Surname	Centre Number	Candidate Number
First name(s)		2

GCE A LEVEL

S23-1410U40-1

1410U40-1

MONDAY, 19 JUNE 2023 – AFTERNOON

CHEMISTRY – A2 unit 4

Organic Chemistry and Analysis

1 hour 45 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1. to 7.**	**10**	
Section B	**8.**	**13**	
	9.	**15**	
	10.	**15**	
	11.	**15**	
	12.	**12**	
	Total	**80**	

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01

ADDITIONAL MATERIALS

In addition to this examination paper, you will need a:
- calculator;
- **Data Booklet** supplied by WJEC.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen. Do not use gel pen or correction fluid.

You may use a pencil for graphs and diagrams only.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions.
Section B Answer **all** questions.

Write your answers in the spaces provided in this booklet. If you run out of space, use the additional page(s) at the back of the booklet, taking care to number the question(s) correctly.

Candidates are advised to allocate their time appropriately between **Section A (10 marks)** and **Section B (70 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The assessment of the quality of extended response (QER) will take place in **Q10**(a).

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SECTION A

Answer **all** questions.

1. Give the structure of an unsaturated aldehyde of molecular formula C_4H_6O. [1]

2. State a group that will give a positive triiodomethane (iodoform) test and give the observation for a positive result. [2]

.....

3. (a) 1,2-Diaminoethane reacts as a base.

Explain how this compound acts as a base. [1]

.....

.....

(b) Give the structure of the organic compound formed when 1 mole of 1,2-diaminoethane reacts with 2 moles of ethanoyl chloride. [1]

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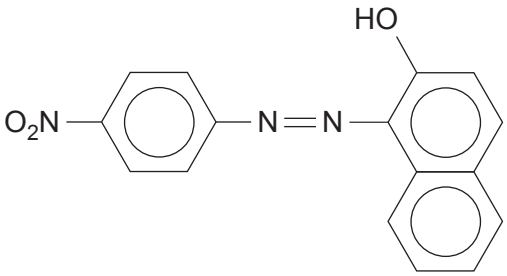
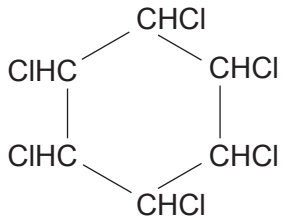
4. The formula of the azo dye, Para Red, is shown below.



Give the structure of the compound that couples with 4-nitrobenzenediazonium chloride to give this dye. [1]

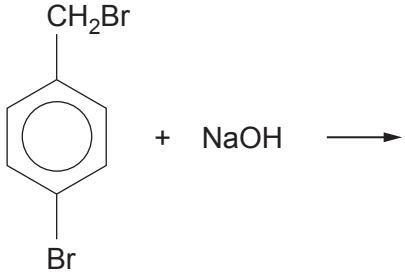
5. Hexachlorocyclohexane can be used as an insecticide.



Deduce the empirical formula of this compound. [1]

.....

6. Give the structure of the organic product of the reaction below. [1]



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Turn over.

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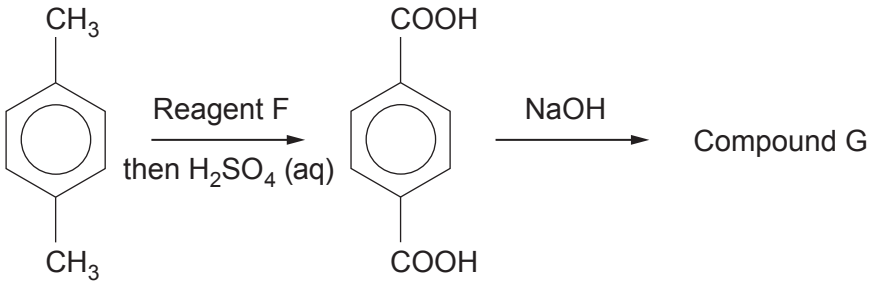
7. Study the reaction sequence below and answer the **two** questions that follow.



(a) Reagent F is ..... [1]

(b) Give the structure of Compound G. [1]

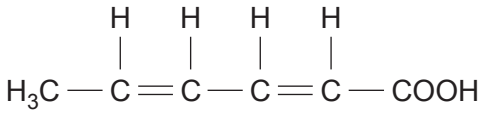
10

Examiner only

Section B

Answer **all** questions.

8. (a) Sorbic acid was isolated in 1859 from mountain ash berry oil. It is a white solid that is slightly soluble in cold water.



(i) The solubility of sorbic acid in water is $1.6\,g\,dm^{-3}$ at 20 °C and $40.0\,g\,dm^{-3}$ at 100 °C.

Calculate how much sorbic acid is precipitated from its aqueous solution if $200\,cm^3$ of a saturated solution at 100 °C is cooled to 20 °C.
Give your answer to an appropriate number of significant figures. [2]

..... g

(ii) Sorbic acid and its salts, for example sodium sorbate, have important uses as antimicrobial agents in food preservation.
Some moulds are, however, able to detoxify the action of these sorbates.
An example is the decarboxylation of sodium sorbate.

I. State what is meant by 'decarboxylation'. [1]

.....

II. In the laboratory sodium sorbate can be decarboxylated by heating it with soda lime.
The organic product of decarboxylation is *E*-penta-1,3-diene.

Write the equation for this decarboxylation of sodium sorbate with soda lime (which you should represent as NaOH in your equation), showing the structure of *E*-penta-1,3-diene. [2]

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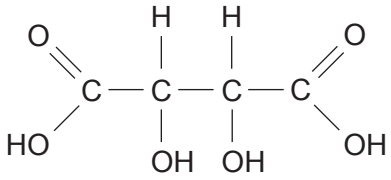
III. *E*-penta-1,3-diene can then react with hydrogen using platinum as a catalyst giving pentane.

State the number of moles of hydrogen required to react with 0.2 mol of *E*-penta-1,3-diene in this way. [1]

.....

(b) Tartaric acid (2,3-dihydroxybutanedioic acid) is used in the food industry.



(i) Indicate any chiral centre(s) present by means of an asterisk (*). [1]

(ii) This acid occurs in a number of optically active forms.
Complete the sentences below.

Forms of tartaric acid that rotate the plane of plane-polarised light are called

.....

[1]

A solution containing an equimolar mixture of two forms of the acid that rotates the plane of plane-polarised light in equal and opposite directions is called a

.....

[1]

(c) Both sorbic acid and tartaric acid are described as showing stereoisomerism.

Explain what is meant by the term stereoisomerism. [1]

.....

.....

(d) Tartaric acid is formed when butenedioic acid reacts with a suitable oxidising agent.

Give the equation for this reaction, representing the oxidising agent as [O] and using water as a reactant. [1]

Examiner only

(e) The solubility of unsaturated carboxylic acids in water decreases as the chain length increases.

Number of carbon atoms in the alkyl chain	Solubility in water at 25 °C / g dm^{-3}
3	94
5	1.6
7	0.7

Suggest why this solubility decreases as the chain length increases. [2]

.....

.....

.....

.....

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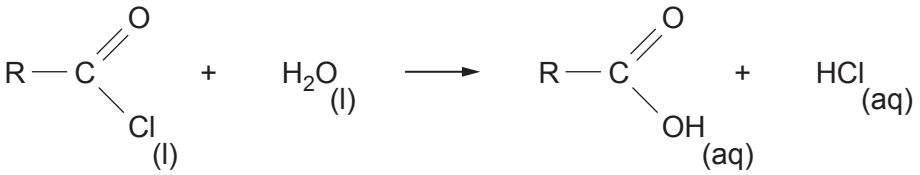
Turn over.

Examiner only

9. (a) 1.598 g of an acid chloride, RCOCl, was added to water.
The aqueous solution contained hydrochloric acid and a carboxylic acid, R — COOH, where R is an alkyl group



(i) State the type of reaction occurring. [1]

.....

(ii) This acidic solution was titrated with 0.400 mol dm^{-3} aqueous sodium hydroxide, using a suitable indicator. Both acids were just neutralised by 75.00 cm^3 of the sodium hydroxide solution.

Use the results to calculate the relative molecular mass of the acid chloride. [3]

M_r .....

(iii) The low resolution ^1H NMR spectrum of the acid chloride showed two signals in the peak area ratio of 6:1.

Use this information and the relative molecular mass of the RCOCl, obtained in part (ii), to find the structure of the acid chloride. [2]

Examiner only

(b) (i) The acid chloride, benzene-1,4-dicarbonyl dichloride, ClOC — C_6H_4 — COCl is made by reacting benzene-1,4-dicarboxylic acid with phosphorus(V) chloride. The other products of this reaction are hydrogen chloride and phosphoryl trichloride, $POCl_3$.

Give the equation for this reaction. [1]

(ii) Benzene-1,4-dicarbonyl dichloride reacts with benzene-1,4-diamine to give a polyamide.

Show the repeating unit for this polyamide. [1]

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(c) Nylon polyamides that are produced from starting materials with a different number of carbon atoms are given numbers.
For example Nylon 4,5 has a 4-carbon diamine fragment and a 5-carbon dicarboxylic acid fragment.

Butane-1,4-diamine can be used as a starting material for this polyamide. This can be produced in a two-stage reaction from butane-1,4-diol.

$$HOCH_2(CH_2)_2CH_2OH \xrightarrow[\text{Stage 1}]{\text{reagent } \mathbf{A}} ClCH_2(CH_2)_2CH_2Cl \xrightarrow[\text{Stage 2}]{\text{reagent } \mathbf{B}} H_2N(CH_2)_4NH_2$$

(i) State the name of reagent(s) **A**. [1]

.....

(ii) State the name of reagent(s) **B**. [1]

.....

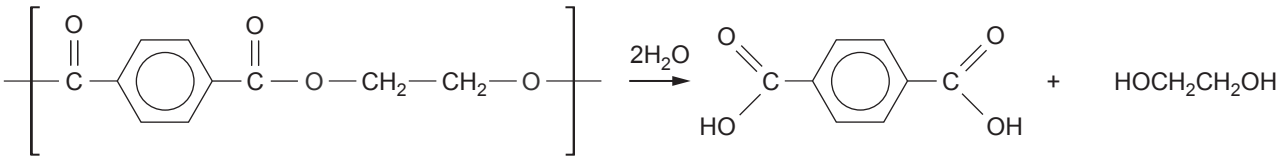
Examiner only

(iii) State the type of mechanism occurring in Stage 2. [1]

.....

(iv) Draw the **skeletal** formula of the 5-carbon containing dicarboxylic acid used to produce Nylon 4,5. [1]

(d) The depolymerisation of polyamides and polyesters present a number of difficult problems as these polymers are very stable and only slowly decompose in the environment.
Poly(ethyleneterephthalate) (PET) is very difficult to hydrolyse but a new process using specific enzymes is proving promising. In this process 90% of PET is depolymerised into benzene-1,4-dicarboxylic acid.



Calculate the mass of benzene-1,4-dicarboxylic acid produced from 75 kg of PET if the yield from this hydrolysis is 90%. [3]

mass of benzene-1,4-dicarboxylic acid produced = ... kg

15

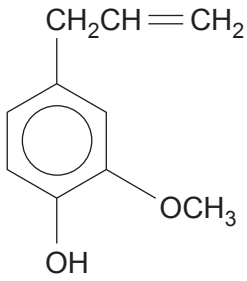
Examiner only

10. (a) Benzene reacts with bromine in the presence of a catalyst.
Give the mechanism for this reaction and explain how the Br — Br bond becomes polarised during the reaction.
Suggest why, in the absence of this catalyst, there is very little reaction between benzene and bromine under normal conditions. [6 QER]

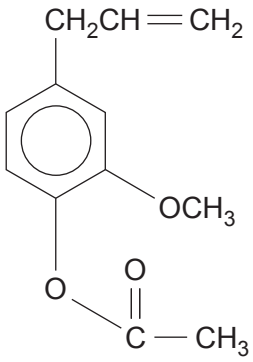
Turn over.

Examiner only

(b) Eugenol is the main constituent of clove oil, together with smaller quantities of eugenyl ethanoate.



Eugenol



Eugenyl ethanoate

(i) Describe what is seen if a few drops of iron(III) chloride solution are added to a solution of eugenol. [1]

.....

(ii) State the colour change that occurs if a few drops of aqueous bromine are added to a solution of eugenol. [1]

.....

(iii) If an excess of bromine is added to eugenol, a new compound is formed that contains the following percentages by mass of each element.

C 24.9% H 2.1% O 6.6%, the remainder being the % of bromine

Use this information to calculate the empirical and molecular formulae of this brominated compound and suggest a possible structure for it. [5]

Examiner only

(iv) Explain how adding aqueous sodium hydroxide at room temperature to a solution of eugenol and eugenyl ethanoate dissolved in trichloromethane, enables the two compounds to be separated.
Trichloromethane and water are immiscible. [2]

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15

Examiner only

11. (a) Aminoethanoic acid is the simplest α-amino acid.

$$H_2N — CH_2 — COOH$$

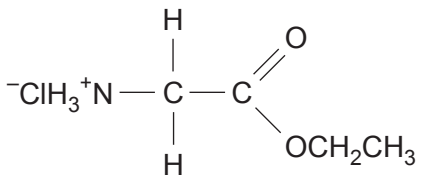
(i) Give the structure of the dipeptide formed from two molecules of aminoethanoic acid. [1]

(ii) Explain why aminoethanoic acid can only form one dipeptide. [1]

.....

.....

(b) Amino acids form esters in the usual way from the carboxylic acid group and an alcohol, in the presence of an acid catalyst. These esters can form a salt with the acid used in esterification.
The formula of one of these salts is shown below. Compound **M** is a white solid that is soluble in water, giving a colourless solution.



Compound **M**

(i) I. Many amino acids exist as zwitterion forms in aqueous solution.

Give the zwitterion form of aminoethanoic acid. [1]

II. Explain why compound **M** cannot form a zwitterion in this way. [1]

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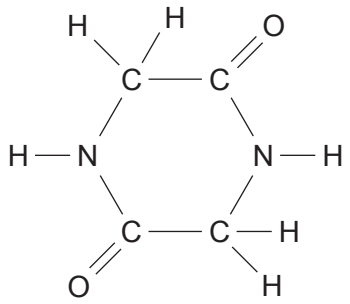
Examiner only

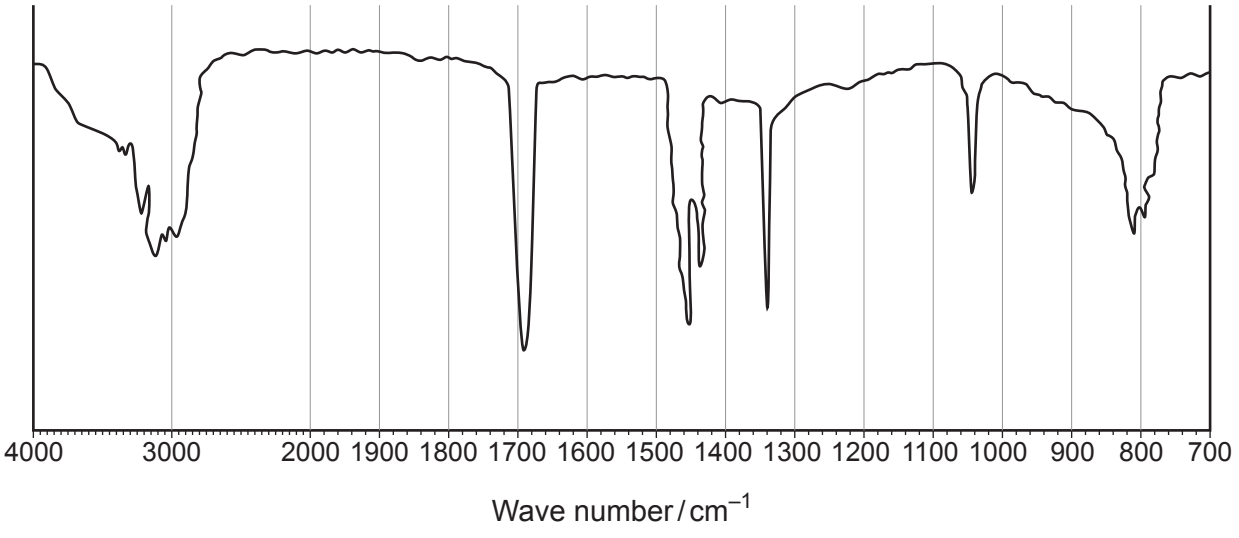
(ii) Under suitable conditions, aminoethanoic acid condenses to give diketopiperazine.



I. The mass spectrum of diketopiperazine shows a molecular ion at m/z 114 and two prominent fragments at m/z 43 and 71.

Suggest a formula for the fragment at m/z 71. [1]

II. An outline infrared absorption spectrum of diketopiperazine is shown below. Use the formula shown and the data sheet to suggest an absorption value for the N — H and C = O bonds. [1]



N — H ..... cm^{-1} C = O ..... cm^{-1}

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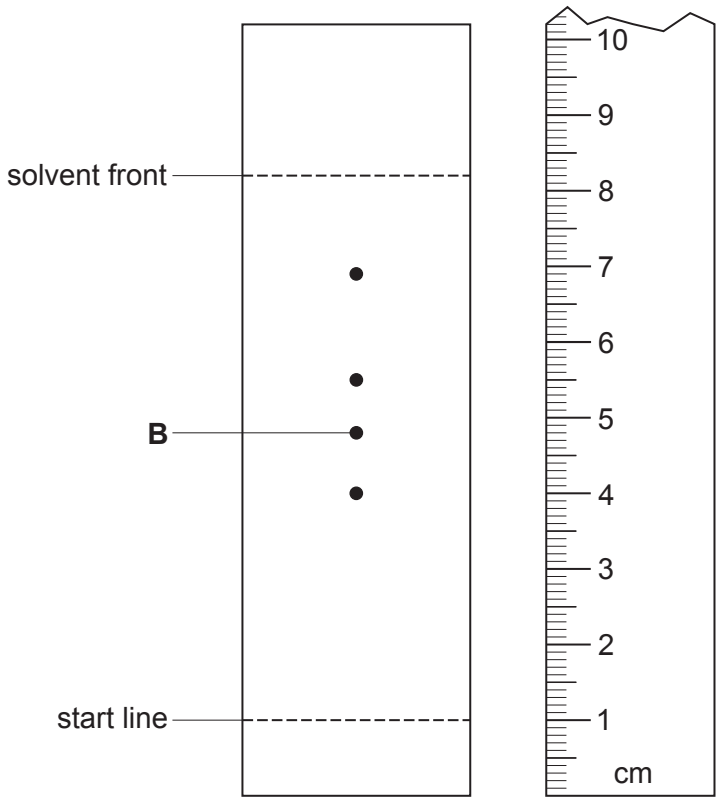
(c) A mixture of α-amino acids can be separated and identified by thin layer chromatography.

(i) These amino acids are colourless and the chromatogram is sprayed with a solution of ninhydrin, so that the amino acids appear as purple dots. The colour is due to the dye Ruhemann's Purple.

A thin layer chromatogram of a mixture of α-amino acids is shown below.



Calculate the R_f value for threonine (spot **B**). [1]

.....

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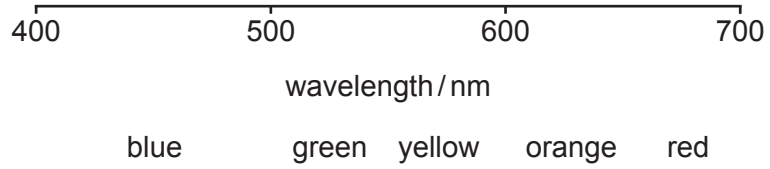
(ii) Ruhemann's Purple has a maximum absorption at 564 nm.

The information below indicates the colours absorbed at various wavelengths in the visible spectrum.
Use this to help you explain why the colour of the dye is purple. [1]



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(iii) Calculate the energy (in kJ mol^{-1}) associated with this absorption at 564 nm. [3]

energy = ... kJ mol^{-1}

Examiner only

(d) Amino acids react with nitric(III) acid to produce nitrogen gas.

(i) 0.500 g of 2-aminohexanoic acid, $CH_3(CH_2)_3CH(NH_2)COOH$, reacted with an excess of nitric(III) acid.

Calculate the volume of nitrogen produced, assume the temperature was measured at 298 K and at 1 atmosphere pressure. [2]

volume of nitrogen produced = ... cm^3

(ii) The actual volume of nitrogen produced was 90.9 cm^3, which was less than the calculated volume in part (i) above.

Suggest **two** reasons for this low result, apart from errors in weighing and in measuring the volume of nitrogen produced. [2]

1. .....

.....

2. .....

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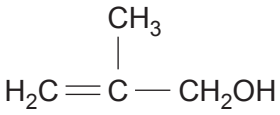
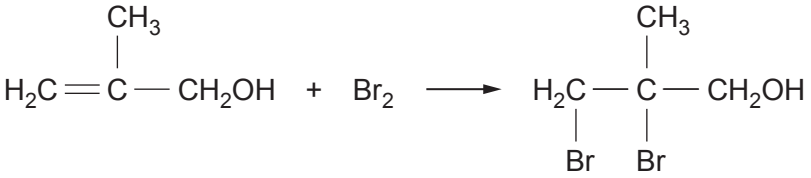
12. (a) 2-Methylpropenoic acid can be obtained from 2-methylprop-2-en-1-ol.



The standard reagents used for the oxidation of a primary alcohol to a carboxylic acid may affect the C = C bond. To prevent this occurring the double bond is protected by bromination.

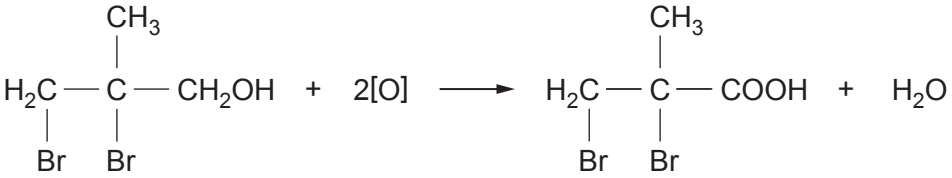


The bromine atoms are removed in a later reaction to give the required acid.

(i) State the type of mechanism occurring during the bromination. [1]

.....

(ii) Suggest an oxidising agent used for the oxidation of the brominated alcohol. [1]



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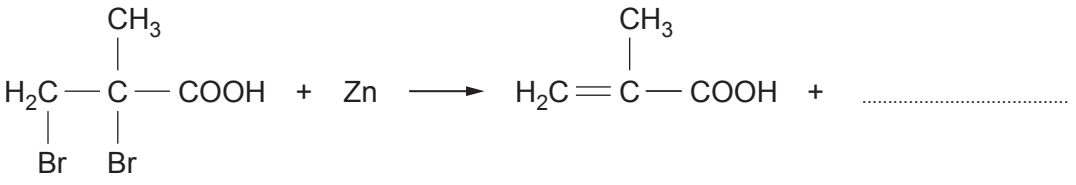
(iii) The dibromoacid produced in part (ii) is then reacted with zinc under suitable conditions to give 2-methylpropenoic acid.

Complete the equation, showing zinc bromide as the co-product. [1]



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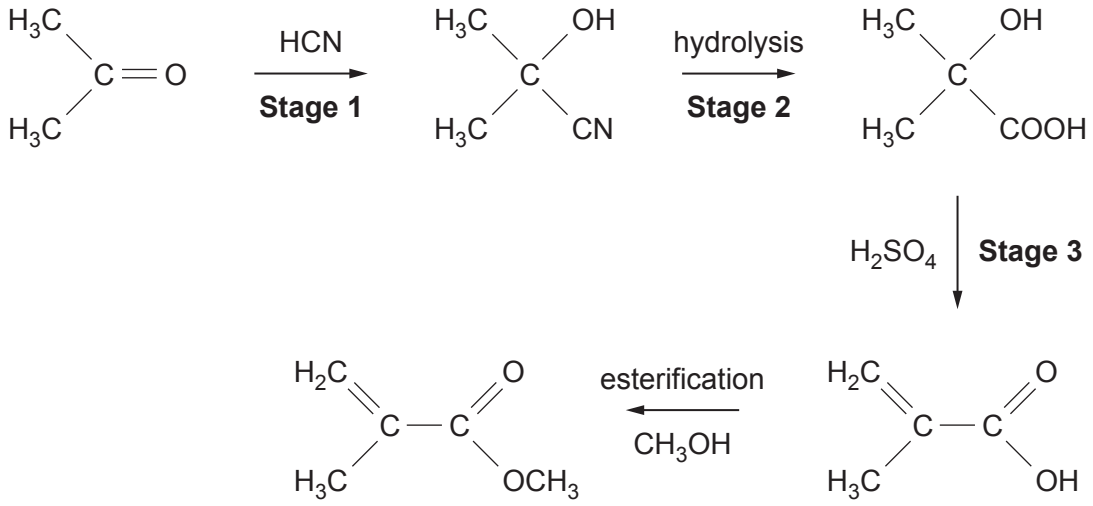
(b) Methyl 2-methylpropenoate can be produced from propanone.



(i) **Stage 1** is a nucleophilic addition reaction.

Give the formula of the nucleophile taking part in this stage. [1]

.....

(ii) State why **Stage 1** is described as an **addition** reaction. [1]

.....

(iii) State a reagent used for hydrolysis in **Stage 2**. [1]

.....

(iv) State the role of sulfuric acid in **Stage 3**. [1]

.....

(v) Addition polymerisation of methyl 2-methylpropenoate gives 'Perspex'.

Give the repeating unit of this polymer. [1]

Examiner only

(vi) Explain why the polymerisation in part (v) is described as addition polymerisation and not condensation polymerisation. [1]

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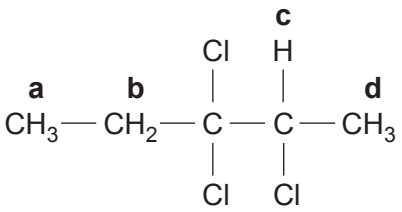
(c) The formula of a halogenoalkane is shown below.



(i) Give the systematic name of this halogenoalkane. [1]

.....

(ii) Complete the table below which describes the high resolution ^{1}H NMR spectrum of this compound. [2]

Hydrogen proton	Splitting pattern
a	
b	
c	
d	

12

END OF PAPER

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Question number	Additional page, if required. Write the question number(s) in the left-hand margin.

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GCE A LEVEL

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MONDAY, 19 JUNE 2023 – AFTERNOON

CHEMISTRY – A2 unit 4
Data Booklet

Avogadro constant	N_A	$6.02 \times 10^{23}\ \text{mol}^{-1}$
molar gas constant	R	$8.31\ \text{J mol}^{-1}\ \text{K}^{-1}$
molar gas volume at 273 K and 1 atm	V_m	$22.4\ \text{dm}^3\ \text{mol}^{-1}$
molar gas volume at 298 K and 1 atm	V_m	$24.5\ \text{dm}^3\ \text{mol}^{-1}$
Planck constant	h	$6.63 \times 10^{-34}\ \text{J s}$
speed of light	c	$3.00 \times 10^{8}\ \text{m s}^{-1}$
density of water	d	$1.00\ \text{g cm}^{-3}$
specific heat capacity of water	c	$4.18\ \text{J g}^{-1}\ \text{K}^{-1}$
ionic product of water at 298 K	K_w	$1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$
fundamental electronic charge	e	$1.60 \times 10^{-19}\ \text{C}$

temperature (K) = temperature (°C) + 273

$1\ \text{dm}^3 = 1000\ \text{cm}^3$
$1\ \text{m}^3 = 1000\ \text{dm}^3$
1 tonne = 1000 kg
$1\ \text{atm} = 1.01 \times 10^5\ \text{Pa}$

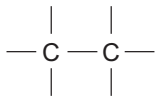
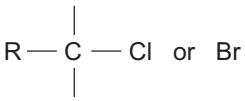
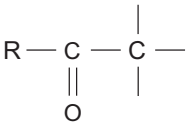
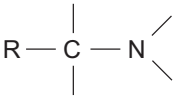
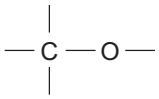
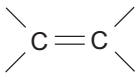
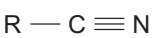
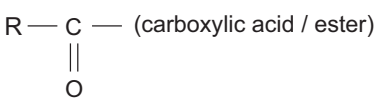
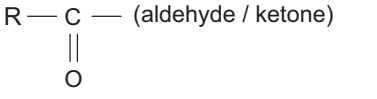
Multiple	Prefix	Symbol
10^{-9}	nano	n
10^{-6}	micro	μ
10^{-3}	milli	m

Multiple	Prefix	Symbol
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G

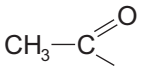
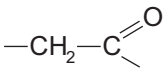
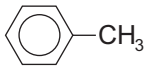
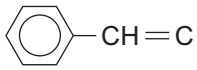
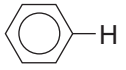
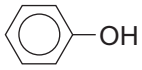
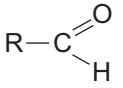
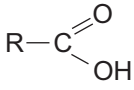
Infrared absorption values

Bond	Wavenumber / cm^{-1}
C — Br	500 to 600
C — Cl	650 to 800
C — O	1000 to 1300
C = C	1620 to 1670
C = O	1650 to 1750
C ≡ N	2100 to 2250
C — H	2800 to 3100
O — H (carboxylic acid)	2500 to 3200 (very broad)
O — H (alcohol / phenol)	3200 to 3550 (broad)
N — H	3300 to 3500

^{13}C NMR chemical shifts relative to TMS = 0

Type of carbon	Chemical shift, δ (ppm)
	5 to 40
	10 to 70
	20 to 50
	25 to 60
	50 to 90
	90 to 150
	110 to 125
	110 to 160
	160 to 185
	190 to 220

^{1}H NMR chemical shifts relative to TMS = 0

Type of proton	Chemical shift, δ (ppm)
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
	2.0 to 2.5
	2.0 to 3.0
	2.2 to 2.3
$HC-Cl$ or $HC-Br$	3.1 to 4.3
$HC-O$	3.3 to 4.3
$R-OH$	4.5 *
$-C=CH$	4.5 to 6.3
$-C=CH-CO$	5.8 to 6.5
	6.5 to 7.5
	6.5 to 8.0
	7.0 *
	9.8 *
	11.0 *

*variable figure dependent on concentration and solvent

THE PERIODIC TABLE