Candidate Name	Centre Number					Candidate Number				
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WJEC CBAC

GCE A LEVEL CHEMISTRY

A2 UNIT 4

Organic Chemistry and Analysis

SPECIMEN PAPER

1 hour 45 minutes

	For Examiner's use only		
	Question	Maximum Mark	Mark Awarded
Section A	1. to 9.	10	
Section B	10.	15	
	11.	15	
	12.	13	
	13.	13	
	14.	14	
	Total	80	

ADDITIONAL MATERIALS

In addition to this examination paper, you will need a data sheet and a calculator.

INSTRUCTIONS TO CANDIDATES

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

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

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

INFORMATION FOR CANDIDATES

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

The assessment of the quality of extended response (QER) will take place in question 14.

SECTION A

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

1. Give the structural formula of a compound that will give a diazonium compound when treated with cold nitric(III) acid. [1]

2. Write the displayed formula of the organic compound obtained when phenylamine reacts with ethanoyl chloride. [1]

3. The melting temperature of a pure compound is 113 °C.

   State the effect on the melting temperature of adding a small quantity of another compound to a sample of the pure material. [1]

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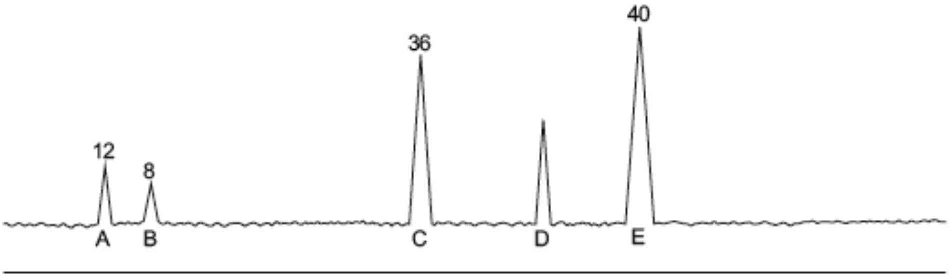
4. The gas chromatogram of a mixture of hydrocarbons is shown below. The peak areas represent the relative amount of each compound present. Compound **D** makes up 20 % of the mixture.

   Calculate the relative peak area of compound **D**. [1]



Relative peak area = ...

5. The nitrile that has the formula C_6H_5CN is reduced by lithium tetrahydridoaluminate(III).

State the systematic name of the organic **product**. [1]

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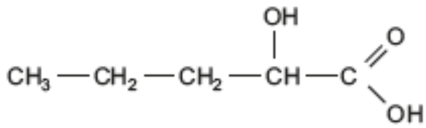
6. Compound **P** reacts with hydrogen cyanide and the product is then hydrolysed to give compound **Q**.



compound **Q**

(a) State the type of reaction mechanism occurring when compound **P** reacts with hydrogen cyanide. [1]

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(b) State the **name** of compound **P**. [1]

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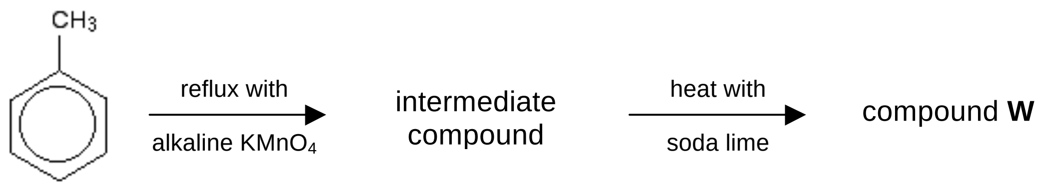
7. Methylbenzene undergoes the reactions below.



State the molecular formula of compound **W**. [1]

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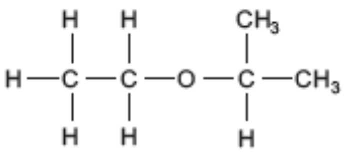
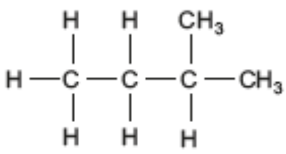
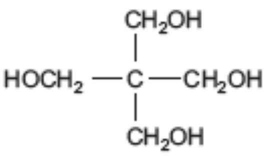
8. Arrange the compounds shown below in order of **increasing** solubility in water. [1]



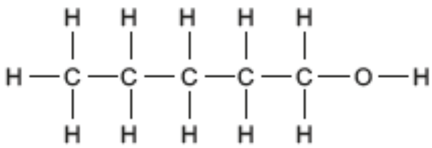
A



B



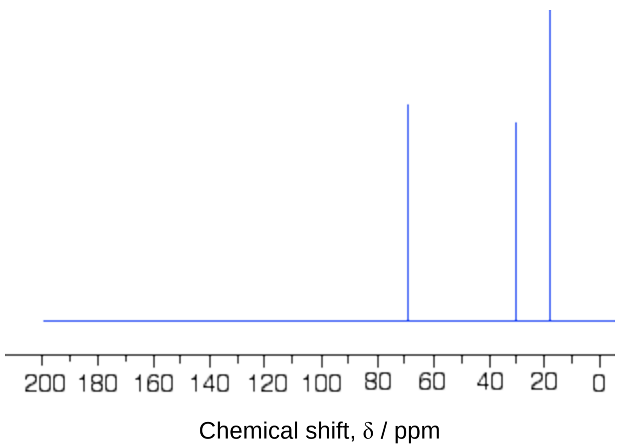
C



D

least soluble .... *most soluble*

9. State the **systematic name** of the alcohol of formula $C_4H_{10}O$ that has the ^{13}C NMR spectrum shown below. [1]



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SECTION B

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

10. *(a)* Propene is obtained by the cracking of a larger molecule hydrocarbon.
In a particular cracking process two thirds of the product was propene and the rest was propane.

Give the formula of a hydrocarbon that could be cracked in this way. [1]

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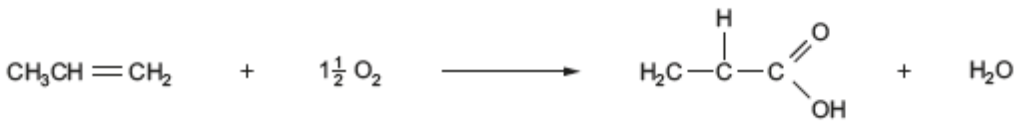
(b) Propenoic acid is produced from propene by oxidation.



This reaction uses a heterogeneous catalyst at a temperature of about 600 K.

State and explain whether the use of this catalyst will affect the enthalpy change for this reaction. [2]

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(c) Compound **F** is produced by the reaction of propenoic acid and hydrogen bromide. This product does not exist as enantiomers.

Suggest a displayed formula for compound **F**, giving a reason for your choice. [2]

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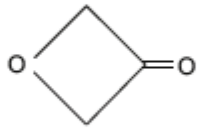
(d) Both propenoic acid and 3-oxetanone are isomers of formula $C_3H_4O_2$.



3-oxetanone

These two compounds have different infrared absorption spectra.

Use the Data Sheet to state the differences in the bonds present, stating their absorption values. [2]

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(e) Propenoic acid is neutralised by sodium hydroxide to produce sodium propenoate.

Calculate the mass of sodium propenoate that will be formed from 38.3 kg of propenoic acid, assuming that complete neutralisation occurs. [2]

Mass of sodium propenaoate = ... kg

(f) Sodium propenoate can be polymerised to give 'sodium polyacrylate'.

Give the repeating unit of this addition polymer. [1]

(g) A solid polymer is made by polymerising a mixture of propenoic acid and sodium propenoate. This product is sold as a superabsorbent polymer that will absorb 300 times its volume of water without a significant increase in volume. The water is held in the polymer structure by hydrogen bonding.

Draw a diagram to show how water molecules can hydrogen bond to propenoic acid molecules. In your answer you should use at least two molecules of each reactant, showing necessary dipoles and relevant lone pairs of electrons. [2]

(h) Propenenitrile, $H_2C{=}CH{-}C{\equiv}N$, is used as the starting material to make 'acrylic' fibres. It is made from propene, ammonia and oxygen from air, in the presence of a suitable catalyst.

$$H_2C{=}CH{-}CH_3 \;+\; NH_3 \;+\; 1\tfrac{1}{2}\,O_2 \longrightarrow H_2C{=}CH{-}C{\equiv}N \;+\; 3\,H_2O$$

A modification of this method has been developed using propane as the starting material, and a different catalyst.

$$H_3C{-}CH_2{-}CH_3 \;+\; NH_3 \;+\; 2\,O_2 \longrightarrow H_2C{=}CH{-}C{\equiv}N \;+\; 4\,H_2O$$

Suggest **three** important factors that should be taken into account when considering adoption of the modified method using propane. Each of your comments should consider both routes. [3]

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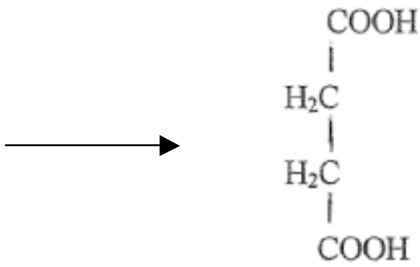
11. *(a)* There is an increasing interest in biochemical routes to compounds that were previously produced from fossil fuels. One of these compounds is butane-1,4-dicarboxylic acid.

$$HOOC{-}CH_2{-}CH_2{-}COOH$$

One route involves the oxidation of compound **G**.

compound **G**



(i) Suggest a formula for compound **G** giving a suitable oxidising agent for the reaction. [2]

Oxidising agent ....

(ii) One biochemical route being developed starts from sugars such as glucose. This process also uses carbon dioxide and can be represented by the following equation.

$$7C_6H_{12}O_6 \ + \ 6CO_2 \ \rightarrow \ 12(CH_2)_2(COOH)_2 \ + \ 6H_2O$$

M_r 180 $\qquad\qquad$ M_r 118

I. Calculate the yield (in kilograms) of butane-1,4-dicarboxylic acid that would be obtained if 1.00 kg of glucose was completely converted to the acid. [3]

Yield = ... kg

II. Use the chemical equation to help you suggest why this reaction can be considered to be a *green* process.

A reference to the exclusion of fossil fuels in this process is not required. [1]

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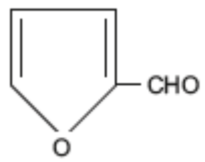
(b) Furfural is an aldehyde that is produced from agricultural by-products. One method is the hydrolysis of certain polysaccharides to give the sugar xylose, which is then itself hydrolysed to give furfural.



furfural

In a large scale laboratory experiment 750 g of corn cobs were refluxed with 2.5 dm^3 of aqueous sulfuric acid of concentration 1.2 mol dm^{-3}. After neutralisation of the acid, 100 g of furfural was obtained.

(i) Calculate the volume of sulfuric acid needed to make 2.5 dm^3 of the aqueous solution. [2]

[density of sulfuric acid = 1.84 g cm^{-3}]

Volume of sulfuric acid = ... cm^3

(ii) Suggest **two** ways in which this method might be modified so that a higher percentage yield of furfural could be obtained. [2]

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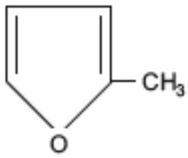
(iii) The boiling temperature of furfural is 162 °C.
Comment on why the boiling temperature of 2-methylfuran may be different from this value, explaining your answer. [3]



2-methylfuran

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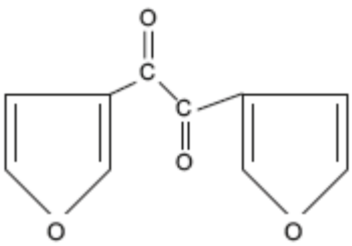
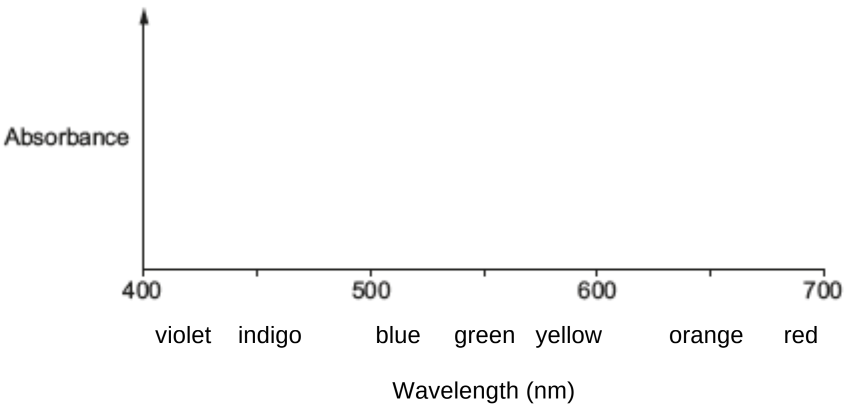
(iv) Under certain conditions furfural can be converted into the yellow compound, furil.



furil

Use the diagram below to draw a line that shows the visible absorption spectrum for furil. [2]



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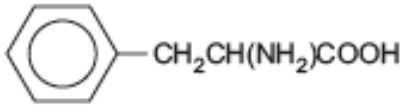
12. *(a)* The artificial sweetener aspartame is a dipeptide. One of its hydrolysis products is phenylalanine.



phenylalanine

(i) Give the formula of the dipeptide formed from phenylalanine. [1]

(ii) The formula of an α-amino acid can be written in an ionic form.

Write the formula of the ionic form of phenylalanine present in a strongly acidic solution. [1]

(b) Data about three derivatives of propanoic acid are given in the table.

Name	Formula	Melting temperature / °C
3-phenylpropanoic acid	$C_6H_5CH_2CH_2COOH$	< 20
3-phenyllactic acid	$C_6H_5CH_2CH(OH)COOH$	122
phenylalanine	$C_6H_5CH_2CH(NH_2)COOH$	270

Discuss the relative melting temperatures of the acids in terms of the intermolecular bonding between the molecules. [4]

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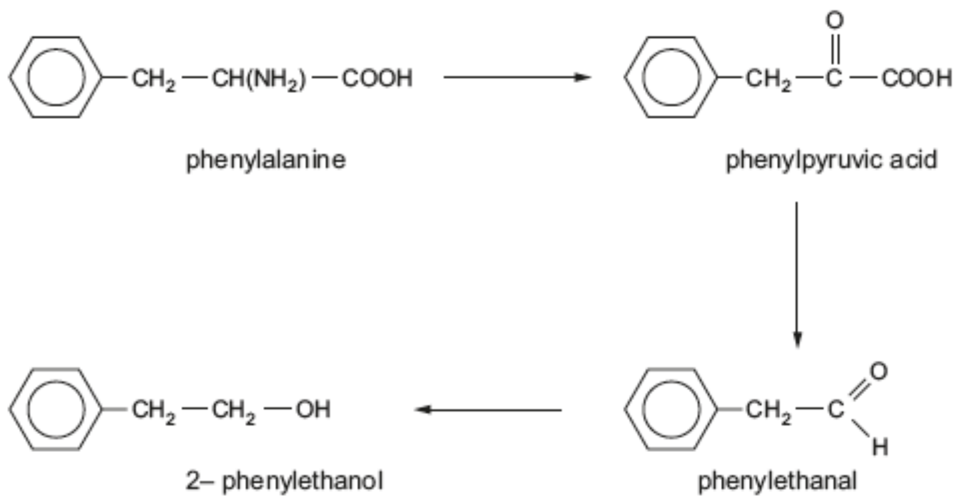
(c) The isolation of flavours and fragrances from plants has been practised for many years. However, this extraction is often expensive and produces only small quantities. There is therefore an increasing interest in biochemical routes that do not rely on oil based products. In a recent study phenylalanine has been converted to the important perfumery chemical, 2-phenylethanol, via a route using enzymes. This is summarised below.



(i) Describe a test that will distinguish between phenylpyruvic acid and phenylethanal, stating the reagent(s) used and the observation with each compound. [2]

Reagent(s)

....

Observation with each compound

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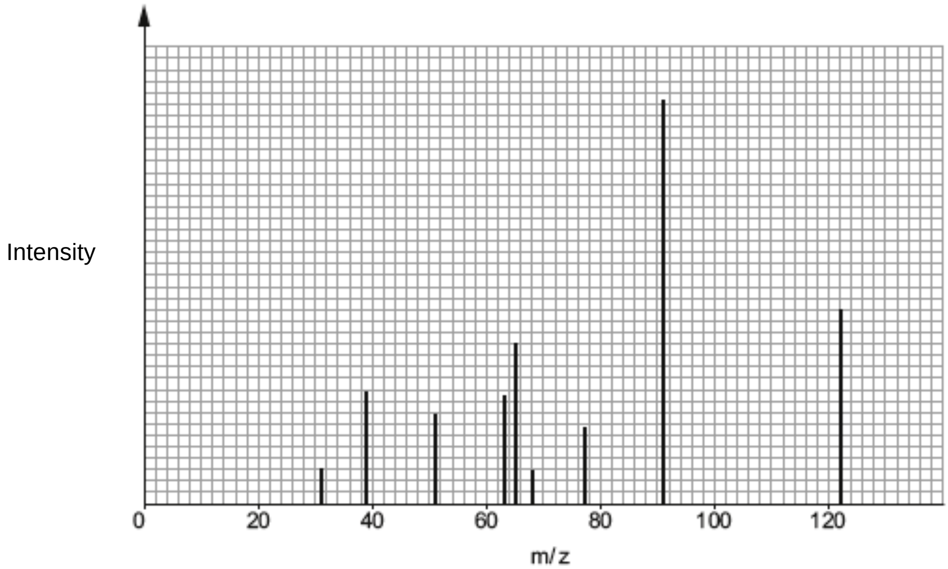
(ii) In this study 2-phenylethanol was separated by gas chromatography and identified by mass spectroscopy. The mass spectrum of 2-phenylethanol is shown below.



Suggest a formula for the ion fragment at m/z 91, giving your reasoning. [2]

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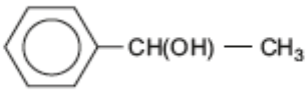
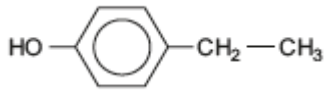
(iii) 1-Phenylethanol, 2-phenylethanol and 4-ethylphenol are isomers of formula of $C_8H_{10}O$.



1-phenylethanol



4-ethylphenol

State which one of these three compounds can be identified by the triiodomethane (iodoform) test giving the reagent(s) used, the observation and the reason for your choice of compound. [3]

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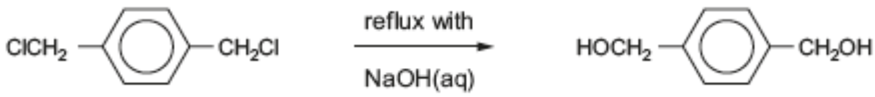
13

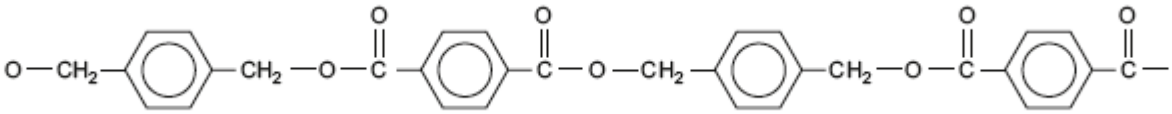
13. *(a)* 1,4-Di(chloromethyl)benzene can be used as a starting material for the production of polyesters.

1,4-di(chloromethyl)benzene

It is converted into 1,4-di(hydroxymethyl)benzene via a reaction with aqueous sodium hydroxide.



1,4-Di(hydroxymethyl)benzene can then be used to produce the polyester drawn below.



State the name of the other compound that is used to make this polyester. [1]

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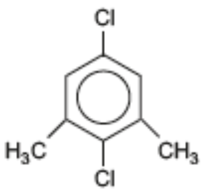
(b) Explain why refluxing 2,5-dichloro-1,3-dimethylbenzene, shown below, with aqueous sodium hydroxide does not result in the replacement of the chlorine atoms by hydroxide groups. [2]



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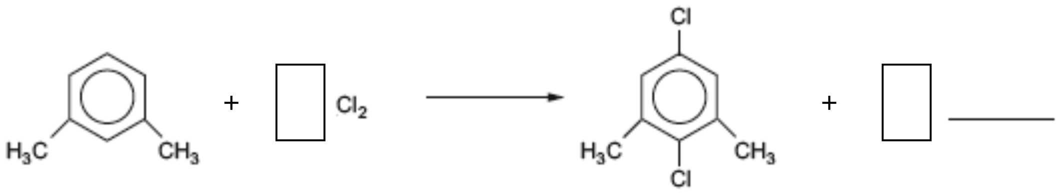
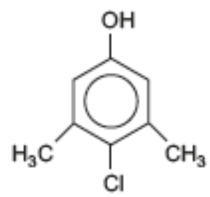
(c) 2,5-Dichloro-1,3-dimethylbenzene can be formed from 1,3-dimethylbenzene by a Friedel-Crafts reaction.

State a catalyst for this reaction and complete the equation below. [2]



Catalyst ....

(d) The active compound in Dettol® is PCMX.



PCMX

(i) State what will be seen when PCMX reacts with iron(III) chloride solution. [1]

....

(ii) Aqueous bromine was added to PCMX resulting in the colour of the bromine disappearing.

Suggest what else would be seen during this reaction and draw the formula of a possible organic product. [2]

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(iii) There are 12.0 g of PCMX in a bottle containing 250 cm^3 of Dettol®.

Calculate the concentration of PCMX in mol dm^{-3}. [2]

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

(iv) Describe and explain the **low** resolution ^1H NMR spectrum of PCMX. No reference to the relative position of the peaks in the spectrum is required. [3]

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13

14. *(a)* In a project some students were asked to prepare 1-butyl ethanoate from butan-1-ol and ethanoic acid. One method found in the literature is given below.

'Mix together 18.0 cm^3 / 14.6 g of butan-1-ol with 8.5 cm^3 / 8.9 g of ethanoic acid in a pear-shaped flask. Reflux the mixture for 20 minutes.
Remove the condenser and distil the mixture, collecting the mixture that boils at 115–130 ^oC. After purification, the yield of 1-butyl ethanoate is about 25 g'.

Some necessary data is given in the table.

Name	M_r	Boiling temperature / ^oC
butan-1-ol	74	117
ethanoic acid	60	118
1-butyl ethanoate	116	126

(i) Give the equation for the reaction. [1]

....

(ii) The students thought that the theoretical yield of 1-butyl ethanoate was less than the actual yield stated in the method.

Calculate the theoretical yield in grams that should be formed. [3]

Yield = ... g

(iii) The students ran a chromatogram of their distillate. They found besides 1-butyl ethanoate, some butan-1-ol and ethanoic acid were present together with a little water.

A student suggested that some solid sodium hydrogencarbonate was added to the distillate.

Describe what would be seen when this substance was added and state why this observation occurred. [2]

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(iv) After further purification the 1-butyl ethanoate was checked for traces of butan-1-ol.

State an instrumental method, other than chromatography, that could be used for this purpose and explain how any traces of butan-1-ol would be indicated. [2]

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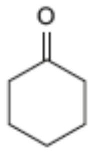
(b) An ant pheromone has been isolated and studied. Some details of the compound are given below.

1. The % of oxygen by mass is 16.3
2. It can be reduced to a primary alcohol
3. It will decolourise aqueous bromine
4. The ^{1}H NMR spectrum suggests six different proton environments.
5. The ^{13}C NMR spectrum suggests six different carbon environments.

Gareth suggested that the pheromone was cyclohexanone.



Study the information provided and discuss, giving reasons, whether each statement fits the suggested compound. [6 QER]

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