OCR
RECOGNISING ACHIEVEMENT

GCE

Chemistry A

Advanced GCE

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

Mark Scheme for June 2011

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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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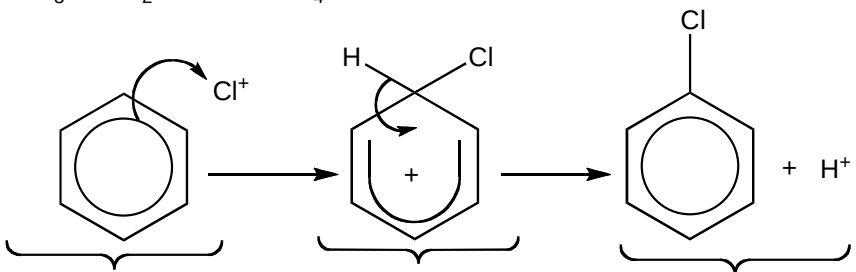
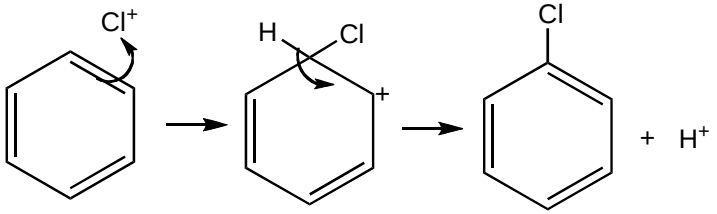
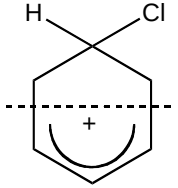
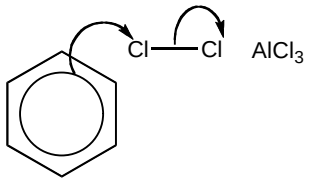
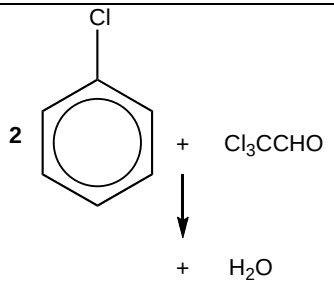
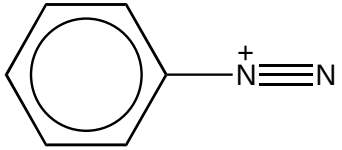
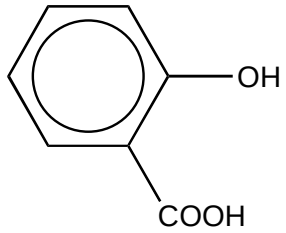
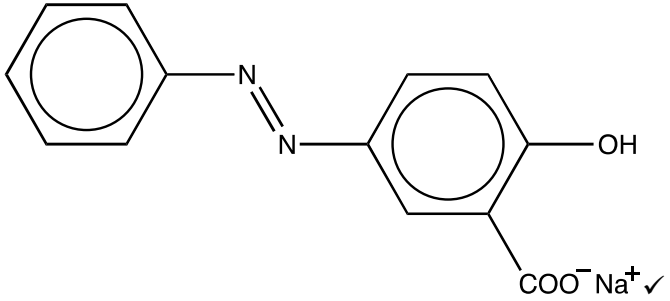
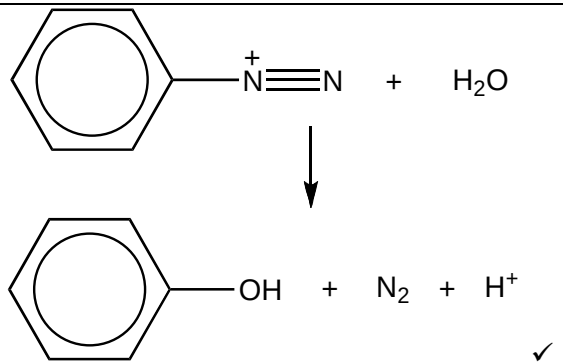
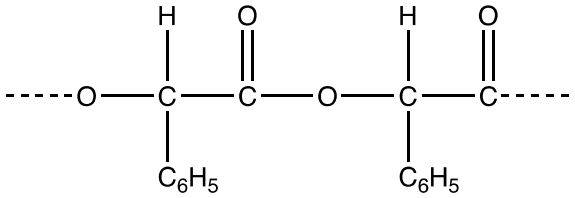
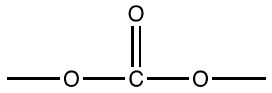
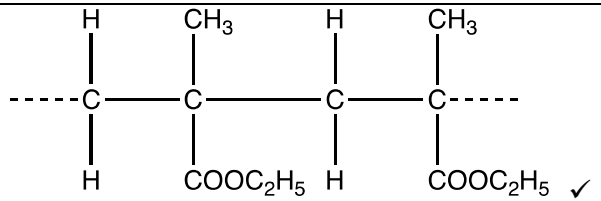
ALLOW Kekulé structures throughout

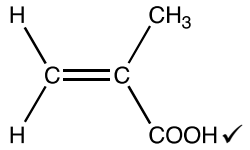
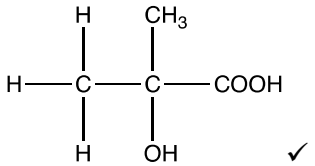
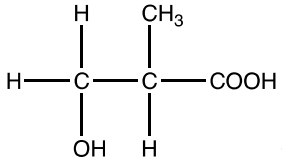
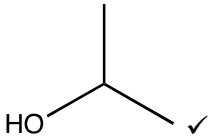
Question			Answer	Mark	Guidance
1	(a)		$AlCl_3 + Cl_2 \longrightarrow AlCl_4^- + Cl^+$ ✓  curly arrow from π-bond to Cl^+ ✓ correct intermediate ✓ curly arrow from C–H bond back to reform π-ring ✓ correct products ✓ $H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl$ ✓ **Note**: 1st curly arrow should start 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**

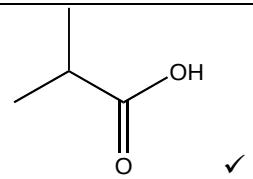
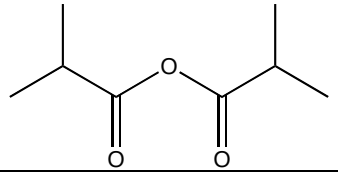
Question			Answer	Mark	Guidance
1	(b)	(i)	 **1st mark**: reactants, correctly balanced, ✓ *ie* **2** C_6H_5Cl + Cl_3CCHO **2nd mark**: product, (correctly balanced) ✓ *ie* H_2O	**2**	**Each mark is independent of the other** **ALLOW** C_6H_5Cl for chlorobenzene **ALLOW** any unambiguous structure for 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)	$(C_2H_5NH_3^+)_2SO_4^{2-}$ ✓	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*
			$C_2H_5NH_3^+$ CH_3COO^- ✓		**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*

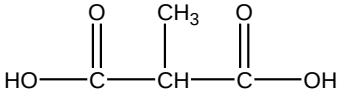
Question			Answer	Mark	Guidance
3	(c)		compound **C**  ✓ compound **D** and compound **E**  ✓  ✓	**3**	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous) **ALLOW** $CH_2C(CH_3)COOH$ **ALLOW D** and **E** by **ECF** from an incorrect 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)

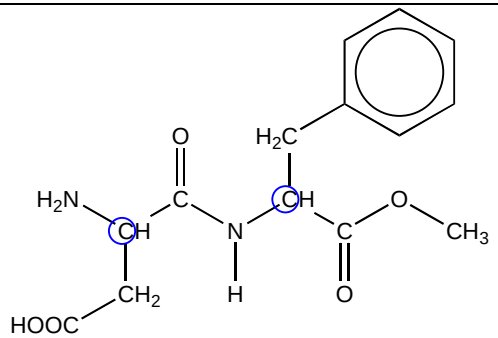
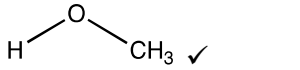
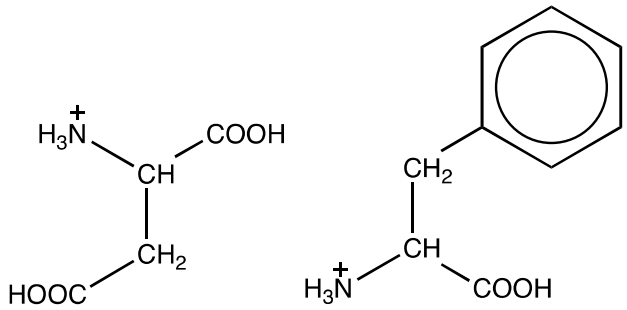
Question			Answer	Mark	Guidance
3	(d)	(ii)	 ✓ **OR** acid anhydride: 	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous) **OR** (2-)methylpropanoic acid **DO NOT ALLOW** incorrect name (will CON a correct structure) **ALLOW** acyl 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 $CH_3COCHO + 4[H] \longrightarrow CH_3CHOHCH_2OH$ ✓ $CH_3COCHO + [O] \longrightarrow CH_3COCOOH$ ✓	**1** **1**	**ALLOW** partial reduction (ie reduction of either C=O group) [H] implies reduction [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** $K_2Cr_2O_7$ ✓ Observation: turns green **OR** blue ✓		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-} If name given, **ALLOW** dichromate **OR** dichromate(VI) **ALLOW** acidified dichromate **ALLOW** any strong acid If formulae used, formulae must be correct
			OR Methylglyoxal is **oxidised** by Tollens' reagent ✓ Observation: Silver (mirror) ✓	**2**	**ALLOW** $AgNO_3$ in ammonia **OR** ammoniacal $AgNO_3$ **ALLOW oxidised** by manganate 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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