Surname	Centre Number	Candidate Number
First name(s)		2

GCE A LEVEL

A410U20-1

O21-A410U20-1

TUESDAY, 12 OCTOBER 2021 – MORNING

CHEMISTRY – A level component 2
Organic Chemistry and Analysis

2 hours 30 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1. to 5.**	**15**	
Section B	**6.**	**17**	
	7.	**20**	
	8.	**17**	
	9.	**17**	
	10.	**20**	
	11.	**14**	
	Total	**120**	

ADDITIONAL MATERIALS

In addition to this examination paper, you will need a:
- calculator;
- **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 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.

Candidates are advised to allocate their time appropriately between **Section A (15 marks)** and **Section B (105 marks)**.

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 120.

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 **Q.8***(a)*(i) and **Q.10***(b)*.

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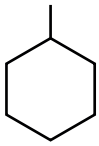
SECTION A

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

1. Methylcyclohexane has been used as a component of correction fluid.



methylcyclohexane

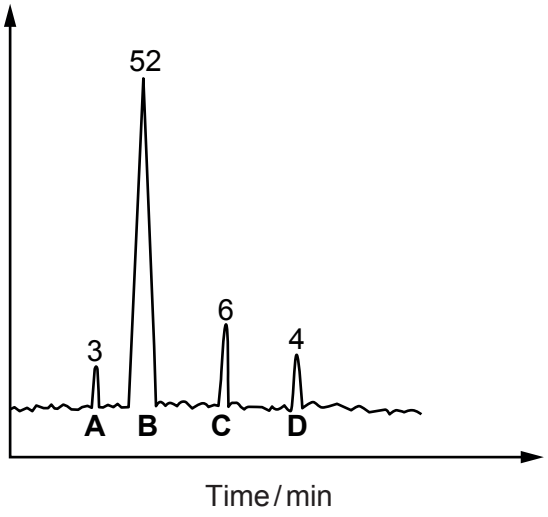
(a) State the empirical formula of methylcyclohexane. [1]

.....

(b) (i) A gas-liquid chromatogram of methylcyclohexane, contaminated with small quantities of cyclohexane, ethylcyclohexane and propylcyclohexane is shown below.

The figures show the relative peak areas.

Calculate the percentage of methylcyclohexane in the mixture. [1]



Percentage = ... %

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(ii) The boiling temperatures of cyclohexane and some alkylcyclohexanes are shown in the table.

Compound	Boiling temperature / °C
cyclohexane	81
methylcyclohexane	101
ethylcyclohexane	131
propylcyclohexane	155

The retention times for these compounds become longer as the boiling temperature rises.

State, giving a reason for your answer, which of the peaks **A**, **B**, **C** or **D** is likely to be given by ethylcyclohexane. [1]

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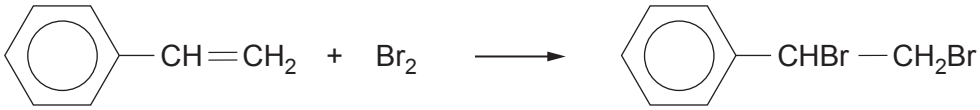
2. Bromine reacts with phenylethene to produce (1,2-dibromoethyl)benzene.



In an experiment 0.500 mol of phenylethene, together with a solvent, was placed in a flask and bromine slowly added with constant stirring.

(a) Bromine is very hazardous and the quantity required is usually measured by volume.

The density of bromine is 3.16 g cm^{-3}. Calculate the volume of bromine needed in this reaction. [2]

Volume = ... cm^3

(b) The melting temperature of pure (1,2-dibromoethyl)benzene is 73 °C. In the reaction the product was recrystallised using ethanol as the solvent.

State how the melting temperature would differ if the product still contained traces of the solvent. [1]

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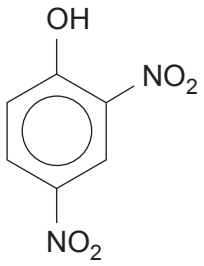
3. 2,4-Dinitrophenol is a coloured solid that has been used in some illegal weight loss preparations.



2,4-dinitrophenol

Its visible spectrum shows a maximum absorption in the blue region of the electromagnetic spectrum.

(a) State and explain the colour of this compound in white light. [1]

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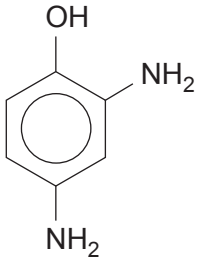
(b) This dinitro compound can be reduced to the corresponding diamino compound, 2,4-diaminophenol.



2,4-diaminophenol

Suggest a reagent(s) that can be used for this reduction. [1]

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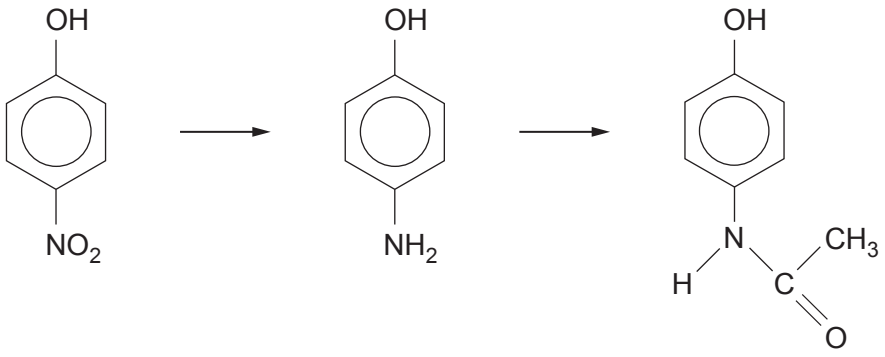
(c) A similar reaction can be used to produce 4-aminophenol, which can be used to make the painkiller paracetamol.



paracetamol

(i) State a compound that can be used in the second stage to make paracetamol. [1]

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(ii) A solution of paracetamol is treated with a solution of bromine.

Give the colour change that occurs. [1]

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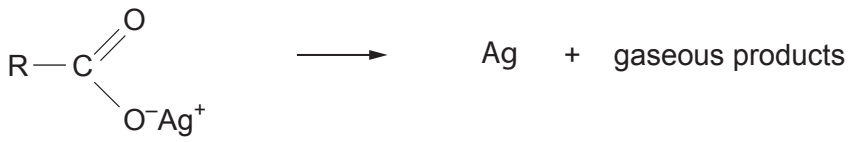
4. 0.774 g of the silver salt of an organic acid was heated and produced gaseous products and 0.365 g of solid silver.



Use this information to calculate the relative molecular mass of the organic **acid**. [2]

M_r = ...

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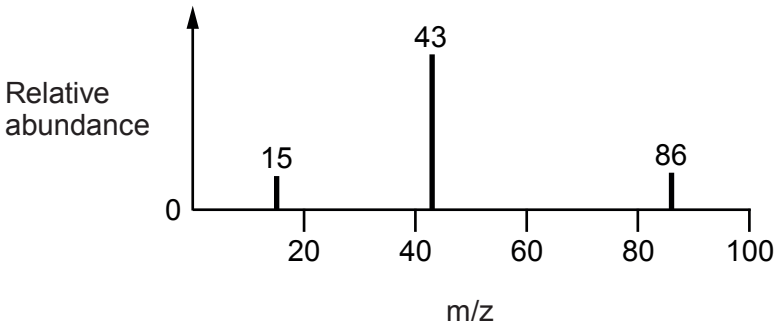
5. The mass spectrum of butane-2,3-dione is shown below.



Draw the structure of butane-2,3-dione and use this to identify the molecular ion. Suggest structures for the fragmentation ions. [3]

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SECTION B

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

6. *(a)* Calcium propanoate, $(CH_3CH_2COO)_2Ca$, is used as a preservative in bread making. On heating it gives a ketone and calcium carbonate as the only products.

Complete the equation below, giving the structure of the ketone that is obtained. [1]

$(CH_3CH_2COO)_2Ca \longrightarrow$ +

(b) Calcium propanoate (M_r 186) reacts with aqueous sulfuric acid giving propanoic acid and calcium sulfate.

$(CH_3CH_2COO)_2Ca + H_2SO_4 \longrightarrow 2CH_3CH_2COOH + CaSO_4$

(i) In an experiment, 8.38 g of an impure sample of calcium propanoate reacted with an excess of aqueous sulfuric acid, giving 5.70 g of calcium sulfate (M_r 136).

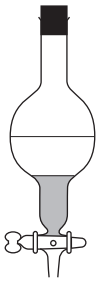
Calculate the percentage purity of the calcium propanoate, giving your answer to an **appropriate** number of significant figures. [3]

Percentage purity = ... %

Examiner only

(ii) After removal of insoluble calcium sulfate, 20 cm^3 of hexan-1-ol was added to the reaction product. Hexan-1-ol and water are immiscible.

The propanoic acid dissolved preferentially in the hexan-1-ol and the two layers were separated using the apparatus below.



I. State the name of this piece of apparatus. [1]

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II. Suggest how you could tell which was the hexan-1-ol layer. [1]

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(iii) The hexan-1-ol layer, containing the dissolved propanoic acid, was then refluxed to produce the ester 1-hexyl propanoate.

Give the equation for the reaction between propanoic acid and hexan-1-ol, to produce the ester 1-hexyl propanoate. Show the structure of the ester. [2]

(c) At 0 °C the solubility of calcium propanoate in water is 49 g / 100 g of water. This rises to 56 g / 100 g of water at 100 °C.

Calculate the mass of calcium propanoate precipitated if a saturated solution of calcium propanoate in 20 g of water is cooled from 100 °C to 0 °C. [2]

Mass = ... g

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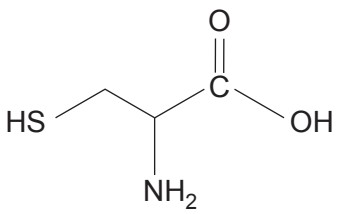
(d) Cysteine is a sulfur-containing α-amino acid.



cysteine

(i) Write the **displayed** formula for cysteine. [1]

(ii) Cysteine reacts with hydrochloric acid to give the salt cysteine hydrochloride, which is used in flour processing.

Suggest a **skeletal** formula for this salt. [1]

(iii) Cysteine contains a chiral centre and exists in two mirror image forms.

Draw the 3D structures of these two forms. [1]

Examiner only

(e) Cysteine has been proposed as an antidote to counteract damage caused by excessive ethanol consumption. It works by oxidising ethanal, which is produced from ethanol, to ethanoic acid.

(i) The concentration of small quantities of ethanal present in ethanoic acid can be measured by colorimetry, where the intensity of the colour produced in solution with 2,4-dinitrophenylhydrazine is measured at a wavelength of 480 nm.

Calculate the frequency of this absorption at 480 nm. [2]

Frequency = ... Hz

(ii) The absorption at 480 nm is related to the concentration of ethanal present by the equation below.

absorption = constant × concentration

The absorption of an ethanal solution of concentration 5×10^{-4} mol dm^{-3} is 1.25.

Find the concentration of a solution that gives an absorption reading of 0.70. [2]

Concentration = ... mol dm^{-3}

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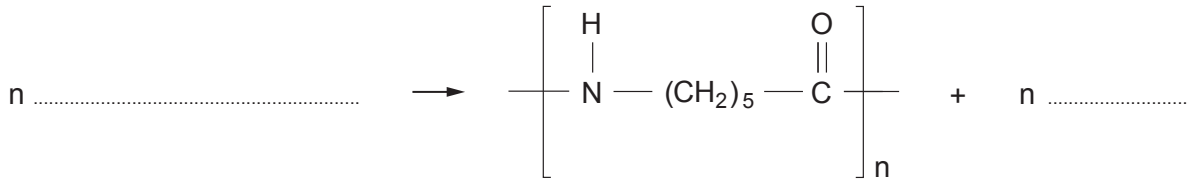
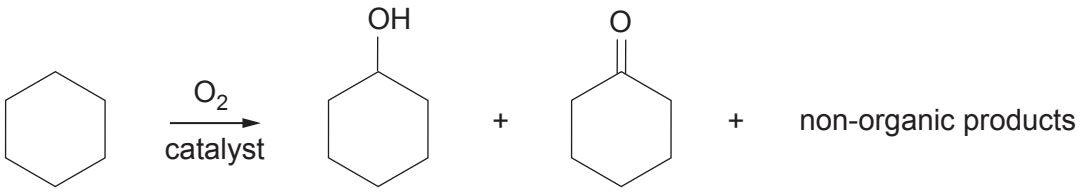
7. *(a)* The condensation polymer Nylon-6 can be formed from 6-aminohexanoic acid.

Complete the equation for this reaction. [1]



6-aminohexanoic acid Nylon-6

(b) (i) 6-Aminohexanoic acid is not readily available and Nylon-6 is made in industry by a series of reactions starting with cyclohexane, which is first converted to cyclohexanol and cyclohexanone.



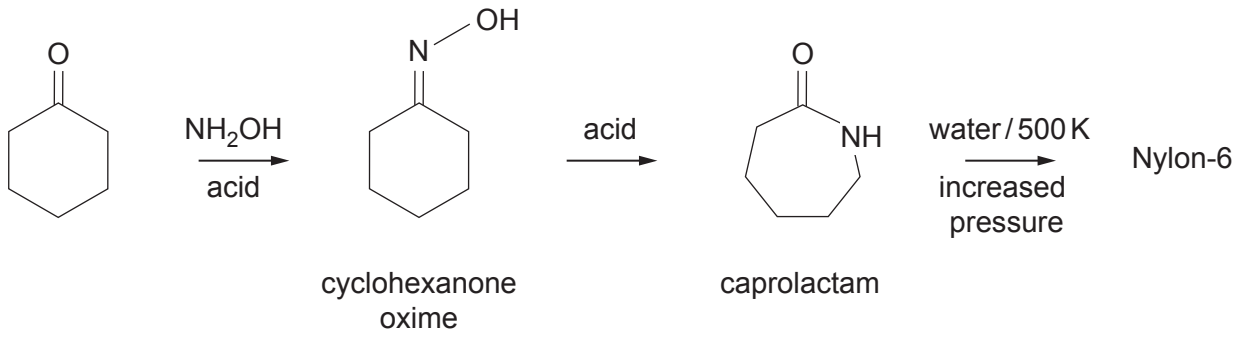
In an experiment only 5 % of the cyclohexane is oxidised and analysis of the organic products shows that the molar ratio of cyclohexanol to cyclohexanone is 2:1.

If 2400 mol of cyclohexane reacts in this way, calculate the mass of cyclohexanol produced. Give your answer in kg. [3]

Mass of cyclohexanol = ... kg

Examiner only

(ii) Cyclohexanone is then converted to Nylon-6 in a three-stage process.



cyclohexanone oxime

caprolactam

I. In the first stage cyclohexanone reacts with hydroxylamine, NH_2OH.

Suggest why hydroxylamine reacts as a nucleophile in this step. [1]

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II. Use the Data Booklet to describe how the intensity of the infrared absorptions change as cyclohexanone oxime is converted to caprolactam.

Refer only to the functional groups present and their absorption values.

The C–N infrared absorption is seen between 1 020 and 1 250 cm^{-1} and the C=N infrared absorption is seen at 1 665 cm^{-1}. [2]

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III. In a batch process 200 kg of cyclohexanone oxime was converted to caprolactam.

Explain why, if there is 100 % conversion of the oxime to caprolactam, exactly 200 kg of caprolactam will be obtained. [1]

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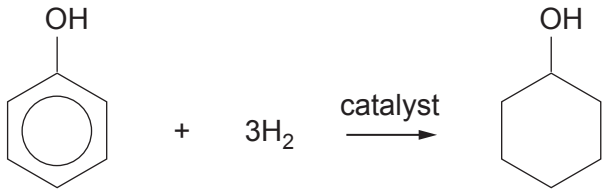
(c) Another method of producing cyclohexanol is by the reduction of phenol.



Apart from cost, state **two** factors that should be considered when choosing to make cyclohexanol from phenol or from cyclohexane [as in part *(b)*(i)]. [2]

1. .....

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2. .....

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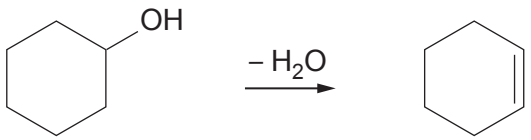
QUESTION CONTINUES ON PAGE 18

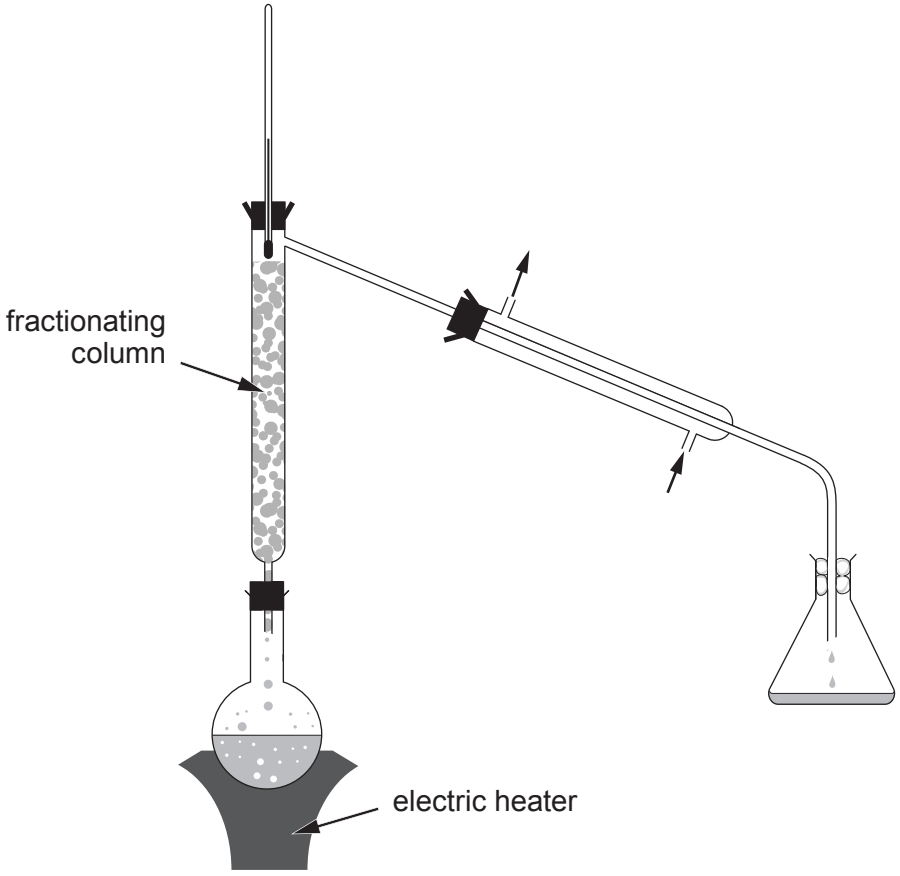
(d) Cyclohexene can be produced in the laboratory by the dehydration of cyclohexanol. This is done in the presence of sulfuric acid, which acts as a dehydrating agent.



boiling temperature
161 °C

boiling temperature
83 °C

In an experiment cyclohexene was produced using the apparatus below.



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The mixture was heated electrically and the temperature at the top of the column was not allowed to exceed 90 °C. Cyclohexene distilled over and was collected in the conical flask.

(i) Explain why the temperature at the top of the column was kept at 90 °C or below. [1]

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(ii) Suggest why the conical flask containing cyclohexene had a loose cotton wool plug rather than being secured by a stopper. [1]

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(iii) The cyclohexene distillate was not pure. Suggest and explain what other compound could be present in the distillate. [2]

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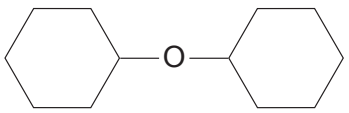
(iv) In the experiment 0.20 mol of cyclohexanol was dehydrated using sulfuric acid. After purification 10 cm^3 of cyclohexene was obtained.

Calculate the percentage yield of cyclohexene. [1]

1 mol of cyclohexene has a volume of 66 cm^3

Percentage yield = ... %

(v) After the experiment the liquid left in the reaction flask contained unreacted cyclohexanol, aqueous sulfuric acid and the compound whose formula is shown below.



Suggest how this compound had been produced in the reaction. [1]

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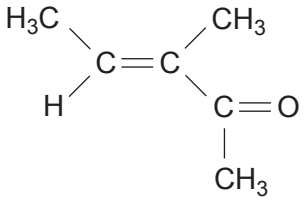
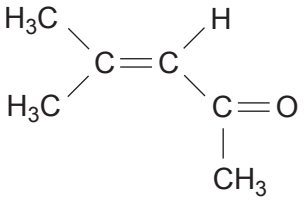
(e) Cyclohexanone and liquid **L** are isomers of formula $C_6H_{10}O$. The label on the bottle containing liquid **L** was torn but stated that it contained

'……methylpent-3-en-2-one'.

This meant that compound **L** was one of the two compounds whose formulae are shown below.





(i) 6.86 g of liquid **L** reacted with 0.070 mol of bromine (Br_2) to give a new compound of formula $C_6H_{10}OBr_2$.

Use these quantities to show that this information fits both of the suggested structures for compound **L**. [2]

(ii) Compound **L** reacts with hydrogen to give a saturated ketone, compound **M**.

I. Suggest the type of reaction mechanism occurring in this hydrogenation. [1]

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II. The ^1H NMR spectrum of ketone **M** suggested that it was 4-methylpentan-2-one.

Write the structure of compound **L** giving a reason for your answer. [1]

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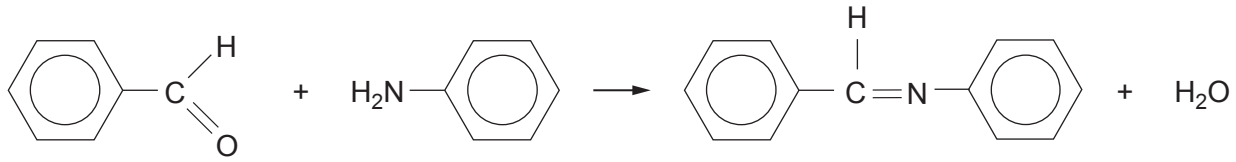
8. *(a)* Benzylidene aniline is produced as a solid by heating together the liquids benzaldehyde and phenylamine (aniline).

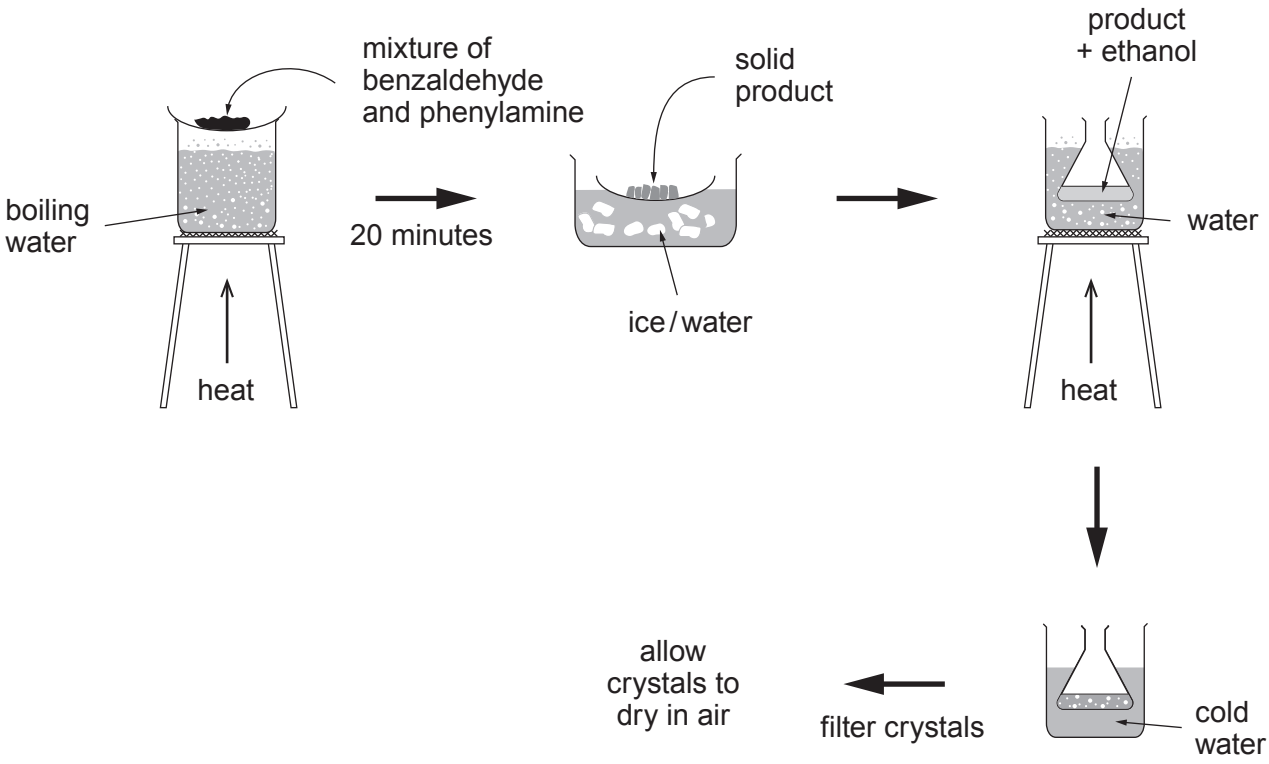
Starting with 0.040 mol of each reactant will result in about 6 g of the product.



benzylidene aniline

Reactant	M_r	Density / g cm^{-3}
benzaldehyde	106	1.05
phenylamine	93	1.02

(i) The flow chart below outlines one method for its preparation.



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Use the flow chart as a basis to write a more detailed method for the preparation of 6 g of this compound.

Your answer should state the volumes of the starting materials and a suggestion for the volume of ethanol used for recrystallisation.

You should also indicate appropriate sizes of the glassware that you would use. [6 QER]

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Examiner only

(ii) The table below summarises two methods for making benzylidene aniline.

Method	Time taken / min	Reaction temperature / °C	Catalyst	Purification solvent	Yield / %
1	2	20	$FeSO_4(s)$	ethanol	57
2	20	100	none	ethanol	85

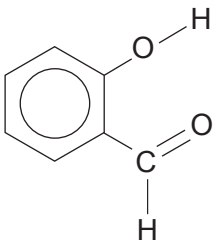
I. State **one** advantage of method 1 compared to method 2. [1]

.....

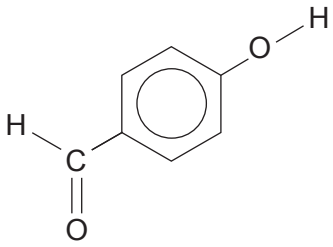
II. State **one** disadvantage of method 1 compared to method 2. [1]

.....

(b) The melting temperatures of the two isomeric hydroxybenzaldehydes are given below.



1-2 °C



112-116 °C

Suggest reasons for this difference in melting temperature in terms of forces between molecules and forces within molecules. [4]

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(c) Both benzoic acid and 2-hydroxybenzaldehyde have the formula $C_7H_6O_2$.

(i) Complete the table below giving the observation, if any, for the reaction with each of these compounds.

You can assume that the materials being used are in an appropriate solution. If there is no reaction, you should write 'no observation'. [2]

Reagent	Benzoic acid	2-Hydroxybenzaldehyde
sodium hydrogencarbonate	.....	.....
alkaline iodine	.....	.....
iron(III) chloride	brown solid	.....

(ii) The brown solid produced when iron(III) chloride reacts with benzoic acid is iron(III) benzoate.

Write the formula of this compound. [1]

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(d) Phenyl methanoate also has the molecular formula $C_7H_6O_2$.

Give the structure of this compound and use it to explain why it is likely to give a silver mirror when it reacts with Tollens' reagent. [2]

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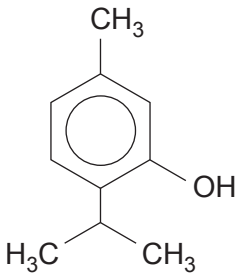
9. *(a)* The phenolic compound thymol has antiseptic properties.



(i) Traditionally, thymol has been extracted from a number of plants, including the oil obtained from the herb thyme. The solvent used for this extraction is ethanol or dichloromethane.

In one extraction 5.5 g of thyme oil was obtained from 100 g of the plant.
On analysis the oil contained 12 % of thymol.

Calculate the concentration of thymol in the plant in $mg\,g^{-1}$, giving your answer to an **appropriate** number of significant figures. [2]

Concentration = ... $mg\,g^{-1}$

(ii) Suggest why ethanol is seen as a 'greener' solvent for this extraction than dichloromethane. [1]

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(iii) Thyme oil contains a number of other compounds, including other phenols.
Most of these compounds, including the phenols, are colourless.

If a thin layer chromatogram is produced from this oil, the colourless spots have to be made visible. When the thin layer plate is sprayed with a solution of a suitable diazonium compound, the spots become coloured.

Explain why these spots now appear coloured. [2]

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Examiner only

(iv) Another method of obtaining thymol is by the reaction of 3-methylphenol with 2-chloropropane in a Friedel-Crafts alkylation.

Give the equation for this reaction, stating any catalyst that might be used. [2]

(v) I. Suggest why thymol is only slightly soluble in water at room temperature. [2]

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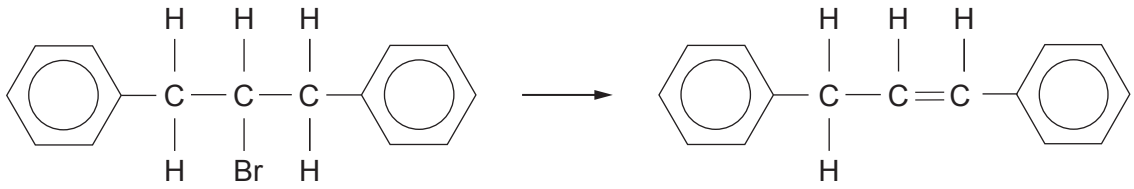
II. Thymol reacts with aqueous sodium hydroxide.

Suggest the formula of the organic compound that is produced. [1]

Examiner only

(b) (i) State the **name** of the reagent that will convert 2-bromo-1,3-diphenylpropane into 1,3-diphenylpropene. [1]



2-bromo-1,3-diphenylpropane 1,3-diphenylpropene

.....

(ii) Explain why 1,3-diphenylpropene can exist as *E*-*Z* isomers. [1]

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.....

(iii) Give the formula of the repeating section of the polymer that can be obtained from 1,3-diphenylpropene. [1]

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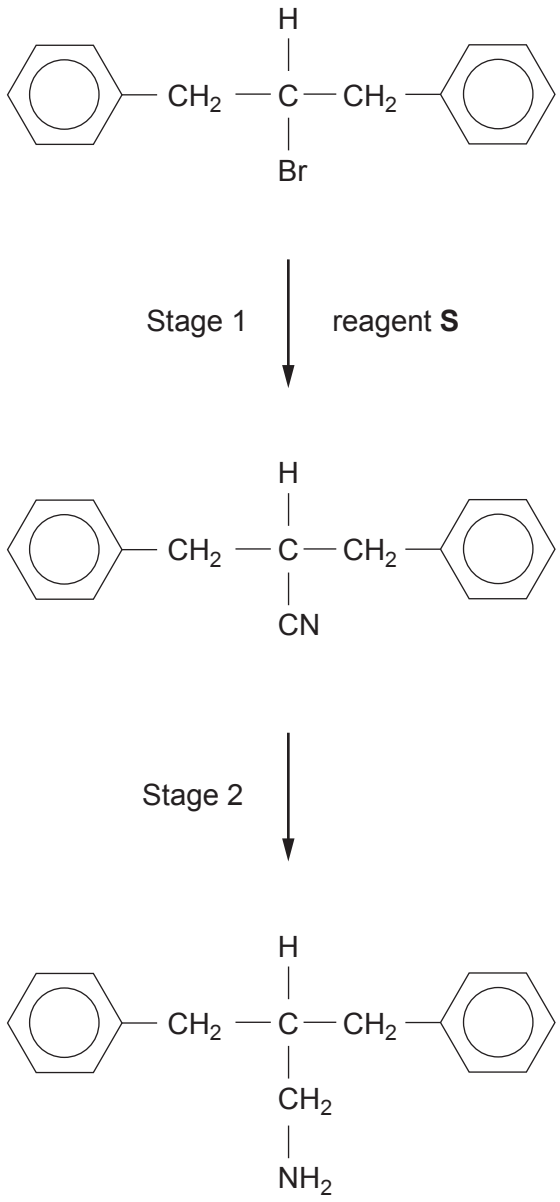
QUESTION CONTINUES ON PAGE 30

(iv) Study the reaction sequence below and answer the questions that follow.



compound **T**

(M_r 225)

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I. State the reagent **S** used in stage 1. [1]

.....

II. State the type of reaction occurring in stage 2. [1]

.....

III. Compound **T** reacts with nitric(III) acid in a 1:1 ratio giving nitrogen gas.

In an experiment, 200 cm^3 of nitrogen was obtained at a temperature of 317 K and at 1 atm pressure.

Show that the mass of compound **T** giving this volume was 1.73 g.

You **must** show your working. [2]

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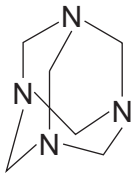
10. *(a)* Hexamethylenetetramine (hexamine) is a solid that can be used as a fuel for camping stoves.



(i) It can be made by reacting aqueous solutions of methanal and ammonia.

$$6CH_2O + 4NH_3 \longrightarrow \underset{\text{hexamine}}{(CH_2)_6N_4} + 6H_2O$$

Calculate the atom economy of this reaction to make hexamine. [2]

Atom economy = ... %

(ii) Both the high resolution ^{1}H NMR and ^{13}C NMR spectra of hexamine show only a single peak.

Suggest why these signals are single peaks. [1]

.....

.....

(iii) Hexamine acts as a *tertiary base*.

Explain the meaning of these two terms in this context. [2]

Tertiary .....

.....

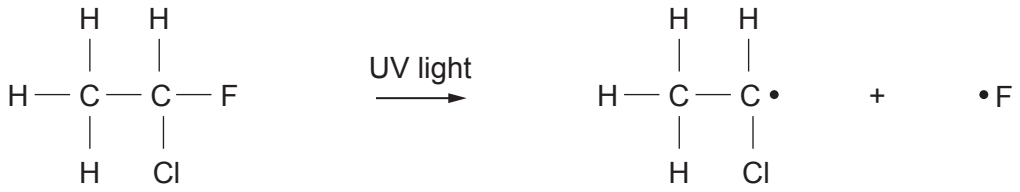
Base .....

.....

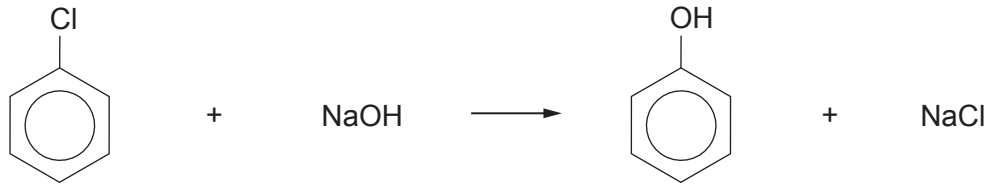
(b) Four reactions are shown below. Each of them is **wrong** in some way.

For each of these reactions, explain what is incorrect, and correct them as appropriate. [6 QER]

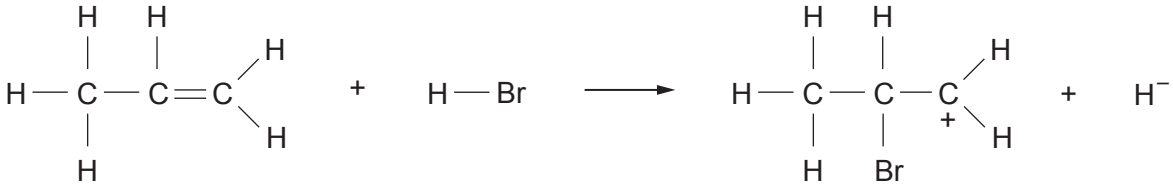
1.



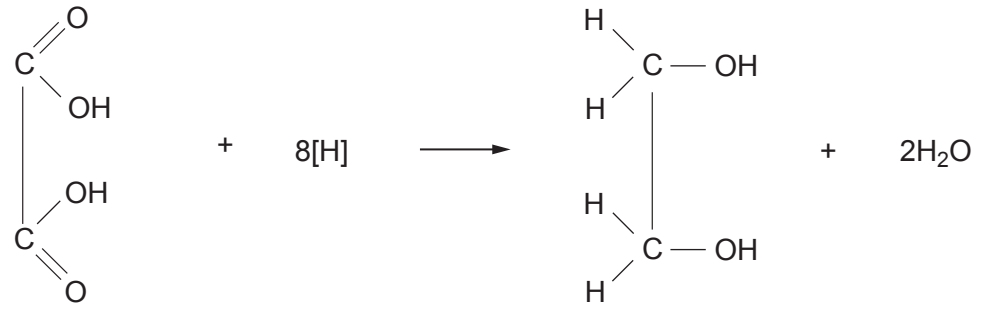
2.



3.



4.



where [H] is $NaBH_4$

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(c) In an experiment, chlorine reacted with ethanoic acid to give a mixture of chloroethanoic acid ($CH_2ClCOOH$) and dichloroethanoic acid ($CHCl_2COOH$).

4.75 g of this mixture of $CH_2ClCOOH$ and $CHCl_2COOH$ reacted with silver ions. The chlorine present gave 8.83 g of silver chloride, AgCl.

(i) Calculate the percentage of chlorine in this mixture. [2]

Percentage = ... %

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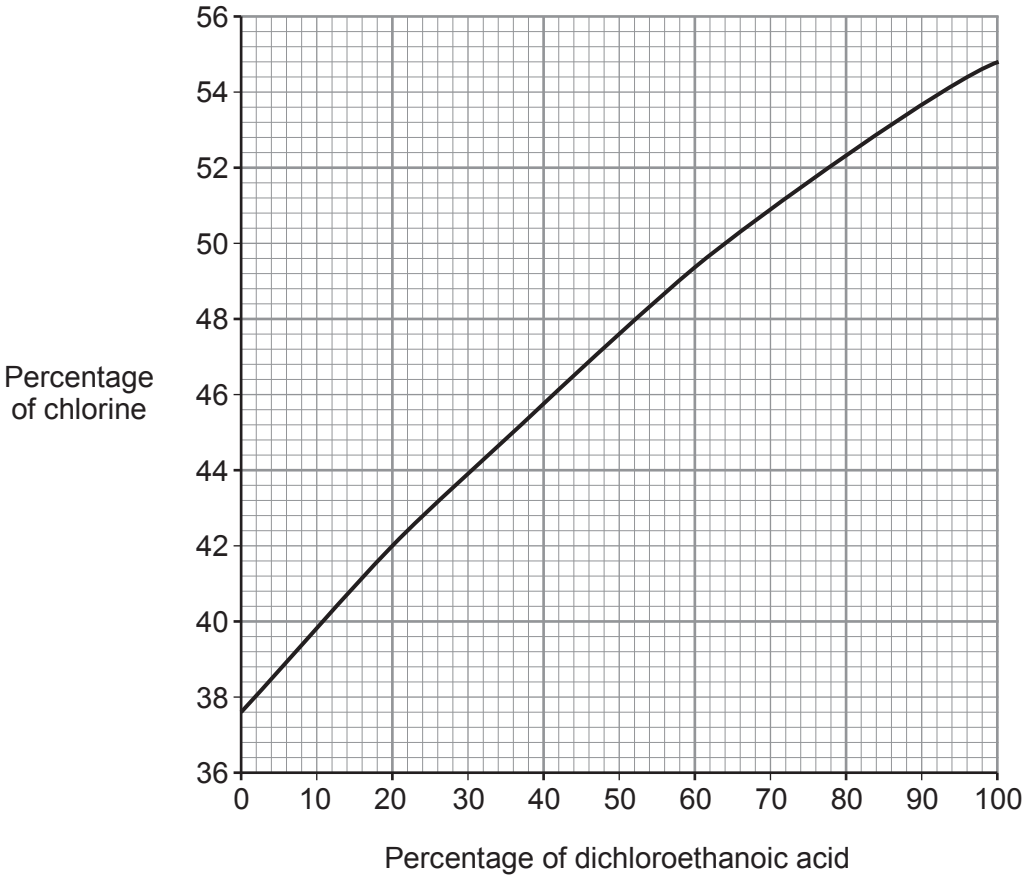
(ii) Use the graph to find the percentages of chloroethanoic acid and dichloroethanoic acid present in the mixture. [1]



Percentage of chloroethanoic acid = ... %

Percentage of dichloroethanoic acid = ... %

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(d) Under suitable conditions dichloroethanoic acid, $Cl_2CHCOOH$, reacts with alkalis to give compound **W**.

Information about compound **W** is given below.

- It has a relative molecular mass of 74
- There are three oxygen atoms in each molecule
- Its ^{1}H NMR spectrum shows signals at 9.5 and 11.0 ppm
- An aqueous solution turns Universal Indicator paper from green to red
- Its ^{13}C NMR spectrum shows only two signals

Use **all** of this information to deduce a structure for compound **W** giving reasons for your answer. [6]

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.....

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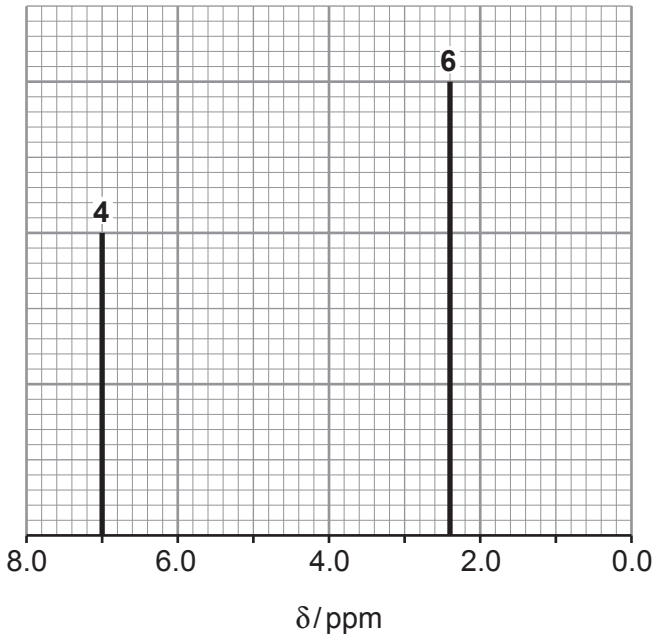
11. *(a)* The high resolution ^{1}H NMR spectrum of a dimethylbenzene is shown below.

Explain how this spectrum shows that the compound is 1,4-dimethylbenzene. [3]



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(b) 1,4-Dimethylbenzene (M_r 106) reacts with chlorine in a radical reaction to give 1,4-di(chloromethyl)benzene (M_r 175).

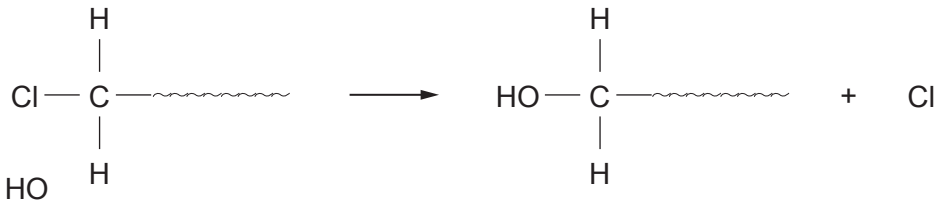
In an experiment 0.240 mol of 1,4-dimethylbenzene reacted with chlorine.

Calculate the **increase** in mass of the liquid that corresponds to the formation of 1,4-di(chloromethyl)benzene. [2]

Increase in mass = ... g

(c) 1,4-Di(chloromethyl)benzene reacts with aqueous sodium hydroxide giving the corresponding primary alcohol, 1,4-di(hydroxymethyl)benzene.

Use the diagram below to complete the mechanism, showing curly arrow(s), lone pairs and any partial / full charges. [3]



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(d) State the reagent(s) needed to convert 1,4-dimethylbenzene to benzene-1,4-dicarboxylic acid, $HOOC(C_6H_4)COOH$. [1]

.....

(e) 1,4-Di(hydroxymethyl)benzene, $HOH_2C–C_6H_4–CH_2OH$, and benzene-1,4-dicarboxylic acid, $HOOC–C_6H_4–COOH$, react together to give a polyester.

(i) Use the formula of these two compounds to give the formula of the repeating section of this polyester. [1]

(ii) Draw a ring around the part of the repeating section in part (i) that shows the ester linkage in this polymer. [1]

(f) (i) State a reagent that can be used to convert benzene-1,4-dicarboxylic acid to the corresponding diacyl chloride, benzene-1,4-dicarbonyl dichloride. [1]

.....

(ii) The diacyl chloride reacts with ammonia to give the corresponding diamide and ammonium chloride as products.

Give the equation for this reaction. [2]

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