OCR
RECOGNISING ACHIEVEMENT

GCE

Chemistry A

Advanced GCE

Unit **F324:** Rings, Polymers and Analysis

Mark Scheme for January 2011

Oxford Cambridge and RSA Examinations

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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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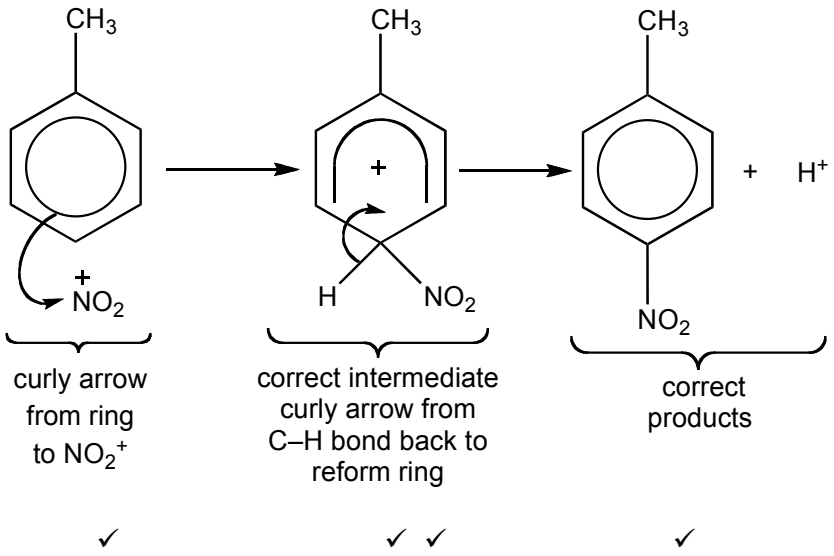
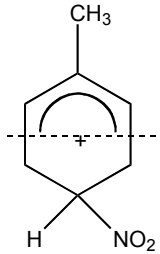
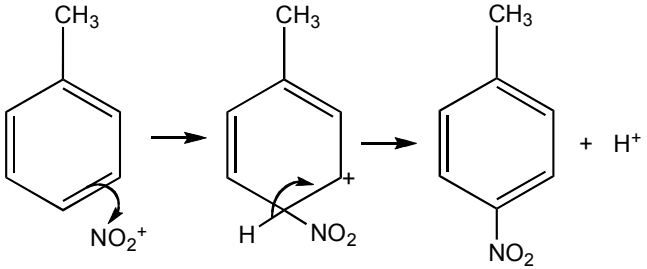
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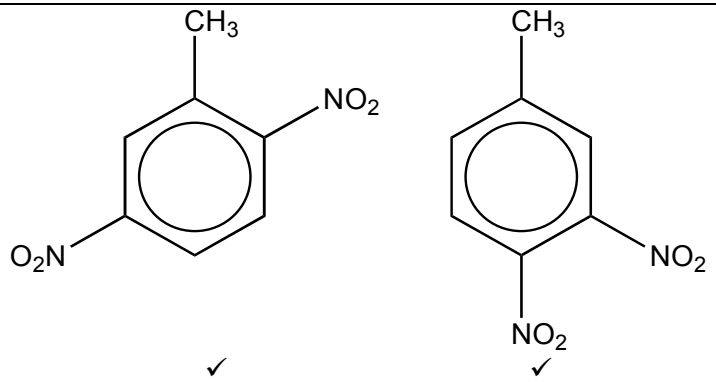
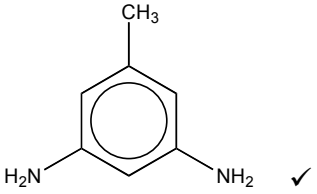
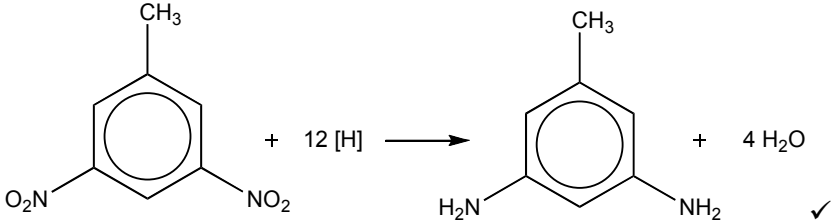
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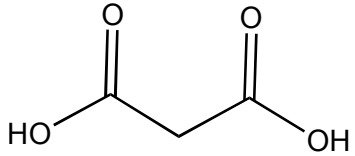
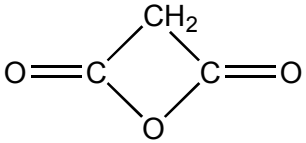
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ALLOW Kekulé structures throughout

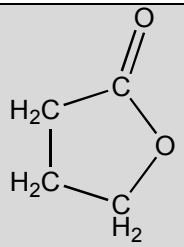
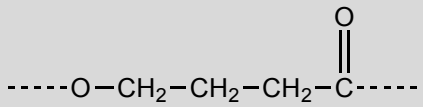
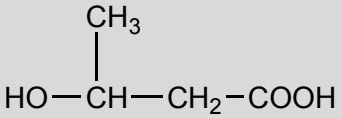
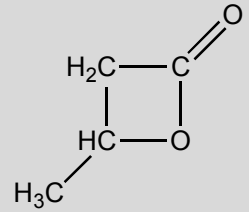
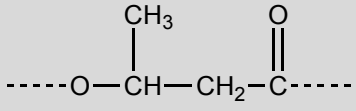
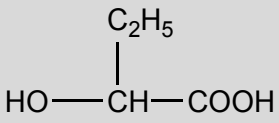
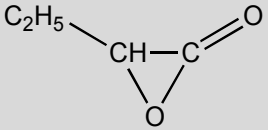
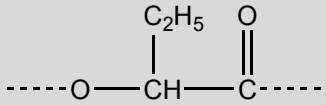
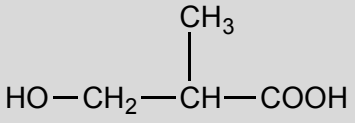
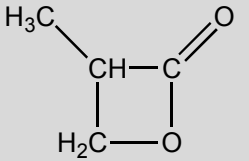
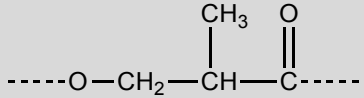
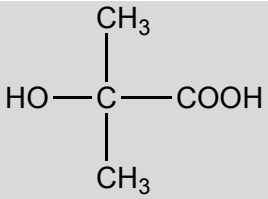
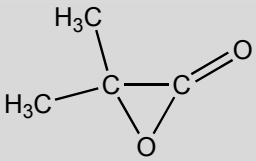
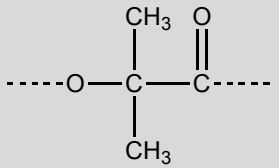
Question	Answer	Mark	Guidance
1 (a)	 ✓ ✓ ✓ ✓ 1 mark for intermediate 1 mark for curly arrow	4	***ANNOTATIONS MUST BE USED*** **ALLOW** skeletal CH_3 **ALLOW** $^{+}NO_2$ **OR** NO_2^{+} **ALLOW** 1st curly arrow from the ring OR from within the ring to any part of the NO_2^{+} including the + charge **DO NOT ALLOW** intermediate with broken ring less than halfway down:  Horseshoe must have open end towards NO_2 **ALLOW** Kekulé mechanism:  **ALLOW** double bonds shown in other Kekulé arrangement **IF** CH_3 has been omitted completely (*ie* benzene shown), **DO NOT AWARD** intermediate mark **OR** products mark **(max 2)** **IF** NO_2 is shown in incorrect position in intermediate or product, **DO NOT AWARD** intermediate mark but award other marks **(max 3)**

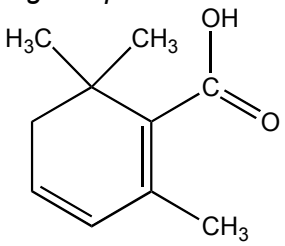
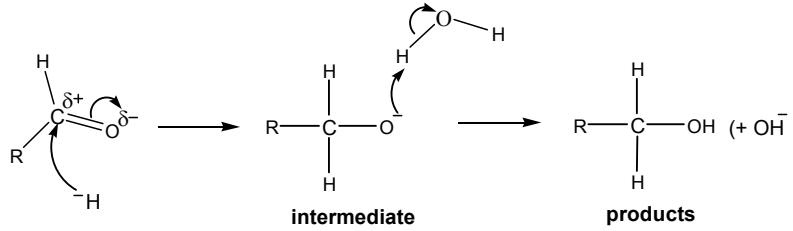
Question			Answer	Mark	Guidance
1	(b)		 ✓ ✓	2	**ALLOW** any correct unambiguous structures **ALLOW** NO_2– **Note**: connectivity is **NOT** being assessed in this part
1	(c)		**1st stage** *isomer*: **isomer 3** ✓ *product*:  ✓ *reagents*: Sn **AND** (conc) HCl ✓ *equation*:  ✓		***ANNOTATIONS MUST BE USED*** **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** $CH_3C_6H_3(NH_2)_2$ **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

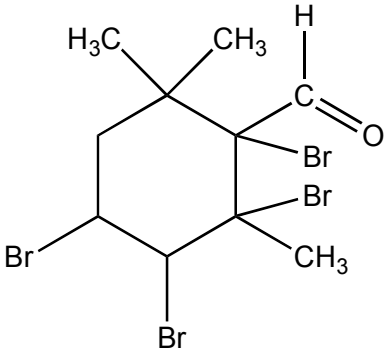
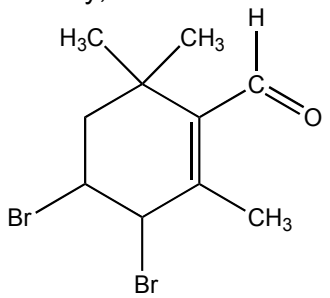
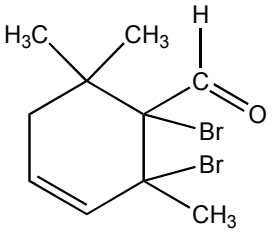
Question			Answer	Mark	Guidance
	(c)	(i)	**2nd stage** *organic compound*: $HOOC–CH_2–COOH$ ✓	6	 **DO NOT ALLOW** molecular formula **ALLOW** name of compound: propanedioic acid **OR** propane-1,3-dioic acid **ALLOW** absence of 'e' after 'propan' **ALLOW** acyl dichloride: $ClOC–CH_2–COCl$ **ALLOW** cyclic acid anhydride of propanedioic acid: 
			type of polymer: polyamide ✓		**ALLOW** Nylon or Kevlar **DO NOT ALLOW** polypeptide **DO NOT ALLOW** amide
			Total	**12**	

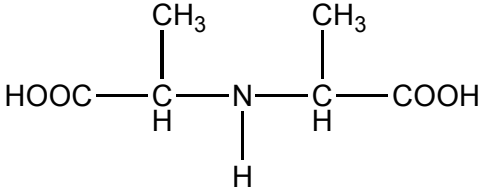
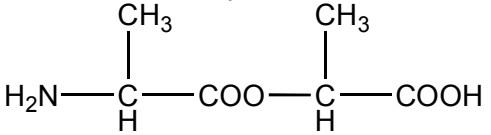
Question			Answer	Mark	Guidance
2	(a)		propane-1,2,3-triol ✓	1	**ALLOW** absence of 'e' after 'propan' **ALLOW** 1,2,3-propanetriol **ALLOW** absence of hyphens 1, 2 and 3 must be clearly separated: **ALLOW** full stops: 1.2.3 **OR** spaces: 1 2 3 **DO NOT ALLOW** 123
2	(b)	(i)	methanol **OR** ethanol **AND** renewable ✓	 1	**BOTH points required for the mark** **ALLOW** correct structural **OR** displayed **OR** skeletal formula **DO NOT ALLOW** molecular formulae **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

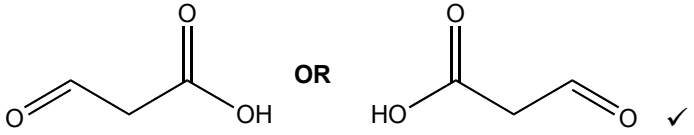
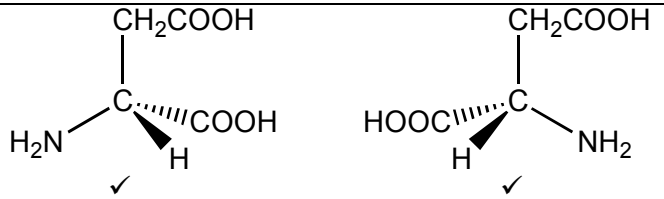
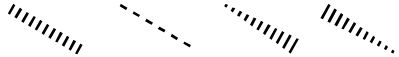
Question			Answer	Mark	Guidance
2	(c)		$CH_3CH_2COOH + CH_3CH_2OH \rightarrow CH_3CH_2COOCH_2CH_3 + H_2O$ ✓ $(CH_3CH_2CO)_2O + CH_3CH_2OH \rightarrow CH_3CH_2COOCH_2CH_3 + CH_3CH_2COOH$ ✓	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **DO NOT ALLOW** molecular formulae **ALLOW** further esterification, *ie* $(CH_3CH_2CO)_2O + 2CH_3CH_2OH \rightarrow 2CH_3CH_2COOCH_2CH_3 + H_2O$ ***ALLOW*** *linear formula for anhydride,* ie $CH_3CH_2COOCOCH_2CH_3$ If incorrect carboxylic acid/anhydride/alcohol is used, **ALLOW ECF** for second equation

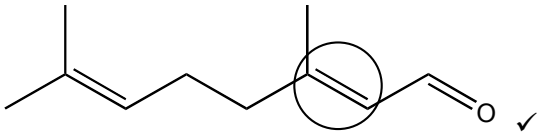
Question			Answer			Mark	Guidance
2	(d)		**A**	**B**	**C**	3	Mark **A**, **B** and **C** independently ie • **A** can be **any** of the alternatives in the 1st column • **B** can be **any** of the alternatives in the 2nd column • **C** can be **any** of the alternatives in the 3rd column **ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **DO NOT ALLOW** molecular formulae **ALLOW** correct names for **A**, **B** and **C** **For B** accept diester **For C**, **IGNORE** '*n*' **OR** brackets (even if wrong); **ALLOW** solid side bonds Minimum is **one** correct repeat unit. Polymer must be open at both ends
							
			OR	**OR**	**OR**		
							
			OR	**OR**	**OR**		
							
			OR	**OR**	**OR**		
							
			OR	**OR**	**OR**		
							
					Total	**8**	

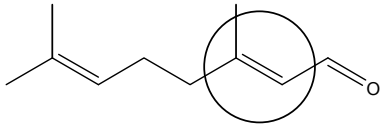
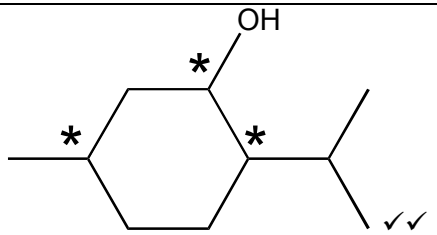
Question			Answer	Mark	Guidance
3	(a)		*observation*: silver **OR** Ag ✓ *type of reaction*: oxidation✓ *organic product*:  ✓	3	**ALLOW** black **OR** grey **ALLOW** redox **ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **DO NOT ALLOW** molecular formulae **ALLOW** carboxylate, $–COO^-$
3	(b)		 1 mark for curly arrow from H^- to C of C=O ✓ 1 mark for correct dipole on C=O **AND** curly arrow from double bond to $O^{\delta-}$ ✓ 1 mark for correct intermediate with negative charge on O **AND** curly arrow from O^- to H of H–O–H **AND** curly arrow from H–O to O of H–O–H ✓ 1 mark for correct **organic** product ✓	4	***ANNOTATIONS MUST BE USED*** **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	Mark	Guidance
3	(c)		*reagent*: Br_2 ✓ *observation*: decolourised **OR** orange to colourless ✓ *organic product*: ✓ 	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  **OR**  **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_2O **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,** correct organic product must be shown that could be from reaction of both or one of the double bonds.
			Total	**10**	

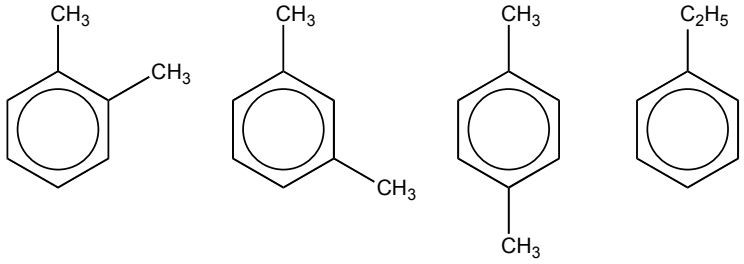
Question			Answer	Mark	Guidance
4	(a)	(i)	$ClCH(CH_3)COOH + 3NH_3 \rightarrow H_2NCH(CH_3)COO^- + NH_4^+ + NH_4Cl$ ✓	1	**ALLOW** use of **two** NH_3: $ClCH(CH_3)COOH + 2NH_3 \rightarrow H_2NCH(CH_3)COO^- + NH_4^+ + HCl$ **ALLOW** products as above **OR** $H_2NCH(CH_3)COOH + NH_4Cl$ **ALLOW** use of **one** NH_3: $ClCH(CH_3)COOH + NH_3 \rightarrow H_2NCH(CH_3)COO^- + H^+ + HCl$ **ALLOW** products as above **OR** $H_2NCH(CH_3)COOH + HCl$ For alternatives below, for NH_4Cl, **ALLOW** $NH_4^+Cl^-$ **OR** $NH_4^+ + Cl^-$ for HCl, **ALLOW** H^+Cl^- **OR** $H^+ + Cl^-$ for $H_2NCH(CH_3)COO^- + NH_4^+$ **ALLOW** $H_2NCH(CH_3)COO^-NH_4^+$ **OR** $H_2NCH(CH_3)COONH_4$ **ALLOW** R in equation in place of CH_3 (either or both sides) **ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **DO NOT ALLOW** molecular formulae
	(a)	(ii)	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **ALLOW** product from carboxylate ion as nucleophile: 

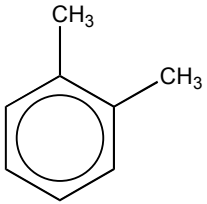
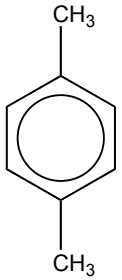
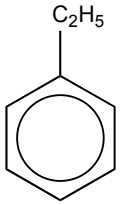
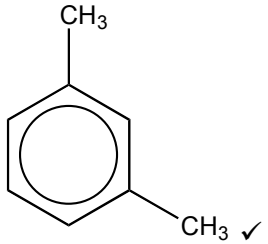
Question			Answer	Mark	Guidance
4	(b)	(i)	 ✓	1	**DO NOT ALLOW** any structure containing C **OR** H (except in OH)
	(b)	(ii)	 ✓ ✓	2	**ALL** bond linkages must be correct, eg the chiral C must be linked to the C of the COOH, the C of the CH_2COOH and the N of the NH_2 (connectivity is being tested) The 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_2COOH (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**	

Question			Answer	Mark	Guidance
5	(a)	(i)	Adsorption ✓(onto the stationary phase) ***Quality of Written Communication*** 'Adsorption' must be spelled correctly	1	**ALLOW** adsorbtion or adsorb(s) or adsorbed spelled correctly at least once **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** MS is compared to a database/reference ✓	1	**ALLOW** chromatography for GC **ALLOW** they have different retention times **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** they are stereoisomers **OR** primary alcohols ✓	1	Compounds **AND** reason required for the mark **ALLOW** they are *E*/*Z* isomers **OR** *cis-trans* isomers **ALLOW** straight-chain alcohols **OR** unsaturated alcohols
		(iii)	stereoisomers have the same structural formula **AND** different 3D arrangements ✓	1	**BOTH** points required for the mark **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:

Question			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	Mark	Guidance
6 (a)	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 ✓ ***Quality of Written Communication*** singlet **OR** triplet **OR** quintet **OR** pentet **OR** multiplet (see Guidance) must be spelled correctly at least once	3	***ANNOTATIONS MUST BE USED*** **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* 'CH_2 between two oxygens'

Question	Answer	Mark	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 $C_6H_4–CH_3^+$/$C_6H_5–CH_2^+$ ✓		**ALLOW** $C_6H_4–CH_3$/$C_6H_5–CH_2$ **ALLOW** peak at 91 represents loss of CH_3
	Molecular formula is C_8H_{10} (or implied, *ie* 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
	 ✓		**ALL FOUR** structures needed for 1 mark **ALLOW** correct names
	^{13}C NMR spectrum shows 5 C environments ✓		**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
	Peak near 20 is a C attached at another carbon, **C**–C **OR** peaks at ~125–140 for aromatic **C**s ✓		

Question			Answer	Mark	Guidance
6	(b)		Number of peaks for other three isomers matched to structures: *Any 2 correct for 2 marks* ✓✓ *1 correct for 1 mark* ✓    4 peaks 3 peaks 6 peaks Correct structure shown:  ✓	6	**ALLOW** 'carbon environments' for peaks
			Total	**9**	

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