AQA

Please write clearly in block capitals.

Centre number ☐☐☐☐☐ Candidate number ☐☐☐☐

Surname _____

Forename(s) _____

Candidate signature _____

A-level
CHEMISTRY

Paper 2 Organic and Physical Chemistry

Monday 19 June 2017   Morning   Time allowed: 2 hours

Materials

For this paper you must have:
* the Periodic Table/Data Booklet, provided as an insert (enclosed)
* a ruler with millimetre measurements
* a 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.
* Do all rough work in this booklet. 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.

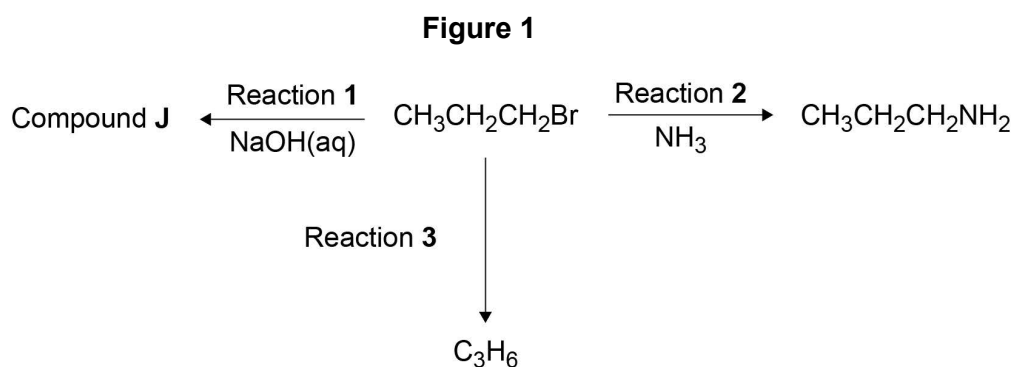| For Examiner's Use	
Question	Mark
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
TOTAL	

Answer **all** questions in the spaces provided

0 1 **Figure 1** shows some compounds made from a halogenoalkane.

Figure 1

Compound **J** ⟵ $\dfrac{\text{Reaction } 1}{\text{NaOH(aq)}}$ $CH_3CH_2CH_2Br$ $\dfrac{\text{Reaction } 2}{\text{NH}_3}$ ⟶ $CH_3CH_2CH_2NH_2$

Reaction **3**
↓

C_3H_6

0 1 . 1 Draw the displayed formula of compound **J**.

[1 mark]

0 1 . 2 Name the mechanism for Reaction **2** and give an essential condition used to ensure that $CH_3CH_2CH_2NH_2$ is the major product.

[2 marks]

Name of mechanism _____

Condition _____

0 1 . 3 Calculate the mass, in grams, of $CH_3CH_2CH_2NH_2$ produced from 25.2 g of $CH_3CH_2CH_2Br$ in Reaction **2** assuming a 75.0% yield.

Give your answer to the appropriate number of significant figures.

[3 marks]

Mass _____ g

0 1 . 4 When Reaction **2** is carried out under different conditions, a compound with molecular formula $C_9H_{21}N$ is produced.

Draw the skeletal formula of the compound.

Identify the functional group in the compound including its classification.

[2 marks]

Skeletal formula

Functional group including classification _____

0 1 . 5 Identify the reagent and conditions used in Reaction **3**.

[1 mark]

0 1 . 6 Name and outline a mechanism for Reaction **3**.
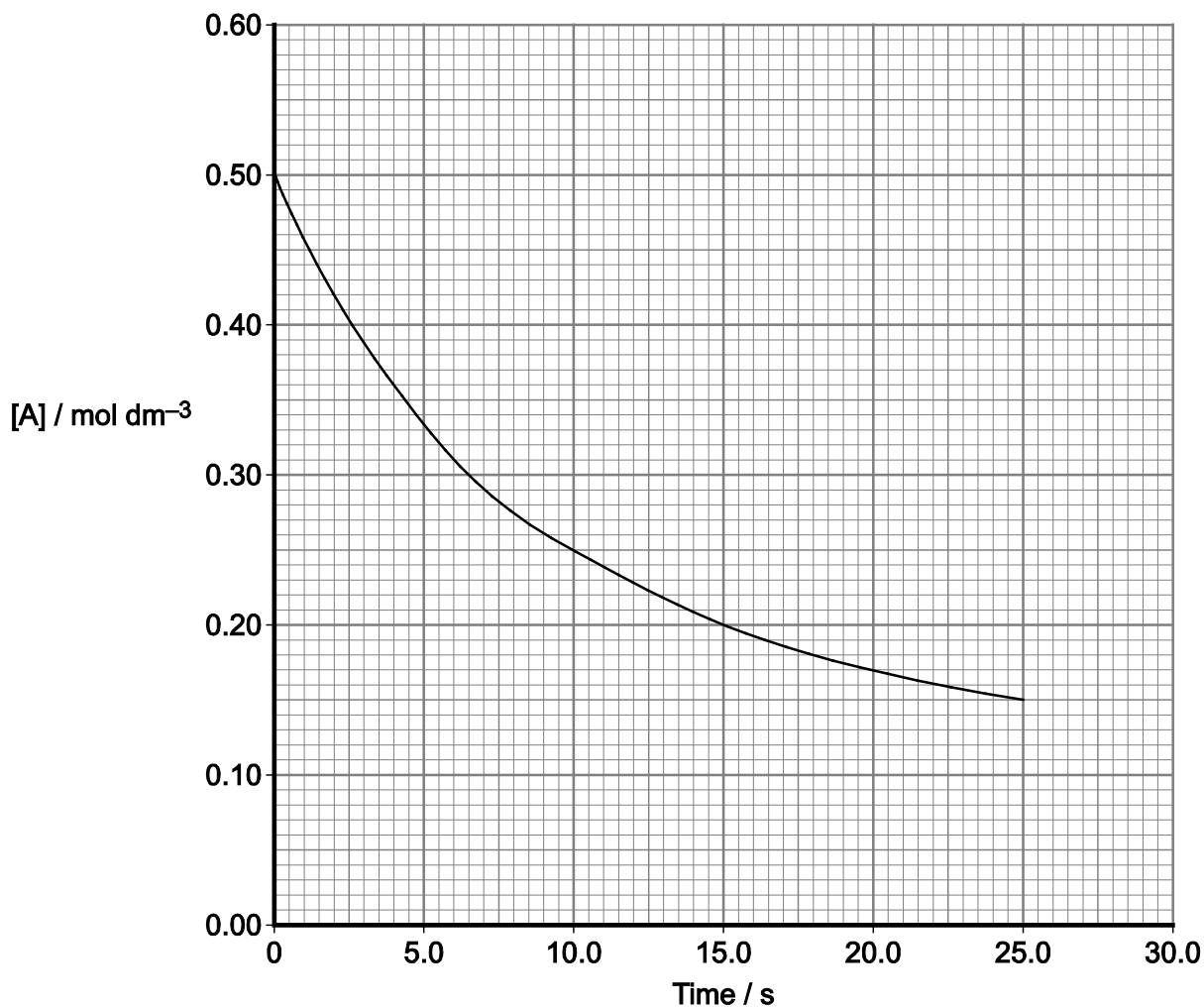
[4 marks]

Name of mechanism _____

Mechanism

13

Turn over ▶

0 2   The rate equation for the reaction between compounds **A** and **B** is

$$rate = k[\mathbf{A}]^2[\mathbf{B}]$$

Figure 2 shows how, in an experiment, the concentration of **A** changes with time, t, in this reaction.

Figure 2

0 2 . 1   Draw a tangent to the curve at $t = 0$

[1 mark]

0 2 . 2   Use this tangent to deduce the initial rate of the reaction.

[1 mark]

Initial rate _____ mol dm^{-3}s^{-1}

Do not write outside the box

0 2 . 3 The experiment was repeated at the same temperature and with the same initial concentration of **B** but with a different initial concentration of **A**.
The new initial rate was 1.7 times greater than in the original experiment.

Calculate the new initial concentration of **A**.

[2 marks]

Initial concentration of **A** _____ mol dm^{-3}

Turn over for the next question

$\dfrac{}{4}$

Turn over ▶

0 5

0 3 A series of experiments is carried out with compounds **C** and **D**. Using the data obtained, the rate equation for the reaction between the two compounds is deduced to be

$$rate = k[\mathbf{C}][\mathbf{D}]$$

In one experiment at 25 °C, the initial rate of reaction is 3.1×10^{-3} mol dm^{-3} s^{-1} when the initial concentration of **C** is 0.48 mol dm^{-3} and the initial concentration of **D** is 0.23 mol dm^{-3}

0 3 . 1 Calculate a value for the rate constant at this temperature and give its units.

[3 marks]

Rate constant _____ Units _____

Do not write outside the box

0 3 . 2 An equation that relates the rate constant, k, to the activation energy, E_a, and the temperature, T, is

$$\ln k = \frac{-E_a}{RT} + \ln A$$

Use this equation and your answer from Question **3.1** to calculate a value, in kJ mol^{-1}, for the activation energy of this reaction at 25 °C.

For this reaction $\ln A = 16.9$

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

(If you were unable to complete Question **3.1** you should use the value of 3.2×10^{-3} for the rate constant. This is not the correct value.)

[4 marks]

Activation energy _____ kJ mol^{-1}

7

Turn over ▶

0 4 The aldehyde $CH_3CH_2CH_2CH_2CHO$ reacts with KCN followed by dilute acid to form a racemic mixture of the two stereoisomers of $CH_3CH_2CH_2CH_2CH(OH)CN$

0 4 . 1 Give the IUPAC name of $CH_3CH_2CH_2CH_2CH(OH)CN$

[1 mark]

0 4 . 2 Describe how you would distinguish between separate samples of the two stereoisomers of $CH_3CH_2CH_2CH_2CH(OH)CN$

[2 marks]

0 4 . 3 Explain why the reaction produces a racemic mixture.

[3 marks]

| 0 | 4 | . | 4 |

An isomer of $CH_3CH_2CH_2CH_2CHO$ reacts with KCN followed by dilute acid to form a compound that does not show stereoisomerism.

Draw the structure of the compound formed and justify why it does not show stereoisomerism.
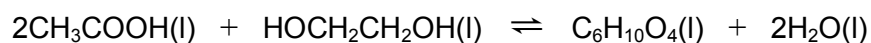
[2 marks]

Structure

Justification

_____

_____

Turn over for the next question

___
8

Do not write outside the box

0 5 Ethanoic acid and ethane-1,2-diol react together to form the diester ($C_6H_{10}O_4$) as shown.

$$2CH_3COOH(l) \ + \ HOCH_2CH_2OH(l) \ \rightleftharpoons \ C_6H_{10}O_4(l) \ + \ 2H_2O(l)$$

0 5 . 1 Draw a structural formula for the diester $C_6H_{10}O_4$

[1 mark]

0 5 . 2 A small amount of catalyst was added to a mixture of 0.470 mol of ethanoic acid and 0.205 mol of ethane-1,2-diol.

The mixture was left to reach equilibrium at a constant temperature.

Complete **Table 1**.

Table 1

		Amount in the mixture / mol		
	CH_3COOH	$HOCH_2CH_2OH$	$C_6H_{10}O_4$	H_2O
At the start	0.470	0.205	0	0
At equilibrium	0.180			

[3 marks]

Space for working

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0 5 . 3 Write an expression for the equilibrium constant, K_c, for the reaction.

The total volume of the mixture does not need to be measured to allow a correct value for K_c to be calculated.

Justify this statement.

[2 marks]

Expression

Justification

0 5 . 4 A different mixture of ethanoic acid, ethane-1,2-diol and water was prepared and left to reach equilibrium at a different temperature from the experiment in Question **5.2**

The amounts present in the new equilibrium mixture are shown in **Table 2**.

Table 2

Amount in the mixture / mol				
	CH_3COOH	$HOCH_2CH_2OH$	$C_6H_{10}O_4$	H_2O
At new equilibrium	To be calculated	0.264	0.802	1.15

The value of K_c was 6.45 at this different temperature.

Use this value and the data in **Table 2** to calculate the amount, in mol, of ethanoic acid present in the new equilibrium mixture.
Give your answer to the appropriate number of significant figures.

[3 marks]

Amount of ethanoic acid _____ mol

9

0 6   Use the Data Booklet to help you answer this question.

This question is about amino acids and peptide (amide) links.

0 6 . 1   Draw the structure of the zwitterion formed by phenylalanine.

[1 mark]

0 6 . 2   Draw the structure of serine at high pH.

[1 mark]

0 6 . 3   Draw the structures of both dipeptides formed when phenylalanine reacts with serine.

In each structure show all the atoms and bonds in the amide link.

[2 marks]

0 6 . 4 An amide link is also formed when an acyl chloride reacts with a primary amine.

Name and outline a mechanism for the reaction between CH_3CH_2COCl and $CH_3CH_2NH_2$

Give the IUPAC name of the organic product.

[6 marks]

Name of mechanism

Mechanism

IUPAC name of organic product

10

Turn over ►

0 7 Test-tube reactions can be used to identify the functional groups in organic molecules.

0 7 . 1 You are provided with samples of each of the four compounds.

$$H_3C - \underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}} - COOH \qquad H_3C - \underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2OH \qquad H_3C - \underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}} - COOH \qquad H_3C - \underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}} - CHO$$

K **L** **M** **N**

Describe how you could distinguish between all four compounds using the minimum number of tests on each compound.

You should describe what would be observed in each test.

[6 marks]

6

0 8 This question is about nitrobenzenes.

0 8 . 1 Nitrobenzene reacts when heated with a mixture of concentrated nitric acid and concentrated sulfuric acid to form a mixture of three isomeric dinitrobenzenes.

Write an equation for the reaction of concentrated nitric acid with concentrated sulfuric acid to form the species that reacts with nitrobenzene.

[1 mark]

0 8 . 2 Name and outline a mechanism for the reaction of this species with nitrobenzene to form 1,3-dinitrobenzene.

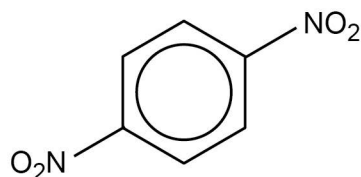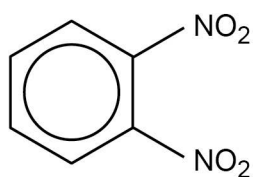**[4 marks]**

Name of mechanism

Mechanism

**Turn over for the next question**

0 8 . 3 The dinitrobenzenes shown were investigated by thin layer chromatography (TLC).

In an experiment, carried out in a fume cupboard, a concentrated solution of pure 1,4-dinitrobenzene was spotted on a TLC plate coated with a solid that contains polar bonds. Hexane was used as the solvent in a beaker with a lid.

The start line, drawn in pencil, the final position of the spot and the final solvent front are shown on the chromatogram in **Figure 3**

Figure 3

Solvent front

○

× Start line
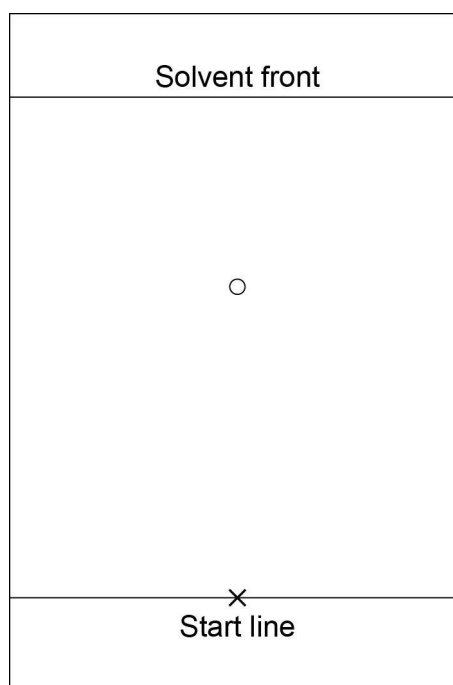
Use the chromatogram in **Figure 3** to deduce the R_f value of 1,4-dinitrobenzene in this experiment.

Tick (✓) **one** box.

[1 mark]

A 0.41 ☐

B 0.46 ☐

C 0.52 ☐

D 0.62 ☐

Do not write outside the box

0 8 . 4 State in general terms what determines the distance travelled by a spot in TLC.

[1 mark]

0 8 . 5 To obtain the chromatogram, the TLC plate was held by the edges and placed in the solvent in the beaker in the fume cupboard. The lid was then replaced on the beaker.

Give one other practical requirement when placing the plate in the beaker.

[1 mark]

0 8 . 6 A second TLC experiment was carried out using 1,2-dinitrobenzene and 1,4-dinitrobenzene. An identical plate to that in Question **8.3** was used under the same conditions with the same solvent. In this experiment, the R_f value of 1,4-dinitrobenzene was found to be greater than that of 1,2-dinitrobenzene.

Deduce the relative polarities of the 1,2-dinitrobenzene and 1,4-dinitrobenzene and explain why 1,4-dinitrobenzene has the greater R_f value.

[2 marks]

Relative polarities

Explanation

Turn over ▶

0 8 . 7 A third TLC experiment was carried out using 1,2-dinitrobenzene. An identical plate to that in Question **8.3** was used under the same conditions, but the solvent used contained a mixture of hexane and ethyl ethanoate.

A student stated that the R_f value of 1,2-dinitrobenzene in this third experiment would be greater than that of 1,2-dinitrobenzene in the experiment in Question **8.6**

Is the student correct? Justify your answer.

[2 marks]

_____

_____

_____
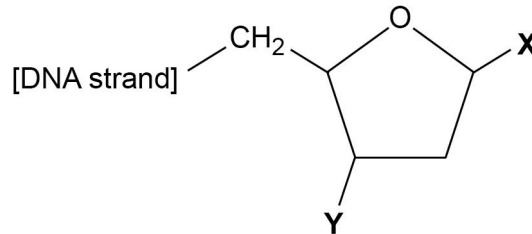
_____

12

Do not write outside the box

0 9   Use the Data Booklet to help you answer these questions.

DNA exists as two strands of nucleotides in the form of a double helix with hydrogen bonding between the two strands.

0 9 . 1   A deoxyribose molecule in a strand of DNA is shown.

Name the types of group attached to 2-deoxyribose at positions **X** and **Y**.
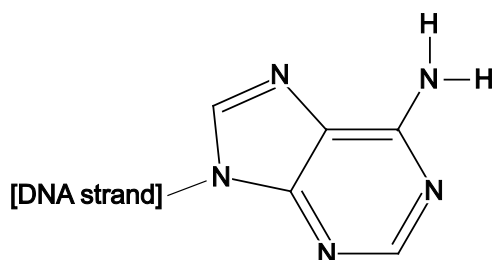
[2 marks]

X _____

Y _____

0 9 . 2   In the DNA double helix, adenine is linked by hydrogen bonds to a molecule in the other strand of DNA.

Complete the diagram below to show the other molecule and the hydrogen bonds between it and adenine.

[2 marks]

4

Turn over ▶

1 0 This question is about six isomers of $C_6H_{10}O_2$

1 0 . 1 Give the full IUPAC name of isomer **P**.

$$\begin{array}{ccc} CH_3CH_2 & & COOH \\ & \diagdown & \diagup \\ & C = C & \\ & \diagup & \diagdown \\ H & & CH_3 \\ & \mathbf{P} & \end{array}$$

[1 mark]

1 0 . 2 A sample of **P** was mixed with an excess of oxygen and the mixture ignited. After cooling to the original temperature, the total volume of gas remaining was 335 cm^3

When this gas mixture was passed through aqueous sodium hydroxide, the carbon dioxide reacted and the volume of gas decreased to 155 cm^3

Both gas volumes were measured at 25 °C and 105 kPa

Write an equation for the combustion of **P** in an excess of oxygen and calculate the mass, in mg, of **P** used.

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

[5 marks]

Mass of **P** used _____ mg

Do not write outside the box

1 0 . 3 Isomer **Q** ($C_6H_{10}O_2$) is a cyclic compound. The infrared spectrum of **Q** is shown in **Figure 4** and the ^{13}C NMR spectrum of **Q** is shown in **Figure 5.**
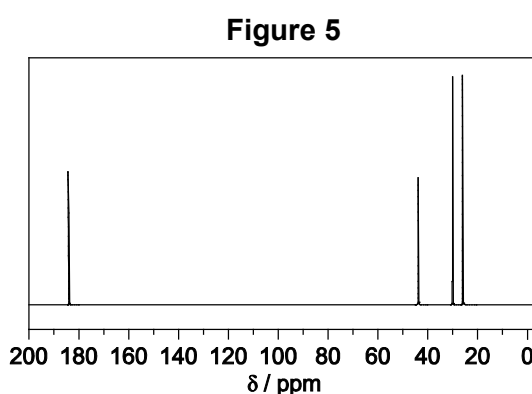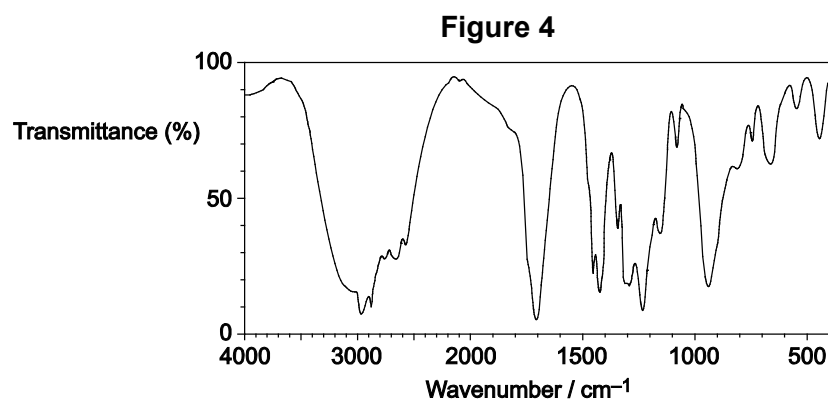
Figure 4

Figure 5

Use these spectra and Tables **A** and **C** in the Data Booklet to deduce the structure of **Q**.
In your answer, state one piece of evidence you have used from each spectrum.

[3 marks]

Structure of **Q**.
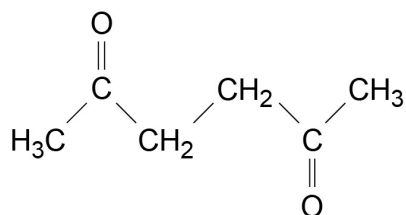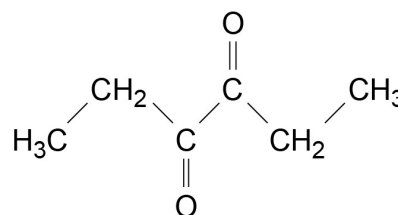
Evidence from **Figure 4**

Evidence from **Figure 5**

Turn over ▶

10.4 Isomers **R** and **S** are shown.

R   **S**

Although the ^{13}C spectra of **R** and **S** both show the same number of peaks, the spectra can be used to distinguish between the isomers.

Justify this statement using Table **C** from the Data Booklet.

Give the number of peaks for each isomer.

[3 marks]

Justification

Number of peaks

1 0 . 5 Although the ^{1}H spectra of **R** and **S** both show the same number of peaks, the spectra can be used to distinguish between the isomers.

Justify this statement using the splitting patterns of the peaks.

Give the number of peaks for each isomer.

[3 marks]

Justification

Number of peaks

Question 10 continues on the next page

Turn over ▶

1 0 . 6 The action of heat on 5-hydroxyhexanoic acid can lead to two different products.

On gentle heating, 5-hydroxyhexanoic acid loses water to form a cyclic compound, **T** ($C_6H_{10}O_2$).

Under different conditions, 5-hydroxyhexanoic acid forms a polyester.

Draw the structure of **T**.

Draw the repeating unit of the polyester and name the type of polymerisation.

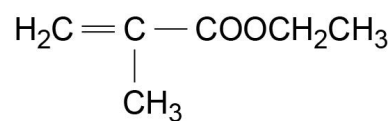**[3 marks]**

Structure of **T**

Repeating unit of polyester

Type of polymerisation _____

Do not write outside the box

1 0 . 7 Isomer **U** is shown.

$$H_2C = C - COOCH_2CH_3$$
$$|$$
$$CH_3$$

U

The polymer formed by **U** and the polymer formed by 5-hydroxyhexanoic acid in Question **10.6** both contain ester groups that can be hydrolysed.

Draw the repeating unit of the polymer formed by **U**.

Justify the statement that, although both polymer structures contain ester groups, the polymer formed by **U** is not biodegradable.

[3 marks]

Repeating unit of polymer formed by **U**.

Justification

21

Turn over for the next question

Turn over ▶

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box*

1 1 This question is about the three amines, **E**, **F** and **G**.

NH$_2$ CH$_2$CH$_2$NH$_2$ NHCH$_2$CH$_3$

E   **F**   **G**

1 1 . 1 Amines **E**, **F** and **G** are weak bases.

Explain the difference in base strength of the three amines and give the order of increasing base strength.

[6 marks]

1 1 . 2 Amine **F** can be prepared in a three-step synthesis starting from methylbenzene.

Suggest the structures of the two intermediate compounds.

For each step, give reagents and conditions only. Equations and mechanisms are **not** required.

[5 marks]

END OF QUESTIONS

11

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ANSWER IN THE SPACES PROVIDED