Organic Synthesis

Mark Scheme 2

Level	International A Level
Subject	Chemistry
Exam Board	Edexcel
Topic	Transition Metals & Organic Nitrogen Chemistry
Sub Topic	Organic Synthesis
Booklet	Mark Scheme 2

Time Allowed: **68 minutes**

Score: **/56**

Percentage: **/100**

Grade Boundaries:

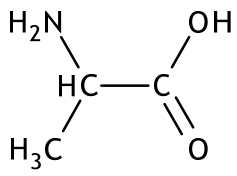
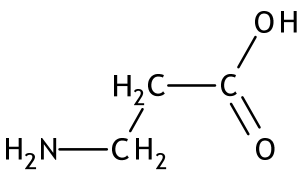
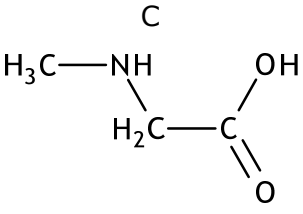
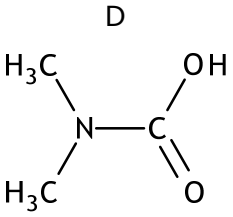
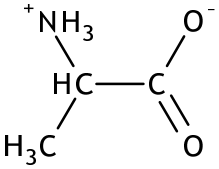
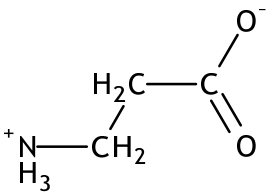
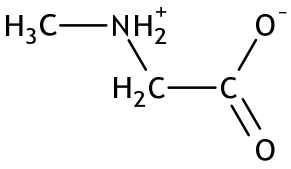
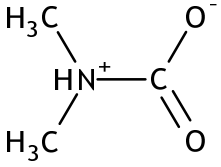
A*	A	B	C	D	E	U
>85%	'77.5%	70%	62.5%	57.5%	45%	<45%

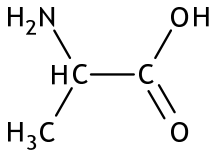
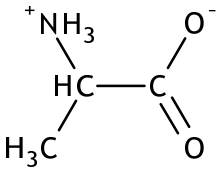
Question Number	Acceptable Answers	Reject	Mark
1(a)	<table><tr><th>Element</th><th>%</th><th></th><th>mol</th><th>Ratio</th></tr><tr><td>C</td><td>40.44</td><td>÷12</td><td>= 3.37</td><td>2.999</td></tr><tr><td>H</td><td>7.87</td><td>÷ 1</td><td>= 7.87</td><td>7.004</td></tr><tr><td>O</td><td>35.96</td><td>÷ 16</td><td>= 2.2475</td><td>2.000</td></tr><tr><td>N</td><td>15.73</td><td>÷ 14</td><td>= 1.12357</td><td>1.000</td></tr><tr><td></td><td></td><td></td><td>(1)</td><td>(1)</td></tr></table> **Empirical formula = $C_3H_7O_2N$ (1)** **Symbols in any order** **Stand alone mark** **No TE on incorrect ratio** **IGNORE significant figure and rounding errors except 1sf in mole calculation**		**3**

Question Number	Acceptable Answers	Reject	Mark
1(b)(i)	Peak at *m/e* = 89 labelled M^+ ALLOW Any clear label e.g. $C_3H_7O_2N^+$		**1**

Question Number	Acceptable Answers	Reject	Mark
1(b)(ii)	M_r = 89 = M_r ($C_3H_7O_2N$) so molecular formula is **$C_3H_7O_2N$** Symbols in any order IGNORE structural and displayed formulae	Answer with no explanation M_r = 90 $C_3H_7O_2N^+$	**1**

Question Number	Acceptable Answers	Reject	Mark
1(c)(i)	Gas evolved is carbon dioxide / CO_2 (1) (so carboxylic) acid / -COOH group is present (1) Dark blue colour indicates the formation of a (copper(II)) **complex** ALLOW indicates **ligand exchange** has occurred (1) Suggests that an amine / -NH_2 group is present ALLOW NH (1) IGNORE ammine amino acid	NH_3 complexes Amide group	**4**

Question Number	Acceptable Answers	Reject	Mark
1(c)(ii)	Any 2 of A, B, C or D (1 mark for each) <u>Molecules</u> A  B  C  D  <u>Zwitterions</u> A  B  C  D  Or fully displayed structures		**2**

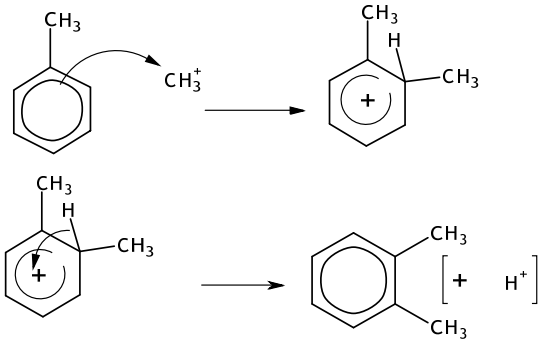
Question Number	Acceptable Answers	Reject	Mark
1(c)(iii)	**First mark** **P** has structure A  or  **Second mark** EITHER Splitting pattern quartet due to CH next to CH_3 and doublet due to CH_3 next to CH ALLOW A comparison e.g A has quartet & doublet but B has two triplets OR As the areas / heights of the two peaks are in a 3:1 ratio (approximately), there must be 3 protons in one environment and 1 in another No TE if A is not one of the isomers given in (c)(ii)	Just quartet & doublet Just two peaks	**2**

Question Number	Acceptable Answers	Reject	Mark
1(d)	**P** (is an amino acid) exists as a zwitterion ALLOW Zwitterion formula OR molecules are held together by (strong) **ionic** forces IGNORE Just 'electrostatic forces'		**1**

Total for Question 1 = 14 marks

Question Number	Acceptable Answers	Reject	Mark
2(a)(i)	M = chloro- /bromo- / iodo- methane / CH_3Cl / CH_3Br / CH_3I		**1**

Question Number	Acceptable Answers	Reject	Mark
2(a)(ii)	$CH_3X + AlCl_3 \rightarrow CH_3^+ + AlXCl_3^-$ Ignore curly arrows even if incorrect Ignore state symbols even if incorrect		**1**

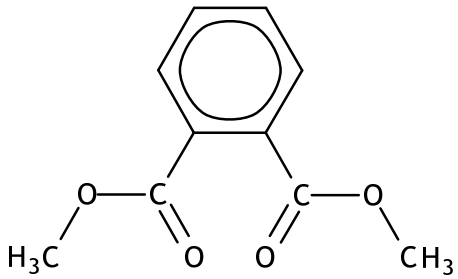
Ques. No.	Acceptable Answers	Reject	Mark
2(a) (iii)	 TE on incorrect electrophile in (a)(ii) If benzene used instead of methylbenzene OR If final product not 1,2-dimethylbenzene (max 2) Curly arrow from on or within the circle to positively charged carbon ALLOW Curly arrow from anywhere within the hexagon Arrow to any part of the CH_3^+ including to the + charge (1) Intermediate structure including charge with horseshoe covering at least 3 carbon atoms, **and** facing the tetrahedral carbon **and** some part of the positive charge must be within the horseshoe (1) Curly arrow from C—H bond to anywhere in the benzene ring reforming delocalized structure (1) Correct Kekulé structures score full marks Ignore any involvement of AlX_4^- in the final step	Curly arrow on or outside the hexagon Dotted bonds to H and CH_3	**3**

Question Number	Acceptable Answers	Reject	Mark
2(a)(iv)	The methyl group donates / pushes electrons into the benzene ring (because of its positive inductive effect / donating inductive effect) (1) (Increased electron density) makes the ring more susceptible to electrophilic attack (1) IGNORE Activating group / ring activation	Mention of lone pair Just 'reacts faster'	**2**

Question Number	Acceptable Answers	Reject	Mark
2(a)(v)	Any identified (name or formula) strong mineral acid: sulfuric acid / $H_2SO_4(aq)$ / hydrochloric acid / $HCl(aq)$ / nitric acid / $HNO_3(aq)$ ALLOW Formulae without (aq) concentrated (acid) IGNORE dilute 'acid' $H^+(aq)$ / H^+ addition of extra alkali before adding acid		**1**

Question Number	Acceptable Answers	Reject	Mark
2(b)(i)	Oxidation state / oxidation number /valency easily changed ALLOW 'Just' variable oxidation state / oxidation number /valency OR easily oxidized **and** reduced IGNORE references to d orbitals / active sites		**1**

Question Number	Acceptable Answers	Reject	Mark
2(b)(ii)	Surface area of catalyst decreases OR Number of active sites is reduced ALLOW Active sites blocked OR Catalyst is poisoned	 Active sites saturated / occupied by **reactants** denatured	**1**

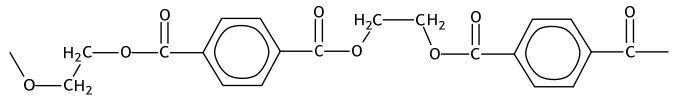
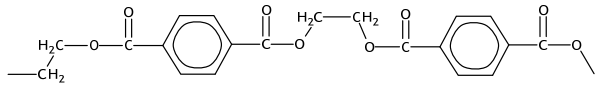
Question Number	Acceptable Answers	Reject	Mark
2(c)(i)	 ALLOW $COOCH_3$ for ester group skeletal / displayed structures omission of benzene ring circle.		**1**

Question Number	Acceptable Answers	Reject	Mark
2(c)(ii)	The forces between plasticiser / phthalate and polymer molecules are weak (1) So London /dispersion /van der Waals forces (rather than covalent bonds) ALLOW dipole-dipole forces OR Forces between water and plasticiser / phthalate molecules are strong(er) / hydrogen bonds (1)	 hydrogen bonds	**2**

Question Number	Acceptable Answers	Reject	Mark
2(c)(iii)	Any **two** of The intermolecular forces between the plasticiser and the polymer molecules are weaker than the those between polymer molecules (1) The polymer molecules move over one another more easily (1) Plasticiser molecules disrupt the polymer structure (1)	break cross-linking between polymer molecules / (covalent) bonds	**2**

Question Number	Acceptable Answers	Reject	Mark
2(d)(i)	PCl_5 / phosphorus(V) chloride / phosphorus pentachloride OR PCl_3 / phosphorus(III) chloride / phosphorus trichloride OR $SOCl_2$ / thionyl chloride / thionyl dichloride		**1**

Question Number	Acceptable Answers	Reject	Mark
2(d)(ii)	Reaction goes to completion / (much) faster / not reversible / not an equilibrium / higher yield / catalyst not needed / uses less energy ALLOW Heat / increased temperature not required. Reverse arguments. IGNORE Cost / reacts easily. More reactive.		**1**

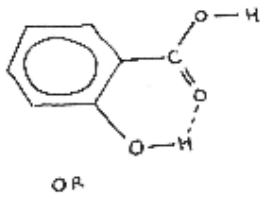
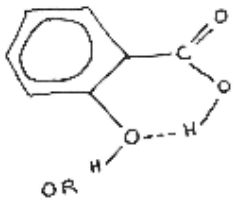
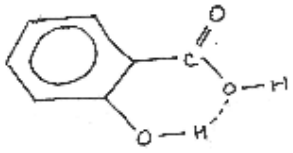
Question Number	Acceptable Answers	Reject	Mark
2(d)(iii)	 OR  ALLOW $-COOCH_2CH_2OOC-$ for diester link **three** ester links (i.e. – CO-O-CH_2-) only if polymer is open-chained (non-cyclic) **and** at least a dimer (1) remaining structure (1) this mark is **not** stand alone IGNORE $()_n$	Omission of benzene ring circle	**2**

Question Number	Acceptable Answers	Reject	Mark
2(d)(iv)	Methanol / CH_3OH	alcohol	**1**

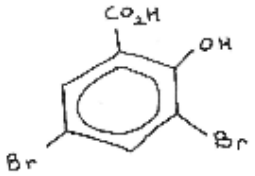
Total for Question 2 = 20 marks

Question Number	Correct Answer	Reject	Mark
3(a)	$C_7H_6O_3$ IGNORE Any other formulae eg $C_6H_4OHCOOH$		1

Question Number	Correct Answer	Reject	Mark
3(b)	$NaCO_3$ scores 0 $2C_6H_4OHCOOH + Na_2CO_3 \rightarrow 2C_6H_4OHCOO^{(-)}Na^{(+)} + CO_2 + H_2O$ Entities **(1)** Balancing correct entities/H_2CO_3/$C_7H_6O_3$ ALLOW Incorrect hydrogens in organic formula on both sides **(1)** ALLOW other correct formulae for 2-hydroxybenzoic acid Fully correct ionic equation (2) IGNORE State symbols even if incorrect	H_2CO_3/ $C_7H_6O_3$	2

Question Number	Correct Answer	Reject	Mark
3(c)(i)	 OR  OR  Ignore bond angles around H ALLOW Two hydrogen bonds within one molecule between **phenol** and **carboxylate** groups		1

Question Number	Correct Answer	Reject	Mark
3(c)(ii)	**First mark** 4-hydroxybenzoic acid has a higher melting temperature with some attempt at justification which may not be correct **(1)** **Second mark** EITHER There are (more) hydrogen bonds between molecules OR chains of molecules held together by hydrogen bonds OR So more hydrogen bonds have to be broken OR More energy is needed to break the extra hydrogen bonds OR The intramolecular hydrogen bonds in 2-hydroxybenzoic acid do not need to be broken **(1)** Or reverse argument	Lower/same melting temperature loses first mark	2

Question Number	Correct Answer	Reject	Mark
3(d)	**Scroll down answer to check name first**  OR COOH for carboxylic acid group **(1)** 3,5-dibromo-2-hydroxybenzoic acid ALLOW 2-hydroxy-3,5-dibromobenzoic acid **(1)** TE for name on their incorrect mono/di/tri/tetra substituted product for **1** max	Look out for substitution of the **phenol group or the carboxylic acid group** **0 out of 2**	2

Question Number	Correct Answer	Reject	Mark
3(e)(i)	Methanol **(1)** (Concentrated) sulfuric acid ALLOW (concentrated) hydrochloric acid IGNORE Acidic conditions **And** Heat/reflux/warm/any temperature above 25^{o}C Second mark dependent on an alcohol in MP1 **(1)**	Nitric acid	2

Question Number	Correct Answer	Reject	Mark
3 (e)(ii)	Methyl 2-hydroxybenzoate molecules are held together by (strong) London/ dispersion forces IGNORE Dipole forces and hydrogen bonds **(1)** Less / limited hydrogen bond **between** water and methyl 2-hydroxybenzoate (so sparingly soluble) **(1)** The hydrogen bonding between water molecules is (very) strong **(1)** Insufficient energy released to break hydrogen bonds in water/ London forces in methyl 2-hydroxybenzoate **(1)** (Some of the) hydrogen bonds are internal in methyl 2-hydroxybenzoate **(1)** The oxygens in methyl 2-hydroxybenzoate can form hydrogen bonds to the hydrogens of water molecules OR The hydrogen on the oxygen in methyl 2-hydroxybenzoate can form hydrogen bonds to the oxygens of water molecules **(1)**		3

Question Number	Correct Answer	Reject	Mark
3 (e)(iii)	ALLOW Correct formulae for names **First mark** Sodium hydrogencarbonate (solution) ALLOW Sodium carbonate (solution) IGNORE water **(1)** **Second mark** to neutralise/ remove remaining acids **(1)** IGNORE references to saturated sodium chloride solution to reduce solubility of ester **Third mark** (Dried with) (anhydrous) sodium sulfate OR magnesium sulfate OR calcium sulfate OR calcium chloride **(1)**	Anything else	3

Question Number	Correct Answer	Reject	Mark
3 (e)(iv)	Distillation OR Distil off the ethyl ethanoate ALLOW Fractional distillation/redistillation	Steam distillation Solvent extraction	1

Question Number	Correct Answer	Reject	Mark
3(e)(v)	**First marking point** A is methyl 2-hydroxybenzoate OR B is 2-hydroxybenzoic acid **and** a bond / wavenumber considered (eg O-H, C-O, C=O, C-H in CH_3) **(1)** **Second marking point** This is independent of the first mark Any one bond with wavenumber from: In spectrum B the carboxylic acid OH between 3300 and 2500 (cm^{-1}) In spectrum A no broad peak between 3300 and 2500 (cm^{-1}) In spectrum A, C-O (benzoate) between 1150-1100 (cm^{-1}) and/or 1310-1250 (cm^{-1}) In spectrum A alkyl C-H between 2962 – 2853 (cm^{-1}) **(1)** IGNORE In spectrum A phenol/OH peak between 3300 and 3100 (cm^{-1}) OR C-H arene	C=O in acid/ ester	2

Question Number	Correct Answer	Reject	Mark
3(e)(vi)	moles of 2-hydroxybenzoic acid = $\frac{9.00}{138}$ = 0.0652 **and** moles of methyl 2-hydroxybenzoate = 0.6 x 0.0652 = 0.0391 **(1)** Mass of methyl 2-hydroxybenzoate = 0.0391 x 152 = 5.948 (g) **(1)** Volume of methyl 2-hydroxybenzoate = 5.948/1.174 = 5.066 = 5.07 cm^3 Correct volume with no working 3 marks **(1)** ALLOW Internal TE s eg For 100% gives 9.91(3) g and 8.44(4) cm^3 **(2)** IGNORE SF		3

(Total for Question 3 = 22 marks)