OCR
RECOGNISING ACHIEVEMENT

GCE

Chemistry A

Advanced GCE

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

Mark Scheme for June 2011

Oxford Cambridge and RSA Examinations

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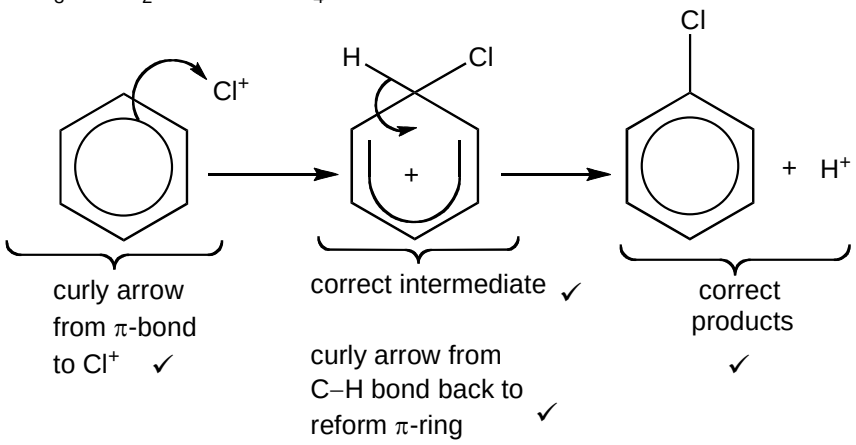
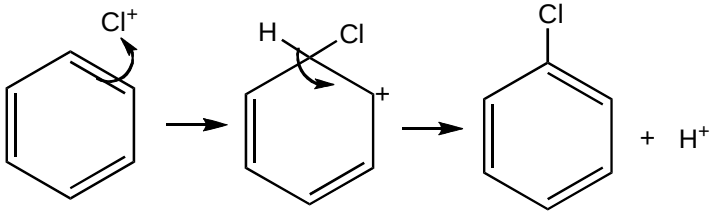
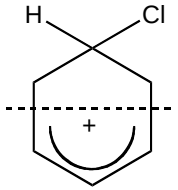
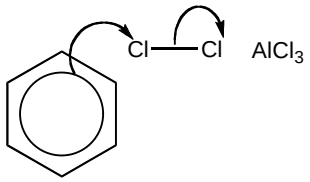
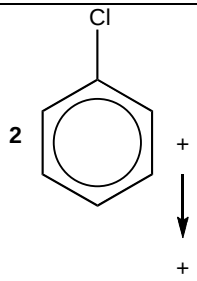
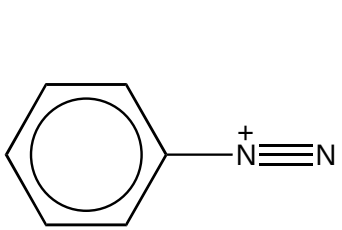
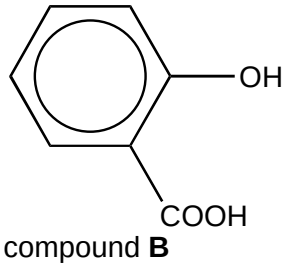
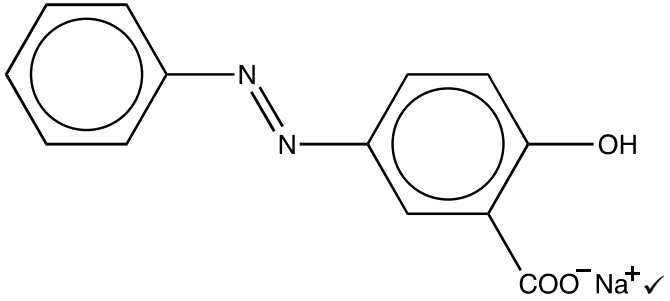
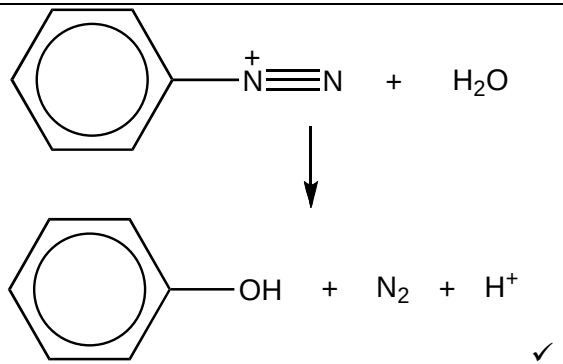
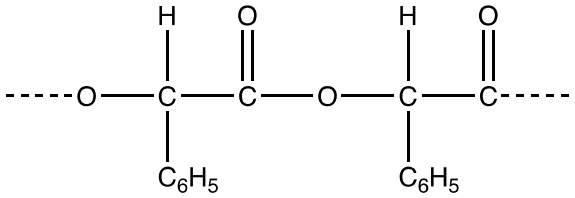
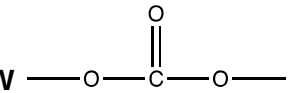
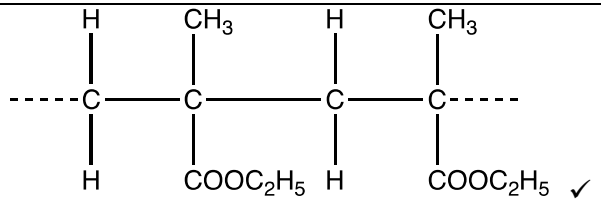
ALLOW Kekulé structures throughout

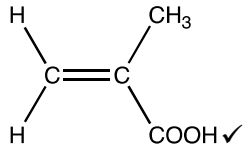
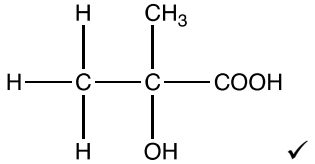
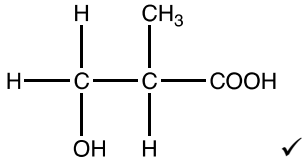
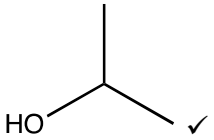
Question	Answer	Mark	Guidance
1 (a)	$AlCl_3 + Cl_2 \longrightarrow AlCl_4^- + Cl^+$ ✓  curly arrow from π-bond to Cl^+ ✓ correct intermediate ✓ curly arrow from C–H bond back to reform π-ring ✓ correct products ✓ $H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl$ ✓ **Note**: 1st curly arrow should start within the ring or on the ring --- **Note: ALLOW** mechanism using Kekulé structures:  	6	***ANNOTATIONS MUST BE USED*** **DO NOT ALLOW** the following intermediate:  π-ring must be more than 1/2 way up **AND** 'horseshoe' the right way up, *ie* gap towards C with Cl **ALLOW** + sign anywhere inside the 'hexagon' of intermediate **ALLOW** 1st curly arrow starting within the hexagon **ALLOW** mechanism with Cl–Cl----$AlCl_3$ for 1st 2 marks, ie  Second curly arrow to either –Cl or $AlCl_3$ **Note**: If Br^+ is used, **DO NOT ALLOW** 1st mechanism mark but all other marks available by **ECF**

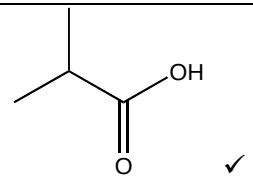
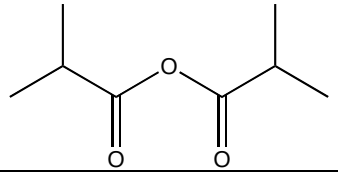
Question			Answer	Mark	Guidance
1	(b)	(i)	 **1st mark**: reactants, correctly balanced, ✓ *ie* **2** C_6H_5Cl + Cl_3CCHO **2nd mark**: product, (correctly balanced) ✓ *ie* H_2O	**2**	**Each mark is independent of the other** **ALLOW** C_6H_5Cl for chlorobenzene **ALLOW** any unambiguous structure for Cl_3CCHO, e.g. CCl_3CHO **BUT** ….. **DO NOT ALLOW** CCl_3COH **Standalone mark** **Standalone mark**
		(ii)	6 ✓	**1**	
	(c)		substitution/nitration/NO_2 at different positions (on the ring) **OR** forms different isomers **OR** multiple substitution/nitration ✓	**1**	**ALLOW** examples, e.g. 1-chloro-2-nitrobenzene and 1-chloro-2-nitrobenzene **ALLOW** 'it' for nitro group **ALLOW** examples, e.g. 1-chloro-2,3-dinitrobenzene **IGNORE** nitrate/NO_3
	(d)		In phenol, (lone) pair of electrons on O is (partially) **delocalised** into the ring ✓ **QWC**: delocalised/delocalized/delocalise, etc must be spelt correctly in the correct context for benzene **OR** phenol at least once electron density increases/is high ✓ **ORA** Cl_2/electrophile is (more) polarised ✓ **ORA**	**3**	***ANNOTATIONS MUST BE USED*** **ALLOW** diagram to show movement of lone pair into ring but **delocalised** ring must be mentioned **ALLOW** lone pair of electrons on O is (partially) drawn/ attracted/pulled into **delocalised** ring **IGNORE** 'activates the ring' **DO NOT ALLOW** charge density or electronegativity **ALLOW** Cl_2 is (more) attracted **OR** Cl_2 is not polarised by benzene **OR** induces dipoles (in chlorine/electrophile)
			Total	**13**	

Question			Answer	Mark	Guidance
2	(a)	(i)	donates a lone pair (on N) **OR** accepts a proton/H^+ ✓	1	**IGNORE** 'forms a dative covalent bond' (no direction of lone pair) **ALLOW** 'forms a dative covalent bond with/to **H^+**' **ALLOW** mark for N:→H^+ (can be from correct equation)
		(ii)	$(C_2H_5NH_3^+)_2SO_4^{2-}$ ✓ $C_2H_5NH_3^+$ CH_3COO^- ✓	2	**ALLOW** $(C_2H_5NH_3)_2$ SO_4 **DO NOT ALLOW** $(C_2H_5NH_3)$ HSO_4 **OR** $(C_2H_5NH_3^+)$ HSO_4^- *brackets not required* **ALLOW** $(C_2H_5NH_3)$ (CH_3COO) **OR** $(C_2H_5NH_3^+)$ (CH_3COO^-) *brackets not required* **ALLOW** separate ions with or without a '+' sign between them, e.g. $C_2H_5NH_3^+$ + CH_3COO^-
	(b)	(i)	 diazonium ion ✓  compound **B** ✓	2	In diazonium ion, **IGNORE** Cl^- **ALLOW** '+' sign up to halfway along triple bond from left-hand N In compound **B**, **ALLOW** –OH ionised as $–O^-$ **ALLOW** –COOH ionised as COO^-
		(ii)	conditions = alkaline /OH^- **AND** use = dye/pigment/colouring ✓	1	**BOTH** responses required for one mark **ALLOW** named alkali, e.g. NaOH/KOH **ALLOW** base **IGNORE** references to temperature **ALLOW** use = indicator

Question			Answer	Mark	Guidance
2	(b)	(iii)	Organic product:  ✓ Other products: CO_2 **AND** H_2O ✓	**2**	**IGNORE** phenoxide: O^- **OR** O^-Na^+ **ALLOW** COO^- **OR** COONa **ALLOW** H_2CO_3 **Note**: must be formulae and not names (in question)
	(c)		 ✓	**1**	**ALLOW** N_2^+ on structural formula **ALLOW** $C_6H_5N_2^+ + H_2O \rightarrow C_6H_5OH + N_2 + H^+$ **ALLOW** $C_6H_5N_2Cl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$ If + charge shown, **IGNORE** its position
			Total	**9**	

Question			Answer	Mark	Guidance
3	(a)		**monomers** join/bond/add/react/form polymer/form chain **AND** another product/small molecule e.g. H_2O/HCl ✓ **QWC** must spell **AND** use 'monomer(s)' correctly throughout	1	**IGNORE** 'two' when referring to monomers, ie (two) monomers ……..
	(b)	(i)	 ester link ✓ **Note**: Any ester link shown **must** be correct rest of the structure ✓	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous) **ALLOW** benzene ring for C_6H_5 'End bonds' **MUST** be shown (do not have to be dotted) **ALLOW one** or more repeat units but has to have a whole number of repeat units (*ie* does not have to be two) For ester, **DO NOT ALLOW**  **ALLOW** structure with no O at left end and COO at right end **IGNORE** brackets **IGNORE** *n*
		(ii)	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous) **ALLOW one** or more repeat units but has to have a whole number of repeat units (*ie* does not have to be two) 'End bonds' **MUST** be shown (do not have to be dotted) **IGNORE** brackets **IGNORE** *n*

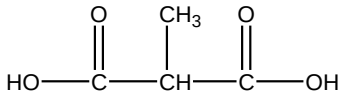
Question			Answer	Mark	Guidance
3	(c)		compound **C**  ✓ compound **D** and compound **E**  ✓  ✓	**3**	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous) **ALLOW** $CH_2C(CH_3)COOH$ **ALLOW D** and **E** by **ECF** from an incorrect structure of **C** provided that **C** contains a double bond and molecular formulae of **D** and **E** is $C_4H_8O_3$ with H_2O added across double bond
	(d)	(i)	 ✓	**1**	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous) e.g. $(CH_3)_2CHOH$ **DO NOT ALLOW** –HO **IGNORE** working (*ie* other structures) provided correct structure of propan-2-ol is shown **IGNORE** name (even if wrong)

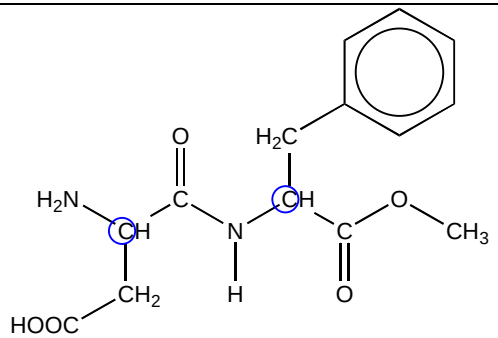
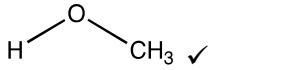
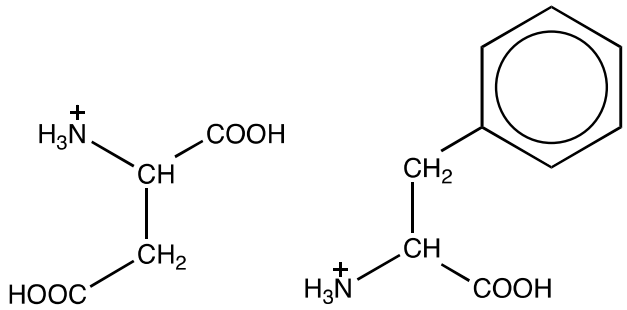
Question			Answer	Mark	Guidance
3	(d)	(ii)	 ✓ **OR** acid anhydride: 	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous) **OR** (2-)methylpropanoic acid **DO NOT ALLOW** incorrect name (will CON a correct structure) **ALLOW** acyl chloride: $(CH_3)_2CHCOCl$ **IGNORE** working provided correct structure of propan-2-ol is shown
		(iii)	Hydrogen bonds form **with** water ✓ **Note**: Can be shown in diagram as dashed line, *ie* ---- (no label required) **DO NOT CON** 'hydrogen bond' from an incorrect hydrogen bond in diagram Mandelic acid forms more hydrogen bonds (with water) ✓ **ORA** Mandelic acid has an extra OH **OR** 2 OH groups **OR** has a COOH group ✓ **ORA**	3	***ANNOTATIONS MUST BE USED*** **ALLOW** a diagram showing hydrogen bonds with water, dipole and lone pair are not required **ALLOW** a hydrogen bond to C=O, ie C=O---H–O **IGNORE** bond angles Diagram does **not** need to show all of mandelic acid (**IGNORE** if wrong) **ALLOW** any comparison of numbers of hydrogen bonds provided that mandelic acid has more hydrogen bonds **DO NOT ALLOW** 'No –OH groups in ester (as there are)' **DO NOT ALLOW** reference to $–OH^-$ / hydroxide **IGNORE** reference to carbon chain and van der Waals' forces **Note**: If a response compares **Ester 1** with **Ester 2** rather than with mandelic acid, maximum of 2 marks: **1st mark** hydrogen bonds **2nd mark** **Ester 2** has more Os/oxygens **OR** **Ester 2** forms more hydrogen bonds

Question			Answer	Mark	Guidance
3	(d)	(iv)	To test for (adverse) side effects **OR** to test toxicity **OR** to test for irritation ✓	1	**ALLOW** a stated adverse side effect, *eg* allergy, carcinogenic, etc **IGNORE** references to optical isomers, chirality, etc **IGNORE** vague statements such as harmful to skin, dangerous to skin, corrosive to skin, reacts with skin **ALLOW** company liable to litigation/damages
			Total	13	

Question			Answer	Mark	Guidance
4					***ANNOTATIONS MUST BE USED*** Throughout question, **ALLOW** correct structural **OR** displayed **OR** skeletal formula **DO NOT ALLOW** molecular formulae
			Equations		
			$CH_3COCHO + 4[H] \longrightarrow CH_3CHOHCH_2OH$ ✓	**1**	**ALLOW** partial reduction (ie reduction of either C=O group) [H] implies reduction
			$CH_3COCHO + [O] \longrightarrow CH_3COCOOH$ ✓	**1**	[O] implies oxidation
			Reduction reagents and observation		
			Methylglyoxal is **reduced** by $NaBH_4$ ✓	**1**	reduced **AND** reagent are **both** required for the mark **ALLOW** link to equation with [H] for reduction **ALLOW** $LiAlH_4$ as alternative for $NaBH_4$ **ALLOW** any recognisable attempt at name **IGNORE** any reference to acids
			Oxidation reagents and observation		
			Methylglyoxal is **oxidised** by H_2SO_4 **AND** $K_2Cr_2O_7$ ✓		oxidised **AND** reagent are **both** required for the mark **ALLOW** link to equation with [O] for oxidation **ALLOW** $Na_2Cr_2O_7$ instead of $K_2Cr_2O_7$ **ALLOW** H^+ **AND** $Cr_2O_7^{2-}$ **OR** H^+ **AND** CrO_4^{2-}
			Observation: turns green **OR** blue ✓		If name given, **ALLOW** dichromate **OR** dichromate(VI) **ALLOW** acidified dichromate **ALLOW** any strong acid If formulae used, formulae must be correct
			OR		**ALLOW** $AgNO_3$ in ammonia **OR** ammoniacal $AgNO_3$
			Methylglyoxal is **oxidised** by Tollens' reagent ✓	**2**	**ALLOW oxidised** by manganate
			Observation: Silver (mirror) ✓		Observation: decolourised **Note**: If one reaction is identified as oxidation, assume the other is reduction (and vice versa)
			Total	**5**	

Question			Answer	Mark	Guidance
5	(a)		idea of separating (the components/compounds) ✓ idea of (identifying compounds) by comparison with a (spectral) database ✓	2	**ALLOW** (identifies compounds) using fragmentation (patterns)/fragment ions (but **IGNORE** molecular ions) ✓ **Note**: Each marking point does **not** need to be linked to GC or MS (The question asks about GC–MS as a combined technique)
	(b)	(i)	54.2% of 118 **OR** 54.2/118 x 100 = 64/63.96 (hence there are 4 oxygens) ✓ 118 – 64 = 54 hence 4 carbon (48) and 6 hydrogen (6) ✓	2	**IGNORE** calculation that proves that $C_4H_6O_4$ has a molar mass of 118 (ie 12 x 4 + 6 x 1 + 16 x 4) **ALLOW** 64/118 x 100 = 54.2% for 1st mark **IGNORE** method using empirical formula **ALLOW** any reasonable working leading to 4C **Note**: 54.2(%) ÷ 16 would **not** get the 1st mark but the answer could be used to get the 2nd mark
		(ii)	carboxyl group **OR** carboxylic acid ✓ must be **name** (in question)	1	**IGNORE** working, e.g. O–H, C=O, C–O on IR spectrum

Question			Answer	Mark	Guidance
5	(c)	(i)	***Chemical shifts*** Any **two** peaks identified for **1 mark** ✓ peak at δ = 0.8 ppm due to R–C**H** / CH_3CH peak at δ = 3.4 ppm due to **H**C–C=O peak at δ = 11 ppm due to COO**H** / carboxylic acid ***Splitting*** quartet shows adjacent CH_3 **OR** 3 adjacent Hs ✓ doublet shows adjacent CH **OR** 1 adjacent H ✓ ***Identification***  ✓	1 2 1	***ANNOTATIONS MUST BE USED*** **CHECK SPECTRUM** for responses **ANNOTATE** with '^' For peak at (δ =) 0.8 (ppm), **ALLOW** doublet and vice versa For peak at (δ =) 3.4 (ppm), **ALLOW** quartet ' and vice versa For peak at (δ =) 11 (ppm), **ALLOW** singlet and vice versa **ALLOW** peak at δ = 2.4 ppm for peak at δ = 3.4 ppm **ALLOW** tolerance on δ values: ± 1 ppm For quartet, **ALLOW** quadruplet **ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous)
		(ii)	$(CD_3)_2SO$ / D / It does **not** absorb **OR** does not give a peak ✓	1	**ALLOW** $(CD_3)_2SO$ / does **not** contain H **ALLOW** undeuterated solvents would absorb **OR** give peaks **ALLOW** responses in terms of $(CH_3)_2SO$ producing peaks ……. **but IGNORE** number of peaks
		(iii)	TMS is the standard (for chemical shift measurements) ✓	1	**ALLOW** TMS is the reference **OR** TMS has δ = 0 (ppm) **OR** for calibration **IGNORE** unreactive, volatile, it gives a sharp peak
		(iv)	peak at δ = 11.0 (ppm) disappears ✓	1	**ALLOW** COOH (peak) disappears **ALLOW** OH (peak) disappears
			Total	12	

Question			Answer	Mark	Guidance
6	(a)	(i)	 ✓	1	Circles can be around C **OR** CH atoms but must **not** include other atoms **ALLOW** any suitable way of highlighting chiral carbons, e.g. asterisk, * **Note**: Mark the circles and ignore other working on diagram
		(ii)	carboxyl **OR** carboxylic acid, amine, amide, ester must be **names** 2 marks for 4 correct functional groups ✓✓ 1 mark for 3 correct functional groups ✓	2	**ALLOW** peptide for amide
	(b)		 ✓  1 mark for left-hand amino acid with NH_3^+ **OR** NH_2 ✓ 1 mark for right-hand amino acid with NH_3^+ **OR** NH_2 ✓ 1 mark for **both** amino acids shown with NH_3^+ ✓	4	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous) **ALLOW** + charge on H of NH_3 groups, ie NH_3^+ **Note**: If there are more than three structures shown, credit any correct structures and ignore incorrect structures

Question			Answer	Mark	Guidance
6	(c)		(adverse) side effects **OR** toxicity **OR** irritation ✓	1	**ALLOW** a stated adverse side effect, *eg* allergy, carcinogenic, hyperactivity etc **IGNORE** references to optical isomers, chirality, etc **IGNORE** vague statements such as harmful to body, dangerous to body **DO NOT ALLOW** obesity, corrosive to body **ALLOW** company liable to litigation/damages **Note**: Scroll down to bottom of page to check for any further writing
			Total	8	

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