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2002

XVIII

1583

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55 Minutes

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/46

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%

CHEMISTRY

**Edexcel
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Mark Scheme

**Paper 2: Advanced Organic
and Physical Chemistry**

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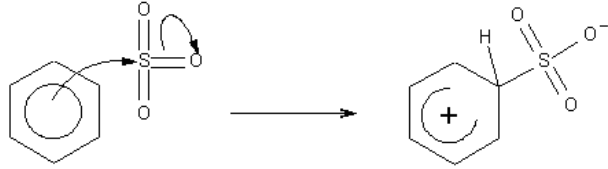
Question Number	Acceptable Answers	Reject	Mark
1 (a)(i)	sulfuric acid / fuming H_2SO_4 / oleum / $\text{H}_2\text{S}_2\text{O}_7$	Conc. (for fuming) Fuming dilute sulfuric acid Just sulfuric acid Just H_2SO_4	1

Question Number	Acceptable Answers	Reject	Mark
1 (a)(ii)	Sulfur is δ^+ and on at least one oxygen δ^- (1) Oxygen is (much) more electronegative than sulfur ALLOW Oxygen is very electronegative (1)	Full + or – charge(s) 1/3 – on each oxygen	2

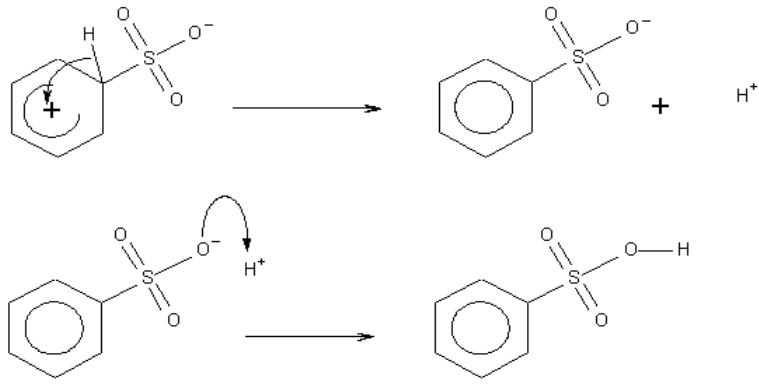
Question Number	Acceptable Answers	Reject	Mark
1 (a)(iii)	The sulfur trioxide can accept a pair of electrons OR (Three oxygen atoms so) sulfur has a large δ or partial / slight positive charge OR π bonds allow S–O bonds to be polarized more easily ALLOW Electron-deficient sulfur	An electron	1



Marks for (b)(i) and (b)(ii) can be awarded from either of the two annotated diagrams on item

Question Number	Acceptable Answers	Reject	Mark
1 (b)(i)	 <p>First curly arrow as shown to start inside the hexagon to the S atom (1)</p> <p>Second curly arrow from bond to O (i.e. not from the S atom itself) (1)</p> <p>ALLOW Second curly arrow to any of the three O atoms in SO₃</p> <p>IGNORE A full + charge on S</p>		2



Question Number	Acceptable Answers	Reject	Mark
1 (b) (ii)	 <p>Curly arrow as shown from the C-H bond to reform the ring in first line, not from the H atom in this bond (1)</p> <p>Intermediate anion formed in first line (H^+ does not have to be shown) (1)</p> <p>Last line with curly arrow and correct structure of benzenesulfonic acid (1)</p> <p>ALLOW Use of H_2SO_4 for H^+ with HSO_4^- as other product in final step</p> <p>The marks for (b)(ii) may be awarded from annotations on the right hand structure given in question in (b)(i)</p> <p>If contradictory arrows drawn on structure in question (b)(ii), then penalise any such inconsistency</p> <p>The three marks for the two steps in (b)(ii) can be shown in one step / diagram / structure</p> <p>ALLOW -SO₃H undisplayed</p>	Use of H ₂ O for H ⁺	3



Question Number	Acceptable Answers	Reject	Mark
1(c)(i)	$\text{C}_6\text{H}_5\text{SO}_3\text{H} + 3\text{NaOH} \rightarrow \text{C}_6\text{H}_5\text{ONa} + \text{Na}_2\text{SO}_3 + 2\text{H}_2\text{O}$ <p style="text-align: right;">(1)</p> ALLOW Charges on $\text{C}_6\text{H}_5\text{O}^-\text{Na}^+$ $\text{C}_6\text{H}_5\text{ONa} + \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{NaCl}$ <p style="text-align: right;">(1)</p> ALLOW $\text{C}_6\text{H}_5\text{O}^- + \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{Cl}^-$ OR $\text{C}_6\text{H}_5\text{O}^- + \text{H}^+ \rightarrow \text{C}_6\text{H}_5\text{OH}$	Charges on $\text{C}_6\text{H}_5\text{SO}_3\text{H}$	2

Question Number	Acceptable Answers	Reject	Mark
1(c)(ii)	Any two from: (Both) products useful / both are useful / propanone is useful So less waste / high(er) atom economy Fewer steps / one step / does not require many steps (in Hock synthesis) Continuous rather than a batch process <p style="text-align: right;">(2)</p> IGNORE "Only one waste product in Hock" Comments relating to hazardousness of reactants / safety / energy requirements References to yield References to efficiency References to rate	Cheaper	2

Question Number	Acceptable Answers	Reject	Mark
2(a)	2,6-dimethylhept-5-enal (2) Either part scores (1) e. 2,6-dimethyl (1) hept-5-enal (1) IGNORE missing/misplaced/misused hyphens or commas ALLOW ene for en ALLOW methy or methly for methyl		2

Question Number	Acceptable Answers	Reject	Mark
2(b) (i)	CH ₃ C(CH ₃)=CHCH ₂ CH ₂ CH(CH ₃)CH ₂ OH (1) OR CH ₃ C(CH ₃)CHCH ₂ CH ₂ CH(CH ₃)CH ₂ OH OR CH ₃ C(CH ₃)=CHCH ₂ CH ₂ C(CH ₃)HCH ₂ OH ALLOW displayed or skeletal formulae K ₂ Cr ₂ O ₇ /Na ₂ Cr ₂ O ₇ /name (oxidation state must be correct if given (VI)) (1) This is a stand alone mark H ₂ SO ₄ /name (ignore any references to concentration) (1) ALLOW H ⁺ and Cr ₂ O ₇ ²⁻ (2) 'Acidified dichromate' (1)	C ₉ H ₁₈ O KMnO ₄ (0) for last 2 marks HCl (0) for 3 rd mark	3

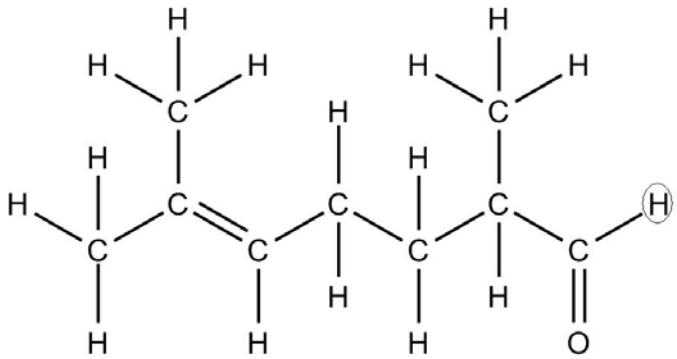
Question Number	Acceptable Answers	Reject	Mark
2(b) (ii)	(Steam) distil off melonal (as it forms) Allow add a limited amount of oxidizing agent/excess alcohol/excess X (1) To prevent further oxidation/To prevent carboxylic acid forming (1) Stand alone marks		2

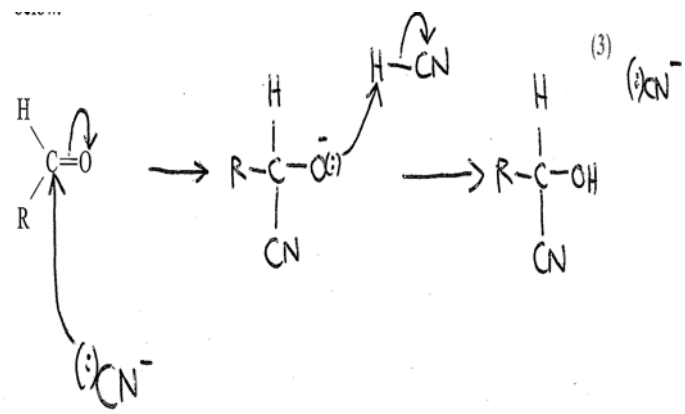


Question Number	Acceptable Answers	Reject	Mark									
2(c)	<table border="1"><thead><tr><th>Wavenumber range / cm^{-1}</th><th>Bond</th><th>Function group present in melonal</th></tr></thead><tbody><tr><td>1740 – 1720 OR 2900 – 2820 / 2775 – 2700</td><td>C=O C-</td><td>(saturated) Aldehyde/CHO</td></tr><tr><td>1669 – 1645 OR 3095 - 3010</td><td>C=C C-</td><td>Alkene ALLOW 'carbon to carbon double bond'</td></tr></tbody></table>	Wavenumber range / cm^{-1}	Bond	Function group present in melonal	1740 – 1720 OR 2900 – 2820 / 2775 – 2700	C=O C-	(saturated) Aldehyde/CHO	1669 – 1645 OR 3095 - 3010	C=C C-	Alkene ALLOW 'carbon to carbon double bond'	(1) (1)	2
	Wavenumber range / cm^{-1}	Bond	Function group present in melonal									
1740 – 1720 OR 2900 – 2820 / 2775 – 2700	C=O C-	(saturated) Aldehyde/CHO										
1669 – 1645 OR 3095 - 3010	C=C C-	Alkene ALLOW 'carbon to carbon double bond'										
	<p>ALLOW any single value or range within the ranges above</p> <p>ALLOW one mark if both wavenumber ranges and bond columns are correct but neither bond identified</p>	Just carbonyl Just C=C in 3 rd column										

Question Number	Acceptable Answers	Reject	Mark
2(d)	$\text{C}_3\text{H}_5\text{O}^+$ / $\text{CH}_3\text{CHCHO}^+$ (1) $\text{C}_6\text{H}_{11}^+$ (1) [ALLOW Structural, skeletal or displayed formulae] Penalise omission of + charge once only ALLOW any order of atoms if correct totals.	C_4H_9^+ $\text{C}_5\text{H}_7\text{O}^+$	2

Question Number	Acceptable Answers	Reject	Mark
2(e) (i)	<p>The diagram shows the structural formula of 2-hexenal, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{CHO}$. The hydrogen atom on the carbon atom adjacent to the double bond (the alpha carbon) is circled in red.</p>	Circle around any other additional atoms	1

Question Number	Acceptable Answers	Reject	Mark
2(e)(ii)		Circle around any other additional atoms	1

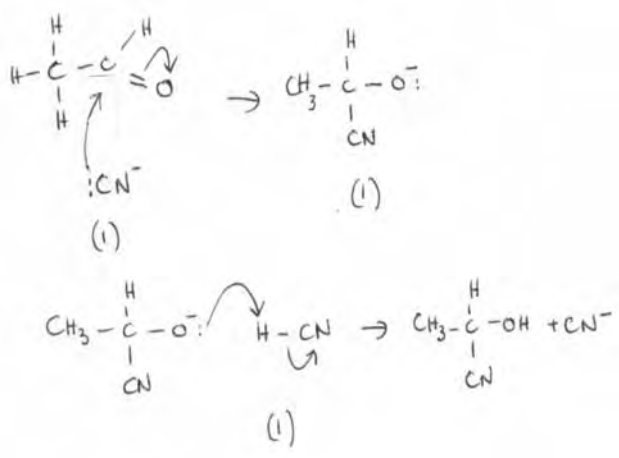
Question Number	Acceptable Answers	Reject	Mark
2(f)(i)	<p>.....</p>  <p>Arrow from anywhere on the cyanide ion to the carbon of the carbonyl. Arrow to the O must come from the carbonyl bond (1)</p> <p>Formula of intermediate (1)</p> <p>Arrow from oxygen to H and from H-CN bond to CN (1)</p> <p>ALLOW arrow from O⁻ to H⁺ or to H₂O</p>	Starting from HCN/ CN ^{δ-}	3

Question Number	Acceptable Answers	Reject	Mark
2(f)(ii)	<p>These marks are stand alone EITHER No</p> <p>First mark: Reaction site/carbonyl/aldehyde/molecule is planar (1)</p> <p>Second mark: Attack (equally likely) from both sides OR Attack (equally likely) from above and below (1)</p> <p>Third mark: (gives) racemic mixture/(gives) equal amounts of each isomer/(gives) equal amounts of each enantiomer (1) OR Yes Melongal has a chiral carbon atom (1)</p> <p>Correct identification of chiral centre (1)</p> <p>This chiral centre unaffected by reaction (1)</p>	<p>attack on a (planar) carbocation OR attack on a (planar) intermediate OR S_N1 OR S_N2 OR "planar product"</p> <p>Any/either direction or any/either angle</p>	3



Question Number	Acceptable Answers	Reject	Mark
3 (a) (i)	Addition (1) Nucleophilic (1) Either order	SN1 SN2	2

Question Number	Acceptable Answers	Reject	Mark
3 (a) (ii)	Hydrogen cyanide / HCN (1) Potassium cyanide / KCN/ sodium cyanide/ NaCN (1) OR Potassium cyanide / KCN (1) With hydrochloric acid / sulfuric acid (to generate HCN) (1) Ignore concentration of acids Mark for HCl etc is consequential on KCN OR Hydrogen cyanide / HCN (1) With sodium hydroxide / other base (to make cyanide ions) (1) Mark for NaOH etc is consequential on HCN	Just CN ⁻ Just CN ⁻ Just acid/ H ⁺ any weak acid Just OH ⁻	2

Question Number	Acceptable Answers	Reject	Mark
<p>3 (a) (iii)</p>	 <p>(1)</p> <p>(1)</p> <p>(3)</p> <p>Both arrows in first step of mechanism above correctly drawn (1)</p> <p>Correct intermediate with charge (1)</p> <p>Both arrows in second step with correct organic product (CN⁻ is not required) (1)</p> <p>Use of HCN for first step max 2 marks</p> <p>Allow omission of lone pair on CN⁻ and O⁻ Allow curly arrow from negative charge or elsewhere on cyanide ion</p> <p>Allow arrow from O⁻ in 2nd step to H⁺ (no other product or only one product) or H₂O (with OH⁻ formed)</p>	<p>C=O breaking before attack by CN⁻</p> <p>Arrows from atoms when they should be from bonds and vice versa</p>	<p>3</p>

Question Number	Acceptable Answers	Reject	Mark
* 3 (a) (iv)	<p>Attack (by nucleophile on the C) is from both sides (equally)/ above and below (at the planar reaction site in the aldehyde group) (1)</p> <p>So a mixture of two enantiomers/(optical)isomers in equal proportions forms OR racemic mixture forms (1)</p> <p>First and second marks are independent</p>	<p>Attack on intermediate in reaction mechanism is from both sides Attack from both ends/two angles</p> <p>Just "both enantiomers form"</p>	2

Question Number	Acceptable Answers	Reject	Mark
3 (b)	<p>Any named (aqueous) strong acid or its formula.</p> <p>Allow (aqueous) sodium hydroxide followed by named acid or formula</p> <p>Ignore references to concentration</p>	<p>Water</p> <p>H⁺</p> <p>Potassium dichromate + sulfuric acid</p> <p>Carboxylic acids</p>	1

Question Number	Acceptable Answers	Reject	Mark
3 (c) (i)	2-hydroxypropanoic acid	<p>2-hydroxylpropanoic acid</p> <p>2-hydroxopropanoic acid</p> <p>2-hydroxypropan-1-oic acid</p>	1



Question Number	Acceptable Answers	Reject	Mark
3 (c) (ii)	$\begin{array}{c} \text{CH}_3 \qquad \qquad \text{CH}_3 \\ \qquad \qquad \qquad \\ -\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{O}- \\ \quad \qquad \quad \quad \\ \text{H} \quad \text{O} \qquad \quad \text{H} \quad \text{O} \end{array}$ <p>OR</p> $\begin{array}{c} \text{CH}_3 \qquad \qquad \text{CH}_3 \\ \qquad \qquad \qquad \\ -\text{O}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}- \\ \quad \qquad \quad \quad \\ \text{H} \quad \text{O} \qquad \quad \text{H} \quad \text{O} \end{array}$ <p>All bonds in ester link must be shown More than 2 units may be shown but structure shown should be a repeat unit Ignore brackets/n</p>	A dimer Missing H atoms Missing bonds at ends	1

Question Number	Acceptable Answers	Reject	Mark
3 (c) (iii)	Ester (link/bond) in PLA can be hydrolysed/broken down (by enzymes) OR Ester (link/bond) in PLA can be broken down	Just "it can be hydrolysed"	1

Question Number	Acceptable Answers	Reject	Mark
3 (c) (iv)	Ethene is (from crude oil so) non-renewable/ milk is from a renewable source/ energy required to make ethene is high/ high temperatures needed to make ethene/ energy requirements for process from sour milk less/ process from milk doesn't use toxic chemicals / process from milk doesn't use cyanide Allow process from ethene requires many steps so expensive/so loss of material occurs at each step /so more reagents needed Ignore references to cost, unless answer gives a reason for lower cost.	Milk is more readily available Greater atom economy No other chemicals needed in process from milk Just "process from ethene requires many steps" Just "cheaper"	1