GCE

Chemistry A

H432/02: Synthesis and analytical techniques

Advanced GCE

Mark Scheme for November 2020

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This mark scheme is published as an aid to teachers and students, to indicate the requirements of the examination. It shows the basis on which marks were awarded by examiners. It does not indicate the details of the discussions which took place at an examiners' meeting before marking commenced.

All examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

Mark schemes should be read in conjunction with the published question papers and the report on the examination.

1. Annotations available in RM Assessor

Annotation	Meaning
	Correct response
	Incorrect response
	Omission mark
	Benefit of doubt given
	Contradiction
	Rounding error
	Error in number of significant figures
	Error carried forward
	Level 1
	Level 2
	Level 3
	Benefit of doubt not given
	Noted but no credit given
	Ignore

2. Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
( )	Words which are not essential to gain credit
__	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

1. **Subject-specific Marking Instructions**

INTRODUCTION

Your first task as an Examiner is to become thoroughly familiar with the material on which the examination depends. This material includes:

- the specification, especially the assessment objectives
- the question paper
- the mark scheme.

You should ensure that you have copies of these materials.

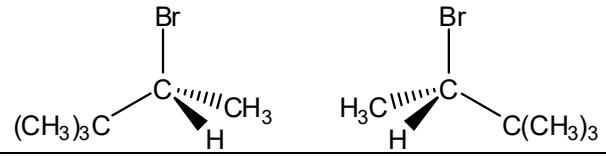
You should ensure also that you are familiar with the administrative procedures related to the marking process. These are set out in the OCR booklet **Instructions for Examiners**. If you are examining for the first time, please read carefully **Appendix 5 Introduction to Script Marking: Notes for New Examiners**.

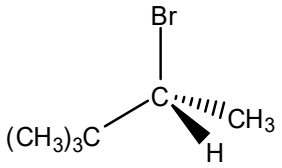
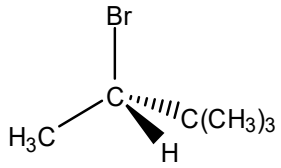
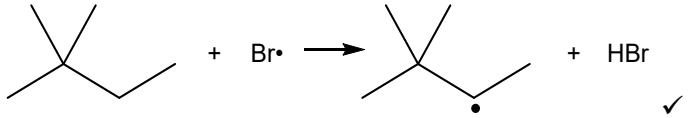
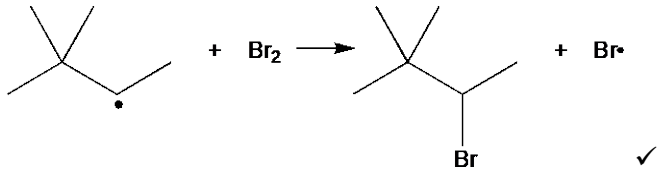
Please ask for help or guidance whenever you need it. Your first point of contact is your Team Leader.

SECTION A

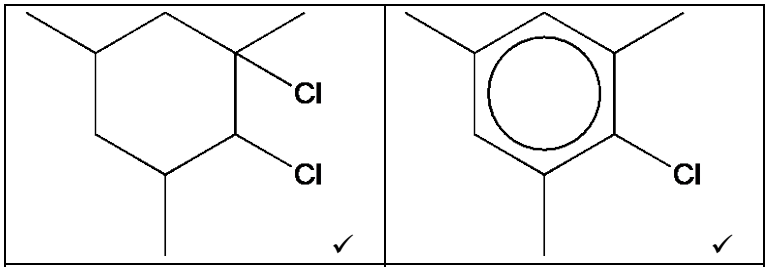
Question	Answer	Marks	AO element	Guidance
1	A	1	1.2	
2	B	1	1.1	
3	A	1	1.1	
4	C	1	2.3	
5	D	1	1.2	
6	D	1	2.1	
7	A	1	1.1	
8	C	1	2.2	
9	D	1	1.2	
10	C	1	2.5	ALLOW 5
11	A	1	2.6	
12	A	1	2.2	
13	A	1	1.1	
14	B	1	2.3	
15	C	1	1.2	

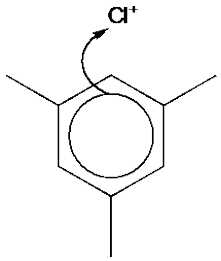
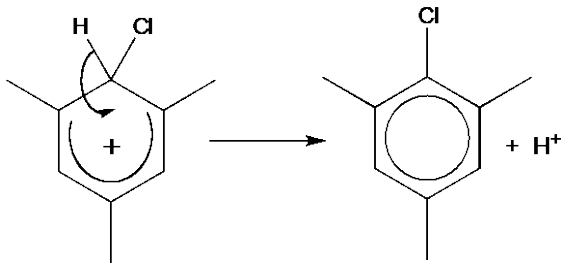
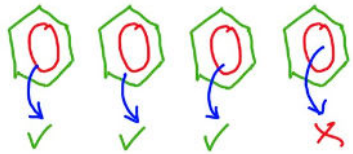
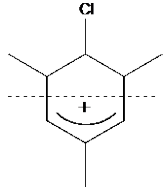
SECTION B

Question			Answer	Marks	AO element	Guidance
16	(a)	(i)	2-bromo-3,3-dimethylbutane ✓	1	1.2	**IGNORE** lack of hyphens or addition of commas **ALLOW** 3,3-dimethyl-2-bromobutane **DO NOT ALLOW** 2-bromo-3-dimethylbutane methy for methyl methly for methyl brom for bromo
	(b)	(i)	**Stereoisomers** Same structural formula **AND** Different arrangement (of atoms) in space **OR** different spatial arrangement (of atoms) **AND** **Type:** Optical ✓	1	1.2	**ALLOW** structure/displayed/skeletal formula **DO NOT ALLOW** same empirical formula **OR** same general formula **IGNORE** same molecular formula **IGNORE** references to chiral molecules/compounds
		(ii)	One 3D structure with correct groups attached to the chiral C ✓ Two 3D structures of $(CH_3)_3CCHBrCH_3$ that are mirror images **AND** correct connectivity in both ✓  	2	2.5 1.2	**ALLOW** small slip in one of the groups OR use of C_4H_9 3D structures must have four central bonds with **at least two wedges.** For bond into paper accept:  **ALLOW** two 3D structures with 2 groups swapped e.g.

Question			Answer	Marks	AO element	Guidance
			 			
	(c)		**Initiation** $Br_2 \rightarrow 2Br\bullet$ ✓ **Propagation**  ✓  ✓	3	1.2 2.5×2	**ALLOW** $Br_2 \rightarrow Br\bullet + Br\bullet$ **IGNORE** dots for initiation step, i.e. **ALLOW** $Br_2 \rightarrow Br + Br$ **OR** $Br_2 \rightarrow 2Br$ **DOT REQUIRED** at correct position on chain. **ALLOW 1 mark** if both propagation equations are correct by atom but dot(s) missing or on incorrect C in chain **ALLOW 1 mark** if both propagation equations are correct including position of dot(s) but structures are not shown using skeletal formula **ALLOW** ECF from incorrect intermediate

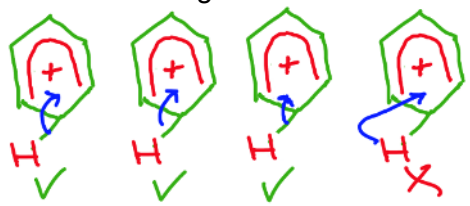
Question			Answer	Marks	AO element	Guidance
	(d)		further substitution/s **OR** produces different termination products **OR** More than one termination step **OR** Mixture of products are formed ✓ substitution at different positions along chain ✓	**2**	**1.1×2**	**ALLOW** dibromo/multibromo compounds formed **OR** an example of a further substitution product **OR** an example of a different termination product **ALLOW** more than one hydrogen (atom) can be replaced **ALLOW** radicals react with each other to form other products **IGNORE** references to separation of products **IGNORE** references to atom economy or yield **ALLOW** a hydrogen (atom) on a different carbon (atom) can be replaced

Question			Answer	Marks	AO element	Guidance
17	(a)	(i)	 ✓ ✓ Organic product with **B** | Organic product with **C**	**2**	**2.5×2**	
		(ii)	**Reactivity of B** in B electrons are localised OR in B π-bond is localised ✓ **Reactivity of C** in C electrons are delocalised OR In C π-system / ring is delocalised In **B**, electron density is higher **AND** B is more susceptible to electrophilic attack **OR** B attracts/accepts the electrophile/Cl_2 more **OR** B polarises the electrophile/Cl_2 more ✓ **ORA**	**3**	**1.1×3**	**ALLOW** labelled diagram to show delocalised system **IGNORE** charge density **IGNORE** electronegativity **IGNORE** B is more reactive/reacts more readily (no reference to electrophile) **IGNORE** references to electron density spread around the π–ring **ALLOW** chlorine

Question	Answer	Marks	AO element	Guidance
(iii)	**Generation of electrophile** $AlCl_3 + Cl_2 \rightarrow AlCl_4^- + Cl^+$ ✓ **Attack of Cl^+**  Curly arrow from π-bond to Cl^+ ✓ --- **Intermediate and organic product**  Correct intermediate ✓ Curly arrow from C–H bond to reform π-ring ✓ --- **Regeneration of catalyst** $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$ ✓	5	1.2 1.2 2.5 1.2 1.2	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW** $FeCl_3 + Cl_2 \rightarrow FeCl_4^- + Cl^+$ **ALLOW** use of Fe **NOTE**: curly arrows can be straight, snake-like, etc. …….. but **NOT** double-headed or half-headed arrows **1st curly arrow** must • start from, **OR** close to, **circle of benzene ring**  **DO NOT ALLOW** following intermediate:  π-ring must cover 4 of the 6 sides of the benzene ring **AND** correct orientation, *i.e.* gap towards C–Cl **ALLOW** + sign anywhere inside the 'hexagon' of the intermediate.

<table>
<tr><th colspan="3">Question</th><th>Answer</th><th>Marks</th><th>AO element</th><th>Guidance</th></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td>IGNORE partial charges on the chlorine in the intermediate

DO NOT ALLOW mark for intermediate if any CH_3 is missing

Curly arrow must start from, OR be traced back to, any part of C-H bond and go inside the ‘hexagon’
 

ALLOW use of $AlCl_4^-$ in the mechanism

ALLOW ECF for regeneration of an incorrect metal chloride catalyst e.g. $AgCl_3$</td></tr>
<tr><td></td><td>(b)</td><td></td><td>$3C_3H_6O \rightarrow C_9H_{12} + 3H_2O$

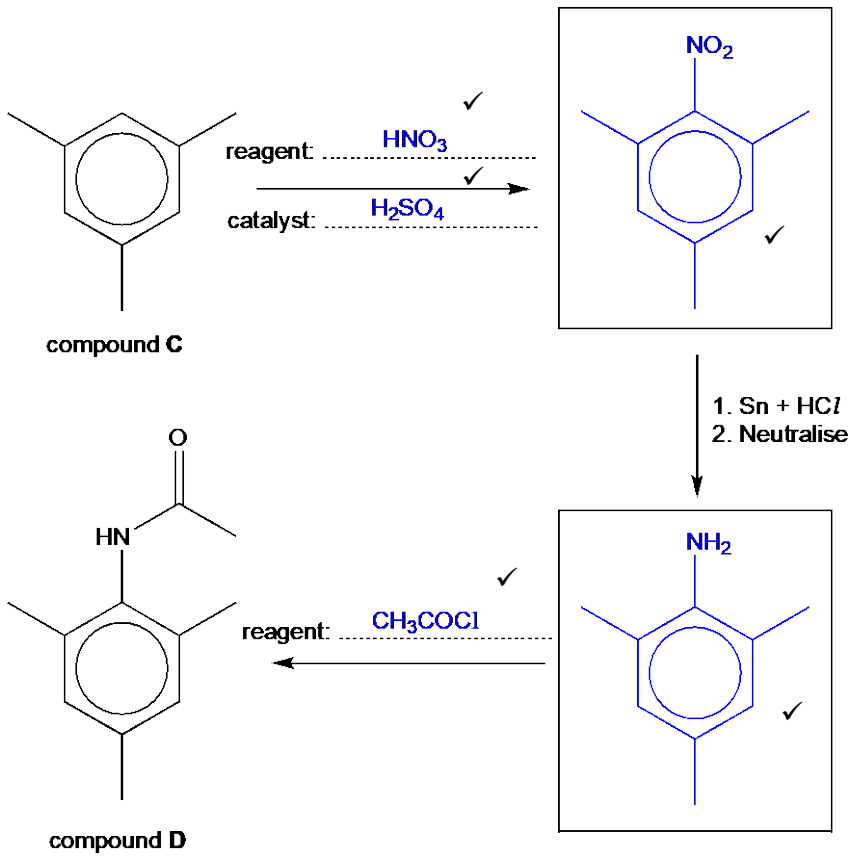
molecular formulae of C_3H_6O AND C_9H_{12} ✓

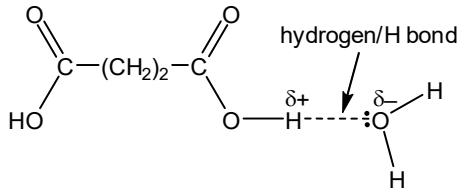
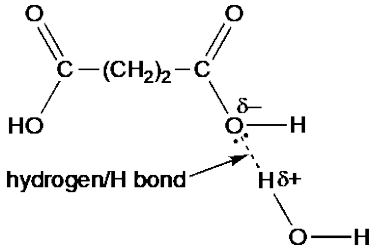
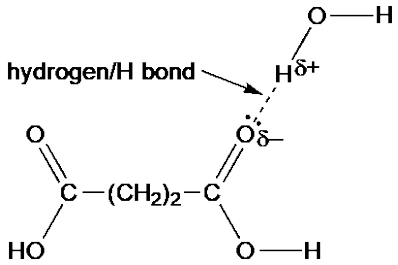
H_2O as by-product ✓

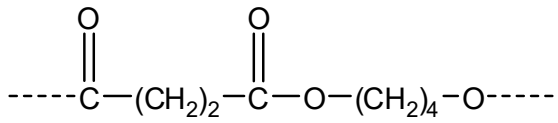
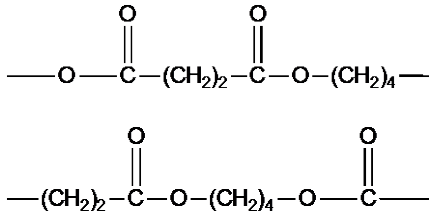
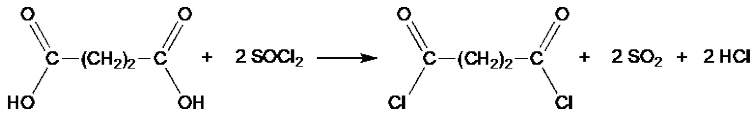
correct balanced equation ✓</td><td>3</td><td>2.6

2.5

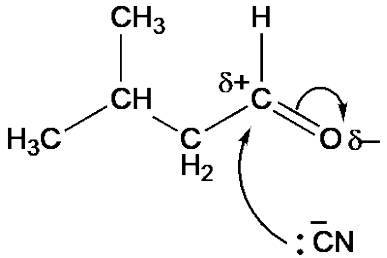
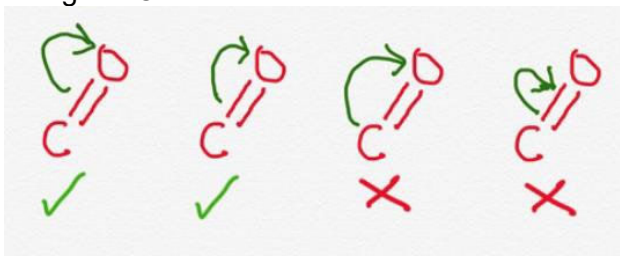
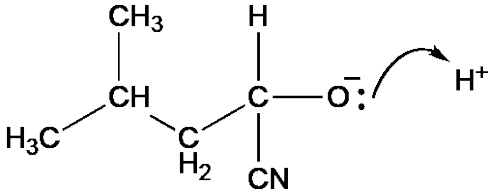
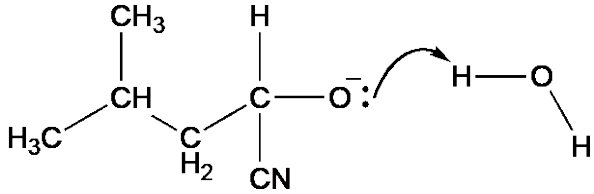
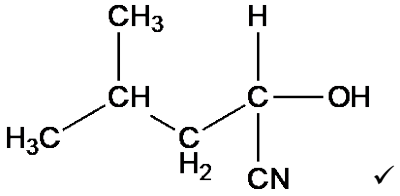
2.6</td><td></td></tr>
<tr><td></td><td>(c)</td><td>(i)</td><td><table><tr><td></td><td>Compound C</td><td>Compound D</td></tr><tr><td>Number of peaks</td><td>3 ✓</td><td>8 ✓</td></tr></table></td><td>2</td><td>3.2</td><td></td></tr>
</table>

Question	Answer	Marks	AO element	Guidance
(ii)		5	3.2×5	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **IGNORE** names for organic intermediates (question asks for structures **ALLOW** names of reagents and catalyst Around top arrow, **ALLOW** 1 of 2 marks if HNO_3 and H_2SO_4 swapped. i.e. reagent: H_2SO_4 catalyst: HNO_3 **IGNORE** references to concentration **ALLOW** $(CH_3CO)_2O$ for left arrow **IGNORE** CH_3COOH **IGNORE** acyl chloride **DO NOT ALLOW** $AlCl_3/FeCl_3$/Fe4

Question			Answer	Marks	AO element	Guidance
18	(a)	(i)	**Reagents** $K_2Cr_2O_7$ **AND** acid **AND** reflux ✓ **Equation** $HO(CH_2)_4OH + 4[O] \rightarrow HOOC(CH_2)_2COOH + 2H_2O$ [O] **AND** H_2O ✓ Correctly balanced equation ✓	**3**	 **1.1** **2.5** **2.6**	**ALLOW** $Na_2Cr_2O_7$ **OR** $Cr_2O_7^{2-}$ **ALLOW** H_2SO_4 **OR** HCl **OR** H^+ **ALLOW** words. e.g. 'acidified dichromate' **ALLOW** a small slip in formula for dichromate e.g KCr_2O_7,
		(ii)	 **OR**  Diagram showing correct dipole charges on each end of one hydrogen bond between a water molecule and a diacid ✓ Hydrogen bond between one lone pair on O atom in one of the molecules and the H atom of another **AND** Hydrogen bonding stated or labelled on diagram	**2**	**2.1×2**	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **DO NOT ALLOW** δ+ on H atoms of CH_2 group **ALLOW** H-bond for hydrogen bond **ALLOW** H bond between C=O and H_2O, i.e.  **IF** diagram is not labelled, **ALLOW** hydrogen bond/H bond from text

Question			Answer	Marks	AO element	Guidance
	(b)	(i)	 Ester link (must be displayed) ✓ Rest of structure ✓	2	1.2 2.5	**ALLOW** the 'O' or C=O at either end, e.g.  **IGNORE** brackets **IGNORE** *n* End bonds' **MUST** be shown (solid or dotted) **DO NOT ALLOW** more than one repeat unit
		(ii)	the ester/ ester bond/ ester group /polyester can be broken down ✓ **OR** It can be hydrolysed ✓	1	3.2	**IGNORE** references to photodegradable 'Bond breaks' is not sufficient – no reference to ester bond
		(iii)	 $SOCl_2$ in equation ✓ Structure of diacyl dichloride ✓ Complete balanced equation ✓	3	1.1 1.2 2.6	**ALLOW** alternative approach using PCl_5 or PCl_3

Question			Answer	Marks	AO element	Guidance
19	(a)	(i)	(series of organic compounds with the) same functional group **OR** same/similar chemical properties/reactions ✓ each **successive/subsequent** member differs by CH_2 ✓	2	1.1 ×2	**IGNORE** reference to physical properties **IGNORE** same general formula **DO NOT ALLOW** same empirical **OR** molecular formula Differs by CH_2 is **not** sufficient (*no successive*)
		(ii)	$C_{24}H_{48}O$ ✓	1	2.1	
	(b)		F/aldehyde **AND** Tollens' (reagent) **AND** Silver (mirror/precipitate/ppt/solid) ✓ G/alkene/C=C **AND** Bromine/Br_2 **AND** goes colourless/decolourised ✓ G/ketone **AND** 2,4-dinitrophenylhydrazine **AND** orange/yellow/red precipitate ✓ G/ketone **AND** Tollens' (reagent) **AND** no silver mirror/no change/no reaction ✓	4	2.3 3.3 3.3 3.3	**IGNORE** use of 2,4-DNP with F **ALLOW** ammoniacal silver nitrate **OR** Ag^+/NH_3 **ALLOW** black ppt **OR** grey ppt **ALLOW** bromine water/ $Br_2(aq)$ **ALLOW** errors in spelling for 2,4-DNP **ALLOW** 2,4(-)DNP **OR** 2,4(-)DNPH **ALLOW** Brady's reagent or Brady's Test **ALLOW** solid **OR** crystals **OR** ppt as alternatives for precipitate **ALLOW** ammoniacal silver nitrate **OR** Ag^+/NH_3 **ALLOW** black ppt **OR** grey ppt **ALLOW** alterative approach using acidified potassium dichromate for tests with F and/or G, with correct observations, alongside use of 2,4-DNP

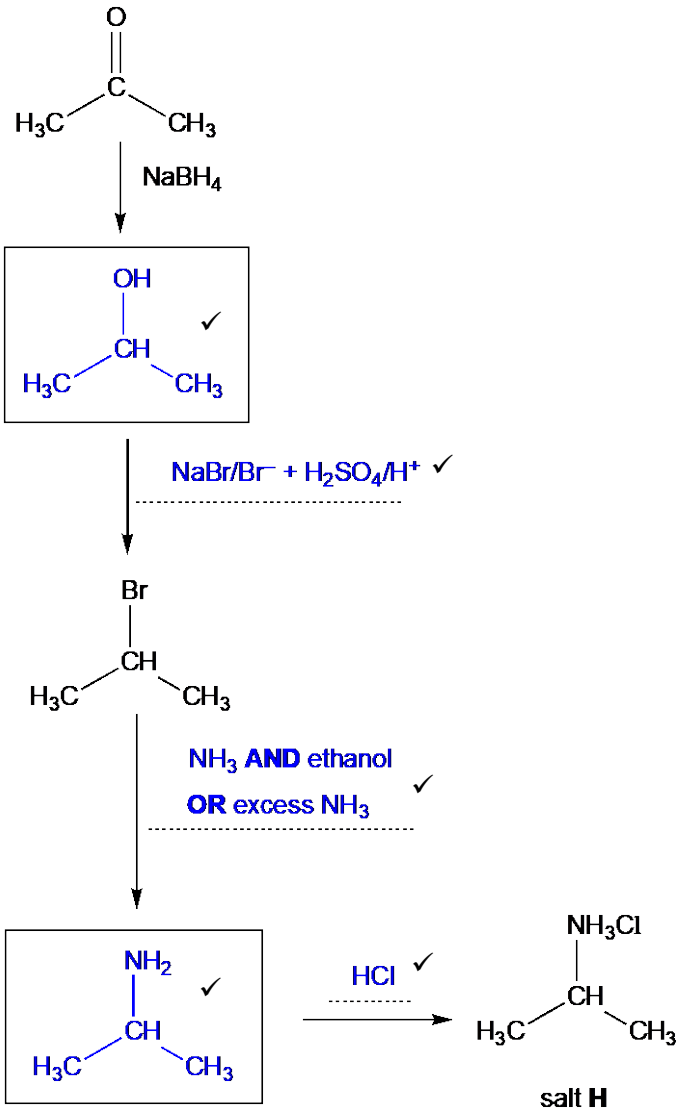
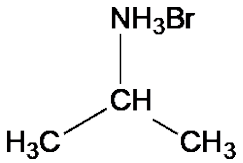
Question			Answer	Marks	AO element	Guidance
	(c)	(i)	**Mechanism** ***3 marks***	**5**		**ANNOTATE ANSWER WITH TICKS AND CROSSES**
						Curly arrow must come from lone pair on C of $^{-}$CN **OR** CN^{-} **OR** from minus sign on C of $^{-}$CN ion (then lone pair on CN^{-} does not need to be shown)
			Curly arrow from $^{-}$CN to C atom of C=O ✓		**1.2**	Curly arrow from C=O bond must start from, OR be traced back to, any part of C=O bond and go to O
			Dipole shown on C=O bond, $C^{\delta+}$ and $O^{\delta-}$, **AND** curly arrow from C=O bond to O atom ✓		**1.2**	
						---
			Curly arrow from lone pair **OR** – charge on O^{-} of **correct** intermediate to H^{+} ✓		**2.5**	**ALLOW** curly arrow to H atom of H_2O, i.e.
			---			
			Product ***1 mark***			**IGNORE** attempt to draw curly arrow showing breaking of H–O in H_2O
			 ✓		**2.5**	**IGNORE** lack of dipole on H_2O

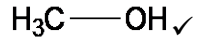
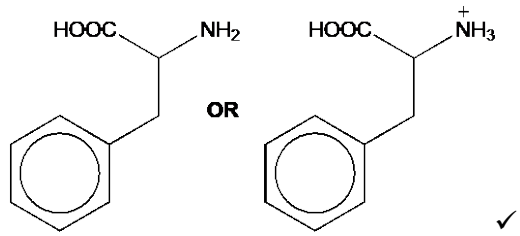
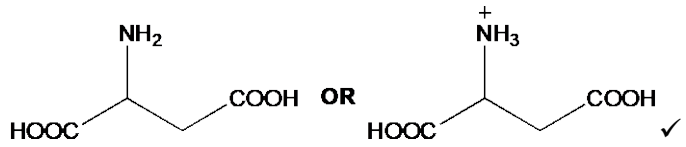
			Name of mechanism ***1 mark***			
			Nucleophilic addition ✓		**1.1**	

Question			Answer	Marks	AO element	Guidance
		(ii)	**Heterolytic** One (bonded) atom/O receives both/2 electrons ✓ **Fission** Breaking of a **covalent** bond ✓	**2**	**1.2**	**ALLOW** 2 electrons go to one (bonded) atom/O **DO NOT ALLOW** both pair**s** of electrons go to O **IGNORE** formation of ions/radicals For O atom, **ALLOW** species **DO NOT ALLOW** element or molecule **ALLOW** π bond in C=O breaks **IGNORE** breaking of C=O bond (no reference to only one bond breaking) 'Bond breaking' is **not** sufficient *(no reference to covalent)*

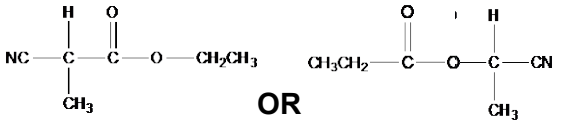
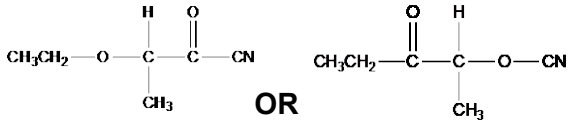
Question			Answer	Marks	AO element	Guidance
20	(a)*		*Refer to marking instructions on page 4 of mark scheme for guidance on marking this question.* **Level 3 (5-6 marks**) A correct calculation of the mass of cyclopentanol **AND** A **detailed** description of most purification steps *There is a well-developed 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 cyclopentanol with some errors **AND** A **detailed** description of some purification steps **OR** A correct calculation of the mass of cyclopentanol **AND** A **detailed** description of a few purification steps *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)** Calculates the mass of cyclopentanol with some errors **OR** A **detailed** description of some purification steps *There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.* **0 marks** No response or no response worthy of credit.	**6**	**2.8×2** **3.3×4**	**Indicative scientific points may include:** **<u>Calculation of mass of cyclopentanol</u>** **Using moles** • n(cyclopentene) = $\frac{4.00}{68}$ = 0.0588…. (mol) • n(cyclopentanol) = 0.0588 × $\frac{100}{64}$ = 0.0919…(mol) • Mass of cyclopentanol = 86 × 0.0919 = **7.90** g **Using mass** • Theoretical mass cyclopentene= 4.00 × $\frac{100}{64}$ = 6.25 g • Theoretical n(cyclopentanol) = $\frac{6.25}{68}$ = 0.0919 (mol) • Mass of cyclopentanol = 86 × 0.0919 = **7.90** g **ALLOW** for small slip in Mr / rounding errors **<u>Examples of some calculation errors</u>** **Incorrect inverse ratio**: • 0.0588 × $\frac{64}{100}$ = 0.0376…. (mol) • Mass = 86 × 0.0376 = 3.24 g **Ignoring % yield gives**: • $\frac{4.00}{68}$ = 0.0588…. (mol) • Mass = 86 × 0.0588 = 5.06 g **<u>Purification</u>** • Add a neutralising agent **by formula or name** e.g. Na_2CO_3 • In separating funnel, **organic layer is on top** • Drying with an **anhydrous salt by formula or name**, e.g. $MgSO_4$, Na_2SO_4, $CaCl_2$ • Redistil **at approx. 44ºC** **Examples** of detail in **bold** (**NOT INCLUSIVE**)

Question			Answer	Marks	AO element	Guidance
	(b)		C=C/alkene peak in region 1620-1680 cm^{-1} ✓ O–H/alcohol peak in region 3200-3600 cm^{-1} ✓	2	3.2×2	**LOOK ON THE SPECTRUM** for labelled peaks which can be given credit **IGNORE** references to C-O at 1000cm^{-1}

Question			Answer	Marks	AO element	Guidance
21	(a)			**5**	**2.5×5**	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** HBr **ALLOW** for the bottom left structure 

Question			Answer	Marks	AO element	Guidance
	(b)	(i)	Ester Amide Amine Carboxylic acid 4 groups correct ✓✓✓ 3 groups correct ✓✓ 2 groups correct ✓	3	1.2×3	**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**  **Amino Acids 3 marks**   Both amino acids shown with NH_3^+ ✓	4	2.5×4	**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^+ 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_3Cl, all marks can be awarded.

Question			Answer	Marks	AO element	Guidance
		(iii)	**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	2.2×3	**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) ✓ n(aspartame) per kg = 5.68 x 10^{-4} / 75 = 7.57 x 10^{-6} (mol) ✓ number of cans = 1.7 x 10^{-4} / 7.57 x 10^{-6} = 22.4✓ **OR** n(aspartame) limit per day = 1.7x10^{-4} x 75 =0.01275 (mol) ✓ mass(aspartame) limit per day =0.01275 x 294 = 3.7485 (g) ✓ number of cans = 3.7485 / 0.167 = 22.4 ✓

Question		Answer	Marks	AO element	Guidance
22	(a)	$CDCl_3$ used as a solvent ✓ D_2O used to identify OH **OR** NH protons ✓	2	1.1×2	Example and use required for each mark **ALLOW** for 1 mark, D_2O as a solvent
	(b)*	*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)** Structure **I** has a viable chemical structure of $C_6H_9NO_2$ which has the key features consistent with spectral data **AND** Most of the data analysed *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)** Compound **I** has a viable chemical structure of $C_6H_9NO_2$ with most of the key features consistent with spectral data **AND** Some of the spectral data analysed. *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)** Correct determination of empirical formula and/or molecular formula. **OR** Analyses some of the IR and NMR data. **OR** Analyses most of the NMR data.	6	3.1× 4 3.2× 2	**Indicative scientific points:** **Empirical and Molecular Formulae** $= \frac{C}{56.69/12.0} : \frac{H}{7.09/1.0} : \frac{N}{11.02/14.0} : \frac{O}{25.20/16.0}$ **OR** 4.72 : 7.09 : 0.787 : 1.575 = 6 : 9 : 1 : 2 • Empirical formula = $C_6H_9NO_2$ • *m/z* = 127.0 and empirical formula mass (127) used to determine molecular formula as $C_6H_9NO_2$ **Structures of compound I**  **OR** **OR**  **OR** **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous

Question		Answer	Marks	AO element	Guidance
		There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant. **0 marks** No response or no response worthy of credit.			**Key features** • C ≡N • C=O in aldehyde, ketone, ester, amide, acid anhydride • CH_3 group that would give a doublet • CH_3 group that would give a triplet • CH_2 group that would give a quartet **^{1}H NMR and IR analysis** ^{1}H NMR spectrum • δ = 4.2 ppm, quartet, 2H CH_3–**CH_2**–O • δ = 2.9 ppm, quartet, 1H CO–**CH**–CH_3 • δ = 1.7 ppm, doublet, 3H CO–CH–**CH_3** • δ = 1.3 ppm, triplet, 3H **CH_3**–CH_2 IR spectrum • peak at 1750 (cm^{-1}) is C=O • peak at 2280 (cm^{-1}) is C ≡N **ALLOW** ranges from *Data Sheet* **IGNORE** references to C–O peaks

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