 0 marks: No response or no response worthy of credit. 		 Dissolve impure solid in minimum volume of hot water / solvent Cool solution and filter solid Wash with cold water / solvent and dry NOTE Filtration of hot solution to remove solid particles is not required.
	Total	6	



6.2.5 Organic Synthesis

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