

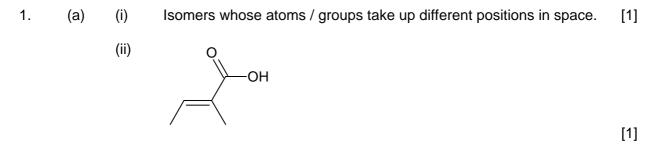
GCE MARKING SCHEME

CHEMISTRY (NEW) AS/Advanced

JANUARY 2010

CH4

SECTION A

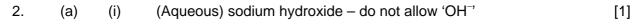


(iii) Ethanol (1) in the presence of (concentrated) sulfuric acid / hydrogen chloride (acting as a catalyst). (1) [2]

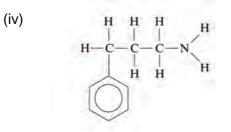
H	H	H	H	H	OH	H	н
н-с	-c	-c	-c	-ċ	- <u>C</u> *-	-c=	=C
Ĥ	I H	Ĥ	н	H	H		Ĥ

[1]

		A carbon atoms that has four different groups / atoms bonded to it [[1]
	(ii)	They rotate the plane of polarised light (in opposite directions) [[1]
	(iii)	An equimolar / equal masses of the two enantiomers (1)	
		No (apparent) effect on the plane of polarised light (1) [2]	[2]
(c)	(i)	I Groups / atoms that are responsible for the absorption of (visible) light / giving colour [[1]
		II It absorbs 'blue' light / all other colours of the visible spectrum /transmits orange [[1]
	(ii)	The CH ₂ protons 'see' three protons on the adjacent CH ₃ group and by the $n+1$ rule are split into a quartet. (1) The CH ₃ protons 'see' two protons on the adjacent CH ₂ group and by th	ne
			[2]



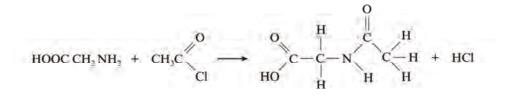
- (ii) Potassium / sodium cyanide do not allow ' CN^{-1} [1]
- (iii) Elimination / dehydration [1]



[1]

(b) Compound **T** (1); this has protons in only 'two' environments, \therefore 2 peaks (1) [2]





balanced (1) correct displayed structure of ethanoyl derivative (1) [2]

(ii)

[1]

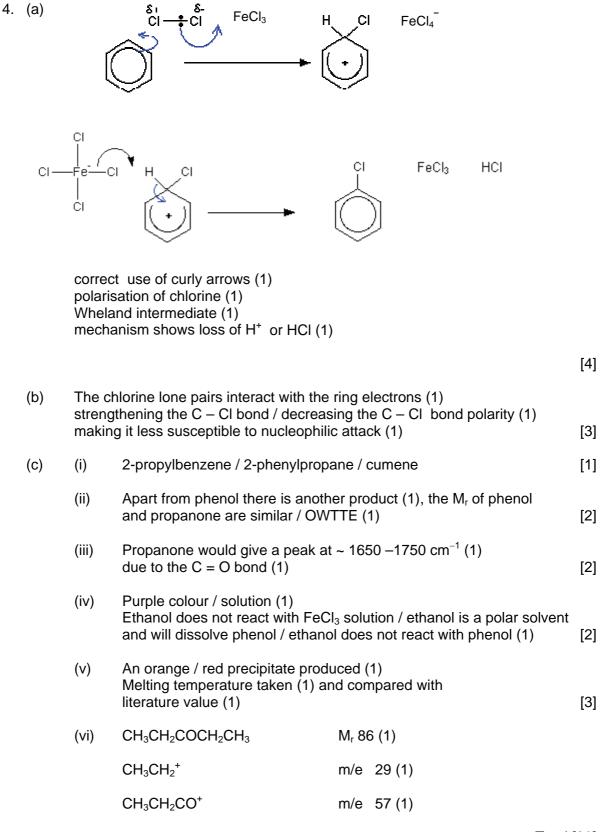
(d) The secondary structure results from hydrogen bonding (1). This occurs between the N – H and C = O groups of the polypeptide chain(s) (1) [2]
 QWC Legibility of text; accuracy of spelling, punctuation and grammar; clarity of meaning. [1]

Total [12]

3.	(a)	(i) e.g. (Thorough) mixing of the solution	[1]	
		(ii) Number of moles of		
		NaOH = $\frac{26.25 \times 0.100}{1000}$ = 0.002625 / 2.625 x 10 ⁻³ (1)	
		Number of moles of CH_3COOH is also 0.002625 (1)	
		Concentration of the diluted solution = $\frac{1000 \times 0.002625}{25.00}$ = 0.105 mol dm ⁻³ (1)	
		Concentration of the undiluted solution = $10 \times 0.105 = 1.05(0) \text{ mol dm}^{-3}$ (1) [4]	
	(b)	<u>Conditions</u> although the temperatures are the same / moderate, method 2 needs higher pressures (1) (or vice versa)		
		<u>Yield / Products</u> Method 1 gives a higher yield / Method 2 gives a lower yield (1) Method 1 gives few or no co-products / Method 2 gives a number of co-products (1) The atom economy of the naphtha method is low (1) There will be problems of the separation of products if method 2 is u	used (1)	
		- maximum 4 marks	[4]	
		QWC Information organised clearly and coherently, using specialis vocabulary when appropriate	st [1]	
	(c)	$CH_3(CH_2)_{10}COOCH_2$		
		CH ₃ (CH ₂) ₁₀ COOCH		
		$CH_3(CH_2)_{10}COOCH_2$	[1]	
	(d)	ethyl palmitate is c (1)	
		because $R_f = \frac{3.6}{6.0} = 0.60$ (1) [2]	
	(e)	$- \mathbf{o} - \mathbf{c} - \mathbf{c} - \mathbf{c} - \mathbf{o} - \mathbf{c} - \mathbf{c} - \mathbf{c} - \mathbf{o} - \mathbf{c} $	0	
		repeating unit (1) structure (1)	[2]	
			Total [15]	

Section A Total [40]

SECTION B



Total [20]

5. (a)

(i)

e.g. CH ₃ CH ₂ CH ₂ CH ₂ Br + 2NH ₃	$\leftarrow CH_3CH_2CH_2CH_2NH_2 + NH_4Br$	[1]
	r = 0 + 13 + 12 + 12 + 12 + 12 + 12 + 12 + 12	ניו

accept one mole of ammonia as a reactant and one mole of HX as a product

- (ii) In the liquid phase butylamine molecules are attracted to each other (mainly) by hydrogen bonding (1). This is because the NH₂ group is polar / correct mention of electronegativity / polarity shown in a diagram (1). Attraction occurs between the nitrogen (lone pair) / (atom) of one molecule and the δ+ hydrogen atom of another molecule (could be seen in a diagram) (1).
 ∴ stronger forces between molecules / more energy needed to separate molecules (and hence a higher boiling temperature). (1) [4]
 (iii) The indicator turns blue / purple (1). This is because butylamine /
- amines are basic (1), as the lone pair on the nitrogen atom is a proton acceptor / or nitrogen is an electron pair donor (could be seen on a diagram) (1). [3]
- (b) (i) 105 kg of ammonium butanoate gives 87 kg of butanamide
 ∴ 1 kg of ammonium butanoate gives 87 kg of butanamide 105
 - \therefore 50.0 kg of ammonium butanoate gives <u>87 x 50.0</u> kg of butanamide = 41.4 kg (1) 105

% yield =
$$\frac{26.9 \times 100}{41.4}$$
 (1) = 65 (1) [3]

- II See if the reaction time can be reduced. [1]
- (c) (i) The (orange) mixture turns green (1) as the ethanol has reduced the acidified dichromate (to green Cr^{3+} (aq)). (1) [2]
 - (ii) Ethanol gives a mixture of ethanal (1) and ethanoic acid (1). The ethanal present will give a silver mirror with Tollens' reagent (1) The ethanoic acid present will fizz / effervesce / produce CO₂ when sodium hydrogencarbonate or carbonate is added (1) [4] (Accept responses based on Fehlings' / Benedict's reagents, acidified dichromate, 2,4-dinitrophenylhydrazine and iodoform test.)

QWC Selection of a form and style of writing appropriate to purpose and to complexity of subject matter [1]

Total [20]

Section B Total [40]

GCE Chemistry - New MS - January 2010 1/3/10

3]

- *.*
- F



GCE MARKING SCHEME

CHEMISTRY AS/Advanced

SUMMER 2010

CH4

SECTION A

1.	(a)	(i)	$C_{10}H_{16}$ (not shortened structural formula)	[1]
		(ii)		
				[1]
		(iii)	I Compound that contains no double bonds / single bonds only (Accept contains maximum number of hydrogens)	[1]
			II $C_{10}H_{16} + 3H_2 \longrightarrow C_{10}H_{22}$	[1]
			(accept structural formulae, consequential from (a)(i))	
		(iv)	Moles $H_2 = \frac{8.96}{22.4} = 0.4$	[1]
			4 double bonds	[1]
	(b)	(i)	Ethane (accept formula)	[1]
		(ii)	LiAlH ₄	[1]
		(iii)	H H Br H—C—C—C—H H H H	[1]
		(iv)	(1-)Propyl ethanoate	[1]

Total [10]

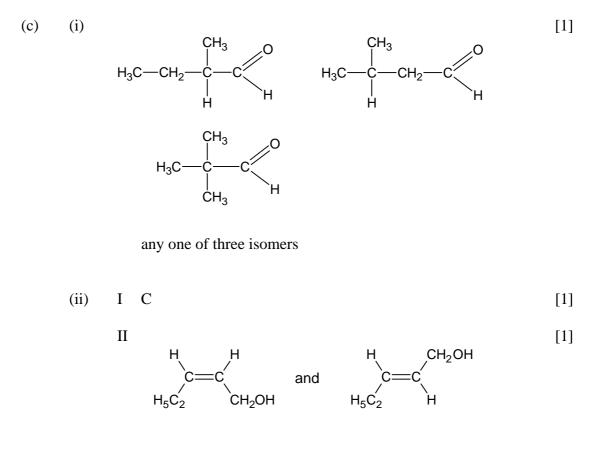
2. (a) In primary alcohols the –OH group is joined to a carbon atom bonded to two hydrogen atoms, in secondary alcohols the carbon atom is bonded to only one hydrogen. [1]

(b)	$\frac{C}{\frac{68.1}{12}}$	H <u>13.7</u> 1.01	O <u>18.2</u> 16	
	5.675	13.56	1.1375	[1]
	4.99	11.92	1	

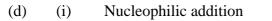
Empirical formula = $C_5H_{12}O$

[1]

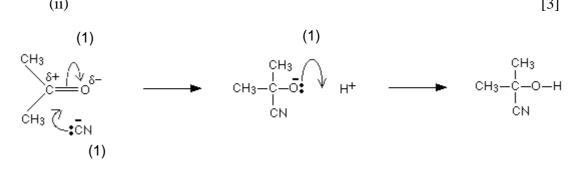
Formula mass, 88.1(2), is same as M_r , therefore molecular formula is C₅H₁₂O [1]



(iii)	Add Tollens' reagent / Fehling's solution	[1]
	A no reaction, B gives silver mirror / red ppt.	[1]
(iv)	Add iodine in aqueous sodium hydroxide / KI and NaOCl	[1]
	C no reaction, D gives pale yellow ppt.	[1]







Total [15]

[1]

Atom economy = $\frac{94.06 \times 100}{122.07}$ (f) Hexane-1,6-diamine / 1,6-diaminohexane (h) In addition polymerisation only the polymer is formed (Accept description e.g. monomers join together with no water loss) In condensation polymerisation the polymer and a small molecule are formed (Accept description e.g. water molecule lost as monomers join together) (Accept for 1 mark only water is eliminated during condensation polymerisation but not during addition polymerisation) Making aspirin / cellulose acetate / as an acylating agent

In phenol anion formed is stabilised by delocalisation of the negative charge

In carboxylic acids anion formed is stabilised by delocalisation of the negative

Phenol loses H+ more easily than alcohol and carboxylic acid does so more

In alcohol anion formed is not stabilised by delocalisation (1)

Delocalisation is stronger in acid than in phenol (1)

Iron(III) chloride / bromine water

Purple solution / white precipitate

charge over the two oxygen atoms (1)

over the benzene ring (1)

easily than phenol (1) (Accept diagrams)

4-chloro-3,5-dimethylphenol

(d) [1]

max 4 marks

(e)

(c)

3.

(a)

(b)

(g)

Total [15]

Total Section A [40]

[1]

[1]

[4]

[1]

[1]

[1]

[1]

[1]

[1]

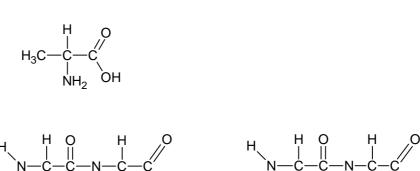
SECTION B

4.	(a)	(i)				[3]
			H H H H H—C—C—C—C—Br H H H H	H Br	$H_3C^{H_5}$	
			(1)	(1)	(1)	
		(ii)	Use a polarimeter to dif One will rotate plane of left / opposite direction 1-bromobutane will hav	f plane polarised ligh s (1)	t to the right and one	to the [3]
			Accept use mass spectr 1-bromobutane (1) Answer gives peak pres isomers (1) (Accept converting to a	sent in 1-bromobutan	e that is not in other	
			QWC The information specialist vocabulary w		and coherently, using	[1]
	(b)	(i)	I $C_2H_5Cl + NH_3$ —	\rightarrow C ₂ H ₅ NH ₂ +	HCl	[1]
			II Nucleophilic substit	tution		[1]
		(ii)	Nitrobenzene (1) Tin and concentrated h	vdrochloric acid (1)		[2]
		(iii)	Sodium nitrite and hydr under 5 °C (1) No change phenylamine		en) with ethylamine (1)
			Accept alternative – bro phenylamine, no chang	· · · - · ·		[3]

(c)

(i)

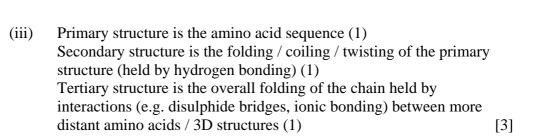
(ii)



| H

Ĥ

ĊH₃



Н

Total [20]

[1]

[2]

-H

5.	(a)	each o Sidew Leadi above	r molecule (1) carbon bonded covalently to 2 other carbons and 1 hydrogen.(1) vays overlap of p-orbitals. (1) ng to delocalised π – bonds. (1) e and below plane of molecule (1) imum 4 marks for bonding)	
		attrac In ber	hes have localised double bond /greater electron density / t electrophiles more readily (1) nzene stable delocalised system would be disturbed / has extra alisation energy / reacts by substitution (1)	[6]
		clarity Select	Legibility of text; accuracy of spelling, punctuation and grammar, y of meaning (1) tion of a form and style of writing appropriate to purpose and to lexity of subject matter (1)	[6]
	(b)	(i)	Benzene is too hazardous / methylbenzoate is less toxic	[1]
		(ii)	The product is crude / impure	[1]
		(iii)	Add crystals to minimum amount of hot ethanol (1) Filter if necessary and leave to cool (1) Filter and dry (in air) (1)	[3]
		(iv)	Take a melting point and compare it with a book value	[1]
		(v)	$\frac{2.75}{1.1} = 2.5 \text{ cm}^3$	[1]
		(vi)	Moles methylbenzoate = $\frac{2.75}{136} = 0.0202$ (1)	
			Moles methyl 3-nitrobenzoate = $\frac{270}{181} = 0.0149$ (1)	
			% yield = 73.8 % (1)	[3]
		(vii)	I Electrophilic substitution	[1]
			II NO_2^+	[1]
			Tota	d [20]
			Total Section 1	R [40]

Total Section B [40]



GCE MARKING SCHEME

CHEMISTRY AS/Advanced

JANUARY 2011

CH4

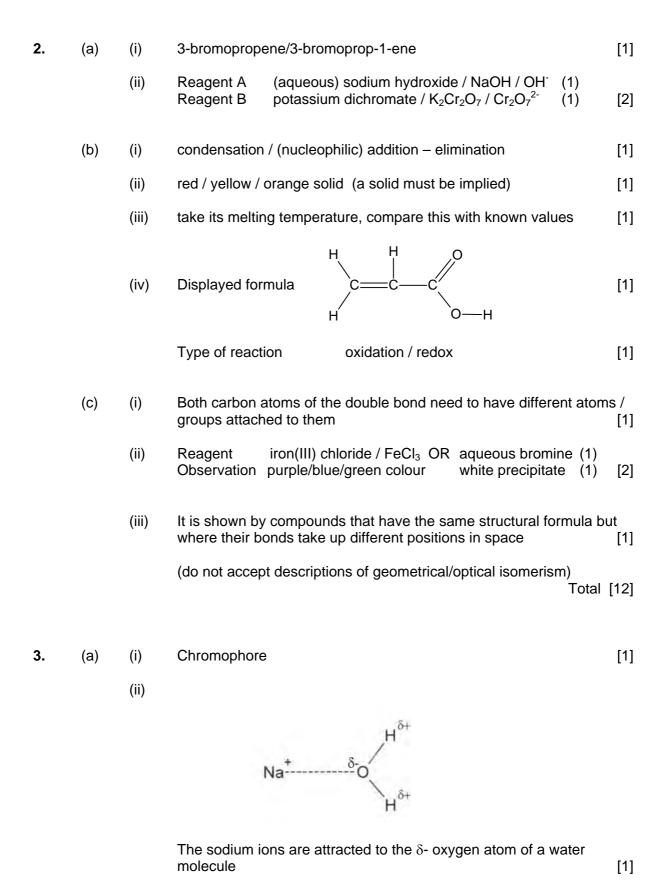
SECTION A

(b) (i) ÇН₃ СН3СІ нсі

[1]

	(ii)	aluminium ch	loride / iron(III) chloride / correct formulae	[1]
(c)	(i)	electrons (1) making it less	s (lone pair of) electrons interact with the ring π cloud s polar / stronger bond (1) e less susceptible to nucleophilic substitution (1)	of [3]
	(ii)	percentage y	m nanufacture / availability of starting materials / ield / shelf life of product / life of product in use / / suitability / range of colours	[2]
(d)	(i)	esters		[1]
	(ii)	reagents	iodine / sodium hydroxide OR sodium chlorate(I) / potassium iodide I_2 / NaOH or OH ⁻ NaCIO / CIO ⁻ / KI / I ⁻ (1)	
		observation	yellow precipitate / solid / crystals (1) (antiseptic smell is a neutral answer)	[2]

Total [13]



(iii) I $0 - 10 \,^{\circ}\text{C} / < 10 \,^{\circ}\text{C}$ [1]

II (An ion that is) an electron **pair** acceptor / seeks out an electron rich site [1]

(accept an electron deficient group/species)

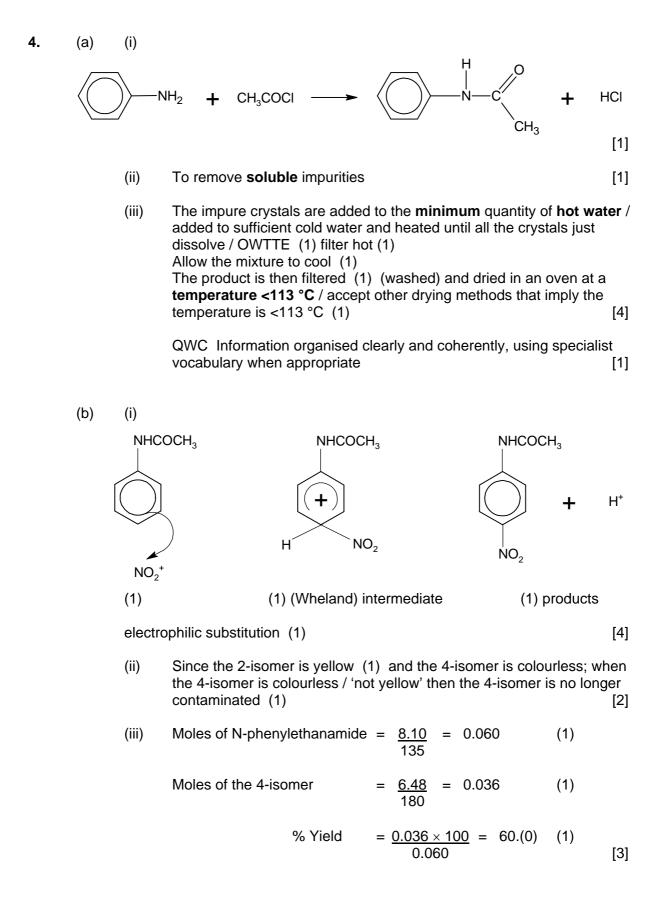
- PMT
- (b) (i) Brilliant Blue FF (1) as it has R_f value 0.80 and this has been identified on the chromatogram (1) [2] must have the correct deduction, either 2 or 0 here (ii) Any TWO from e.g. repeat the chromatography using a different solvent / take its visible spectrum and compare its λ_{max} with those of the two dyes / take its infrared spectrum and compare with the spectrum of the two dyes / take its NMR spectrum and compare its spectrum with the NMR spectrum of each individual dye (1), (1) [2] $(CH_3CH_2COO)_2Ca + Ca(OH)_2 \rightarrow 2 CaCO_3 + 2 C_2H_6$ (C) correct balancing (1) correct formula of ethane (1) [2] (d) δ polarisation (1) δhydrogen bonding (1) Â Η δ+ δ+ [2] (e) COO H₂N-ĊН accept the formula with Na⁺ ions [1] ĊH₂ ĊH₂ ĊOO (f) Н 0 Н CH₃OH HO Ĥ $\dot{N}H_2$ Ĥ (1) (1) =0 С ÓН

[2]

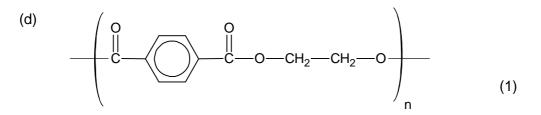
Total [15]

Section A Total [40]

SECTION B



(ii) To convert the (sodium) salt back to the (parent) acid [1]



(c)

(i)

in condensation polymerisation a small molecule / water is lost / produced (1) [2]

Total [20]

PMT

5 . (a)) (i)	Hydrogen cyanide ionises/dissociates (giving a hydrogen ion / H ⁺ and a cyanide ion / CN ⁻) (1) (The mechanism is described as nucleophilic addition) because the CN ⁻ ion acts as a nucleophile / base / electron pair donor (attacking (accept 'approaches') a δ + site) (1) Electron density increases / negative charge produced on the oxygen atom (1) This oxygen atom acts as an electron pair donor, attracting a hydrogen ion (1) In effect a molecule of hydrogen cyanide has added across the carbon
		to oxygen double bond (1) (Accept any four correct points) [4]
		QWC Legibility of text; accuracy of spelling, punctuation and grammar; clarity of meaning[1]
	(ii)	Hydrolysis is a reaction with water (or a water containing reagent), where water 'splits' the 'organic molecule (1) In this reaction, hydrochloric / (dilute) sulfuric acid is used (1) [2]
(b)) (i)	Number of moles of sodium hydroxide = $\frac{20.00 \times 0.250}{1000}$ = 0.005 (1)
		Number of moles of lactic acid $= 0.005$
		Mass of lactic acid = $0.005 \times 90 = 0.45 \text{ g}$ (1)
		Percentage of lactic acid in the yoghurt = $\frac{0.45 \times 100}{50}$ = 0.90 (1) [3]
	(ii)	It would produce a much smaller titre and this will lead to larger % errors - both statements required [1]

(c) The dione does not react with Fehling's reagent (1)
 The dial produces a brown solid (1) [2]

(d) Molecular formula must be $\frac{172}{43} = 4$ \therefore C₈H₁₂O₄ (1)

All oxygen atoms in ester group(s) - each ester group needs two oxygen atoms

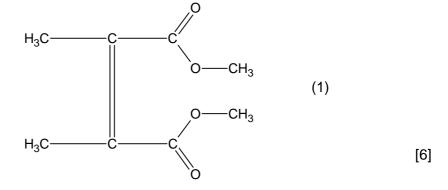
: 2 ester groups (1)

Decolourises aqueous bromine \therefore C===C (1)

Gives methanol as the only alcohol on hydrolysis ... methyl ester (1)

¹H NMR suggests each signal = 6 protons, 'remotely bonded' (1)

Ester is



QWC Selection of a form and style of writing appropriate to purpose and to complexity of subject matter [1]

Total [20]

Section B Total [40]

GCE Chemistry MS - January 2011



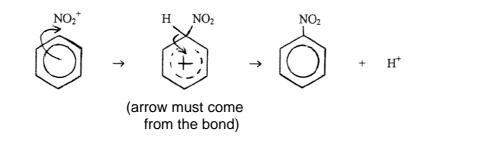
GCE MARKING SCHEME

CHEMISTRY AS/Advanced

SUMMER 2011

CHEMISTRY - CH4

Q.1	(a)	(i)	Chromophore	[1]
		(ii)	Yellow transmitted (or reflected) / other colours (e.g. blue and red) absorbed	[1]

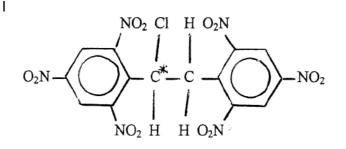


(ii)
$$C_3H_2NO_2$$
 [1]

(iii) H_2SO_4 is losing a proton (to another species and becoming an HSO_4^- ion, acids are proton donors). [1]

(c) The benzene ring is more stable than an alkene because of its delocalised electron structure / π electron system / OWTTE (1) If benzene underwent addition this would mean disrupting this stable electron system and this would require relative more energy / activation energy would be (much) higher. (1) [2]

- QWC Legibility of text; accuracy of spelling, punctuation and grammar; clarity of meaning. [1]
- (d) (i) There is no rotation about a double bond / each 'end' of the double bond has two different 'groups' attached to it [1]
 - (ii)



[1]

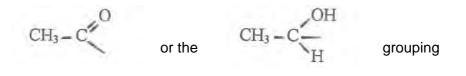
[1]

- II They are mirror image forms (1) that rotate plane polarised light in opposite directions (1) [2]
- III Elimination [1]

Total [13]

- Q.2
- (a) (i) Sodium borohydride / sodium tetrahydridoborate(III) / lithium aluminium hydride / sodium and ethanol / zinc and ethanoic acid (accept correct formulae)
 - (ii) The absorption at ~ 1700 cm⁻¹ is due to the C = O bond (1) As the reaction proceeds the intensity of this absorption becomes smaller because the butanal is being used up / butan-1-ol does not contain a C = O bond (1) [2]

- (ii) Propanone [1]
- (iii) Compounds propanone / ethanol / propan-2-ol Any two for one mark [1]
 - *Explanation* the compounds that give a positive iodoform test have to contain a



[1]

[1]

- (iv) So that a valid comparison can be made between results from other teams / OWTTE
 [1]
 (do not accept 'fair test')
- (c) There is a balance between the 'carbon' produced by burning and the 'carbon' absorbed by the plant (1)
 When butan-1-ol is burnt carbon dioxide is produced, but this is used by plants / in photosynthesis to produce cellulose (1)
- (d) (i) $CH_3CH_2CH_2CH_2OH + CH_3COOH \rightarrow CH_3COOCH_2CH_2CH_2CH_3 + H_2O$ [1] accept C_4H_2OH but not $C_4H_{10}O$ - functional groups must be present
 - (ii) (concentrated) sulphuric acid / H₂SO₄ / hydrogen chloride (gas) / HCl(g) [1]

do not accept H₂SO₄(aq) / HCI

Total [12]

[1]

[1]

|--|

- (c) (i) It is providing a pair of electrons to bond to a proton / acting as a lone pair donor / proton acceptor [1]
 - (ii) I A process of boiling / evaporation and condensation without loss (of reactants) [1]
 - II By using an electrical heater / or a suitable heating bath / heating mantle - do not accept 'water bath' [1]
- (d) Halothane would cause the most damage as it contains a weaker C-CI / C-Br bond (1), which is broken in the upper atmosphere (1) (producing radicals that attack ozone).
 Desflurane does not contain C-CI / C-Br bonds, only the more stable C-F bonds. [2]

(e) (i) Purple colour / solution / complex - do not accept 'precipitate' [1]

(ii) I

Compound	Colour given with Universal Indicator paper	Reaction with sodium hydrogencarbonate solution
propofol	yellow / orange	no reaction
compound L	~~~~~~	~~~~~~
compound M	orange / red	fizzing

One mark for each correct column

II Gas evolved turns 'lime water' milky

[1]

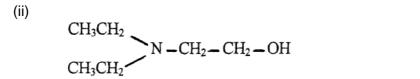
[2]

[1]

[1]

(f) (i)

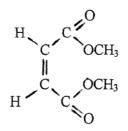




(g) It would melt at a lower temperature (than 89 °C) / below 89 °C (1) and over a range of temperature / not a sharp melting temperature (1) [2]

Total [15]

- **Q.4** (a) (i)
- Stereoisomerism is where the compound has the same structural formula but whose atoms / groups take up different positions in space / in three dimensions (1)



[2]

[2]

(ii) The signal at 3.8 δ due to the methoxy protons (1) would disappear and be replaced by a signal at 11.0 δ (1) due to the O<u>H</u> protons (1). These protons would have peak area 2 (rather than peak area 6 for the methoxy protons) (1) The signal at 6.9 δ would be (largely) unchanged (1) as the C –H bond is not affected by the hydrolysis of the ester. [5]

QWC Selection of a form and style of writing appropriate to purpose and to complexity of subject matter [1]

- (iii) $C_6H_8O_4 \rightarrow 144$ 113 is 31 less, could be CH₃O (1) ion could be $C_5H_5O_3^+$ (1)
- (b) (i) Raw material prices become cheaper / reduce the reaction temperature / use a method where the % yield is increased [1]
 - Use a different (more economic) starting material / find a way of reducing the time taken for fermentation / effect an easier separation method.
 Do not accept reference to increased amounts of enzyme /bigger batch. [1]
 - (iii) Number of moles of fumaric acid expected = 140 (1)

Actual number of moles of fumaric acid obtained = $\frac{13.0 \times 1000}{116}$ = 112 (1)

% Yield =
$$\frac{112 \times 100}{140}$$
 = 80 (1)

Alternatively

180 g / kg of glucose give 2 x 116 g / kg of fumaric acid (1)

$$\therefore$$
 1 g / kg of glucose gives 2×116 g / kg of fumaric acid 180

:. 12.6 kg of glucose gives $2 \times 116 \times 12.6$ kg of fumaric acid = 16.2(4) kg (1) 180

% Yield =
$$\frac{13.0 \times 100}{16.2}$$
 = 80 (1) [3]

	(iv)	starting material (1) e.g. ethanol / ethanal OR ethyl ethanoate OR ethanoyl chloride		
		reagent (1) Cr ₂ O ₇ ²⁻ / H ⁺ acid(aq) / base (aq) followed by acidification	water	
		type of reaction (1) oxidation / redox hydrolysis	hydrolysis [3]	
		II platinum / nickel	[1]	
(c)	e.g.	Tollens reagent - silver mirror		
		OR 2,4 - dinitrophenylhydrazine - yellow/ orange / red precipitate		
		OR Fehling's / Benedict's reagent - brown / red precipitate	[1]	
			Total [20]	

Q.5 (a) (i)

$$\qquad \qquad + \quad CH_3Cl \rightarrow \qquad \bigcirc \qquad + \quad HCl \qquad (1)$$

catalyst - aluminium chloride (1)

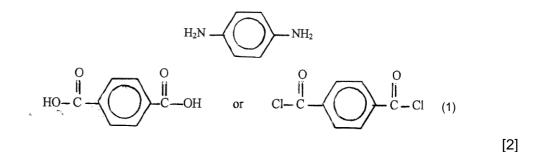
(ii) Mass of methylbenzene =
$$27.6 \text{ g}$$
 (1)

Moles of methylbenzene =
$$\frac{27.6}{92.1}$$
 = 0.30(0) (1)

 \therefore 0.30 mole of C₆H₅CH₂Cl should be made this will have a mass of 0.30 x 126.6 = 38.0 g (1)

 \therefore Mass of flask + product needs to be 120.4 + 38.0 = 158.4 g (1) [4]

- (iii) I potassium cyanide
 - II lithium tetrahydridoaluminate(III) / lithium aluminium hydride [1] (accept correct formulae)
- (b) The nitrogen atom is electron rich / has a lone pair (1) and will act as a proton acceptor / electron pair donor (1) [2]
- (c) 2-Phenylethylamine reacts with nitrous acid giving an alcohol (1) and evolving nitrogen gas as bubbles (1)
 4-Ethylphenylamine gives a diazonium compound (1)
- (d)



(e) (i) 2-amino-3-hydroxypropanoic acid

(ii) Hydrogen bonding occurs because of the difference in electronegativity between hydrogen and oxygen / nitrogen(in O-H and N-H bonds), (1). leading to polar covalent bonds / δ +, δ - (1) There are attractive forces between the oxygen or nitrogen of one molecule and the hydrogen atom bonded to an oxygen or nitrogen atom of another molecule (1) [3]

(Marks can be obtained from a suitable diagram)

QWC Information organised clearly and coherently, using specialist vocabulary when appropriate

[1]

Total [20]

[2]

[1]

[3]

[1]



GCE MARKING SCHEME

CHEMISTRY AS/Advanced

JANUARY 2012

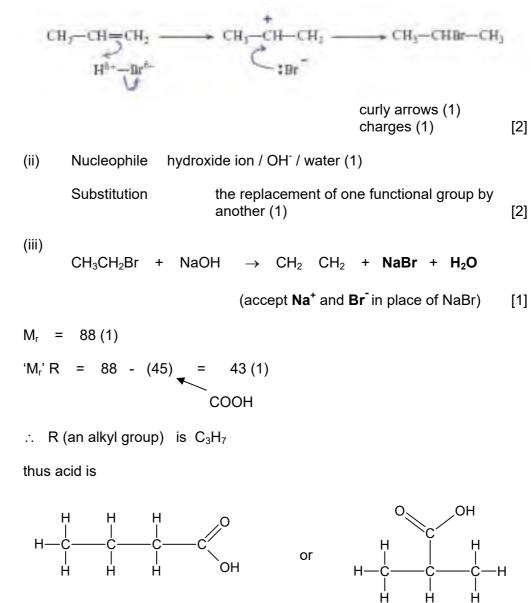
(b)	(i)	It contains an unpaired electron [7	1]	
	(ii)	$I \bullet CH_3 + CI_2 \rightarrow CH_3CI + CI \bullet $	1]	
		II A radical reacts to produce a new radical (that can continue the process)	1]	
	(iii)	C ₇ H ₁₆ [*	1]	
	(iv)	(Bond fission where a covalent bond breaks) and each atom receives an electron	s 1]	
		Total [13	3]	
(a)	Hydrogen bonding occurs between(1)oxygen, nitrogen or fluorine(1)of one molecule and hydrogen, which is bonded to oxygen / nitrogen / fluorine of another molecule (1)			
	Alkane	es do not contain an O-H, N-H or F-H bond and cannot therefore	4]	
	QWC	Candidates should have use 'a selection and form of writing appropriate to purpose and to complexity of subject matter'	1]	
(b)	(i)	The (purified) petroleum is separated by heating (1) due to the different boiling temperatures of different fractions (1)		
		OR the mixture is vaporised (1) and then condensed according to boiling temperatures (1) (as at the oil refinery) [2]	2]	
	(ii)	$CuCl_2$ $Cu + 2$ $CuCl Cu + 1$ (1)		
		(reduction occurs when) the oxidation number becomes less positive (1)	2]	
(c)	(i)	Same molecular formula but a different structural formula / structure [1]	
	(ii)	Both of the carbon atoms of the double bond have different atoms / groups bonded to them (1) There is no free rotation about the double bond (1) [2]	2]	
	(iii)	M _r of compound A is 146.3 / 146 (1)		
		Cost per mole is $\frac{146.3 \times 48 \times 100}{100 \times 73}$ = £96.20 (1)		
		(Accept £96.00 per mole if M _r of 146 has been used) [2	2]	

Q.9

Total [14]

Q.10 (a) (i)

(b)



(1) [3]

- (c) In graphite each carbon atom is bonded to three other carbon atoms (1) (using covalent bonding) The other (outer) electron for each carbon atom is delocalised (1), throughout the structure and is able to move (1), conducting electricity In iodine the two iodine atoms are bonded together (using covalent bonding) and there are no free electrons to carry the charge (1) Mention of covalent bonding for either element (1) [5]
 - QWCLegibility of text; accuracy of spelling, punctuation and grammar;
clarity of meaning (1)Organisation of information clearly and coherently; use of specialist
vocabulary where appropriate (1)[2]

Total [15]

SECTION B TOTAL [70]

GCE Chemistry – CH4

SECTION A

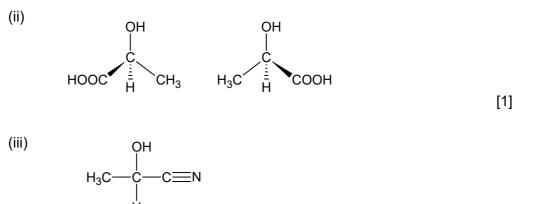
Q.1	(a)	(i)	Α		[1]
		(ii)	D		[1]
		(iii)	С		[1]
		(iv)	С		[1]
	(b)	(i)	Nucle	ophilic substitution	[1]
		(ii)	1-chlo	C–CI bond in chlorobenzene is stronger than in probutane (1) due to delocalization of electron density the ring with the bond (1)	
			OR		
				alised electrons in chlorobenzene (1)	
			repei	lone pair of electrons on nucleophile / ammonia (1)	[2]
		(iii)	C ₄ H ₉ N	$H_2 + CH_3COCI \longrightarrow C_4H_9NHCOCH_3 + HCI$	[1]
		(iv)	I	Tin and concentrated hydrochloric acid (1)	
				Add sodium hydroxide (after cooling) (1)	
				Steam distillation to separate the product (1)	[3]
			II	C ₆ H₅NN ⁺ Cl ⁻	[1]
			Ш	Azo dye / azo compound	[1]

Total [13]

PMT



(i)



[1]

(iv) Reflux / heat with H_2O/H^+ [1]

(v) It contains an equal amount of the two enantiomers / it is a racemic mixture (1)

The rotating effect of one form exactly cancels out the effect of the other (1) [2]

(b) (i) OH H₃C—C—COONa H (1]

(ii)

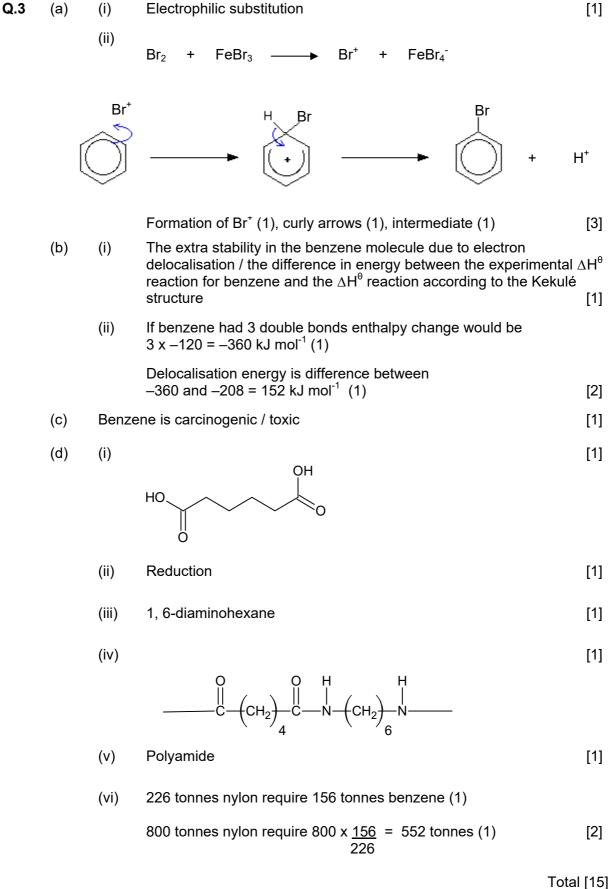
[1]

(c)	(i)	2-aminopropanoic acid	[1]
	(ii)	Nitrous acid / nitric(III) acid / HNO ₂	[1]

(iii) It exists as a zwitterion (1)

strong electrostatic attractions / ionic bonds between different zwitterions (1) [2]

Total [12]



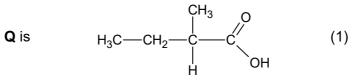
SECTION A TOTAL [40]

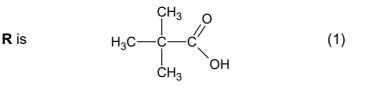
SECTION B

Q.4(a)(i)Moles NaOH = 5.675 x 10⁻³ (1)[2]
$$M, O = 0.50 \\ 0.005675 = 88.1 (1)$$
[2](ii)K contains C=O due to 2, 4-dinitrophenylhydrazine reaction (1)
Contains CH₃CO due to positive iodoform test (1)
From M, K must be CH₃COCH₃ (1)
O contains COOH due to neutralisation / decarboxylation reaction (1)
From M, O must be CH₃CH₂CH₂COOH / (CH₃)₂CHCOOH (1)[5](iii)L is CH₃CH(OH)CH₃ (1)
M is C₃H₆ (1)[3](iv)Concentrated H₂SO₄ / Al₂O₃ / concentrated H₃PO₄[1](b)(i)To form the acid from the salt / to precipitate the acid / the salt is water
soluble[1](iii)Moles = 3.2/40 = 0.08 (1)
Concentration = 0.08/0.04 = 2 mol dm⁻³ (1)[2](iv)Mass = 2.90 x 1.06 = 3.074 g (1)
Moles = 3.074/150.1 = 0.0205 (1)[2](v)Maximum mass = 0.0205 x 122 = 2.50 g (1)
% yield = 1.45/2.50 = 58.0% (1)[2](vi)Hydrolysis not complete / equilibrium forms / C₆H₅COOH slightly
soluble invator / two stages so some loss at both / mass lost during
recrystallisation[1]

Total [20]

Q.5 (a) **P** is
$$H_3C$$
— CH_2





is
$$H_3C$$
— CH_3 O (1)
 H_3C — CH — CH_2 — C OH

Infrared spectrum at 1750 cm⁻¹ shows C=O and at 3000 cm⁻¹ shows O–H therefore X is an acid (1)

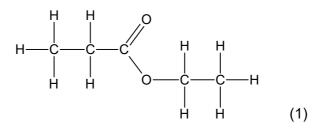
Y is an alcohol, formed from ethanal must be ethanol (1)

5 carbons in ester therefore \mathbf{X} must be propanoic acid (1)

Structure of T is

S

(ii)



(Maximum 4 marks)

[4]

- QWC
 Legibility of text; accuracy of spelling, punctuation and grammar, clarity of meaning (1)

 Selection of a form and style of writing appropriate to purpose and to complexity of subject matter (1)
 [2]
- I Reagent to form **Y** is $NaBH_4 / LiAIH_4$ [1]
 - II Sulfuric acid acts as a catalyst / removes water so pushes equilibrium to right [1]

[4]

(c)	$CH_3(CH_2)$	0.1 to 2.0 ppm triplet (1)	
	(CH ₃)CH ₂ O	3.5 to 4.0 ppm quadruplet (1)	
	CH ₂ CO	2.5 to 3.0 ppm singlet (1)	
	CH₃CO	2.0 to 2.5 ppm singlet (1)	[4]

(d) Isomer **P** (1)

Only **P** can form hydrogen bonds between molecules (1)

Hydrogen bonds are the strongest intermolecular bonds / need more energy to break hydrogen bonds (1) [3]

QWC The information is organised clearly and coherently, using specialist vocabulary where appropriate [1]

Total [20]

SECTION B TOTAL [40]



GCE MARKING SCHEME

CHEMISTRY AS/Advanced

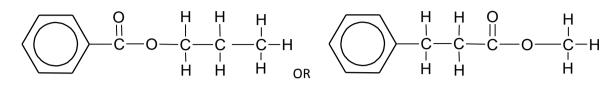
SUMMER 2012

PMT

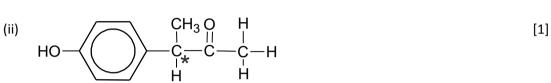
Question 1

(a) Any valid ester structure with formula $C_{10}H_{12}O_2$

Examples:



(b) (i) Compound X



(iii) Rotate the plane of polarised light in opposite directions

[1]

[1]

[1]

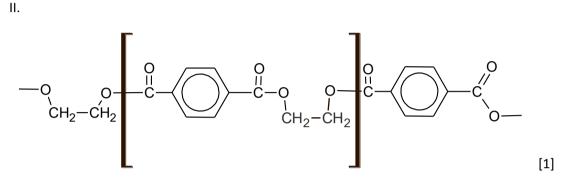
(c)

Reagent(s)	Observation if the test is positive	Compound(s) that would give a positive result
I ₂ / NaOH (aq)	Yellow solid	x
Na ₂ CO ₃ (aq)	Bubbles of colourless gas / effervescence	W
FeCl₃ (aq)	Dark purple/blue/green - do not accept 'precipitate'	X, Z

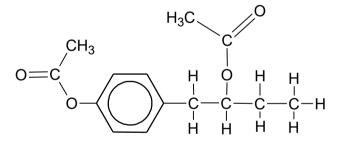
(1 mark for each box) [6]

- (d) (i) Heat / Alkaline / Potassium manganate(VII) / then acidify
 (1 mark for Potassium manganate + 1 other point; 2 marks for all)
 - (ii) I. Addition polymer One large molecule formed only / Condensation polymer one large molecule with small molecules (e.g. water) lost.
 (1)

Addition polymer – one starting material / Condensation – two starting materialsOR Addition polymer – one functional group in each molecule/ Condensation polymer –
two functional groups in each molecule(1)[2]



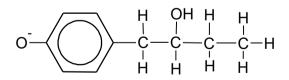
- (e) (i) NaBH₄ / LiAlH₄ or name(1) Reduction (1) [2]
 ignore conditions unless LiACH₄ do not accept 'redox' in water
 - (ii)



Accept structures with only one –OH group reacted.

[1] [1]

(iii)



[19 marks]

Question 2

(a) (i) Alanine forms a zwitterion (1)
 Forces between alanine molecules are ionic bonding (1)
 Ionic bonding much stronger than hydrogen bonding / van der Waals (1)

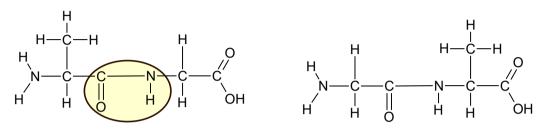
Max 2 marks [2]

[2]

[1]

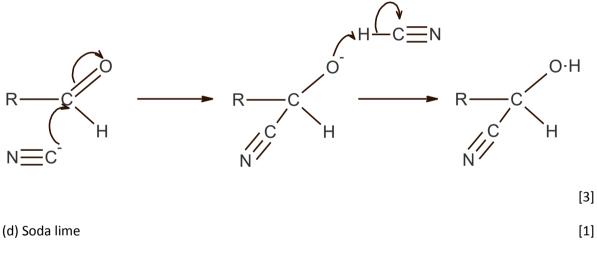
[1]

(ii) 1 mark for each correct structure



(iii) 1 mark for correct identification of peptide link

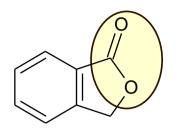
- (b) Enzymes / Structural proteins / Hormones or specific example
- (c) 1 mark for arrows in first stage; 1 mark for correct intermediate; 1 mark for arrow giving gain of proton in second stage (from HCN or from H⁺).



[10 marks]

Question 3

(a) (i)

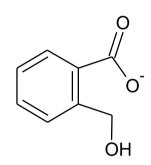


Phthalide

(ii)

[1]

[1]



(b) Distillation / Chromatography

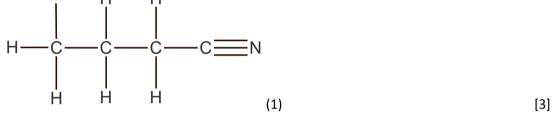
[1]

- (c) Hydrogenation of 3-butyl phthalide removes a benzene ring (1)
 Benzene ring is more stable than alkene/ Reference to delocalisation energy (1) [2]
- (d) 62.1%[1](e) (i) Greater variety of different phthalides that can be produced[1](ii) Higher atom economy / less waste / carbon monoxide is toxic[1]- do not accept references to yield
- (f) Silver nitrate and ammonia / Tollen's reagent (1); Q = Silver mirror (1); R = No reaction (1)
 OR 2,4,-DNP (1); Orange precipitate with Q (1); No reaction with R (1)
 OR Fehling's solution (1); Orange solid with Q (1); No reaction with R (1) [3]

[11 marks]

Question 4

(a)	(i)	Nucleophilic substitution / Hydrolysis	[1]	
	(ii)	Dissolved in alcohol (1) Propene or unambiguous structure (1)	[2]	
	(iii)	Potassium manganate(VII) / Potassium dichromate(VI) - must be name Oxidation (1)	(1) [2]	
	(iv)	(Add Potassium dichromate(VI)) and distil off the propanal from the reaction mixture	[1]	
(b)	(i) Step	1: Potassium cyanide in ethanol / Heat (1)		
	Step 2: Heat with aqueous hydrochloric acid (or other acid) (1)			
		부 부 부		



- (ii) Two points from different bullet points 1 mark each.
- Atom economy / Amount of waste / Whether waste material was recyclable / Whether waste was toxic.
- Amount of energy required / temperature required / pressure required / conditions used
- Rate of production / time
- Availability of catalyst
- Cost of reactants / Availability of reactants / toxicity of reactants.
- Two step processes usually have lower yields than one step processes / percentage yield [2]
- Purification method / separation

(c) (i) Butanoic acid is $C_4H_8O_2$ so $M_r = 88$ (1) Percentage carbon = 48/88 x 100 = 54.5%; percentage hydrogen = 8/88 = 9.1%; Percentage oxygen = 32/88 = 36.4% (At least two of these for 1) OR empirical formula for butanoic acid = C_2H_4O (1) and calculate empirical formula from percentage masses = C_2H_4O (1) [2]

- (ii) Structure 1 mark + 4 marks for explanations.
 - Product is ethyl ethanoate. (1)
 - Two points from the following required for each mark– MAX 4 marks
 - Sweet-smelling = ester
 - $\circ \quad \text{Peak at 1.0ppm implies} \text{CH}_3$
 - Peak area 3 = CH₃
 - Peak area 2 = CH_2
 - Triplet shows CH_3 is next to a CH_2 group.
 - \circ Singlet shows CH_3 no hydrogen atoms bonded to adjacent carbon.
 - \circ Peak at 2.1 ppm suggests this is next to C=O.
 - \circ Quartet shows CH₂ is adjacent to a CH₃ group.
 - Peak at 4.0 ppm shows it is –O-CH₂-
 - \circ IR Peak at 1752 cm⁻¹ = C=O
 - IR Peak at 2981 $\text{cm}^{-1} = \text{C-H or O-H}$
 - Cannot be –OH as we know there is no –OH in NMR spectrum

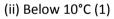
[5]

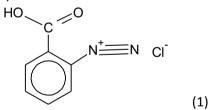
- *QWC:* selection of a form and style of writing appropriate to purpose and to complexity of subject matter. (1)
- QWC: organisation of information clearly and coherently; use of specialist vocabulary where appropriate. (1) [2]

[20 marks]

Question 5

(a)	 (i) (Concentrated) nitric acid / (concentrated) sulfuric acid / Temperature of 40-80°C (Any 2 = 1 mark; All 3 = 2 marks) 					
	Electrophilic substitution (1)					
	 (ii) I. Peak area is proportional to amount of substance (1) Percentage = (30 / 38) x 100 = 79% (Can obtain both marks from correct percentage) 					
	II. 45 = $COOH^+$, 46= NO_2^+ , 122 = $C_6H_4NO_2^+$ and 167 = $C_7H_5NO_4^+$. (Any 2 = 1 mark; All 4 = 2 marks)					
		 Lower melting point / melts over a range 1 mark for each point. Dissolve in the minimum volume Of hot water Filter hot Allow to cool Filter Dry residue under suction / in oven below 142°C 	[1] ax 4 marks [4]			
	QWC: le	gibility of text, accuracy of spelling, punctuation and grammar, clarity	of meaning.[1]			
(b)	(i) Tin aı	nd concentrated hydrochloric acid	[1]			





[2]

(iii) N=N double bond is chromophore (1)
 Compound absorbs blue /green / complementary colours to red / all colours but red (1)
 Remaining frequencies are transmitted, giving the red colour seen. (1)
 Any 2 out of 3 [2]

(c) Nitrogen has a lone pair (1) which can accept a proton (1) [2]

[20 marks]



GCE MARKING SCHEME

CHEMISTRY AS/Advanced

JANUARY 2013

GCE CHEMISTRY - CH4

JANUARY 2013 MARK SCHEME

Section A

1.
$$(a)(i) CH_3 - CH - CH_3$$
 [1]
OH
(ii) O O

(II)
$$\begin{array}{c} 0 \\ \| \\ H_3C - C - O - CH_3 \\ \end{array} \text{ or } H - C - O - CH_2 - CH_3 \end{array}$$
[1]



(iv)
$$H_3C$$
 H
 $C = C$ (or Z form) [1]
 H CH_3

(b)(i)

$$\begin{array}{ccccc}
OH & OH H H CH_3 \\
| & | & | & | \\
H-C & C^*-C-N-C-CH_3 \\
| & | & | \\
H & H & CH_3 \\
HO
\end{array}$$

$$\begin{array}{c}
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(ii) The isomers rotate the plane of polarised light in opposite directions [1]

 (iii) Side effects from other optical isomer / lower dose needed / improved pharmacological activity / only one isomer has correct orientation to bind with biological molecule [1]

(1 mark for acid (accept aldehyde), 1 mark for ketone)

- (c)(i) Ethylamine, ethanol, phenol, ethanoic acid
- (ii) Ethylamine is basic because it accepts a proton readily (1) due to the lone pair of electrons on the nitrogen. (1)
 Phenol is acidic because it loses a proton / the anion formed is stabilised (1)
 by delocalisation of the negative charge over the benzene ring. (1)
 (Accept description e.g. in phenoxide ion lone pairs of electrons on oxygen become delocalised with electrons in benzene ring.) [4]

Total [14]

[4]

[1]

Total [12]

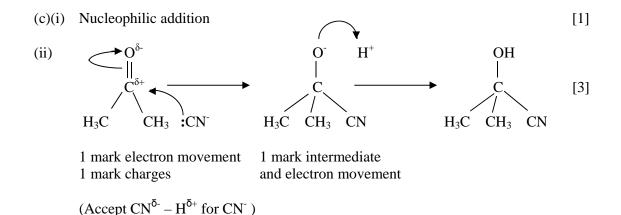
[1]

a)

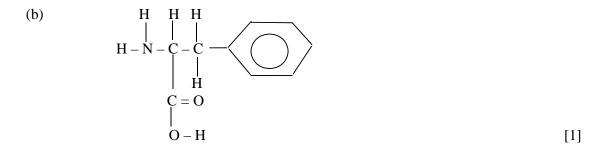
	Butan-2-ol	Ethanal	Ethanol	Propanone
2,4-DNP	No reaction	Yellow-orange	No reaction	Yellow-orange
		precipitate		precipitate
Tollens' reagent	No reaction	Silver mirror	No reaction	No reaction
I ₂ /NaOH	Yellow	Yellow	Yellow	Yellow
	precipitate	precipitate	precipitate	precipitate

(1 mark for each column)

- (b)(i) Electrophilic addition [1]
- (ii) Carbonium ion / carbocation / electrophile
- (iii) Bromination / HBr addition / hydrogenation[1]
- (iv) Secondary carbocation more stable than primary carbocation [1]



- 3. (a) Intermolecular bond formed (1) when hydrogen attached to a highly electronegative atom (1) is bonded to an electronegative atom attached to hydrogen (in another molecule) (1) forming a very strong dipole dipole attraction (1) [3] (maximum 3 marks)
 OWC I egibility of text: accuracy of spelling, punctuation and grammar, clarity of
 - *QWC* Legibility of text; accuracy of spelling, punctuation and grammar, clarity of meaning [1]



(c) Behaves as / can react with an acid or a base (1)

-COOH is an acidic group / donates proton, -NH $_2$ is a basic group / accepts proton (1) [2]



(e) Moles $MSG = 1/169.08 = 5.91 \times 10^{-3}$	(1)	
Concentration = $5.91 \times 10^{-3} / 0.1 = 5.91 \times 10^{-2}$	(1)	[2]

- (f) (Neutral) $\operatorname{FeCl}_3 / \operatorname{Br}_2$ (1) Purple colour / white precipitate (1)
- (g) 2,4-Dinitrophenylhydrazine / acidified sodium dichromate(1)Yellow-orange precipitate / orange to green colour change(1)[2]

Total [14]

[2]

Total Section A [40]

Section B

4. (a) For synthetic polymer:

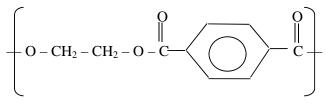
Monomers: 1,6-Diaminohexane / ethane-1, 2-diol (1)

Hexanedioic acid / benzene-1,4-dioic acid (1)

Structure:

$$\begin{bmatrix} O & O & H & H \\ || & || & | & | \\ C - (CH_2)_4 - C - N - (CH_2)_6 - N \end{bmatrix}$$
(1)

or



For natural polymer:

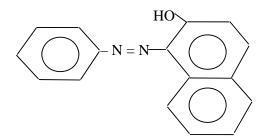
Monomers: aminoethanoic acid / 2-aminopropanoic acid (1)

Structure: e.g.

QWC Selection of a form and style of writing appropriate to purpose and to complexity of subject matter [1]

(b) (i)		H ₂ Cl			[1]
(ii)	1,4-dichlo	robenzene			[1]
(iii)	Chlorine (in the absence of ultraviolet light)		(1)	
	AlCl ₃ / Fe	eCl ₃ (as a halogen carrier)		(1)	[2]
(iv)	Heat with	NaOH (aq)		(1)	
	add HNO	(aq) followed by AgNO ₃ (aq)		(1)	
	F gives v	white precipitate, G does not		(1)	
	In F , the	C–Cl bond is polarised / contains	-	cleophilic substitutio	n
	In G due of the chl	to delocalisation of the π electron orine	cloud of the ring wit		ons
	the C–Cl	bond is too strong to break/ does		hilic substitution (1) [6]	
	QWC	The information is organised cle vocabulary where appropriate	arly and coherently,	using specialist	[1]
(c)(i)	To preven	t decomposition of benzenediazor	ium chloride / HNO	2	[1]

(ii)



[1]

(iii) A chromophore is the group of atoms responsible for the colour of the compound (by causing absorption in the visible region of the spectrum) [1]

Total [20]

5. (a)((i) Moles HCl = 5.4×10^{-3} (1) $M_r \mathbf{B} = \frac{0.395}{0.0054} = 73.1$ (1) (2]]
(ii)	B is basic therefore must be amine (1)	
	C reacts with Na_2CO_3 therefore must be an acid (1)	
	D is oxidised to C therefore must be an alcohol (1)	
	A hydrolyses to acid but does not contain oxygen therefore must be nitrile (1)	
	$\mathbf{B} \text{ is } CH_3CH_2CH_2CH_2NH_2 \tag{1}$	
	$C is CH_3CH_2CH_2COOH $ (1)	
	$\mathbf{D} \text{ is } CH_3CH_2CH_2CH_2OH \tag{1}$	
	$\mathbf{A} \text{ is } \mathrm{CH}_3\mathrm{CH}_2\mathrm{CH}_2\mathrm{CN} \tag{1}$]
	 (4 marks structures – if 3 carbons in chains penalise only once 4 marks reasons – accept alternative reasons) 	
(b)	CH ₃ CH ₂ CH ₂ Cl	
	Peak areas (1) 3	
	Chemical shifts (1) 2 2	
	8 7 6 5 4 3 2 1 0	
	Chemical shift (δ) / ppm (CH ₃) ₂ CHCl	
	(ch ₃) ₂ ener 6	
	Peak areas (1)	
	Chemical shifts (1)	
	1	
	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$]
(c)(i)	2 steps instead of 3 / CH ₃ COCH ₃ can be sold / reagents are cheaper / gives a higher yield / easier to extract phenol / phenol formed more quickly / fewer reactants [2 (Accept any 2)]	:]
(ii)	Lower temperature required / catalyst costs less / catalyst less likely to break up / catalyst less toxic or safer [1]	.]
(d)	Moles phenol = $58.75/94.06 = 0.625$ (1)	
	Maximum mass aspirin = $0.625 \times 180.08 = 112.55$ g (1)	
	65% yield, therefore mass aspirin = 73.16 g (1) [3]]

Total [20]

Total Section B [40]

GCE CHEMISTRY MS - January 2013

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20

PMT



GCE MARKING SCHEME

CHEMISTRY AS/Advanced

SUMMER 2013

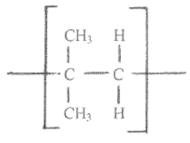
[1]

GCE CHEMISTRY – CH4

SUMMER 2013 MARK SCHEME

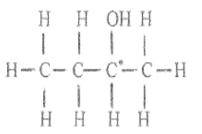
Q.1	(a)	(i)	(2-)Methylpropan-2-ol	[1]
		(ii)	30.1 / 30	[1]

- (iii) (Concentrated) sulfuric acid / phosphoric acid / aluminium oxide / pumice [1]
- (iv)



(with or without n)

(v)



(1) for structure, (1) for asterisk [2]

	(vi)	I	acidified potassium dichromate / H^+ , $Cr_2O_7^{2-}(aq)$	[1]	
		II	ethanal has a C = O bond at 1650-1750 cm ⁻¹ (metaldehyde does not have this bond)	(1)	
			metaldehyde has a C – O bond at 1000-1300 cm ⁻¹ (ethanal does not have this bond)	(1) [2]	
)	.,	leagent)bservat	2,4-dinitrophenylhydrazine / 2,4-DNP OR iodine / NaO tion yellow / orange / red precipitate OR yello	H or KI / NaOCI (1) ow precipitate (1) [2]	
	()	•	ethanol / sulfuric acid OR NaHCO ₃ OR	$Ag^{+}/NH_{3}/ Tollens' (1)$	
	C)bservat	tion sweet smelling liquid OR effervescence OR	silver mirror (1) [2]	
				Total [13]	

(b)

Q.2	(a)		et with iron(III) chloride solution Purple solution with phenol, no reaction with methyl propenoate			
		OR	OR			
		React with aqueous bromine / bromine water White precipitate with phenol (and bromine decolourised), bromine decolourised with methyl propenoate				
		(1) for reagent and (1) for observation with compound	[2]		
	(b)	(i)	It absorbs all colours except yellow / absorbs the blue end of the spectrum and reflects yellow – do not accept 'emits'	[1]		
		(ii)	Tin / iron and concentrated hydrochloric acid	[1]		
	(c)	(i)	Moles of 2,4-dinitrophenol = $7.36/184 = 0.040$ (1) Moles of 2,4-dinitrophenyl ethanoate = $7.91/226 = 0.035$ (1)			
			Percentage yield = $0.035 \times 100 / 0.040 = 87.5 / 88 \%$ (1)	[3]		
		(ii)	R _f value is given bydistance travelled by the 2,4-dinitrophenol distance travelled by the solvent front(1)			
			$= \frac{2.8}{5.0} = 0.56 $ (1)	[2]		
	(d)	(i)	Nickel / platinum	[1]		
		(ii)	The –OH groups are able to hydrogen bond with water (1) but these are a very small part of the 'urushiol' molecule (1)	[2]		

Total [12]

PMT

15

Q.3	(a)	(i)	48.5 / 49 %	[1]
		(ii)	Find a use for the calcium sulfate	[1]
	(b)		Total volume of aqueous sodium hydroxide needed = $\frac{26.40 \times 250}{25.00}$ = 264.0 cm ³ (1)
			from the graph this is equivalent to 0.011 mole of the acid (1)	
			$\therefore M_r \text{ of the acid } = \underbrace{\text{mass}}_{\text{no. of moles}} = \underbrace{2.31}_{0.011} = 210 (1)$	
			$C_6H_8O_7$. n H ₂ O = 210	
			192 ∴ n = 18 (1)	
			since M_r of water is 18 n = 1 (1)	[5]

[1]

(c) The two 'ends' of the double bond have different groups bonded to the carbon atoms (of the double bond) / they have different structural formulae, so cannot be stereo / geometric isomers [1]

(e)
$$C_5H_6O_5 \rightarrow CH_3COCH_3 + 2CO_2$$
 [1]

$$\begin{array}{c|c} H & H \\ C & -C - O - H \\ H & H \\ H - C - O - H \\ H & H \\ C - C - O - H \\ H & H \end{array}$$

 (g)
 (Fractional) distillation / (preparative) gas chromatography / HPLC
 [1]

 (h)
 (i)
 eg An optically active isomer that will rotate the plane of polarised light / an isomer with a chiral centre
 [1]

 (ii)
 An equimolar mixture of both enantiomers (that has no apparent effect on the plane of polarised light)
 [1]

 Total [15]

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Q.4 (a) Benzene is a compound whose molecules contain six carbon atoms bonded in a (hexagonal) ring (1) All the carbon to carbon bond lengths are equal / intermediate (1) Each carbon atom is bonded to two other carbon atoms and a hydrogen atom (1) by σ -bonds (1) All the C - Ĉ - C angles are the same / 120° (1) The remaining p electron of each carbon atom / overlap of p orbitals forms a delocalised cloud of electrons / π -system (1) above and below the plane (1) Credit can be gained from labelled diagram [*Candidates can gain a maximum of (4) for this part*]

> This delocalisation increases the **stability** (1) of the molecule and this stability is maintained by benzene undergoing substitution reactions in preference to addition reactions (that would destroy the delocalised system) The g cloud is **electron rich** and will be attracted to electron deficient electron biles (

The π -cloud is **electron rich** and will be attracted to electron deficient electrophiles (1) [*Candidates can gain (2) for this part*] [6]

QWC Selection of a form and style of writing appropriate to purpose and to complexity of subject matter (1)

Legibility of text; accuracy of spelling, punctuation and grammar; clarity of meaning. (1) QWC [2]



catalyst eg AlCl₃ (anhydrous) (1)

[2]

(c) (i) (There are two environments for the protons), the 3 aromatic protons at ~6.8 δ and the 9 methyl / aliphatic protons at ~ 2.3 δ (1) These give a peak area of 3:9, ie.1:3 (1) These environments are separate / discrete (1) therefore no splitting pattern

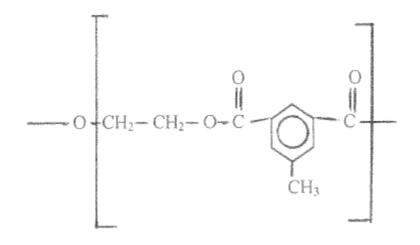
[3]

(ii) Dissolve in the minimum volume (1)
 Of hot water (1)
 (Filter hot) (1)
 Cool (1)
 Filter (1)
 Dry (1)

(up to 4 max but candidates must give the first two points in order to gain full credit)

[4]

(iii)



[1]

(iv) Reagent S is alkaline potassium manganate(VII) (1)
 Reagent T is eg hydrochloric acid (1)

[2]

Total [20]

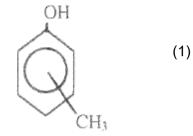
[1]

- **Q.5** (a) (i) The **nitrogen atom** has a **lone pair** of electrons making it an electron pair donor / proton acceptor
 - (ii) Compound **L** must contain the grouping -N-C (1)

The nitrogen atom must be bonded directly to the ring as a (primary) aromatic amine is formed on hydrolysis (1)

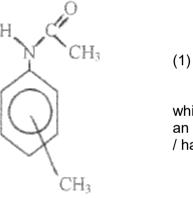
As the hydrolysis compound is a phenol (and has an OH group directly bonded to the ring) a methyl group must also be bonded directly to the ring, as the molecular formula is C_7H_8O / the compound has the structure

ΗΟ



The compound is likely to be an amide, as these are hydrolysed by bases to amines (1)

A suggested formula is



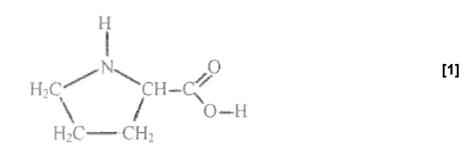
which is $C_9H_{11}NO$, an isomer of cathinone / has M_r of 149(1)

[6]

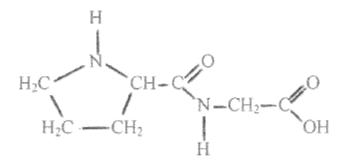
QWC Information organised clearly and coherently, using specialist vocabulary where appropriate QWC [1]

[1]

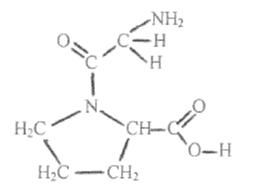
(b) (i)



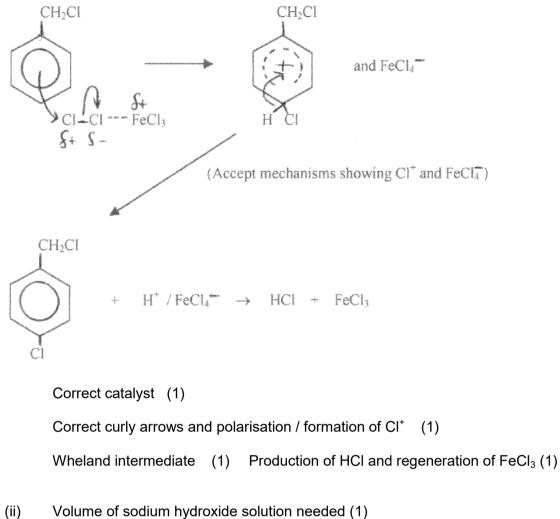
(ii)



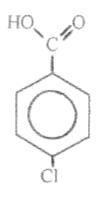
OR



(c) (i)



- (ii) Volume of sodium hydroxide solution needed (1) How long to reflux (1)
- (iii) The aromatic C Cl bond is stronger than the aliphatic C Cl bond (1) This is because a p-electron(s) of the chlorine atom in the aromatic compound becomes part of / incorporated into the delocalised π system of the ring (1) [2]
- (iv)



(1)

chlorine has two isotopes 35/37 in a 3:1 ratio (1)

[2]

[4]

[2]

Total [20]



GCE MARKING SCHEME

CHEMISTRY AS/Advanced

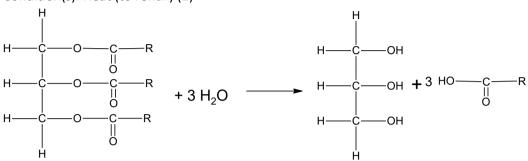
JANUARY 2014

CH4

Section A

Q.1 (a) Reagent(s): (aqueous) sodium hydroxide followed by acid (1)

Condition(s): Heat (to reflux) (1)



[IF NO ACID LISTED IN REAGENT, THEN EQUATION SHOULD CONTAIN SODIUM SALTS] (1) [3]

(b)	(i)	Reagent(s): (aqueous) bromine (1) Observation(s): Changes from orange to colourless (1)	[2]
	(ii)	Nickel / Platinum / Palladium	[1]
	(iii)	Moles of hydrogen gas = $1.15 \div 24.0 = 4.79 \times 10^{-2} \text{ mol (1)}$ Moles of stearic acid produced = $4.79 \times 10^{-2} \div 2 = 2.40 \times 10^{-2} \text{ mol (1)}$ Mass of stearic acid = $2.40 \times 10^{-2} \times 284 = 6.80 \text{ g (1)}$	[3]
(c)	(i) (ii)	C 69.7 ÷ 12 = 5.808 H 11.7 ÷ 1.01 = 11.584 O 18.6 ÷ 16 = 1.163 (Empirical formula = $C_5H_{10}O$ (1) $C_{10}H_{20}O_2$	1) [2] [1]
(d)	e.g. bi	odiesel is renewable/won't run out / carbon neutral do not accept 'produces less carbon dioxide'	[1]

Total [13]

Q.2	(a)	Chromophore [1]	Chromo	[1]
	(b)	(i) Melting temperature lower than literature value / melting occurs over a temperature range [1]	(i)	
		 (ii) Identify percentage or amount of impurities (1) Identify the number of compounds present or number of impurities (1) [2] 	(ii)	[2]
	(c)	(i) Acidified potassium dichromate (1) Heat and distil (1) do not accept 'reflux' [2]	(i)	[2]
		M_r of phenylmethanol = 108.08 M_r of benzenecarbaldehyde = 106.06 (1)100% conversion would be 10.0 \div 108.08 \times 106.06 = 9.815g (1)86% yield = 9.815 \times 86 \div 100 = 8.44g (1)[3]	(ii)	
		 (iii) Two resonances in the range 5.8-7.0 ppm (1) These are doublets (1) One singlet at around 11.0 ppm (1) All resonances have the same area (1) 	(iii)	[4]

Total [13]

[1]

[2]

[3]

(b)	(i)	Peak at 2500-3550 cm ⁻¹ present in product but not reactant [2	1]
	(ii)	Add FeCl ₃ (1) Forms a purple solution (1) do not accept 'precipitate' [2	2]
	(iii)	1 mark for correct location of hydrogen bond; 1 mark for dipole OR lone p e.g. H H^{δ^+} H^{δ^+} H^{δ^+}	air

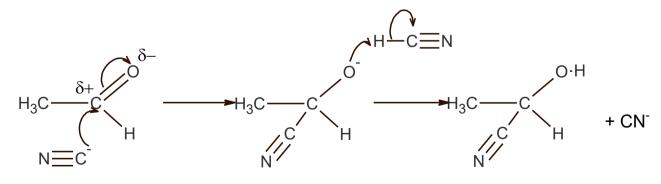
(c) Aromatic Claisen product is more acidic / better proton donor than product of 1,2-Wittig rearrangement (1)

The 1,2-Wittig rearrangement product is an alcohol, so the charge on the **anion** formed is localised / the **anion** is unstable (1) The product of the aromatic Claisen rearrangement is a phenol, so the charge on the anion can be delocalised which stabilises it (1)

(Must be reference to 'anions'; (1) mark awarded for 'stability of anions' if no reference to delocalisation)

QWC: organisation of information clearly and coherently; use of specialist vocabulary where appropriate [1]

(d) 1 mark for arrows in first stage; 1 mark for correct intermediate; 1 mark for arrow giving gain of proton in second stage (from HCN or from H⁺); 1 mark for bond polarity – max 3 marks; lose 1 if incorrect final structure



Mechanism: Nucleophilic addition (1)

[4]

Total [14]

Total Section A [40]

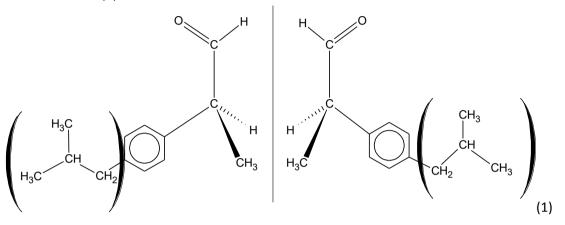
Q.3

(a)

Isomers

- Q.4 (a) $CH_3CH(CH_3)CH_2Cl(1) AlCl_3 / FeCl_3 (1) Room temperature / in the dark (1) [3]$
 - (b) (i) 2,4-DNP (1) Orange precipitate (1) [2]
 - (ii) Tollen's reagent (1) Silver mirror with **C**, no reaction with **B** (1) [2]

(c) Optical isomerism is where a molecule and its mirror image are different / non-superimposable (1)
 Compound C has a chiral centre / 4 different groups attached to one carbon atom (1)



The two isomers rotate the plane of polarised light in opposite directions (1) [4]

QWC: organisation of information clearly and coherently; use of specialist vocabulary where appropriate (1) [1]

- (d) Dilute acid (1) heat (1) hydrolysis (1) [3]
- (e) Acidified potassium dichromate (VI) (1) / heat (1)

One step reactions are generally better as they have a better yield / there is waste in each stage (1)

Two step process may be cheaper / use more sustainable reagents/ may give a better yield in this case / produce less harmful waste materials / potassium dichromate may react with other parts of the molecule as well / may be easier to separate product (1)

Do not credit same idea twice e.g. if 'better yield' gains first mark, a different point is required to gain second mark [4]

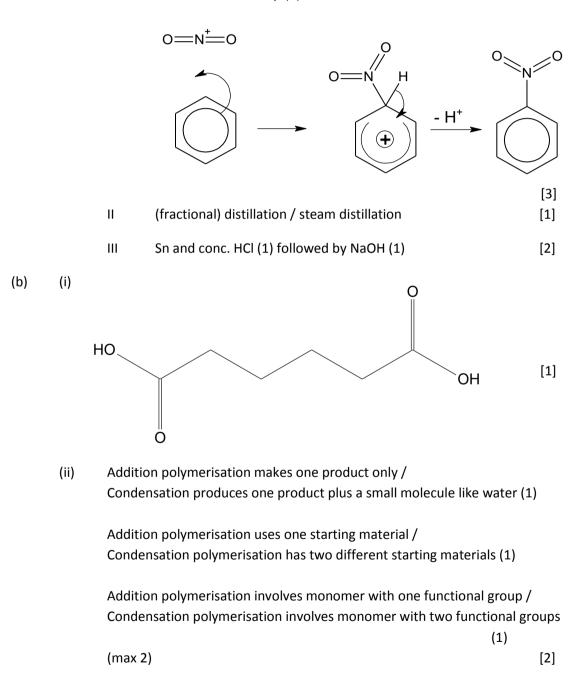
QWC: selection of a form and style of writing appropriate to purpose and to complexity of subject matter [1]

Total [20]

Q.5 (a) (i) Both molecules have lone pairs on nitrogen (1)

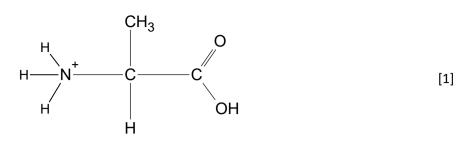
The lone pairs can form (coordinate) bonds with H^+ ions (1) [2]

- (ii) Lone pair on N in phenylamine is delocalised over benzene ring (1) therefore less able to accept $H^+(1)$ [2]
- (iii) I Arrow in first step (1) Cation structure in second step (1) Arrow in second step (1)





(ii)



 $\begin{array}{c|c} H & \begin{array}{c} CH_{3} & CH_{3} \\ \hline N & C & \end{array} \\ \hline N & C & C & N \\ H & H & \begin{array}{c} C & N \\ \hline C & -C & C \\ H & H & \begin{array}{c} H \\ \end{array} \\ \hline H & H \\ \end{array} \\ \end{array} \begin{array}{c} CH_{3} \\ \hline C & -C \\ H & \begin{array}{c} C \\ H \\ \end{array} \end{array}$

(iii) Alanine has strong (electrostatic) forces between the zwitterions (1)

Butanoic acid has hydrogen bonding between molecules / electrostatic forces in alanine are stronger than forces in butanoic acid (1)

[2]

(iv) Soda lime (1) $CH_3CH_2NH_2$ (1)

[2]

Total [20]

Total Section B [40]

GCE CHEMISTRY MS January 2014



GCE MARKING SCHEME

CHEMISTRY AS/Advanced

SUMMER 2014

GCE CHEMISTRY – CH4

SUMMER 2014 MARK SCHEME

SECTION A

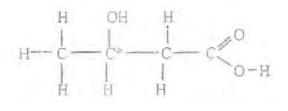
Q.1	(a)	(i)	$CH_{3}CH_{2}CH_{2}CH_{2}CH_{3} + Cl_{2} \rightarrow CH_{3}CH_{2}CH_{$	[1]
		(ii)	CH ₃ CH ₂ CH ₂ CH ₂ CHCH ₃	[1]
	(b)	(Anhy	ydrous) aluminium chloride / iron(III) chloride allow AlCl ₃ / FeCl ₃	[1]
	(c)	(i)	orange / red precipitate	[1]
		(ii)	(1) $-COCH_3$ groups in any positions	
			It must contain a C=O group but it is not an aldehyde as it does not react wit Tollens' reagent (1)	th [2]

(d)	(i)	(Alkaline) potassium manganate(VII) (solution)	allow $KMnO_4 / MnO_4^-$	[1]
	(ii)	Dilute acid allow HCl / H^+		[1]
	(iii)	•	ium tetrahydridoaluminate(III) / lithium aluminium hydride allow LiAlH4	
	(iv)	CH ₂ Br		[1]

(e) Only the infrared spectrum of benzoic acid would have a peak at $1650-1750 \text{ cm}^{-1}(1)$ This is due to the carbonyl group present in the benzoic acid (1) [2]

Total [12]

Q.2 (a)



[1]

(b)	(i)	Acidified potassium dichromate $allow H^+, Cr_2O_7^{2-}$	[1]		
	(ii)	I An equimolar mixture of two enantiomers / optical isomers do not accept 'equal mixture'	[1]		
		II It has no (apparent) effect on the plane of polarised light	[1]		
(c)	(i)	But-2-enoic acid; this is because each of the carbon atoms of the double bond has two different groups / atoms allow reason based on the other isomer	[1]		
	(ii)	Any TWO from the following for (1) each reagent used / temperature / quantities / time of reaction / catalyst / solvent	[2]		
(d)	Reage Obser		[2]		
(e)	The NMR spectrum will consist of two peaks, as there are two discrete 'areas' of protons; these will be seen at between 2.0 to 2.5 (CH ₃) and between 2.5 to 3.0 (CH ₂) (1) The peak area ratio will be 3:2 for the CH ₃ and CH ₂ protons respectively (1) There will be no splitting of either signal as the protons causing these signals are not bonded directly to other carbon atoms that also have protons (1)				
	1 max if only one peak described correctly				
		<i>Legibility of text; accuracy of spelling, punctuation and grammar; y of meaning.</i>	[1]		
		Total [13]		

Q.3 (a) (i) 2 mol of ethanol gives 1 mol of ethoxyethane (1)

Moles of ethanol = $\frac{69}{46}$ = 1.5

- \therefore Moles of ethoxyethane if theoretical yield = 0.75
- \therefore Moles of ethoxyethane if 45% yield = $0.75 \times 0.45 = 0.34$ (1)

Mass of ethoxyethane = $0.34 \times 74 = 25g$ (1) allow error carried forward [3]

(ii) Ethene /
$$C_2H_4$$
 [1]

(iii)
$$\begin{array}{c} H & H \\ H - C & C - Br \\ H & H \\ \hline & & & \\ 1 & H \\ \hline & & & \\ 1 & H \\ \hline & & & \\ 1$$

(c) Iron(III) chloride solution / $FeCl_3$ (1) Reagent

> Observation Purple coloration / solution (1) [2]

(d) (i)
$$C_{10}H_{12}O_1$$
 [1]

(ii)
$$\begin{array}{c} H & H \\ i & I \\ CH_3 - C - C - C \\ I & I \\ H & Br \end{array} \xrightarrow{OH} OH CH_3 - C - C - C - OH \\ I & I \\ Br & H \end{array} \xrightarrow{OH} OH$$
[1]

(b)

(e) Displayed formula, for example

 $CH_2 - CH_2 - CH_3$ (1) HOOC

Functional group

carboxylic acid (1)

[2]

Total [15]

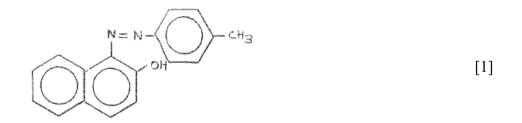
SECTION B

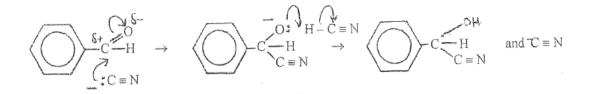
Q.4 (a) (i) (Fractional) distillation / (preparative) gas chromatography / HPLC / TLC column chromatography / solvent extraction [1] the fragmentation pattern would be different / valid examples given [1] (ii) (iii) Ι Η CH₂-N-C + HCl $CH_2NH_2 + CH_3C$ [1] II Heated electrically / by a naked flame with a water bath (1) Add compound \mathbf{G} to the ethanol until the hot ethanol will (just) not dissolve any more solute (1) Filter hot (1) Allow to cool (1)Filter (1) Dry in air / window sill / < 60 °C in an oven (1) [5] Maximum 4 out of 5 total if second marking point not given Note 5 marks maximum here QWC Information organised clearly and coherently, using specialist

QWC Information organised clearly and coherently, using specialist vocabulary where appropriate [1]

(iv) I The amine is reacted with sodium nitrite / HCl(aq) or nitrous acid (1) at a temperature of < 10 °C (1) [2]

Π





Accept a mechanism that shows HCN polarisation and nucleophilic addition as a concerted process

polarisation / charges shown (1) curly arrows on first structure (1) regeneration of $^{-}C \equiv N$ or capture of H⁺ and curly arrow (1) [4]

(ii) Chromophores (1)The colour will be black (1) as the compound absorbs blue / other colours (1)

[3]



Total [20]

Q.5 (a) C 71.3 H 9.6 \therefore O 19.1 (1) \div by A_r $\frac{71.3}{12} = 5.94$ $\frac{9.6}{1.0} = 9.6$ $\frac{19.1}{16} = 1.193$

÷ smallest
$$5.94 = 5$$
 $9.6 = 8$ $1.193 = 1$ (1)
1.193 1.193

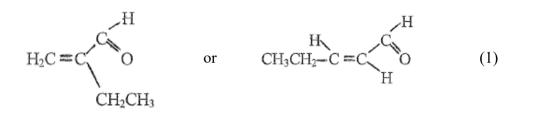
Only one oxygen atom per molecule

 \therefore Molecular formula is C₅H₈O (1)

Silver mirror produced $\therefore -C_0^H$ present (1)

Ion m/z 29 suggests ethyl group present / CH_3CH_2 (1)

Structure must be



[6]

[3]

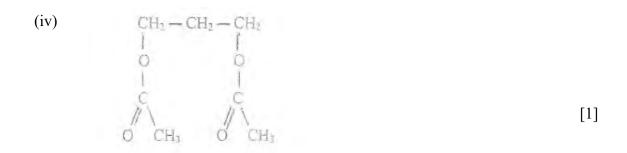
(b) (i)
$$C_{11}H_{24} \longrightarrow C_6H_{14} + C_2H_4 + C_3H_6$$
 [1]

(ii) Total peak areas
$$26 + 13 + 46 = 85$$

% propene =
$$\frac{13 \times 100}{85}$$
 = 15.(3) [1]

(iii) Any THREE points for (1) each

e.g. can it run at a lower temperature (reducing energy costs) is the yield comparable / better than the yield from the propene process is the time taken comparable / better than used in the propene process is there a continued availability of starting materials can the product be easily / better separated from the reaction mixture is relatively more expensive equipment needed is it a batch or continuous process



(c)

(i)

$$-\overset{\circ}{\mathbb{C}} \underbrace{\bigcirc}_{-\mathbb{C}} \overset{\circ}{=} \underbrace{\bigcirc}_{-(\mathbb{C}H_2)_3 - \mathbb{O} - \mathbb{C}} \overset{\circ}{=} \underbrace{\bigcirc}_{-\mathbb{C}} \overset{\circ}{=} \underbrace{\bigcirc}_{-(\mathbb{C}H_2)_3 - \mathbb{O} - \mathbb{C}} \overset{\circ}{=} \underbrace{\bigcirc}_{-(\mathbb{C}H_2)_3 - \mathbb{O} - \mathbb{C}} \overset{\circ}{=} \underbrace{\bigcirc}_{-(\mathbb{C}H_2)_3 - \mathbb{O} - \mathbb{C}} \overset{\circ}{=} \underbrace{\bigcirc}_{-\mathbb{C}} \overset{\circ}{=} \underbrace{\frown}_{-\mathbb{C}} \overset{\circ}{=} \underbrace{\bigcirc}_{-\mathbb{C}} \overset{\circ}{=} \underbrace{\bigcirc}_{-\mathbb{C}} \overset{\circ}{=} \underbrace{\bigcirc}_{-\mathbb{C}} \overset{\circ}{=} \underbrace{\bigcirc}_{-\mathbb{C}} \overset{\circ}{=} \underbrace{\bigcirc}_{-\mathbb{C}} \overset{\circ}{=} \underbrace{\odot}_{-\mathbb{C}} \overset{\bullet$$

(ii) The production of PTT is an example of condensation polymerisation (1)
 The production of poly(propene) is an example of addition polymerisation (1)
 Condensation polymerisation needs bifunctional compounds / COOH,OH etc (1)

Addition polymerisation needs a $\supset C = C \subset C$ present in the monome	r	(1)
Addition polymerisation has an atom economy of 100% Condensation polymerisation has an atom economy of $< 100\%$	(1)	
(as a co-product is formed)	(1)	[6]

QWC Selection of a form and style of writing appropriate to purpose and to complexity of subject matter [1]

Total [20]

PMT