

GCE

Chemistry A

Unit F324: Rings, Polymers and Analysis

Advanced GCE

Mark Scheme for June 2016

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All examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

Mark schemes should be read in conjunction with the published question papers and the report on the examination.

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Abbreviations, annotations and conventions

Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
()	Words which are not essential to gain credit
_	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

Q	uesti	ion	Answer	Mark	Guidance
1	(a)		Stearic acid/octadecanoic acid AND Saturated (fat)	1	ALLOW stearic acid AND no C=C double bonds IGNORE comments about LDL and cholesterol DO NOT ALLOW stearic acid is a trans fatty acid
	(b)		$C_{17}H_{35}COOH + NaOH \rightarrow C_{17}H_{35}COO^-Na^+ + H_2O$	1	ALLOW C ₁₇ H ₃₅ COONa IGNORE state symbols
	(c)		At least one ester link fully displayed in a triglyceride structure O C O C O	2	$H = C - O$ $H = C - O$ $C = C_{17}H_{35}$ $H = C - O$ $C = C_{17}H_{35}$ $C = C_{17}H_{35}$ $C = C_{17}H_{35}$ $C = C_{17}H_{35}$
			Correct triglyceride structure ✓		ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above for the rest of the structure
	(d)	(i)	M1 Correct structure of a mono unsaturated fatty acid with 18 C	2	Must be skeletal formula for M1
			M2 Correct position of double bond (12) in a mono unsaturated fatty acid AND trans arrangement ✓		DO NOT ALLOW cis isomer for M2

C	Question		Answer	Mark	Guidance			
		(ii)	Each carbon atom <u>in the double bond</u> is attached to (two) different group s /atoms ✓	1	ALLOW Each carbon atom of the double bond is attached to a H atom DO NOT ALLOW functional group for group DO NOT ALLOW the carbon atoms are attached to different groups IGNORE two of the substituent groups are the same			
			Total	7				

Q	uestio	n	Answer	Mark	Guidance
2	(a)	(i)	$H_2N(CH_2)_6NH_2$	2	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous
			HOOC(CH ₂) ₄ COOH		ALLOW acid chloride, CIOC(CH ₂) ₄ COCI
		(ii)	Type of condensation polymer Polyamide AND	1	Both answers required for one mark ALLOW nylon IGNORE numbers IGNORE polypeptide DO NOT ALLOW kevlar
			Use of condensation polymer Fibres in clothing ✓		ALLOW any common use for nylon e.g. fibre, clothing, rope, fishing net, bristles, brushes, bags, cable ties etc. DO NOT ALLOW distinctive uses associated with kevlar or other polymers e.g. bullet-proof vests, crash helmets, bottles, cups IGNORE plastic
	(b)	(i)	Ethanoic anhydride OOO H3CCOCCH3	2	ALLOW skeletal formula
			Other organic compound CH ₃ COOH		ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous IGNORE names

Question	Answer	Mark	Guidance
(ii)	FIRST CHECK THE ANSWER ON THE ANSWER LINE IF answer = 2.66 (g) award 3 marks IF answer = 4.36 (g) award 2 marks (% yield not used) IF answer = 7.14 (g) award 2 marks (% yield used	3	ANNOTATE WITH TICKS AND CROSSES ETC.
	incorrectly) $n(phenylamine) (= 3.00/93.0) = 0.0323 \text{ mol}$		ALLOW 3 SF: 0.0323 up to calculator value of 0.032258064 correctly rounded
	$n(compound A) = (0.0323 \times 0.61) = 0.0197 mol$		ALLOW 3 SF up to calculator value
	Mr (compound A) = 135 AND		Penalise rounding to 2 SF once ALLOW ECF on incorrectly rounded values
	Mass of compound A = (135)(0.0197) = 2.66 g		Final answer must be expressed to 3 significant figures
	OR		ALLOW ecf from incorrect Mr
	n(phenylamine) (= 3.00/93.0) = 0.0323 mol		
	Mr (compound A) = 135 AND		
	Theoretical mass of compound A = (0.0323 x 135) = 4.36		
	Actual mass of compound A = (4.36 x 0.61) = 2.66 g		IF answer = 2.65 (g) award 2 marks unless this alternative method is used (3 marks) 93 g gives 135 g
			3.00 g gives 135/93 x 3.00 = 4.35 g 4.35 x 0.61 = 2.65 g

Question	Answer	Mark	Guidance
(iii)	M1 $H_2SO_4 + HNO_3 \rightarrow HSO_4^- + H_2O + NO_2^+$ ✓	5	ANNOTATE WITH TICKS AND CROSSES ETC. Equation to show formation of the electrophile ALLOW $2H_2SO_4 + HNO_3 \rightarrow 2HSO_4^- + H_3O^+ + NO_2^+$ ALLOW $H_2SO_4 + HNO_3 \rightarrow HSO_4^- + H_2NO_3^+$ AND $H_2NO_3^+ \rightarrow H_2O + NO_2^+$
	M2 curly arrow from π ring OR from within the ring to ${}^{\dagger}NO_2$		AND 112NO3 7112O + 1NO2
	NHCOCH ₃ H NO ₂ NO ₂ H NO ₂ NO ₂ NO ₃ NHCOCH ₃		Penalise missing or incorrect –NHCOCH ₃ on intermediate only (M3)
	M3 correct intermediate (with charge) ✓ M4 curly arrow from C-H to reform ring AND correct products ✓		DO NOT ALLOW intermediate with the π-system covering less than half the ring
			ALLOW + charge anywhere inside the 'horseshoe' Horseshoe must have open end towards NO ₂ ALLOW Kekulé mechanism

Qı	estio	n	Answer	Mark	Guidance
					NHCOCH ₃ NHCOCH ₃ NHCOCH ₃
					OR NHCOCH3 NHCOCH3 NO2
			M5 Regeneration of the catalyst: H ⁺ + HSO ₄ ⁻ → H ₂ SO ₄		ALLOW $H_3O^+ + HSO_4^- \rightarrow H_2SO_4 + H_2O$
		(c)	reagents for step 1 Nitrous acid/HNO ₂ (and HCI)	4	ALLOW NaNO ₂ + HCI
			conditions for step 1 ≤10 °C		IGNORE reference to concentration
			compound C		ALLOW –OH ionised as –O
			HO'		ALLOW KOH(aq)/NaOH(aq)/OH-(aq)

Question	Answer	Mark	Guidance
	conditions for step 2 alkaline/alkali ✓		ALLOW dilute NaOH or stated concentration IGNORE NaOH/KOH (must be aqueous) If temperature stated must be below 10°C DO NOT ALLOW heat/boil/warm
	Total	17	

Qı	uestio	n	Answer	Mark	Guidance
3	(a)		O H − O H .	2	
			Curly arrow from OH^- to $C(\delta+)$ Dipole correct AND curly arrow from C=O bond to $O(\delta-)$		First curly arrow must come from either a lone pair on O or negative charge on O
	(b)		Measure distance moved by spot / distance moved by solvent Compare (R _f) value with data book values/known values	2	ALLOW attempt at calculation of R _f value using distances measured on the chromatogram IGNORE explanation of how chromatography works
			Two amino acids have the same/similar R _f value OR similar adsorption OR move the same/similar distance	1	ALLOW One spot contains two amino acids ALLOW Two amino acids have not separated IGNORE relative solubility ALLOW two of the amino acids have similar structures
	(c)	(i)	The pH at which the amino acid exists as a <u>zwitterion</u>	1	DO NOT ALLOW PH/ph ALLOW zwitter ion
			Context		

(iii) M1 structure $\begin{array}{c ccccccccccccccccccccccccccccccccccc$	——COO	1	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous Two COO groups are required in the structure ALLOW -COO Na+ OR -COONa
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	00 ⁻		ALLOW delocalised carboxylate ALLOW ONA OR
и о и		2	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous ALLOW tripeptide with the 3 amino acids in any order ALLOW cyclic tripeptide
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0 11	9	Isoleucine has two chiral centres, aspartic acid has one chiral centre and glycine has none. ALL three correct for one mark ALLOW chiral centres correctly identified if the three amino acids are part of a polypeptide chain

Q	uestio	n	Answer	Mark	Guidance
4	(a)		2(-)hydroxypropanoic acid	1	DO NOT ALLOW 2-hydroxylpropanoic acid IGNORE other dashes, commas and spaces
	(b)		Lactic acid synthesised in the laboratory will contain optical isomers/two optical isomers OR Lactic acid produced by bacteria will be present as one optical isomer	1	ALLOW enantiomer for optical isomer ALLOW racemic mixture IGNORE stereoisomer
	(c)		$\begin{array}{c} H \\ C \\ C \\ C \\ O \\ C \\ H \end{array}$	1	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous
	(d)	(i)	H O	1	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous DO NOT ALLOW more than one repeat unit DO NOT ALLOW if structure has no end bonds IGNORE brackets unless they are used to pick out the repeat unit from a polymer chain IGNORE n

Question	Answer	Mark	Guidance
(ii)	(Ester links in PLA are) hydrolysed	3	ANNOTATE WITH TICKS AND CROSSES ETC. ALLOW (ester) hydrolysis/(ester) hydrolyses
	Any two from:		IGNORE acid/alkaline (hydrolysis)
	 Ester (links in the polymer) OR (PLA is a) polyester 		
	Monomer/lactic acid/product (is soluble because it) forms hydrogen bonds to water		IGNORE PLA forms hydrogen bonds to water
	polymer is photodegradable		IGNORE biodegradable
	the C=O bond absorbs radiation/uv/light		IGNORE infrared radiation
			Maximum of 2 marks if hydrolysed/hydrolysis/hydrolyses does not appear in the answer ALLOW (ester) hydrolyzed
	Total	7	

Qı	Question		Answer			Mark	Guidance
5	(a)	(a) (i) ¹ H NMR spectrum for 2-aminopropan-1-ol		opan-1-ol	3	One mark for each correct row ALLOW δ values as a range or a value within the specified	
			Chemical shift,	Relative peak	Splitting		range.
			δ/ppm	area	pattern		ALLOW δ values +/- 0.2 ppm.
			0.8 – 2.0	3	doublet		ALLOW a response that implies a splitting into two for a
			2.3 – 3.0	1	multiplet		doublet etc.
			3.3 – 4.2	2	doublet		ALLOW sextet/hextet/six (or more than 5) as alternative to
							multiplet
		/** \			$\checkmark\checkmark\checkmark$		Relative peak area = CH ₃ /3H etc. penalise once
		(ii)				2	ALLOW correct structural OR displayed OR skeletal
			M ⁺ pook at 75 (pook 1)				formulae OR a combination of above as long as unambiguous
			M ⁺ peak at 75 (peak 1) CH ₃ CH(NH ₂)CH ₂ OH ⁺ /C ₃ H	∘NO ⁺			dilambiguous
				gitO	✓		
			Fragment peak at 44 (pea	k 2)			Positive charge is essential but ALLOW maximum of one
			$CH_3CH(NH_2)^+/C_2H_6N^+$				mark if both formulae are correct AND neither species has
					✓		a positive charge
5	(b)	(i)	Ethanolic ammonia			1	ALLOW ammonia in a sealed tube
			OR ammonia/NH ₃ AND et	thanol	✓		ALLOW dilute ethanolic ammonia/NH ₃
					v		IGNORE heat
							ALLOW alcohol for ethanol DO NOT ALLOW any reference to water or hydroxide ions
		(ii)	(compound D)			1	ALLOW correct structural OR displayed OR skeletal
		(11)		CII		'	formulae OR a combination of above as long as
				$_{\parallel}^{\mathrm{CH}_{3}}$			unambiguous
			***				g.c.ac
			Н	C—CH ₂ OH			
			Ì	N H			
			H_3C —	CH ₂ OH			
]	H	✓		

Question	Answer	Mark	Guidance
(c) (i)	Alcohol AND Amide/peptide	1	IGNORE phenol IGNORE hydroxyl/hydroxy IGNORE attempts to classify alcohol or amide as primary, secondary or tertiary DO NOT ALLOW hydroxide
(ii)	ОН	2	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above ALLOW correct structural OR displayed OR skeletal
	NH3*		formulae OR combination of above as long as unambiguous
	√		ALLOW + on N or H i.e. ⁺ NH ₃ or NH ₃ ⁺ ALLOW NH ₃ ⁺ Cl ⁻
	Total	10	

Qı	uestion	Answer	Mark	Guidance
6	(a)	<u>Equation</u>	2	ALLOW LiAlH ₄ / lithium tetrahydridoaluminate(III)/lithium aluminium hydride
		CH ₃ (CH ₂) ₃ CHO + 2[H] → CH ₃ (CH ₂) ₃ CH ₂ OH		ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above ALLOW $C_4H_9CHO + 2[H] \rightarrow C_5H_{11}OH$ ALLOW molecular formulae: $C_5H_{10}O + 2[H] \rightarrow C_5H_{12}O$ DO NOT ALLOW —COH for aldehyde
	(b)		7	ANNOTATE WITH TICKS AND CROSSES ETC.
				ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous
				IGNORE names if structures are given
		M1 Compound F structure is a secondary alcohol with the formula $C_5H_{11}OH$		ALLOW 3-methylbutan-2-ol if structure not given
		M2 Compound $\mathbf{F} = CH_3CH(OH)CH(CH_3)CH_3$	/	ALLOW ECF from an incorrect secondary alcohol for M3 e.g. pentan-2-ol → pentan-2-one e.g. pentan-3-ol → pentan-3-one
		M3 Compound G = CH ₃ COCH(CH ₃)CH ₃		ALLOW (3-)methylbutanone if structure not given IGNORE any discussion of the reactions of compound G with 2,4-dinitrophenylhydrazine and/or Tollens' reagent.
				ALLOW 3 SF up to calculator value correctly rounded

Question	Answer	Mark	Guidance
	M4 n(NaOH) = (0.125 x 22.8/1000) = 0.00285 (mol) M5 M(compound H) = (0.211/0.00285 =) 74(.0) (g mol ⁻¹) M6 Compound H = / CH ₃ CH ₂ COOH		IF M(compound H) = 74 award 2 marks (M4 + M5) ALLOW ECF from incorrect calculation of amount of NaOH ALLOW propanoic acid if structure not given
	M7 Compound $I =$ $H \longrightarrow C \longrightarrow $		ALLOW ECF from incorrect compound F (alcohol) and/or incorrect compound H (carboxylic acid) to form compound I (ester). Compounds F, G, H and I must be placed in the correct box or correctly labelled for M2. M3, M6 and M7
(c)	The structural isomer is: $ \begin{array}{c} CH_3 \\ H_3C -\!$	1	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous ALLOW 2,2-dimethylpropan-1-ol
	Total	10	

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