

GCE

Chemistry A

Advanced GCE

Unit F324: Rings, Polymers and Analysis

Mark Scheme for January 2011

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ALLOW Kekulé structures throughout

| Q | uestic | n | Answer | | ALLOW HORard Structu | | Guidance |
|-----|--------|----|--------|---|---|-----------|--|
| Q 1 | | on | | correct intermediate curly arrow from C–H bond back to reform ring ✓ ✓ r intermediate r curly arrow | CH ₃ + H ⁺ NO ₂ correct products | Mark 4 | ALLOW skeletal CH ₃ ALLOW ¹st curly arrow from the ring OR from within the ring to any part of the NO ₂ † including the + charge DO NOT ALLOW intermediate with broken ring less than halfway down: CH ₃ ALLOW Kekulé mechanism: CH ₃ CH |
| | | | | | | | |

| Question Answer | | Mark | Guidance |
|-----------------|--|------|--|
| 1 (b) | O_2N O_2 O_2N O_2 O_2 | | ALLOW any correct unambiguous structures ALLOW NO ₂ — Note: connectivity is NOT being assessed in this part |
| | NO ₂ | 2 | |
| 1 (c) | 1st stage isomer: isomer 3 ✓ product: CH ₃ reagents: Sn AND (conc) HCI ✓ equation: CH ₃ + 12 [H] + 4 H ₂ O NH ₂ NH ₂ NH ₂ V NH ₂ V | | ALLOW structure of isomer 3 shown separately OR in equation ALLOW structure of product shown separately OR in equation ALLOW correct name (3,5-diaminomethylbenzene) IGNORE incorrect name DO NOT ALLOW CH ₃ C ₆ H ₃ (NH ₂) ₂ ALLOW Zn + HCl/H ₂ + metal catalyst/LiAlH ₄ /Na in ethanol IGNORE NaBH ₄ ALLOW Sn and HCl followed by NaOH DO NOT ALLOW Sn and HCl and NaOH IF isomer 3 OR product are given in equation but not shown previously then credit here Also credit reagents here if shown (eg above arrow) ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous |

| Question | Answer | Mark | Guidance |
|----------|---|------|---|
| (c) (i) | 2nd stage organic compound: HOOC−CH₂−COOH ✓ | 6 | DO NOT ALLOW molecular formula ALLOW name of compound: propanedioic acid OR propane-1,3-dioic acid ALLOW absence of 'e' after 'propan' ALLOW acyl dichloride: CIOC-CH ₂ -COCl ALLOW cyclic acid anhydride of propanedioic acid: CH ₂ O C C C C C |
| | type of polymer. polyamide ✓ | | ALLOW Nylon or Kevlar DO NOT ALLOW polypeptide DO NOT ALLOW amide |
| | Total | 12 | |

| | Quest | ion | Answer | Mark | Guidance | |
|---|-------|------|-------------------------------|------|---|--|
| 2 | (a) | | propane-1,2,3-triol ✓ | 1 | ALLOW absence of 'e' after 'propan' ALLOW 1,2,3-propanetriol ALLOW absence of hyphens 1, 2 and 3 must be clearly separated: ALLOW full stops: 1.2.3 OR spaces: 1 2 3 DO NOT ALLOW 123 | |
| 2 | (b) | (i) | methanol OR ethanol AND | | BOTH points required for the mark ALLOW correct structural OR displayed OR skeletal formula DO NOT ALLOW molecular formulae | |
| | | | renewable ✓ | 1 | ALLOW easy/cheap to manufacture/produce as alternative for renewable/from plants/from fermentation/burns more easily/efficiently | |
| | (b) | (ii) | equilibrium shifts to right ✓ | 1 | ALLOW equilibrium shifts in forward direction ALLOW more products form ALLOW greater yield OR fully reacts OR goes to completion DO NOT ALLOW improves atom economy | |

| | Questi | ion | Answer | | Guidance |
|---|--------|-----|---|---|--|
| 2 | (c) | | CH ₃ CH ₂ COOH + CH ₃ CH ₂ OH → CH ₃ CH ₂ COOCH ₂ CH ₃ + H ₂ O ✓ | | ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous DO NOT ALLOW molecular formulae |
| | | | $(CH_3CH_2CO)_2O + CH_3CH_2OH \rightarrow CH_3CH_2COOCH_2CH_3 + CH_3CH_2COOH$ | 2 | ALLOW further esterification, <i>ie</i> $(CH_3CH_2CO)_2O + 2CH_3CH_2OH \rightarrow 2CH_3CH_2COOCH_2CH_3 + H_2O$ |
| | | | | | ALLOW linear formula for anhydride, ie |
| | | | | | CH ₃ CH ₂ COOCOCH ₂ CH ₃ |
| | | | | | If incorrect carboxylic acid/anhydride/alcohol is used, ALLOW ECF for second equation |

| C | Question | | Answer | Mark | Guidance | | |
|---|----------|--|--|--|---|---|--|
| 2 | (d) | | A | В | С | | Mark A, B and C |
| | | | HO-CH ₂ -CH ₂ -CH ₂ -COOH | H_2C C C C C C C C C C | O O-CH ₂ -CH ₂ -CH ₂ -C | | A can be any of the alternatives in the 1st column B can be any of the alternatives in the 2nd column |
| | | | OR | OR | OR | | C can be any of the |
| | | | CH ₃ HO—CH—CH ₂ −COOH | H ₂ C—C | CH ₃ O O—CH—CH ₂ —C | 3 | alternatives in the 3rd column ALLOW correct structural OR displayed OR skeletal formula |
| | | | OR | OR | OR | | ALLOW combination of |
| | | | C₂H₅ HO—CH—COOH | C_2H_5 CH—C O | C ₂ H ₅ O O——CH——C | | formulae as long as unambiguous DO NOT ALLOW molecular formulae |
| | | | OR | OR | OR | | |
| | | | СН ₃ НО—СН ₂ —СН—СООН | CH—C | CH ₃ O OCH ₂ CH | | ALLOW correct names for A, B and C For B accept diester For C, |
| | | | OR | OR | OR | | IGNORE 'n' OR brackets |
| | | | СН ₃ НО—С—СООН СН ₃ | H ₃ C C C O | CH ₃ O CH ₃ C | | (even if wrong); ALLOW solid side bonds Minimum is one correct repeat unit. Polymer must be open at both ends |
| | | | | | Total | 8 | |

| Question | Answer | Mark | Guidance |
|----------|---|------|---|
| 3 (a) | observation: silver OR Ag ✓ type of reaction: oxidation ✓ organic product: H ₃ C CH ₃ OH CH ₃ ✓ | 3 | ALLOW black OR grey ALLOW redox ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous DO NOT ALLOW molecular formulae ALLOW carboxylate, -COO- |
| 3 (b) | 1 mark for correct dipole on C=O AND curly arrow from O⁻ to H of H−O−H AND curly arrow from H−O to O of H−O−H AND curly arrow from H−O to O of H−O−H AND curly arrow from H−O to O of H−O−H AND curly arrow from H−O to O of H−O−H AND curly arrow from H−O to O of H−O−H AND curly arrow from H−O to O of H−O−H AND curly arrow from H−O to O of H−O−H AND curly arrow from H−O to O of H−O−H ✓ | 4 | ALLOW mechanism showing curly arrows from lone pair on H ⁻ and O ⁻ of intermediate Dipole not required on H–O–H DO NOT ALLOW incorrect dipole on H–O–H ALLOW 1 mark for correct intermediate with '–' charge on O AND curly arrow from O ⁻ to H ⁺ IGNORE missing OH ⁻ DO NOT ALLOW incorrect second product |

| Question | Answer | | Guidance |
|----------------|--|-----------|--|
| Question 3 (c) | Answer reagent. Br₂ ✓ observation: decolourised OR orange to colourless ✓ organic product. ✓ H₃C CH₃ H Br CH₃ Br CH₃ | Mark 3 | DO NOT ALLOW ECF from incorrect reagent, eg 2,4-DNP DO NOT ALLOW goes clear ALLOW red/orange/yellow/brown in any combination ALLOW organic product from reaction of one of the double bonds only, ie H ₃ C CH ₃ H ₃ C CH ₃ CH ₃ CH ₃ ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous |
| | | | DO NOT ALLOW molecular formulae ALTERNATIVE reagents For 1st mark, ALLOW H ₂ OR Cl ₂ OR I ₂ OR HCl OR HBr OR HI OR H ₂ O For 2nd mark, there must be a statement of no change OR no observation or similar that implies there is no visible change EXCEPT for I ₂ which has an observation of 'decolourised' OR brown to colourless For 3rd mark, |
| | | 42 | correct organic product must be shown that could be from reaction of both or one of the double bonds. |
| | Total | 10 | |

| (| Quest | ion | Answer | Mark | Guidance |
|---|-------|------|--|------|--|
| 4 | (a) | (i) | $CICH(CH_3)COOH + 3NH_3 \rightarrow H_2NCH(CH_3)COO^- + NH_4^+ + NH_4CI$ | 1 | ALLOW use of two NH ₃ : $CICH(CH_3)COOH + 2NH_3 \rightarrow H_2NCH(CH_3)COO^- + NH_4^+ + HCI$ ALLOW products as above OR H ₂ NCH(CH ₃)COOH + NH ₄ CI ALLOW use of one NH ₃ : $CICH(CH_3)COOH + NH_3 \rightarrow H_2NCH(CH_3)COO^- + H^+ + HCI$ ALLOW products as above OR H ₂ NCH(CH ₃)COOH + HCI For alternatives below, for NH ₄ CI, ALLOW NH ₄ +CI OR NH ₄ + + CI for HCI, ALLOW H+CI OR H+ + CI for H ₂ NCH(CH ₃)COO- + NH ₄ + ALLOW H ₂ NCH(CH ₃)COO-NH ₄ + OR H ₂ NCH(CH ₃)COONH ₄ ALLOW R in equation in place of CH ₃ (either or both sides) ALLOW combination of formulae as long as unambiguous DO NOT ALLOW molecular formulae |
| | (a) | (ii) | CH ₃ CH ₃ | 1 | ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous ALLOW product from carboxylate ion as nucleophile: CH ₃ CH ₃ H ₂ N—C—COO—C—COOH |

| C | uesti | ion | Answer | Mark | Guidance |
|---|-------|------|--|----------------|--|
| 4 | (b) | (i) | ON HO O | 1 | DO NOT ALLOW any structure containing C OR H (except in OH) |
| | (b) | (ii) | CH ₂ COOH H ₂ N COOH HOOC NH ₂ NH ₂ | 2 | ALL bond linkages must be correct, eg the chiral C must be linked to the C of the COOH, the C of the CH ₂ COOH and the N of the NH ₂ (connectivity is being tested) The 2nd mark is for the mirror image of an amino acid. This could be any amino acid EXCEPT glycine DO NOT penalise connectivity more than once ALLOW R in equation in place of CH ₂ COOH (either or both sides) Each structure must have four central bonds, with at least two wedges, one in; one out For bond into paper, accept: |
| 4 | (c) | | Disadvantages Any two from: • (one stereoisomer might have harmful) side effects ✓ • reduces the (pharmacological) activity/effectiveness ✓ • cost OR difficulty in separating stereoisomers ✓ Synthesis of a single optical isomer Any two from: • using enzymes or bacteria ✓ • using a chiral catalyst OR transition metal complex/transition metal catalyst ✓ • using chiral synthesis OR chiral starting material OR natural amino acid ✓ | 2 max 2 max | ANNOTATIONS MUST BE USED ALLOW optical isomer OR enantiomers as alternative for stereoisomers ALLOW a response that implies an increased dose ALLOW biological catalyst ALLOW 'chiral pool' OR L-amino acids OR D-sugars |
| | | | Total | 8 | |

| | Quest | tion | Answer | Mark | Guidance | |
|---|-------|-------|---|------|---|--|
| 5 | (a) | (i) | Adsorption ✓ (onto the stationary phase) | | ALLOW adsorbtion or adsorb(s) or adsorbed spelled correctly at least once | |
| | | | Quality of Written Communication 'Adsorption' must be spelled correctly | 1 | DO NOT ALLOW anything that begins with ab | |
| | (a) | (ii) | 0.2 ✓ | 1 | ALLOW any value in the range 0.1 – 0.3 IGNORE significant figures DO NOT ALLOW fraction/percent as final answer | |
| | (a) | (iii) | Spot may contain more than one compound/component ✓ | 1 | ALLOW compounds have similar R_f values/adsorptions OR compounds have not (fully) separated OR B is spread over a large region OR compounds are similar IGNORE retention times | |
| 5 | (b) | (i) | GC separates the components/compounds AND | | ALLOW chromatography for GC ALLOW they have different retention times | |
| | | | MS is compared to a database/reference ✓ | 1 | ALLOW MS analyses compounds/gives structural information/gives different mass spectra ALLOW (uses) fragmentation patterns/fragments/peaks/parts of the compound DO NOT ALLOW MS identifies compounds (in question) DO NOT ALLOW molecular ion alone/M _r etc. | |
| | | (ii) | nerol and geraniol AND | | Compounds AND reason required for the mark | |
| | | | they are stereoisomers OR primary alcohols ✓ | 1 | ALLOW they are <i>E/Z</i> isomers OR <i>cis-trans</i> isomers ALLOW straight-chain alcohols OR unsaturated alcohols | |
| | | (iii) | stereoisomers have the same structural formula AND | | BOTH points required for the mark | |
| | | | different 3D arrangements ✓ | 1 | ALLOW different arrangements in space | |
| | | (iv) | | 1 | Circle must include the correct C=C double bond AND must not extend further than the adjacent atoms in the main chain, ie limit is: | |

| , | Quest | tion | Answer | Mark | Guidance |
|---|-------|------|--|------|--|
| | | | | | |
| | (b) | (v) | * * * * | 2 | ALL THREE chiral centres required for 2 marks ANY TWO chiral centres required for 1 mark If more than three asterisks are shown, mark incorrect asterisk(s) first |
| 5 | (c) | | Correctly calculates amount of myrcene = 34/136 OR 0.25 (mol) ✓ Correctly calculates 60% yield of menthol = 0.25 × 60/100 OR 0.15 (mol) ✓ Correctly calculates mass of menthol = 0.15 × 156 = 23.4 (g) ✓ | 3 | ANNOTATIONS MUST BE USED ALLOW amount of myrcene × 60/100 ALLOW amount of menthol × 156 ALLOW alternative approach based on reacting masses (using same ECF principles as above): correctly calculates mass of myrcene that could be obtained from 34 g myrcene: mass = 34 × 156/136 = 39 (g) × 156 ✓; ÷ 136 ✓ 60% of 39 g = 39 × 60/100 = 23.4 (g) ✓ ALLOW final answer to 2 or more significant figures correctly rounded Correct answer of 23.4 (g) with no working scores all 3 marks |
| | | | Total | 12 | |

| | Question | Answer | | Guidance | |
|---|----------|---|---|--|--|
| 6 | (a) | | | ANNOTATIONS MUST BE USED | |
| | | a singlet for position 2 OR a singlet because it has no adjacent H's✓ A triplet for positions 4 and 6 OR a triplet because it has 2 adjacent H's ✓ A quintet for position 5 OR a quintet because it has four adjacent H's ✓ | 3 | ALLOW a response that implies a single peak OR 'no splitting' ALLOW a response that implies a splitting into three DO NOT ALLOW implications of more than one triplet ALLOW 'pentet' OR a response that implies a splitting into five OR multiplet ALLOW 1 mark for singlet and triplet and quintet/pentet/multiplet with no identification of protons Any suggestion that the oxygens cause a splitting scores a maximum of 2 marks. ■ All 3 remaining splitting patterns correct 2 marks. ■ Any 2 correct 1 mark. IF number labels for protons in diagram are not identified, ALLOW identification by chemical shifts for 2 marks max: ■ singlet at 3.3–4.2 AND a triplet at 3.3–4.2 ✓ ■ quintet/pentet/multiplet at 0.7–2.0 ✓ Clear and unambiguous identification of the protons other than by position number should be credited, ie 'CH₂ between two oxygens' | |
| | | Quality of Written Communication singlet OR triplet OR quintet OR pentet OR multiplet (see Guidance) must be spelled correctly at least once | | | |

| Question | Answer | | Guidance | |
|----------|---|--|--|--|
| 6 (b) | ANY 5 marks plus correct structure (in box) | | ANNOTATIONS MUST BE USED | |
| | Molecular ion/M ⁺ peak at (m/z of) 106 ✓ | | ALLOW molecular mass OR relative molecular mass | |
| | Fragment peak at 91 is C ₆ H ₄ −CH ₃ ⁺ /C ₆ H ₅ −CH ₂ ⁺ ✓ | | ALLOW C ₆ H ₄ –CH ₃ /C ₆ H ₅ –CH ₂ ALLOW peak at 91 represents loss of CH ₃ | |
| | Molecular formula is C ₈ H ₁₀ (or implied, <i>ie</i> any one of the structures below) ✓ | | ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous ALLOW a correct name eg a dimethylbenzene | |
| | CH ₃ CH ₃ CH ₃ C ₂ H ₅ | | ALL FOUR structures needed for 1 mark ALLOW correct names | |
| | The spectrum shows 5 C environments ✓ Peak near 20 is a C attached at another carbon, C–C OR peaks at ~125–140 for aromatic Cs ✓ | | ALLOW NMR spectrum shows five different types of carbon DO NOT ALLOW 'NMR spectrum has five peaks' – the mark is for realising what the peaks show, not for just describing the spectrum | |

| | Question | | Answer | | | Mark | Guidance |
|---|----------|--|---|---|--|------|---------------------------------------|
| 6 | | | Number of peaks for of structures: Any 2 correct for 2 mand 1 correct for 1 mark CH ₃ CH ₃ CH ₃ CH ₃ | nrks √ √ | atched to C ₂ H ₅ 6 peaks | | ALLOW 'carbon environments' for peaks |
| | | | Correct structure show | vn: CH ₃ CH ₃ ✓ | | 6 | |
| | Total | | | | | 9 | |

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