

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 12 June 2018

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.
- 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	
4	
5	
6	
7	
TOTAL	



J U N 1 8 C H O 4 O 1

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

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0 1

This question is about three isomers of C_4H_8O

A	B	C
$CH_3CH_2COCH_3$	$CH_3CH_2CH_2CHO$	$CH_3CH=CHCH_2OH$

0 1 . 1

Give the IUPAC name for isomer **B** and for isomer **C**.

[2 marks]

B Butanal

C But-2-en-1-ol

0 1 . 2

Isomers **A** and **B** both react with KCN followed by dilute acid.

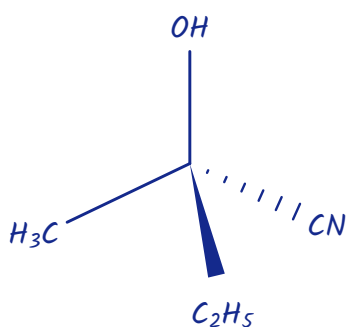
Name the mechanism for this reaction.

Draw the two enantiomers formed by isomer **A** in this reaction and show how the two enantiomers are related to each other.

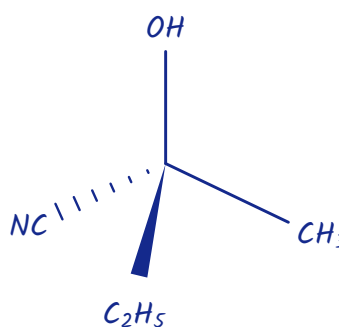
[3 marks]

Mechanism Nucleophilic addition

Enantiomer 1



Enantiomer 2



mirror

The two enantiomers are non-superimposable mirror images of each other (the product is a racemic mixture).



0 1 . 3

Describe a test-tube reaction to distinguish isomer **C** from isomer **A**.

State the observations.

[2 marks]Test Add bromine water to each and shakeObservation(s) with isomer **A** No visible change (stays orange)Observation(s) with isomer **C** Bromine water decolourises (orange to colourless)Do not write
outside the
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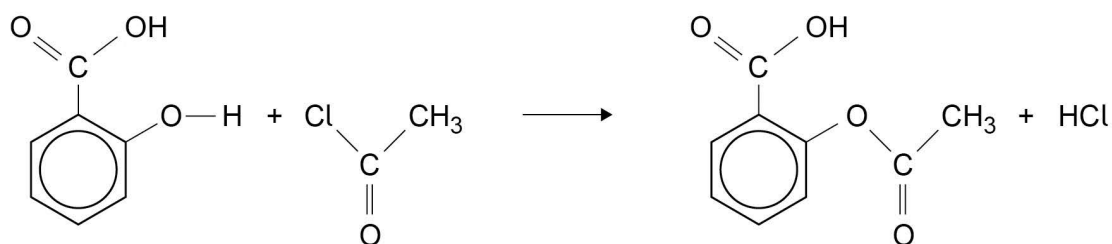
7

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

0 2

Aspirin can be produced by the acylation of 2-hydroxybenzoic acid (salicylic acid), as shown in **Figure 1**. In this reaction, ethanoyl chloride is a powerful acylating agent.

Figure 1



0 2 . 1

In the industrial manufacture of aspirin, ethanoic anhydride is used instead of ethanoyl chloride as the acylating agent.

Give **two** reasons why ethanoic anhydride is used instead of ethanoyl chloride.

[2 marks]

Reason 1 The reaction is less vigorous and less exothermic, so it is easier and safer to control

Reason 2 Ethanoic anhydride is cheaper, less corrosive and does not produce corrosive HCl fumes

0 2 . 2

In the laboratory, the aspirin produced is impure. It is purified by recrystallisation using water as the solvent.

Complete the steps carried out in a recrystallisation practical.

[3 marks]

Step 1 Dissolve in the minimum volume of hot water

Step 2 Filter whilst hot

Step 3 Cool the filtrate (in ice) so the aspirin crystallises

Step 4 Vacuum filter

Step 5 Wash the crystals with a little ice-cold water

Step 6 Dry in a desiccator



0 2 . 3

Outline how you could confirm that a sample of aspirin is pure.

[2 marks]

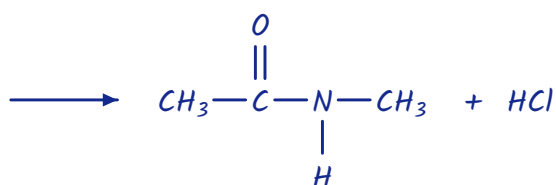
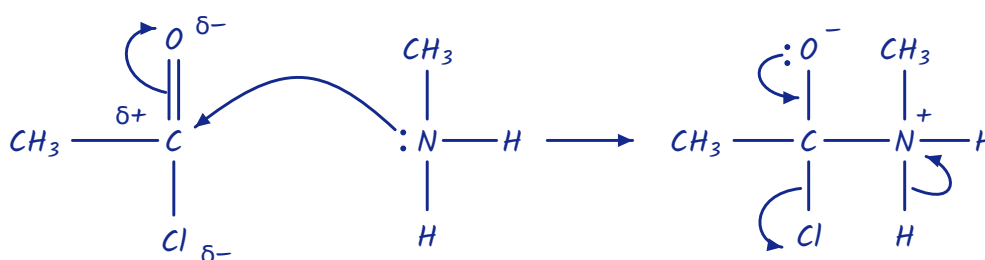
*Measure the melting point of the sample using melting point apparatus.**A pure sample melts sharply (over a narrow range) at a value that agrees with the data book value for aspirin.*

0 2 . 4

Ethanoyl chloride reacts with amines to produce amides.

Name and outline the mechanism for the reaction between ethanoyl chloride and methylamine.

[5 marks]

Name of mechanism Nucleophilic addition-elimination*(Cl⁻ and H⁺ lost, forming HCl; C=O reformed)*

Question 2 continues on the next page

Turn over ►



Amines can be prepared from different compounds.

0 2 . 5 Propylamine ($\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$) can be prepared in two different **one-step** reactions.

For each reaction, identify:

- the organic starting material, and
- the reagent and condition(s).

[4 marks]

Reaction 1

Organic starting material Propanenitrile, $\text{CH}_3\text{CH}_2\text{CN}$

Reagent and condition(s) H_2 with a nickel catalyst (or LiAlH_4 in dry ether)

Reaction 2

Organic starting material 1-bromopropane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$

Reagent and condition(s) Excess ammonia (in ethanol), heated in a sealed tube

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0 3

Gas chromatography (GC) was used to separate a mixture of five compounds, **D**, **E**, **F**, **G** and **H**.

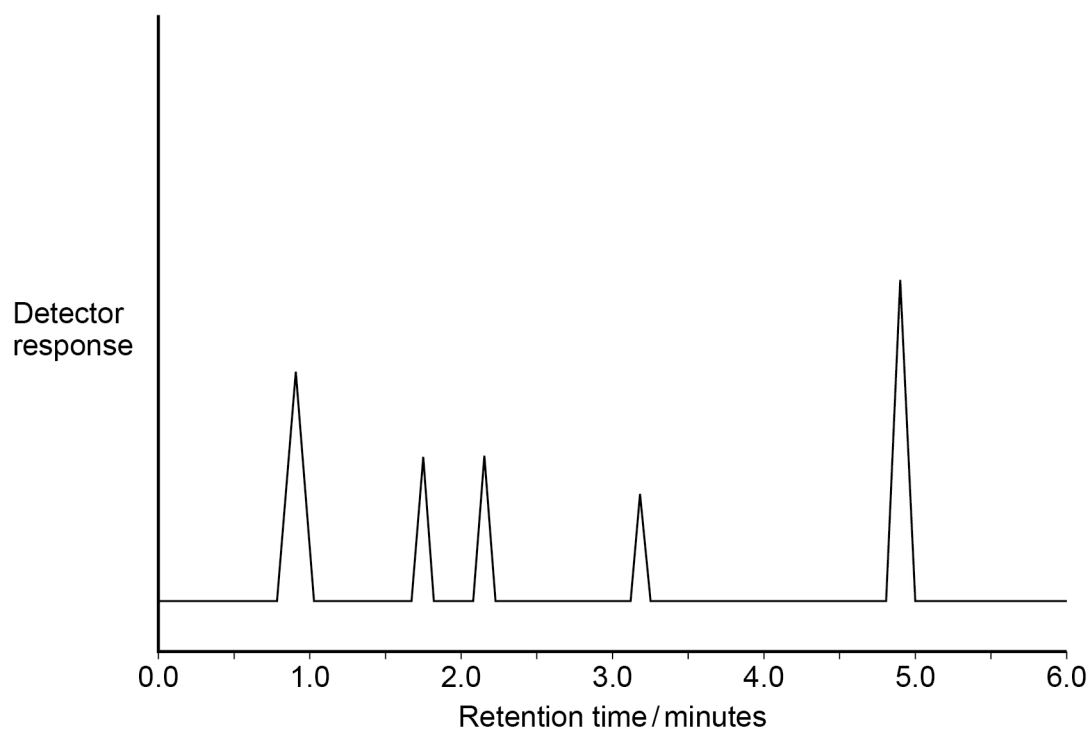
Table 1 shows the names and formulae of these compounds.

Table 1

Compound	Name	Formula
D	1-bromopentane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
E	trichloroethanoic acid	Cl_3CCOOH
F	hexane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
G	methoxybutane	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
H	methylbenzene	$\text{C}_6\text{H}_5\text{CH}_3$

Figure 2 shows the output from the detector in this separation.

Figure 2



0 3

. 1

State the meaning of the term retention time.

[1 mark]

The time taken for a component to travel through the column, from the injection point to the detector.



0 3 . 2

Two of the compounds are present in the mixture in equal amounts.

Explain how **Figure 2** shows this.

[1 mark]

Two of the peaks (at about 1.8 and 2.1 minutes) have the same area under the peak.

0 3 . 3

Give a reason why nitrogen is used rather than oxygen as the carrier gas.

[1 mark]

Nitrogen is inert, so it does not react with the components, whereas oxygen could react with (combust) them.

0 3 . 4

Polyethane-1,2-diol (PEG) is a liquid and is part of the stationary phase.

Identify what else is needed to complete the stationary phase.

Tick (✓) **one** box.

[1 mark]

Aluminium oxide

☒

Argon

☐

Carbon dioxide

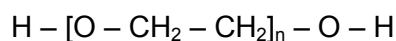
☐

Epoxyethane

☐

0 3 . 5

Polyethane-1,2-diol (PEG) can be represented as



Explain why PEG is polar.

[2 marks]

O is more electronegative than C, so the C-O bonds are polar; the molecule is not symmetrical, so the bond polarities (dipoles) do not cancel.

Turn over ►



0 3 . 6

Deduce the compound in the mixture with retention time 4.9 minutes.

Give a reason for your choice.

[2 marks]Compound E, trichloroethanoic acid (Cl_3CCOOH)

Reason E is the most polar compound (it has the most polar bonds: three C-Cl bonds as well as C=O and O-H), so it is attracted most strongly to the polar PEG stationary phase and is retained for the longest time.

0 3 . 7

Some modifications to the GC apparatus were considered to improve the separation of the same mixture of components.

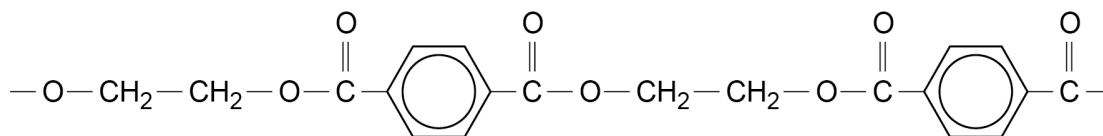
Predict the effect, if any, of each modification on the retention times of the components.

[3 marks]Increasing the column temperature Decreased (shorter)Decreasing the column length Decreased (shorter)Decreasing the carrier gas flow rate Increased (longer)

0 4

Clothes are often made from polyesters such as Terylene.

Two repeating units of the polymer Terylene are shown.



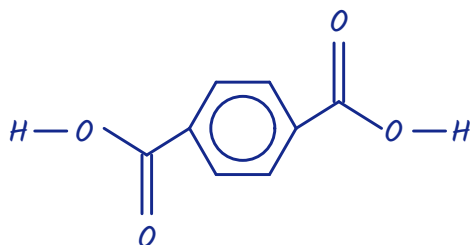
0 4 . 1

Draw the skeletal formulas of the two monomers that react to form Terylene.

[2 marks]

Monomer 1

Monomer 2



0 4 . 2

Explain why Terylene is biodegradable but polychloroethene is not.

[3 marks]

Terylene is a polyester; the ester links contain polar C=O and C-O bonds.

These polar bonds can be attacked by water (nucleophiles), so the ester links are hydrolysed and the polymer breaks down.

Polychloroethene has a backbone of non-polar C-C bonds which are strong and hard to break, so it is not hydrolysed.

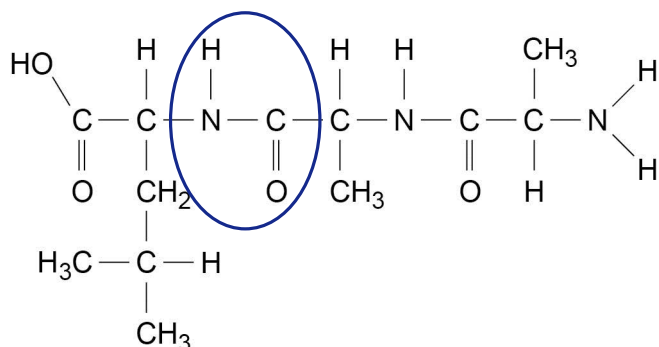
Question 4 continues on the next page

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Proteins are chains of amino acids linked together.

The structure of a tripeptide is

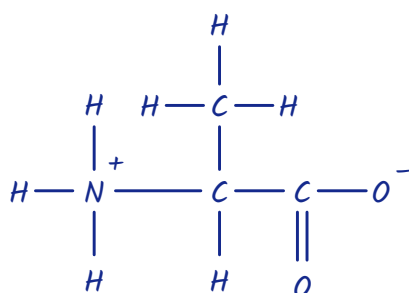


0 4 . 3 Draw a circle around one peptide link on the diagram.

[1 mark]

0 4 . 4 Draw the displayed formula of the zwitterion formed by the amino acid which makes up the central section of the tripeptide in Question **04.3**.

[1 mark]



0 4 . 5 Name the type of structure where protein chains form α -helixes and β -pleated sheets.

[1 mark]

Secondary structure



0 4 . 6

Name the interactions that hold protein chains in a β -pleated sheet.

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Explain how these interactions are formed.

[3 marks]

Hydrogen bonds.

N and O are both very electronegative, so the C=O and N-H bonds are polar (N-H has a $\delta+$ H and C=O has a $\delta-$ O).

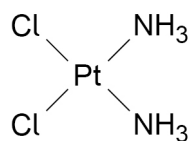
A lone pair on the $\delta-$ O of a C=O group on one chain is attracted to the $\delta+$ H of an N-H group on a neighbouring chain, forming a hydrogen bond.

Question 4 continues on the next page

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Cisplatin is used as an anticancer drug.



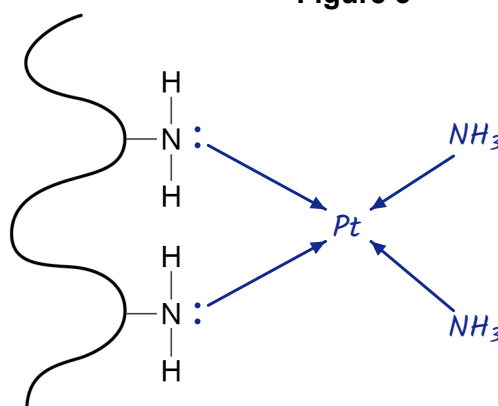
0 4 . 7 Cisplatin bonds with DNA by ligand replacement.

Figure 3 shows part of a DNA strand.

Complete **Figure 3** to show the complex formed when one molecule of cisplatin binds with the part of DNA shown.

[1 mark]

Figure 3



0 4 . 8 State how cisplatin affects cancer cells.

[2 marks]

Cisplatin binds to N atoms on bases in DNA, which distorts the shape of the DNA.

This prevents DNA replication, so the cancer cells cannot divide.

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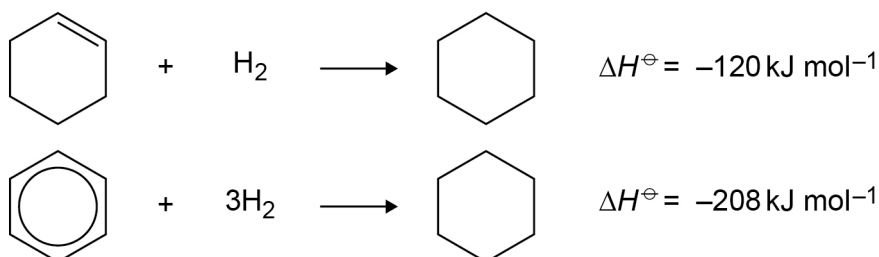
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0 5 . 1 The molecule cyclohexa-1,3,5-triene does not exist and is described as theoretical.

State and explain the stability of benzene compared with the theoretical cyclohexa-1,3,5-triene.

Use the following data.



[4 marks]

Benzene is more stable than the theoretical cyclohexa-1,3,5-triene.

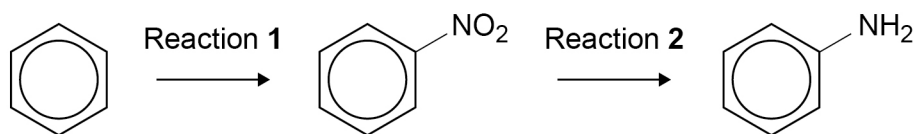
Cyclohexene has one C=C, so the expected $\Delta H^\ominus$ of hydrogenation for cyclohexa-1,3,5-triene, with three C=C, is $3 \times (-120) = -360 \text{ kJ mol}^{-1}$.

The actual $\Delta H^\ominus$ of hydrogenation of benzene is -208 kJ mol^{-1} , which is 152 kJ mol^{-1} less exothermic than expected, so benzene is 152 kJ mol^{-1} lower in energy.

This is because the π electrons in benzene are delocalised (spread out) over the whole ring, which gives it extra stability.



Benzene can be converted into phenylamine by a two-step synthesis as shown.



0 5 . 2 The mechanism of Reaction 1 involves attack by an electrophile.

Give the reagents used to produce the electrophile needed in Reaction 1.

[2 marks]

*Concentrated nitric acid (HNO₃) and concentrated sulfuric acid (H₂SO₄),
which react to form NO₂⁺*

The percentage yield of the two-step synthesis where benzene is converted into phenylamine was found to be 68%.

0 5 . 3 State the **two** measurements that need to be recorded to calculate the percentage yield.

[2 marks]

Measurement 1 *Mass of benzene used at the start*

Measurement 2 *Mass of (pure) phenylamine produced*

0 5 . 4 Explain why phenylamine is a weaker base than hexylamine.

[2 marks]

*Both amines have a lone pair of electrons on N that accepts a proton.
In phenylamine the N lone pair is delocalised into the benzene ring, so
it is less available to accept H⁺.
In hexylamine the alkyl group pushes electrons towards N (inductive
effect), so the lone pair is more available.*

Turn over for the next question

Turn over ►



0 6

This question is about carboxylic acids and alkalis.

0 6 . 1

Carboxylic acids are **weak** acids.

State what is meant by weak in this statement.

[1 mark]

Weak acids are only slightly dissociated (ionised) into H^+ ions in solution.

0 6 . 2

Barium hydroxide, $Ba(OH)_2$, is a strong alkali.Calculate the pH of a $0.0120 \text{ mol dm}^{-3}$ solution of barium hydroxide at 298K

Give your answer to two decimal places.

The ionic product of water, $K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 298K

[3 marks]



$$[OH^-] = 2 \times 0.0120 = 0.0240 \text{ mol dm}^{-3}$$

$$[H^+] = K_w / [OH^-] = 1.00 \times 10^{-14} / 0.0240 = 4.17 \times 10^{-13} \text{ mol dm}^{-3}$$

$$pH = -\log_{10}(4.17 \times 10^{-13}) = 12.38$$

pH 12.38

0 6 . 3

The value of the acid dissociation constant (K_a) for benzenecarboxylic (benzoic) acid (C_6H_5COOH) is $6.31 \times 10^{-5} \text{ mol dm}^{-3}$ Calculate the pH of a $0.0120 \text{ mol dm}^{-3}$ solution of this acid.

Give your answer to two decimal places.

[3 marks]

$$K_a = [H^+][C_6H_5COO^-] / [C_6H_5COOH] \text{ and } [H^+] = [C_6H_5COO^-]$$

$$\text{so } K_a = [H^+]^2 / [C_6H_5COOH]$$

$$[H^+] = \sqrt{(6.31 \times 10^{-5} \times 0.0120)} = \sqrt{(7.572 \times 10^{-7})} = 8.70 \times 10^{-4} \text{ mol dm}^{-3}$$

$$pH = -\log_{10}(8.70 \times 10^{-4}) = 3.06$$

pH 3.06

0 6 . 4

1.09 g of sodium benzenecarboxylate ($\text{C}_6\text{H}_5\text{COONa}$) is added to 200 cm^3 of a $2.4 \times 10^{-3} \text{ mol dm}^{-3}$ solution of benzenecarboxylic acid.

Calculate the pH of the buffer solution produced.

$M_r(\text{C}_6\text{H}_5\text{COONa}) = 144.0$

[5 marks]

$$K_a = [\text{H}^+][\text{A}^-] / [\text{HA}], \text{ so } [\text{H}^+] = K_a \times [\text{HA}] / [\text{A}^-]$$

$$\text{Moles of } \text{C}_6\text{H}_5\text{COONa} = 1.09 / 144.0 = 7.569 \times 10^{-3} \text{ mol}$$

$$[\text{C}_6\text{H}_5\text{COO}^-] = 7.569 \times 10^{-3} / (200 / 1000) = 0.03785 \text{ mol dm}^{-3}$$

$$[\text{C}_6\text{H}_5\text{COOH}] = 2.4 \times 10^{-3} \text{ mol dm}^{-3} \text{ (dissociation of the acid is negligible)}$$

$$[\text{H}^+] = (6.31 \times 10^{-5} \times 2.4 \times 10^{-3}) / 0.03785 = 4.00 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}(4.00 \times 10^{-6}) = 5.40$$

pH 5.40

12

Turn over for the next question

Turn over ►



0 7

The isomers of $C_6H_{12}O_2$ can be distinguished using NMR spectroscopy.

0 7 . 1

Tetramethylsilane (TMS) is used as a standard in recording both ^1H and ^{13}C NMR spectra. TMS is non-toxic and inert.

Give **two other** reasons why TMS is used as a standard in recording NMR spectra.

[2 marks]

Reason 1 *All 12 H atoms (and all 4 C atoms) are in the same environment, so TMS gives a single sharp peak.*

Reason 2 *Its peak is upfield, well away from (to the right of) other peaks, so it does not interfere; it is also volatile, so it is easily removed.*

Compound **X** is an isomer of $C_6H_{12}O_2$

Figure 4 shows the ^1H NMR spectrum for compound **X**.

Figure 4

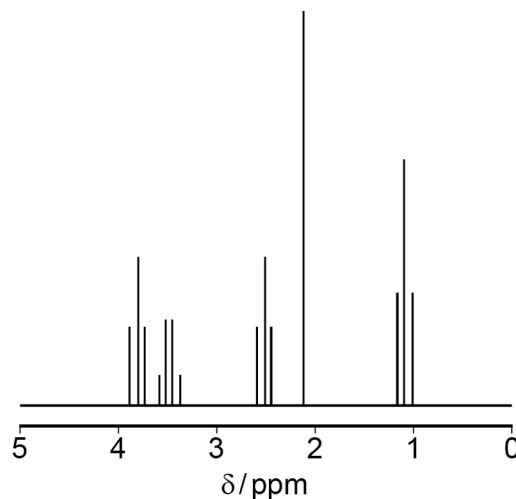


Table 2 shows information about the five peaks shown in **Figure 4**.

Table 2

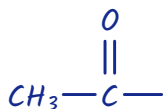
δ / ppm	3.8	3.5	2.6	2.2	1.2
Integration ratio	2	2	2	3	3



Use **Table B** in the Data Sheet, **Figure 4** and **Table 2** to answer Questions **07.2**, **07.3** and **07.4**.

- 0 7 . 2** Deduce the part of the structure responsible for the peak at $\delta = 2.2$ ppm

[1 mark]



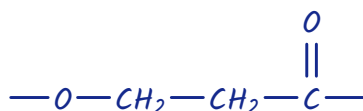
- 0 7 . 3** Deduce the part of the structure responsible for the peaks at $\delta = 3.5$ ppm and $\delta = 1.2$ ppm

[1 mark]



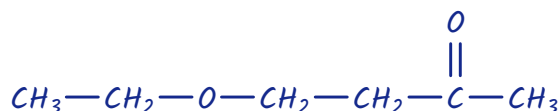
- 0 7 . 4** Deduce the part of the structure responsible for the peaks at $\delta = 3.8$ ppm and $\delta = 2.6$ ppm

[1 mark]



- 0 7 . 5** Draw the structure of the isomer of $\text{C}_6\text{H}_{12}\text{O}_2$ that would produce the ^1H NMR spectrum shown in **Figure 4**.

[1 mark]



Turn over ►



Questions **07.6**, **07.7** and **07.8** are about different isomers of $C_6H_{12}O_2$

07.6 Two isomers of $C_6H_{12}O_2$ are both esters.

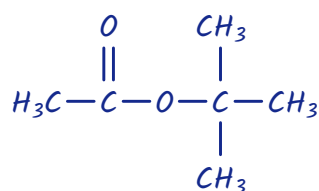
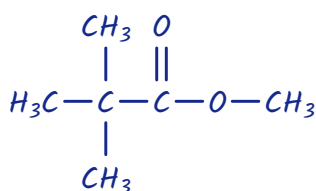
Each isomer has only two peaks in their ^1H NMR spectrum. The integration ratio for both esters is 3:1

Draw the two esters.

[2 marks]

Ester 1

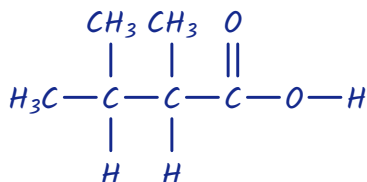
Ester 2



07.7 Another isomer of $C_6H_{12}O_2$ is a carboxylic acid with a chiral centre. This isomer has five peaks in its ^{13}C NMR spectrum.

Draw the structure of this isomer.

[1 mark]



07.8

Another isomer of $C_6H_{12}O_2$ is a cyclic compound.

This isomer has only two peaks in its ^{13}C NMR spectrum. The infrared spectrum of this isomer does not show an absorption in the region $1680-1750\text{ cm}^{-1}$

Draw the structure of this isomer. Use **Table A** in the data sheet.

[1 mark]



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END OF QUESTIONS



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