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# A-level CHEMISTRY

Paper 2 Organic and Physical Chemistry

Tuesday 11 June 2019

Afternoon

Time allowed: 2 hours

### **Materials**

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.
- 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.
- 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.

For Examiner's Use		
Question	Mark	
1		
2		
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12	_	
13		
TOTAL		

- Answer all questions in the spaces provided.
- 0 1 This question is about amines.
- **0 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 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

$$\mathrm{NH}_3$$
  $\mathrm{NH}_2$ 

Cyclic secondary amine



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0 1.3	1,6-Diaminohexane can also be formed in a two-stage synthesis starting from 1,4-dibromobutane.	outs t
	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]	
0 1.5	Justify the statement that there are no chiral centres in 3-aminopentane.  [1 mark]	
		12
	Turn over for the next question	



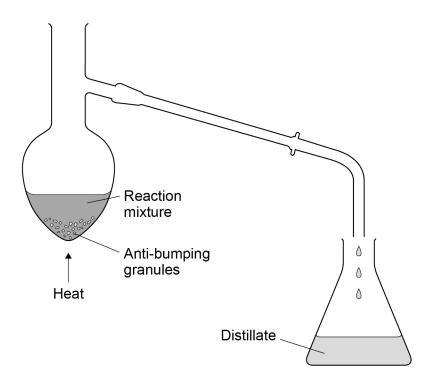
0 2

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 of the apparatus used to distil the cyclohexene from the reaction mixture at 83 °C.

[2 marks]



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]



	ŭ
0 2.3	The cyclohexene separated in Question <b>02.2</b> 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 <b>one</b> observation that the student made to confirm that the cyclohexene was dry.  [1 mark]
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 <sup>3</sup> of cyclohexene ( $M_r = 82.0$ ). Density of cyclohexene = 0.810 g cm <sup>-3</sup>
	Calculate the percentage yield of cyclohexene obtained.  Give your answer to the appropriate number of significant figures.  [5 marks]
	% yield
	Question 2 continues on the next page

Turn over ►

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

Complete the mechanism for this reaction.

[3 marks]



12



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.	
Deduce the molecular formula of isoprene and suggest a possible structure.  [4 marks]	
Molecular formula	
Structure	
	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.  Deduce the molecular formula of isoprene and suggest a possible structure.  [4 marks]

Question 3 continues on the next page



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.

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



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outsia	le	the
bo	λ	,

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

$$-CH_2$$
  $CH_2$   $H$ 

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]

9

Turn over for the next question



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  $\bf P$  over the first five seconds of the reaction.

The data obtained are shown in Table 1.

Table 1

Even a wise a mat	Time after	Concentration / mol dm <sup>-3</sup>		
Experiment	mixing / s	Р	Q	
4	0	1.00 × 10 <sup>-2</sup>	1.25 × 10 <sup>-2</sup>	
ı	5.0	0.92 × 10 <sup>-2</sup>	not measured	
2	0	2.00 × 10 <sup>-2</sup>	1.25 × 10 <sup>-2</sup>	
2	5.0	1.84 × 10 <sup>-2</sup>	not measured	
3	0	0.50 × 10 <sup>-2</sup>	2.50 × 10 <sup>-2</sup>	
3	5.0	0.34 × 10 <sup>-2</sup>	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 <sup>-3</sup> s <sup>-1</sup>
1	1.6 × 10 <sup>-4</sup>
2	
3	



0 4.2	Determine the order of reaction with respect to <b>P</b> and the order of reaction with respect to <b>Q</b>	Do not write outside the box
	with respect to Q. [2 marks]	
	Order with respect to P	
	Order with respect to <b>Q</b>	
0 4 . 3	A reaction between substances <b>R</b> and <b>S</b> was second order with respect to <b>R</b> and	
	second order with respect to <b>S</b> .	
	At a given temperature, the initial rate of reaction was $1.20 \times 10^{-3}$ mol dm <sup>-3</sup> s <sup>-1</sup> when the initial concentration of <b>R</b> was $1.00 \times 10^{-2}$ mol dm <sup>-3</sup> and	
	the initial concentration of <b>S</b> was $2.45 \times 10^{-2}$ mol dm <sup>-3</sup>	
	Calculate a value for the rate constant, <i>k</i> , for the reaction at this temperature.	
	Give the units for <i>k</i>	
	[3 marks]	
	k Units	6



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0	5

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

$$k = Ae^{-E_aIRT}$$

For this reaction, at 25 °C,  $k = 3.46 \times 10^{-8} \text{ s}^{-1}$ The activation energy  $E_a = 96.2 \text{ kJ mol}^{-1}$ The gas constant  $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ 

Calculate a value for the Arrhenius constant, A, for this reaction. Give the units for A.

[4 marks]

Α	Units	



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.	marks]
	Reagent	
	Observation with 2-methylbutan-1-ol	
	Observation with 2-methylbutan-2-ol	
0 6.2	Compounds <b>A</b> and <b>B</b> both have the molecular formula C <sub>4</sub> H <sub>8</sub> Br <sub>2</sub> <b>A</b> has a singlet, a triplet and a quartet in its <sup>1</sup> H NMR spectrum. <b>B</b> has only two singlets in its <sup>1</sup> H NMR spectrum.	
	Draw a structure for each of <b>A</b> and <b>B</b> .	marks]
	АВ	
	Question 6 continues on the next page	

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Compounds  ${\bf C}$  and  ${\bf D}$  both have the molecular formula  $C_6H_3Br_3$   ${\bf C}$  has two peaks in its  $^{13}C$  NMR spectrum.  ${\bf D}$  has four peaks in its  $^{13}C$  NMR spectrum. 0 6 . 3 Draw a structure for each of C and D [2 marks] C D



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box

Do not write outside the Compounds E, F, and G are isomers.  $CH_3 - CH_2 - C$  O  $CH_3 - C$  O  $CH_3 - C$  O  $CH_3 - C$   $CH_2 - C$   $CH_2 - C$   $CH_3 - C$  CFigure 1 shows the infrared spectra of these isomers, but not necessarily in the same Label each spectrum with the correct letter E, F or G in the box. [1 mark] Figure 1 Transmittance 4000 Wavenumber / cm<sup>-1</sup> Transmittance 4000 Wavenumber / cm<sup>-1</sup> Transmittance / % 4000 Wavenumber / cm<sup>-1</sup>





0 7	Isomers ${\bf X}$ and ${\bf Y}$ have the molecular formula $C_5H_8O$
	Isomer X Isomer Y  O OH
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  • ¹³C NMR spectra  • infrared spectra.  Use data from Tables A and C in the Data Booklet in your answer.  [6 marks]



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Paracetamol is a medicine commonly used to relieve mild pain.

Traditionally, paracetamol has been made industrially in a three-step synthesis from phenol.

0 8. 1 Name the mechanism of the reaction in Step 1.

[1 mark]

0 8 . 2 Complete the equation for the reaction in Step 2.

[1 mark]



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.  $\mathsf{RNH}_2$  is used to represent 4-aminophenol in this mechanism.

[2 marks]

$$\begin{array}{c} \text{CH}_3 - \text{C} \\ \text{Cl} \\ \text{R} - \text{NH}_2 \end{array}$$

0 8. 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]

Question 8 continues on the next page

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.

$$HO \longrightarrow HO \longrightarrow HO \longrightarrow OH + H_2O$$
hydroquinone

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

Complete the equation for this second step.

paracetamol

hydroquinone

[1 mark]



$\boxed{0 \ 8}$ . $\boxed{7}$ Calculate the mass, in kg, of hydroquinone ( $M_r = 110.0$ ) needed to produ	ce 250 kg of	Do not write outside the box
paracetamol.	[3 marks]	
		10
Mass	kg	
Turn ever for the next question		
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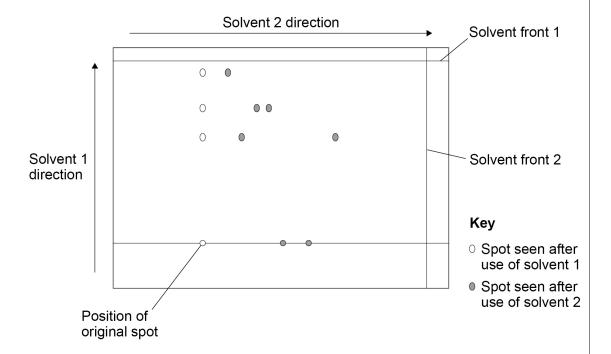


0 9

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 shows the final TLC plate.

Figure 2



0 9 Suggest a suitable reagent for the hydrolysis of a protein.

[1 mark]



0 9.2	Suggest how the positions of the amino acids on the TLC plate were located.	[1 mark]	outside i box
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]	
			4

Turn over for the next question



	24	
1 0	Some compounds with different molecular formulas have the same relative memory mass to the nearest whole number.	olecular
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	
1 0 . 2	A student dissolved some of the dicarboxylic acid from Question <b>10.1</b> in water made up the solution to 250 cm <sup>3</sup> in a volumetric flask. In a titration, a 25.0 cm <sup>3</sup> sample of the acid solution needed 21.60 cm <sup>3</sup> of 0.109 mol dm <sup>-3</sup> sodium hydroxide solution for neutralisation.	and
	Calculate the mass, in g, of the dicarboxylic acid used.  Give your answer to the appropriate number of significant figures.	1 marks]
	Mass	g



1 0 . 3 Compounds with molecular formula C<sub>6</sub>H<sub>14</sub>O<sub>2</sub> 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 <sup>1</sup>H NMR spectrum of this diol.

[1 mark]

Draw the structure of a different diol also with molecular formula C<sub>6</sub>H<sub>14</sub>O<sub>2</sub> that has a <sup>1</sup>H NMR spectrum that consists of two singlet peaks.

[1 mark]

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

Turn over for the next question



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<sub>3</sub>CH<sub>2</sub>OH

Complete the equation. In your answer show clearly the structure of the ester. Give the IUPAC name of the ester.

[3 marks]

Equation

$$CH_3CH_2$$
— $C$ 
 $O$ 
 $CH_3CH_2$ — $C$ 
 $O$ 
 $CH_3CH_2$ — $C$ 
 $O$ 

Name of ester

1 1 . 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  $C_{19}H_{36}O_2$ 

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]

- 1 1 . 3
- The compound  $C_{19}H_{34}O_2$  is the methyl ester of  $\emph{Z},\emph{Z}$ -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]

1 1 . 4

Give an equation for the complete combustion of the ester  $C_{\rm 19}H_{\rm 34}O_{\rm 2}$ 

[1 mark]

Question 11 continues on the next page



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<u>  1  </u> .  <u>5</u>	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 <b>Figure 3</b> . <b>Figure 3</b>
	Transmittance / % 50-3000 Wavenumber / cm-1  State how the infrared spectrum of carbon dioxide in <b>Figure 3</b> is <b>not</b> what you might
	predict from the data provided in <b>Table A</b> in the Data Booklet.  [1 mark]

11



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1 2 Figure 4 shows two complementary strands in part of a DNA double helix structure.

Figure 4

1 2 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 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]

1 2 . 3 State the meaning of the term complementary when it is used to refer to DNA strands.

[1 mark]

-||.

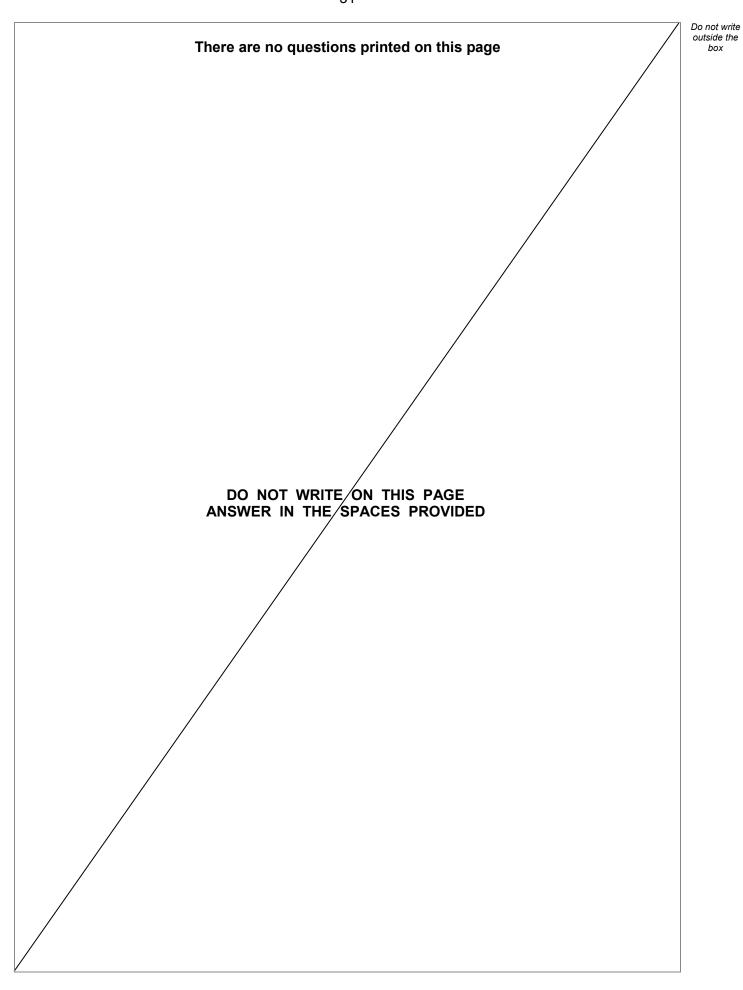
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1 3	Aqueous NaBH <sub>4</sub> reduces aldehydes but does not reduce alkenes.		outside the box
1 3 . 1	Show the first step of the mechanism of the reaction between NaBH $_4$ and 2-methylbutanal. You should include two curly arrows.		
	Explain why NaBH <sub>4</sub> reduces 2-methylbutanal but has no reaction with 2-methylbut-1-ene.	[5 marks]	
		[o marko]	
	First step of mechanism		
	Explanation		
1 3 . 2	A student attempted to reduce a sample of 2-methylbutanal but added		
	insufficient NaBH₄ The student confirmed that the reduction was incomplete by using a		
	chemical test.		
	Cive the regent and charmation for the chamical test		
	Give the reagent and observation for the chemical test.	[2 marks]	
	Reagent		
	Observation		
			7

# **END OF QUESTIONS**







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