Surname	Centre Number	Candidate Number
Other Names		2

GCE A LEVEL

1410U40-1

S19-1410U40-1

TUESDAY, 11 JUNE 2019 – AFTERNOON

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 7.	10	
Section B	8.	13	
	9.	15	
	10.	13	
	11.	13	
	12.	16	
	Total	80	

1410U401
01

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.

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

Section A Answer **all** questions in the spaces provided.
Section B Answer **all** questions in the spaces provided.

Candidates are advised to allocate their time appropriately between **Section A (10 marks)** and **Section B (70 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 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 **Q.11**_(a)_(i).

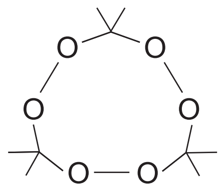
If you run out of space, use the additional page(s) at the back of the booklet, taking care to number the question(s) correctly.

Examiner only

SECTION A

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

1. The skeletal formula of the compound TATP is shown below.



Give the **molecular** formula of this compound. [1]

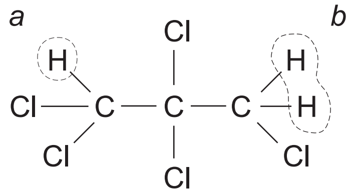
....

2. Alkanes are produced when carboxylic acids are strongly heated with sodalime.

State the name of a carboxylic acid that will produce propane, when heated in this way. [1]

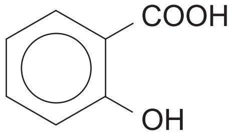
....

3. Complete the table below, which describes the ^{1}H NMR spectrum of 1,1,2,2,3-pentachloropropane. [2]

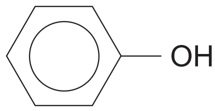


Proton(s)	Splitting pattern	Relative peak area ratio
a		
b		

4. Using the letters provided, place these three compounds in order of **increasing** acidity. [1]



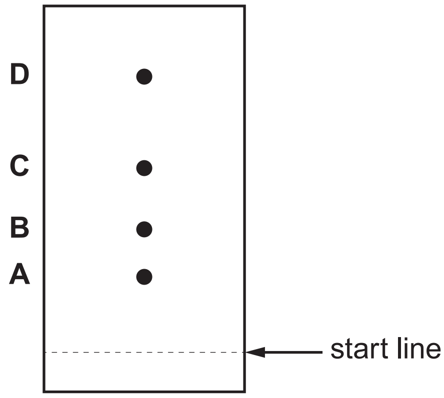
$(CH_3)_3N$



A **B** **C**

least acidic .... most acidic

5. A student produced the following chromatogram of a mixture of four amino acids.
The student forgot to mark the position of the solvent front.



The R_f values of the four amino acids are as follows.

Amino acid	R_f value
alanine	0.59
glycine	0.42
leucine	0.88
serine	0.36

State and explain which of the spots is likely to be alanine. [1]

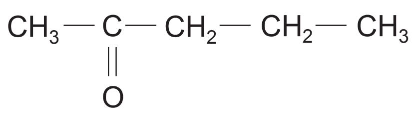
....

....

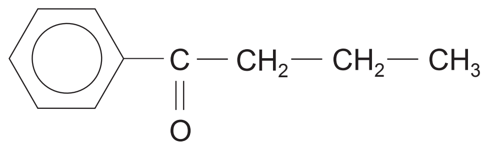
....

Examiner only

6. Describe a simple chemical test that will distinguish between pentan-2-one and 1-phenylbutanone. [2]



pentan-2-one



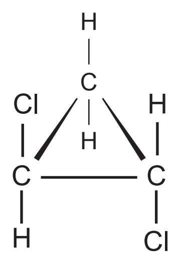
1-phenylbutanone

Reagent(s) used ....

Observations with both compounds ....

....

7. The displayed formula of 1,2-dichlorocyclopropane is given below.



(a) Draw the displayed formula of another structural isomer of formula $C_3H_4Cl_2$. [1]

(b) Draw the displayed formula of a stereoisomer of 1,2-dichlorocyclopropane. [1]

10

Examiner only

SECTION B

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

8. *(a)* Chloroethanoic acid is produced from ethanoic acid by passing chlorine gas into it under suitable conditions.

$$CH_3COOH \quad + \quad Cl_2 \longrightarrow ClCH_2COOH \quad + \quad HCl$$

$$M_r\ 60.0 \qquad\qquad\qquad M_r\ 94.5$$

(i) This reaction involves radicals. In the first stage chlorine radicals are formed. They then attack the ethanoic acid molecule producing a molecule of hydrogen chloride and a new radical.

Suggest the formula of the new radical formed from the acid during this reaction. [1]

....

(ii) I. In an experiment 89.0 g of ethanoic acid reacted with chlorine.

Calculate the increase in mass that occurs if chloroethanoic acid is the only organic product. [2]

Increase in mass = ... g

II. Chloroethanoic acid reacts with ammonia producing aminoethanoic acid.

$$CH_3COOH \longrightarrow ClCH_2COOH \longrightarrow CH_2(NH_2)COOH$$

In the experiment described in I, 89.0 g of ethanoic acid then gave 49.2 g of aminoethanoic acid (M_r 75.0).

Calculate the percentage yield of aminoethanoic acid. Give your answer to an **appropriate** number of significant figures. [2]

Percentage yield = ... %

1410U401
05

Examiner only

III. Aminoethanoic acid is isolated from the solution of the products by adding methanol to the liquid. The acid is precipitated as a white solid.

Suggest why aminoethanoic acid is insoluble in methanol. [2]

....

....

....

....

(b) Explain why an aqueous solution of aminoethanoic acid does not affect the plane of plane polarised light. [1]

....

....

(c) Draw the structure of the dipeptide formed from two molecules of aminoethanoic acid. [1]

Examiner only

(d) Aminoethanoic acid reacts with nitric(III) acid to produce nitrogen gas.

$$CH_2(NH_2)COOH + HNO_2 \longrightarrow CH_2(OH)COOH + N_2 + H_2O$$

Calculate the maximum volume of nitrogen gas produced at 100 °C and 98 kPa pressure when 0.300 mol of aminoethanoic acid reacts in this way. Give your answer in dm^3. [3]

Volume produced = ... dm^3

(e) Hydroxyethanoic acid, $CH_2(OH)COOH$, can also be prepared by reacting chloroethanoic acid with aqueous sodium hydroxide.

Explain why the reaction mixture needs to be acidified to produce hydroxyethanoic acid. [1]

....

....

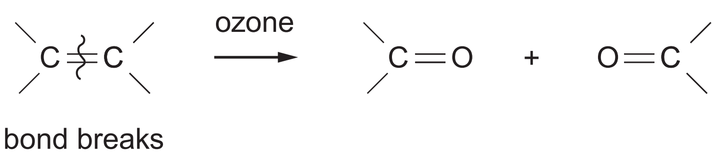
....

1410U401 07

13

Examiner only

9. *(a)* Alkenes react with ozone to give an intermediate compound, which can then react further to give aldehydes or ketones.



1 mol of an alkene **T** reacts with ozone to give 2 mol of the same carbonyl compound, **U**.

(i) Explain what can be deduced about the structural formula of alkene **T**. [1]

....

....

(ii) Carbonyl compound **U** reacted with 2,4-dinitrophenylhydrazine to produce a solid derivative.

State the colour of this solid derivative. [1]

....

(iii) I. The ^{1}H NMR spectrum of compound **U** did **not** show a chemical shift at 9.8 δ.

State what can be deduced from this statement. [1]

....

....

Examiner only

II. The melting temperatures of the 2,4-dinitrophenylhydrazine derivatives can be used to identify the original carbonyl compound. The melting temperatures of some of these derivatives are shown in the table.

Carbonyl compound	Melting temperature of derivative / °C
$CH_3(CH_2)_3C(=O)CH_3$	106
$CH_3(CH_2)_3C(=O)H$	108
$CH_3CH_2C(=O)CH_3$	115
$CH_3(CH_2)_2C(=O)H$	126

The 2,4-dinitrophenylhydrazine derivative of compound **U** was slightly impure and melted at a temperature of 110-113 °C.

Use the information given to deduce the formula of compound **U**.
Explain your reasoning. [3]

....

....

....

....

....

....

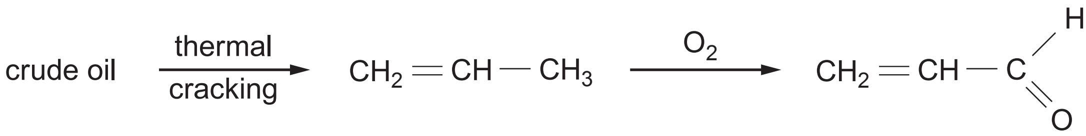
(iv) Use your answer to part (iii) and other relevant information given in the question to give the structure of alkene **T**. Name alkene **T**. [2]

Name ....

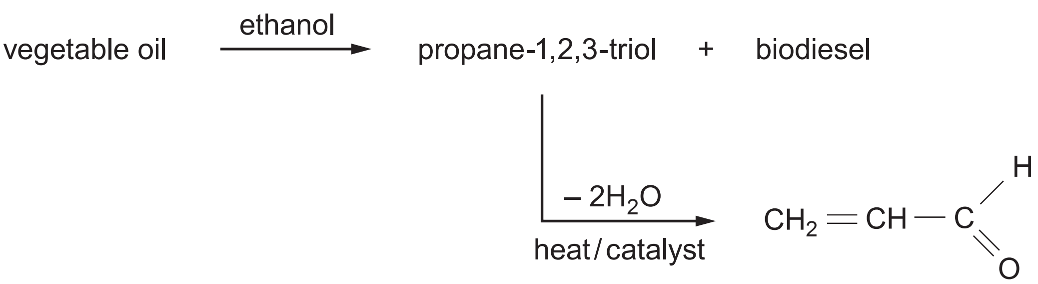
Examiner only

(b) Propenal, $CH_2{=}CH{-}CHO$ is made by two main methods.

Method 1 From crude oil



Method 2 From vegetable oil



(i) Suggest **one** reason why the general public would probably favour the production of propenal by Method 2. [1]

....

....

(ii) If you were considering which of these two methods to choose to produce propenal, state **two** other factors, apart from cost, that you would need to know to be able to come to a decision. [2]

Factor 1 ....

....

Factor 2 ....

....

Examiner only

(iii) The densities of biodiesel and propane-1,2,3-triol are shown in the table. These two liquids are immiscible (insoluble in each other).

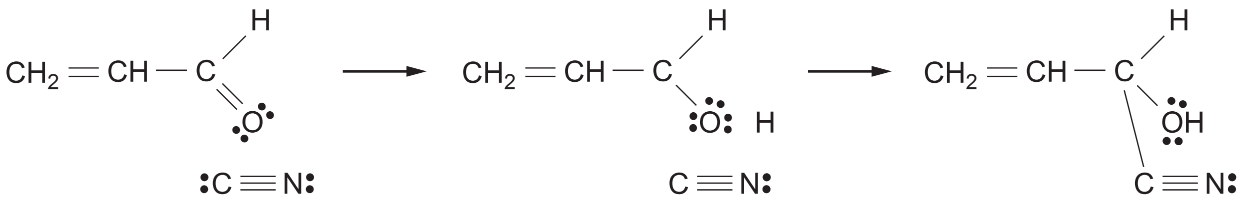
Liquid	Density / $g\,cm^{-3}$
biodiesel	0.85
propane-1,2,3-triol	1.26

Sketch and name a piece of apparatus that could be used to separate a mixture containing $25\,cm^3$ of each liquid. The two liquids should also be labelled. [2]

Name of apparatus ....

(iv) Propenal reacts with hydrogen cyanide by a nucleophilic addition reaction.

Complete the mechanism for this reaction using curly arrows and partial/complete charges as appropriate. [2]



1410U401
11

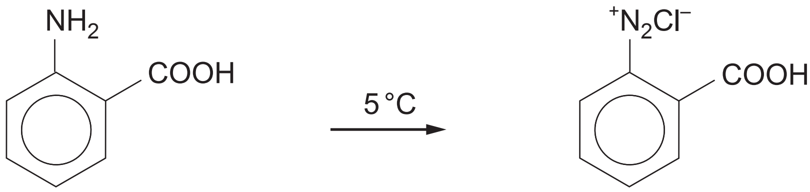
15

 (1410U40-1) **Turn over.**

Examiner only

10. *(a)* The acid-base indicator methyl red can be made from 2-aminobenzenecarboxylic acid.

(i) In the first stage of the reaction, a benzenediazonium compound is made from this acid.

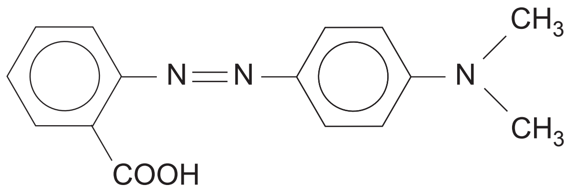


2-aminobenzenecarboxylic acid

State the reagent(s) necessary to produce this diazonium compound from the acid. [1]

....

(ii) The benzenediazonium compound is then coupled with an amine to make methyl red.



methyl red

Draw the structure of the amine used. [1]

(iii) The visible spectrum of this azo dye at a certain pH shows an absorption maximum at 410 nm.

Calculate the frequency that corresponds to this wavelength. [2]

Frequency = ... Hz

Examiner only

(b) Some azo dyes are permitted for use as food colours but their concentration is strictly controlled. The concentration present can be found by colorimetry. The absorption of a series of standard solutions is measured and a straight line calibration graph is drawn.

(i) The molar mass of an azo dye is 272 g mol^{-1}.

Calculate the mass of the azo dye needed to prepare 250 cm^3 of a standard solution of concentration 0.0075 mol dm^{-3}. [2]

Mass required = ... g

(ii) Absorption (*A*) and concentration (*c*) are related by the equation

$A = k\,c$ where k is a constant

The calibration graph shows that an absorption of 1.44 is measured for a solution of concentration 0.0096 mol dm^{-3}.

Calculate the concentration of a solution that gave an absorption of 1.03. [2]

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

(c) (i) When ethanoic acid is heated with urea, NH_2CONH_2, the products are ethanamide, carbon dioxide and ammonia.

Give the equation for this reaction. [1]

....

(ii) Suggest why an amide can act as a base. [1]

....

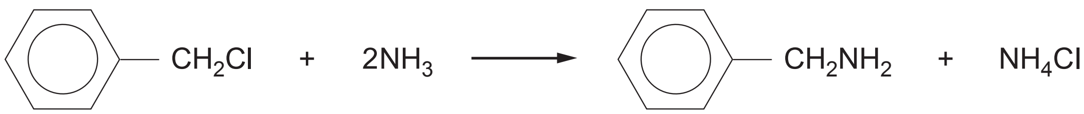
....

Examiner only

(iii) When ethanamide is heated with a dehydrating agent the organic product is ethanenitrile.

Use the **Data Booklet** to state and explain how characteristic infrared absorption values change during the reaction. In your answer you should relate the relevant bonds to their corresponding absorption frequencies. [2]

(iv) Some amines can be made by the reaction of a chlorine-containing compound and ammonia. For example (chloromethyl)benzene reacts with ammonia to give phenylmethylamine.

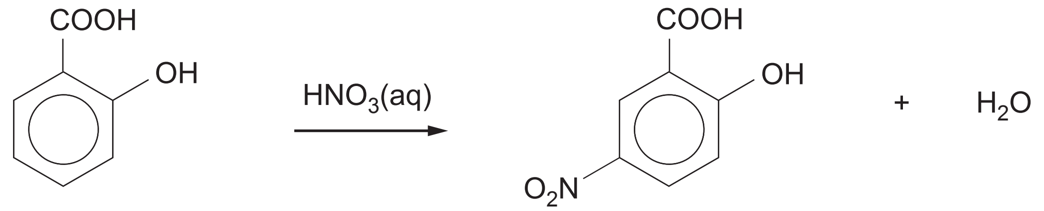


Suggest why phenylamine cannot easily be made by this method from chlorobenzene and ammonia. [1]

13

Examiner only

11. *(a)* 2-Hydroxy-5-nitrobenzenecarboxylic acid is made by reacting 2-hydroxybenzenecarboxylic acid and aqueous nitric acid.



(i) A basic outline of the method is given below.

Add 4.00 g of 2-hydroxybenzenecarboxylic acid to 100 cm^3 of nitric acid of concentration 2 mol dm^{-3}. Heat the mixture to 60 °C for 10 minutes. As the reaction proceeds brown fumes containing toxic nitrogen dioxide are produced. Add the products to 300 cm^3 of cold water. A yellow solution and white crystals of 2-hydroxy-5-nitrobenzenecarboxylic acid are obtained.

Use this outline method to produce a more detailed method suitable for others to use to be able to produce dry white crystals of the acid. As part of your answer you should give the type and size of apparatus used and mention any necessary health and safety factors.

Details of subsequent recrystallisation are **not** required. [6 QER]

....

....

....

....

....

....

....

....

....

....

....

....

....

Examiner only

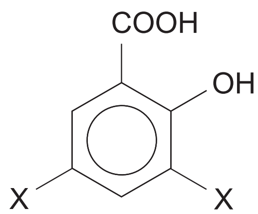
(ii) In this experiment the percentage yield of dry 2-hydroxy-5-nitrobenzenecarboxylic acid (M_r 183) was 41 %.

Calculate the mass produced based on the original mass of the 2-hydroxybenzenecarboxylic acid (M_r 138). [3]

Mass = ... g

(iii) Several other products were obtained during this reaction. One of these products is compound **J**.

Spectroscopy and analysis show that compound **J** is a substituted hydroxybenzenecarboxylic acid of M_r 228. Each molecule contains seven oxygen atoms.



compound **J**

Use the information given to suggest a structure for compound **J**. Show your reasoning. [2]

....

....

....

Examiner only

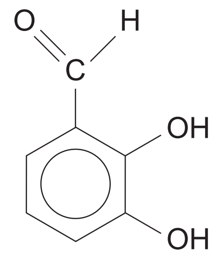
(iv) The yield of 2-hydroxy-5-nitrobenzenecarboxylic acid in this experiment is low.

Suggest how the experiment could be modified to increase the yield of the required product. [1]

....

....

(b) 2,3-Dihydroxybenzaldehyde has the same molecular formula as 2-hydroxybenzenecarboxylic acid.



Suggest a simple reaction that will give a positive result for 2-hydroxybenzenecarboxylic acid but **not** for 2,3-dihydroxybenzaldehyde. You should give the reagent(s) used and the result of the test with the acid. [1]

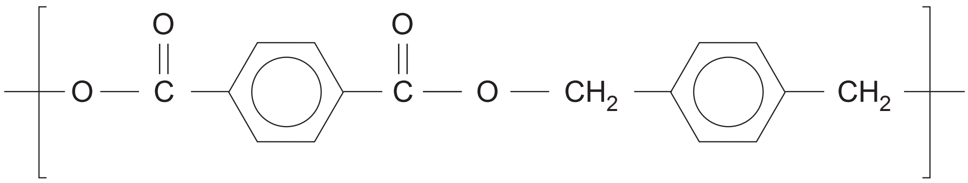
....

....

13

Examiner only

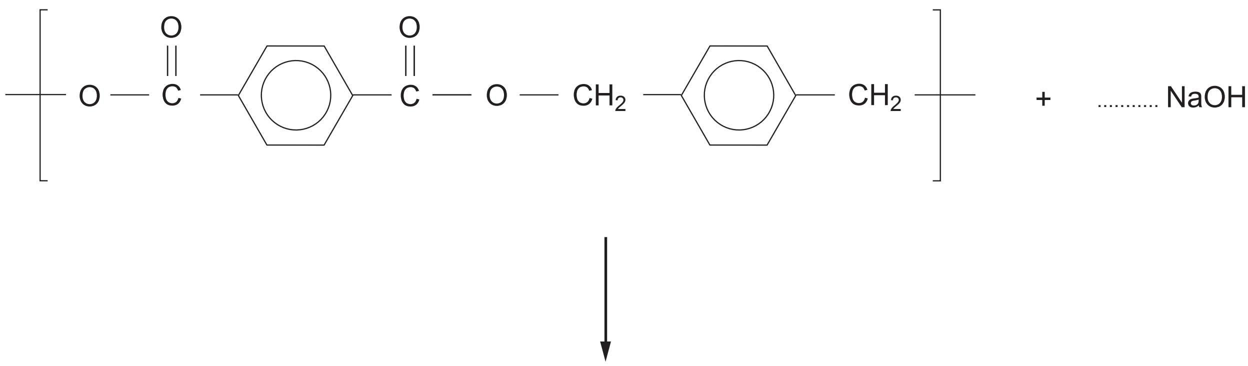
12. *(a)* A student was given a sample of a polyester **P**. He was told that the repeating unit was as follows.



(i) Draw a **circle** around an ester linkage in the repeating unit. [1]

(ii) Polyesters such as compound **P** can be hydrolysed by heating with aqueous sodium hydroxide.

Complete the balanced equation for this hydrolysis. [2]



(iii) The formation of polyester **P** is an example of condensation polymerisation.

State how this type of polymerisation differs from addition polymerisation. Refer to both types in your answer. [1]

....

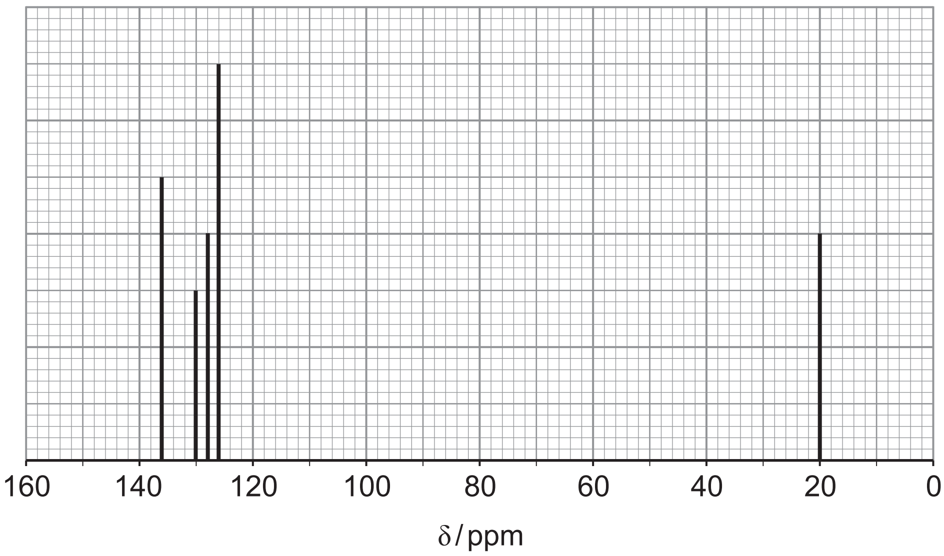
....

Examiner only

(iv) One of the raw materials used to make polyester **P** is methylbenzene.
Under suitable conditions methylbenzene can be converted to a mixture of dimethylbenzene isomers and benzene.

$$2C_6H_5CH_3 \longrightarrow C_6H_4(CH_3)_2 + C_6H_6$$

Gas chromatography can be used to separate the dimethylbenzene isomers.
One of the dimethylbenzene isomers has the ^{13}C NMR spectrum below.



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

....

....

....

....

....

....

Examiner only

(v) The isomer of dimethylbenzene used to produce polyester **P** is 1,4-dimethylbenzene. In industry this isomer is oxidised by air to produce benzene-1,4-dicarboxylic acid.

$$HOOC—C_6H_4—COOH$$

During this reaction a number of other aromatic oxidation products are made. One of these has the empirical formula C_4H_3O.

Suggest a structure for this product giving your reasoning. State how it could be produced in the reaction between 1,4-dimethylbenzene and atmospheric oxygen. [5]

....

....

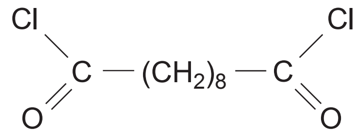
....

....

....

Examiner only

(b) (i) A laboratory experiment to demonstrate the formation of a polyamide uses decanedioyl dichloride.



State the name of a reagent used to produce this compound from the corresponding dicarboxylic acid, decanedioic acid. [1]

....

(ii) After use, a bottle containing decanedioyl dichloride (M_r 239.1) can become contaminated with decanedioic acid.

Analysis of a 3.50 g sample of contaminated decanedioyl dichloride showed that it contained 0.977 g of chlorine by mass.

Calculate the percentage purity of this sample of decanedioyl dichloride. [2]

Percentage purity = ... %

(iii) Suggest how the decanedioyl dichloride had become contaminated with decanedioic acid. [1]

....

....

....

16

END OF PAPER

BLANK PAGE

PLEASE DO NOT WRITE ON THIS PAGE

Question number	Additional page, if required. Write the question number(s) in the left-hand margin.

Examiner only

Question number	Additional page, if required. Write the question number(s) in the left-hand margin.

Examiner only