

Please write clearly in block capitals.

Centre number

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Candidate number

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Surname *StemUp Model Solution*

Forename(s)

Candidate signature

INTERNATIONAL A-LEVEL CHEMISTRY (9620)

Unit 4: Organic 2 and Physical 2

Tuesday 22 January 2019 07:00 GMT Time allowed: 1 hour 30 minutes

Materials

For this paper you must have:

- the Periodic Table/Data Sheet, provided as an Insert
- a ruler with millimetre measurements
- a scientific calculator, which you are expected to use where appropriate.

Instructions

- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- If you need extra space for your answer(s), use the lined pages at the end of this book. Write the question number against your answer(s).
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information

- The marks for questions are shown in brackets.
- The maximum mark for this paper is 80.

For Examiner's Use	
Question	Mark
1	
2	
3	
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8	
9	
TOTAL	

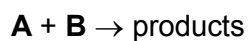


Answer **all** questions in the spaces provided.

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0 1

The rate of reaction between solutions of **A** and **B** is investigated.



Three experiments are completed at a given temperature. The results of these experiments are shown in **Table 1**.

Table 1

	Initial concentration of A / mol dm ⁻³	Initial concentration of B / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
Experiment 1	2.40×10^{-3}	2.80×10^{-3}	1.60×10^{-4}
Experiment 2	3.60×10^{-3}	4.20×10^{-3}	3.60×10^{-4}
Experiment 3	5.40×10^{-3}	4.20×10^{-3}	8.10×10^{-4}

0 1 . 1

Use the data in **Table 1** to deduce the order of reaction with respect to **A** and the order of reaction with respect to **B**.

Place **one** tick (✓) in the box which shows the order with respect to **A** and the order with respect to **B**.

[2 marks]

Order with respect to **A**

Zero

☐

First

☐

Second

☒

Order with respect to **B**

Zero

☒

First

☐

Second

☐


0 1 . 2

The reaction between compounds **C** and **D** is studied at a given temperature. The rate equation for the reaction is found to be

$$\text{rate} = k [\text{C}]^2 [\text{D}]$$

When the initial concentration of **C** is $8.55 \times 10^{-2} \text{ mol dm}^{-3}$ and the initial concentration of **D** is $2.80 \times 10^{-2} \text{ mol dm}^{-3}$, the initial rate of reaction is $9.43 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$

Calculate the value of the rate constant at this temperature and deduce its units.

[3 marks]

$$k = \text{rate} \div ([\text{C}]^2 [\text{D}])$$

$$k = 9.43 \times 10^{-4} \div ((8.55 \times 10^{-2})^2 \times 2.80 \times 10^{-2})$$

$$k = 9.43 \times 10^{-4} \div 2.047 \times 10^{-4} = 4.61$$

$$\text{units} = \text{mol dm}^{-3} \text{ s}^{-1} \div (\text{mol dm}^{-3})^3 = \text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

Rate constant 4.61 Units $\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$

5

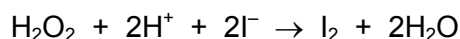
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0 2

Iodide ions react with hydrogen peroxide to form iodine as shown.



A student reacted iodide ions with hydrogen peroxide at different temperatures to determine the activation energy (E_a) for this reaction.

The student measured the time taken for a set amount of iodine to be formed at different temperatures. The results from the experiment are shown in **Table 2**.

An equation that relates activation energy (E_a) to the time taken (*time*) and temperature (T), where C is a constant, is shown.

$$\ln\left(\frac{1}{\text{time}}\right) = -\frac{E_a}{RT} + \ln C$$

Table 2

Experiment	Temperature / K	Time / s	$\frac{1}{\text{time}}$ / s ⁻¹	$\ln\left(\frac{1}{\text{time}}\right)$	$\frac{1}{T}$ / K ⁻¹
1	306	350	2.86×10^{-3}	-5.86	3.27×10^{-3}
2	316	102	9.80×10^{-3}	-4.62	3.16×10^{-3}
3	326	35	2.86×10^{-2}	-3.56	3.07×10^{-3}
4	336	12	8.33×10^{-2}	-2.48	2.98×10^{-3}

0 2 . 1

On **Figure 1**, plot a graph of $\ln\left(\frac{1}{\text{time}}\right)$ against $\frac{1}{T}$

You should plot $\ln\left(\frac{1}{\text{time}}\right)$ on the y-axis and $\frac{1}{T}$ on the x-axis.

Draw a line of best fit through your points.

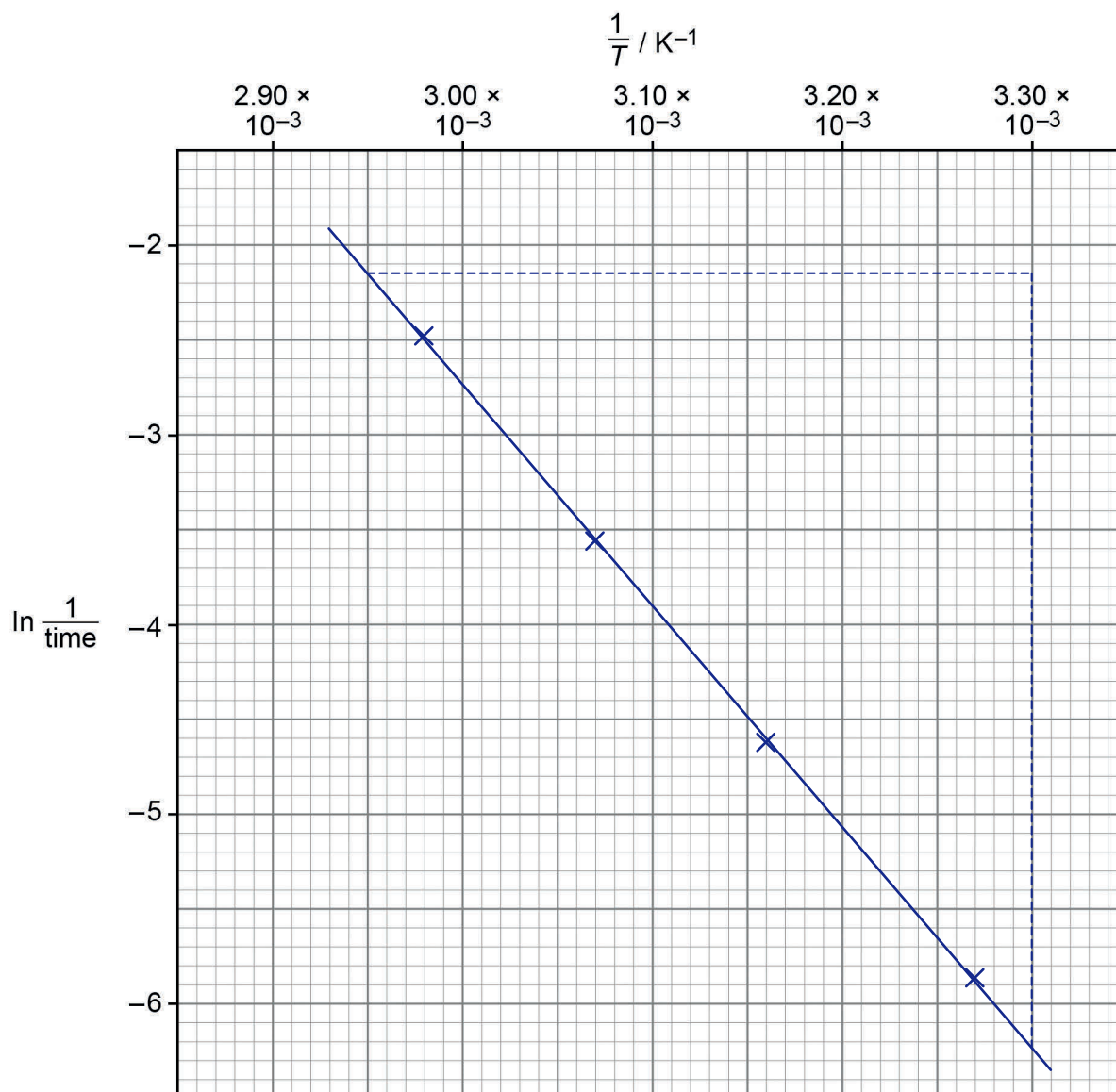
Use the gradient of your line to calculate the activation energy, in kJ mol⁻¹, for this reaction.

The gas constant, $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

[5 marks]



Figure 1



$$\text{gradient} = (-6.23 - (-2.15)) \div (3.30 \times 10^{-3} - 2.95 \times 10^{-3}) = -1.17 \times 10^4 \text{ K}$$

$$E_a = -\text{gradient} \times R = 1.17 \times 10^4 \times 8.31 = 9.72 \times 10^4 \text{ J mol}^{-1}$$

$$E_a = 97\,200 \div 1000 = 97.2 \text{ kJ mol}^{-1}$$

Activation Energy 97.2 kJ mol⁻¹

0 2 . 2

Suggest why the student did not repeat the experiment at temperatures higher than 336 K

[1 mark]

At higher temperatures the time would be very short (too fast), so the percentage error in measuring the time would be very high.

Turn over ►



0 3

This question is about carboxylic acids and esters.

0 3 . 1

Butanoic acid is a weak acid.

Write an expression for the acid dissociation constant (K_a) for butanoic acid.

[1 mark]

$$K_a = \frac{[CH_3CH_2CH_2COO^-][H^+]}{[CH_3CH_2CH_2COOH]}$$

0 3 . 2

At 298 K for butanoic acid, $K_a = 1.51 \times 10^{-5} \text{ mol dm}^{-3}$ Calculate the pH of a $0.150 \text{ mol dm}^{-3}$ solution of butanoic acid at 298 KGive your answer to **two** decimal places.

[3 marks]

$$[H^+] = [CH_3CH_2CH_2COO^-], \text{ so } [H^+] = \sqrt{K_a \times [CH_3CH_2CH_2COOH]}$$

$$[H^+] = \sqrt{(1.51 \times 10^{-5} \times 0.150)} = 1.50 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pH = -\log_{10}(1.50 \times 10^{-3}) = 2.82$$

pH 2.82

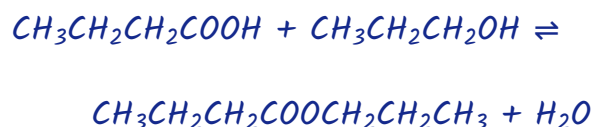
0 3 . 3

Write an equation to show the reaction of butanoic acid with propan-1-ol.

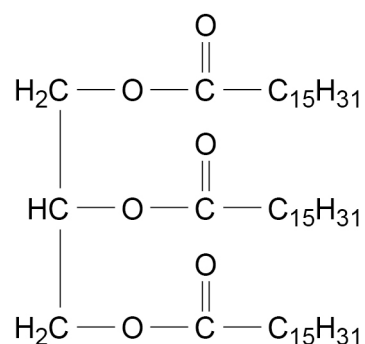
Identify a catalyst for this reaction.

[2 marks]

Equation

Catalyst concentrated sulfuric acid (H_2SO_4)

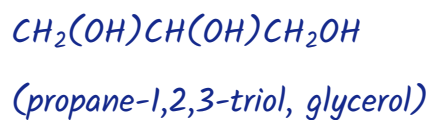
0 3 . 4 The structure of a tri-ester is shown.



Give the formula of each of the products formed when this tri-ester is hydrolysed in acid conditions.

[2 marks]

Product 1



Product 2



Turn over for the next question

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0 4

Propylamine can be formed in different reactions either from propanenitrile or from 1-bromopropane.

0 4 . 1

State the reagent and condition, other than temperature, for the formation of propylamine from each of these starting materials.

[3 marks]

From propanenitrile

Reagent hydrogen (H_2)

Condition nickel catalyst (Ni)

From 1-bromopropane

Reagent ammonia (NH_3), in ethanol

Condition excess ammonia (in a sealed tube)

0 4 . 2

N-methylethylamine is a secondary amine and an isomer of propylamine.

Suggest why the secondary amine is a stronger base than propylamine.

[2 marks]

The secondary amine has two alkyl groups on the N; alkyl groups are
electron releasing (positive inductive effect), so they push electron
density onto the N.

So the lone pair on the N is more available to accept a proton (H^+).

5



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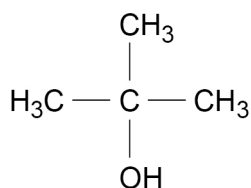
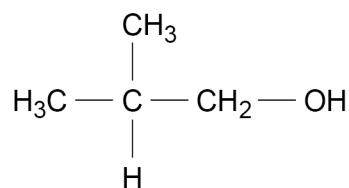


0 5

Simple test-tube reactions can be used to distinguish the following pairs of isomers.

Give a reagent, or combination of reagents, that can be added to the compounds in each pair to distinguish between them.

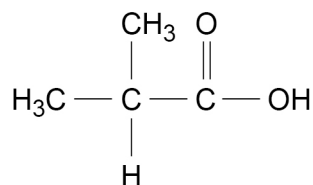
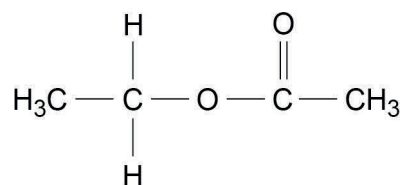
State what is observed in each case.

0 5 . 1**R****S****[3 marks]**

Reagent acidified potassium dichromate(VI) ($\text{K}_2\text{Cr}_2\text{O}_7$ / H_2SO_4), warm

Observation with **R** no visible change (stays orange)

Observation with **S** orange to green

0 5 . 2**T****U****[3 marks]**

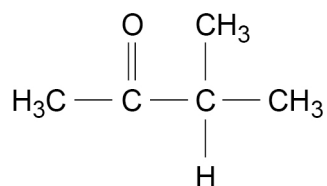
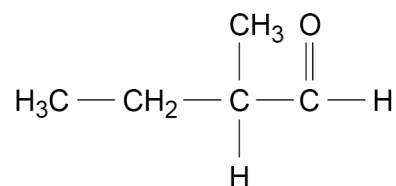
Reagent sodium carbonate solution (Na_2CO_3)

Observation with **T** effervescence (bubbles of CO_2)

Observation with **U** no visible change



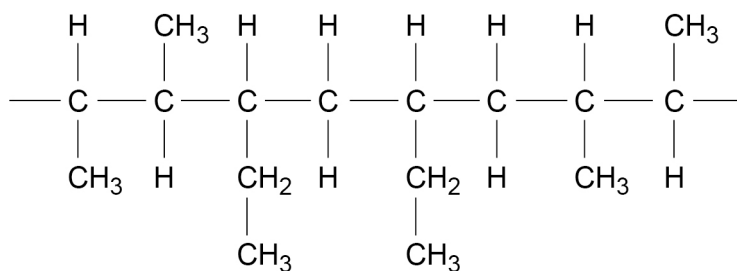
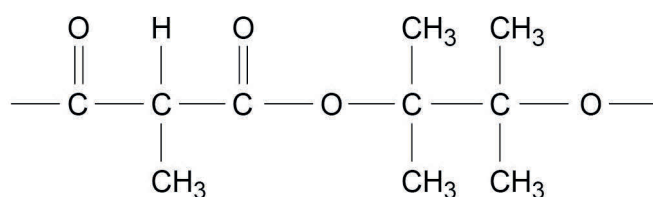
0 5 . 3

V**W****[3 marks]**Reagent Tollens' reagent (ammoniacal silver nitrate), warmObservation with **V** no visible changeObservation with **W** silver mirror forms

9

Turn over for the next question**Turn over ►**

0 6

Sections of two polymers, **E** and **F**, are shown.**E****F**

0 6

. 1

Polymer **E** is made from two different alkene monomers.

Draw the skeletal formula of each alkene monomer.

[2 marks]**Alkene monomer 1****Alkene monomer 2***(but-2-ene)**(but-1-ene)*

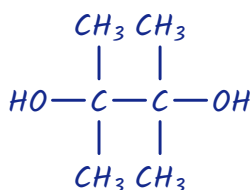
0 6 . 2

Polymer **F** is a polyester. This polyester is produced by reacting a diol with a dicarboxylic acid.

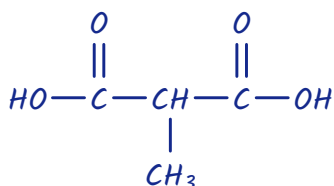
Give the structure of the diol and the structure of the dicarboxylic acid used to produce this polyester.

[2 marks]

Diol



Dicarboxylic acid



0 6 . 3

Suggest an environmental advantage of polymer **F** compared with polymer **E**.

Explain your answer.

[3 marks]

Advantage Polymer F is biodegradable (it can be broken down).

Explanation F has polar C=O groups (ester links) in its chain, so the δ^+ C can be attacked by nucleophiles such as water: F can be hydrolysed.

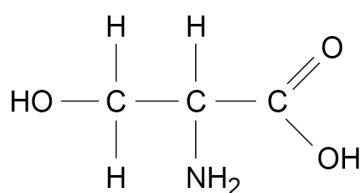
E has only strong, non-polar C-C and C-H bonds, so it cannot be hydrolysed.

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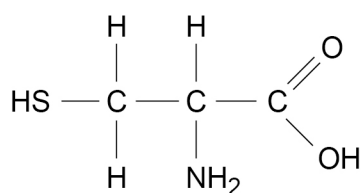


07

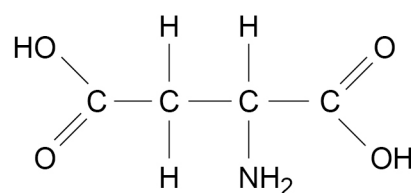
The structures of three amino acids are shown.



Serine



Cysteine



Aspartic acid

07.1

Use IUPAC rules to deduce the name for serine.

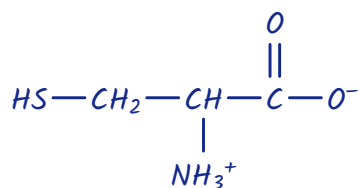
[1 mark]

2-amino-3-hydroxypropanoic acid

07.2

Draw the structure of the zwitterion formed by cysteine.

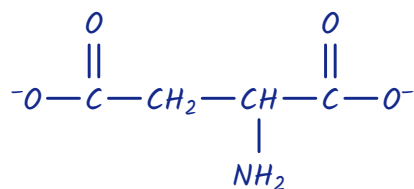
[1 mark]



07.3

Draw the structure of the species formed by aspartic acid at high pH.

[1 mark]

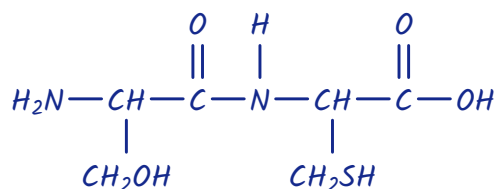


0 7 . 4

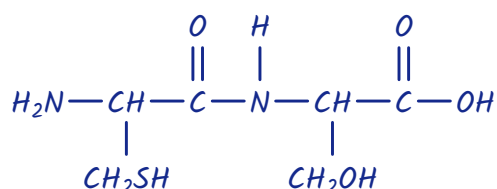
Draw the structure of each of the two dipeptides formed when cysteine and serine react together.

[2 marks]

Dipeptide 1



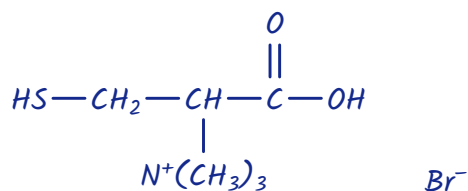
Dipeptide 2



0 7 . 5

Draw the structure of the species formed when cysteine reacts with an excess of bromomethane.

[1 mark]



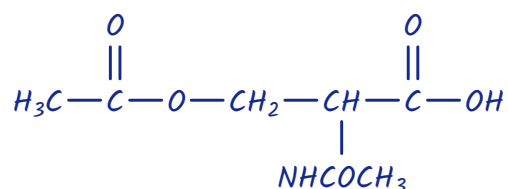
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0 7 . 6

Draw the structure of the species formed when serine reacts with an excess of ethanoyl chloride.

[2 marks]



0 7 . 7

A mixture of amino acids can be separated using thin-layer chromatography.

Describe how amino acids can be made visible on the chromatogram.

Explain why different amino acids have different R_f values.

[3 marks]

How amino acids are made visible Spray with ninhydrin (and warm), or shine UV light on the plate.

Explanation Amino acids have different polarities (different R groups).
So they have different affinities for the stationary phase and for the mobile phase (solvent), so they move different distances up the plate.



0 7 . 8 **Table 3** shows different types of bonding in proteins.

Complete **Table 3** by placing a tick (✓) in the correct column to show which level of protein structure (primary, secondary or tertiary) contains each type of bonding.

[2 marks]

Table 3

Type of bonding	Primary	Secondary	Tertiary
Hydrogen bonds in an α -helix		✓	
Peptide links between amino acids	✓		
Hydrogen bonds between $-\text{CH}_2\text{OH}$ groups in serine amino acids			✓
Disulfide bonds between cysteine amino acids			✓

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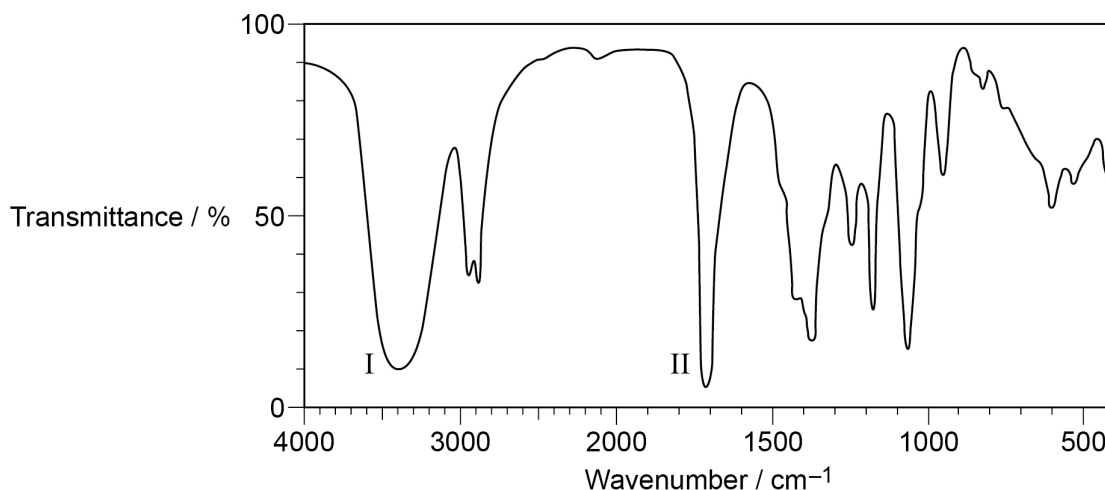


0 8

Compound **G** has the molecular formula $C_4H_8O_2$

The infrared spectrum of **G** is shown in **Figure 2**.

Figure 2



0 8 . 1

Use **Table A** on the Data Sheet to identify the bond causing the absorption labelled **I** and the bond causing the absorption labelled **II**.

[2 marks]

Bond **I** O-H (alcohols)

Bond **II** C=O

0 8 . 2

Proton (^1H) NMR spectra are recorded using solutions that contain the non-toxic and inert standard tetramethylsilane (TMS).

Give **two** other reasons why TMS is a suitable standard.

[2 marks]

Reason 1 It gives a single intense peak, because all 12 H atoms are in the same environment.

Reason 2 It is volatile (low boiling point), so it is easily removed from the sample.



Question 8 continues on the next page

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0 8 . 3 Identify a suitable solvent to use when recording a ^1H NMR spectrum.

Give a reason for your choice.

[2 marks]

Solvent CDCl_3

Reason It contains no ^1H atoms (no protons), so gives no peaks.

The ^1H NMR spectrum of **G** shows four peaks. **Table 4** gives chemical shift (δ) values for the four peaks, their splitting patterns and integration values.

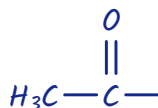
Table 4

δ / ppm	2.20	2.60	3.40	3.84
Splitting pattern	singlet	triplet	singlet	triplet
Integration value	0.75	0.50	0.25	0.50

Use **Figure 2**, **Table 4** and **Table B** of your Data Sheet to help you answer questions **08.4**, **08.5** and **08.6**.

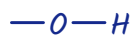
0 8 . 4 Draw the part of the structure of **G** that can be deduced from the peak at $\delta = 2.20$ ppm

[1 mark]



0 8 . 5 Draw the part of the structure of **G** that can be deduced from the peak at $\delta = 3.40$ ppm

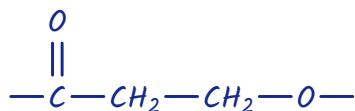
[1 mark]



0 8 . 6

Draw the part of the structure of **G** that can be deduced from the peaks at $\delta = 2.60$ ppm and $\delta = 3.84$ ppm

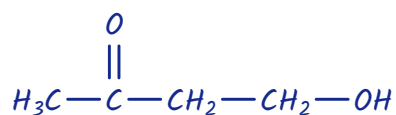
[2 marks]



0 8 . 7

Deduce the structure of **G**.

[1 mark]



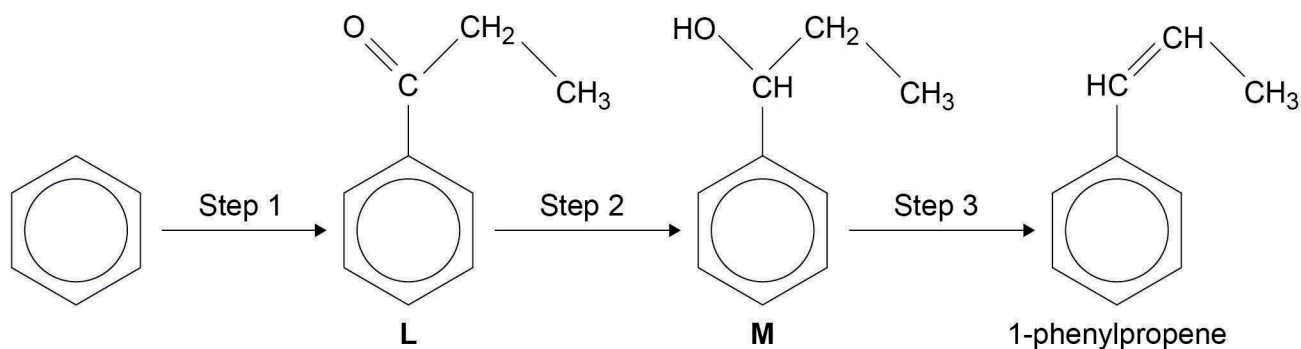
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0 9

1-Phenylpropene can be prepared as shown in **Figure 3**.**Figure 3**

0 9 . 1

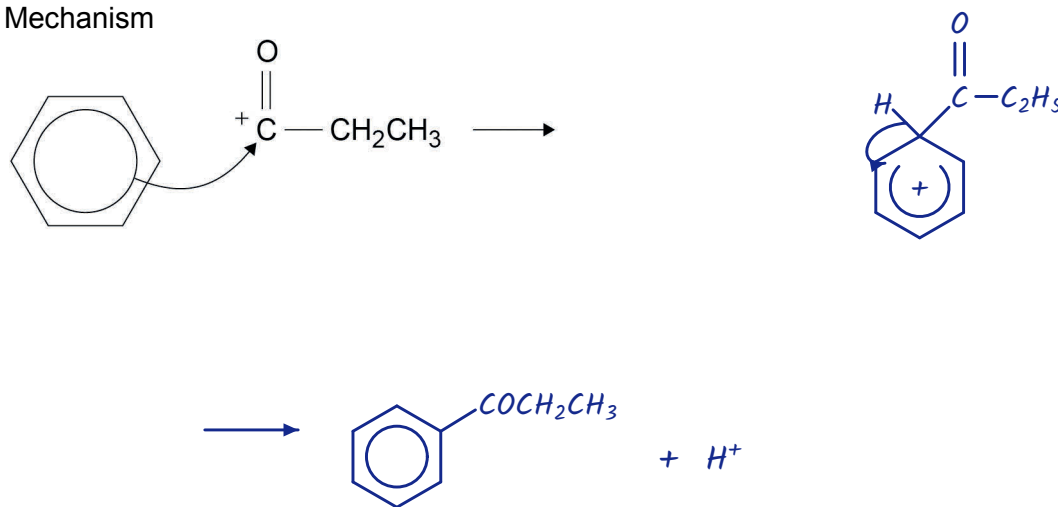
Step 1 involves an attack on benzene by the electrophile $[\text{CH}_3\text{CH}_2\text{CO}]^+$

Write an equation for a reaction that forms this electrophile.

Complete the mechanism for the reaction of this electrophile with benzene.

[3 marks]Equation $\text{CH}_3\text{CH}_2\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CO}^+ + \text{AlCl}_4^-$

Mechanism



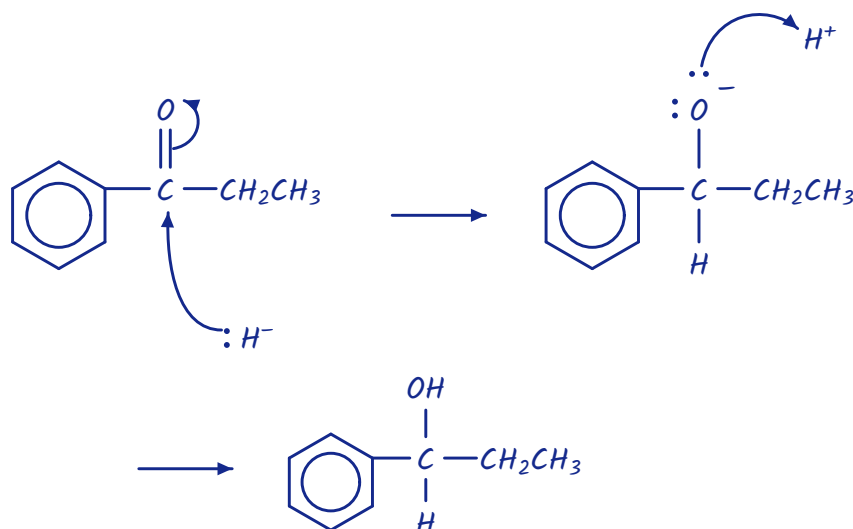
0 9 . 2 Step 2 involves the reaction of **L** with NaBH_4

Name and outline the mechanism for this reaction.

[5 marks]

Name of mechanism nucleophilic addition

Mechanism



Question 9 continues on page 25

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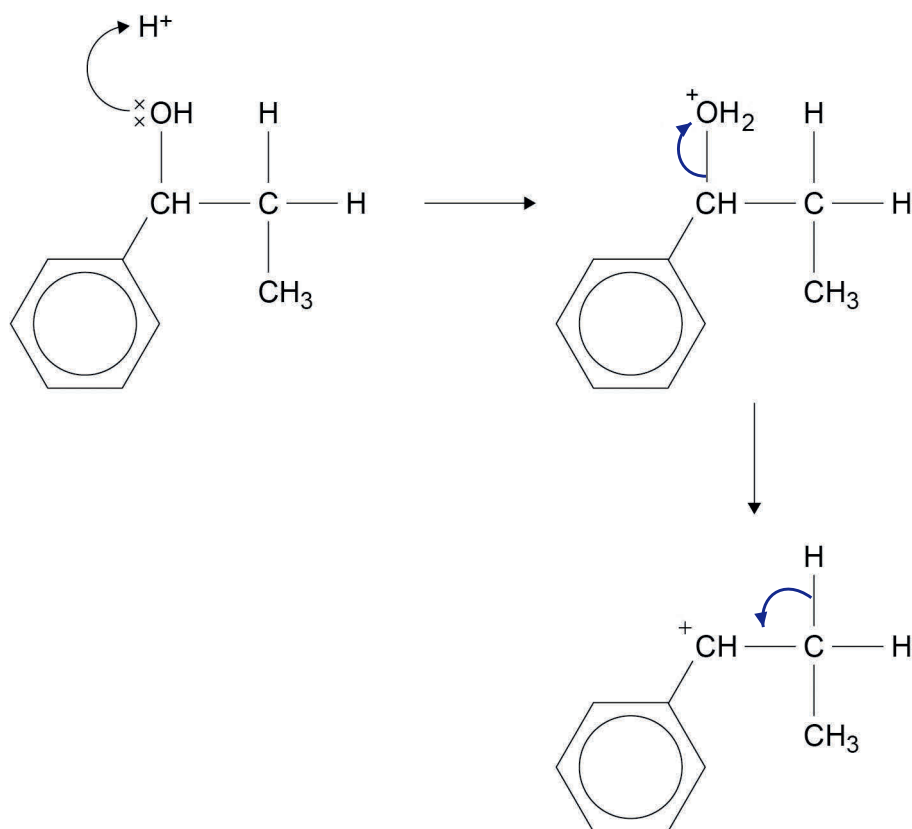
0 9 . 3

1-Phenylpropene can be formed by reacting **M** with concentrated sulfuric acid. Part of the mechanism is shown in **Figure 4**.

Draw **two** curly arrows on **Figure 4** to complete the mechanism. You do **not** need to draw the final products.

[2 marks]

Figure 4



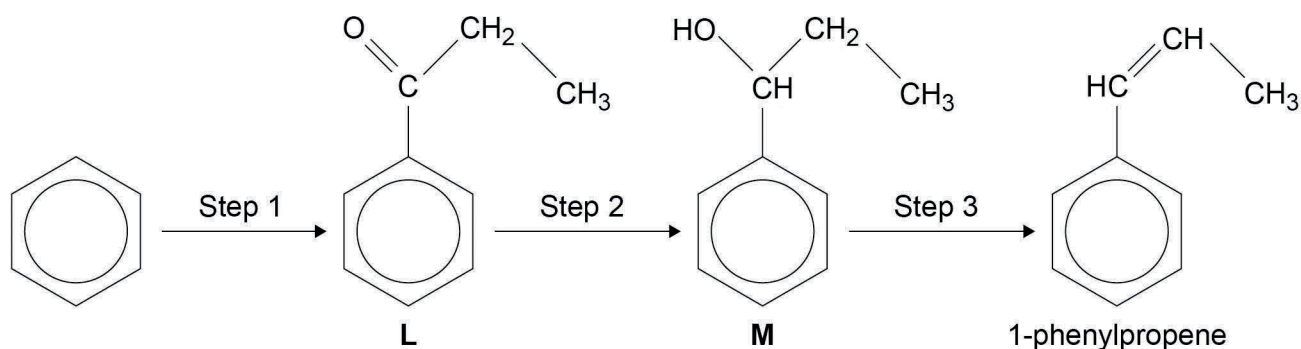
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Figure 3 is repeated here.

Figure 3



0 9 . 4 **M** exists as two enantiomers.

State the meaning of the term enantiomers.

[1 mark]

Molecules (stereoisomers) that are non-superimposable mirror images of each other.

0 9 . 5 Describe how the two enantiomers could be distinguished.

[2 marks]

Shine plane polarised light through a solution of each enantiomer separately (in a polarimeter).

The two enantiomers rotate the plane of polarised light by the same angle but in opposite directions.



0 9 . 6

The overall percentage yield in the preparation of 1-phenylpropene from benzene is 68.0%

Calculate the minimum mass of benzene needed to produce 1.68 g of 1-phenylpropene.

[3 marks]

$$M_r(C_9H_{10}) = 118.0; \quad M_r(C_6H_6) = 78.0$$

$$\text{moles of 1-phenylpropene} = 1.68 \div 118.0 = 0.0142 \text{ mol}$$

1 mol benzene gives 1 mol 1-phenylpropene, so mass of benzene =

$$0.0142 \times 78.0 = 1.11 \text{ g}$$

$$68.0\% \text{ yield, so mass needed} = 1.11 \times 100 \div 68.0 = 1.63 \text{ g}$$

Mass of benzene 1.63 g

16

END OF QUESTIONS



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