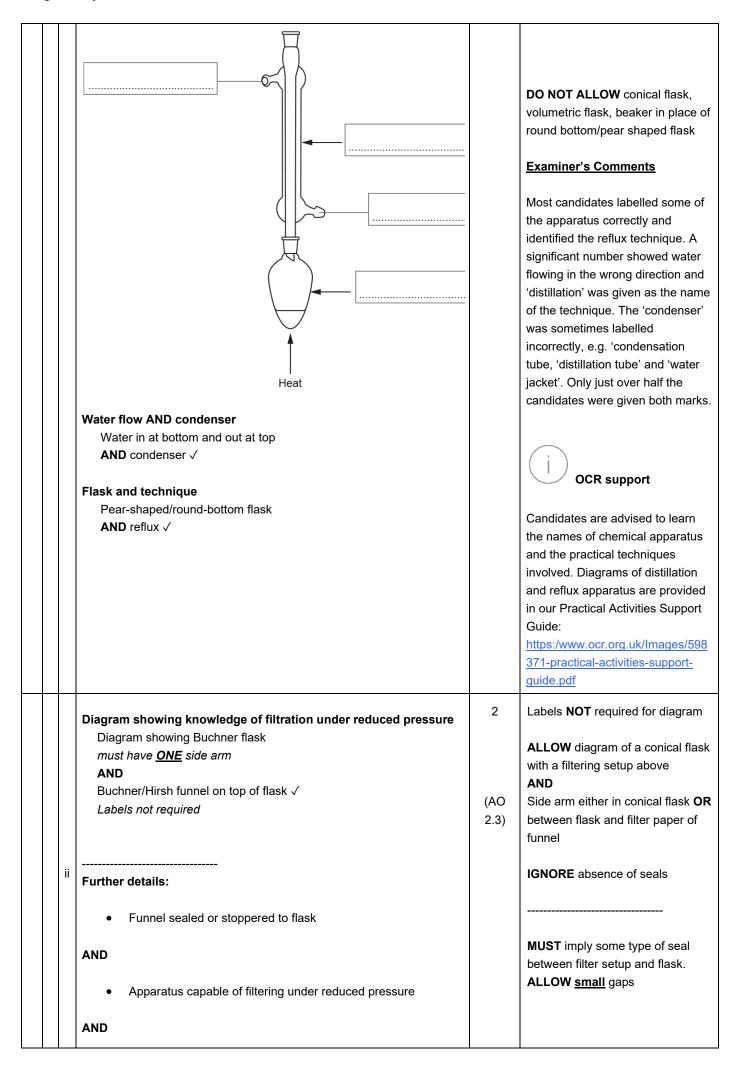
Mark scheme - Synthesis

	Questi on		Answer/Indicative content	Marks	Guidance
1	а		OH OH OH CH CH CH CH CH CH CH	5 (AO2.5 ×5)	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW HBr
			NH ₃ AND ethanol OR excess NH ₃ NH ₃ Cl HCl H ₃ C CH H ₃ C CH Salt H		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 ₃ C — OH ✓ HOOC NH ₂ HOOC NH ₃ OR	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 +

		NH₂ COOH OR COOH HOOC COOH HOOC Shown with NH₃+ ✓		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 CI, 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 x 10 ⁻⁴ (mol) √ n(aspartame) limit per day = 1.7x10 ⁻⁴ x 75 = 0.01275 (mol) √ number of cans = 0.01275 / 5.68 x 10 ⁻⁴ = 22.4 √	3 (AO2.2 ×3)	If there is an alternative answer, apply ECF and look for alternative methods Alternative methods n(aspartame) in 1 can = $0.167 / 294$ = 5.68×10^{-4} (mol) \checkmark n(aspartame) per kg = $5.68 \times 10^{-4} / 75$ = 7.57×10^{-6} (mol) \checkmark number of cans = $1.7 \times 10^{-4} / 7.57 \times 10^{-6}$ = $22.4 \checkmark$ OR n(aspartame) limit per day = $1.7 \times 10^{-4} \times 75$ = 0.01275 (mol) \checkmark mass(aspartame) limit per day = 0.01275×294 = 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 ✓ ALLOW slips in spelling of 'Buchner'	(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' Flask and funnel used in normal filtration 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	→ NoH	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.

ii

sides

ALLC larges
ORA
Awar
mark

MAXIMUM OF 4 MARKS FROM 5 MARKING POINTS

Requirement for E/Z isomerism
2 marks

C=C/double bond ✓
Each C (in C=C) is attached to (two) different groups/atoms ✓

Identification as E- or Z- isomer
2 marks

AO1.2
x2

IGNO
IGNO
IGNO

Z- isomer AND groups are on same side

OR the ring carbons √

ring would be strained

OR ring would break/deform

Reason why other E/Z isomer does not exist 1 mark

OR Cannot form ring if high priority groups are on opposite

OR ring locks groups on one side of C=C bond ✓

IGNORE no H attached to C=C **IGNORE** functional',

i.e. **ALLOW** different functional groups

ALLOW in context of groups with largest atomic number

Award BOTH identification marks for:

Z- isomer **AND** (high) priority groups on same side

Mark independently of previous part

Response **MUST** be linked to the ring/cyclic structure

IGNORE just '*E* isomer is impossible'

IGNORE C=C bond cannot rotate **IGNORE** Groups can't swap sides

AO2.5

х2

Examiner's Comments

Candidates displayed a good knowledge of the requirements for *E/Z* isomerism in terms of a C=C double bond and different groups on the carbon atoms of the C=C bond. Many assigned terpineol as 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 one E/Z 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 ring 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 E conformation.

First group:

Reagent

AND

Functional group: Alkene OR cycloalkene √

Examples of reagents

 Br_2 or other halogen, HBr, H_2 **AND** Ni (catalyst), $H_2O(\mathbf{g})$ /steam **AND** H^+ (catalyst)

Organic product for reagent with C=C in α -terpineol \checkmark

ALLOW product from H_2 or H_2 O if H^+ catalyst has been omitted from reagent. -----

Second group

Reagent

AND

Functional group: (Tertiary) alcohol √

Examples of reagents

NaBr/KBr/Br⁻ **AND** acid/H⁺ (substitution),

OR HBr

ii

i

Acid/H⁺ (catalyst) (elimination),

CH₃COOH **AND** acid/H⁺ (catalyst) (esterification)

CH₃COOCOCH₃ (esterification)
CH₃COCI (esterification)

Organic product for reagent with OH in α -terpineol \checkmark ALLOW product if catalyst omitted from reagent

CONTACT TEAM LEADER FOR OTHER REACTIONS

ALLOW GROUPS EITHER WAY ROUND IN BOXES

Functional group MUST be named

DO NOT ALLOW UV with

halogens

ALLOW H₂SO₄/H₃PO₄/acid for H⁺

ALLOW addition of HBr/ H₂O either way across C=C

ALLOW ANY HALIDE, i.e. Cl⁻, Br⁻

ALLOW H₂SO₄/H₃PO₄/acid for H⁺ **ALLOW** HBr for H⁺ and Br

ALLOW name or formula of any carboxylic acid or acyl chloride for esterification

AO3.2 ×4

ALLOW Na \rightarrow product with -ONa **OR** -O $^-$

DO NOT ALLOW Cr₂O₇²⁻/H⁺ (tertiary alcohol)

Examiner's Comments

In this question, candidates were given the opportunity to demonstrate some knowledge of organic reaction in a new context. The choice of reaction was up to the candidate.

Most candidates were able to identify the alkene group in terpineol and to suggest a reagent that would react with this functional group. A correct structure for the organic product then usually followed.

Although most candidates identified the alcohol group, many struggled with a reagent and resulting product. Although the

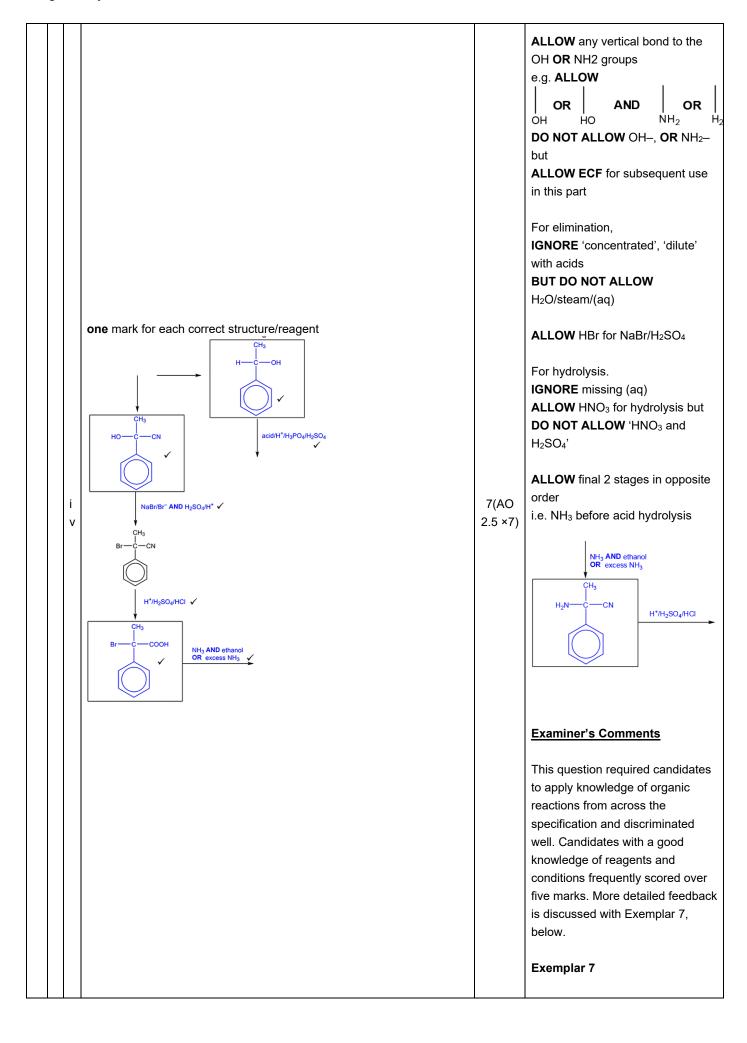
			alcohol –OH group has many reactions, (e.g. elimination, substitution, esterification) many candidates were fixated on oxidation with acidified dichromate despite a tertiary alcohol not being capable of oxidation with this reagent. Some candidates quoted acidified dichromate but then copied the structure 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 $\begin{array}{c ccccccccccccccccccccccccccccccccccc$	(AO 2.5) (AO 1.2) (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

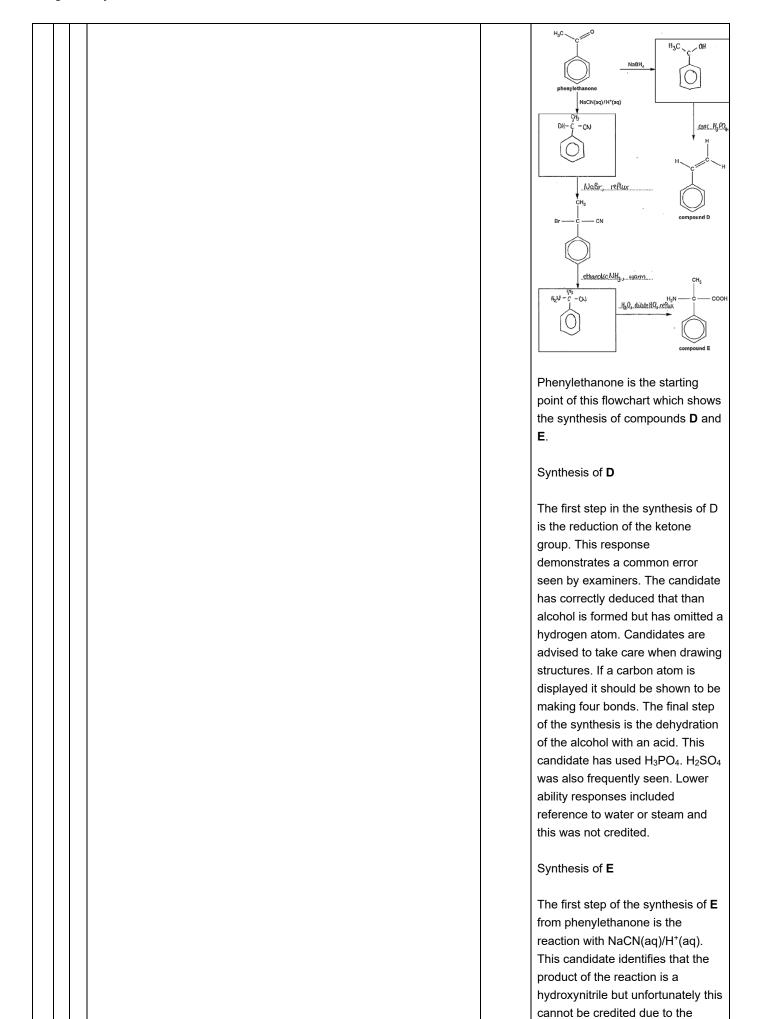
	D Addition / polyalkene	1(AO	able to draw two repeats units of the polymer formed from D and scored at least one mark. While most candidates drew the polymer from E correctly, securing full marks, some candidates were unable to show the amide link correctly. This common error is demonstrated in Exemplar 6. Exemplar 5 Two repeat units of polymer formed from E This response demonstrates a common error seen by examiners. The candidate has included an O atom as part of the amide link. So they have also included an O atom before the 'end bond'. This is a costly error as the candidate is unable to be given either of the marks available for this polymer.
ii	AND E: Condensation / polyamide ✓	1(AO 1.1)	DO NOT ALLOW 'additional'
	E. Condensation / polyamide v	5	
	Formation of electrophile $CH_3COCI + AICI_3 \rightarrow CH_3-C^+=O + AICI_4^- \checkmark$ Mechanism $Curly \ arrow \ from \ \pi\text{-bond to} \ CH_3C^+=O \ \checkmark$	(AO 2.5)	ANNOTATE ANSWER WITH TICKS AND CROSSES ALLOW '+' charge anywhere on
	H ₃ C—		CH₃C ⁺ O i.e. CH₃CO ⁺
ii i		(AO 2.5)	NOTE: curly arrows can be straight, snake-like, etc. but NOT double headed or half headed arrows
	Correct intermediate √		1st curly arrow must
	Curly arrow from C–H bond to reform π-ring √ H COCH ₃ COCH ₃	(AO 3.1)	go to the C of C=O AND
	+	(AO 2.5)	start from, OR close to circle of benzene ring

(AO 1.2) IGNORE curly arrow shown on C=O **DO NOT ALLOW** the following intermediate: π-ring should cover approximately 4 of the 6 sides of the benzene ring structure **AND** the correct orientation, i.e. gap towards C with COCH3 **ALLOW** + sign anywhere inside the 'hexagon' of intermediate curly arrow must start from, OR be traced back to, any part of C-H bond and go inside the 'hexagon' **Examiner's Comments** This question required candidates to apply their knowledge of the mechanism of electrophilic substitution to the formation of phenylethanone from benzene. Examiners were encouraged by the number of excellent responses to this question, with the majority of candidates securing four out of five marks. Common errors included accuracy of curly arrows (Exemplar 7 below) and omission of HCl as product from the regeneration of the catalyst. The responses of lower ability

candidates also contained errors in

	the equation for the formation of the electrophile. Such responses used chlorine rather than ethanoyl chloride. Exemplar 6
	Formation of electrophile $CH_3COCI + AICI_3 \rightarrow CH_3CC$ $H_3C \rightarrow CH_3COCI + AICI_3 \rightarrow CH_3CC$ Intermediate
	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
	This response demonstrates a near perfect attempt at this question. The equations for the formation of the electrophile and regeneration of the catalyst are correct. The first curly arrow is
	drawn accurately from the circle of the benzene ring to the correct carbon atom of the electrophile. The intermediate is correct, with the π ring over the five carbon atoms and in the correct orientation. Unfortunately the curly
	arrow drawn to reform the π bond starts at the H atom rather than from the bond. This small error has prevented this candidate from being given full marks.





incorrect linking of the OH group

				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	
5	i	3-hydroxybutanal √	1	IGNORE lack of hyphens or addition of commas ALLOW 4-oxobutan-2-ol OR 1-oxobutan-3-ol DO NOT ALLOW • 3-hydroxybutal • 3-hydroxylbutanal Examiner's Comments Most candidates made good

								being that to be shot rather the Common hydroxylt carbon countries and 2- or the contries the co	at hydroxown as a an the sin errors i outanal (chain fror the alde	yl group hydrox uffix -ol. ncluded counting the wi oxybutar	I 2-
ii	Addition	✓					1	most cho	ALLOW on, cond sation er's Con t was and cosing no	radical Vadditic ensation nments swered ucleoph	on– n, well with
ii	charge at e.g. For Correct One of i.e. A OR Step 2: CH ₃ C CH For CH ₂	any formula profe correct, CH₃CHO, ALLO ect equation √ correct acid—bas 1 and B1 OR A CH₃CHO + OH CH₃CHO + OH CH₃CHO + CH₂CHO d₃CHOHCH₂CHO CHO: ALLOW O CHOHCH₂CHO,	Se pair √ 2 and B2 T = CH ₂ CHC CH ₂ CHO ⁻ ; CH ₂ CHO ⁻ ; CH ₂ CHO ⁻ ; C	D + H ₂ O + H ₂ O √ B1 B2 H ₃ CO ⁻ ; C ₂ H	A2 A1	and	3	in any for shown. Example in 6a(iv) Step 1: OH ⁻ , i.e. CH ₃ CH O ²⁻ V B2 OR B1 Step 2: CH ₃ CH	ALLOW HO + OH A1 A2 HO + CH CH ₃ CHC CH ₂ O+: A	H [†] trans A2 A1 A2 A1 A2 A1 A1 A2 A1	sfer from 3CH ₂ O ⁺ + B1 B2 + O ² - CHO +

				acid-base equilibria with a multistep 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 CH ₃ CO + H ₂ O ACA ACA ACA ACA ACA ACA ACA ACA ACA A
	i v	H ₃ C C C C C C C C C C C C C C C C C C C	1	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous For connectivity, ALL
		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.

- · 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. Change in 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: Calculation of mass of 4- nitrophenol Using moles
ii	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. There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated. Level 2 (3-4 marks) Calculates the mass of 4-nitrophenol with some errors AND suggests reagents and intermediate with some omissions. OR 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 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. Level 1 (1-2 marks) Attempts to calculate the mass of 4-nitrophenol OR Suggests reagents OR intermediate but may be incomplete OR Describes few purification steps. There is an attempt at a logical structure with a line of reasoning. The	6	• $n(\text{paracetamol}) = \frac{5.00}{151} = 0.0331 \text{ (mol)}$ • $n(4\text{-nitrophenol}) = 0.0331 \times \frac{100}{40} = 0.082$ • Mass of 4-nitrophenol = $139 \times 0.0828 = 11.5 \text{ g}$ ALLOW 11.4-11.6 for small slip/rounding Using mass • Theoretical mass paracetamol = 5.00×10^{-2} Theoretical $n(4\text{-nitrophenol}) = \frac{12.5}{151} = 0.00 \times 10^{-2}$ • Mass of 4-nitrophenol = $139 \times 0.0828 = 11.5 \text{ g}$ NOTE: Incorrect inverse ratio of $\frac{100}{40}$ gives: • $0.0331 \times \frac{40}{100} = 0.0132 \text{ (mol)}$ • Mass = $139 \times 0.0132 = 1.84 \text{ g}$ Reagents and intermediate • Reagents: Sn + (conc) HCl (then NaOH) Intermediate: 4-aminophenol or • structure
	 information is in the most part relevant. 0 marks No response or no response worthy of credit. 		 Purification 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

were showing the correct steps but in the wrong order and use of a drying agent such as CaCl2 (confusion with part of the purification of an organic liquid). These candidates seemed unaware that adding a solid drying agent to an organic solid would result in impure paracetamol rather than purifying. Exemplar 11 shows an excellent response that addresses all 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 maar mass 4 puracetand = 151 gmol " moles in 19: 151 = 0:0331 mel maes required = 0.0331 -0.0 = 0.0827 modes of 4-nitrophenal required = 0.08278 mol mass of 4-nitrophend required = 0.08278 To purity the paracetainal, filter the sen under reduced pressure woring Buchner as Dissolve the remaining solid in the mana amount & hot solvent and filter again remaining Mm Solution and filter mitte both. Wash the remaining solid north co and leave to dry. Exemplar 12

	1		
	Total	8	In your enswer, include the mass of 4-nitrophenol required, the reagents and addition of the purification of paracetamol. # -nitrophenol is excelled with reduced (Sn) him in presence of and acid and for the plane of the plane
			ALLOW and a such in all
7	One mark for each correct structure/reagent as shown below Compound H Compou	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. 'End bonds' MUST be shown (do not have to be dotted) ALLOW the 'O' at either end i.e. IGNORE brackets IGNORE n Examiner's Comments Compound H was also the focus for this question. Most candidates were able to provide the structure of the acyl chloride obtained from

				H but only some identified SOCI ₂ as the correct reagent. Common incorrect reagents included HCl and AlCI 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) $ \begin{tabular}{ll} \it Mechanism \\ \it Curly arrow from lone pair on OH^- to δ+ carbon atom (1) \\ \it Curly arrow and dipole on C-I bond (1) \\ \it Correct products (1) \\ \end{tabular} $	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 do not allow attack by NaOH
		Total	5	
9	i	$K_a = \frac{[H^{\dagger}] [C_4 H_9 S^{-}]}{[C_4 H_9 S H]} \checkmark$ 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+].

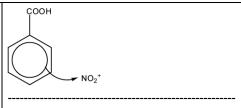
ii	CH ₃ CH ₂ CH ₂ CH ₂ SH + H ₃ C	2	ALLOW correct skeletal OR displayed formula OR mixture of the above as long as non- ambiguous ALLOW C4H9SH ALLOW CH3COOH Thioester functional group must be fully displayed, OR as a skeletal formula but allow SC4H9 in thioester Examiner's Comment: In this part, candidates were
	S-CH₂CH₂CH₂CH₃ ✓ Structure of thioester ✓ Complete equation ✓		expected to apply their knowledge and understanding of esterification to thiols and thioesters. Over half the candidates obtained a correct structure of the thioester. Most of these candidates constructed a balanced equation although some omitted the water product. Common errors included formation of a conventional ester and H ₂ S, and retaining the O atom from the OH in the carboxyl group to form – COOS–. As with 4(b)(i), structural and skeletal formulae were used. Candidates are less likely to omit H atoms if the skeletal formula is used.
ii	SH SH	1	IF correct skeletal formula is shown, IGNORE displayed formula in a second structure Examiner's Comment: Just over half the candidates drew the correct structure, displaying a good understanding of interpreting organic nomenclature when drawing a structure. Common errors included omission of the CH ₂ adjacent to the terminal –SH group and placing the branch or double bond in wrong positions. Some candidates spoilt an otherwise good response by showing a structural formula or a

				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	Reactants ✓ Products AND balanced equation ✓	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 0	i	curly arrow from ${}^-CN$ to carbon atom of C-C/ bond \checkmark Dipole shown on C-C/ bond, $C^{\delta+}$ and $CI^{\delta-}$, AND curly arrow from C-C/ bond to C/ atom \checkmark C_2H_5 C_1 C_2H_5 C_2H_5 C_1 C_2H_5 C_1 C_2H_5 C_1 C_2 C_1 C_2 C_1 C_2 C_1 C_2 C_2 C_1 C_2 C_1 C_2 C_1 C_2 C_2 C_1 C_2 C_2 C_2 C_1 C_2 C_2 C_2 C_2 C_2 C_3 C_4	2	ANNOTATE ANSWER WITH TICKS AND CROSSES Curly arrow must come from lone pair on C of ⁻CN OR CN⁻ OR from minus sign on C of ⁻CN ion (then lone pair on CN⁻ does not need to be shown) IGNORE NaCl ALLOW S _N 1 mechanism: Dipole shown on C−Cl bond, C⁵+ and Cl⁵-, AND curly arrow from C−Cl bond to Cl atom ✓ Correct carbocation AND curly arrow from ⁻CN to carbocation. Curly arrow must come from lone pair on C of ⁻CN OR CN⁻

			not need to be shown) \(\squares \) correct organic product AND CI \(\squares \) \(\squares \
	Compound G		ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous IGNORE name(s) ALLOW
	H C H		OH OH OH
ii	Reagents Reaction 2: H₂ AND Ni ✓	3	ALLOW any suitable metal catalyst e.g. Pt ALLOW LiAlH4 for reagent in reaction 2 DO NOT ALLOW NaBH4 for reagent in reaction 2 IGNORE names (question asks for formulae) IGNORE references to temperature and/or pressure
	Reaction 3: Correct formula of an aqueous acid e.g. HC/(aq)/H₂SO₄(aq) √		ALLOW H ⁺ (aq) IGNORE dilute ALLOW formula of an acid AND water e.g. HC/ AND H ₂ O H ₂ SO ₄ AND H ₂ O

			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.
ii	Explanation Nitrogen electron pair OR nitrogen lone pair AND accepts a proton / H*✓ Structure of salt OH H H — — — — — — — — — — — — — — — — —	2	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 C NH3CI i.e. charges n IF charges are shown both need to be present ALLOW charge either on N atom or NH3 ⁺ IF displayed then + charge must be on the nitrogen Examiner Comments Only 20% of candidates were awarded both marks for this question. The commonest error was a failure to state that the N atom has a lone pair of electrons that can gain a proton. Answers

					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 CI ⁻ had to be included.
		i v	Ester link Rest of structure (polymer J is biodegradable because) the ester / ester bond / ester group / polyester can be hydrolysed.	3	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. 'End bonds' MUST be shown (do not have to be dotted) IGNORE brackets IGNORE n 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	а	i	Generation of electrophile $HNO_3 + H_2SO_4 \longrightarrow H_2O + HSO_4^- + NO_2^+ \checkmark$ Electrophilic substitution $Curly \ arrow \ from \ p\text{-bond to } NO_2^+?$	5	ANNOTATE ANSWER WITH TICKS AND CROSSES ALLOW HNO ₃ + 2H ₂ SO ₄ ? H ₃ O ⁺ + 2HSO ₄ ⁻ + NO ₂ ⁺ ALLOW HNO ₃ + H ₂ SO ₄ ?H ₂ NO ₃ ⁺ + HSO ₄ ⁻
					Then $H_2NO_3^+$? $H_2O + NO_2^+$



Correct intermediate?

Curly arrow back from C-H bond to reform p-ring **AND** H⁺ as product?

Regeneration of catalyst

$$H^{+} + HSO_{4}^{-} \longrightarrow H_{2}SO_{4} \checkmark$$

ALLOW *NO2 OR NO2*

First curly arrow must come from the ring to NO₂⁺

DO NOT ALLOW the following intermediate:

p-ring should cover approximately 4 of the 6 sides of the benzene ring structure

AND

the correct orientation, *i.e.* gap towards C with NO₂

ALLOW + sign anywhere inside the

'hexagon' of intermediate

Examiner Comments

The majority of candidates were well prepared for this standard mechanism and frequently scored marks of four or five. Most were able to show equations to generate the electrophile and regenerate the catalyst. Candidates should note the importance of the correct placement of curly arrows and the horseshoe in the intermediate to show the remaining electrons present in the ring structure. These were often poorly represented, leading to marks not being awarded.

Please refer to the marking instructions on page 5 of this mark scheme

Level 3 (5–6 marks)

Outlines the main steps of recrystallisation to produce a pure sample of 3-nitrobenzoic acid from the impure solid.

AND

ii

Calculates correct percentage yield of 3-nitrobenzoic acid.

for guidance on how to mark this question.

AND

Method of checking purity to include comparison to relevant data. A well-structured response with the steps for recrystallisation and the determination of purity being given in the correct order. Correct use of

Indicative scientific points, with bulleted elements, may include:

1. Purification

i. Purilication

6

- Recrystallisation
- Dissolve impure solid in minimum volume of hot water/solvent
- Cool solution and filter solid

terminology throughout.

Level 2 (3-4 marks)

Attempts all three scientific points but explanations may be incomplete.

Explains two scientific points thoroughly with very few omissions.

The description of checking for purity or recrystallisation is clear and any calculations structured. Key terminology used appropriately.

Level 1 (1-2 marks)

A simple explanation based on at least two of the main scientific points.

Explains one scientific point thoroughly with few omissions. There is an attempt at a logical structure. The description of the 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.

Wash with cold water/solvent and dry

2. Percentage yield

- n(benzoic acid) used = $\frac{4.97}{122}$ = 0.0400 n(3-nitrobenzoic acid) made = $\frac{4.85}{167}$ = 0.0
- percentage yield = $\frac{0.0290}{0.0407} \times 100 = 71.3$ (

ALLOW 71 to calculator value of 71.29001554 correctly rounded.

CHECK for extent of errors by **ECF**

Alternative correct calculation may calculate theoretical mass of 3nitrobenzoic acid that can be produced as 0.0407 × 167 = 6.80 (g) followed by: percentage yield = $\frac{4.85}{6.80} \times 100 = 71.3$

Calculation must attempt to calculate n(benzoic acid) in mol.

3. Checking purity

- Obtain melting point
- Compare to known values
- 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 (R_f value) to known data

 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: Br ₂ AND A/Br ₃ /FeBr ₃ /Fe √		IGNORE reaction conditions even if incorrect
b	i	Intermediate NO2 Br ✓ Reduction: Sn AND (concentrated) HC/ ✓	3	IGNORE 'dilute' for HC/ IGNORE H2 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	NH₂ is 2,4 directing ✓ Products (1 mark for each): NH₂ Br	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. ALLOW ortho and para directing for 2,4 directing
		y Br √		IGNORE 6-directing ALLOW Kekulé structure IGNORE names

			Examiner Comments The most able candidates completed this question with a clear statement that the —NH2 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 the —NH2 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 CH3-CH2-C CI CONDITIONS AICI3 NaBH4 Acid (catalyst) acid (catalyst)	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.
	H CH ₃		ALLOW sodium borohydride OR sodium tetrahydridoborate IGNORE [H] for reducing agent in second step
			ALLOW H ⁺ / H ₂ SO ₄ / H ₃ PO ₄ / named mineral acid for reagent in third step

			Use as an organic feedstock √ OR	_	ALLOW the production of plastics or monomers
	b			1	or new polymers
			Combustion for energy production √		Combustion alone is not sufficient
			Total	7	
1 3		i	OH O CH ₃	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
			Acid (catalyst) ✓		ALLOW H ⁺ / H ₂ SO ₄ / H ₃ PO ₄ / named mineral acid
		ii	Diagram showing correct apparatus for distillation ✓ i.e. Round-bottom/pear-shaped flask Condenser (correctly orientated) Stopper/thermometer Delivery tube and suitable collection vessel Condenser Condenser Condenser Round-bottom/pear-shaped) flask AND condenser AND heat (source) ✓	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	а	i	Chem δ 0.8 2.3	NMR spectruical shift, /ppm 8 – 2.0 3 – 3.0 3 – 4.2	im for 2-aminopro Relative peak area 3 1 2	opan-1-ol Splitting pattern doublet multiplet doublet	\ \ \ \	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 CH ₃ CH(NH ₂)CH ₂ OH Fragment peak at 44 CH ₃ CH(NH ₂) ⁺ /C ₂ H ₆ N	¹ ⁺ /C₃H ₉ NO ⁺ <u>4</u> (peak 2)			*	2	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	OR ammonia/NH ₃		ol 🗸			1	ALLOW ammonia in a sealed tube ALLOW dilute ethanolic

				ammonia/NH ₃ IGNORE heat ALLOW alcohol for ethanol DO NOT ALLOW any reference to water or hydroxide ions Examiner's Comments A well answered question. Some candidates forgot to use a solvent or suggested the use of aqueous ammonia.
	ii	(compound D) $ \begin{array}{c} CH_3 \\ H \\ C - CH_2OH \\ H \\ \end{array} $ $ H_3C - C - CH_2OH \\ H \\ \\ \end{array} $	1	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous Examiner's Comments This question discriminated well. Although there were very few blank pages, many incorrect structures were seen.
С	i	Alcohol AND Amide/peptide ✓	1	IGNORE phenol IGNORE hydroxyl/hydroxy IGNORE attempts to classify alcohol or amide as primary, secondary or tertiary DO NOT ALLOW hydroxide Examiner's Comments Generally well answered but incorrect functional groups included carbonyl and amine.
	ii	OH OH NH3*	2	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous ALLOW + on N or H i.e. +NH3 or NH3 +ALLOW NH3+CI- Examiner's Comments

				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	-	• pent-2-ene H ₃ C C=O O=C CH ₂ CH ₃	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
		• hexa-2,4-diene H ₃ C C=0 O=C-C=0 H H H H		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.
	ii		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 6	i	Step 1 Add HNO ₃ OH COOH H2O	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
		Step 2 Tin AND concentrated HC/ ✓		ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous

OH + 6 [H] O ₂ N OH + 2 H ₂ O COOH + 2 H ₂ O		Equations MUST be completely correct for one mark each
		DO NOT ALLOW 3H ₂
		Examiner's Comments
		This question discriminated well. Most candidates knew that nitric acid was involved in the first reaction but some also included sulfuric acid and tried to construct a mechanism involving the nitronium ion, rather than write the expected equation for the reaction. The omission of water as a product was an occasional error. Many correct equations were seen for Step 2, but tin and concentrated hydrochloric acid was required to score the reagent mark.
		DO NOT ALLOW nitrogen / N lone pair accepts hydrogen (proton/H ⁺ required)
		ALLOW nitrogen donates an electron pair / lone pair to H ⁺
ii Nitrogen electron pair OR nitrogen lone pair accepts a proton / H⁺ ✓	1	IGNORE NH ₂ group donates electron pair
		Examiner's Comments
		Candidates needed to mention the electron pair on the nitrogen atom to score this mark.
		ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous
compound A CI N		ALLOW —N ₂ C/ OR —N ₂ +C/-
compound A CI N	2	DO NOT ALLOW —N≡N⁺ OR — N≡N⁺ CI₋
OH OH		DO NOT ALLOW —N ₂ -Cl (covalent bond)
compound B		Examiner's Comments

			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}{180} = 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 Purification Impure aspirin from hot reaction mixture Cool reaction mixture Filter product under reduced pressure Recrystallisation of impure
	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	

1 8	а		3	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous
		Product from NH ₃ /ethanol		ALLOW
		NH ₂ O		NH ₂ O
		C ₆ H ₅ OH		C ₆ H ₅ O (NH ₄ ⁺) ALLOW ECF from 2-bromo compound as product from Reaction 1
		Product from Reaction 1		DO NOT ALLOW 2-bromo compound (inconsistent with final product shown)
		C ₆ H ₅ OH		
		Product from NaOH(aq)		DO NOT ALLOW ECF from 2- bromo compound as product from Reaction 1 (inconsistent with final product shown)
		ОН О 		
		C ₆ H ₅ O ⁻ (Na ⁺)		
	b			ANNOTATE ANSWER WITH TICKS AND CROSSES
		Curly arrow from C=C bond to H of H-Br		
				ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous
		Correct dipole shown on H–Br AND curly arrow showing the breaking of H-Br bond		

	C_6H_5 OH OH OH OH OH OH OH OH		DO NOT ALLOW partial charges shown on C=C double bond DO NOT ALLOW δ+ on C of carbocation
	Correct carbocation AND curly arrow from Br ⁻ to C ⁺ of carbocation C ₆ H ₅ Br ⁻ OH		ALLOW formation of the 2-bromo isomer O C ₆ H ₅ Br
	Electrophilic addition		Curly arrow must come from a lone pair on Br ⁻ OR from the negative sign of Br ⁻ ion (then lone pair on Br ⁻ ion does not need to be shown)
c i	H COOH C C H	1	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous 'End bonds' MUST be shown (do not have to be dotted) IGNORE brackets IGNORE n
ii	Ester link Rest of structure	2	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous 'End bonds' MUST be shown (do not have to be dotted)
	Total	10	