2016

6. *(a)* Geoff was given an unknown alcohol of molecular formula $C_4H_{10}O$. It was labelled **A**. He performed the following tests and noted his results in order to find the identity of **A**.

Test	Results
1. Heat **A** with acidified potassium dichromate(VI), distilling the product as it forms	Colourless liquid **B** is formed
2. Heat **A** with ethanoic acid and sulfuric acid	Sweet smelling liquid **C** is formed
3. Reflux **A** with acidified potassium dichromate(VI), followed by distillation	Colourless liquid **D** is formed
4. Add sodium hydrogencarbonate solution to liquid **D**	Effervescence of CO_2 and compound **E** is formed

After analysing his results Geoff concluded that compound **A** must be butan-1-ol. Assume that he is correct in order to answer parts (i) and (ii).

(i) Name compounds **B** and **C**. [2]

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(ii) Give the formula of compound **E**. [1]

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(iii) By considering all the alcohols of formula $C_4H_{10}O$, state if you agree with Geoff's conclusion. Give reasons to justify your answer. [5]

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(iv) Draw a labelled diagram of the apparatus Geoff should use to carry out the **distillation** in test 3. [3]

(b) 1-Chlorobutane can be warmed with aqueous sodium hydroxide to form butan-1-ol.

(i) Classify the type of reaction mechanism occurring and draw the mechanism for this reaction. [4]

Type of reaction mechanism .....

(ii) Use the infrared absorption frequencies given in the Data Sheet to explain how you would know if **all** the 1-chlorobutane has been converted into butan-1-ol. [2]

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(iii) 1-Iodobutane also reacts with aqueous sodium hydroxide to form butan-1-ol. State, giving a reason, if this reaction is faster or slower than the one between 1-chlorobutane and aqueous sodium hydroxide under the same conditions. [1]

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6.	*(a)*	(i)		**B** = Butanal (1) **C** = Butyl ethanoate (1)		2		2		
		(ii)		C_3H_7COONa Accept NaC_3H_7COO		1		1		
		(iii)		Other possible structures are butan-2-ol, methylpropan-2-ol, methylpropan-1-ol (2) (Accept displayed formulae) (1) for 2 correct structures Cannot be methylpropan-2-ol / must be primary or secondary alcohol since it is oxidised (1) Cannot be butan-2-ol / must be primary alcohol since it is oxidised to acid (1) Could be methylpropan-1-ol since it is a primary alcohol (1)		2	1 1 1	5		
		(iv)		Thermometer with bulb opposite outlet to condenser (1) Condenser with correct water connections (1) Suitable overall diagram	3			3		3
6.	*(b)*	(i)		Nucleophilic substitution (1) Polarisation of C—Cl (1) Curly arrow from OH^- (1) Curly arrow to show C—Cl breaking / intermediate (1)	1 1 1	1		4		
		(ii)		No peak at 650–800 cm^{-1} due to C—Cl bond (1) Peak at 2500–3500 cm^{-1} due to O—H bond Accept peak at 1000–1300 cm^{-1} due to C—O bond (1)		2		2		
		(iii)		Faster since C— I bond weaker than C—Cl bond	1			1		
				Question 6 total	**7**	**8**	**3**	**18**	**0**	**3**

(b) A compound is known to be either 1-chlorobutane or 1-iodobutane. Describe a test to show that the compound is 1-chlorobutane. Give any reagent(s) used and expected observation(s). [3]

(c) 1-Chlorobutane can undergo an elimination reaction with hydroxide ions.

(i) Draw the displayed formula of the organic product of this reaction. [1]

(ii) State the conditions required for this reaction. [1]

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(d) Explain why 1-chlorobutane has a higher boiling temperature than chloroethane. [2]

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(e) CFCs have been shown to be serious pollutants due to their contribution to ozone depletion. Chemists are now replacing them with HFCs. Suggest **two** properties which HFCs should have. [2]

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(f) The mass spectrum of a CFC shows two major signals at m/z 135 and 137 in the ratio of 3:1 and molecular ion peaks at 170, 172 and 174.

The CFC contains 14.0 % carbon, 44.5 % fluorine and 41.5 % chlorine by mass.

It only has one peak in its ^{13}C NMR spectrum.

Use the information to find the structural formula for the CFC. Explain your reasoning.

[5]

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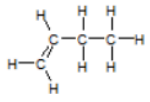
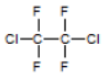
7.	*(b)*			Heat with aqueous sodium hydroxide (1) Add nitric acid and aqueous silver nitrate (1) White precipitate observed (1)	3			3		3
	(c)	(i)				1		1		
		(ii)		Dissolved in ethanol + heated	1			1		1
	(d)			It has stronger/more Van der Waals forces (1) Because it has a larger surface area / hydrocarbon chain (1)		2		2		

7.	*(e)*			Any two of following for (1) each • non-flammable • non-toxic • suitable volatility	2			2		
	(f)			C F Cl 14.0 44.5 41.5 12 19 35.5 1.17 2.34 1.17 (1) 1 2 1 Empirical formula is CF_2Cl (1) Mass spectrum shows two chlorines in molecule / shows that M_r is 171 (1) Molecular formula is $C_2F_4Cl_2$ (1) Only one carbon environment so formula is  (1)		1 1 1 1			1	
							1	5		

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6. Give a chemical test which could be used to show the presence of a carboxylic acid group, —COOH. Your answer should include all reagents and observations. [2]

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6				add Na_2CO_3 / $NaHCO_3$ (1) bubbles seen (1)	2			2		2

(c) Propene reacts with hydrogen bromide to give 2-bromopropane as the major product.

(i) Draw the mechanism for this reaction. [3]

(ii) State briefly why 2-bromopropane is the main product of this reaction. [1]

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(d) 1-Bromopropane is used in the synthesis of many organic compounds.

(i) Classify the type of reaction mechanism taking place when propan-1-ol is formed from 1-bromopropane. [1]

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(ii) Give the reagent(s) and conditions necessary to convert 1-bromopropane to propene. [1]

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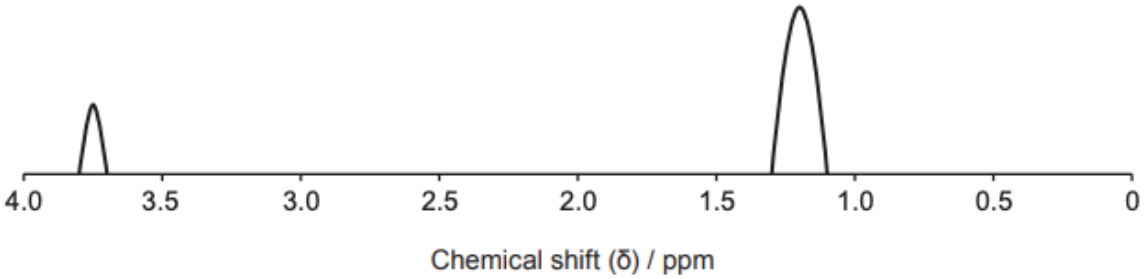
(e) A student was given a sample of bromopropane but was not told which isomer it was. The low resolution ^1H NMR spectrum of the sample is shown below.



Deduce which isomer the student was given and hence the relative areas under each peak. Give your reasoning. [2]

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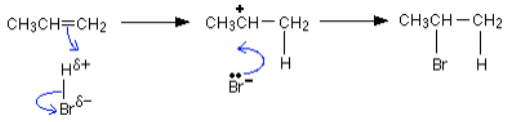
	(c)	(i)		 dipole and curly arrow in HBr (1) curly arrow from double bond (1) curly arrow from Br^- to carbocation (1)	3			3		
		(ii)		secondary carbocation is more stable than primary carbocation	1			1		
	(d)	(i)		nucleophilic substitution	1			1		
		(ii)		alcoholic potassium/sodium hydroxide (+ heat)	1			1		1
	(e)			2-bromopropane since only two different proton environments (1) relative areas of the peaks must be 6:1 (1)			2	2		

8. *(a)* A student was asked to prepare ethanoic acid from ethanol using the following method.

- Pour 10 cm^3 of dilute sulfuric acid into a round-bottomed flask.
  Add 5 g of a suitable reagent and 2-3 anti-bumping granules.
- Swirl the flask gently until all the reagent has dissolved.
- Add 2 cm^3 of concentrated sulfuric acid and cool the flask under running water.
- Set up the apparatus for heating under reflux. Add 12.0 cm^3 of ethanol, drop by drop, to the solution in the round-bottomed flask.
- When all of the ethanol has been added, boil gently under reflux for 20 minutes, not allowing any vapour to escape.
- Distil the mixture in the flask and collect the aqueous solution of ethanoic acid formed.

(i) Name the type of reaction taking place, giving a suitable reagent. [2]

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(ii) Draw a labelled diagram of the apparatus you would use for heating under reflux. Explain how this apparatus prevents the escape of vapour. [4]

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(iii) Give **two** reasons why the escape of vapour should be prevented. [2]

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(iv) Ethanol has a density of $0.79\,g\,cm^{-3}$ at room temperature. Calculate the number of moles of ethanol in $12.0\,cm^3$. [2]

n = ... mol

(v) In another experiment, the same reaction mixture was only gently heated and the product distilled off as it was formed. Explain why ethanoic acid is not produced in this instance. [2]

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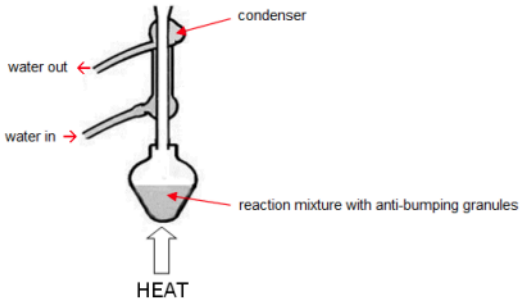
(b) In another preparation of ethanoic acid from ethanol, 10.2 g of pure ethanoic acid were obtained. The percentage yield of ethanoic acid was 65 %.

Calculate the mass of ethanol used in the preparation. [3]

Mass = ... g

8	(a)	(i)		oxidation (1) potassium dichromate(VI) (1)	2			2		2
		(ii)		 flask with vertical condenser (1) unsealed apparatus (1) heat (1) reaction mixture being heated returns to the flask / vapour is (cooled and) condensed (1)	4			4		4

		(iii)		any two of following for (1) • yield would be reduced / reactants (products) would be lost • complete oxidation could not occur • vapour is flammable / acidic			2	2		2
		(iv)		0.206 (2) if answer is incorrect award (1) for mass of ethanol = 9.48 g ecf possible from incorrectly calculated mass		2		2	2	
		(v)		ethanal / aldehyde is formed (1) only partial oxidation occurs (1)		2		2		
	(b)			0.170 mol of ethanoic acid (1) from 0.262 mol of ethanol (1) 12.0 (1) ecf possible throughout		3		3	1 1	

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(d) Butane is another common alkane. Two other compounds with a similar molecular mass to butane are ethanoic acid and propan-1-ol.

The boiling temperatures in °C for butane, ethanoic acid and propan-1-ol are

–1, 97 and 118, **but not necessarily in that order**.

Deduce the boiling temperature of **each** compound, giving reasons in support of your conclusions. [3]

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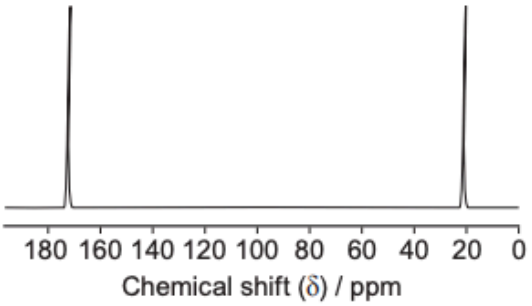
(e) Compounds **A** and **B** are two of butane, ethanoic acid and propan-1-ol.

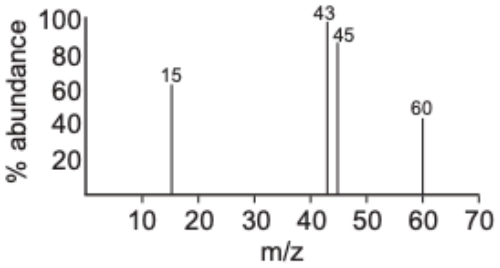
Their ^{13}C NMR spectra and simplified mass spectra are shown below.

Compound **A**

^{13}C NMR spectrum

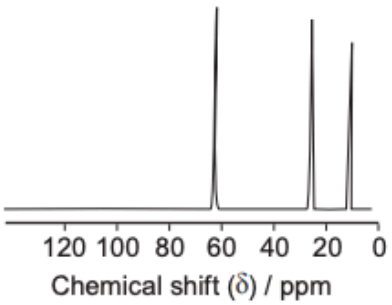


Mass spectrum

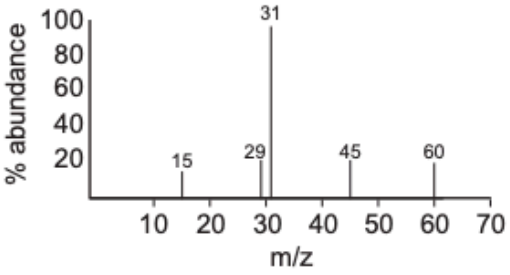


Compound **B**

^{13}C NMR spectrum



Mass spectrum



Use the information to identify compounds **A** and **B** clearly explaining your reasoning. Describe the main features that would be seen in the ^{13}C NMR spectrum and the mass spectrum of the **remaining** compound. [6 QER]

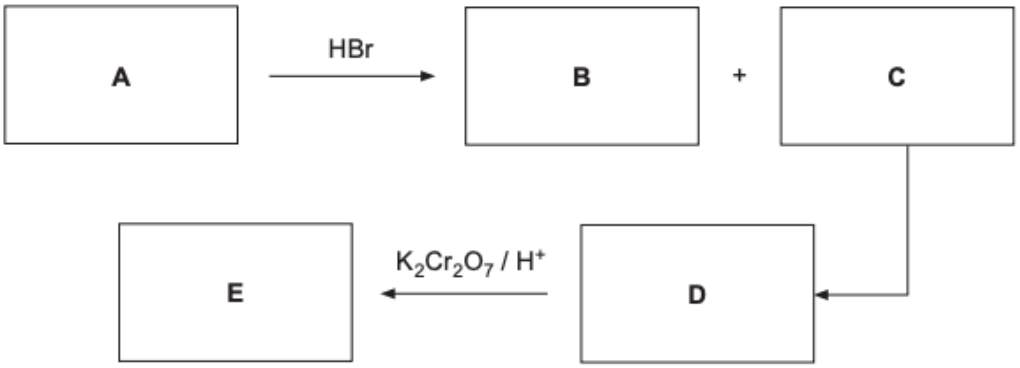
(f) State and explain how you would expect the infrared spectrum of ethanoic acid to differ from that of propan-1-ol. [2]

	(d)			butane −1°C, propan-1-ol 97°C, ethanoic acid 118°C (1) butane shows no hydrogen bonding between molecules (1) ethanoic acid has more/stronger hydrogen bonds between molecules than propan-1-ol (1) (accept answers in terms of more dipoles)		3		3		

	(e)			**Indicative content** • **A** is ethanoic acid, **B** is propan-1-ol • ^{13}C NMR for butane has 2 peaks between 5 and 40 ppm • ^{13}C NMR ethanoic acid has 2 peaks but propan-1-ol has 3 peaks • both have peaks at m/z 60 due to molecular ion (butane does not) • both have peaks at m/z 45 due to $COOH^+$ and $CH_2CH_2OH^+$ respectively (butane does not) • mass spectrum for butane has peaks at m/z 15, 29, 43 and 58 • propan-1-ol has a peak at m/z 29 due to $CH_3CH_2^+$ and m/z 31 due to CH_2OH^+ (ethanoic acid does not) • ethanoic acid has a peak at m/z 43 due to CH_3CO^+ (propan-1-ol does not)		4	2	6		
				5-6 marks Correctly identifies compounds giving a comprehensive explanation and gives details of spectra for butane. *The candidate constructs a relevant, coherent and logically structured method including all key elements of the indicative content. A sustained and substantiated line of reasoning is evident and scientific conventions and vocabulary is used accurately throughout.* **3-4 marks** Correctly identifies compounds giving good basic explanation and gives details relating to one spectrum for butane. *The candidate constructs a coherent account including most of the key elements of the indicative content. Some reasoning is evident in the linking of key points and use of scientific conventions and vocabulary are generally sound.* **1-2 marks** Correctly identifies compound(s) giving some explanation. *The candidate attempts to link at least two relevant points from the indicative content. Coherence is limited by omission and/or inclusion of irrelevant material. There is some evidence of appropriate use of scientific conventions and vocabulary.* **0 marks** *The candidate does not make any attempt or give an answer worthy of credit.*						

	(f)			only ethanoic acid would have an absorption at 1650-1750 cm^{-1} due to presence of the C=O bond (1) ethanoic acid would have an absorption at 2500-3200 cm^{-1} due to the presence of the O—H bond, while the absorption due to O—H in propan-1-ol would be at 3200-3550 cm^{-1} (1)	2			2		

8. *(a)* Study the reaction scheme shown below and the other information about compounds **A-E** that follows.



Compound **A** is a straight-chained gaseous hydrocarbon.

Compounds **B** and **C** are isomers.

Compound **E** reacts with sodium hydroxide in a 1:1 molar ratio.

0.412 g of compound **E** in aqueous solution requires 23.40 cm^3 of sodium hydroxide solution of concentration 0.200 mol dm^{-3} for complete neutralisation.

(i) Calculate the relative molecular mass of compound **E**. [2]

Relative molecular mass = ...

(ii) Identify compounds **A**-**E** giving your reasoning. [7]

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(iii) Name the type of reaction taking place when compound **B** is converted back to compound **A**. [1]

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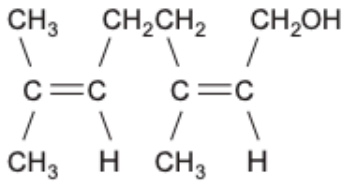
(b) Geraniol is one of the main constituents of rose oil and is widely used in perfumes and flavourings. Its structure is shown below.



(i) Name the functional groups present in the compound. [1]

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(ii) State the **molecular** formula of the compound. [1]

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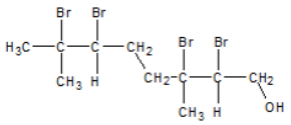
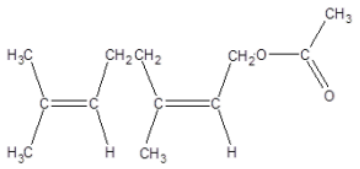
(iii) Draw the structure of an organic product formed when geraniol reacts with

I. Br_2 [1]

II. CH_3COOH in the presence of sulfuric acid [1]

8.	(a)	(i)		moles NaOH = $0.2 \times 23.4/1000 = 4.68 \times 10^{-3}$ therefore 4.68×10^{-3} moles of **E** (1) M_r(**E**) = $0.412/4.68 \times 10^{-3} = 88.03$ (1)		2		2	1	
		(ii)		**A** is but-1-ene (1) **B** is 2-bromobutane (1) **C** is 1-bromobutane (1) **D** is butan-1-ol (1) **E** is butanoic acid (1) award (1) each for any two of following • **E** must be acid since neutralised by NaOH • **D** must be primary alcohol since oxidised to acid • **A** must be alkene since reacts with HBr • **B/C** must be bromoalkane since formed from alkene (and **C** forms alcohol)		5	2	7		
		(iii)		elimination	1			1		
	(b)	(i)		alkene / C=C **and** alcohol / hydroxyl	1			1		
		(ii)		$C_{10}H_{18}O$	1			1		
		(iii)	I	 accept addition across 1 double bond only		1		1		
			II	 ignore error in chain		1		1		

(e) A student was given separate samples of pentan-2-ol and 2-methylbutan-2-ol but was not told which was which.

Describe a chemical test that the student could use to clearly distinguish between the alcohols. Give any reagent(s) used and expected observation(s) for both compounds. [3]

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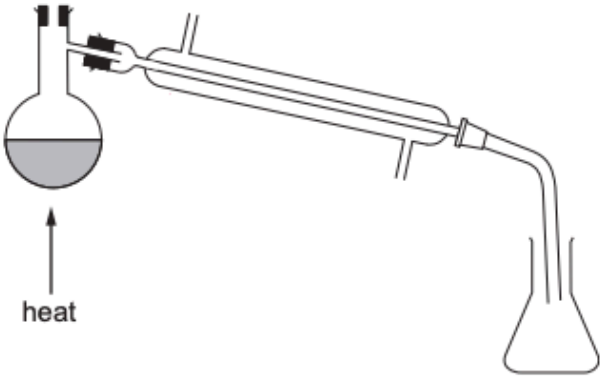
(f) Another student wanted to make pure 2-chloro-2-methylbutane from 2-methylbutan-2-ol in a multi-step process. One of the steps used was distillation.

(i) An incomplete diagram of the distillation apparatus is shown below.



Complete the diagram by drawing a thermometer and clearly labelled arrows to show the flow of water into and out of the condenser. [2]

(ii) The student predicted that since this was a multi-step process the overall yield would be less than 70 %.

In the process, 5.00 cm^3 of 2-methylbutan-2-ol were used and 4.05 cm^3 of 2-chloro-2-methylbutane were made.

Is the student correct? Use the following information to justify your answer. [3]

Compound	Density / g cm^{-3}
2-methylbutan-2-ol	0.805
2-chloro-2-methylbutane	0.866

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

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	(e)			reflux both with acidified potassium dichromate (1) colour changes from orange to green with pentan-2-ol (1) no change with 2-methylbutan-2-ol (1)		3		3		
	(f)	(i)		thermometer bulb adjacent to outlet leading to condenser (1) water in through lower tube and out through upper tube (1)	2			2		2
		(ii)		mass of alcohol = 5 × 0.805 = 4.025 moles of alcohol = 4.025 ÷ 88 = 0.0457 (1) theoretical mass of chloroalkane = 0.0457 × 106.5 = 4.87 actual mass chloroalkane = 4.05 × 0.866 = 3.51 g (1) percentage yield = 3.51/4.87 × 100 = 72% therefore student is incorrect (1)			3	3	2	

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7. Ethanoic acid, CH_3COOH, is a typical organic acid.

Write the equation for the reaction between ethanoic acid and magnesium oxide. [1]

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7				$2CH_3COOH + MgO \rightarrow (CH_3COO)_2Mg + H_2O$		1		1		

8. *(a)* Discuss how 1-bromobutane can react with hydroxide ions under different conditions to give two different organic products.

Draw the mechanism for the formation of **one** of the organic products. [6 QER]

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(b) Chloroethane is formed when ethane reacts with chlorine in sunlight. However, during the reaction a mixture of products is obtained.

(i) Name the type of reaction mechanism taking place. [1]

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(ii) Explain why butane can also form during this reaction. [2]

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(c) Halogenoalkanes can also be formed from alkenes.

When 3-methylbut-1-ene is reacted with hydrogen bromide a mixture of two different products is formed.

(i) Identify the products. [2]

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(ii) State and explain which of the two products is more likely to be formed. [1]

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(d) Halogenoalkanes containing both chlorine and fluorine are known as CFCs. One of the most abundant CFCs in the atmosphere is trichlorofluoromethane, CCl_3F.

Explain why CCl_3F remains longer in the troposphere (lower atmosphere) of the Earth than in the stratosphere (upper atmosphere). [2]

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8	*(a)*			**Indicative content** • types of mechanism - nucleophilic substitution and elimination • reaction conditions NaOH dissolved in water for nucleophilic substitution NaOH dissolved in ethanol for elimination • products - butan-1-ol and but-1-ene / equations • mechanism for nucleophilic substitution polarisation of C–Br curly arrow from OH^- curly arrow showing C–Br breaking / intermediate	6			6		
	(b)	(i)		radical substitution accept photochlorination	1			1		
		(ii)		during the reaction ethyl radicals form (1) two of these radicals can combine to give butane (1)	2			2		
	(c)	(i)		award (1) for each product 1-bromo-3-methylbutane 2-bromo-3-methylbutane accept correct structures award (1) if Br in correct place but error in structures		2		2		
		(ii)		2-bromo-3-methylbutane since intermediate carbocation formed is more stable		1		1		
	(d)			CFCs are very stable and they do not break down easily in the lower atmosphere since the C—F and C—Cl bonds are strong / energy from uv light not strong enough to break C—F or C—Cl bond (1) in the upper atmosphere higher energy uv light breaks the C—Cl bond forming chlorine radicals (1)		1	1	2		

10. *(a)* A student is asked to prepare a sample of ethanal by oxidising ethanol.

(i) Write an equation for this reaction. [1]

Use [O] to represent the oxidising agent and show the structure of the organic product.

(ii) Describe, giving brief experimental details, how he can carry out the reaction. [4]

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(iii) Ethanol can also be oxidised to ethanoic acid. Describe how the student could use a chemical test to confirm that his sample of ethanal did **not** contain ethanoic acid. [2]

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(b) State a difference and a similarity between the ^{13}C NMR spectra of ethanal and ethanol. [2]

Difference .....

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Similarity .....

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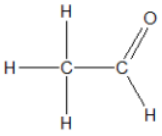
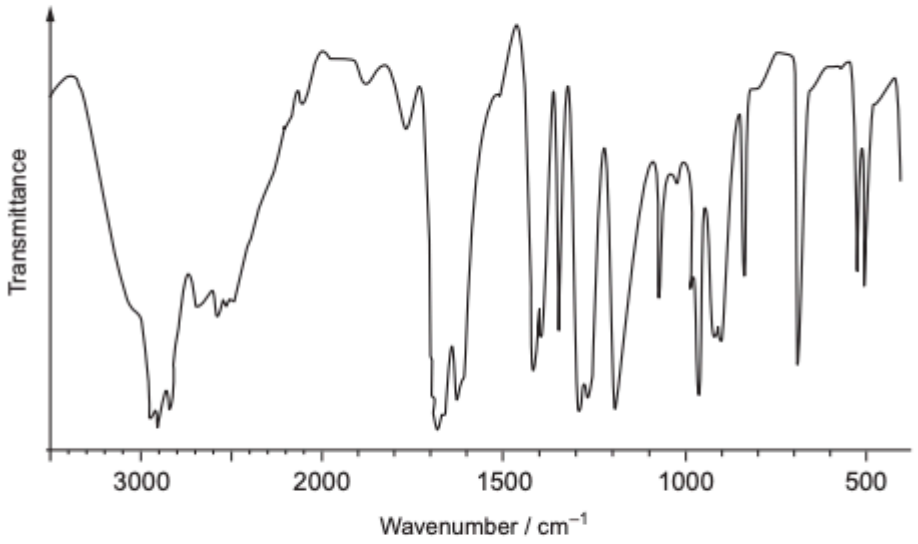
10	*(a)*	(i)		$C_2H_5OH + [O] \rightarrow$  $+ H_2O$		1		1		
		(ii)		place acid in flask and add sodium dichromate(VI) until it has dissolved (1) (cool mixture) and add ethanol dropwise (shaking between additions) (1) set up distillation apparatus (1) heat gently until liquid boils over (1)	4			4		4
		(iii)		add sodium (hydrogen)carbonate (1) no effervescence (1) do **not** accept references to pH	2			2		2
	(b)			award (1) for either of following • ethanol has peak at 50-90 ppm, ethanal does not • ethanal has peak at 190-220 ppm, ethanol does not both contain two peaks / one other peak below 40 ppm (1)		2		2		

11. Compound **A** contains 55.8 % carbon, 7.00 % hydrogen and 37.2 % oxygen by mass.

Part of its infrared spectrum is shown below.



- An aqueous solution of compound **A** has a pH of less than 7.
- In an addition reaction, 2.00 g of compound **A** reacts with 3.71 g of bromine in a 1 : 1 molar ratio.

Use all the data given to identify **all** the possible structures of compound **A**. Explain what information can be found from each piece of data. [10]

11

- C H O

  $\frac{55.8}{12}$ $\frac{7.00}{1.01}$ $\frac{37.2}{16}$ (1)

  4.65 : 6.93 : 2.325 ⇨ C_2H_3O (1)

- very broad peak 2500 to 3000 cm^{-1} so is a carboxylic acid / peak around 1700 cm^{-1} (C = O) and around 3000 cm^{-1} (O—H) so is carboxylic acid (1)
- pH < 7 so must be acid - must contain at least two oxygens (1)
- addition reaction with bromine so must contain C=C
  1:1 molar ratio so only one double bond (1)
- moles $Br_2 = \frac{3.71}{159.8} = 2.32 \times 10^{-2}$ (1)

  $M_r = \frac{2}{2.32 \times 10^{-2}} = 86.2$ (1)

  molecular formula = $C_4H_6O_2$ (1)
- possible structures of **A**

  $H_2C{=}CHCH_2COOH$ $H_2C{=}C(CH_3)COOH$

  Z-$CH_3CH{=}CHCOOH$ *E*-$CH_3CH{=}CHCOOH$

  award (2) for all four correct or (1) for any two correct

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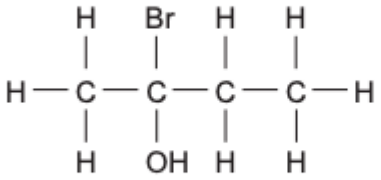
1. Name the compound whose formula is shown below.



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2-bromobutan-2-ol

5. Complete the equation for the reaction between propanoic acid and sodium carbonate. [1]

$2C_2H_5COOH + Na_2CO_3 \longrightarrow$ .....

5				$2C_2H_5COONa + H_2O + CO_{2C}$

8. *(a)* A student wanted to form a halogenoalkane from an alcohol. He added hydrochloric acid to the alcohol and a mixture of organic and inorganic products formed. The halogenoalkane is the only substance in the mixture that does not dissolve in the inorganic aqueous solution.

(i) Suggest how the student could separate the halogenoalkane from the other compounds. [1]

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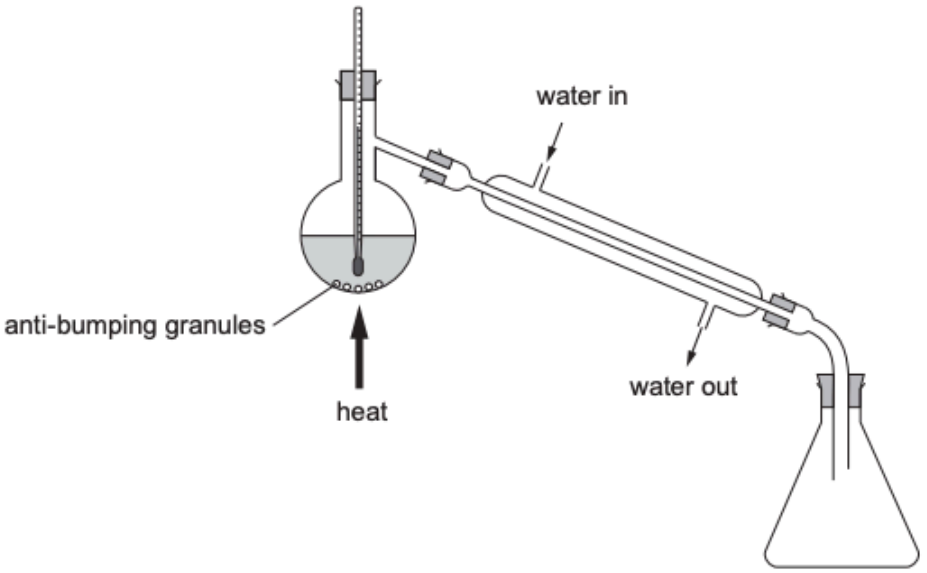
(ii) The student wants to purify the halogenoalkane by distillation. He sets up the apparatus as shown in the diagram. You may assume that all the equipment is suitably clamped.



I. Anti-bumping granules were placed in the flask.

Suggest why these granules prevent bumping. [1]

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II. State **two** changes that must be made to the apparatus for safe and effective use. Give your reason in each case. [4]

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(b) Another student wanted to make 1-chloropentane.

She started with pentan-1-ol and obtained 1.62 g of 1-chloropentane. The percentage yield of 1-chloropentane was 67 %.

A fellow student told her that since 67 % is about two-thirds, she must have started with about 2.43 g of pentan-1-ol.

Is the student correct? Justify your answer. [3]

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(d) When 2-bromobutane is heated with potassium hydroxide dissolved in ethanol, two structural isomers are formed.

(i) State the meaning of the term *structural isomers*. [1]

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(ii) Draw the structure of both isomers. [2]

(iii) Circle the isomer which exhibits *E-Z* isomerism. Explain your choice. [1]

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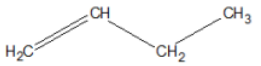
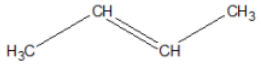
8	*(a)*	(i)		separating funnel accept any answer that recognises the presence of two separate layers			1	1		1
		(ii)	I	award (1) for any of following small(er) bubbles form prevent large bubbles provide surface for bubbles to form		1		1		1
			II	accept any **two** from three possible changes/explanations (bulb of the) thermometer should be opposite the opening to the condenser (1) temperature of the vapour is measured (1) water should go in at the bottom of the condenser and out at the top (1) keeps condenser full of water / prevents 'air-lock' / allows better cooling (1) flask receiving condensed product should not be sealed (1) pressure could build inside a sealed system (1)			4	4		4

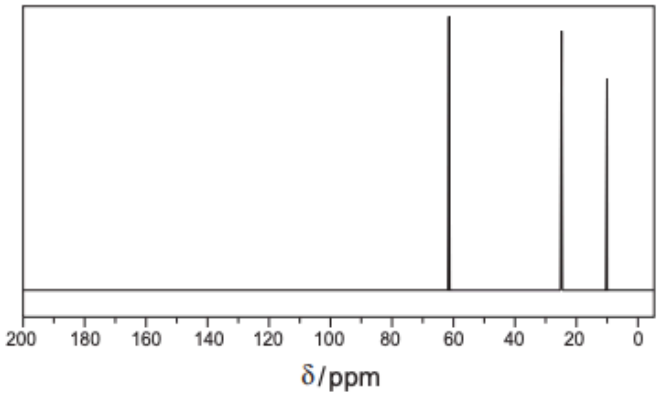
	(b)			moles 1-chloropentane formed = 0.0152 (1) moles pentan-1-ol used = 0.0227 (1) mass pentan-1-ol used = 2.00 g ⇨ student incorrect (1) alternative answer moles pentan-1-ol = 0.0276 (1) moles 1-chloropentane = 0.0152 (1) percentage yield = 55% ⇨ student incorrect (1)		2	1	3	2	
	(d)	(i)		compounds with the same molecular formula but different structural formulae	1			1		
		(ii)		 (1)  (1)		1 1		2		
		(iii)		but-2-ene circled (or identified in any way) it has two <u>different</u> groups attached to <u>both</u> carbons in the double bond	1			1		

9. *(a)* Compound **X** is an alcohol. When compound **X** is warmed with acidified potassium dichromate(VI) there is a colour change.

In the mass spectrum of compound **X**

- the molecular ion peak is at m/z 74
- the peak with the greatest relative intensity is at m/z 43 and is due to a secondary carbocation

Compound **X** has the following ^{13}C NMR spectrum.



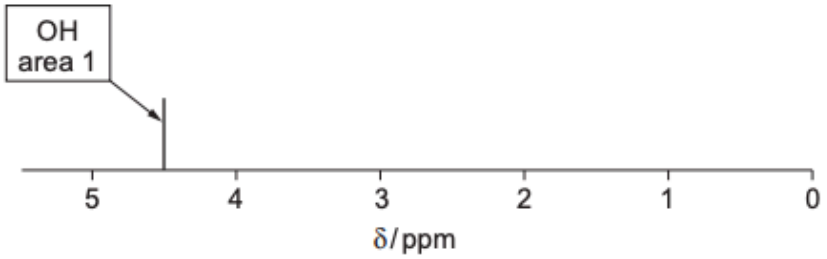
Explain what can be deduced from each piece of information and identify the structure of compound **X**. [7]

Structure of compound **X**

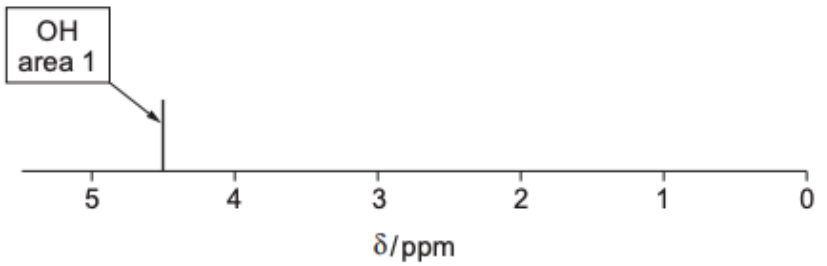
(b) Complete the sketches of the **low resolution** ^{1}H NMR spectra for propan-1-ol and propan-2-ol.

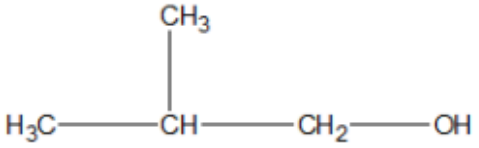
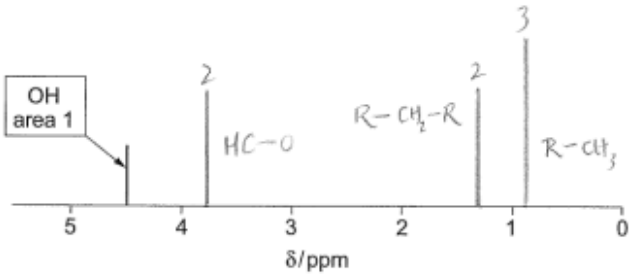
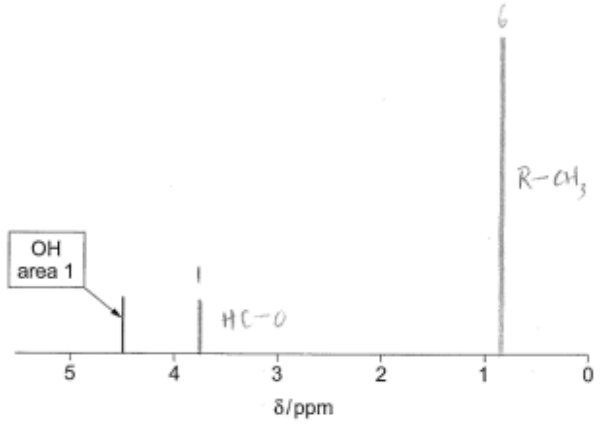
Identify which protons are responsible for each peak giving the approximate chemical shift (ppm) and the relative area of each peak. [4]

Propan-1-ol, $CH_3CH_2CH_2OH$



Propan-2-ol, $CH_3CH(OH)CH_3$



9	*(a)*			accept any **five** of following for (1) mark each reacts with potassium dichromate(VI) ⇨ can't be tertiary alcohol (1) molecular ion peak at m/z 74 ⇨ M_r is 74 (1) M_r of alkyl chain must be 57 ⇨ molecular formula is $C_4H_{10}O$ (1) peak at m/z 43 ⇨ $C_3H_7^+$ / peak at m/z 31 ⇨ CH_2OH^+ (1) secondary carbocation ⇨ $(CH_3)_2CH^+$ / branched chain (1) only three peaks in ^{13}C NMR spectrum ⇨ only three carbon environments (1)  (2) accept any unambiguous structure showing 2-methylpropan-1-ol
	(b)			propan-1-ol  propan-2-ol  award (1) for approximate chemical shifts and (1) for peak areas for each spectrum

3. Explain why propanoic acid is soluble in water but propane is not. [2]

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only propanoic acid forms hydrogen bonds / propanoic acid forms hydrogen bonds but propane does not (1)

with water (1)

(c) Ethanol can be heated under reflux with propanoic acid in the presence of concentrated sulfuric acid to form an ester.

(i) Draw a labelled diagram of the apparatus you could use for heating under reflux. [3]

(ii) Explain how this apparatus prevents escape of vapour and give a reason why the escape of vapour should be prevented. [2]

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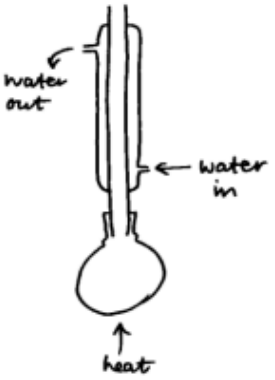
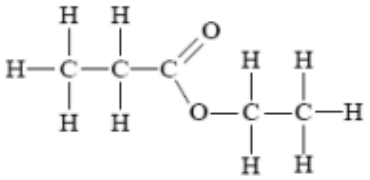
(iii) Draw the structure of the ester that forms. [1]

	(c)	(i)		 flask with vertical condenser (1) direction of water flow (1) clear indication that flask and condenser are two different pieces of apparatus (1)
		(ii)		vapour / mixture being heated is condensed and returns to the flask (1) award (1) for any of following yield would be reduced / product would be lost reactants would be lost solvent would be lost neutral answer – vapour is flammable
		(iii)		

10. (a) Halogenoalkanes can be hydrolysed to give alcohols.

Devise an experiment to compare the rates of hydrolysis of 1-chlorobutane, 1-bromobutane and 1-iodobutane.

Include the expected results and use these to state the trend in the rates of reaction. Explain this trend. [6 QER]

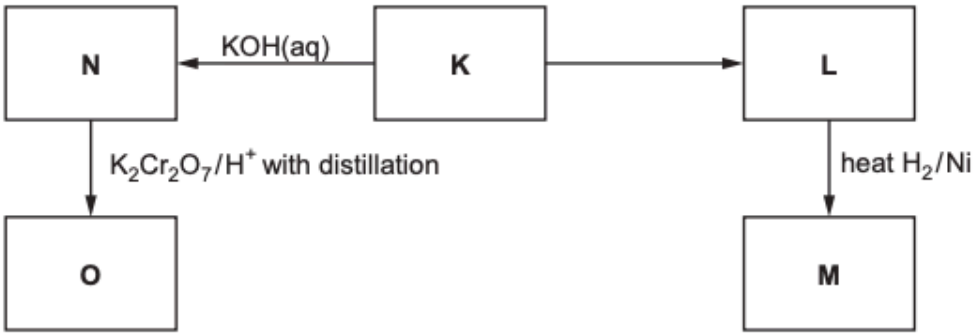
Indicative content

Method
- Equal amounts of halogenoalkane in each tube
- Add ethanol as a solvent
- Add $AgNO_3(aq)$ to each tube
- Heat mixture to same temperature
- Measure time taken for each precipitate to form

Results
- C_4H_9I produces yellow precipitate quickly
- C_4H_9Br takes longer to produce a cream precipitate
- C_4H_9Cl takes a very long time to produce a white precipitate

Use of Results
- Trend is 1-iodobutane > 1-bromobutane > 1-chlorobutane
- Bond enthalpy C – Cl > C – Br > C – I

12. Study the reaction scheme shown below and the other information that follows.



Compound **L** is a hydrocarbon. It does not show *E-Z* isomerism and its mass spectrum shows a molecular ion peak at m/z 56.

The ^{1}H NMR spectrum for compound **K** shows 3 peaks and the ratio of the peak areas is 6:1:2.

The ^{13}C NMR spectrum for compound **N** shows 3 peaks.

Compound **O** does not react with sodium carbonate.

(a) Identify compounds **K**, **L**, **M** and **N**. Give your reasoning. [8]

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(b) Name the homologous series to which compound **O** belongs. [1]

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(c) State the reagent(s) and conditions needed for the conversion of compound **K** to compound **L**. [1]

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12	(a)			award (1) for each compound identified and (1) for each relevant point in reasoning (up to maximum of 4) e.g. **K** ⇨ ^{1}H NMR peak area 6 so must have two CH_3 groups attached to same carbon / must have branched chain (1) **L** ⇨ hydrocarbon with M_r of 56 so must be C_4H_8 and must have branched chain (1) **L** ⇨ 2-methylpropene (1) **M** ⇨ formed by addition of H_2 to alkene **L** (1) **M** ⇨ 2-methylpropane (1) **K** ⇨ undergoes nucleophilic substitution to form (primary) alcohol **N** (1) **K** ⇨ 1-chloro-2-methylpropane (or 1-bromo-2-methylpropane or 1-iodo-2-methylpropane) (1) **N** ⇨ 2-methylpropan-1-ol (1) accept correct structures for **K**, **L**, **M** and **N** credit any other relevant points in reasoning e.g. **N** ⇨ ^{13}C NMR has only 3 peaks meaning carbons in 3 environments so must be branched chain (1) if **L** identified as but-1-ene award maximum (6) if **L** identified as but-2-ene award maximum (5)
	(b)			aldehyde
	(c)			KOH in ethanol (+ heat)

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(c) Propan-2-ol can react with ethanoic acid in the presence of concentrated sulfuric acid to form an ester and water. This reaction is reversible so an equilibrium mixture is produced and the ester is removed by distillation.

(i) Write the equation for the reaction between propan-2-ol and ethanoic acid.

Clearly show the structure of the ester formed. [2]

(ii) Explain fully why the ester can be separated from the equilibrium mixture by distillation. [2]

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(iii) I. Explain why the yield of ester in the equilibrium mixture is increased by removing the ester. [1]

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II. Concentrated sulfuric acid is a dehydrating agent.

Suggest why the yield of ester in the equilibrium mixture is increased by adding concentrated sulfuric acid. [1]

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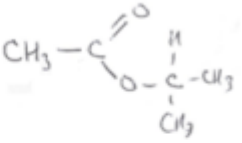
(c)	(i)		$CH_3CH(OH)CH_3 + CH_3COOH \rightleftharpoons$  $+ H_2O$ ester structure (1) balanced equation (1)
	(ii)		boiling temperature of ester is lower (than alcohol and acid) (1) alcohols and acids form hydrogen bonds between molecules (which are stronger than van der Waals forces between ester molecules) / esters do not form hydrogen bonds between molecules (1)

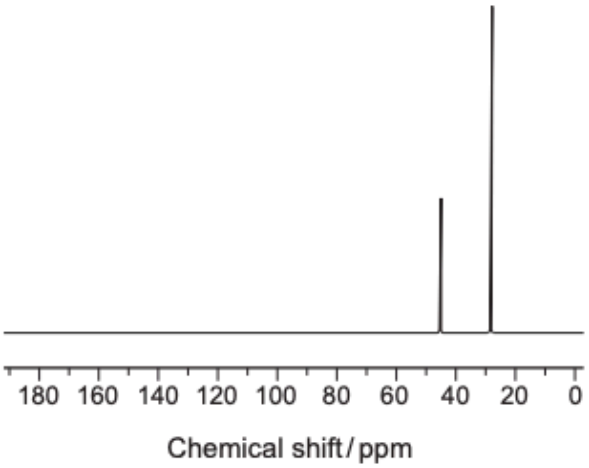
(iii)	I	removing ester decreases its concentration so equilibrium position moves to the right to form more ester
	II	dehydrating agent so removes water so equilibrium position moves to the right (to form more water and more ester)

(b) The information given below relates to liquid **X**.

Quantitative analysis shows that it contains 29.2% carbon and 5.8% hydrogen by mass. The remainder is bromine.

The mass spectrum shows two molecular ion signals at m/z 122 and m/z 124 in the ratio of 1:1.

Its ^{13}C NMR spectrum is shown below.



(i) Use **all** the information to identify liquid **X**. [5]

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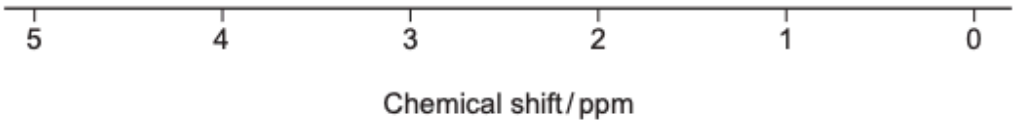
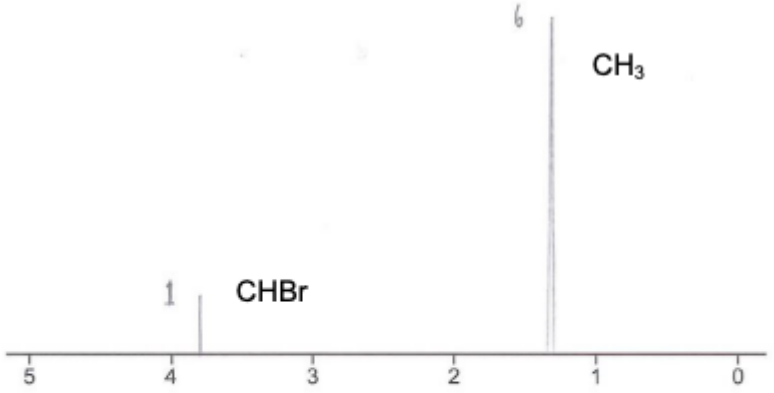
(ii) Sketch the low resolution ^{1}H NMR spectrum of liquid **X**.

Identify which protons are responsible for each peak giving the approximate chemical shift (ppm) and the relative area of each peak. [2]



	(b)	(i)		C H Br $\frac{29.2}{12}$ $\frac{5.80}{1.01}$ $\frac{65.0}{79.9}$ 2.43 5.74 0.814 (1) simplest whole number ratio is 3 : 7 : 1 ⇨ empirical formula is C_3H_7Br (1) award (1) for either of following • M_r of empirical formula is 122 ⇨ molecular formula is C_3H_7Br • mass spectrum peak at 122 due to $C_3H_7{}^{79}Br$ / at 124 due to $C_3H_7{}^{81}Br$ award (1) for either of following • ^{13}C NMR peak at 30 ppm due to CH_3 and at 45 ppm due to CHBr • only two peaks / carbon environments **X** is 2-bromopropane (1)

(ii)



chemical shift (1)

peak area / height (1)

ecf possible from part (i)

9. (a) A student is provided with unlabelled samples of the three liquids listed below.

1-chloropropane hex-1-ene propanoic acid

Describe chemical tests, apart from the use of an indicator, that the student should carry out to positively identify each of the three liquids.

You should include balanced equations for any reactions that occur. [6 QER]

Indicative content

- add aqueous sodium hydroxide and heat
  add nitric acid followed by aqueous silver nitrate
  white precipitate forms with 1-chloropropane only
  $C_3H_7Cl + OH^- \rightarrow C_3H_7OH + Cl^-$
  $Ag^+ + Cl^- \rightarrow AgCl$

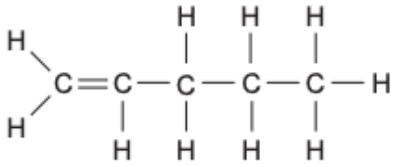
- add bromine water and shake well
  changes from orange to colourless with hex-1-ene only

$C_6H_{12} + Br_2 \rightarrow C_6H_{12}Br_2$

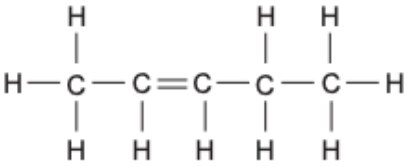
- add suitable carbonate e.g. Na_2CO_3
  effervescence with propanoic acid only
  $2C_2H_5COOH + Na_2CO_3 \rightarrow 2C_2H_5COONa + CO_2 + H_2O$

11. Five non-cyclic structural isomers have the molecular formula C_5H_{10}.

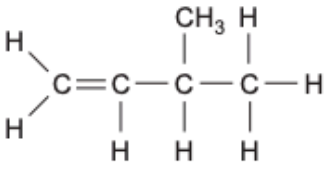
Three of these are shown below.



pent-1-ene



pent-2-ene



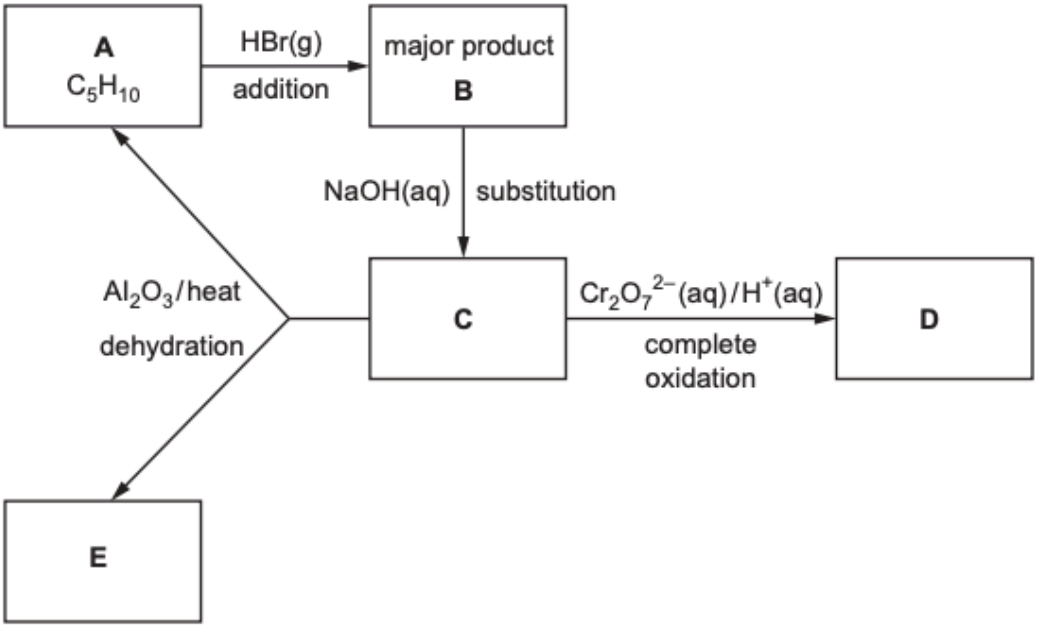
3-methylbut-1-ene

(a) Draw the structures of the other **two** isomers.

Do **not** include both the *E* and the *Z* isomer of the same structure. [2]

(b) Compound **A** is one of the five isomers on the previous page.

Study the reaction scheme and the information below.



Compound **D** does **not** react with aqueous sodium carbonate.

Compound **E** does **not** show *E-Z* isomerism.

(i) Use the information to name the homologous series to which compounds **B**–**E** belong. Give your reasoning. [6]

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(ii) State what you would observe when compound **C** is oxidised to compound **D**. [1]

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(iii) Compound **B** can also undergo an elimination reaction.

State the reagent(s) and conditions needed for this reaction. [1]

.....

(iv) Compound **A** can **only** be 3-methylbut-1-ene.

It cannot be pent-2-ene because its reaction with HBr would give two products in significant quantities.

I. Explain why compound **A** cannot be pent-1-ene. [2]

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II. Explain why compound **A** cannot be either of the two isomers drawn in part (a). [2]

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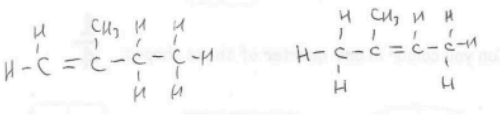
11	(a)			award (1) for each correct structure  do not credit both the *E* and the *Z* isomer of the same structure		2		2		
	(b)	(i)		**B** must be a bromoalkane since **A** is an alkene and addition of HBr gives a bromoalkene (1) B must be a secondary bromoalkene because a secondary carbocation is more stable (1) bromoalkanes undergo substitution reactions with aqueous sodium hydroxide therefore **C** is an alcohol (1) **C** must be a secondary alcohol (1) award (1) for either of following • **C** is not a primary alcohol since when completely oxidised by acidified dichromate(VI) a primary alcohol forms a carboxylic acid which reacts with aqueous sodium carbonate • **C** is not tertiary alcohol because it cannot be oxidised by acidified dichromate(VI) **D** must be a ketone since it does not react with aqueous sodium carbonate / because it forms from a secondary alcohol (1) **D** is not an aldehyde because complete oxidation would form a carboxylic acid (1)		6		6		

				E must be an alkene since alcohols are dehydrated to alkenes (1) award up to **six** of possible eight marks but all compounds must be correct for full marks credit named compounds instead of homologous series						
		(ii)		colour change from orange to green	1			1		
		(iii)		NaOH in ethanol	1			1		
		(iv)	I	pent-1-ene is incorrect as it would form 2-bromopentane as the only major product with HBr (which would then form pentan-2-ol) (1) alkene **E** formed on dehydration of pentan-2-ol would be pent-2-ene but this has *E-Z* isomers (1)			2	2		
			II	**A** cannot be 2-methylbut-1-ene or 2-methylbut-2-ene because a tertiary bromoalkane would be formed as the major product on addition of HBr (1) after the substitution reaction, this bromoalkane would become a tertiary alcohol / an alcohol which cannot be oxidised by acidified dichromate(VI) (1)			2	2		