

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 _____

I declare this is my own work.

INTERNATIONAL A-LEVEL CHEMISTRY (9620)

Unit 4: Organic 2 and Physical 2

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.
- 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).
- Do all rough work in this book. Cross through any work you do not want to be marked.

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

Information

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



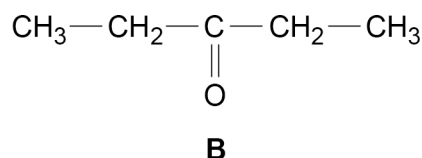
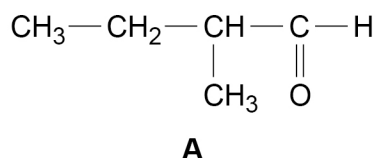
J U N 2 2 C H 0 4 0 1

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

0 1

This question is about carbonyl compounds and their reactions.

Two isomeric carbonyl compounds are shown.



0 1 . 1

Draw the skeletal formula of **A**.

[1 mark]



0 1 . 2

Use IUPAC rules to name **A**.

[1 mark]

2-methylbutanal

0 1 . 3

Identify a reagent, or combination of reagents, that can be used to distinguish between **A** and **B**.

Give the observation made for each compound.

[3 marks]

Reagent *Tollens' reagent (ammoniacal silver nitrate solution), warm*

Observation for **A** *a silver mirror forms*

Observation for **B** *no visible change (no reaction)*



0 1 . 4 Identify a reagent that can be used to convert a carbonyl compound into an alcohol.

State the class of alcohol that is formed from **A**.

State the class of alcohol that is formed from **B**.

[2 marks]

Reagent NaBH_4 (sodium tetrahydridoborate)

Class of alcohol formed from **A** primary

Class of alcohol formed from **B** secondary

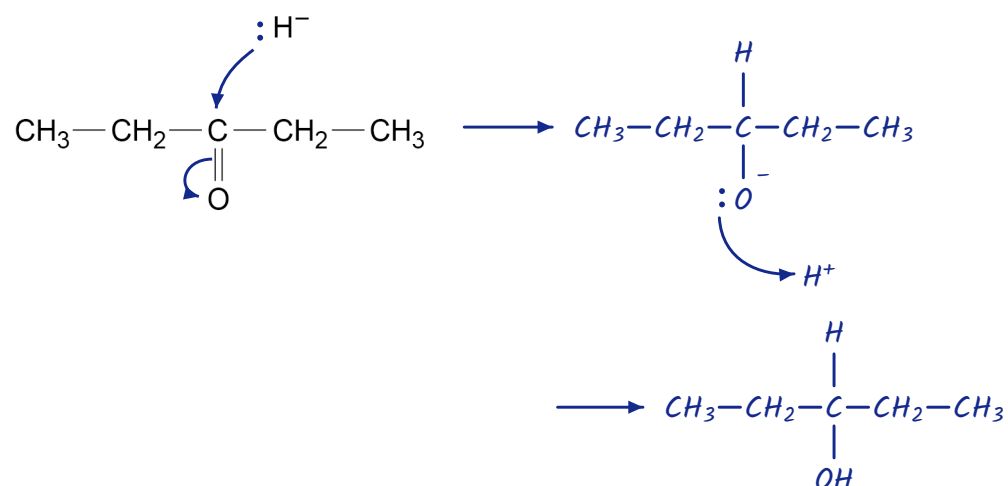
0 1 . 5 In the first step of the mechanism for the conversion of **B** into an alcohol, a hydride ion (H^-) reacts with **B**.

Name and complete this mechanism.

[5 marks]

Name of mechanism nucleophilic addition

Mechanism



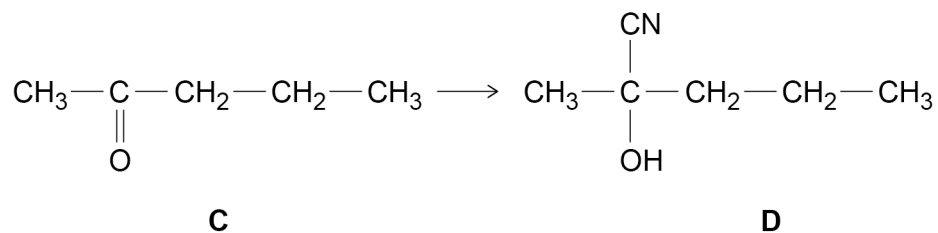
Question 1 continues on the next page

Turn over ►



0 1 . 6

A third isomer, **C**, reacts with potassium cyanide, followed by dilute acid to form **D** as shown.



Explain why **D** does not show optical activity when formed in this reaction.

[2 marks]

D has a chiral carbon atom, but a racemic mixture (a 50:50 mixture of the two enantiomers) is formed, so the rotations cancel.

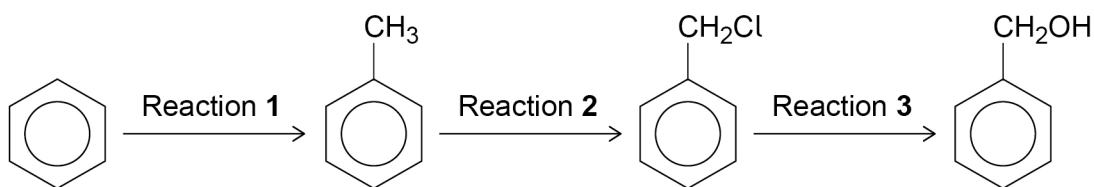
The C=O group in C is planar, so CN⁻ is equally likely to attack from above or below the plane.

14



0 2

The reaction scheme shows some reactions of aromatic compounds, starting from benzene.



0 2 . 1

Name the type of mechanism for Reaction 1.

Identify a reagent and a catalyst for this reaction.

[3 marks]

Type of mechanism electrophilic substitution

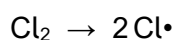
Reagent chloromethane (CH_3Cl)

Catalyst aluminium chloride (AlCl_3)

0 2 . 2

The mechanism of Reaction 2 is free-radical substitution.

An equation for the first step of this reaction is



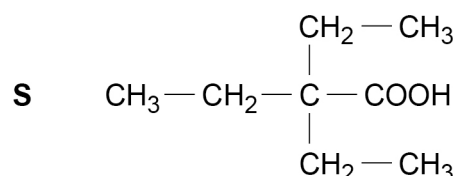
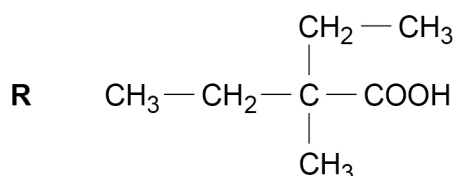
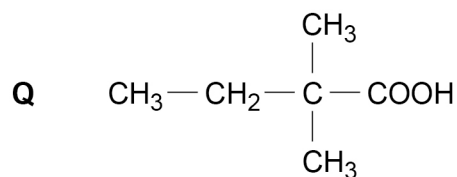
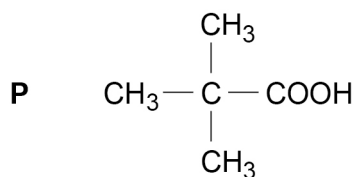
Write equations for the **two** propagation steps in this reaction.

[2 marks]



0 3

^{13}C and ^1H NMR spectroscopy can be used to distinguish between the four carboxylic acids **P**, **Q**, **R** and **S**.



0 3 . 1

Which carboxylic acid has only singlet peaks in its ^1H NMR spectrum?

[1 mark]

Tick (✓) **one** box.

P	Q	R	S
☒	☐	☐	☐

0 3 . 2

Which carboxylic acid is formed by the oxidation of 2,2-dimethylbutan-1-ol?

[1 mark]

Tick (✓) **one** box.

P	Q	R	S
☐	☒	☐	☐

0 3 . 3

Identify, by giving their letters, the **two** carboxylic acids that have the same number of peaks in their ^{13}C NMR spectra.

State the number of peaks in their ^{13}C NMR spectra.

[2 marks]

Identities Q and R

Number of peaks 5



0 3 . 4

Two of these carboxylic acids have the same number of peaks in their ^1H NMR spectra and have the same splitting pattern.

Identify, by giving their letters, these two carboxylic acids.

Complete the table to show the numbers of singlets, doublets, triplets and quartets in each spectrum.

[2 marks]

Identities Q and R

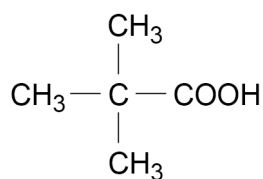
	singlets	doublets	triplets	quartets
number	2	0	1	1

Question 3 continues on the next page

Turn over ►



0 3 . 5 The structure of **P** is repeated here.

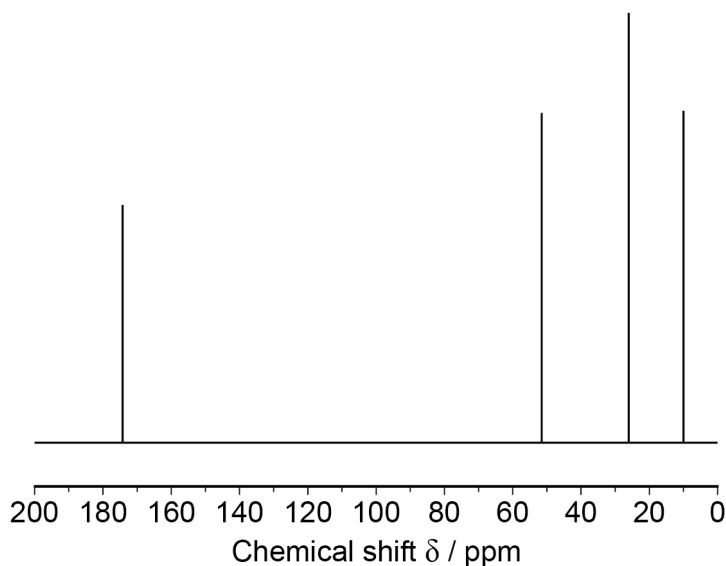


Compound **T** is a functional group isomer of carboxylic acid **P**.

The infrared spectrum of **T** has major absorptions in the wavenumber ranges $1000 - 1300 \text{ cm}^{-1}$ and $1680 - 1750 \text{ cm}^{-1}$.

The ^{13}C NMR spectrum of **T** is shown in **Figure 1**.

Figure 1



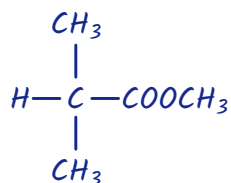
Deduce the structure of **T**.

Use **Tables A** and **C** in the Chemistry Data Sheet.

State **one** piece of evidence you have used from each spectrum.

[3 marks]



Structure of **T**

Evidence from infrared spectrum Absorption at 1680 to 1750 cm^{-1} shows $\text{C}=\text{O}$ and 1000 to 1300 cm^{-1} shows $\text{C}-\text{O}$; no broad $\text{O}-\text{H}$ absorption, so **T** is an ester.

Evidence from ^{13}C NMR spectrum Peak at about 173 ppm is the $\text{C}=\text{O}$ carbon of an ester; peak at about 52 ppm is the CH_3 carbon joined to O .

9

Turn over for the next question

Turn over ►



0 4

This question is about the hydrolysis of an ester, **X**, by warming it with aqueous sodium hydroxide.

0 4 . 1

In a series of experiments, the concentrations of **X** and aqueous sodium hydroxide are varied at a constant temperature.

Table 1 shows the results of these experiments.

Table 1

Experiment	Initial [X] / mol dm ⁻³	Initial [NaOH] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.040	0.040	3.0×10^{-3}
2	0.060	0.040	4.5×10^{-3}
3	0.080	0.060	9.0×10^{-3}
4	0.100	0.060	to be calculated

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

Calculate the initial rate of reaction in **Experiment 4**.

[3 marks]

Exp 1 to 2: [X] $\times 1.5$, [NaOH] same, rate $\times 1.5$, so first order in X

Exp 2 to 3: [X] $\times 4/3$, [NaOH] $\times 1.5$, rate $\times 2 = 4/3 \times 1.5$, so first order in NaOH

$$k = 3.0 \times 10^{-3} \div (0.040 \times 0.040) = 1.875 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

$$\text{rate} = 1.875 \times 0.100 \times 0.060 = 0.01125 = 1.1 \times 10^{-2}$$

Order of reaction with respect to **X** 1

Order of reaction with respect to NaOH 1

Initial rate in **Experiment 4** 1.1×10^{-2} mol dm⁻³ s⁻¹



0 4 . 2

Table 2 shows the results for the reaction between a different ester, **Y**, and aqueous sodium hydroxide under different conditions.

Table 2

Initial [Y] / mol dm ⁻³	Initial [NaOH] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
0.040	2.2	5.0 × 10 ⁻³

Under these conditions, the rate equation is

$$\text{rate} = k[\text{Y}]$$

Use the data in **Table 2** to calculate a value for the rate constant, *k*, for this reaction. Give the units for *k*.

[2 marks]

$$k = \text{rate} \div [\text{Y}] = 5.0 \times 10^{-3} \div 0.040 = 0.125$$

$$k \quad 0.125$$

$$\text{Units} \quad \text{s}^{-1}$$

5

Turn over for the next question

Turn over ►



0 5

The reversible reaction between nitrogen monoxide and oxygen is investigated.

**0 5 . 1**

A mixture of 0.060 mol of NO and 0.035 mol of O₂ is placed in a closed container at a constant temperature. The mixture is left to reach equilibrium.

At equilibrium, the mixture contains 0.040 mol of NO₂

Calculate the amount, in moles, of NO and of O₂ in this equilibrium mixture.

Calculate the mole fraction of NO in this equilibrium mixture.

[4 marks]

$$\text{NO used} = 0.040 \text{ mol, so NO left} = 0.060 - 0.040 = 0.020 \text{ mol}$$

$$\text{O}_2 \text{ used} = 0.040 \div 2 = 0.020 \text{ mol, so O}_2 \text{ left} = 0.035 - 0.020 = 0.015 \text{ mol}$$

$$\text{total} = 0.020 + 0.015 + 0.040 = 0.075 \text{ mol}$$

$$\text{mole fraction of NO} = 0.020 \div 0.075 = 0.267$$

Amount of NO 0.020 mol

Amount of O₂ 0.015 mol

Mole fraction of NO 0.267

0 5 . 2

A second equilibrium mixture contains 0.020 mol of NO, 0.030 mol of O₂ and 0.040 mol of NO₂

The pressure of this equilibrium mixture is 120 kPa

Calculate the partial pressure, in kPa, of NO in this equilibrium mixture.

[2 marks]

$$\text{total} = 0.020 + 0.030 + 0.040 = 0.090 \text{ mol}$$

$$\text{mole fraction of NO} = 0.020 \div 0.090 = 0.222$$

$$p(\text{NO}) = 0.222 \times 120 = 26.7 \text{ kPa}$$

Partial pressure of NO 26.7 kPa



0 5 . 3

A third equilibrium mixture of NO, O₂ and NO₂ is formed at a given temperature and a total pressure of 240 kPa

In this mixture, the partial pressure of NO is 70 kPa and the partial pressure of O₂ is 105 kPa

Write an expression for the equilibrium constant (K_p) for this reaction.

Use the expression to calculate a value for K_p for this reaction.
Give the units for K_p

[4 marks]

$$K_p = \frac{p(\text{NO}_2)^2}{p(\text{NO})^2 \times p(\text{O}_2)}$$

$$p(\text{NO}_2) = 240 - (70 + 105) = 65 \text{ kPa}$$

$$K_p = 65^2 \div (70^2 \times 105) = 4225 \div 514\,500 = 8.21 \times 10^{-3}$$

$$\text{units} = \text{kPa}^2 \div (\text{kPa}^2 \times \text{kPa}) = \text{kPa}^{-1}$$

Value of K_p 8.21×10^{-3}

Units kPa^{-1}

0 5 . 4

The total pressure of an equilibrium mixture containing NO, O₂ and NO₂ is increased at constant temperature.

Predict the effect, if any, of this change on the mole fraction of NO in the equilibrium mixture and on the value of K_p

Give a reason for each prediction.

[4 marks]

Effect on mole fraction of NO decreases

Reason There are fewer moles of gas on the right (2) than on the left (3), so the equilibrium shifts to the right to reduce the pressure.

Effect on value of K_p no change (K_p is unchanged)

Reason K_p only changes with temperature, and the temperature is constant.

14

Turn over ►



0 6

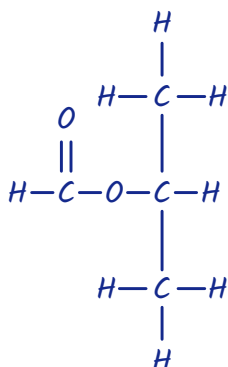
This question is about carboxylic acids and esters.

0 6 . 1

Methanoic acid reacts with propan-2-ol to form an ester.

Draw the displayed formula of this ester.

[1 mark]

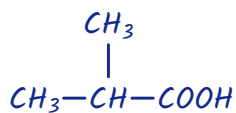


0 6 . 2

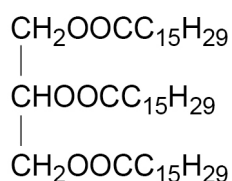
Propan-1-ol reacts with a branched-chain carboxylic acid to form an ester with the molecular formula $\text{C}_7\text{H}_{14}\text{O}_2$

Draw the structure of this carboxylic acid.

[1 mark]



- 0 6 . 3 A naturally-occurring oil contains a triester with the structure shown.



This triester reacts with an excess of methanol in the presence of a catalyst to form two products.

One of these products can be used in biodiesel.

Draw the structure of each of these products.

Use $\text{C}_{15}\text{H}_{29}$ where appropriate in your answer.

[2 marks]

Product 1

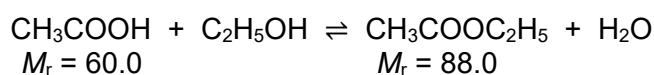


Product 2



- 0 6 . 4 A sample of ethyl ethanoate was prepared using the reaction between 5.70 g of ethanoic acid and an excess of ethanol.

Some M_r values are shown.



The mass of ethyl ethanoate obtained was 4.60 g

Calculate the percentage yield of ethyl ethanoate.

[2 marks]

$$n(\text{CH}_3\text{COOH}) = 5.70 \div 60.0 = 0.0950 \text{ mol}$$

$$\text{maximum mass of ester} = 0.0950 \times 88.0 = 8.36 \text{ g}$$

$$\% \text{ yield} = 4.60 \div 8.36 \times 100 = 55.0\%$$

Yield 55.0 %

6

Turn over ►



0 7

This question is about propylamine.

0 7 . 1

Complete the ionic equation to show how propylamine reacts with sulfuric acid.

[1 mark]



0 7 . 2

1-Bromopropane can be converted into propylamine.

Give the reagent and a condition for this reaction.

Explain why this condition is needed to give a high yield of propylamine.

[3 marks]

Reagent ammonia (NH_3)Condition a large excess of ammoniaExplanation to prevent further substitution, i.e. to stop formation of secondary and tertiary amines and quaternary ammonium salts

0 7 . 3

Propylamine reacts with ethanoyl chloride.

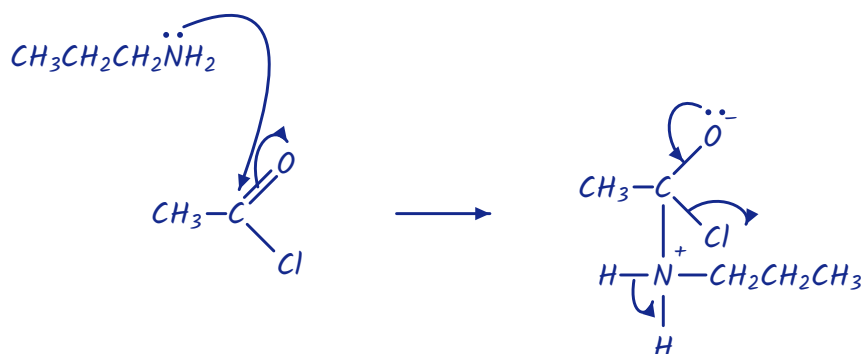
Name and outline the mechanism for this reaction.

Use IUPAC rules to name the organic product.

[6 marks]

Name of mechanism (nucleophilic) addition-elimination

Mechanism

Name of organic product N-propylethanamide

07.4

Explain why propylamine is a stronger base than ammonia.

[2 marks]

The propyl (alkyl) group is electron-releasing (it has a positive inductive effect).

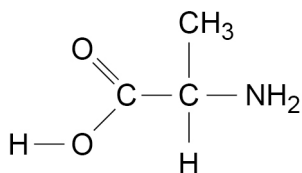
This increases the electron density on the N atom, so its lone pair is more available to accept a proton (H^+).

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

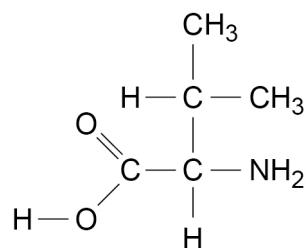
0 8

This question is about amino acids and proteins.

The structures of alanine and valine are shown.



alanine



valine

0 8

. 1

Use IUPAC rules to name valine.

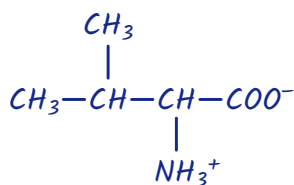
Draw the structure of valine in the solid state.

Name this type of structure.

[3 marks]

Name 2-amino-3-methylbutanoic acid

Structure



Type of structure zwitterion



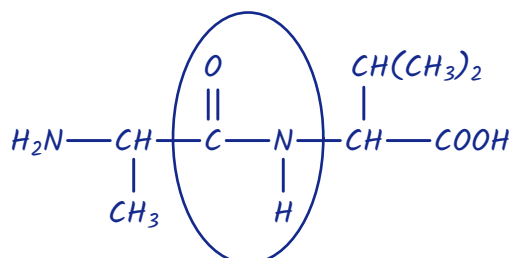
0 8 . 2 Alanine and valine react together to form two dipeptides.

Draw the structure of each dipeptide.

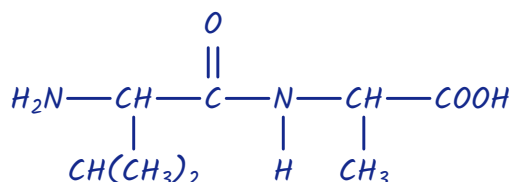
Draw a ring around the peptide link on **one** of your structures.

[3 marks]

Structure 1



Structure 2

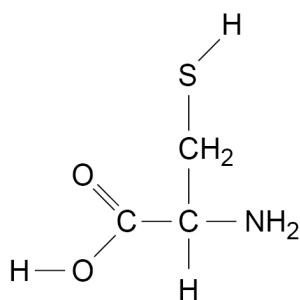


Question 8 continues on the next page

Turn over ►



The structure of the amino acid cysteine is shown.

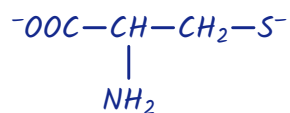


0 8 . 3

In aqueous sodium hydroxide, the thiol group ($-\text{S}-\text{H}$) in cysteine acts as an acid.

Draw the structure of the ion formed by cysteine in an excess of aqueous sodium hydroxide.

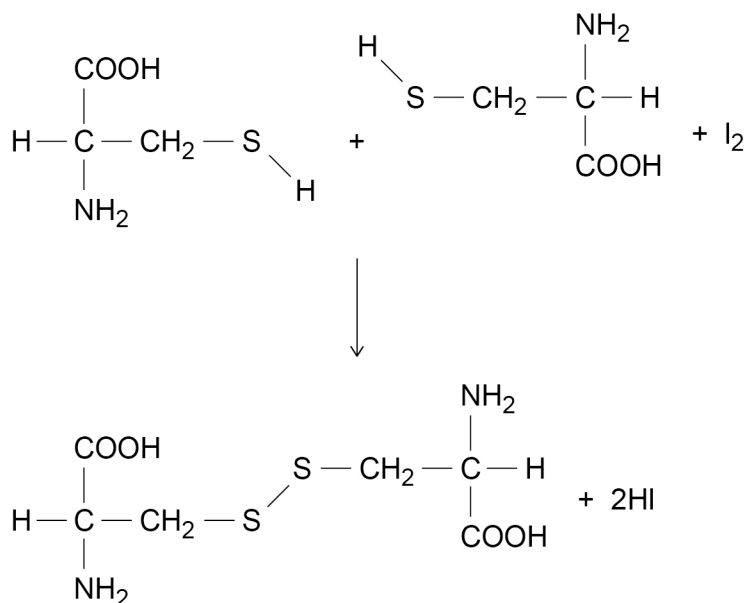
[1 mark]



08.4

Two molecules of cysteine react with iodine to form a disulfide bridge as shown in the equation.

[3 marks]



Give the oxidation state of iodine in I_2 and in HI

Deduce the role of iodine in this reaction.

State the type of protein structure maintained by the S–S bond formed in this reaction.

Oxidation state of iodine in I_2 0

Oxidation state of iodine in HI -1

Role of iodine oxidising agent

Type of protein structure tertiary

10

Turn over for the next question

Turn over ►



0 9

This question is about monomers and polymers.

0 9 . 1

Butane-1,4-diol ($\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$) can be converted into butanedioic acid ($\text{HOOCCH}_2\text{CH}_2\text{COOH}$).

Give the reagent, or combination of reagents, and a condition needed for this reaction.

[2 marks]Reagent(s) acidified potassium dichromate(VI) ($\text{K}_2\text{Cr}_2\text{O}_7$ / H_2SO_4)Condition heat under reflux (with excess oxidising agent)

0 9 . 2

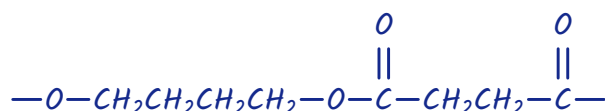
Butane-1,4-diol and butanedioic acid react together to form a polymer.

State the type of polymerisation.

Draw the repeating unit of this polymer.

[2 marks]Type of polymerisation condensation

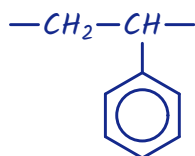
Repeating unit



0 9 . 3

Phenylethene ($\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$) forms the polymer poly(phenylethene).

Draw the repeating unit of this polymer.

[1 mark]**END OF QUESTIONS**

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