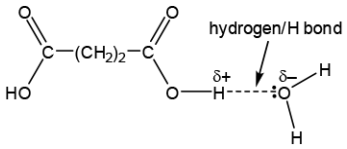
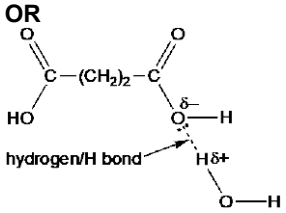
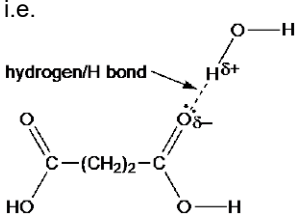
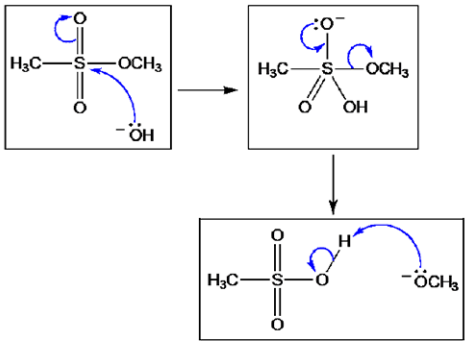
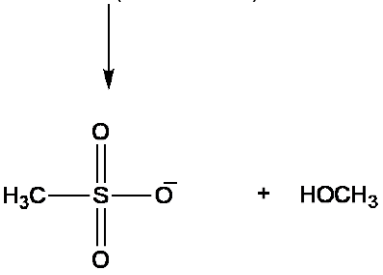
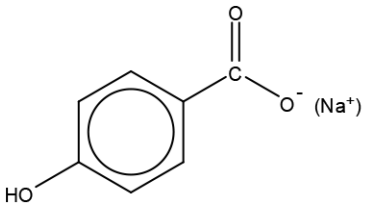
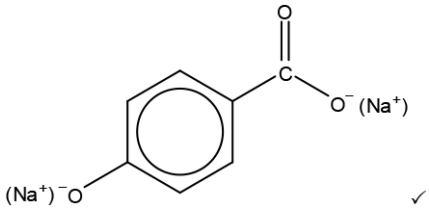
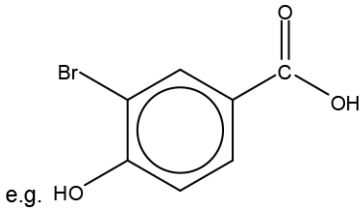
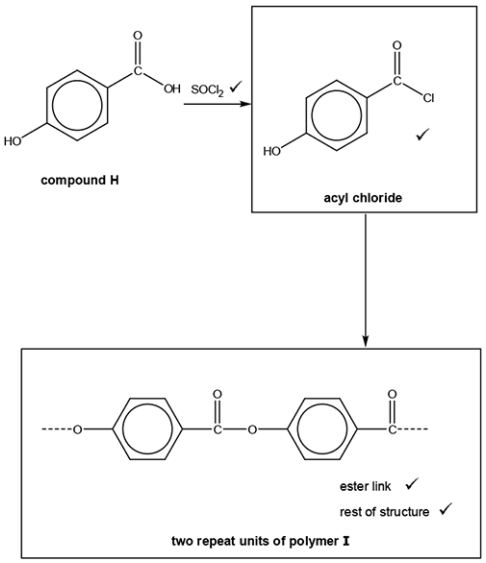
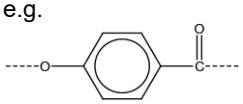
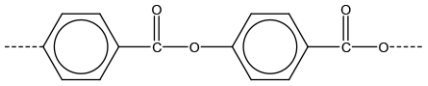
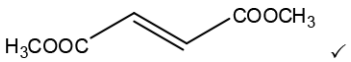
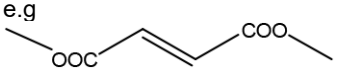
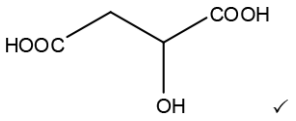
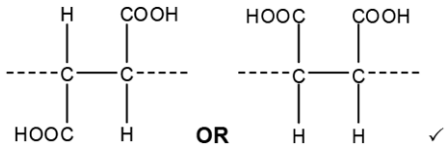
Mark scheme – Carboxylic Acids and Esters

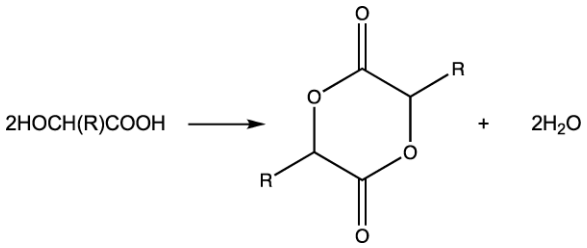
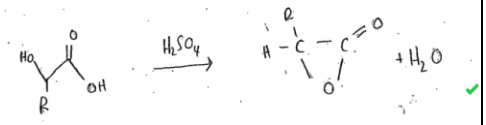
Question			Answer/Indicative content	Marks	Guidance
1		i	**Reagents** $K_2Cr_2O_7$ **AND** acid **AND** reflux ✓ **Equation** $HO(CH_2)_4OH + 4[O] \rightarrow HOOC(CH_2)_2COOH + 2H_2O$ [O] **AND** H_2O ✓ Correctly balanced equation ✓	3 (AO1.1) (AO2.5) (AO2.6)	**ALLOW** $Na_2Cr_2O_7$ **OR** $Cr_2O_7^{2-}$ **ALLOW** H_2SO_4 **OR** HCl **OR** H^+ **ALLOW** words. e.g. 'acidified dichromate' **ALLOW** a small slip in formula for dichromate e.g KCr_2O_7, **Examiner's Comments** Many candidates did not correctly balance this equation or missed water as a product entirely.
		ii	 **OR**  Diagram showing correct dipole charges on each end of one hydrogen bond between a water molecule and a diacid ✓ Hydrogen bond between one lone pair on O atom in one of the molecules and the H atom of another **AND** Hydrogen bonding stated or labelled on diagram	2 (AO2.1 ×2)	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **DO NOT ALLOW** δ+ on H atoms of CH_2 group **ALLOW** H-bond for hydrogen bond **ALLOW** H bond between C=O and H_2O, i.e.  **IF** diagram is not labelled, **ALLOW** hydrogen bond/H bond from text **Examiner's Comments** Candidates who answered this question well had clear, labelled diagrams. Too often, labels, dipoles and lone pairs were missing.
			Total	**5**	

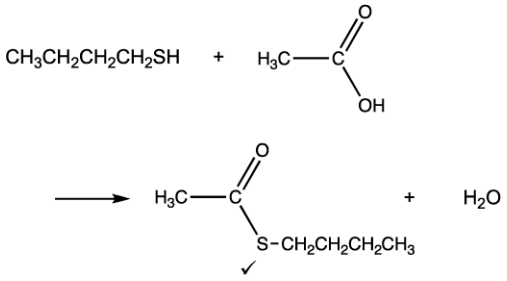
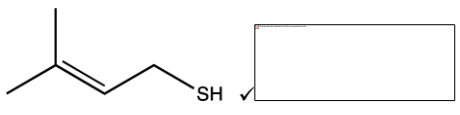
2			 6 curly arrows correct ✓✓✓✓ 5 curly arrows correct ✓✓✓ 4 curly arrows correct ✓✓ 3 curly arrows correct ✓	4 (AO 3.1×4)	**IGNORE** any added charges **OR** dipoles. *Marks solely for curly arrows* **IGNORE** any curly arrows on bottom structures (not in boxes):  **Examiner's Comments** Most candidates showed a good understanding and appreciation of drawing curly arrows. It must be stressed that curly arrows that do not start from a lone pair, negative charge or a bond cannot be credited. Lower-attaining candidates often drew imprecisely positioned curly arrows, curly arrows in the wrong direction or to the wrong atoms. For their response to be credited with marks, candidates should position curly arrows to ensure credit when outlining reaction mechanisms.
			Total	**4**	
3	a		**Product from Na_2CO_3**  ----------	**3**	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** $–COO^–$ **OR** –COONa **DO NOT ALLOW** negative charge on C atom **DO NOT ALLOW** –COO–Na (covalent bond) **IGNORE** connectivity of phenol OH group

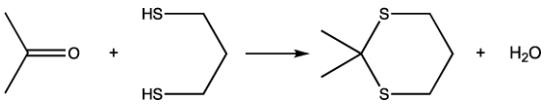
					(marks are for correct conversions)
			Product from NaOH(aq)  ✓ ----------		**ALLOW** 1 mark if top two structures are shown in wrong boxes
			Product from Br_2  e.g. HO ✓		**ALLOW** substitution of any H from benzene ring **ALLOW** multiple substitution, *i.e.* di-, tri- and tetrabromo products. **IGNORE** connectivity of phenol OH group *(marks are for correct conversions)*
					Examiner's Comments This question assessed different reactions of compound **H**, 4-hydroxybenzoic acid, and discriminated well. Two of the reactions focused on acid-base chemistry, using the reagents Na_2CO_3 and NaOH. Many candidates recognised that the carboxylic acid group would react in both cases but only some managed to identify when the phenol group was involved correctly. A number of responses suggested that a phenoxide ion was formed with sodium carbonate but not with sodium hydroxide. The third reaction was substitution with bromine. This reaction appeared more familiar to all candidates with the majority scoring this mark. A small proportion of candidates substituted the phenol OH group or carboxylic acid group.

	b		One mark for each correct structure/reagent as shown below  	**4**	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** PCl_5 **OR** PCl_3 for reagent mark. **IGNORE** references to temperature for reagent mark **IGNORE** additional reagents shown with $SOCl_2/PCl_5/PCl_3$ e.g. H_2O, $AlCl_3$, HCl etc. **IGNORE** names *(question asks for structures of organic compounds and formula of reagent)* **DO NOT ALLOW** more than two repeat units **ALLOW** 1 mark for one correct repeat unit e.g.  'End bonds' **MUST** be shown (do not have to be dotted) **ALLOW** the 'O' at either end i.e.  **IGNORE** brackets **IGNORE** *n* **Examiner's Comments** Compound **H** was also the focus for this question. Most candidates were able to provide the structure of the acyl chloride obtained from **H** but only some identified $SOCl_2$ as the correct reagent. Common incorrect reagents included HCl and $AlCl_3$. Most candidates recognised that polymer **I** was a polyester but only some were able to draw two repeat units correctly. Candidates are advised to practice drawing different polymers, taking care to ensure the correct number of repeat units are present when a specific number is required.
			Total	**7**	
4			**Product from excess CH_3OH/H_2SO_4**  ✓	**3**	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous e.g 

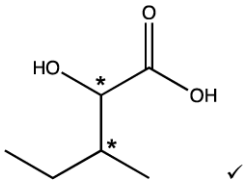
			Product from steam, H_3PO_4  ✓ **Repeat unit of polymer C**  ✓		**IGNORE** connectivity in each product **ALLOW** the *E* or *Z* isomer as product from excess CH_3OH/H_2SO_4 'End bonds' MUST be shown (do not have to be dotted) **IGNORE** brackets **IGNORE** *n* **ALLOW** more than one repeat unit but has to be a whole number of repeat units **Examiner's Comments** The majority of candidates were able to identify at least one product from the reactions of compound C. The polymerisation reaction appeared to be the most familiar, although some candidates attempted to draw a condensation polymer using the carboxylic acid groups rather than the alkene. The reaction of C with excess methanol was also well attempted. However, a significant number of candidates used chemical symbols to show their product. A proportion of these did not show the H atoms of the alkene group, showing only C=C in the centre of the structure. Candidates are advised to use the type of formulae given in a question as this will reduce the potential for error or omissions. The product from the hydration of C appeared to be the hardest to deduce. Many candidates recognised this reaction would produce an alcohol, but often included two OH groups – one on each C from the double bond – in their structure. Other candidates confused this reaction with hydrogenation and formed a saturated product from C.
			Total	**3**	
5		i		**3**	**ALLOW** correct structural **OR** skeletal **OR** displayed formula **OR** mixture of the above as long as non- ambiguous

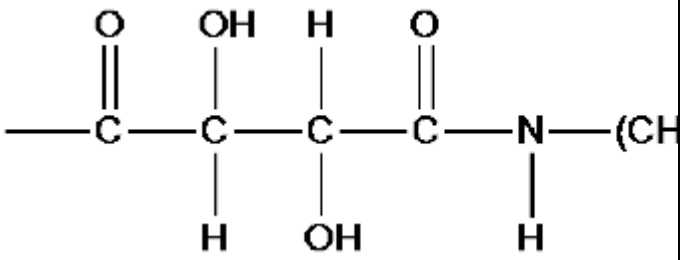
			Equation $2HOCH(R)COOH + Mg \rightarrow (HOCH(R)COO)_2Mg + H_2$ Organic product ✓ Balance ✓ ***Type of reaction*** Redox ✓		**ALLOW** $2HOCH(R)COOH + Mg \rightarrow 2HOCH(R)COO^- + Mg^{2+} + H_2$ **ALLOW** multiples **IGNORE** poor connectivity to OH groups *Given in question* **Examiner's Comment:** Candidates found this part difficult and the problem presented many opportunities for errors. Many candidates tried to show charges for the salt formed but often the 2+ charge was missing on Mg^{2+} or Mg^+ was shown. The balanced equation required a balancing 2 before compound A but this was often omitted. Candidates using skeletal formulae fared better than attempts to show structural formulae such as HOCHRCOOH, with many omitting the H atom from CHR. Few candidates identified the reaction as redox, with many giving neutralisation instead.
		ii	***Equation***  Organic product ✓ Balance ✓ ***Type of reaction*** Condensation **OR** esterification ✓	**3**	**ALLOW** correct structural **OR** skeletal **OR** displayed formula **OR** mixture of the above as long as non- ambiguous **ALLOW** 1 mark of the 2 equation marks for formation of '3 ring' with balanced equation:  **ALLOW** condensation polymerisation **ALLOW** addition–elimination **IGNORE** elimination **IGNORE** dehydration **Examiner's Comment:** As with 4(b)(ii), candidates found this question difficult. It was not often that the dimer was seen but, when it was, the structure was usually correct. Balancing required $2H_2O$ and the balancing 2 was often omitted. In contrast with 4(b)(i), many more

					candidates identified the type of reaction, here condensation or esterification.
			Total	**6**	
6		i	$K_a = \frac{[H^+]\,[C_4H_9S^-]}{[C_4H_9SH]}$ ✓ *Square brackets required*	**1**	**ALLOW** correct structural **OR** skeletal **OR** displayed formula **OR** mixture of the above as long as non- ambiguous **Examiner's Comment:** This part was very well answered. Candidates responded with either near molecular formulae, such as C_4H_9SH, structural formulae or with skeletal formulae. Some candidates made careless errors such as omitting the negative charge or showing $[H^+]^2$ as numerator rather than $[C_4H_9S^-]\,[H^+]$.
		ii	 Structure of thioester ✓ Complete equation ✓	**2**	**ALLOW** correct skeletal **OR** displayed formula **OR** mixture of the above as long as non-ambiguous **ALLOW** C_4H_9SH **ALLOW** CH_3COOH Thioester functional group **must** be fully displayed, **OR** as a skeletal formula but allow SC_4H_9 in thioester **Examiner's Comment:** In this part, candidates were expected to apply their knowledge and understanding of esterification to thiols and thioesters. Over half the candidates obtained a correct structure of the thioester. Most of these candidates constructed a balanced equation although some omitted the water product. Common errors included formation of a conventional ester and H_2S, and retaining the O atom from the OH in the carboxyl group to form –COOS–. As with 4(b)(i), structural and skeletal formulae were used. Candidates are less likely to omit H atoms if the skeletal formula is used.
		ii i		**1**	**IF** correct **skeletal** formula is shown, **IGNORE** displayed formula in a second structure **Examiner's Comment:**

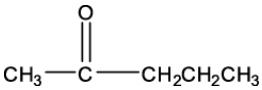
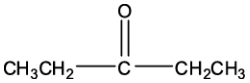
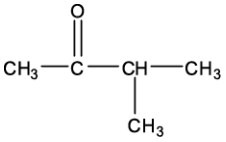
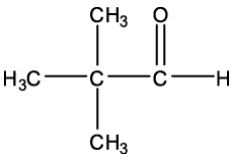
					Just over half the candidates drew the correct structure, displaying a good understanding of interpreting organic nomenclature when drawing a structure. Common errors included omission of the CH_2 adjacent to the terminal –SH group and placing the branch or double bond in wrong positions. Some candidates spoilt an otherwise good response by showing a structural formula or a mixture of skeletal and structural formulae.
		i v	 Reactants ✓ Products **AND** balanced equation ✓	**2**	**ALLOW** correct structural **OR** skeletal **OR** displayed formula **OR** mixture of the above as long as non- ambiguous **Examiner's Comment:** In this part, candidates were expected to apply their knowledge and understanding of condensation to an entirely new context. One mark was allocated for the reactants and this was usually scored. The second mark for the novel cyclic compound and water was much more difficult, aimed at stretch and challenge. A significant number of candidates interpreted the information to obtain a correct cyclic structure but this mark was the domain of the most able candidates.
			Total	**6**	
7		i	***Burette readings*** Final (reading) /cm^3 23.15 45.95 32.45 Initial (reading) /cm^3 0.60 23.15 10.00 ✓ • Correct titration results recorded with initial and final readings, clearly labeled **AND** all readings recorded to two decimal places with last figure either 0 or 5 ***Titres*** Titre / cm^3 22.55 22.80 22.45 ✓ • Correct subtractions to obtain final titres to 2 DP ***Units***	**4**	Table **not** required **ALLOW** initial reading before final reading **ALLOW ECF**

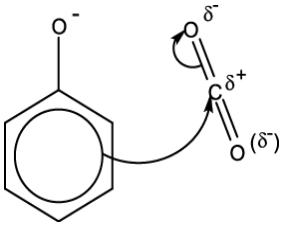
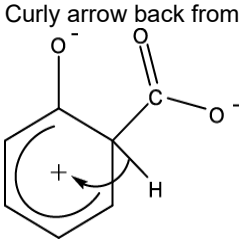
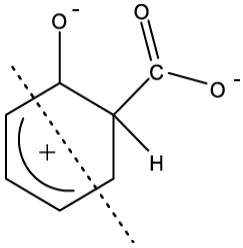
			• Units of cm^3 for initial, final and titres ✓ ***Mean titre*** • mean titre $= \frac{22.55 + 22.45}{2} = 22.50$ **OR** 22.5 cm^3 ✓ *i.e. using concordant (consistent) titres*		**ALLOW** units with each value **ALLOW** brackets for units, i.e. (cm^3) **ALLOW ECF** from incorrect concordant titres **Examiner's Comment:** This question should have been four straightforward marks, but it was actually found very challenging by candidates. Most read the scales correctly but then did not present their findings clearly, often scattering unlabelled numbers around, omitting units with absence of any heading linking them to the burettes. 0.60 was very often shown as 0.6 and 22.80 as 22.8. Candidates were expected to take the mean of their closest titres but a significant number took an average of all three titres instead. The mark scheme allowed for a mean titre obtained from incorrect titres. Candidates need to appreciate the importance of communicating their results in a clear and comprehensive way with headings and units, and showing numerical values to the accuracy of the apparatus used.
		ii	**ALLOW 3SF** or more throughout **IGNORE** trailing zeroes, e.g. **ALLOW** 0.084 for 0.0840 …… $n(NaOH) = 0.0840 \times \frac{22.50}{1000} = 1.89 \times 10^{-3}$ (mol) ✓ n(**A**) in 250 $cm^3 = 10 \times 1.89 \times 10^{-3} = 1.89 \times 10^{-2}$ (mol) ✓ $M(\mathbf{A}) = \frac{2.495}{1.89 \times 10^{-2}} = 132$ (g mol^{-1}) ✓ M(alkyl group) (= 132 – 75) = 57 ✓	**6**	**ALLOW ECF** from incorrect mean titre in **4a(i)** e.g. From 22.60 cm^3 (mean of all 3 titres in **(i)**, n(NaOH) = 1.8984×10^{-3} (mol) **ALLOW ECF** from incorrect n(NaOH) **ALLOW ECF** from incorrect n(**A**) **ALLOW ECF** from incorrect M(**A**) – 75

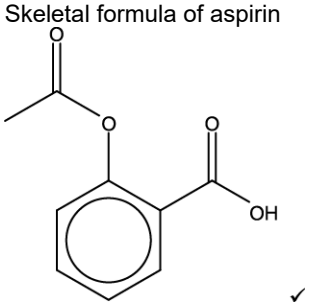
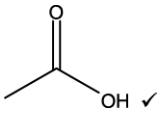
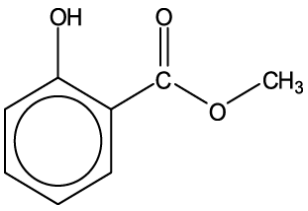
			R = C_4H_9 ✓ **ALLOW** alkyl group in drawn structure with straight chain or branch (es) in wrong position, e.g. for R = C_4H_9, $CH_3CH_2CH_2CH_2$ **OR** $(CH_3)_3C$ Structure with chiral carbon atoms identified (see * below)  ✓		**ALLOW ECF** for alkyl group closest to calculated *M*(alkyl group), e.g. for *M* = 45, **ALLOW** C_3H_7 (43) **ALLOW** correct structural **OR** skeletal **OR** displayed formula **OR** mixture of the above as long as non-ambiguous **IGNORE** poor connectivity to OH groups *Given in question* …… …… **Common error for 4 marks max** *25.00 instead of 22.50 and scaling by × 10* 2.10×10^{-3} → 2.10×10^{-2} ✓ → 118.81 ✓ → 43.81 ✓ → C_3H_7 ✓ *25.00 instead of 22.50 and scaling by* $\times \frac{250}{22.50}$ 2.10×10^{-3} → 2.33×10^{-2} ✓ → 106.93 ✓ → 31.93 ✓ → C_2H_5 ✓ No structure with 2 chiral centres possible **Examiner's Comment:** Most candidates made some headway with this problem. Candidates were expected to process their mean titre from 4(a)(i) in a conventional titration calculation to arrive at a molar mass of 132 g mol^{-1}. From there, candidates could determine a C_4H_9 alkyl group and draw the structure of compound A with two chiral carbon atoms. Most candidates scored some marks but processing beyond the molar mass proved to be difficult for weaker candidates. Some candidates showed a structure with a linear C_4H_9 group which contains one chiral carbon atom. A common error was use of 25.0 cm^3, instead of the titre, as the volume of NaOH, obtaining an initial value of 2.10×10^{-3} mol. The mark scheme allowed processing of this value to be credited using error carried forwards. Some candidates omitted to scale their initial value by a factor of ×10, obtaining a molar mass of over 1000 g mol^{-1}, e.g. 1320 instead of 132. A large range of

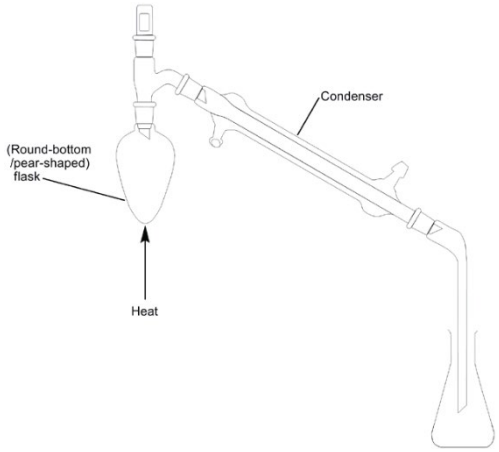
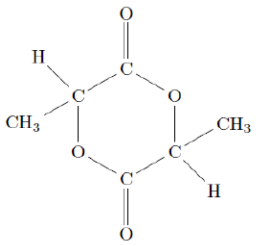
					marks was seen and the question discriminated extremely well.
			Total	**10**	
8		i	$C_2H_3O_3$ ✓	1	
		ii	2,3− dihydroxybutanedioic acid ✓	1	**ALLOW** 2,3−dihydroxybutane−1,4−dioic acid **ALLOW** absence of hyphens or extra hyphen or space, e.g. 2,3−dihydroxy butanedioic acid **ALLOW** full stops or spaces between numbers e.g. 2.3 dihydroxybutanedioic acid
		iii	 Correct amide link ✓ Rest of structure ✓	2	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous 'End bonds' **MUST** be shown **IGNORE** brackets **IGNORE** *n*
		iv	$[H_3N^+(CH_2)_6NH_3^+]$ $[^-OOC(CHOH)_2COO^-]$ **OR** $[H_3N(CH_2)_6NH_3]^{2+}$ $[OOC(CHOH)_2COO]^{2-}$ Positive ion correct ✓ Negative ion correct ✓	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **ALLOW** charge either on N atom or NH_3^+ Negative charge must be on COO^- **ALLOW**$[H_2N(CH_2)_6NH_3^+]$ $[^-OOC(CHOH)_2COOH]$
			Total	**6**	
9	a	i	**Reagent and observation** sodium carbonate **AND** Fizzing/effervescence/bubbling ✓ **Equation** Correctly balanced equation ✓ e.g. $2RCOOH + Na_2CO_3 \rightarrow 2RCOONa + CO_2 + H_2O$	2	**Note:** both reagent and observation are required for first mark **ALLOW** name or formula for any suitable carbonate e.g $NaHCO_3$, potassium carbonate etc. **ALLOW** reagent from equation if not stated elsewhere
		ii	**Reagent and observation** Tollens' (reagent) **AND** Silver (mirror) ✓	2	**Note:** both reagent and observation are required for first mark **ALLOW** ammoniacal silver nitrate **OR**

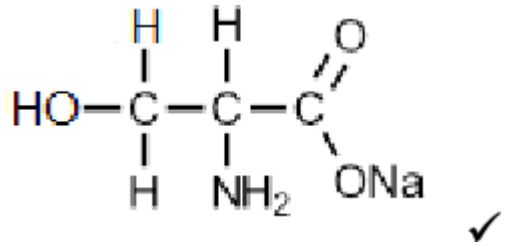
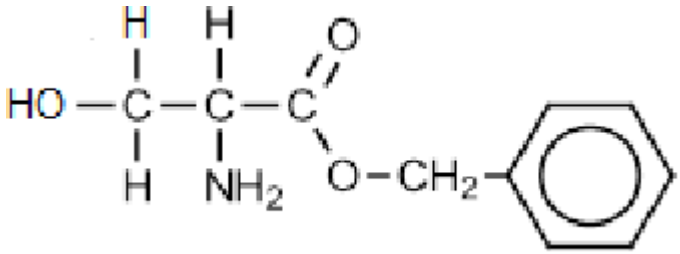
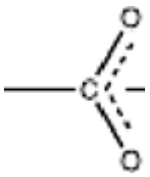
			Equation RCHO + [O] → RCOOH ✓		Ag^+/NH_3 **ALLOW** $H^+/Cr_2O_7^{2-}$ **OR** acidified (potassium/sodium) dichromate **AND** Orange to green *(this would identify the aldehyde from the carboxylic acid, ketone and esters)*
	b		2,4−dinitrophenylhydrazine **AND** Orange/yellow/red precipitate ✓	1	**ALLOW** errors in spelling **ALLOW** 2,4(−)DNP **OR** 2,4(−)DNPH **ALLOW** Brady's reagent or Brady's Test **ALLOW** solid **OR** crystals **OR** ppt as alternatives for precipitate
	c	i	$CH_3COOC(CH_3)_3 + NaOH \rightarrow CH_3COONa + (CH_3)_3COH$ CH_3COONa ✓ Rest of equation correct ✓ **OR** $(CH_3)_3CCOOCH_3 + NaOH \rightarrow (CH_3)_3CCOONa + CH_3OH$ $(CH_3)_3CCOONa$ ✓ Rest of equation correct ✓	2	**Note:** the hydrolysis of either ester may be given **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **DO NOT ALLOW** molecular formulae of products *(question requires structures of products to be shown)*
		ii	**Reagent and observation** $H^+/Cr_2O_7^{2-}$ **OR** acidified (potassium/sodium) dichromate **AND** Orange to green (with CH_3OH) ✓ **Equation** $CH_3OH + [O] \rightarrow HCHO + H_2O$ **OR** $CH_3OH + 2[O] \rightarrow HCOOH + H_2O$ ✓	2	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **DO NOT ALLOW** molecular formulae *(question requires structures of organic compounds to be shown)*
		ii i	**^{13}C NMR (1 mark)** (It is) not possible to identify (the esters) with ^{13}C NMR **AND** (both) spectra would contain four peaks (with similar chemical shifts) ✓ **^{1}H NMR (2 marks)** (It is) possible to identify (the esters) with ^{1}H NMR	3	**ALLOW** 'same number of peaks' in place of 'four peaks'

			(^{1}H NMR spectrum of) $CH_3COOC(CH_3)_3$ has a singlet/peak between 2.0−3.0 (ppm) (^{1}H NMR spectrum of) $(CH_3)_3CCOOCH_3$ has a singlet/peak between 3.0−4.3 (ppm) All **three** correct statements✓✓ Any **two** correct statements ✓		**ALLOW** any value or range of values within 2.0−3.0 **ALLOW** any value or range of values within 3.0−4.3
	d		**<u>Possible structures for ketone (2 marks)</u>**    All **three** correct ✓✓ Any **two** correct ✓ **<u>Aldehyde (3 marks)</u>** Peak at (δ) 1.2 shows HC–R **AND** No H on adjacent C atom as peak is singlet ✓ Peak at (δ) 9.6 shows H–C=O **AND** No H on adjacent C atom as peak is singlet ✓  **OR** (2,2−)dimethylpropanal ✓	5	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **IGNORE** names of ketones
			Total	**17**	
10	a	i	Dipole shown on C=O bond, $C^{\delta+}$ and $O^{\delta-}$, **AND** curly arrow	3	**ANNOTATE ANSWER WITH TICKS AND CROSSES**

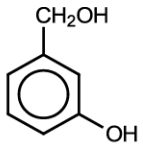
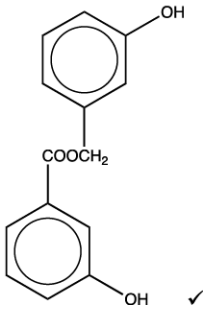
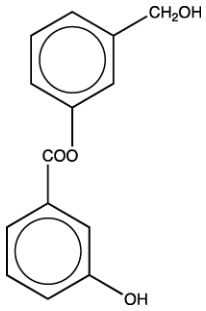
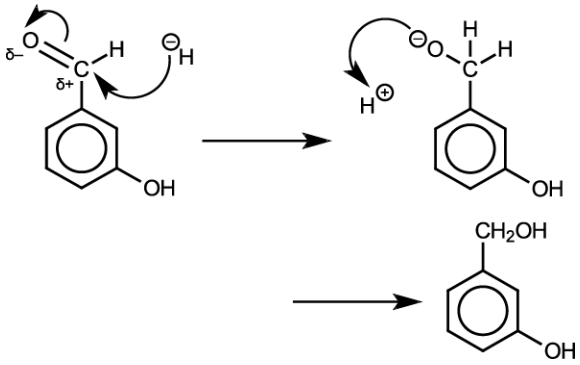
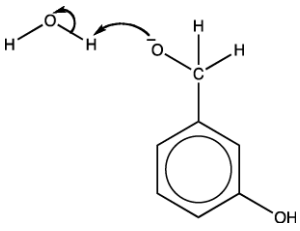
			from the C=O bond to the $O^{\delta-}$ atom **AND** Curly arrow from π−bond to C in CO_2 ✓  Correct intermediate ✓ Curly arrow back from C–H bond to reform π−ring ✓ 		**DO NOT ALLOW** the following intermediate:  π−ring must cover more than 1/2 of the ring **AND** 'horseshoe' in the correct orientation, *ie* gap towards C with COO^- **ALLOW** + sign anywhere inside the 'hexagon' of intermediate
		ii	Neutralisation ✓ (In Stage 1) phenol loses H^+ **AND** (In Stage 3) carboxylate ion gains H^+ ✓	2	**ALLOW** acid-base **ALLOW** both Stage 1 **AND** Stage 3 involve proton transfer
		ii i	**FIRST CHECK THE ANSWER ON THE ANSWER LINE** **IF** answer = 7.31 (g) award 3 marks _____ **actual** n(salicylic acid) produced = $\frac{4.83}{138}$ = 0.035(0) (mol) ✓ **theoretical**	3	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW ECF** at each stage **ALLOW 3 SF** up to calculator value correctly rounded for intermediate values 100 **ALLOW** expected mass compound **E** = $4.83 \times \frac{100}{45.0}$ = 10.733 (g)

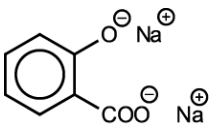
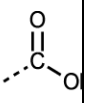
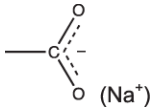
			n(phenol) = n(salicylic acid) = $0.035(0) \times \frac{100}{45.0} = 0.0778$ (mol) ✓ Mass of phenol = 0.0778 × 94.0 = 7.31 (g) ✓		**ALLOW** Mass phenol reacted = 0.035 × 94.0 = 3.29 (g) **ALLOW** Mass of phenol used = 3.29 × $\frac{100}{45.0}$ = 7.31 (g) **Note:** 1.48 g would get 2 marks *(use of 45.0/100 instead of 100/45.0)* 7.30 g would get 2 marks *(use of 0.0777 for moles phenol)*
	b		Skeletal formula of aspirin  ✓ Skeletal formula of ethanoic acid  ✓	2	**IF** skeletal formulae are not used **ALLOW** one mark if both the structures of aspirin **AND** ethanoic acid are correct **IGNORE** names
	c	i	 **AND** Acid (catalyst) ✓	1	**Note:** both the structure and condition are required for the mark **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** H^+ / H_2SO_4 / H_3PO_4 / named mineral acid
		ii	**Diagram** Diagram showing correct apparatus for distillation ✓ *i.e.* • Round-bottom/pear-shaped flask	2	**DO NOT ALLOW** conical flask, volumetric flask, beaker in place of round bottomed/pear shaped flask

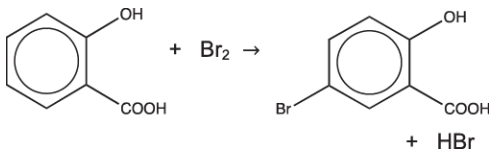
			• Condenser (correctly orientated) • Stopper/thermometer • Delivery tube and suitable collection vessel  **Labels** (Round-bottom/pear-shaped) flask **AND** condenser **AND** heat (source) ✓		**DO NOT ALLOW** diagram mark if top of distillation head not closed **Note:** suitable collection vessels include: conical flask, boiling tube, test-tube, beaker etc.
			Total	**13**	
11			 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **Examiner's Comments** A good discriminator. Many failed to produce the correct cyclic structure.
			Total	**1**	
12			$C_{17}H_{35}COOH + NaOH \rightarrow C_{17}H_{35}COO^-Na^+ + H_2O$ ✓	1	**ALLOW** $C_{17}H_{35}COONa$ **IGNORE** state symbols **Examiner's Comments** Very well answered. Most candidates could write the correct equation.
			Total	**1**	
13		i	$2C_2H_5COOH + Na_2CO_3 \rightarrow 2C_2H_5COONa + CO_2 + H_2O$ ✓	1	**IGNORE** state symbols and use of equilibrium sign **FOR** $CO_2 + H_2O$ **ALLOW** H_2CO_3 **ALLOW** $C_2H_5COO^-Na^+$ **OR** $C_2H_5COO^- + Na^+$ **BUT BOTH** + and − charges **must** be shown **ALLOW** NaC_2H_5COO

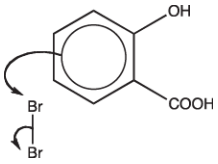
					Examiner's Comments Equations for reactions of weak acids continue to improve. Ionic signs within the formula of sodium propanoate were allowed but both were then needed. Common errors included an incorrect formula of sodium propanoate, usually $(CH_3CH_2COO)_2Na$, sodium carbonate as $NaCO_3$ or an equation with correct species but unbalanced. Candidates are recommended to carefully check the formulae for missing atoms.
		ii	$H^+ + OH^- \rightarrow H_2O$ ✓	1	**ALLOW** $C_2H_5COOH + OH^- \rightarrow C_2H_5COO^- + H_2O$ **IGNORE** state symbols **Examiner's Comments** The required equation using $H^+(aq)$ and $OH^-(aq)$ was commonly seen but a significant number of candidates wrote an equation using $H^+(aq)$ and $CO_3^{2-}(aq)$, perhaps writing an ionic equation for the reaction in (i) rather than a different reaction.
			Total	**2**	
14		i	 ✓  —NH_3^+ in second product ✓	3	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **ALLOW** $—O^-Na^+$ **OR** $—O^-$ (cation not required) **DO NOT ALLOW** —O—Na (covalent bond) **DO NOT ALLOW** —O (without the sodium) **ALLOW** delocalised carboxylate  **Examiner's Comments** The majority scored two marks here. The question had a three mark total for drawing two structures and this may have prompted some candidates to incorrectly form a salt with the alcohol group in **reaction 1**. Many were able to draw a correct structure for the ester formed in **reaction 2**, but very few protonated the amine group in acidic conditions. The protonation of hydrolysis

					products has been well represented in recent papers.
		ii	perfume / fragrance / flavouring ✓	1	**IGNORE** solvent **OR** food additive **Examiner's Comments** Well answered with most of the correct responses referring to perfumes and flavourings which are the uses listed in the specification. Common responses marked as incorrect were suggestions that this ester could be used for making dyes, polymers or textiles.
		ii i	Reaction 3: (hot) ethanolic ammonia ✓ Reaction 4: oxidation ✓ Reaction 5: hydrolysis ✓	3	**ALLOW** NH_3 (dissolved) in ethanol **IGNORE** other conditions **ALLOW** oxidisation / oxidised **DO NOT ALLOW** redox **ALLOW** nucleophilic addition-elimination **DO NOT ALLOW** nucleophilic substitution **IGNORE** acid / base **Examiner's Comments** Most candidates were able to score at least one mark here, usually for correctly identifying **reaction 4** as an oxidation reaction. Although the use of excess reagent was not required for **reaction 3**, some missed ethanol as an essential solvent and **reaction 5** was occasionally described as a reduction.
			Total	**7**	
15		i	reagent = $K_2Cr_2O_7$ **AND** H_2SO_4 ✓	3	**ALLOW** acidified dichromate **ALLOW** H^+ / any acid **IGNORE** concentration of acid **ALLOW** $Na_2Cr_2O_7$ / $Cr_2O_7^{2-}$ / (potassium **OR** sodium) dichromate((VI)) **ALLOW** acidified MnO_4^- **ALLOW** Tollens' reagent / ammoniacal silver nitrate **IGNORE** conditions **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **ALLOW ECF** from incorrect **compound C** Check positions of OH groups

			compound C =  ✓ **ester =**  ✓		**ALLOW** esterification of phenol group  **Examiner's Comments** A well answered question. Most knew the correct reagents for the oxidation of the aldehyde and the majority were able to show the structure produced when the aldehyde is reduced using $NaBH_4$. Some chose to esterify the phenol group rather than the alcohol group in compound **C** and this was given credit.
		ii	curly arrow from H^- to $C^{\delta+}$ ✓ dipole **AND** curly arrow from C=O bond to O ✓ correct intermediate **AND** curly arrow to H^+ ✓ 	3	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** curly arrow must come from lone pair on H or negative charge on H curly arrow must come from the bond, not the carbon atom curly arrow must come from lone pair on O or negative charge on O and go to H or positive charge on H **Where circles have been placed round charges, this is for clarity only and does not indicate a requirement** **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **ALLOW** for second stage  **IF** H_2O is used it **MUST** show the curly

					arrow from the negative charge or lone pair on the oxygen atom of the intermediate to H in H_2O **AND** from the O—H bond to the O in H_2O. **Dipole not required on water molecule** Penalise missing –OH on intermediate only **IGNORE** product – already given credit in part (i) **Examiner's Comments** The full range of marks was seen. Common errors included missing charges, curly arrows beginning or ending in the wrong place and —OH groups missing or placed in the wrong position on the intermediate structure. Most candidates chose to show the reaction of the intermediate with water rather than with H^+ ions
			Total	**6**	
16	a	i	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **DO NOT ALLOW** —O—Na **OR** -COO-Na (covalent bond) **ALLOW** $—O^-$ **ALLOW** —ONa **ALLOW** —COONa **OR**  **ALLOW** delocalised carboxylate  **Examiner's Comments** The question asked for the product of the reaction with excess sodium hydroxide. Many answers included the product formed by the reaction of just one of the functional groups. Most commonly the phenol group was left unreacted. The mark scheme permitted the omission of the cation from the formula of the compound but this omission was rarely seen.

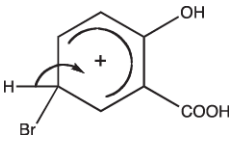
		ii	(Bromine) would be decolourised / turn (from orange / red / yellow / brown) to colourless **OR** white precipitate / solid / emulsion (formed) ✓	1	**IGNORE** goes clear **DO NOT ALLOW** other colours for bromine **IGNORE** cream precipitate **DO NOT ALLOW** salicylic acid turns colourless / decolourised **IGNORE** temperature / fumes **Examiner's Comments** The observation for the reaction of a phenol with bromine was very well known and many candidates offered two correct observations when only one was required to score the mark.
		iii	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **MUST** be all correct to score mark **ALLOW** molecular formulae, i.e. $C_7H_6O_3 + Br_2 \rightarrow C_7H_5O_3Br^+ HBr$ **Examiner's Comments** A very well answered question. Most candidates copied the structural formulae given in the question. Some made errors when they unnecessarily converted the structures into molecular formulae. HBr was occasionally missing as a product.
		iv	$(CH_3)_2CHOH$ / $CH_3CH(OH)CH_3$ / propan(–)2(–)ol **AND** acid / H^+ / H_2SO_4 (catalyst) ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **ALLOW** 2-propanol **DO NOT ACCEPT** incorrect name or incorrect formula of alcohol **IGNORE** reflux / concentrated (acid) **Examiner's Comments** Many candidates correctly gave the formula for propan-2-ol and included an acid catalyst. Common non-scoring answers omitted the acid or the alcohol or gave an incorrect name for the alcohol.



No Br_2 dipole needed

Curly arrow to Br from ring **OR** from within the ring **AND** curly arrow Br-Br bond to Br ✓

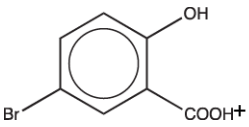
……



b i

✓ correct intermediate (with charge)

✓ curly arrow from C—H to reform ring



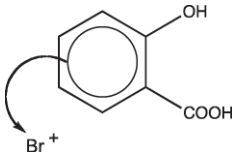
+ HBr / H^+ + Br^-

✓ Correct products

(Br^- may be shown in the first step)

4

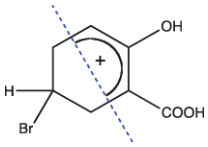
ALLOW mechanism with Br^+ electrophile (Maximum 3 marks)



IGNORE any equations involving a halogen carrier

……

BUT DO NOT ALLOW intermediate with π-system covering less than half of ring:



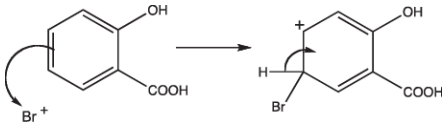
ALLOW + charge anywhere inside the 'horseshoe'

Horseshoe must have open end towards Br

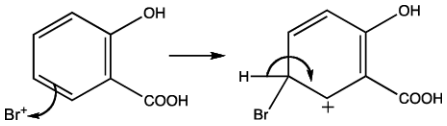
Apply ecf to error in structure of intermediate (M2)

ALLOW Kekulé mechanism as shown

(Maximum 3 marks if Br^+ is the electrophile)



ALLOW double bonds in alternate arrangement

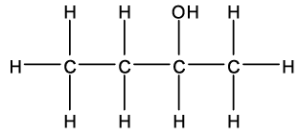


Examiner's Comments

Many fully correct and clearly structured mechanisms were seen. A proportion of candidates did not score full marks because they ignored the information in the question and based their mechanism on the Br^+ electrophile and did not finish with HBr as a product. Relatively few candidates lost

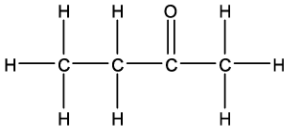
					marks for incorrectly positioned curly arrows.
		ii	(In salicylic acid) lone pair / pair of electrons on O(H) / phenol is ⌣ (partially) **delocalised** into the ring ✓ electron density increases / is high **ORA** ✓ Br_2 / electrophile is (more) polarised **ORA** ✓ ✎**QWC**: delocalised / delocalized / delocalise *etc*. must be spelled correctly in the correct context at least once	3	**ALLOW** diagram to show movement of lone pair into ring but delocalised ring must be mentioned **ALLOW** lone pair / pair of electrons on O(H) / phenol is (partially) drawn / attracted / pulled into **delocalised** ring **IGNORE** 'activates the ring' **ALLOW** more electron rich **DO NOT ALLOW** charge density or electronegativity **ALLOW** (salicylic acid) attracts electrophiles more/more susceptible to electrophilic attack **ALLOW** Br_2 is (more) attracted OR Br_2 is not polarised by benzene **OR** induces dipoles (in bromine / electrophile) Delocalise(d) needed to score the first marking point **Examiner's Comments** This question was very well answered with the majority of candidates scoring at least two marks. The most common errors were the omitting the words delocalised or lone pair or failure to use the word delocalised in the correct context.
			Total	**11**	
17			Molar mass of **B** = 74 ✓ **B-F** clearly identified	6	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **Check and annotate page 19 below this response** Molar mass = $\frac{2.59}{0.035}$ = 74 For structure of **B**, **C**, **D** or **E / F ALLOW** correct displayed **OR** correct structural formula **OR** correct skeletal formula **OR** mixture of the above as long as unambiguous. **DO NOT ALLOW** missing H atom(s) in a

B/alcohol:



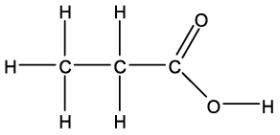
✓

C/ketone:



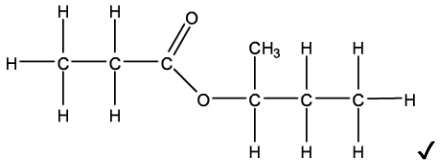
✓

D/carboxylic acid:



✓

E and F:



✓

H_2O/water ✓

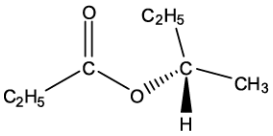
displayed formula for one structure but **ALLOW** missing H atoms in subsequent structures.

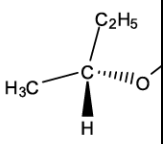
IGNORE names of organic compounds

E and **F** can be identified either way round

ALLOW H_2O or displayed formula for mark

For **E** and **F** – **ALLOW** the two optical isomers





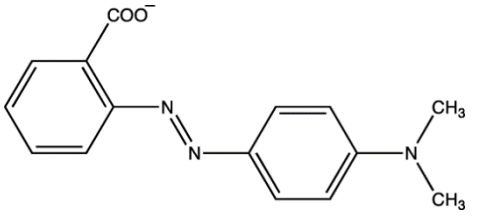
Examiner's Comments

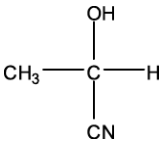
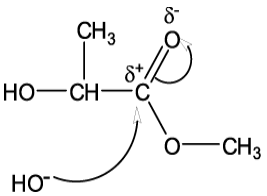
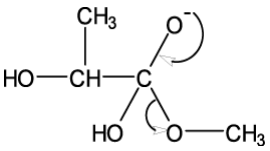
Candidate were required to apply their knowledge of the reactions of alcohols to suggest the structures of the five compound **B–F**. Generally this question was answered well and most candidates scored three or more marks. The majority of candidates chose to use displayed formula. Other candidates opted to use skeletal formula and only a small proportion showed structural formulae.

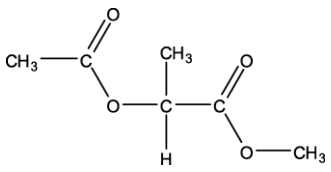
Almost all of the candidates were able to correctly calculate the molar mass of **B** as 74 g mol^{-1} which allowed most to suggest a structure for the compound. Many candidates used the information that **B** forms a ketone and provided the correct structure of butan-2-ol, although a significant proportion of candidates suggested **B** was butan-1-ol.

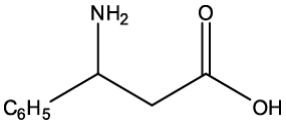
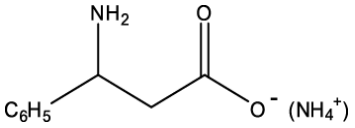
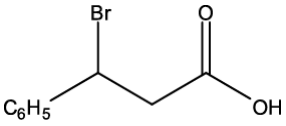
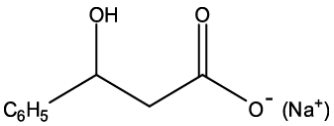
The more able candidates identified the structure of **C** as butanone, but a large proportion of the cohort did not suggest a structure. Some candidates who used displayed formula for **C** often included an extra hydrogen atom on the carbonyl group.

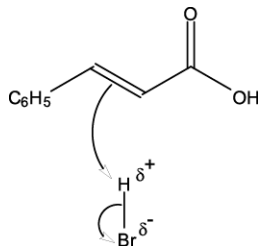
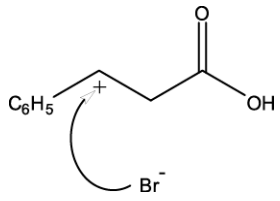
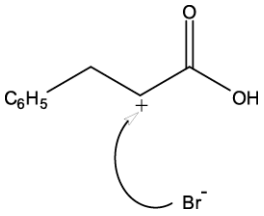
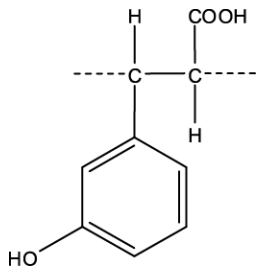
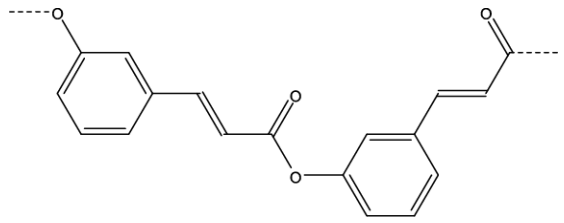
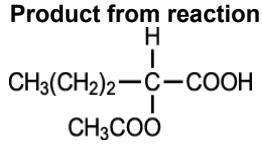
Most candidates were able to suggest a correct structure of carboxylic acid **D** and therefore deduced that the reaction between **B** and **D** was an esterification

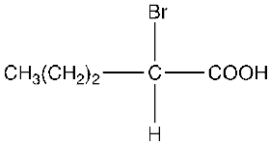
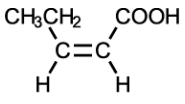
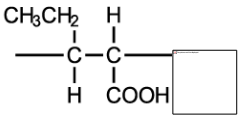
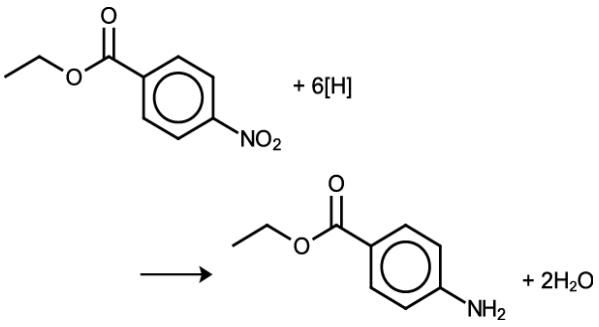
					reaction. The most difficult part of this question was identifying **E** and **F**. The most able candidates provided a correct structure for the ester, however some candidates often missed of one of the hydrogen atoms from their displayed formula. The most common incorrect response was to the structure of butyl propanoaoate. Some candidates identified the other compound formed in the reaction of **B** and **D** as water but a large proportion gave a second ester. In general the structures given by candidates were accurately drawn but candidates should be reminded to check their work carefully to ensure the correct number of atoms and bonds are present if using displayed formula.
			Total	**6**	
18	a	i	Using a pH probe on a data logger **OR** pH meter	1	
		ii	**FIRST CHECK THE ANSWER ON THE ANSWER LINE** **IF** answer = **0.11(0)** (mol dm^{-3}), award **2 marks** …… $n(NaOH) = \frac{0.125 \times 22.0}{1000} = 2.75 \times 10^{-3}$ (mol) concentration of $CH_3COOH = \frac{2.75 \times 10^{-3} \times 1000}{25.0}$ = 0.11(0) (mol dm^{-3})	2	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below. …… **ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW ECF:** *n*(NaOH) × 1000/25.00
	b	i	Brilliant yellow **AND** Vertical section / rapid pH change matches the pH range / end point / colour change (of the indicator)	1	**ALLOW** pH range (of the indicator) matches equivalence point **ALLOW** end point / colour change matches equivalence point **IGNORE** colour change matches end point (*colour change is the same as end point*)
		ii	 Explanation: Acid / H^+ reacts with A^- **AND** equilibrium (position) shifts towards HA (to give a red colour)	4	**ALLOW** direction of equilibrium shift if

			Alkali / OH^- reacts with HA/H^+ **AND** equilibrium (position) shifts towards A^- (to give a yellow colour) At end point, equal amounts of HA and A^- **AND** orange colour		equilibrium shown: $HA \rightleftharpoons H^+ + A^-$ i.e. 'towards HA' is equivalent to 'to left' i.e. 'towards A^-' is equivalent to 'to right' **ALLOW** yellow−red colour
			Total	**8**	
19	a	i		1	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous
		ii	**aqueous** acid **OR** H^+ / **H_2O**	1	**ALLOW** $H^+(aq)$ / $H_2SO_4(aq)$ / HCl(aq)
		ii i	Angle a = 109.5° Angle b = 104.5° Angle c = 120° **Two** correct All **three** correct	2	**ALLOW** 109–110° **ALLOW** 104–105°
	b	i	It is an electron pair donor **OR** donates a lone pair	1	
		ii	 Curly arrow from HO^- to carbon atom of C=O bond Correct dipole **AND** curly arrow from C=O bond to $O^{\delta-}$ ……  Curly arrow from negative charge on oxygen to C–O bond (to reform carbonyl π-bond) Curly arrow from C–O single bond to oxygen atom (to form methoxide ion)	4	Curly arrow must come from lone pair on O of HO^- **OR** OH^- **OR** from minus sign on HO^- ion (No need to show lone pair if curly arrow came from negative charge on O) **IGNORE** dipole on C–O single bond Curly arrow must come from lone pair on O **OR** from minus sign on O^- ion

					(No need to show lone pair if curly arrow came from negative charge on O)
		ii i	Correct organic product: HC*l* 	2	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous
			Total	**11**	
20		i	reaction with bases: neutralisation **AND** reaction with metals: redox	1	Enter text here.
		ii	correctly calculates $n(\mathbf{A}) = \frac{1.125}{90} = 0.0125\ (\text{mol})$ volume of $H_2 = \frac{0.0125}{2} \times 24{,}000 = 150\ \text{cm}^3$ **units** required	2	**ALLOW** 0.15 dm^3 **ALLOW ECF** from $n(\mathbf{A})$
		iii	$C_6H_{12}O_6Mg$	1	**DO NOT ALLOW** $(C_3H_6O_3)_2Mg$
		iv	Type of reaction of COOH: e.g. esterification **AND** reagents and conditions e.g. CH_3OH **AND** H_2SO_4 Organic product of COOH reaction Type of reaction of −OH **AND** reagents and conditions Organic product of −OH reaction	4	**ALLOW** esterification with any stated alcohol e.g. product from CH_3OH/H_2SO_4 → $CH_3(CHOH)COOCH_3$ Many possible reactions of secondary alcohol possible, e.g. oxidation with $K_2Cr_2O_7$ / H_2SO_4 + heat → $CH_3(CO)COOH$ elimination with H_2SO_4 / H_3PO_4 + heat → $CH_2 = CHCOOH$ esterification with CH_3COOH / H_2SO_4 **OR** CH_3COCl → $CH_3(CHOOCCH_3)COOH$ bromination with NaBr / H_2SO_4 → $CH_3(CHBr)COOH$ **ALLOW** self-polymerisation as reaction for either group (if another reaction example given) condensation polymerisation with H_2SO_4 → $[OCH(CH_3)CO]_n$

			Total	**8**	
21	a		**Product from NH_3/ethanol**  ……	3	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW**  **ALLOW ECF** from 2-bromo compound as product from Reaction 1 ……
			Product from Reaction 1  ……		**DO NOT ALLOW** 2-bromo compound *(inconsistent with final product shown)* …… **DO NOT ALLOW ECF** from 2-bromo compound as product from Reaction 1 *(inconsistent with final product shown)*
			Product from NaOH(aq)  		
	b		Curly arrow from C=C bond to H of H-Br Correct dipole shown on H–Br **AND** curly arrow showing the breaking of H-Br bond		**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous

					**DO NOT ALLOW** partial charges shown on C=C double bond
			……		**DO NOT ALLOW** δ+ on C of carbocation
			Correct carbocation **AND** curly arrow from Br^- to C^+ of carbocation		**ALLOW** formation of the 2-bromo isomer
					
			……		Curly arrow must come from a lone pair on Br^- **OR** from the negative sign of Br^- ion (then lone pair on Br^- ion does not need to be shown)
			Electrophilic addition		
	c	i		1	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous 'End bonds' **MUST** be shown (do not have to be dotted) **IGNORE** brackets **IGNORE** *n*
		ii		2	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous 'End bonds' **MUST** be shown (do not have to be dotted)
			Ester link		
			Rest of structure		
			Total	**10**	
22			Enter text here.		
		i	**Product from reaction 1**: 	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous.

			Product from reaction 2: 		
		ii	(*E*)-pent-2-enoic acid	1	**ALLOW** "*E*" with or without brackets
		iii	compound **H** =  addition polymer = 	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous. 'End bonds' **MUST** be shown (solid or dotted) **IGNORE** brackets and / or *n*
		iv	combustion for energy production use as an organic feedstock for the production of plastics and other organic chemicals	2	
			Total	**7**	
23		i	**step 1** = (conc.) H_2SO_4 **AND** CH_3CH_2OH	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous.
		ii	 **BOTH** organic structures balanced equation	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous.
			Total	**3**	