

GCE

Chemistry A

Unit H432/02: Synthesis and analytical techniques

Advanced GCE

Mark Scheme for June 2018

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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.

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Annotations available in RM Assessor

| Annotation | Meaning |
|------------|--|
| ~ | Correct response |
| × | Incorrect response |
| | Omission mark |
| BOD | Benefit of doubt given |
| CON | Contradiction |
| RE | Rounding error |
| SF | Error in number of significant figures |
| ECF | Error carried forward |
| LI | Level 1 |
| L2 | Level 2 |
| L3 | Level 3 |
| NBOD | Benefit of doubt not given |
| SEEN | Noted but no credit given |
| I | Ignore |

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

| Answers which are not worthy of credit |
|--|
| Statements which are irrelevant |
| Answers that can be accepted |
| Words which are not essential to gain credit |
| Underlined words must be present in answer to score a mark |
| Error carried forward |
| Alternative wording |
| Or reverse argument |
| |

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.

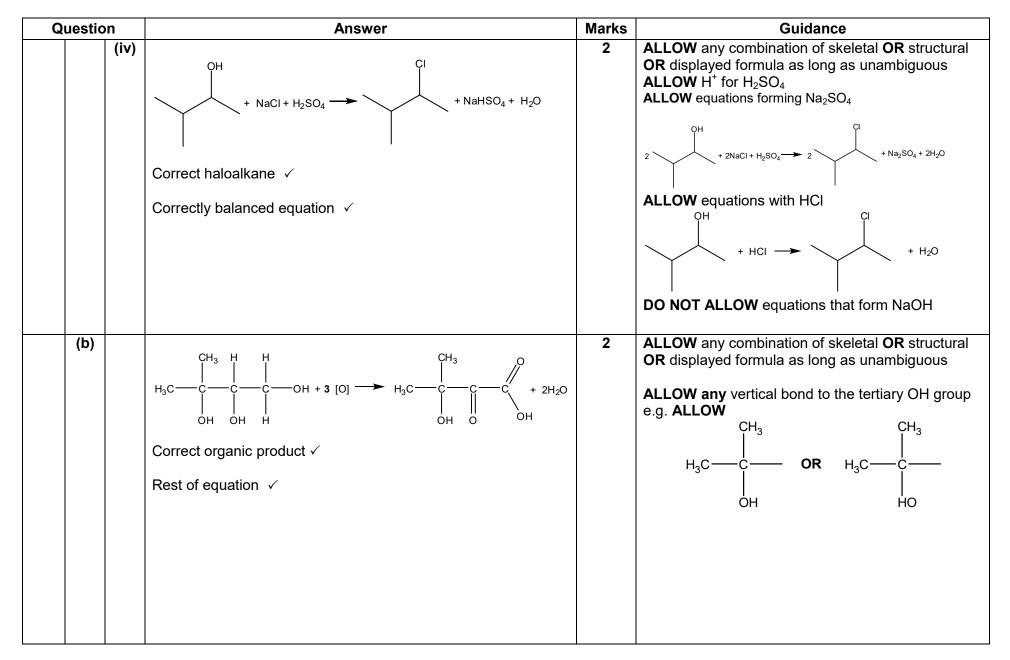
You should ensure also that you are familiar with the administrative procedures related to the marking process. These are set out in the OCR booklet **Instructions for Examiners**. If you are examining for the first time, please read carefully **Appendix 5 Introduction to Script Marking: Notes for New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

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

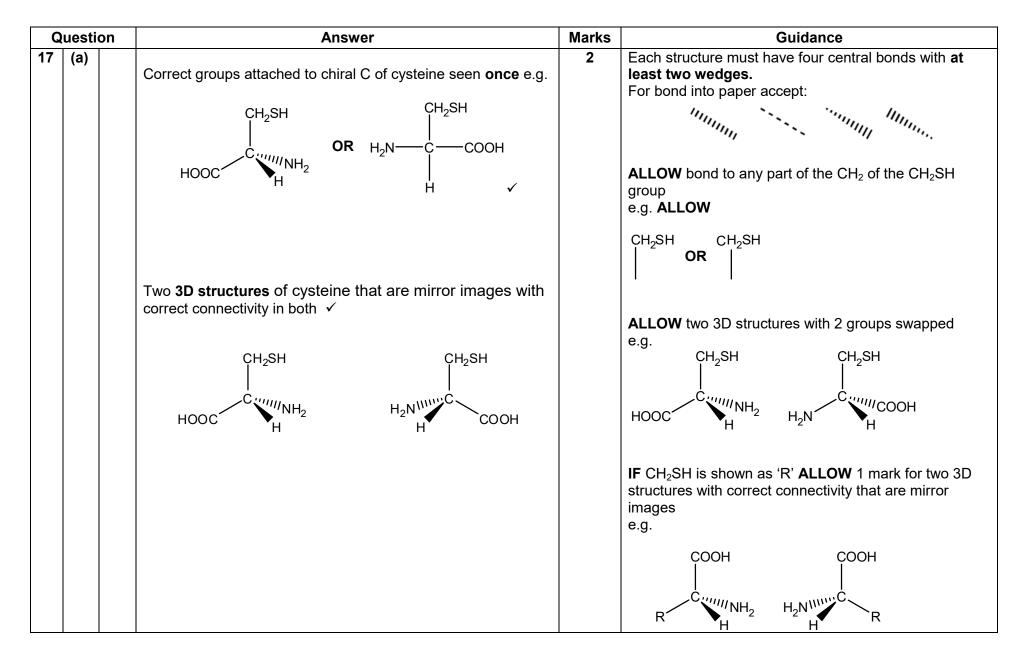
| Question | Answer | Marks | Guidance |
|----------|--------|-------|---|
| 1 | Α | 1 | |
| 2 | C | 1 | |
| 3 | В | 1 | |
| 4 | C | 1 | |
| 5 | В | 1 | |
| 6 | В | 1 | ALLOW 4 (This is the number of peaks in the NMR spectrum) |
| 7 | С | 1 | |
| 8 | D | 1 | |
| 9 | В | 1 | |
| 10 | С | 1 | |
| 11 | В | 1 | ALLOW 2 (This is the number of straight chain isomers with a chiral C atom) |
| 12 | С | 1 | |
| 13 | Α | 1 | |
| 14 | В | 1 | |
| 15 | В | 1 | |
| | Total | 15 | |

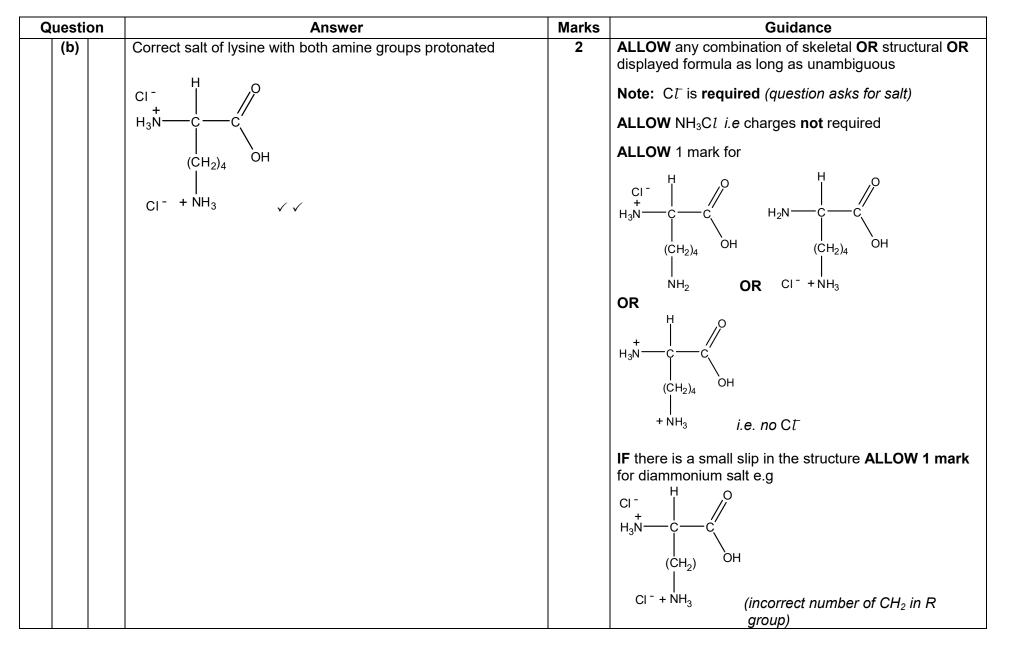
Mark Scheme

| Ques | stion | Answer Ma | | Guidance |
|-------|--------|---|---|--|
| 16 (a | a) (i) | 3-methylbutan-2-ol ✓ | 1 | IGNORE lack of hyphens or addition of commas ALLOW 3-methylbutane-2-ol DO NOT ALLOW 2-methylbutan-3-ol OR 3-methylbut-2-ol OR 3-methbutan-2-ol OR 3-methybutan-2-ol OR 3-methybutan-2-ol |
| | (ii) | (CH ₃) ₂ CHCHOHCH ₃ ✓ | 1 | ALLOW brackets around OH e.g. (CH ₃) ₂ CHCH(OH)CH ₃ ALLOW any unambiguous structural formula e.g. CH ₃ CH(CH ₃)CHOHCH ₃ CH ₃ CH(CH ₃)CH(CH ₃)OH |
| | (iii) | One mark for each correct structure. | 2 | ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW in either order |



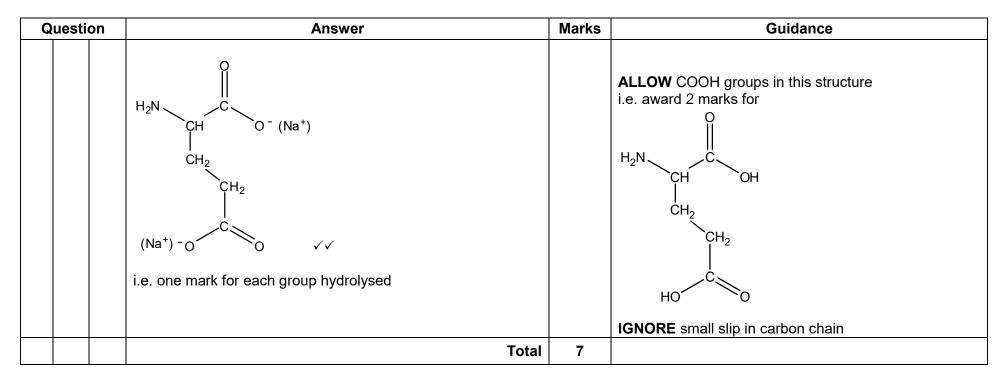
| Question | Answer | Marks | Guidance |
|----------|--|-------|--|
| (c) | Product from excess CH ₃ OH/H ₂ SO₄ H ₃ COOC | 3 | ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous e.g OOC IGNORE connectivity in each product ALLOW the <i>E</i> or <i>Z</i> isomer as product from excess CH ₃ OH/H ₂ SO ₄ |
| | Product from steam, H_3PO_4 HOOC \downarrow COOH \downarrow OH \checkmark | | |
| | H COOH HOOC COOH H COOH HOOC COOH C C H C H H HOOC H HOOC H H | | 'End bonds' MUST be shown (do not have to be dotted) IGNORE brackets IGNORE <i>n</i> ALLOW more than one repeat unit but has to be a whole number of repeat units |
| | Total | 11 | |





| Question | Answer | Marks | Guidance |
|----------|---|-------|---|
| | | | OR CI^{-} $H_{3}N^{-}$ C^{-} C^{-} O $(CH_{2})_{4}$ OH $CI^{-} + NH_{3}$ (H missing from α C atom) |
| (c) | $HO - CH_2 + HO - CH_2 + HO - CH_2 + HO - CH_2 + CH - CH$ | 3 | ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous IGNORE NH ₃ (question asks for organic products) ALLOW $-COO^-$ OR $-COONa$ DO NOT ALLOW negative charge on C atom DO NOT ALLOW negative charge on C atom DO NOT ALLOW $-COO-Na$ (covalent bond) BUT ALLOW ECF if seen in subsequent structures DO NOT ALLOW COOH in this structure DO NOT ALLOW (sodium) salt of alcohol group i.e. $-O - CH_2 - CH_2$ |

Mark Scheme



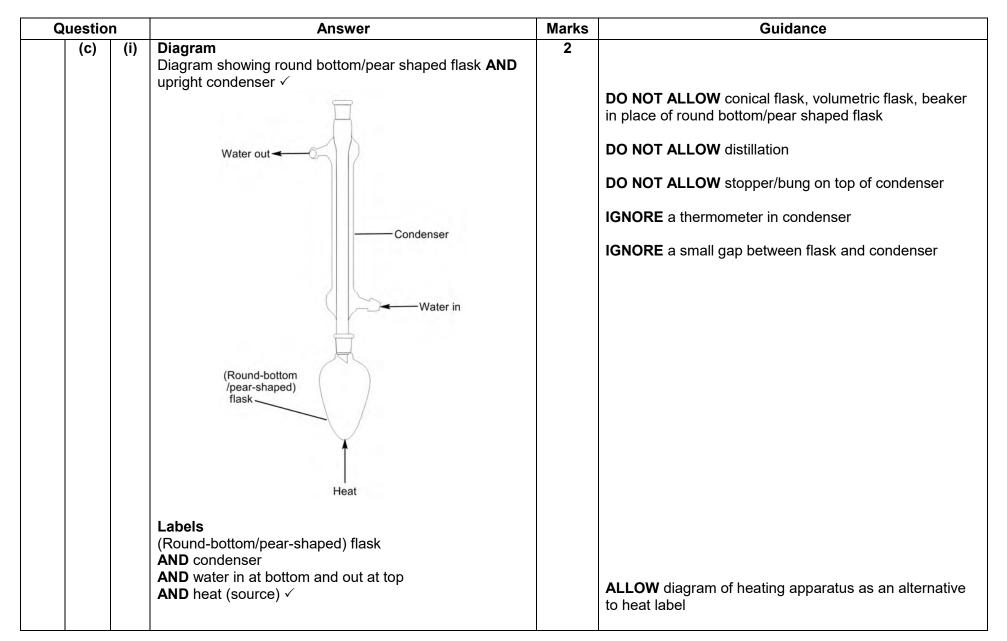
| Questi | on | Answer | | Guidance | |
|--------|------|---|---|---|--|
| 18 (a) | (i) | Number of peaks2 marks2-nitrophenol AND 3-nitrophenol have six peaks/environments/types of carbon ✓4-nitrophenol has four peaks/environments/types of carbon ✓Statement1 mark4-nitrophenol can be distinguished OR 2-nitrophenol and 3-nitrophenol cannot be distinguished with the statement of th | 3 | IGNORE any numbers shown on structures ALLOW 1 mark only IF a response identifies that all the compounds have 6 peaks/environments/types of C OR all the compounds have 4 peaks/environments/ types of carbon IGNORE chemical shifts DO NOT ALLOW ECF from an incorrect number of | |
| | (ii) | (In phenol) a (lone) pair of electrons on O is(partially) delocalised/donated into the π-system / ring ✓ Electron density increases/is higher (than benzene) ✓ ORA (phenol) is more susceptible to electrophilic attack OR (phenol) attracts/accepts electrophile/HNO₃ more OR (phenol) polarises electrophile/HNO₃ more ✓ ORA | 3 | peaks/environments/types of carbon ALLOW the electron pair in the p-orbitals of the O atom becomes part of the π -system / ring ALLOW diagram to show movement of lone pair into ring ALLOW lone pair of electrons on O is (partially) drawn/attracted/pulled/ into π -system / ring IGNORE activating IGNORE charge density IGNORE electronegativity IGNORE phenol reacts more readily (<i>no reference to</i> <i>electrophile</i>) ALLOW NO ₂ ⁺ for electrophile | |

| Question | Answer | Marks | Guidance |
|----------|---|-------|--|
| | Curly arrow from π -bond to S in SO ₃ AND curly arrow from the S=O bond to O atom \checkmark \bigcirc_{H_3} $\bigcirc_{S_4}^{H_5}$ | 3 | ANNOTATE WITH TICKS AND CROSSES NOTE: curly arrows can be straight, snake-like, etc. but NOT double headed or half headed arrows 1st curly arrow must • go to the S of SO ₃ AND • start from, OR close to circle of benzene ring \overrightarrow{O} \overrightarrow{O} \overrightarrow{O} \overrightarrow{O} \overrightarrow{O} 2nd curly arrow must start from, OR be traced back to, any part of S=O bond and go to O \overrightarrow{S} \overrightarrow{S} \overrightarrow{S} \overrightarrow{S} ALLOW 2nd curly arrow from S=O to any O in SO ₃ |
| | | | Intermediate must have correct SO ₃ ⁻ structure fully displayed |

| Question | Answer | Marks | Guidance |
|----------|---|---------|---|
| | Correct intermediate \checkmark Curly arrow from C-H bond to reform π -ring \checkmark | | DO NOT ALLOW the following intermediate: \downarrow + + + + + + + + + + + + + + + + + + + |
| | | Total 9 | |

| Q | uestion | Answer | Marks | Guidance |
|----|---------|---|-------|---|
| 19 | (a) | Links rate of reaction to strength of bond/bond enthalpy ✓ e.g. the weaker the bond the faster the reaction stronger bond takes longer to break lower bond enthalpy reacts faster | 2 | Each marking point must be a comparison |
| | | Correct comparison of rate of reaction for at least two C– Hal bonds e.g. C–F bond is hydrolysed slow est C–I bond is hydrolysed faster than C–Br C–Br has shorter reaction time than C–CI OR | | IGNORE references to halogens as elements: <i>i.e.</i> chlorine is less reactive than bromine etc. DO NOT ALLOW chloride, bromide and iodide |
| | | Correct comparison of C–Hal bond strength/enthalpy of at least two of C–Hal bonds e.g. C–I bond is the weak est C–I has lower bond enthalpy than C–Br C–Br is broken more easily/readily than C–CI C–Hal bond strength decreases down group (7) ✓ | | IGNORE references to bond length, polarity and electronegativity |

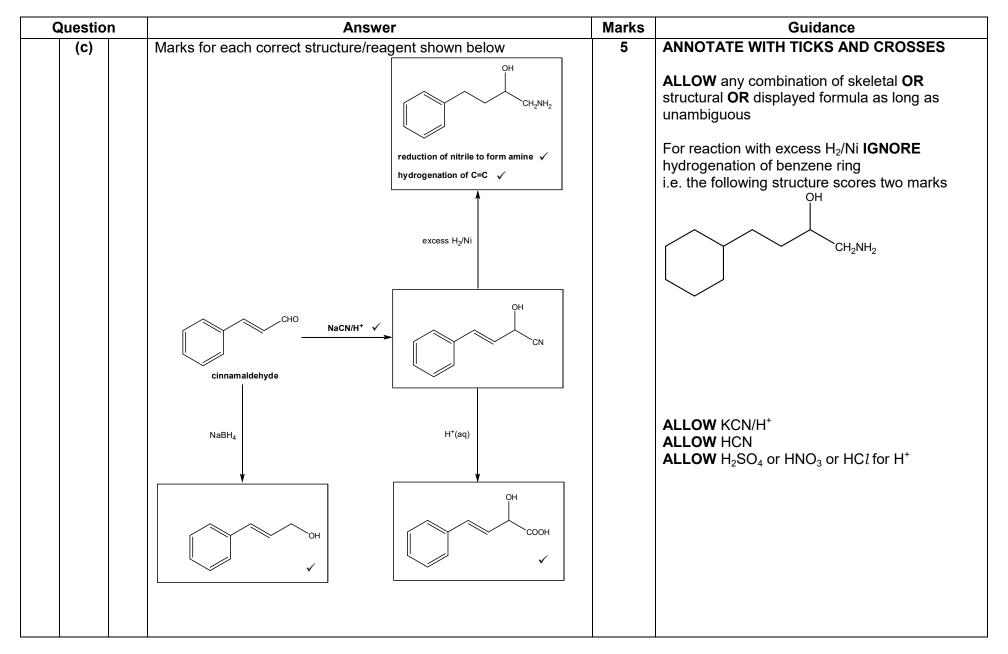
| Question | Answer | Marks | Guidance |
|-----------------|--|------------|---|
| Question (b) | AnswerCurly arrow from HO ⁻ to carbon atom of C–CI bond \checkmark Dipole shown on C–CI bond, C^{δ^+} and Cl^{δ^-} AND curly arrow from C–CI bond to CI atom \checkmark $\overbrace{OH^-}$ IGNORE presence of Na ⁺ but OH ⁻ needed i.e. Na ⁺ OH ⁻ can be allowed if criteria metCorrect organic product AND Cl ⁻ \checkmark IGNORE presence of Na ⁺ but Cl ⁻ needed i.e. Na ⁺ OH ⁻ can be allowed | Marks 3 | Guidance ANNOTATE ANSWER TICKS AND CROSSES 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-Cl AND • start from, OR be traced back to any point across width of lone pair on O of OH ⁻ • OR start from - charge on O of ⁻ OH ion • OR start from - charge on O of ⁻ OH ion • OH OH OH • OH Curly arrow must start from, OR be traced back to, any part of C-Cl bond and go to Cl |



| Question | Answer | Marks | Guidance |
|----------|---|-------|--|
| (c) (ii) | Precipitate G 1 mark silver bromide/AgBr AND $M = 1.88/0.01 = 188 \text{ (g mol}^{-1})$ 188 - 107.9 = 80.1 (so halide is Br ⁻)/ | 3 | ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous Note: working is required for first mark ALLOW use of 108 as A_r of Ag |
| | Alcohol F and Haloalkane E 2 marks | | |
| | E and F clearly identified F/alcohol: butan-2-ol H OH $H_{3}C - C - C - CH_{3}$ H H | | Note: E and F can be identified by correct name or structure BUT IGNORE incorrect names |
| | E/haloalkane: E is haloalkane of C₄H₉X with same halogen as G AND same carbon chain as F ✓ | | |
| | Total | 10 | |

| 0 | Questio | n | Answer | Marks | Guidance |
|----|---------|------|--|-------|--|
| 20 | (a) | | priority groups/atoms are on different/opposite sides \checkmark High(est) priority groups are C ₆ H ₅ AND CHO OR Lowest priority groups are H and CH ₃ \checkmark | 2 | ALLOW suitable alternatives to 'priority' e.g. groups with highest atomic number or more important groups etc. ALLOW high priority groups are diagonal(ly across) IGNORE references to relative mass of groups, <i>A</i>_r, <i>M</i>_r, ALLOW identification by name e.g aldehyde for CHO phenyl/benzene group for C₆H₅ alkyl for CH₃ ALLOW response in terms that O has higher priority than H in context of –CH₃ and –CHO IF 'priority' is not mentioned ALLOW 1 mark for |
| | (b) | (i) | Bromine/ Br₂ AND goes colourless/decolourised ✓ | 1 | 'C₆H₅ and CHO are on different sides' OR H and CH₃ are on different sides Note: both reagent and observation are required ALLOW bromine water/ Br₂(aq) |
| | | (ii) | Tollens' (reagent) AND Silver (mirror/precipitate/ppt/solid) ✓ | 1 | Note: both reagent and observation are required for the mark. ALLOW ammoniacal silver nitrate OR Ag⁺/NH₃ ALLOW black ppt OR grey ppt |

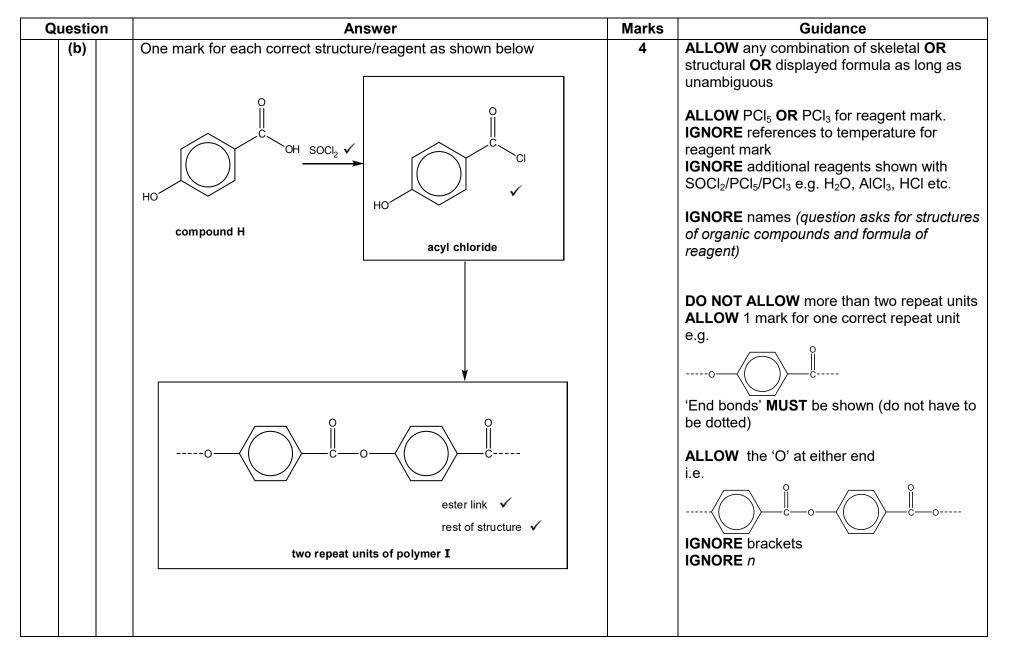
| Question | Answer | Marks | Guidance |
|----------|---|-------|--|
| (iii) | (Add) 2,4-dinitrophenylhydrazine AND orange/yellow/red precipitate√ | 3 | ALLOW errors in spelling ALLOW 2,4(-)DNP OR 2,4(-)DNPH ALLOW Brady's reagent or Brady's Test ALLOW solid OR crystals OR ppt as alternatives for precipitate |
| | Take melting point (of crystals) ✓ Compare to known values/database ✓ | | Mark second and third points independently of response for first marking point DO NOT ALLOW 2 nd and 3 rd marks for taking and comparing boiling points OR chromatograms |
| | | | |



| Question | Answer | Marks | Guidance |
|----------|--|-------|--|
| (d)* | Please refer to marking instructions on page 5 of mark scheme for guidance on how to mark this question. Level 3 (5–6 marks) An outline of the mechanism for the formation of either product which is mostly correct. AND Major and minor products identified with a correct explanation of which product is most/least likely to be formed. 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) An outline of the mechanism for the formation of either product but with a few omissions/errors. AND Identifies major/minor product correctly OR Explanation of which product is most/least likely to be formed. 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) A basic outline of the mechanism for the formation of either product is attempted. OR Basic explanation of which of the products is most/least likely to be formed. There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant. | 6 | Please check all of page 23 which is included with this response. If this page is blank please annotate with SEEN Throughout: ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above if unambiguous Indicative scientific points: <u>Mechanism for formation of either product.</u> • Curly arrow from C=C to attack the I atom of the I-C1 • Curly arrow from I-C1 • Curly arrow from I-C1 • Curly arrow from I-C1 • Curly arrow from negative charge on carbon atom • Curly arrow from negative charge on C1 ⁻ or lone pair on C1 ⁻ to carbon atom with positive charge $ \stackrel{+}{ (- + + + + + + + + + + + + + + + + + +$ |

| Question | Answer | Marks | Guidance |
|----------|---|----------|--|
| Question | Answer 0 marks No response or no response worthy of credit. | Marks | Guidance Organic products Anjor/most likely product Image: Colspan="2">CHO Image: Colspan="2">COLSPANE" Colspan="2">CHO Image: Colspan="2">COLSPANE" Colspan="2">C |
| | | Total 18 | OR the – I is attached to the carbon atom with most hydrogens attached |

| Q | uestio | n Answer | Marks | Guidance |
|----|--------|---|-------|---|
| 21 | (a) | Product from Na ₂ CO ₃ $\downarrow \qquad \qquad$ | 3 | ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW -COO⁻ OR -COONa DO NOT ALLOW negative charge on C atom DO NOT ALLOW -COO-Na (covalent bond) IGNORE connectivity of phenol OH group (marks are for correct conversions) |
| | | Product from NaOH(aq) O O O $O^{-}(Na^{+})$ $(Na^{+})^{-}O$ | | ALLOW 1 mark if top two structures are shown in wrong boxes |
| | | Product from Br ₂ Br e.g. HO | | ALLOW substitution of any H from benzene ring ALLOW multiple substitution, <i>i.e.</i> di-, tri- and tetrabromo products. IGNORE connectivity of phenol OH group (marks are for correct conversions) |



| Question | Answer | Marks | Guidance |
|--------------------|--------|------------|--|
| Question (C) (i | | Marks 2 | If there is an alternative answer, Apply ECF Alternative method [K] in g dm ⁻³ with peak area of 5.9 $9.13 \times 10^{-2} \times \frac{5.9}{4.3}$ OR $9.13 \times 10^{-2} \times 1.37$ $= 0.125$ OR 0.13 (g dm ⁻³) \checkmark Calculator: 0.125272093 [L] in mol dm ⁻³ $\frac{0.125}{166} = 7.5 \times 10^{-4}$ OR $\frac{0.13}{166} = 7.8 \times 10^{-4}$ (mol dm ⁻³) \checkmark Common errors: Award 1 mark for: • 0.099(from $\frac{9.13 \times 10^{-2}}{166} \times 180$) • 6.9 $\times 10^{-4}$ (from $\frac{0.125}{180}$) |
| | | | • 7.2×10^{-4} (from $\frac{0.13}{180}$) • 7.0×10^{-4} (from $\frac{0.25272093}{180}$) |

| Question | Answer | Marks | Guidance |
|---------------|--|------------|---|
| Question (ii) | ester J HO H | Marks 3 | Guidance ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous L and M can be identified either way round IGNORE 'C ₃ H ₇ ' in L and/or M as ambiguous (question requires structures) IGNORE connectivity of phenol OH group (marks are for structures of alkyl groups) |
| | но | | |
| | Total | 12 | |

| Q | Question | Answer | Marks | Guidance |
|----|----------|---|-------|--|
| 22 | (a) | $C_7H_{16} + 7^1/_2O_2 \rightarrow 7CO + 8H_2O$ OR $C_7H_{16} + 4O_2 \rightarrow 7C + 8H_2O \checkmark$ | 1 | ALLOW multiples IGNORE state symbols ALLOW equations for incomplete combustion that give CO and/or C with CO ₂ e.g C ₇ H ₁₆ + 9O ₂ \rightarrow 4CO + 3CO ₂ + 8H ₂ O C ₇ H ₁₆ + 6O ₂ \rightarrow 4CO + 3C + 8H ₂ O |
| | (b) | Heptane compared to hexane heptane (has a longer chain so) has more points of contact / more surface interaction (between molecules) ✓ | 4 | ANNOTATE WITH TICKS AND CROSSES ALLOW ORA throughout |
| | | heptane has stronger/more induced dipole(–dipole) interactions \checkmark | | ALLOW heptane has more electrons IGNORE IDID |
| | | Pentan-1-ol compared to heptane and/or hexane pentan-1-ol has hydrogen bonds that are strong(er than induced dipole–dipole interactions) OR | | ALLOW stronger/more London forces IGNORE van der Waals' forces/VDW for induced dipole– dipole interactions (<i>ambiguous as this term refers to both</i> <i>permanent dipole–dipole interactions and induced</i> <i>dipole–dipole interactions</i>) |
| | | (alcohols have) hydrogen bonds and induced dipole(-dipole) interactions/London forces ✓ Energy required to break forces | | IGNORE 'pentan-1-ol can form hydrogen bonds with water' |
| | | More energy is required to break induced dipole(–dipole) interactions in heptane than hexane OR More energy is required to break hydrogen bonds ✓ | | ALLOW 'more energy to break intermolecular forces' if intermolecular forces are not stated. IGNORE it is harder to break the intermolecular forces <i>no reference to energy</i>) IGNORE more energy needed to separate molecules IGNORE more energy is needed to break bonds |

| Question | Answer | Marks | Guidance |
|----------|--|-------|---|
| (c) (i) | <i>n</i> (CO ₂) = 2.97/44 = 0.0675 (mol) √ | 5 | Consult your team leader if an alternative creditworthy approach is seen |
| | <i>n</i> (H ₂ O) = 1.62/18 = 0.0900 (mol)√ Ratio of C : H 3 : 8 √ | | IGNORE ratio of CO_2 to H_2O is 3:4 ALLOW this mark from the correct molecular formula OR a correct structure if not shown in working |
| | Molecular formula C₃H ₈ O₂√ | | DO NOT ALLOW an incorrect molecular formula |
| | Structure any correct structure of $C_3H_8O_2 \checkmark$ e.g. HO C C C C OH HO H H H H H H H OR H C C OC C OH H H H H H H H H H H H H H H | | Mark independently from molecular formula but structure MUST contain 3C, 8H and 2O ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW any vertical bond to the OH group e.g. ALLOW $\mid OR \mid OR \mid OH$ DO NOT ALLOW OH– |

Mark Scheme

June 2018

| Question | Answer | Marks | Guidance |
|----------------------|---|------------|--|
| Question (c) (ii) | Answer $HO \longrightarrow OH + HO \longrightarrow OO + HO \longrightarrow OO + H_2O$ Carbonyl compound identified as propanone \checkmark Rest of equation \checkmark | Marks 2 | Guidance ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous |
| | | | |

| Question | Answer | Marks | Guidance |
|----------|---|-------|--|
| (d)* | Please refer to the marking instructions on page 5 of this mark scheme for guidance on how to mark this question. | 6 | Indicative scientific points: Empirical and Molecular Formula |
| | Level 3 (5–6 marks) Compound is a structure of $C_6H_{12}O_3$ that is consistent with splitting pattern and chemical shifts in NMR spectrum. AND | | • $C: H: O = 54.54/12 : 9.10/1 : 36.36/16$ 4.545 : 9.10 : 2.273 2 : 4 : 1 |
| | Comprehensive reasoning with 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. | | Empirical formula = C₂H₄O uses <i>m/z</i> = 132.0 to determine molecular formula as C₆H₁₂O₃ |
| | Level 2 (3–4 marks) Compound has a feasible chemical structure that is consistent with the splitting pattern in NMR spectrum but may have incorrect molecular formula. AND Reasoning provided with some of the 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 | | 1 H NMR analysisSpectrum:• $\delta = 4.0$ ppm, quartet, 1H, CH_3 -CH-O• $\delta = 1.3$ ppm, singlet, 6H, $(CH_3)_2$ -C• $\delta = 1.2$ ppm, doublet, 3H, CH_3 -CH-Without D ₂ O:• Peak at 11.0 ppm COOH or OH• peak at 3.6 ppm OHNote: Data Sheet shows O-H chemical shift can occur around 11.0 ppm |
| | formula. OR Analyses most of the NMR data. OR Attempts to determine empirical and/or molecular formula AND analyses some of the NMR data. There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant. | | Structure ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous Contains |

| Question | Answer | Marks | Guidance |
|----------|--|-------|---|
| | 0 marks No response or no response worthy of credit. | | • region that gives doublet and quartet e.g. H C C C H C C C • region that gives singlet e.g. C C C C C C C C C C C C C C C |
| | | | Examples of structures consistent with splitting and chemical shift in NMR $H_3C - C - C - C - C - C - C - C - C - C -$ |

| H432/02 |
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| C | Question | | Answer | Marks | Guidance |
|---|----------|--|--------|-------|--|
| | | | | | $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ |
| | | | | | $H_{3C} O - C - CH_{3}$ $H_{3C} O - C - CH_{3}$ $H_{3C} O - C - CH_{3}$ |
| | | | | | СН ₃ ОН H ₃ CСОН ОСН |
| | | | | | CH ₃ Note: there may be other possible structures that are consistent with the splitting pattern and chemical shifts in NMR – if an alternative structure is seen, please contact your team leader |
| | | | Total | 18 | |

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