

Surname <i>StemUp Model Solution</i>	Centre Number	Candidate Number
First name(s)		2



GCE A LEVEL

1410U40-1



TUESDAY, 18 JUNE 2024 – MORNING

CHEMISTRY – A2 unit 4
Organic Chemistry and Analysis

1 hour 45 minutes

For Examiner's use only		
Question	Maximum Mark	Mark Awarded
Section A 1. to 6.	10	
Section B 7.	14	
8.	15	
9.	15	
10.	12	
11.	14	
Total	80	

ADDITIONAL MATERIALS

- A calculator, pencil and ruler
- **Data Booklet** supplied by WJEC

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen. Do not use gel pen or correction fluid.

You may use a pencil for graphs and diagrams only.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions.

Section B Answer **all** questions.

Write your answers in the spaces provided in this booklet. If you run out of space, use the additional page(s) at the back of the booklet, taking care to number the question(s) correctly.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The assessment of the quality of extended response (QER) will take place in **Q10(a)**.



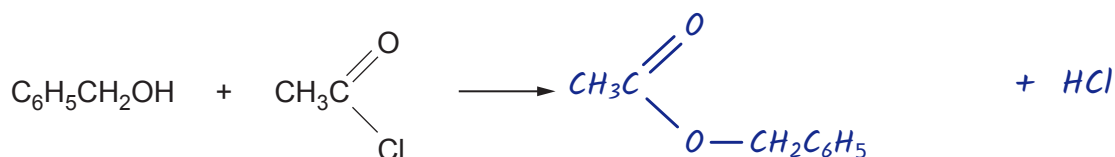
JUN241410U40101

SECTION A

Answer **all** questions.

1. Phenylmethyl ethanoate, used in perfumery, is made by reacting phenylmethanol and ethanoyl chloride.

Complete the equation for this reaction, showing the structure of the organic product. [1]



2. An azo dye has a maximum absorption of visible light at 403 nm.

(a) Calculate the frequency corresponding to this wavelength. [1]

$$f = c \div \lambda = 3.00 \times 10^8 \div (403 \times 10^{-9})$$

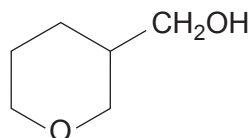
Frequency = 7.44×10^{14} Hz

(b) Explain why this dye is yellow in white light. [1]

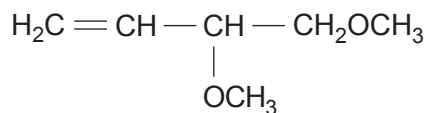
The dye absorbs blue light (the rest of the visible spectrum), so the light that is not absorbed, yellow, is seen.



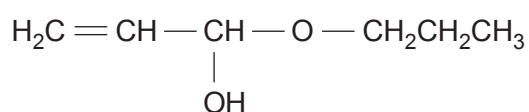
3. Four isomers of formula $C_6H_{12}O_2$ are given below.



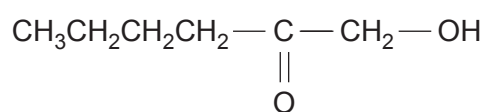
compound **D**



compound **E**



compound **F**



compound **G**

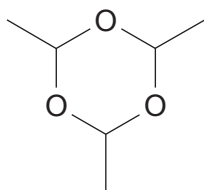
Deduce which isomer has an infrared absorption spectrum showing absorptions at 1620 cm^{-1} and at $3200\text{--}3500\text{ cm}^{-1}$ but **not** at $1650\text{--}1750\text{ cm}^{-1}$. Give reasons for your answer. [2]

Compound F. It contains an O-H (alcohol) bond, absorbing at $3200\text{--}3500\text{ cm}^{-1}$, and a C=C bond, absorbing at 1620 cm^{-1} , but it has no C=O bond, so no absorption at $1650\text{--}1750\text{ cm}^{-1}$. (D has no C=C, E has no O-H and G has a C=O.)

4. Give the formula of the triphenylmethyl radical. [1]



5. The structure of paraldehyde is shown below.



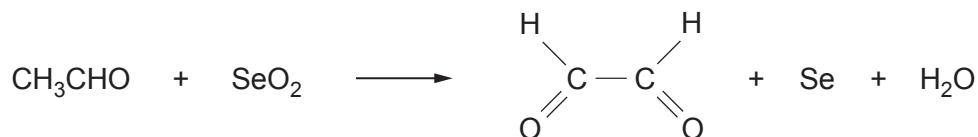
Explain what would be seen in the ^{13}C NMR spectrum of this compound.

References to the positions of the chemical shifts are **not** required.

[2]

Two signals (peaks): all three CH_3 carbon atoms are equivalent (same environment) and all three ring CH carbon atoms, each bonded to two O atoms, are equivalent.

6. Ethanal is oxidised by selenium dioxide giving ethanedial.



Calculate the atom economy of this reaction to produce ethanedial.

Give your answer to an **appropriate** number of significant figures.

[2]

$$M_r: \text{CH}_3\text{CHO} = 44.0, \text{SeO}_2 = 111.0, (\text{CHO})_2 = 58.0$$

$$\begin{aligned} \text{atom economy} &= 58.0 \div (44.0 + 111.0) \times 100 \\ &= 37.4 \% \end{aligned}$$

Atom economy = 37.4 %



SECTION BAnswer **all** questions.

7. (a) Nitrobenzene can be made by the nitration of benzene.

(i) State the reagent(s) used for this reaction.

[1]

concentrated nitric acid and concentrated sulfuric acid

(ii) State the **formula** of the nitrogen-containing electrophile that takes part in this reaction.

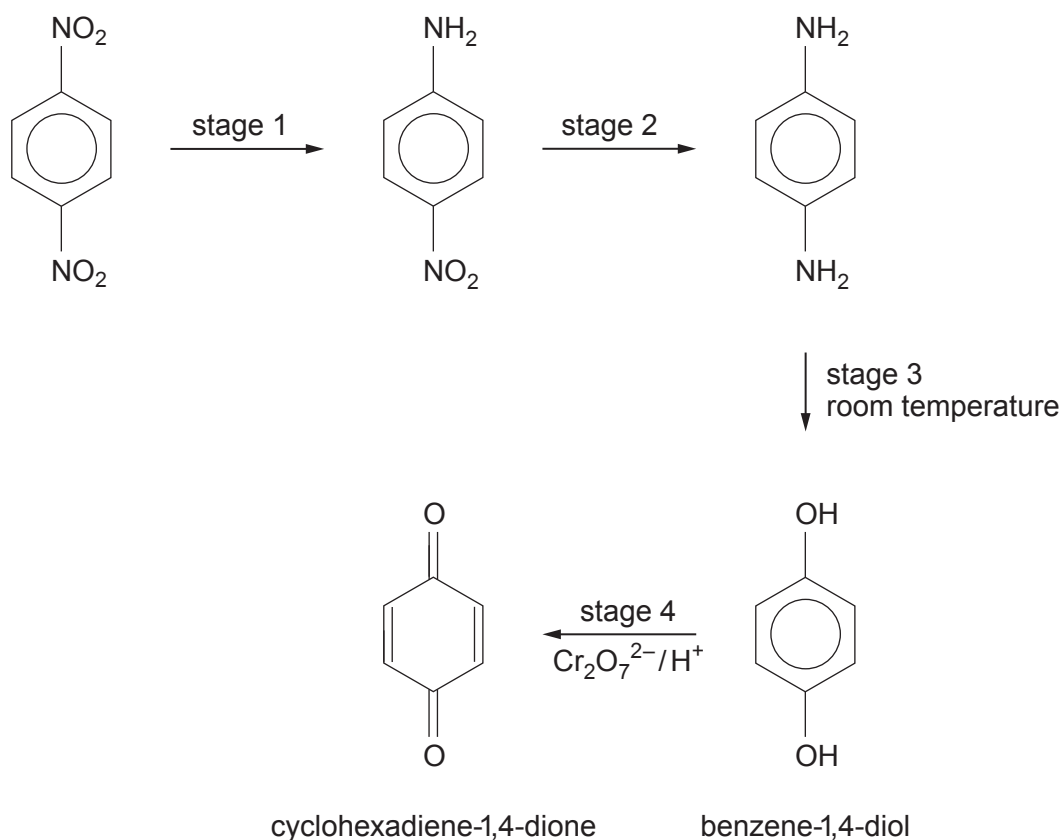
[1]

NO_2^+



- (b) Aromatic nitro-compounds are useful in synthesis as they are often the starting materials for producing other compounds.

Study the reaction sequence below and then answer the questions that follow.



- (i) State the type of reaction occurring during stage 1. [1]
reduction
- (ii) State the reagent(s) used in stage 2. [1]
tin and concentrated hydrochloric acid
- (iii) State the reagent(s) used to produce benzene-1,4-diol in stage 3. [1]
sodium nitrite and hydrochloric acid
- (iv) State the colour change undergone by the reagents in stage 4. [1]
orange to green

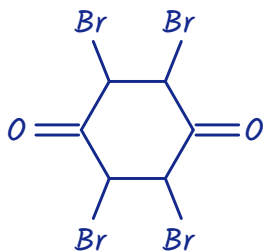


(v) The reaction product in stage 4, cyclohexadiene-1,4-dione acts as an alkene.

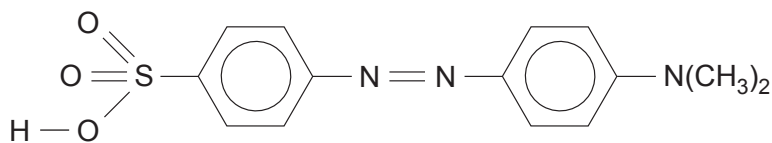
- I. State the type of reaction mechanism that occurs when an alkene reacts with bromine. [1]

electrophilic addition

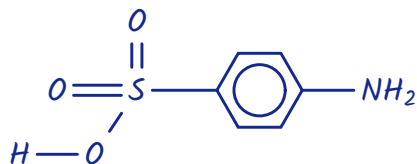
- II. Draw the structure of the compound obtained when 1 mol of cyclohexadiene-1,4-dione reacts with 2 mol of bromine. [1]



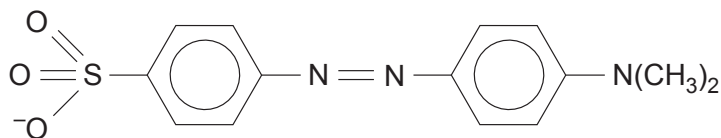
(c) Methyl orange is a water soluble acid-base indicator.



- (i) Give the structure of the starting sulfur-containing compound that is coupled with N,N-dimethylaniline to give methyl orange. [1]



- (ii) Suggest why, in basic solution, methyl orange exists as the species below. [1]

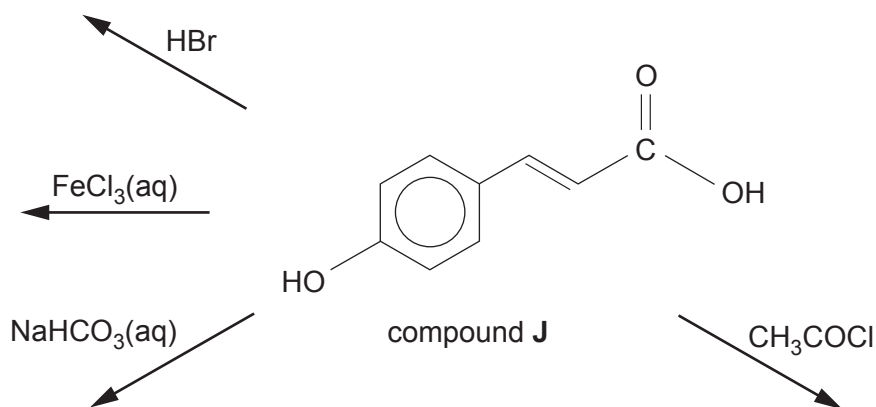


The $-SO_3H$ group acts as an acid: it loses a proton (H^+) to the OH^- ions of the base, giving water and $-SO_3^-$.

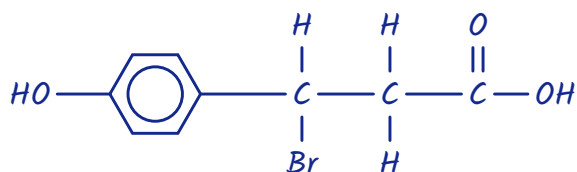


- (d) Compound **J** is present in relatively large quantities in red peppers.

Study the diagram below and then answer the questions that follow.

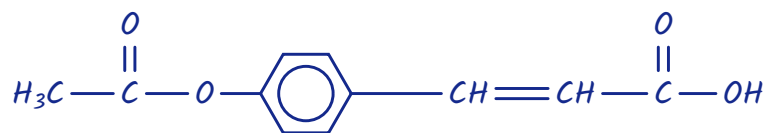


- (i) State what is seen when compound **J** reacts with iron(III) chloride solution. [1]
purple coloration (solution)
- (ii) State what is seen when compound **J** reacts with sodium hydrogencarbonate solution. [1]
fizzing / effervescence (CO_2 given off)
- (iii) Give the structure of the compound formed when compound **J** reacts with hydrogen bromide. [1]



- (iv) Give the structure of the compound formed when compound **J** reacts with ethanoyl chloride.

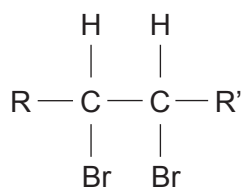
[1]

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09

14



8. (a) Compound **M** is an aliphatic compound, which contains two bromine atoms.



compound **M**

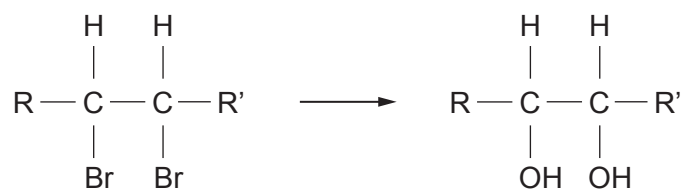
- (i) Compound **M** reacts with an excess of alcoholic potassium hydroxide solution to give compound **N**, which has the formula $\text{R}-\text{C}\equiv\text{C}-\text{R}'$.

Suggest the role of the alcoholic potassium hydroxide in this elimination reaction.

[1]

it acts as a base (it removes protons, H^+)

- (ii) Compound **M** reacts with aqueous sodium hydroxide to give compound **P**.



compound **P**

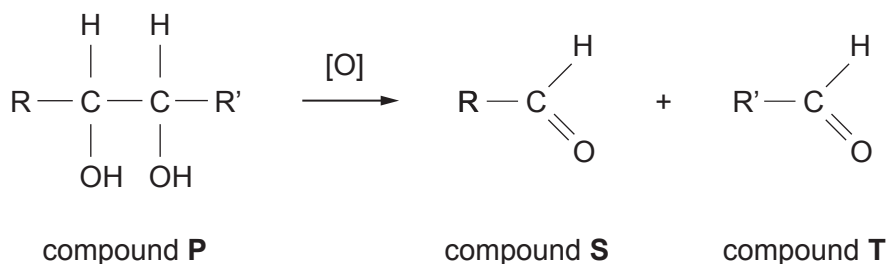
State the type of reaction mechanism occurring.

[1]

nucleophilic substitution



- (iii) Compound **P** can undergo bond fission when it is heated with a suitable oxidising agent to form two aldehydes **S** and **T**.



The mass spectrum of compound **S** showed a molecular ion at m/z 72.

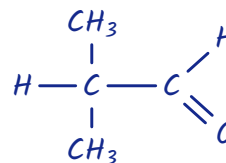
- I. The mass spectrum of compound **S** showed that the alkyl group R was branched.

Deduce the structure of compound **S**. Show your reasoning. [2]

M_r of $-\text{CHO} = 29$, so M_r of R = $72 - 29 = 43$

R is C_3H_7 ; branched, so R = $(\text{CH}_3)_2\text{CH}-$

S is $(\text{CH}_3)_2\text{CHCHO}$, 2-methylpropanal



- II. Compounds **S** and **T** both reacted with 2,4-dinitrophenylhydrazine to give solid derivatives.

State the colour of these derivatives. [1]

orange-red

- III. The melting temperatures of the derivatives of compounds **S** and **T** in part II above are shown in the table.

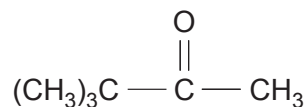
Compound	Melting temperature/ $^{\circ}\text{C}$
S	185–187
T	186–189

Describe how the melting temperature of a 50:50 mixture of the two derivatives differs from those shown in the table. [1]

The mixture melts at a lower temperature than either pure derivative and over a greater (wider) range.



- (b) Pinacolone is prepared from a diol containing 6 carbon atoms.



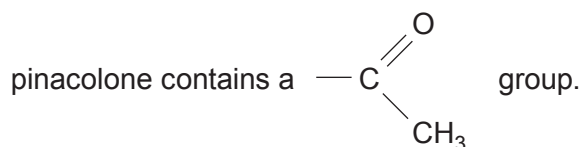
pinacolone

After the reaction, flammable pinacolone is distilled from the reaction mixture. The distillate consists of two layers – an aqueous layer and a less dense layer containing mainly pinacolone.

- (i) Describe how you would separate these two layers. [1]

Use a separating funnel: let the layers settle, then run off the lower aqueous layer through the tap, leaving the pinacolone.

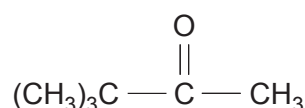
- (ii) Describe a chemical test, giving reagent(s) and observations, to show that



Warm with iodine and sodium hydroxide solution (I_2 / NaOH).

A pale yellow solid (precipitate) of CHI_3 forms.

- (iii) The high resolution ^1H NMR spectrum of pinacolone consists of two signals.



pinacolone

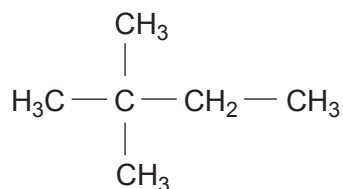
Complete the table below that describes these two signals. [2]

Protons	Splitting pattern	Relative peak area
CH_3CO	<i>singlet</i>	<i>3</i>
$(\text{CH}_3)_3\text{C}$	<i>singlet</i>	<i>9</i>

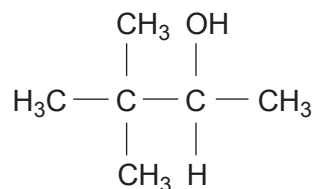


- (iv) Under suitable conditions pinacolone was reduced, giving a mixture of 2,2-dimethylbutane and 3,3-dimethylbutan-2-ol together with some unreacted pinacolone.

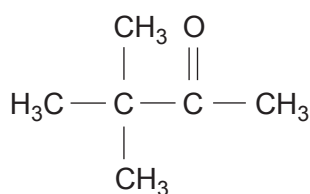
These three compounds were separated by gas chromatography.



2,2-dimethylbutane



3,3-dimethylbutan-2-ol



pinacolone

- I. Mary said that the boiling temperature of 3,3-dimethylbutan-2-ol would be the highest of these three compounds and that this could be used to identify it.

Explain why she is correct.

[2]

Only the alcohol has an O-H group, so it forms hydrogen bonds between molecules (the others cannot). More energy is needed to separate its molecules, so it boils highest.

- II. The ^{13}C NMR spectra of the remaining two compounds were taken.

Suggest how the ^{13}C NMR spectra of these two compounds would be similar and how they would be different.

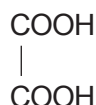
[2]

Similar *both show four signals (four carbon environments)*

Different *the four signals are in different positions (chemical shifts), e.g. C=O at about 210 ppm*



9. (a) Ethanedioic acid is an important industrial chemical.



One method for its manufacture is by the reaction of butan-1-ol, carbon monoxide and oxygen at a pressure of 10 MPa and at a temperature of 100 °C in the liquid phase. The process uses a catalyst of palladium mounted on graphite.

The first stage gives the ester di-1-butyl ethanedioate, which is then hydrolysed to give ethanedioic acid and butan-1-ol.

- (i) Balance the equation for the first stage of this process. [1]

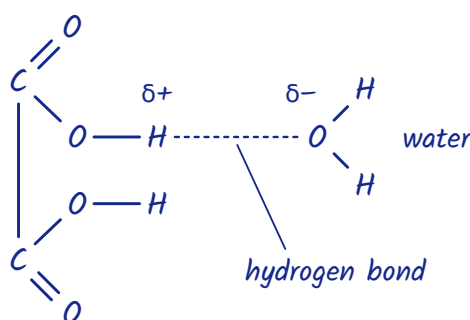


- (ii) Suggest **one** reason why this stage of the process may be seen as relatively uneconomic. [1]

The palladium catalyst is very expensive (and maintaining a very high pressure is costly).

- (iii) Hydrolysis of the ester gives ethanedioic acid and butan-1-ol.

Explain why ethanedioic acid is soluble in water but di-1-butyl ethanedioate is virtually insoluble in water. Include a diagram in your answer. [3]



Ethanedioic acid has O-H groups, so it can form hydrogen bonds with water molecules (as shown), so it dissolves.

The ester has no O-H bond (and large non-polar butyl groups), so it cannot hydrogen bond with water and is virtually insoluble.



- (b) An older method for manufacturing ethanedioic acid produces insoluble calcium ethanedioate (M_r 128) as an intermediate. This is reacted with aqueous sulfuric acid to produce calcium sulfate and an aqueous solution of ethanedioic acid.



Ethanedioic acid crystallises as its dihydrate.

In a laboratory experiment 11.52 g of calcium ethanedioate was reacted with aqueous sulfuric acid of concentration 2.00 mol dm^{-3} .

- (i) Calculate the minimum volume of this aqueous sulfuric acid needed to just react with all the calcium ethanedioate. [2]

$$n((\text{COO})_2\text{Ca}) = 11.52 \div 128 = 0.0900 \text{ mol}$$

$$1 : 1 \text{ ratio, so } n(\text{H}_2\text{SO}_4) = 0.0900 \text{ mol}$$

$$V = 0.0900 \div 2.00 \times 1000 = 45.0 \text{ cm}^3$$

Minimum volume = 45.0 cm^3

- (ii) After removal of insoluble calcium sulfate, the residue was washed with water. The solution was boiled until 50.0 cm^3 (50.0 g) of solution remained. The solubility of ethanedioic acid dihydrate, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ (M_r 126) is $14.3 \text{ g} / 100 \text{ g}$ of solution at 20°C .

Calculate the mass of ethanedioic acid dihydrate that crystallised from this solution at 20°C . [3]

mass that stays dissolved in 50.0 g of solution

$$= 14.3 \times 50.0 \div 100 = 7.15 \text{ g}$$

$$n(\text{dihydrate}) \text{ formed} = n((\text{COO})_2\text{Ca}) = 0.0900 \text{ mol}$$

$$\text{mass formed} = 0.0900 \times 126 = 11.34 \text{ g}$$

$$\text{mass crystallised} = 11.34 - 7.15 = 4.19 \text{ g}$$

Mass = 4.19 g



- (c) The removal of alkyl fluorocarbons and CFCs from the environment presents a difficult problem.

One suggestion is to heat these halogenoalkanes with sodium ethanedioate. For example, difluoromethane reacts with sodium ethanedioate, $(\text{COO})_2\text{Na}_2$, to give hexafluorobenzene, sodium carbonate (Na_2CO_3) and water.

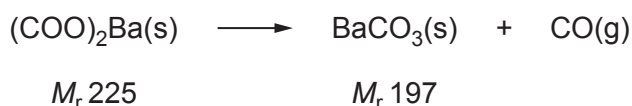
Write an equation for this reaction.

[2]

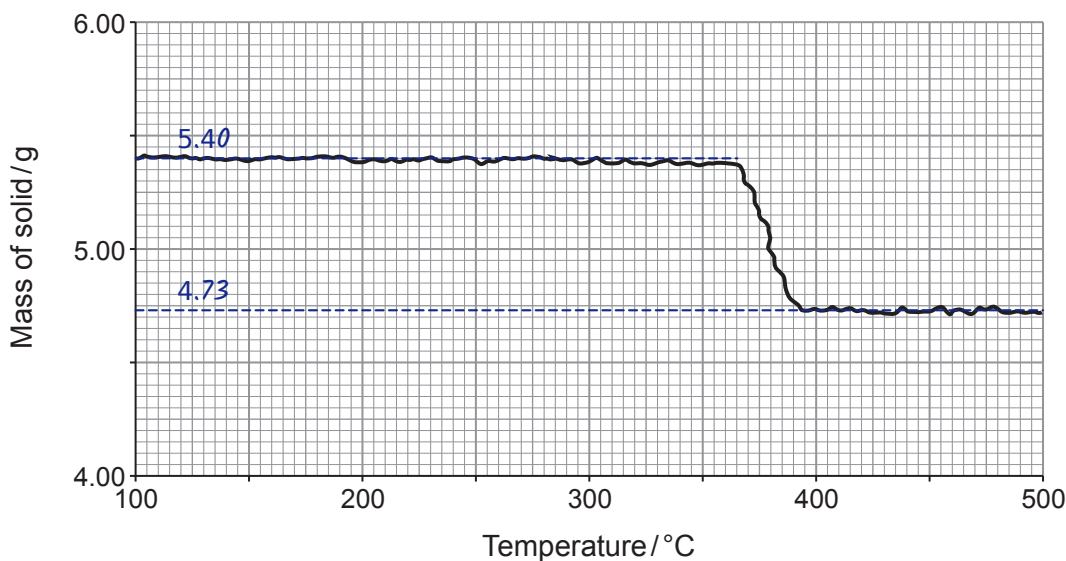


- (d) On heating, barium ethanedioate undergoes decomposition.

Use the graph to show that the equation for this reaction is



[2]



From the graph: initial mass = 5.40 g, final mass = 4.73 g. % mass lost =

$$(5.40 - 4.73) \div 5.40 \times 100 = 12.4 \%$$

From the equation: % mass lost as CO = $28 \div 225 \times 100 = 12.4 \%$. The values are the same, so the equation is correct.



- (e) Decarboxylation occurs when carboxylic acids are heated with sodalime.

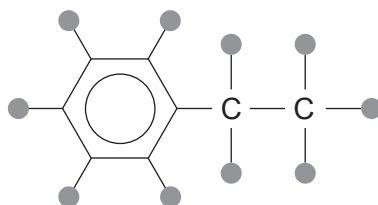
State the name of the organic compound produced when 4-ethylbenzenecarboxylic acid is heated with sodalime. [1]

ethylbenzene

15



10. (a) Compound **B** contains only carbon, hydrogen and bromine. The hydrogen and bromine atoms could be at any of the positions indicated by a circle in the following structure.



- 5.35 g of compound **B** contains 3.74 g of bromine and 0.11 g of hydrogen
- It rotates the plane of plane polarised light
- When 4.36 g of compound **B** is heated with aqueous sodium hydroxide, the bromide ions produced react with silver ions to give 4.77 g of silver bromide (M_r 187.9)

Use **all** of this information to deduce a possible structure for compound **B**.

Explain your reasoning.

[6 QER]

Mass of C = 5.35 - 3.74 - 0.11 = 1.50 g. Moles: C = 1.50 ÷ 12.0 = 0.125; H =

0.11 ÷ 1.01 = 0.109; Br = 3.74 ÷ 79.9 = 0.0468. Ratio C : H : Br = 2.67 : 2.33 : 1

= 8 : 7 : 3.

The structure has 8 carbon atoms, so the molecular formula is $C_8H_7Br_3$ and $M_r = 343$.

The precipitate is AgBr. Mass of Br in 4.77 g AgBr = 4.77 × 79.9 ÷ 187.9 = 2.03 g,

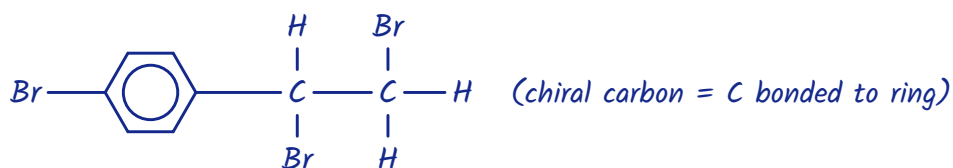
so % Br removed = 2.03 ÷ 4.36 × 100 = 46.6 %. % Br in B = 3 × 79.9 ÷ 343 ×

100 = 69.9 %. 46.6 ÷ 69.9 = 2/3, so only two of the three Br atoms are removed.

NaOH(aq) hydrolyses only aliphatic C-Br bonds (Br on a benzene ring is not

substituted), so two Br atoms are on the side chain and the other Br is on the ring.

B rotates plane polarised light, so it is optically active and has a chiral carbon (four different groups): one Br must be on each side-chain carbon. B is:



- (b) Sucrose, $C_{12}H_{22}O_{11}$, is a sugar that contains eight —OH groups in each molecule. It reacts with ethanoic anhydride to give sucrose octaethanoate.



- (i) A 0.0700 mol sample of sucrose was used in a preparation.

Calculate the minimum volume of ethanoic anhydride needed to react with all the —OH groups present in this sample of sucrose. [2]

ethanoic anhydride	M_r	Density / $g\ cm^{-3}$
	102	1.08

$$n(-OH) = 8 \times 0.0700 = 0.560\ mol = n(anhydride)$$

$$mass = 0.560 \times 102 = 57.1\ g$$

$$volume = 57.1 \div 1.08 = 52.9\ cm^3$$

Minimum volume = 52.9 cm^3

- (ii) There is interest in producing materials by 'green' methods.

Two methods are proposed for making sucrose octaethanoate in the laboratory.

Method X Refluxing the mixture at 139°C using an electric hotplate

Method Y Ultrasonic irradiation at room temperature

Apart from temperature, suggest **two** factors that should be considered when deciding which of these two methods is 'greener'. [2]

1. the percentage yield of each method

2. the reaction rate (time needed for each method)



(c) Lactose is a reducing sugar and reacts with Fehling's reagent.

- (i) State what is seen when lactose reacts with the dark blue solution of Fehling's reagent. [1]

red-brown precipitate (solid)

- (ii) State which functional group must be present in a molecule of lactose for this result with Fehling's reagent. [1]

aldehyde group (-CHO)

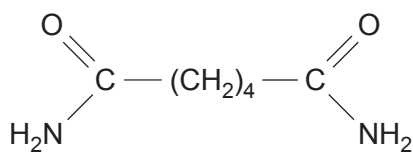


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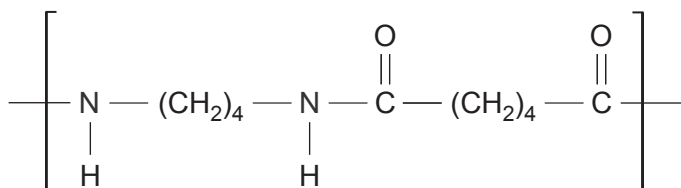
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11. (a) A method to produce the polyamide **W**, starting from adipamide is shown below.



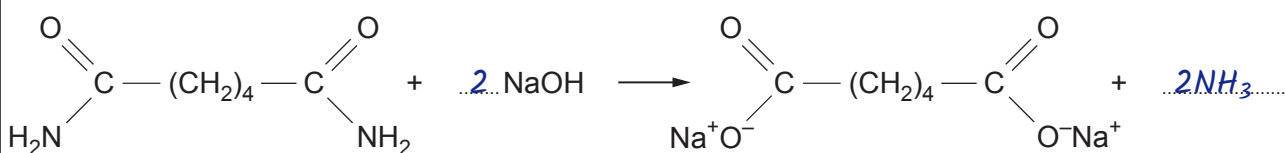
adipamide

polyamide **W**

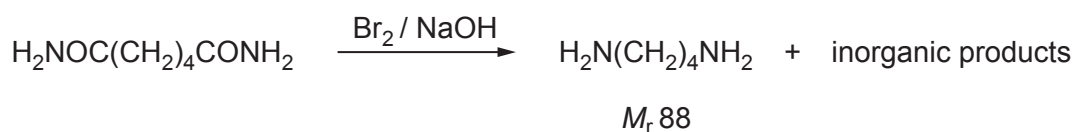
- (i) In the first stage adipamide is hydrolysed using aqueous sodium hydroxide, giving disodium hexanedioate as one of the products.

Complete and balance the equation for this stage.

[2]



- (ii) In another stage, adipamide is reacted with bromine in the presence of alkali to give butane-1,4-diamine, $\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$.



In this stage 0.075 mol of adipamide was used. If the percentage yield of the diamine was 60%, calculate the mass of butane-1,4-diamine produced.

[2]

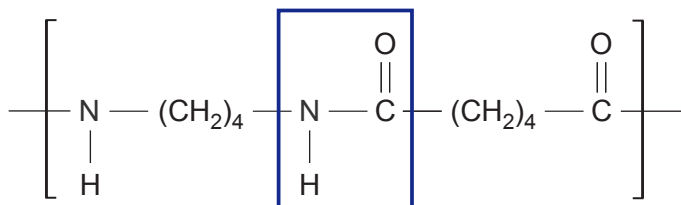
$$n(\text{diamine}) = 0.075 \times 60 \div 100 = 0.045 \text{ mol}$$

$$\text{mass} = 0.045 \times 88 = 3.96 \text{ g}$$

Mass = 3.96 g



- (iii) The sodium salt of hexanedioic acid produced in part (i) is then acidified and the hexanedioic acid produced is reacted with butane-1,4-diamine to give polyamide **W**.



Polyamides contain a peptide link.

Show the peptide link present in the polyamide **on the diagram above**.

[1]

- (iv) An alternative method for producing hexanedioic acid is to treat adipamide with nitric(III) acid.



- I. Give **one** advantage of the method using nitric(III) acid.

[1]

Only one stage is involved, so it is quicker (and probably gives a higher percentage yield).

- II. Suggest how you would know that this alternative reaction using nitric(III) acid is complete.

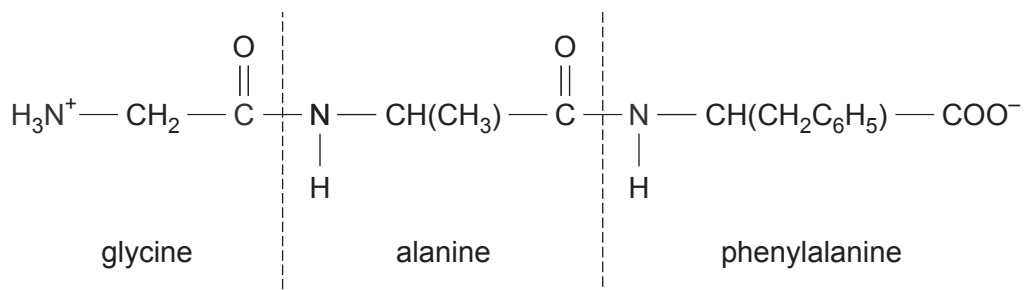
[1]

No more effervescence (bubbles of nitrogen) is given off.



- (b) A tripeptide is formed from three different amino acids.

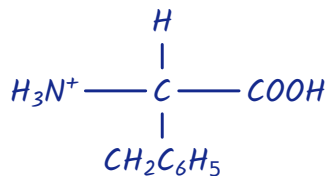
Its formula (shown as a zwitterion) is



- (i) State why the formation of a peptide from amino acids is called a condensation reaction. [1]

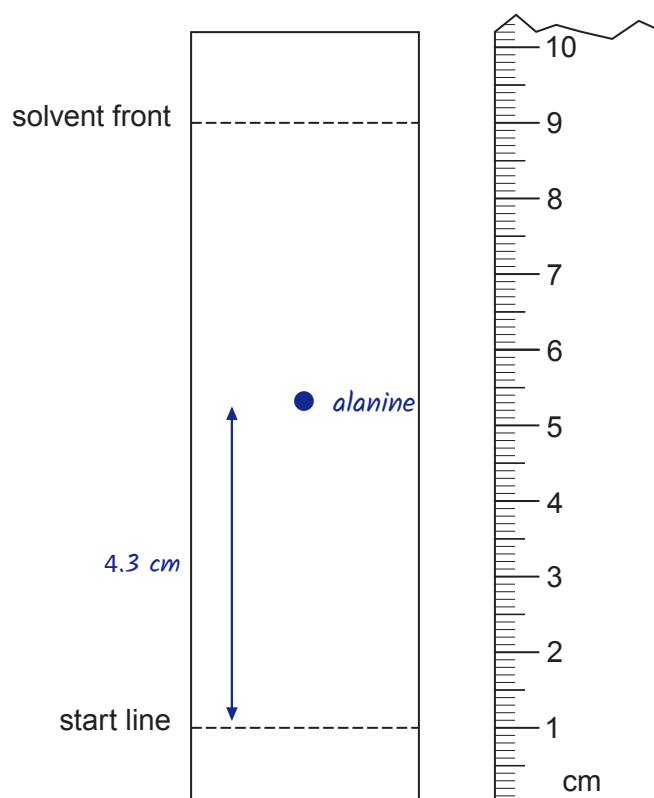
A small molecule, water, is eliminated as the amino acids join.

- (ii) Write the formula of the species formed from phenylalanine in acid solution. [1]



- (iii) The tripeptide is hydrolysed to give its amino acid fragments. A solution containing these three amino acids is separated using thin layer chromatography.

Use the blank chromatogram to show the position of the 'spot' given by alanine, which has an R_f value of 0.54. Show how you arrived at your answer. [2]



Solvent moved 8.0 cm, so spot moved $0.54 \times 8.0 = 4.3$ cm

spot is 4.3 cm above start line (at 5.3 cm on ruler)



- (c) A solution contains a mass of **z g** of **one** of the two enantiomers of alanine. It rotates the plane of plane polarised light in the clockwise direction (+) by 6° ($+6^\circ$).

The other enantiomer rotates the plane of plane polarised light in the anticlockwise direction (–).

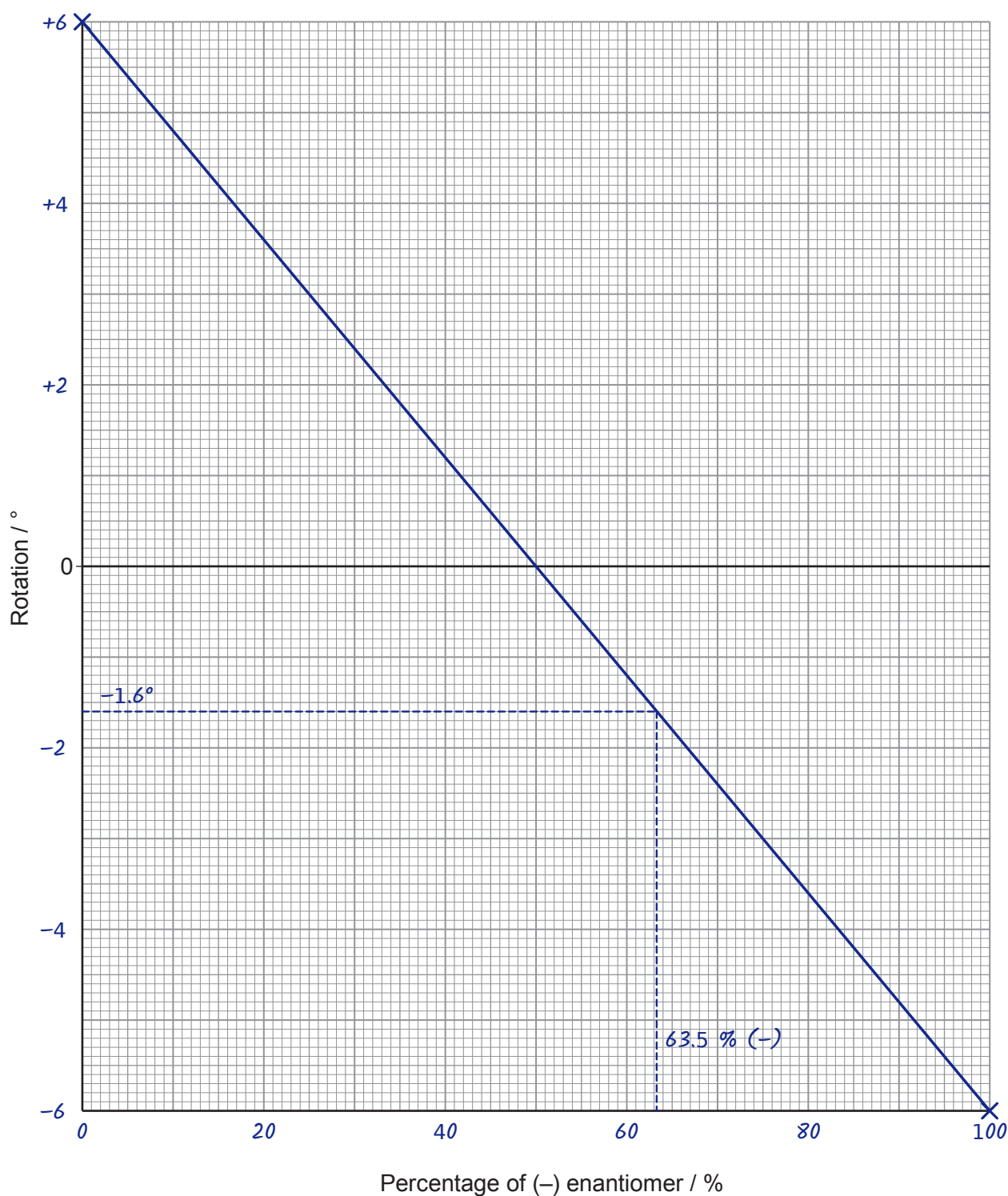
Another solution contains the same total mass **z g** of a **mixture** of both enantiomers. This mixture rotates the plane of plane polarised light by 1.6° in the anticlockwise direction (-1.6°).

Use this information to plot a graph to show how the rotation changes with the percentage of the (–) enantiomer. Hence determine the percentages of the (+) and (–) enantiomers in the mixture. [3]

Percentage of (+) enantiomer **36.5** %

Percentage of (–) enantiomer **63.5** %





END OF PAPER



[illegible]