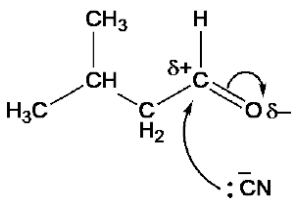
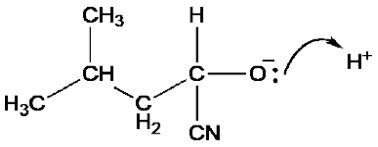
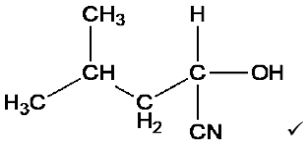
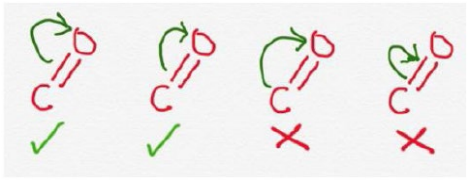
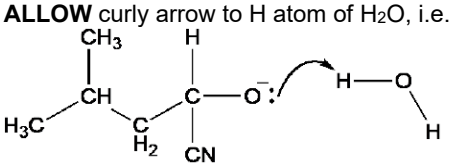
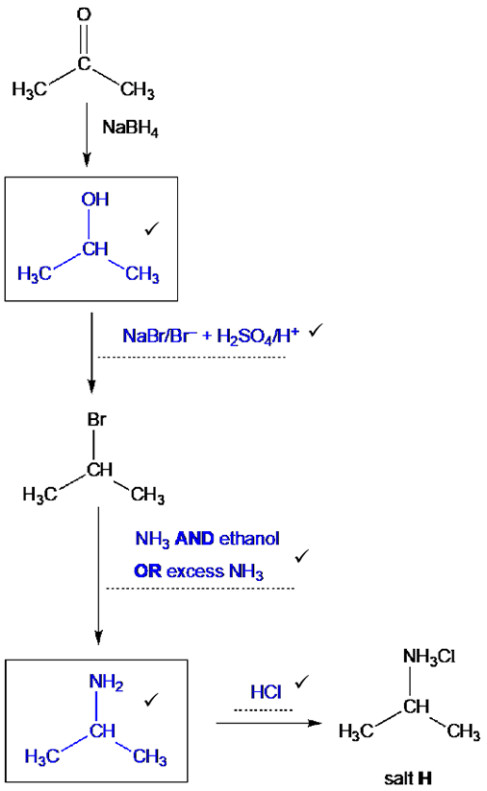
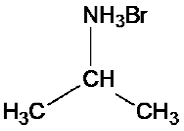
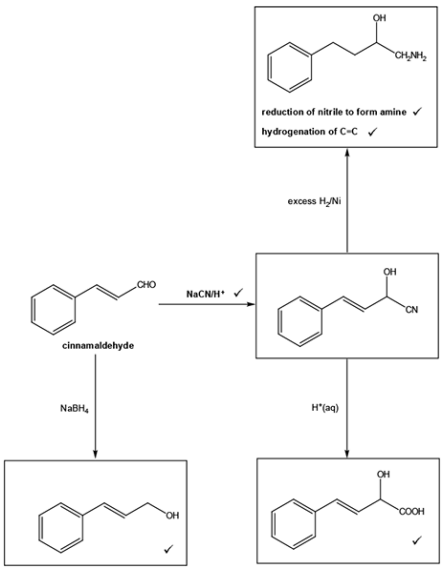
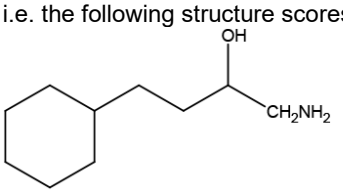
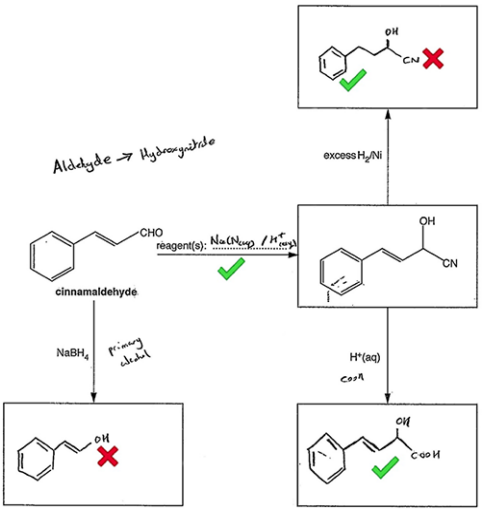
Mark scheme – Carbonyl Compounds

Question			Answer/Indicative content	Marks	Guidance
1	a		F/aldehyde **AND** Tollens' (reagent) **AND** Silver (mirror/precipitate/ppt/solid) ✓ G/alkene/C=C **AND** Bromine/Br2 **AND** goes colourless/decolourised ✓ G/ketone **AND** 2,4-dinitrophenylhydrazine **AND** orange/yellow/red precipitate ✓ G/ketone **AND** Tollens' (reagent) **AND** no silver mirror/no change/no reaction ✓	4 (AO2.3) (AO3.3) (AO3.3) (AO3.3)	**IGNORE** use of 2,4-DNP with F **ALLOW** ammoniacal silver nitrate **OR** Ag^+/NH_3 **ALLOW** black ppt **OR** grey ppt **ALLOW** bromine water/ $Br_2(aq)$ **ALLOW** errors in spelling for 2,4-DNP **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 **ALLOW** ammoniacal silver nitrate **OR** Ag^+/NH_3 **ALLOW** black ppt **OR** grey ppt **ALLOW** alterative approach using acidified potassium dichromate for tests with F and/or G, with correct observations, alongside use of 2,4-DNP **Examiner's Comments** Candidates who found this question difficult often did not give a response that would identify all three of the functional groups (aldehyde, ketone and alkene). The use of Tollens' in identifying aldehydes was well demonstrated, however no reaction with Tollens' was less well demonstrated as a result for ketones.
	b	i	**Mechanism** ***3 marks***  Curly arrow from ^-CN to C atom of C=O ✓ Dipole shown on C=O bond, $C^{\delta+}$ and $O^{\delta-}$,	5 (AO1.2) (AO1.2) (AO2.5) (AO2.5) (AO2.5) (AO1.1)	**ANNOTATE ANSWER WITH TICKS AND CROSSES** Curly arrow must come from lone pair on C of ^-CN **OR** CN^- **OR** from minus sign on C of ^-CN ion (then lone pair on CN^- does not need to be shown) Curly arrow from C=O bond must start from, OR be traced back to, any part of C=O bond and go to O

			AND curly arrow from C=O bond to O atom ✓  Curly arrow from lone pair **OR** – charge on O^- of **correct** intermediate to H^+ ✓ --- **Product** ***1 mark***  --- **Name of mechanism** ***1 mark*** Nucleophilic addition ✓		 --- **ALLOW** curly arrow to H atom of H_2O, i.e.  **IGNORE** attempt to draw curly arrow showing breaking of H–O in H_2O **IGNORE** lack of dipole on H_2O
		ii	**Heterolytic** One (bonded) atom/O receives both/2 electrons ✓ **Fission** Breaking of a **covalent** bond ✓	2 (AO1.2)	**ALLOW** 2 electrons go to one (bonded) atom/O **DO NOT ALLOW** both pairs of electrons go to O **IGNORE** formation of ions/radicals For O atom, **ALLOW** species **DO NOT ALLOW** element or molecule **ALLOW** π bond in C=O breaks **IGNORE** breaking of C=O bond (no reference to only one bond breaking) 'Bond breaking' is **not** sufficient *(no reference to covalent)* **Examiner's Comments** Candidates often referred to NaCN and HCN in their responses. Candidates who identified the correct bond breaking often then incorrectly wrote that the oxygen atom gained the lone pair of electrons.
			Total	**11**	

2				5 (AO2.5×5)	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** HBr **ALLOW** for the bottom left structure 
			Total	**5**	
3	a		Marks for each correct structure/reagent shown below 	**5**	**ANNOTATE WITH TICKS AND CROSSES** **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous For reaction with excess H_2/Ni **IGNORE** hydrogenation of benzene ring i.e. the following structure scores two marks  **ALLOW** KCN/H^+ **ALLOW** HCN **ALLOW** H_2SO_4 or HNO_3 or HCl for H^+ **Examiner's Comments** This question proved difficult and although the majority of candidates scored in some parts, only the very best responses secured all five marks. More detailed feedback is discussed with Exemplar 8.

Exemplar 8



Cinnamaldehyde was the starting point for this flowchart of reactions.

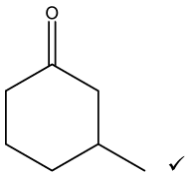
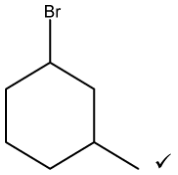
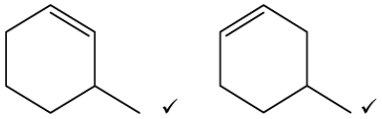
The most frequently scored mark was correct identification of the reagents required for the formation of the hydroxynitrile. This response uses $NaCN/H^+$. Other candidates used HCN which was also acceptable.

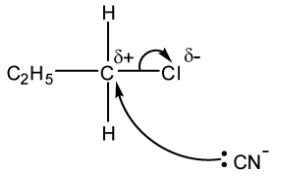
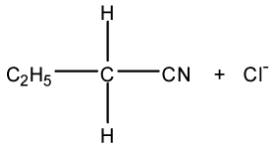
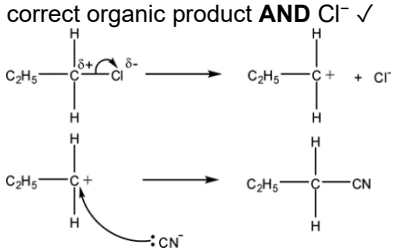
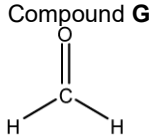
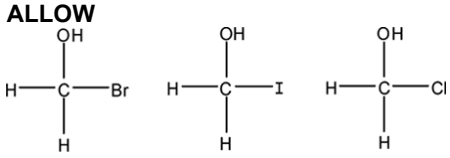
The flowchart shows two different reactions of this hydroxynitrile. The first is the reaction with excess hydrogen in the presence of Ni. Most candidates scored one mark for their product. As in this exemplar, the double bond was often reacted to form a saturated chain. Some candidates identified that the CN group would also react but instead of writing CH_2NH_2 they replaced the CN group with just NH_2, effectivity removing a carbon atom from the chain. The second reaction of the hydroxynitrile is acid hydrolysis of the CN group. This response identifies the correct carboxylic acid. However, this reaction seemed unfamiliar to many candidates and a range of incorrect responses were frequently seen.

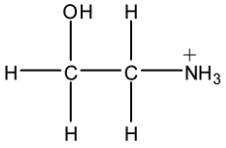
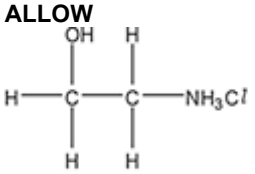
The final reaction is the reduction of cinnamaldehyde with $NaBH_4$. Many candidates recognised this reaction, but as can be seen in this response the alcohol group is shown on the incorrect carbon atom. This was a common error.

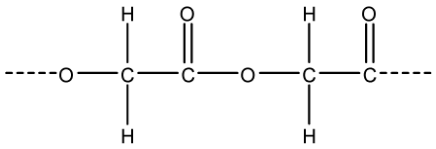
Candidates are advised to number carbon atoms present if provided with a complex structure, such as cinnamaldehyde. Numbering will ensure that each carbon is

					considered when drawing reaction products and would minimise errors, such as those demonstrated in the reduction product.
	b	i	Bromine/ Br_2 **AND** goes colourless/decolourised ✓	**1**	**Note:** both reagent and observation are required **ALLOW** bromine water/ $Br_2(aq)$ **Examiner's Comments** Almost all candidates were able to correctly describe the use of bromine as a test for an unsaturated chain.
		ii	Tollens' (reagent) **AND** Silver (mirror/precipitate/ppt/solid) ✓	**1**	**Note:** both reagent and observation are required for the mark. **ALLOW** ammoniacal silver nitrate **OR** Ag^+/NH_3 **ALLOW** black ppt **OR** grey ppt **Examiner's Comments** Almost all candidates were able to correctly describe the use of Tollens' reagent as a test for an aldehyde functional group.
		iii	(Add) 2,4-dinitrophenylhydrazine **AND** orange/yellow/red precipitate ✓ Take melting point (of crystals) ✓ Compare to known values/database ✓	**3**	**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 **Mark second and third points independently of response for first marking point** **DO NOT ALLOW** 2nd and 3rd marks for taking and comparing boiling points **OR** chromatograms **Examiner's Comments** The use of 2,4-dinitrophenylhydrazine as a test for the carbonyl group is well known by candidates at this level. The majority of the cohort correctly identified this test and the subsequent analysis of the melting point of the products as a method of identifying each compound. Lower ability candidate responses made reference to analysis of the boiling points of the cinnamaldehyde and methylcinnamaldehyde as a means of identification.

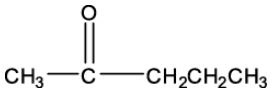
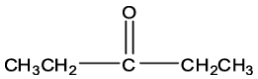
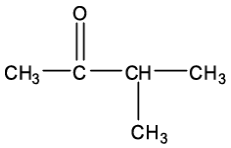
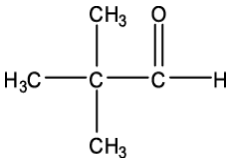
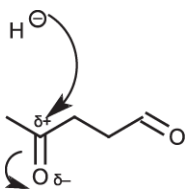
			Total	**10**	
4		i	**Starting material from reduction reaction**  ✓ **Reagent for reduction** $NaBH_4$ ✓ **Product from reaction with $NaBr/H_2SO_4$**  ✓ **Structural isomers**  ✓ ✓	**5**	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous Watch for missing methyl groups **IGNORE** H^+ / acid or H_2O or ethanol **ALLOW** sodium borohydride **OR** sodium tetrahydridoborate **ALLOW** $LiAlH_4$ **ALLOW** in either order **Examiner Comments** There were many good answers to this synthesis question with about 40% of the cohort scoring full marks. The structure of the carbonyl and the reagent needed for reduction were well known by a majority of candidates however some reacted the alcohol group with sodium bromide to obtain $-O^-Na+$ for the second structure. Weaker candidates did not realise that an alcohol could be dehydrated and thus failed to be awarded the final two marks.
		ii	3-methylcyclohexanol ✓	**1**	**ALLOW** 3-methylcyclohexan-1-ol **ALLOW** 1-methylcyclohexan-3-ol **IGNORE** lack of hyphens, or addition of commas **Examiner Comments** Just over half of candidates managed to name the structure as 3-methylcyclohexanol. The most common errors included 3-methylphenol, 3-methylcyclichexanol and 3-methylhexanol.
			Total	**6**	
5		i	curly arrow from ^-CN to carbon atom of C−C*l* bond ✓ Dipole shown on C–C*l* bond, $C^{\delta+}$ and $Cl^{\delta-}$, **AND** curly arrow from C−C*l* bond to C*l* atom ✓	**2**	**ANNOTATE ANSWER WITH TICKS AND CROSSES** Curly arrow must come from lone pair on C of ^-CN OR CN^- **OR** from minus sign on C of ^-CN ion (then lone pair on CN^- does not need to be shown)

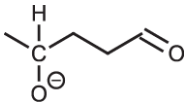
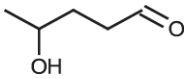
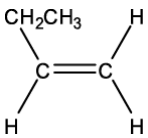
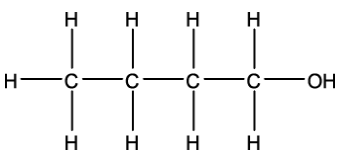
			 correct organic product **AND** C*l*-✓ 		**IGNORE** NaCl **ALLOW** S_N1 mechanism: Dipole shown on C–Cl bond, $C^{\delta+}$ and $Cl^{\delta-}$, **AND** curly arrow from C–C*l* bond to C*l* atom ✓ Correct carbocation **AND** curly arrow from ^-CN to carbocation. Curly arrow must come from lone pair on C of ^-CN **OR** CN^- **OR** from minus sign on C of ^-CN ion (then lone pair on CN^- does not need to be shown) ✓ correct organic product **AND** Cl^- ✓  **Examiner Comments** The mechanism for the reaction of 1-chloropropane was well done with the majority of candidates scoring two or three of the marks. Marks were not awarded when candidates used a negative charge or a lone pair sited on the nitrogen as the starting point for a curly arrow in the first stage of the reaction mechanism. The final marking point was awarded for the production of a Cl^- ion. The placing of curly arrows, dipoles and lone pairs of electrons are important when communicating by mechanisms.
		ii	Compound **G**  ✓ **Reagents** **Reaction 2:** H_2 **AND** Ni ✓ **Reaction 3:** Correct formula of an aqueous acid e.g. HC*l*(aq)/H_2SO_4(aq) ✓	**3**	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **IGNORE** name(s) **ALLOW**  **ALLOW** any suitable metal catalyst e.g. Pt **ALLOW** $LiAlH_4$ for reagent in reaction 2 **DO NOT ALLOW** $NaBH_4$ for reagent in reaction 2 **IGNORE** names *(question asks for formulae)* **IGNORE** references to temperature and/or pressure **ALLOW** H^+(aq) **IGNORE** dilute **ALLOW** formula of an acid **AND** water

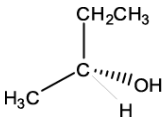
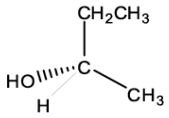
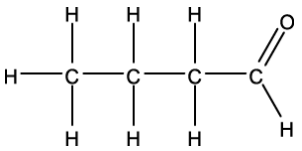
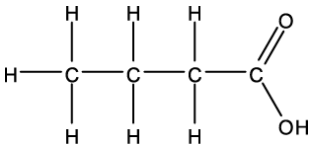
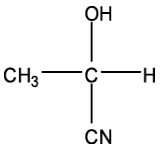
					e.g. HC*l* **AND** H_2O H_2SO_4 **AND** H_2O **Examiner Comments** Although many candidates were able to provide the structure of methanal as the starting material for this synthesis, the structures of chloromethanol, bromomethanol and iodomethanol were accepted as suitable alternatives. It should be noted that hydrolysis is carried out using aqueous acid and that dilute acid is not a suitable alternative.
		iii	**Explanation** Nitrogen electron pair **OR** nitrogen lone pair **AND** accepts a proton / H^+✓ **Structure of salt**  **AND** Cl^- ✓	**2**	**IGNORE** NH_2 group donates electron pair **ALLOW** nitrogen donates an electron pair to H^+ **DO NOT ALLOW** nitrogen donates lone pair to acid **IGNORE** comments about the O in the –OH group Compound **H** is a base is **not sufficient** *(role of lone pair required)* **DO NOT ALLOW** nitrogen/N lone pair accepts hydrogen (*proton/H^+ required*) **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW**  *i.e.* charges **not** required **IF** charges are shown **both** need to be present **ALLOW** charge either on **N** atom or NH_3^+ **IF** displayed then + charge must be on the nitrogen **Examiner Comments** Only 20% of candidates were awarded both marks for this question. The commonest error was a failure to state that the N atom has a lone pair of electrons that can gain a proton. Answers stating that amines accept protons or that a salt is produced when an acid reacts with a base were not credited. Where a full displayed structure is given the positive charge must be shown on the nitrogen atom, although $-NH_3^+$ is acceptable. As the question required the formula of the salt, the Cl^- had to be included.

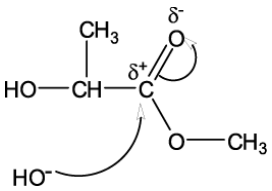
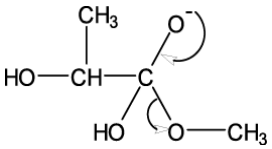
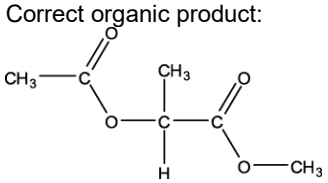
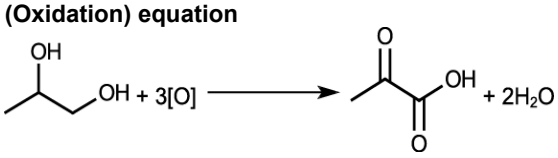
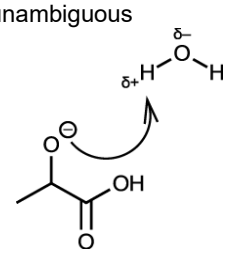
		iv	 Ester link ✓ Rest of structure✓ (polymer **J** is biodegradable because) the ester / ester bond / ester group / polyester can be hydrolysed✓	**3**	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **DO NOT ALLOW** more than two repeat units for second marking point. 'End bonds' **MUST** be shown (do not have to be dotted) **IGNORE** brackets **IGNORE** ***n*** Broken down by water is **not** sufficient **IGNORE** references to photodegradable **Examiner Comments** The most common mark for this question was two out of the three marks available, with candidates giving a correct structure of the polymer but failing to express that the polymer was biodegradable due the ability of the ester functional group to undergo hydrolysis.
			Total	**11**	
6	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) ✓ **Equation** RCHO + [O] → RCOOH ✓	2	**Note:** both reagent and observation are required for first mark **ALLOW** ammoniacal silver nitrate **OR** 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)*

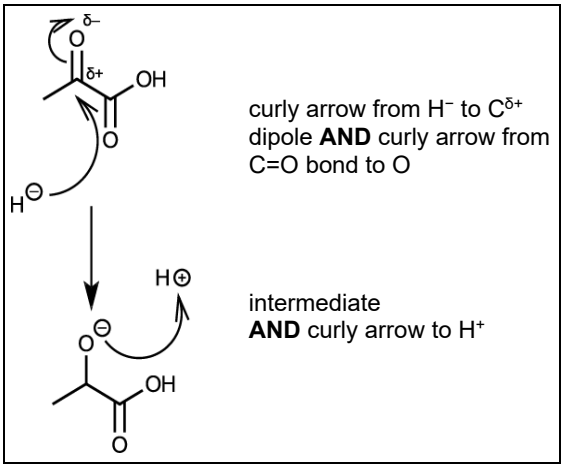
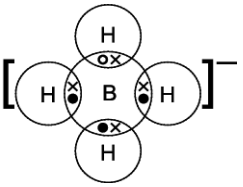
	b		2,4−dinitrophenylhydrazine **AND** Orange/yellow/red precipitate ✓	1	**ALLOW** errors in spelling **ALLOW** 2,4(−)DNP **OR** 2,4(−)DNPH **ALLOW** Brady's reagent or Brady's Test **ALLOW** solid **OR** crystals **OR** ppt as alternatives for precipitate
	c	i	$CH_3COOC(CH_3)_3 + NaOH \rightarrow CH_3COONa + (CH_3)_3COH$ 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)*
		iii	**^{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 (^{1}H NMR spectrum of) $CH_3COOC(CH_3)_3$ has a singlet/peak between 2.0−3.0 (ppm)	3	**ALLOW** 'same number of peaks' in place of 'four peaks' **ALLOW** any value or range of values within 2.0−3.0

			(^{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 3.0−4.3
	d		**Possible structures for ketone (2 marks)**    All **three** correct ✓✓ Any **two** correct ✓ **Aldehyde (3 marks)** 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**	
7			 curly arrow from H^- to C($^{\delta+}$) of correct C=O group ✓	4	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous First curly arrow must come from either a lone pair on H or negative charge on H **IF** aldehyde reduced **OR** both carbonyls reduced

			dipole correct **AND** curly arrow from C=O bond to O($^{\delta-}$) ✓  correct intermediate with negative charge on O ✓  correct product ✓		**DO NOT AWARD** first mark (second, third and fourth marks can be awarded **ECF**) **IGNORE** lack of C—H if entirely skeletal **IGNORE** curly arrows in second stage Apply ecf to error in structure e.g. CH_2 missing from the chain or —COOH / -COH instead of —CHO **IGNORE** other products **Examiner's Comments** Good candidates had no problem with this reaction mechanism. Some did not read the question carefully and reduced the wrong carbonyl group. Other errors included an incorrect starting position for the first curly arrow, the omission of a CH_2 unit from the carbon chain or changing the aldehyde functional group to a carboxyl group.
			Total	**4**	
8	a		**F–K** clearly identified **Compound F:**  **Compound G:**  **Compounds H and I:**	6	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **IGNORE** names **H** and **I** can be identified either way round

			 		
			Compound J: 		
			Compound K: 		
	b		(Add) 2,4-dinitrophenylhydrazine **AND** orange/yellow/red precipitate	3	**NOTE: (b)** is marked completely independently of **(a)**
					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
			Take melting point of crystals		**Mark second and third points independently of response for first marking point**
			Compare to known values		
					DO NOT ALLOW 2nd and 3rd marks for taking and comparing boiling points **OR** chromatograms
			Total	**9**	
9	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** $H^+(aq)$ / $H_2SO_4(aq)$ / $HCl(aq)$
		iii	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)
		iii	Correct organic product:  HC*l*	2	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous
			Total	**11**	
10		i	Oxidising agent = acidified (potassium / sodium) dichromate(VI) **(Oxidation) equation**  **(Reduction) mechanism**	5	**ALLOW** $Cr_2O_7^{2-}$ **OR** $K_2Cr_2O_7$ **OR** $Na_2Cr_2O_7$ for dichromate **ALLOW** H^+ **OR** (conc.) sulfuric acid for "acidified" **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous 

			 curly arrow from H^- to $C^{\delta+}$ dipole **AND** curly arrow from C=O bond to O intermediate **AND** curly arrow to H^+		**ALLOW** for second stage **IF** H_2O is used it **MUST** show the curly arrow from the intermediate to $H^{\delta+}$ in H_2O **AND** from the O—H bond to the O **IGNORE** product **IGNORE** stereochemistry of intermediate
		ii	$Na^+ [$  $]^-$ $1s^2\ 2s^2\ 2p^6$	2	**IGNORE** inner electron shells for both ions Three different symbols required to identify electrons from different elements **DO NOT ALLOW** [Ne] **OR** [He] $2s^2\ 2p^6$
			Total	**7**	