OCR
Oxford Cambridge and RSA

GCE

Chemistry A

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

Advanced GCE

Mark Scheme for June 2017

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This mark scheme is published as an aid to teachers and students, to indicate the requirements of the examination. It shows the basis on which marks were awarded by examiners. It does not indicate the details of the discussions which took place at an examiners' meeting before marking commenced.

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.

OCR will not enter into any discussion or correspondence in connection with this mark scheme.

Annotations

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

Subject-specific Marking Instructions

INTRODUCTION

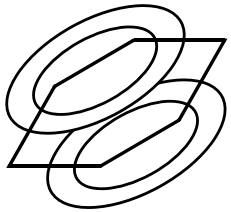
Your first task as an Examiner is to become thoroughly familiar with the material on which the examination depends. This material includes:

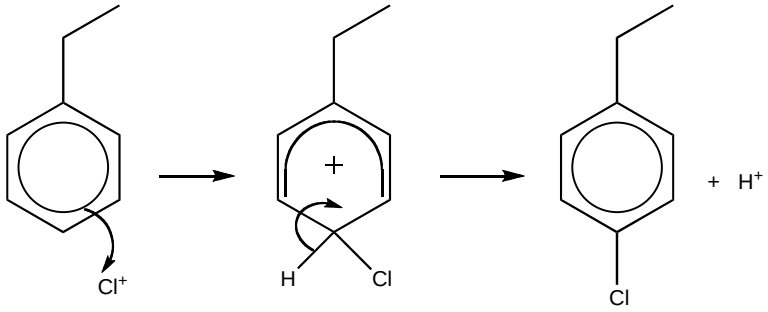
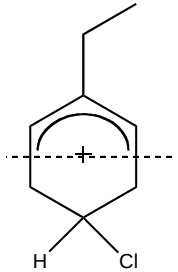
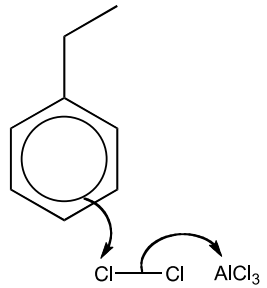
- the specification, especially the assessment objectives
- the question paper
- the mark scheme.

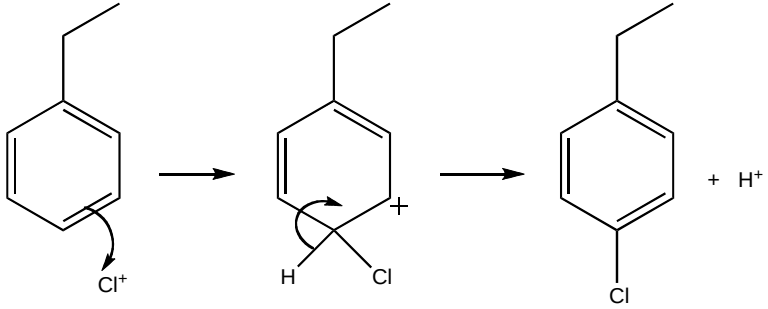
You should ensure that you have copies of these materials.

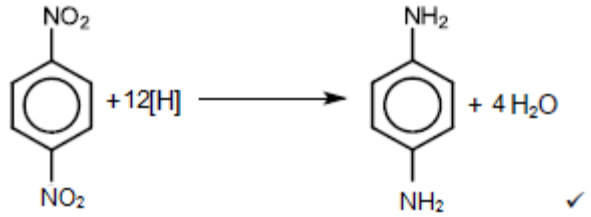
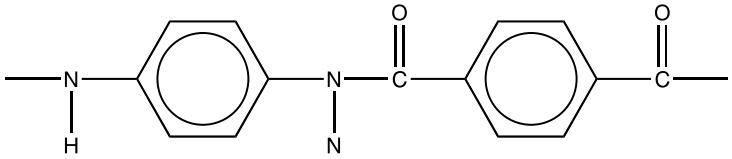
You should ensure also that you are familiar with the administrative procedures related to the marking process. These are set out in the OCR booklet **Instructions for Examiners**. If you are examining for the first time, please read carefully **Appendix 5 Introduction to Script Marking: Notes for New Examiners**.

Please ask for help or guidance whenever you need it. Your first point of contact is your Team Leader.

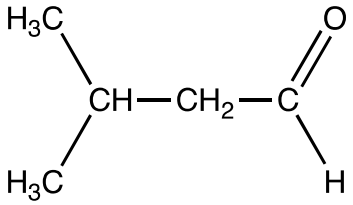
Question			Answer	Marks	AO element	Guidance
1	(a)	(i)	 ✓  ✓	2	AO1 AO1	Diagrams must show the full ring Labels not required Diagram shows correct position of localised π-bonds/π-electrons **OR** correct position of p-orbital overlap Diagram shows correct position of delocalised π-bonds/π-electrons **OR** correct position of p-orbital overlap **IGNORE** C=C in diagram **IGNORE** initial diagrams showing p-orbitals
		(ii)	**Maximum of 3 marks** **Bond lengths:** *up to 2 marks* All carbon–carbon bonds the same length ✓ Bond length intermediate/between (short) C=C and (long) C–C ✓ **Enthalpy change of hydrogenation:** *up to 2 marks* ΔH hydrogenation different from that expected ✓ ΔH less exothermic than expected (when compared to ΔH hydrogenation for cyclohexene) ✓	3	AO1 AO1 AO1	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **IGNORE** any reference to reactivity **DO NOT ALLOW** ΔH halogenation/hydration
	(b)	(i)	6 ✓	1	AO2	

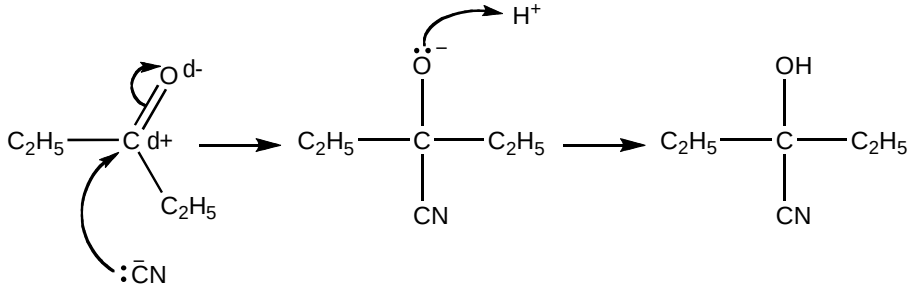
Question			Answer	Marks	AO element	Guidance
	(b)	(ii)	$AlCl_3 + Cl_2 \rightarrow AlCl_4^- + Cl^+$ ✓  Curly arrow from π bond to Cl^+ ✓ Correct intermediate ✓ Curly arrow from C–H bond back to reform ring ✓ $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$ ✓ **Note**: 1st curly arrow should start within the ring or on the ring	**5**	AO1 AO1 AO2 AO2 AO1	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **NOTE**: If Br^+ is used, **DO NOT ALLOW** 1st mechanism mark but other marks available by **ECF** **NOTE** Absence of C_2H_5 OR wrong position of C_2H_5 loses intermediate mark **DO NOT ALLOW** the following intermediate:  • π-ring must be more than halfway way down **AND** • Arc must be the right way up (i.e. gap towards C–Cl) **ALLOW** + sign anywhere within hexagon of intermediate **ALLOW** mechanism with Cl–Cl---$AlCl_3$ for 1st two marks, i.e. 

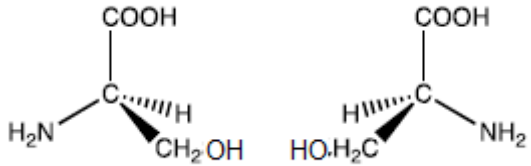
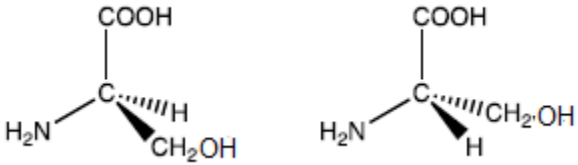
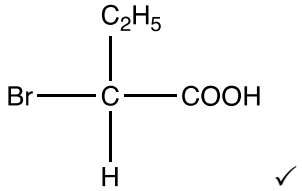
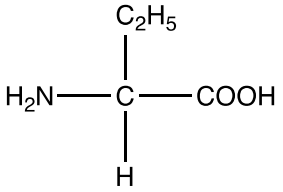
Question			Answer	Marks	AO element	Guidance
			NOTE: **ALLOW** mechanism using Kekulé structures, i.e. 			Refer alternative mechanisms to TL for discussion.
		(iii)	HNO_3 **AND** H_2SO_4 ✓	**1**	AO3	**IGNORE** temperature **IGNORE** catalyst 'concentrated' **not** required for HNO_3 or H_2SO_4 but **DO NOT ALLOW** dilute HNO_3 or dilute H_2SO_4
		(iv)	**IF answer = 61.2% award 3 marks** moles of ethylbenzene used = 2.65/106 = 0.025(0) (mol) ✓ moles of **B** formed = 2.31/151 = 0.0153 (mol) ✓ yield = 0.0153/0.0250 × 100 = 61.2% ✓	**3**	AO2 AO2 AO2	0.0250 mol is exact calculator value 0.0153 mol must be to at least 3sf (calculator value 0.015298013) The final answer must be to 3 SF (calculator value gives 61.1920529%) (rounding of moles of **B** gives 61.2% exactly) **ALLOW ECF** from incorrect M_r or moles unless the yield is > 100%
			Total	**14**		

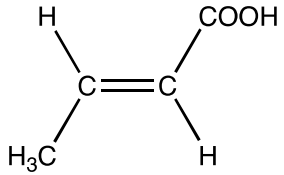
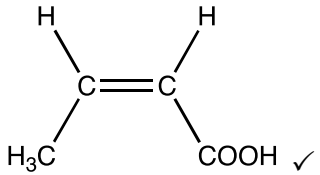
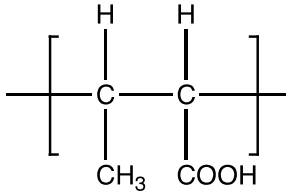
Question			Answer	Marks	AO element	Guidance
2	(a)		nitrogen electron pair **OR** nitrogen lone pair accepts a proton/H^+ ✓	1	AO1	**DO NOT ALLOW** nitrogen/N lone pair accepts hydrogen (proton/H^+ required) **ALLOW** nitrogen donates an electron pair/lone pair to H^+ **IGNORE** NH_2 group donates electron pair
	(b)	(i)	Sn **AND concentrated** HCl ✓	1	AO3	**IGNORE** temperature and reaction type/purpose of reagents
		(ii)	 ✓	1	AO2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **DO NOT ALLOW** H_2 instead of [H]
	(c)	(i)	**monomers** join/bond/add/react/form polymer/form chain **AND** form another product/small molecule/H_2O/HCl ✓	1	AO1	**IGNORE** 'two' when referring to monomers, *i.e.* (two) monomers…
		(ii)	 amide link ✓ correct structure ✓	2	AO2 AO2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **ALLOW** 'terminal' —NH— at other end 'End bonds' **MUST** be shown (solid or dotted) **IGNORE** brackets and/or *n* **ALLOW** CONH for amide link

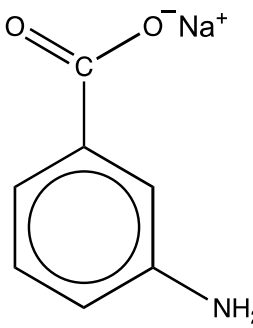
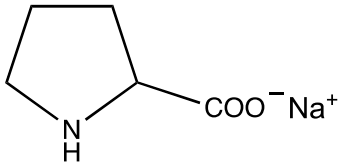
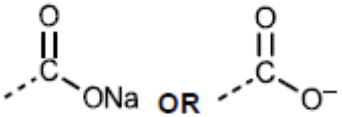
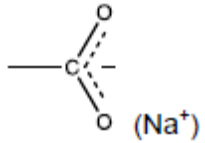
Question			Answer	Marks	AO element	Guidance
	(d)	(i)	$C_8H_{15}NO$ ✓	1	AO2	**ALLOW** any order of elements
		(ii)	$H_2N(CH_2)_6NH_2$ ✓	2	AO2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous
			$HOOC(CH_2)_8COOH$ ✓		AO2	**ALLOW** acyl chloride, $ClOC(CH_2)_8COCl$
			Total	9		

Question			Answer	Marks	AO element	Guidance
3	(a)		**M1** (^{13}C NMR spectrum indicates) four types of carbon ✓ **M2** (Tollens' test shows) compound **D** is an aldehyde ✓ **M3** Correct structure  ✓	3	AO1 AO2 AO2	**ALLOW** 4 carbon environments **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **NOTE:** Correct structure also scores **M2** *(aldehyde shown in structure)* **ALLOW** 3-methylbutanal (2 marks) **NOTE:** Ketone with four carbon environments i.e. methylbutanone (Maximum 2 marks possible: **M1** and **M3**)

Question			Answer	Marks	AO element	Guidance
	(b)		Correct structure of compound **E** (pentan-3-one) ✓ 	**4**	AO2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **IF** structure E is incorrect 3 marks can be scored for the mechanism e.g. apply **ECF** to error in structure e.g. CH_2 missing from the chain
			curly arrow from $^-$CN to C(δ+) of C=O group ✓		AO2	First curly arrow must come from either lone pair on $^-$:CN or '–' charge on $^-$CN **DO NOT ALLOW** lone pair and/or negative charge on nitrogen atom
			dipole correct **AND** curly arrow from C=O bond to O(δ–) ✓		AO1	
			Correct intermediate with negative charge on O **AND** Curly arrow from O^- to H^+ ✓		AO1	Curly arrow must come from either lone pair on O or negative charge on O **ALLOW** curly arrow from O^- to Hδ+ of H_2O Dipole on H_2O must be shown. **IGNORE** other products
			Total	**7**		

Question			Answer	Marks	AO element	Guidance
4	(a)		**M1** Mirror images around a tetrahedral carbon atom ✓  **M2** The four correct groups with correct connectivity ✓	**2**	AO1 AO2	3-D diagrams must contain 1 'out wedge' and 1 'in wedge'/dotted line **AND** 2 lines in plane of paper **ALLOW** 2 'out wedges', 1 'in wedge' and 1 line in plane of paper. **ALLOW** the same 3-D structure repeated with two groups 'swapped'. After rotation the second isomer is a mirror image of the first.  **Connectivity**: the chiral carbon must be linked to the C of the COOH **AND** the C of the CH_2OH **AND** the N of NH_2.
	(b)		**M1** Compound **F**  ✓ **M2** Compound **G**  ✓	**6**	AO2	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **IGNORE** labels for **M1**, **M2**, **M3** and **M4** **ALLOW ECF** for the following conversions: **F → G** (**F** must have correct molecular formula) **H → I** (**I** must have correct empirical formula)

Question	Answer	Marks	AO element	Guidance
	M3 Compound **H**  **OR**  ✓		AO2	C=C must be shown in **H**
	M4 Polymer **I**  ✓		AO2	**ALLOW** multiple repeat units but must be full repeat units **ALLOW** end bonds shown as ..... **DO NOT ALLOW** if structures have no end bonds **IGNORE** brackets unless they are used to pick out the repeat unit from a polymer chain **IGNORE n**
	M5 Formation of **F** is an (electrophilic) addition reaction ✓		AO1	**ALLOW** reaction with HBr is an addition reaction **DO NOT ALLOW** nucleophilic addition
	M6 Formation of **G** is a (nucleophilic) substitution reaction ✓		AO1	**ALLOW** reaction with NH_3 is a substitution reaction **DO NOT ALLOW** electrophilic substitution

Question	Answer	Marks	AO element	Guidance
(c)	 1 mark for correct structure with COOH or COO^-Na^+ ✓  1 mark for correct structure with COOH or COO^-Na^+ ✓ 1 mark for **both** structures shown with COO^- ✓	3	AO2 AO2 AO2	**For both structures,** **ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous) **Note**: If there are more than two structures shown, credit any correct structures and **IGNORE** incorrect structures **DO NOT ALLOW** –COO–Na (covalent bond) (penalise once only) **ALLOW** $–COO^-$ **ALLOW** –COONa **OR**  **ALLOW** delocalised carboxylate 
	Total	**12**		

Question			Answer	Marks	AO element	Guidance
5	(a)		**Throughout, ALLOW formulae OR correct names** --- **M1** react $(CH_3)_3CCHO$ with $H_2SO_4/K_2Cr_2O_7$ **AND** heat/reflux ✓	7	AO3	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **ALLOW** $H^+/Cr_2O_7^{2-}$ or $H_2SO_4/Na_2Cr_2O_7$ **ALLOW** acidified dichromate
			M2 Equation: $(CH_3)_3CCHO + [O] \rightarrow (CH_3)_3CCOOH$ ✓		AO2	
			M3 react $(CH_3)_3CCHO$ with $NaBH_4$ ✓		AO3	**ALLOW** $LiAlH_4$ as alternative to $NaBH_4$
			M4 Equation: $(CH_3)_3CCHO + 2[H] \rightarrow (CH_3)_3CCH_2OH$ ✓		AO2	
			M5 react $(CH_3)_3CCOOH$ with $(CH_3)_3CCH_2OH$ ✓ **AND** acid catalyst/H_2SO_4		AO3	If both already correctly identified, **ALLOW** 'carboxylic acid and alcohol' **ALLOW** conc H_2SO_4 **DO NOT ALLOW** dilute or H_2SO_4(aq) **ALLOW** HCl **IGNORE** HNO_3
			M6 Equation: $(CH_3)_3CCOOH + (CH_3)_3CCH_2OH \rightarrow$ $(CH_3)_3CCOOCH_2C(CH_3)_3 + H_2O$ ✓			
			M7 <u>reflux</u> in either **(M1)** or **(M5)** or <u>catalyst</u> used in **(M5)** ✓ **QWC** must spell catalyst or reflux correctly		AO2 AO1	

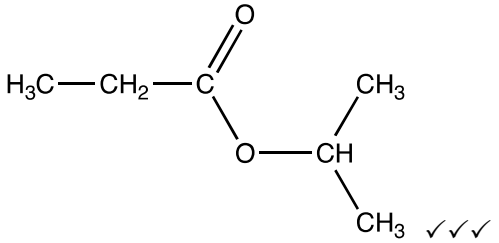
<table>
<tr><th colspan="3">Question</th><th>Answer</th><th>Marks</th><th>AO element</th><th>Guidance</th></tr>
<tr><td>5</td><td>(b)</td><td></td><td>similar compounds have similar retention times ✓

no reference values ✓</td><td>2</td><td>AO1

AO1</td><td>ALLOW same retention times
ALLOW correct description of retention time
ALLOW leave the column at the same time
ALLOW relative solubilities/partition/adsorption will be very similar
IGNORE Rf values
ALLOW no data book values (of retention times)</td></tr>
<tr><td></td><td>(c)</td><td></td><td>Elemental analysis and molecular formula (2 marks)

Use of percentages to find empirical formula = C_3H_6O ✓

Relative molecular mass from mass spectrum = 116
AND
Molecular formula = $C_6H_{12}O_2$ ✓

Ester structure (3 marks)
 
✓✓✓</td><td>2

3</td><td>AO2
×2

AO2
×3</td><td>ANNOTATE ANSWER WITH TICKS AND CROSSES ETC. CHECK SPECTRUM

<table><tr><th>Element</th><th>%</th><th>A_r</th><th>moles</th><th>ratio</th></tr><tr><td>C</td><td>62.07</td><td>12</td><td>5.173</td><td>3</td></tr><tr><td>H</td><td>10.34</td><td>1</td><td>10.34</td><td>6</td></tr><tr><td>O</td><td>27.59</td><td>16</td><td>1.724</td><td>1</td></tr></table>
Alternative method:
carbon: (116 × 62.07/100)/12 = 6
hydrogen: (116 × 10.34/100)/1 = 12
oxygen: (116 × 27.59/100)/16 = 2

ALLOW correct structural OR displayed OR skeletal formula OR mixture of the above (as long as unambiguous)

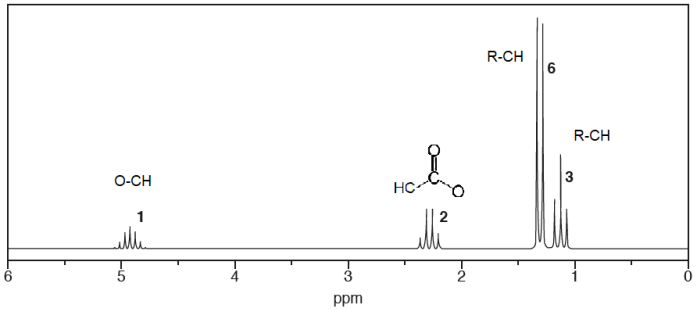
If not fully correct award marks as follows:

If the structure is any ester with molecular formula $C_6H_{12}O_2$, e.g. $CH_3COOCH_2CH(CH_3)_2$ (one mark)

If the ester link is reversed
i.e. $(CH_3)_2CHCOOCH_2CH_3$ (two marks)

Ignore any name</td></tr>
</table>

Question	Answer	Marks	AO element	Guidance
	NMR analysis (4 marks)	**4**		**NOTE: Each peak can be identified from:** • its δ value: ± 0.2 ppm • a range • its relative peak area • its splitting
	M1 Multiplet/heptet/peak at *δ* 4.9/3.9 is due to **H**C-O ✓		AO2	**Check annotated spectrum or table**
	M2 Quartet/peak at (*δ*) 2.3 is due to **H**C-C=O ✓		AO2	



Chemical shift/ppm	Relative peak area	Splitting pattern	Type of proton	Adjacent protons
1.2	3	triplet	R-C**H**	2
1.3	6	doublet	R-C**H**	1
2.3	2	quartet	**H**C-C=O	3
4.9	1	multiplet	O-C**H**	6

Question			Answer	Marks	AO element	Guidance
			M3 (CH_2CH_3) Triplet/peak (at δ 1.2) **AND** quartet/peak (at δ 2.3) = CH_2CH_3 **OR** Triplet/peak (at δ 1.2) shows 2 adjacent Hs/protons = CH_2CH_3 **OR** Quartet/peak (at δ 2.3) shows 3 adjacent Hs/protons = CH_2CH_3 **NOTE: QWC** – **triplet** or **quartet must** be spelled correctly in the correct context for **M3** ✓ **M4** Multiplet/heptet/peak (at δ 4.9/3.9) shows 6 adjacent H/two CH_3 groups **OR** Doublet/peak (at δ 1.3) shows one adjacent H ✓		AO2 AO2	**ALLOW** CH_3CH_2 described as CH_3 and 2 adjacent H **OR** CH_2 and 3 adjacent H **For QWC, ALLOW** quadruplet for quartet
			Total	**18**		

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