A

Surname ______________________

Other Names ______________________

Centre Number ______________________

Candidate Number ______________________

Candidate Signature ______________________

A-level

CHEMISTRY

Paper 2 Organic and Physical Chemistry

7405/2

Tuesday 11 June 2019 Afternoon

Time allowed: 2 hours

At the top of the page, write your surname and other names, your centre number, your candidate number and add your signature.

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For this paper you must have:

- **the Periodic Table/Data Sheet, provided as an insert (enclosed)**
- **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.**
- **Answer ALL questions.**
- **You must answer the questions in the spaces provided. Do NOT write on blank pages.**
- **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 105.**

DO NOT TURN OVER UNTIL TOLD TO DO SO

Answer ALL questions in the spaces provided.

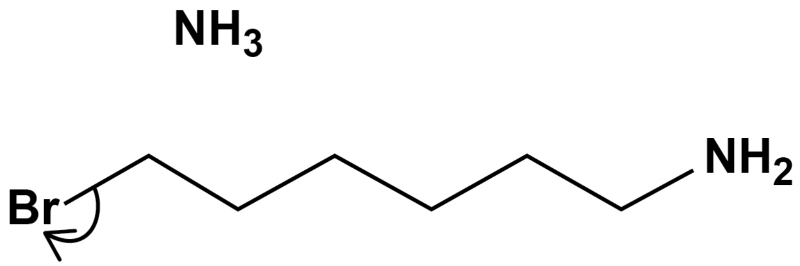
0 1 This question is about amines.

0 1 . 1 Give an equation for the preparation of 1,6-diaminohexane by the reaction of 1,6-dibromohexane with an excess of ammonia. [2 marks]

0 1 . 2 On the opposite page, complete the mechanism for the reaction of ammonia with 6-bromohexylamine to form 1,6-diaminohexane.

Suggest the structure of a cyclic secondary amine that can be formed as a by-product in this reaction. [4 marks]

Mechanism



Cyclic secondary amine

[Turn over]

0 1 . 3 **1,6-Diaminohexane can also be formed in a two-stage synthesis starting from 1,4-dibromobutane.**
Suggest the reagent and a condition for each stage in this alternative synthesis. [3 marks]

Stage 1 reagent and condition

____

____

Stage 2 reagent and condition

____

____

0 1 . 4 **Explain why 3-aminopentane is a stronger base than ammonia. [2 marks]**

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0 1 . 5 **Justify the statement that there are no chiral centres in 3-aminopentane. [1 mark]**

12

0 2 A student prepared cyclohexene by heating cyclohexanol with concentrated phosphoric acid. The cyclohexene produced was distilled off from the reaction mixture.

0 2 . 1 Complete the diagram, on the opposite page, of the apparatus used to distil the cyclohexene from the reaction mixture at 83 °C. [2 marks]

0 2 . 2 The distillate was shaken with saturated sodium chloride solution. The cyclohexene was separated from the aqueous solution using a separating funnel.

State why cyclohexene can be separated from the aqueous solution using the separating funnel. [1 mark]

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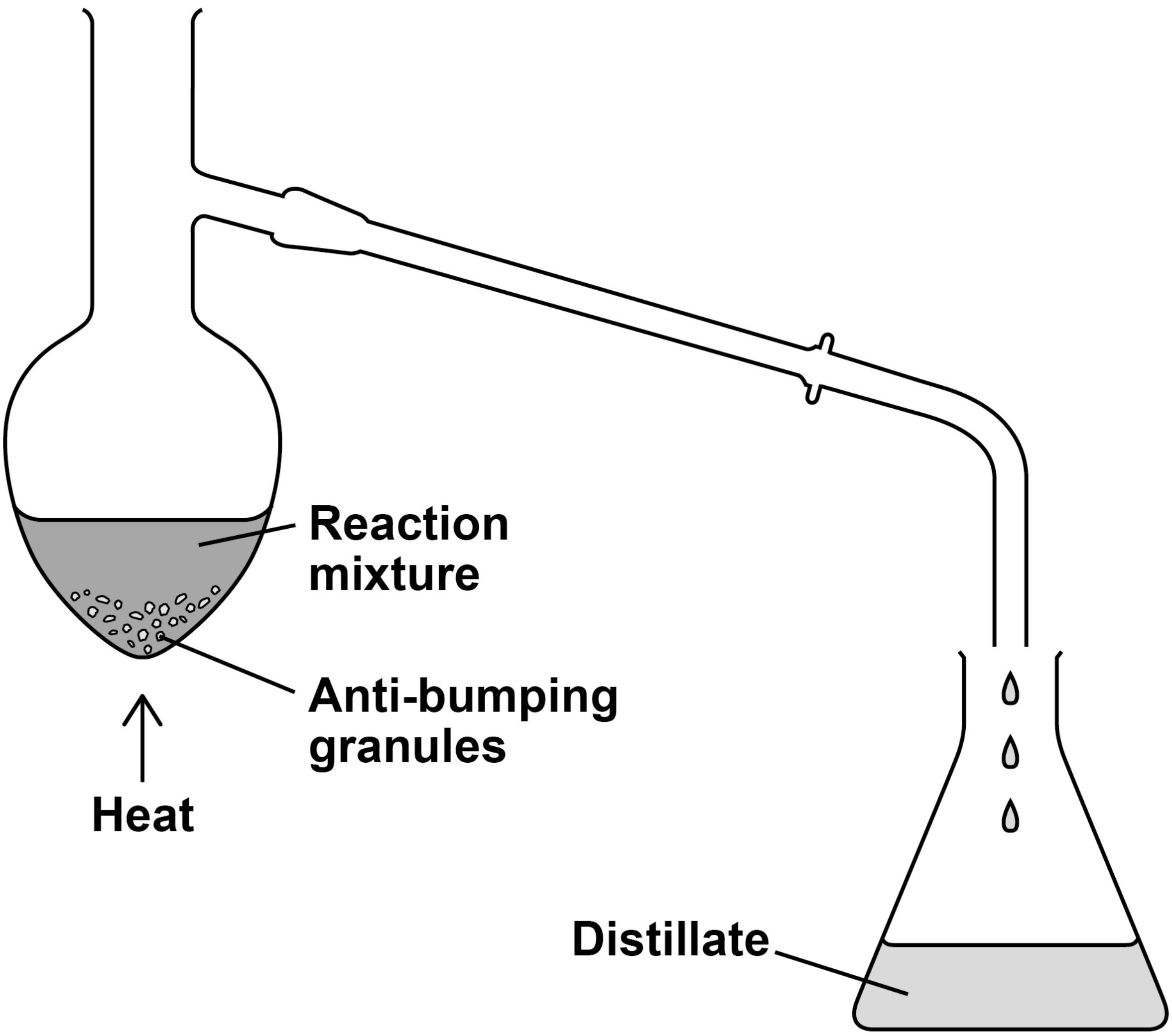
Reaction
mixture
Anti-bumping
granules
Heat
Distillate

0 2 . 3 **The cyclohexene separated in Question 02.2 was obtained as a cloudy liquid.**
The student dried this cyclohexene by adding a few lumps of anhydrous calcium chloride and allowing the mixture to stand.

Give ONE observation that the student made to confirm that the cyclohexene was dry.
[1 mark]

____

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0 2 . 4 **In this preparation, the student added an excess of concentrated phosphoric acid to 14.4 g of cyclohexanol (M_r = 100.0).**

The student obtained 4.15 cm^3 of cyclohexene (M_r = 82.0).

Density of cyclohexene = 0.810 g cm^{-3}

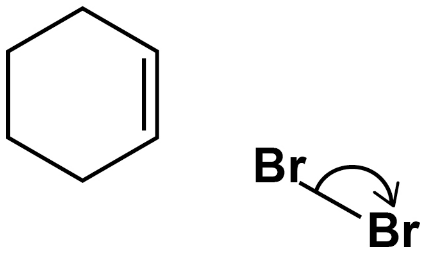
On the opposite page, calculate the percentage yield of cyclohexene obtained.
Give your answer to the appropriate number of significant figures. [5 marks]

% yield ______________________

[Turn over]

0 2 . 5 **Cyclohexene reacts with bromine.**

Complete the mechanism for this reaction.
[3 marks]



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0 3 The outer layers of some golf balls are made from a polymer called polyisoprene.
The isoprene monomer is a non-cyclic branched hydrocarbon that contains 88.2 % carbon by mass.
The empirical formula of isoprene is the same as its molecular formula.

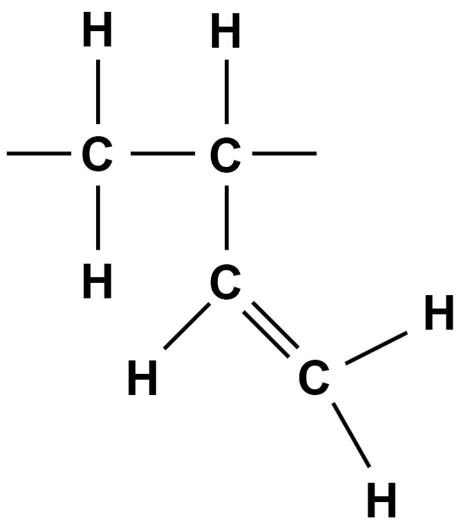
0 3 . 1 Deduce the molecular formula of isoprene and suggest a possible structure. [4 marks]

Molecular formula ____________________________

Structure

[Turn over]

0 3 . 2 The insides of some golf balls are made from a mixture of three other polymers.
The repeating unit for one of these polymers is shown.



On the opposite page, draw the skeletal formula of the monomer used to make this polymer.

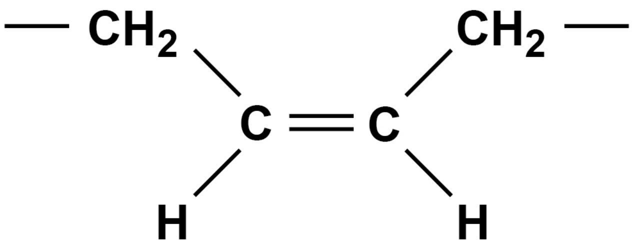
Give the IUPAC name of the monomer.
[2 marks]

Skeletal formula of monomer

IUPAC name ______________________________

[Turn over]

0 3 . 3 A second polymer in the mixture has a repeating unit with the structure shown.



The third polymer in the mixture is a stereoisomer of this polymer.

Draw the structure of the repeating unit of the third polymer.

Give a reason why this type of stereoisomerism arises. [2 marks]

Repeating unit

Reason ______________________________

____

____

____

____

0 3 . 4 **Golf balls recovered from lakes and ponds can be used again even after being in water for several years.**

Explain why these golf balls do not biodegrade. [1 mark]

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0 4 Substances P and Q react in solution at a constant temperature.
The initial rate of reaction was studied in three experiments by measuring the change in concentration of P over the first five seconds of the reaction.
The data obtained are shown in TABLE 1.

TABLE 1

Experiment	Time after mixing / s	Concentration / mol dm^{-3}	
		P	Q
1	0	1.00×10^{-2}	1.25×10^{-2}
	5.0	0.92×10^{-2}	not measured
2	0	2.00×10^{-2}	1.25×10^{-2}
	5.0	1.84×10^{-2}	not measured
3	0	0.50×10^{-2}	2.50×10^{-2}
	5.0	0.34×10^{-2}	not measured

0 4 . 1 **Complete TABLE 2 to show the initial rate of reaction of P in each experiment. [1 mark]**

TABLE 2

Experiment	Initial rate / mol dm^{-3} s^{-1}
1	1.6×10^{-4}
2	
3	

[Turn over]

0 4 . 2 **Determine the order of reaction with respect to P and the order of reaction with respect to Q. [2 marks]**

Order with respect to P ______________________

Order with respect to Q ______________________

0 4 . 3 A reaction between substances R and S was second order with respect to R and second order with respect to S.
At a given temperature, the initial rate of reaction was 1.20×10^{-3} mol dm^{-3} s^{-1} when the initial concentration of R was 1.00×10^{-2} mol dm^{-3} and the initial concentration of S was 2.45×10^{-2} mol dm^{-3}

Calculate a value for the rate constant, *k*, for the reaction at this temperature. Give the units for *k* [3 marks]

k ____________________ Units ____________________

[Turn over]

6

0 5 The rate constant, k, for a reaction varies with temperature as shown by the equation

$$k = Ae^{-E_a/RT}$$

For this reaction, at 25 °C, $k = 3.46 \times 10^{-8}\ s^{-1}$

The activation energy $E_a = 96.2\ kJ\ mol^{-1}$

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

Calculate a value for the Arrhenius constant, A, for this reaction.
Give the units for A. [4 marks]

A ________________ Units ________________

[Turn over]

4

0 6 This question is about isomers.

0 6 . 1 Give a reagent and observations for a test-tube reaction to distinguish between 2-methylbutan-1-ol and 2-methylbutan-2-ol.
[3 marks]

Reagent ______________________________

____

____

Observation with 2-methylbutan-1-ol

____

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____

____

Observation with 2-methylbutan-2-ol

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[Turn over]

0 6 . 2 **Compounds A and B both have the molecular formula $C_4H_8Br_2$**

A has a singlet, a triplet and a quartet in its ^1H NMR spectrum.

B has only two singlets in its ^1H NMR spectrum.

Draw a structure for each of A and B.
[2 marks]

A **B**

0 6 . 3 **Compounds C and D both have the molecular formula $C_6H_3Br_3$**

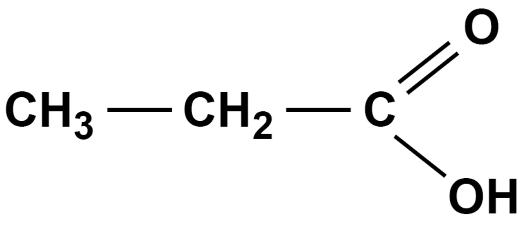
C has two peaks in its ^{13}C NMR spectrum.

D has four peaks in its ^{13}C NMR spectrum.

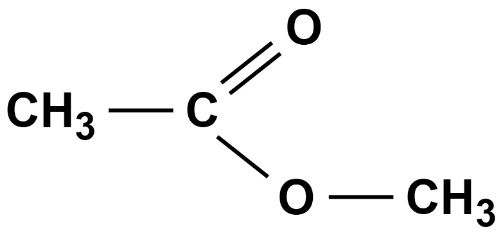
Draw a structure for each of C and D.
[2 marks]

C **D**

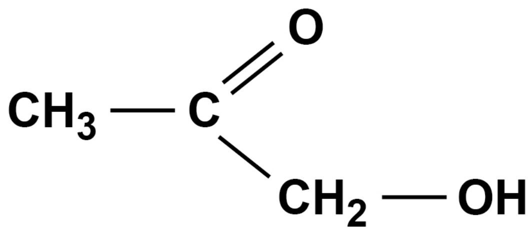
0 6 . 4 **Compounds E, F, and G are isomers.**



E



F

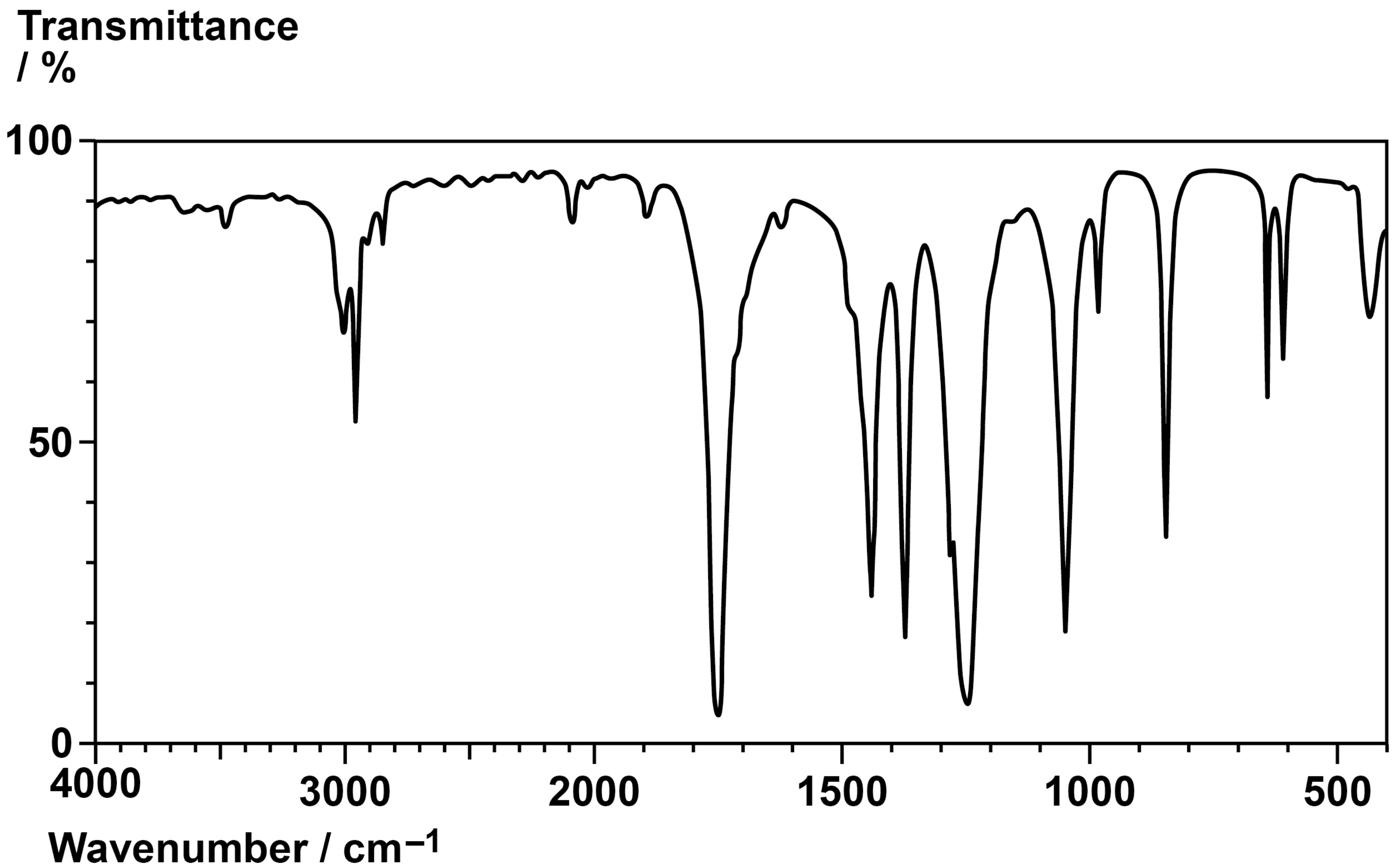


G

FIGURE 1, on pages 31 to 33, shows the infrared spectra of these isomers, but not necessarily in the same order.

Label each spectrum with the correct letter E, F or G in the box. [1 mark]

FIGURE 1



31

[Turn over]

FIGURE 1 continued

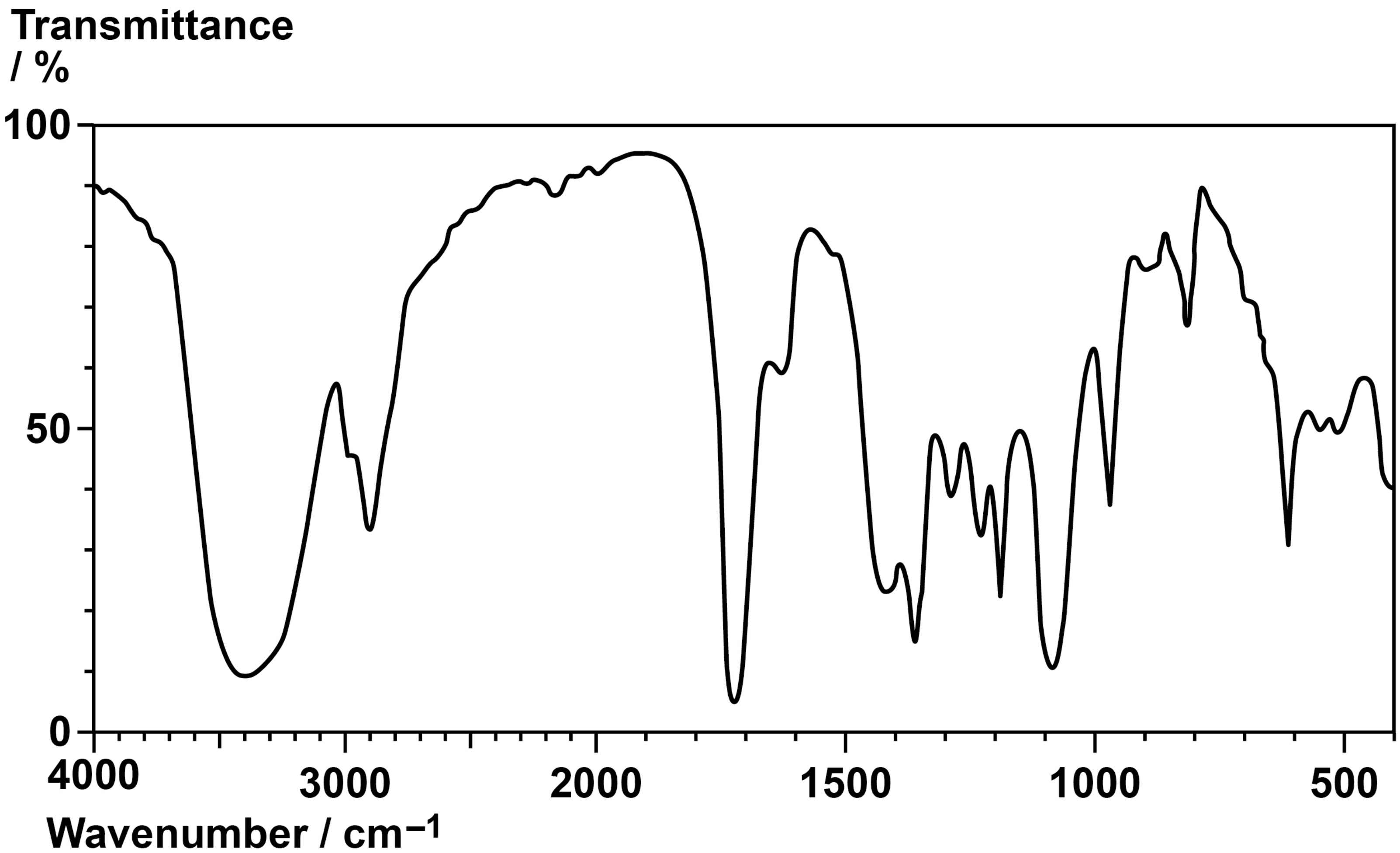
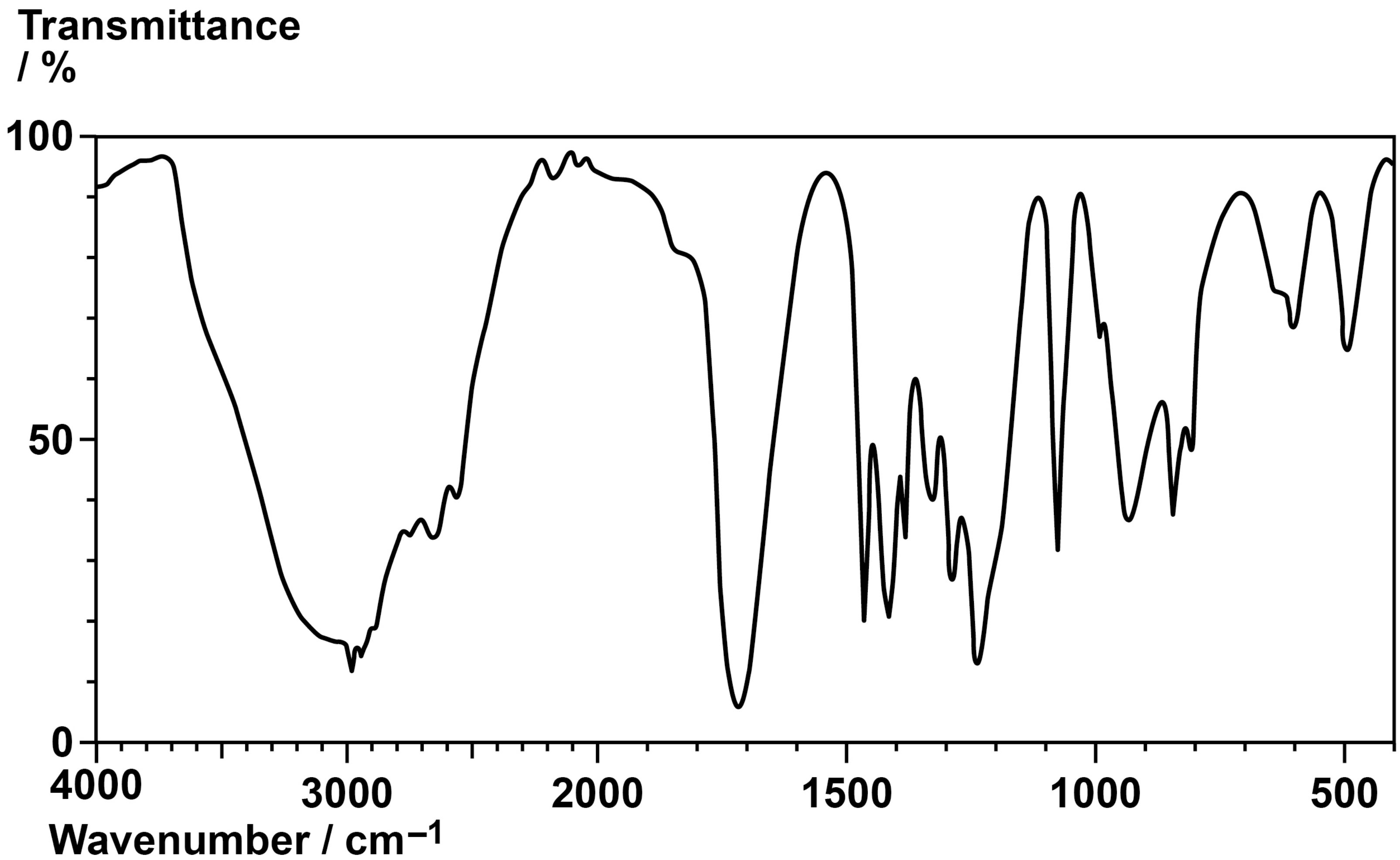


FIGURE 1 continued

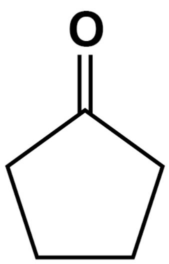


[Turn over]

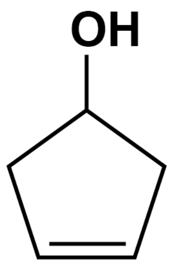
8

0 7 **Isomers X and Y have the molecular formula C_5H_8O**

Isomer X



Isomer Y



0 7 . 1 **Give the IUPAC name for isomer X. [1 mark]**

____

____

0 7 . 2 Explain how and why isomers X and Y can be distinguished by comparing EACH of their

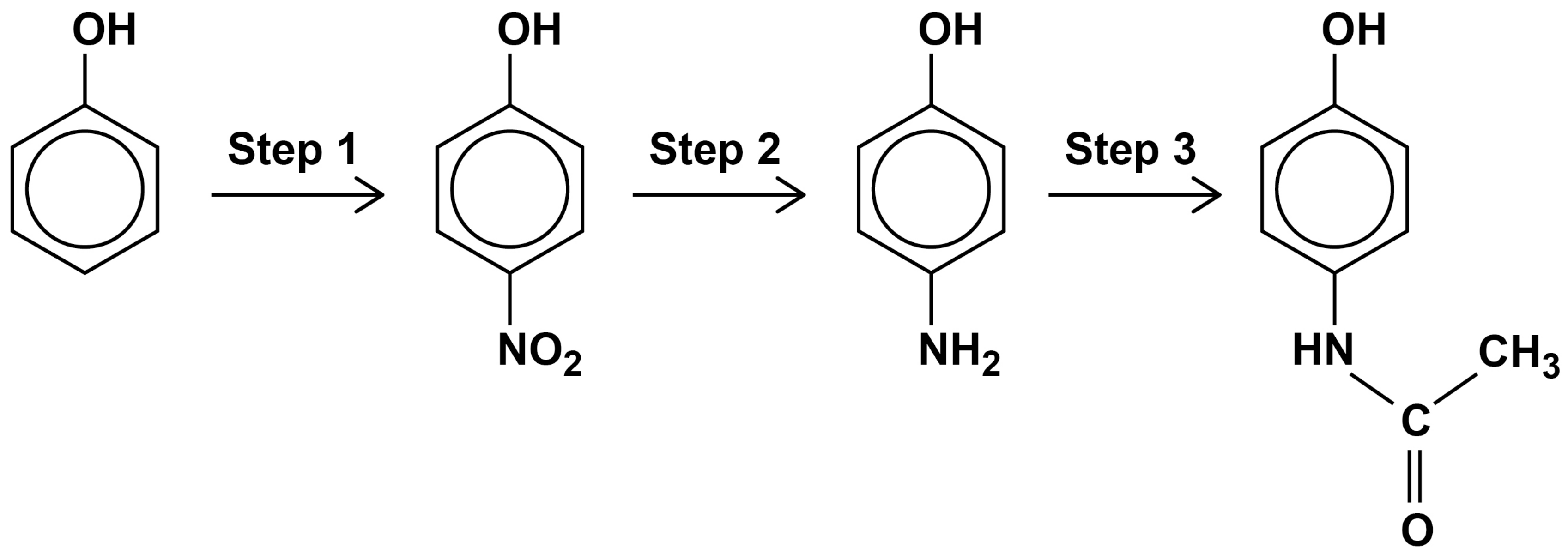
- boiling points
- ^{13}C NMR spectra
- infrared spectra.

Use data from Tables A and C in the Data Booklet in your answer. [6 marks]

7

[Turn over]

0 8 **Paracetamol is a medicine commonly used to relieve mild pain. Traditionally, paracetamol has been made industrially in a three-step synthesis from phenol.**



phenol **4-nitrophenol** **4-aminophenol** **paracetamol**

0 8 . 1 **Name the mechanism of the reaction in Step 1. [1 mark]**

[Turn over]

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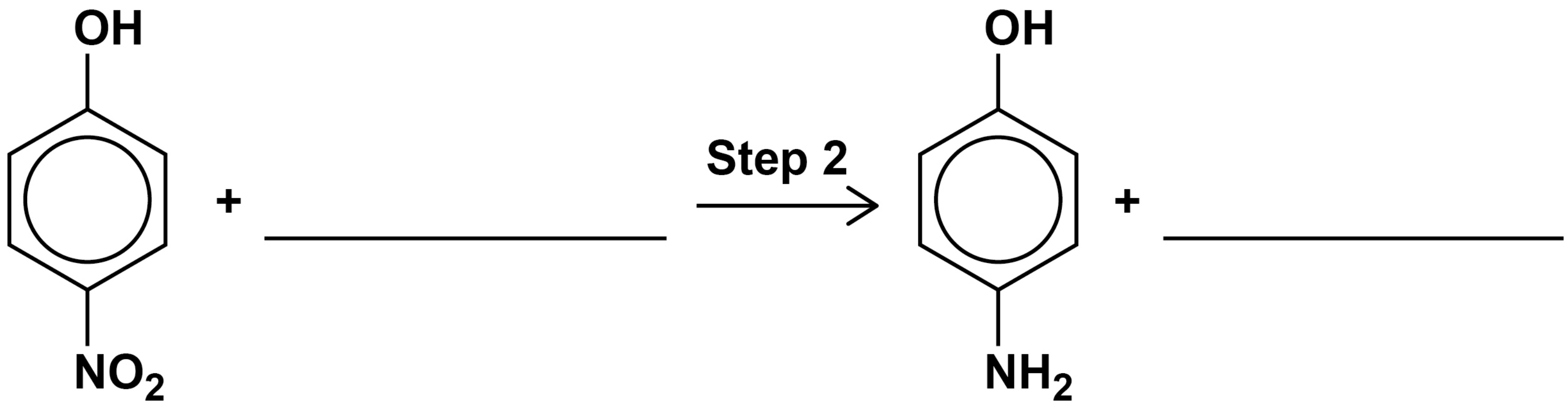
0 8 . 2 **Complete the equation for the reaction in Step 2. [1 mark]**

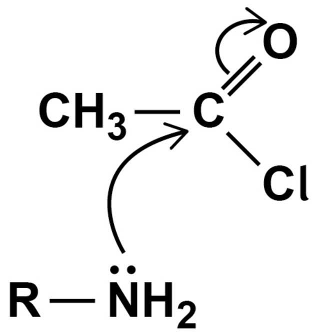


[Turn over]

0 8 . 3 In theory, either ethanoyl chloride or ethanoic anhydride could be used in Step 3.

Complete the mechanism for the reaction of 4-aminophenol with ethanoyl chloride.

RNH_2 is used to represent 4-aminophenol in this mechanism. [2 marks]



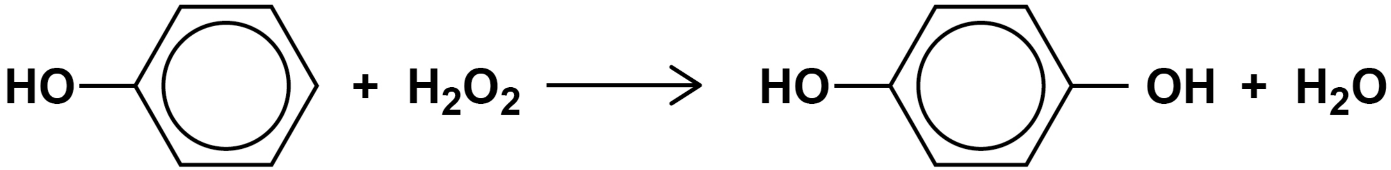
0 8 . 4 In practice, ethanoic anhydride is used in the industrial synthesis rather than ethanoyl chloride.

Give ONE reason why ethanoyl chloride is NOT used in the industrial synthesis.
[1 mark]

0 8 . 5 In Step 3 other aromatic products are formed as well as paracetamol.

Draw the structure of ONE of these other aromatic products. [1 mark]

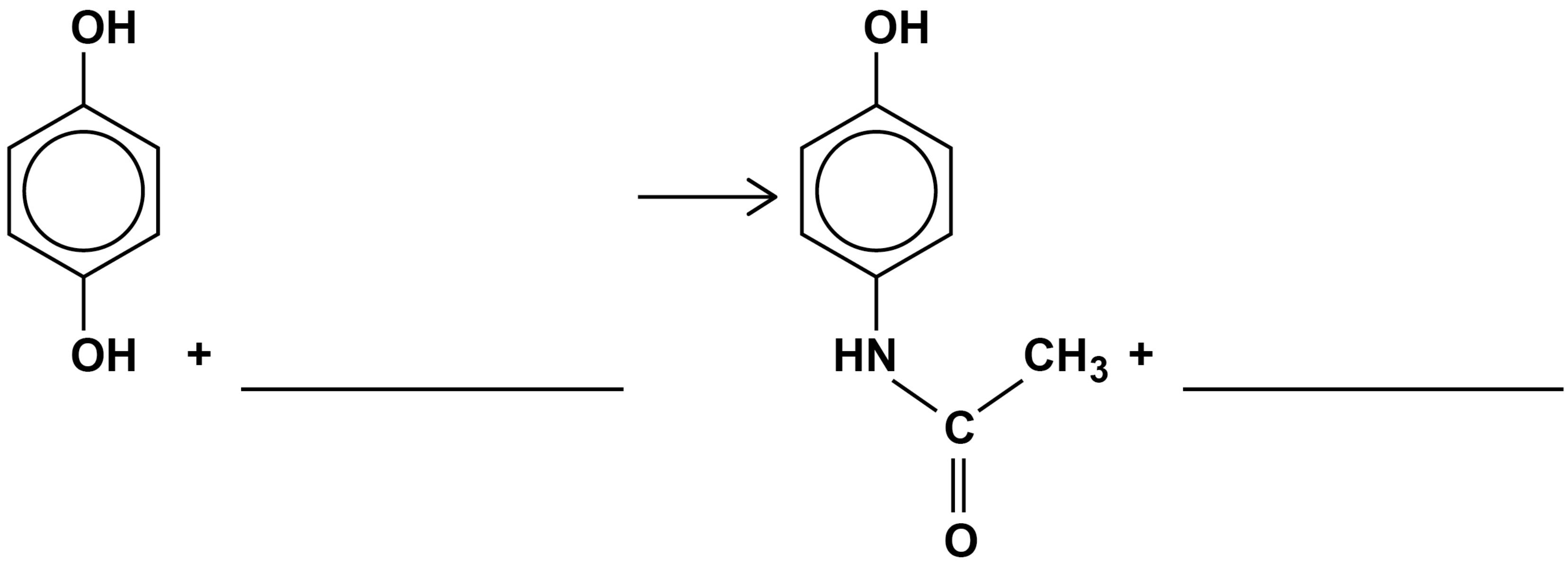
0 8 . 6 Chemists have recently developed a two-step process to produce paracetamol from phenol.
In the first step, phenol is oxidised to hydroquinone.



hydroquinone

In the second step, hydroquinone reacts with ammonium ethanoate to form paracetamol.

On page 45, complete the equation for this second step. [1 mark]



hydroquinone **paracetamol**

[Turn over]

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0 8 . 7 **Calculate the mass, in kg, of hydroquinone (M_r = 110.0) needed to produce 250 kg of paracetamol. [3 marks]**

Mass ____________________ **kg**

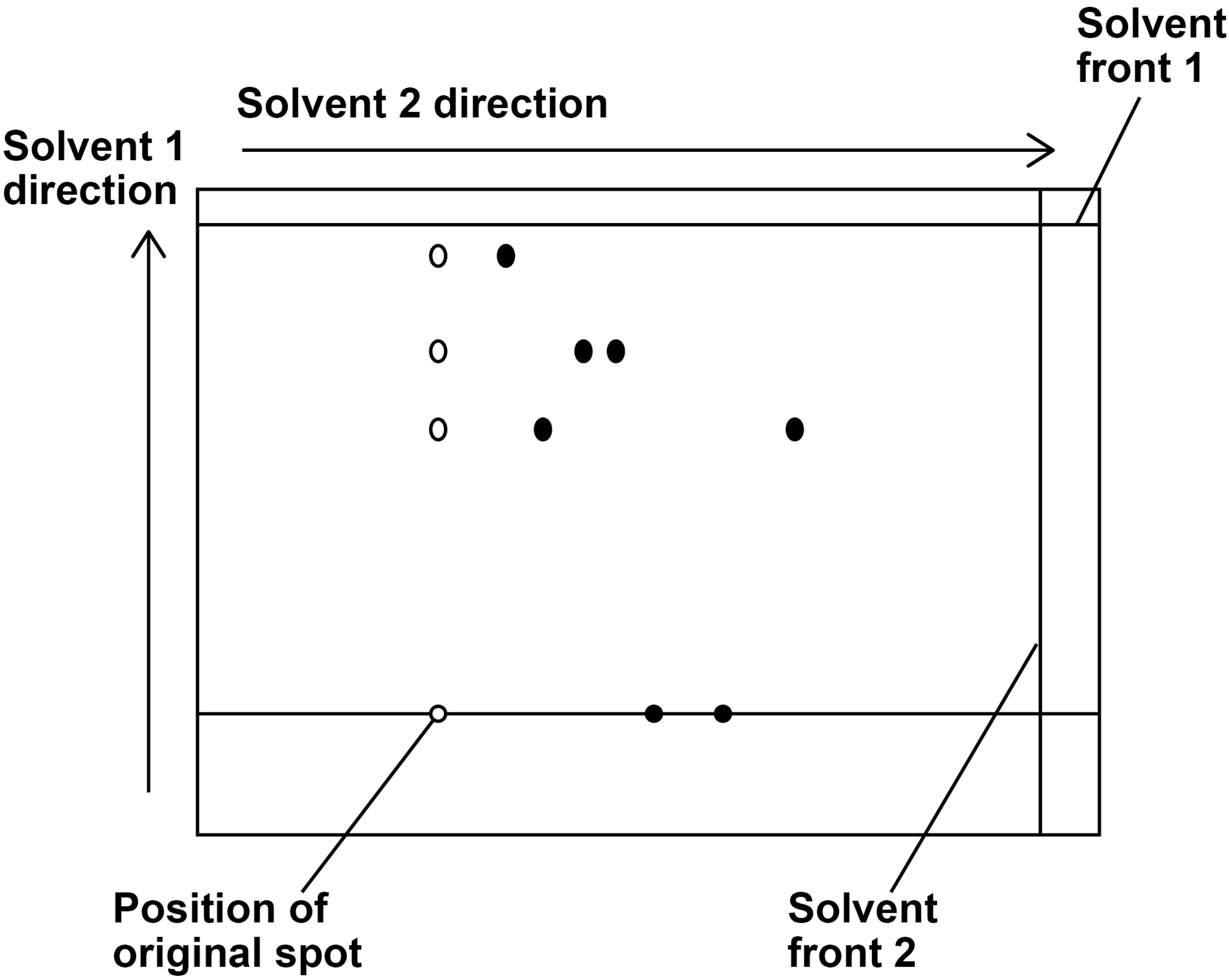
10

0 9 This question is about thin-layer chromatography (TLC).

- A protein was hydrolysed to form a mixture of amino acids.
- A spot of this mixture was added to a TLC plate and the plate placed vertically in a small volume of solvent 1.
- When the solvent front reached nearly to the top of the plate, the plate was removed and allowed to dry.
- The plate was turned anticlockwise through 90° and placed vertically in a small volume of solvent 2.
- When the solvent front reached nearly to the top of the plate, the plate was again removed and allowed to dry.
- FIGURE 2, on the opposite page, shows the final TLC plate.

0 9 . 1 Suggest a suitable reagent for the hydrolysis of a protein. [1 mark]

FIGURE 2



KEY

○ **Spot seen after use of solvent 1**

● **Spot seen after use of solvent 2**

[Turn over]

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0 9 . 2 **Suggest how the positions of the amino acids on the TLC plate were located. [1 mark]**

0 9 . 3 **Deduce the minimum number of amino acids present in the original mixture. [1 mark]**

0 9 . 4 **Suggest why it was necessary to use two different solvents. [1 mark]**

1 0 **Some compounds with different molecular formulas have the same relative molecular mass to the nearest whole number.**

1 0 . 1 **A dicarboxylic acid has a relative molecular mass of 118, to the nearest whole number.**

Deduce the molecular formula of the acid.
[3 marks]

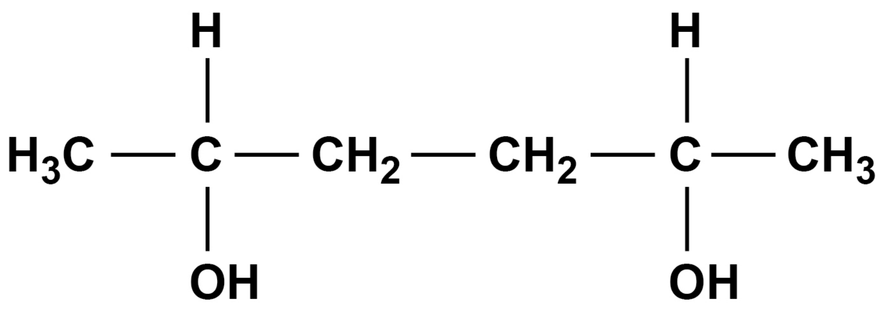
Molecular formula ____________________________

10.2 **A student dissolved some of the dicarboxylic acid from Question 10.1 in water and made up the solution to 250 cm^3 in a volumetric flask. In a titration, a 25.0 cm^3 sample of the acid solution needed 21.60 cm^3 of 0.109 mol dm^{-3} sodium hydroxide solution for neutralisation.**

Calculate the mass, in g, of the dicarboxylic acid used.
Give your answer to the appropriate number of significant figures. [4 marks]

Mass ____________________ g

10 . 3 Compounds with molecular formula $C_6H_{14}O_2$ also have a relative molecular mass of 118 to the nearest whole number. These include the diol shown.



Deduce the number of peaks in the ^1H NMR spectrum of this diol. [1 mark]

____

1 0 . 4 **Draw the structure of a different diol also with molecular formula $C_6H_{14}O_2$ that has a ^1H NMR spectrum that consists of two singlet peaks. [1 mark]**

[Turn over]

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10.5 **The dicarboxylic acid in question 10.1 and the isomers of $C_6H_{14}O_2$ in Questions 10.3 and 10.4 all have a relative molecular mass of 118**

State why the dicarboxylic acid can be distinguished from the two diols by high resolution mass spectrometry using electrospray ionisation. [1 mark]

10

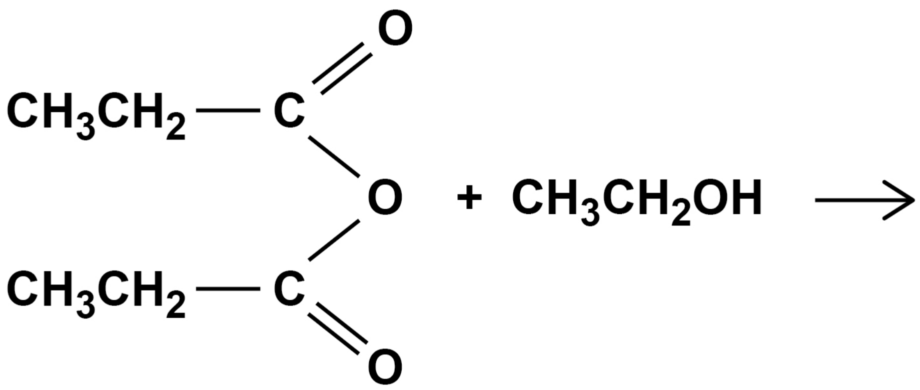
1 1 **This question is about esters including biodiesel.**

1 1 . 1 **An ester is formed by the reaction of an acid anhydride with CH_3CH_2OH**

On page 59, complete the equation. In your answer show clearly the structure of the ester.

Give the IUPAC name of the ester. [3 marks]

Equation



Name of ester ______________________________

11 . 2 **In a reaction to form biodiesel, one mole of a vegetable oil reacts with an excess of methanol to form two moles of an ester with molecular formula $C_{19}H_{34}O_2$ and one mole of an ester with molecular formula $C_{19}H_{36}O_2$**

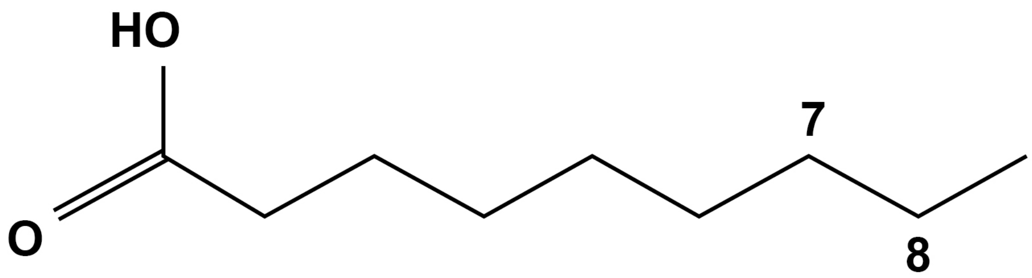
On page 61, draw the structure of the vegetable oil showing clearly the ester links.

You should represent the hydrocarbon chains in the form C_xH_y where *x* and *y* are the actual numbers of carbon and hydrogen atoms. [2 marks]

11 . 3 **The compound $C_{19}H_{34}O_2$ is the methyl ester of *Z*,*Z*-octadeca-9,12-dienoic acid.**

Part of the structure of the acid is shown.

Complete the skeletal formula to show the next part of the hydrocarbon chain to carbon atom number 14.
In your answer, show the *Z* stereochemistry around both C=C double bonds. [2 marks]

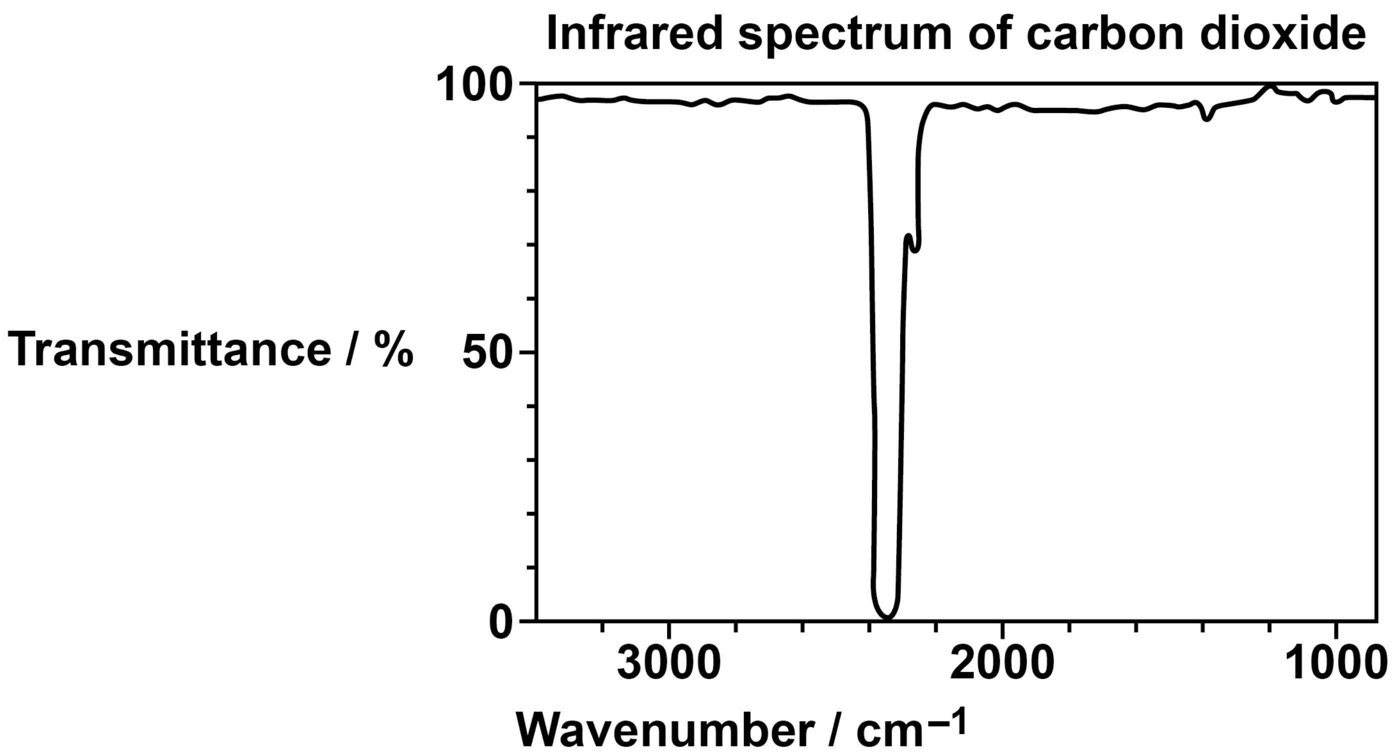


11.4 Give an equation for the complete combustion of the ester $C_{19}H_{34}O_2$ [1 mark]

[Turn over]

11.5 Combustion of biodiesel produces greenhouse gases such as carbon dioxide that cause global warming.
Part of the infrared spectrum of carbon dioxide is shown in FIGURE 3.

FIGURE 3



State how the infrared spectrum of carbon dioxide in FIGURE 3 is NOT what you might predict from the data provided in TABLE A in the Data Booklet. [1 mark]

[Turn over]

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11.6 **Explain how carbon dioxide causes global warming. [2 marks]**

11

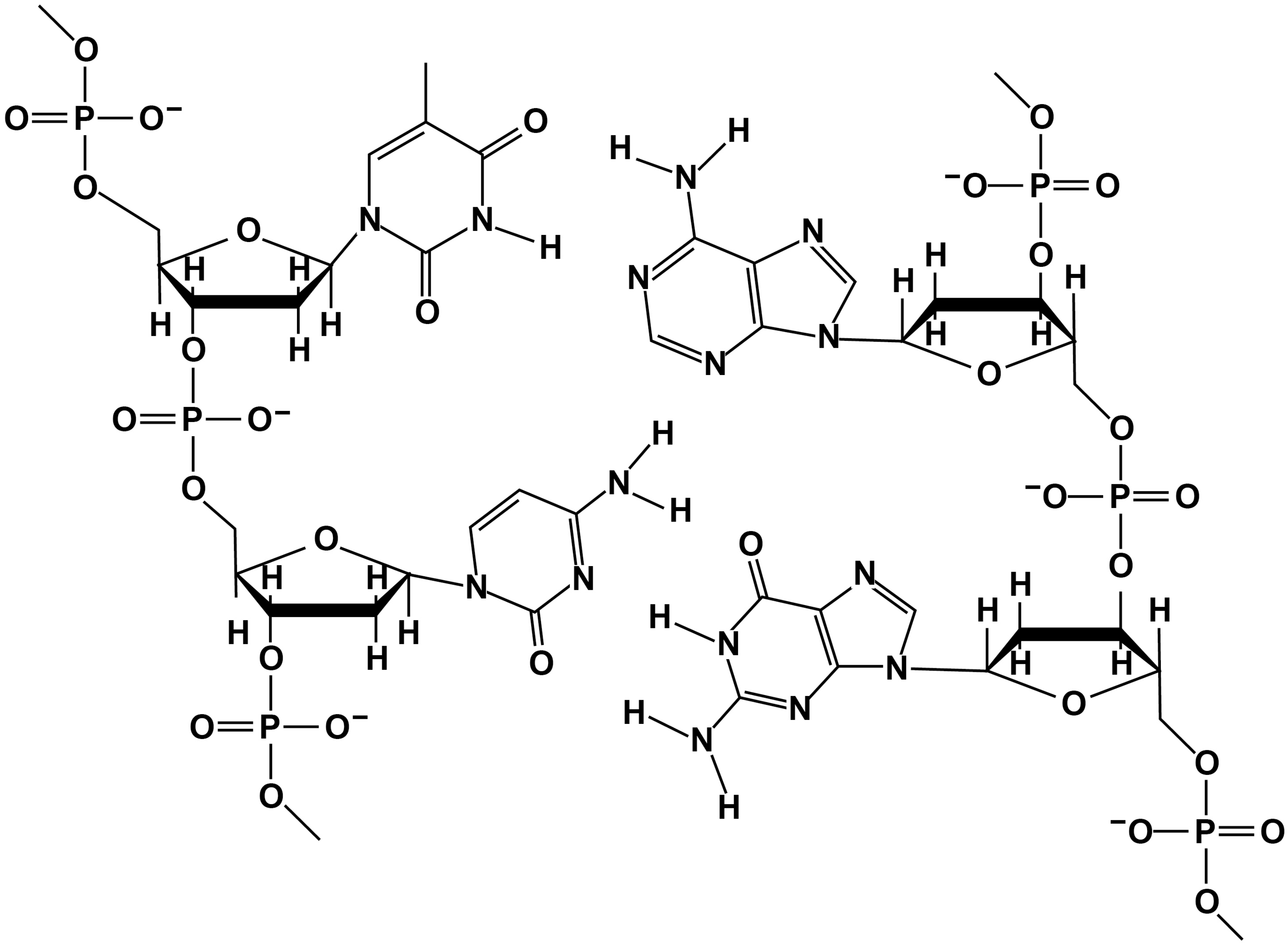
1 2 FIGURE 4, on page 69, shows two complementary strands in part of a DNA double helix structure.

1 2 . 1 Draw all the hydrogen bonds between the complementary strands shown in FIGURE 4.

Use dashed lines to show the hydrogen bonds.
You do NOT need to show lone pairs of electrons or partial charges.
[2 marks]

1 2 . 2 Draw a ring around each of the component parts that make up the cytosine nucleotide in the section of DNA shown in FIGURE 4. [2 marks]

FIGURE 4



[Turn over]

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12.3 State the meaning of the term complementary when it is used to refer to DNA strands. [1 mark]

[Turn over]

5

13 Aqueous $NaBH_4$ reduces aldehydes but does not reduce alkenes.

13.1 Show the first step of the mechanism of the reaction between $NaBH_4$ and 2-methylbutanal. You should include two curly arrows.

Explain why $NaBH_4$ reduces 2-methylbutanal but has no reaction with 2-methylbut-1-ene.
[5 marks]

First step of mechanism

Explanation

[Turn over]

13.2 A student attempted to reduce a sample of 2-methylbutanal but added insufficient $NaBH_4$

The student confirmed that the reduction was incomplete by using a chemical test.

Give the reagent and observation for the chemical test. [2 marks]

Reagent ______________________________

____

____

Observation ______________________________

____

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END OF QUESTIONS

7

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