

Surname <i>StemUp Model Solution</i>	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	

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.

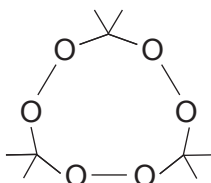


JUN191410U40101

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]

$C_9H_{18}O_6$

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

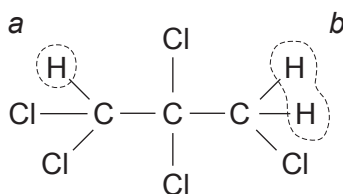
State the name of a carboxylic acid that will produce propane, when heated in this way.

[1]

butanoic acid

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

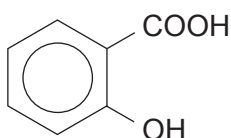
[2]



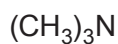
Proton(s)	Splitting pattern	Relative peak area ratio
<i>a</i>	<i>singlet</i>	<i>1</i>
<i>b</i>	<i>singlet</i>	<i>2</i>



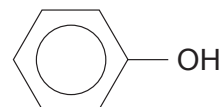
4. Using the letters provided, place these three compounds in order of **increasing** acidity. [1]



A



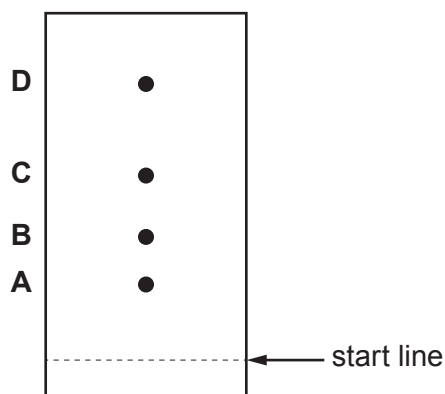
B



C

least acidic *B* *C* *A* 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.

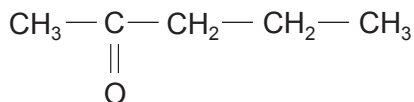
Amino acid	R_f value
alanine	0.59
glycine	0.42
leucine	0.88
serine	0.36

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

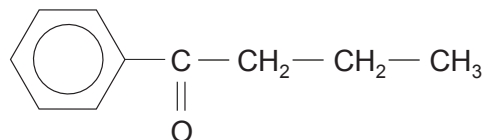
Spot C. Even without the solvent front, the spots move up in order of their R_f values: A = serine (0.36), B = glycine (0.42), C = alanine (0.59) and D = leucine (0.88).



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



pentan-2-one

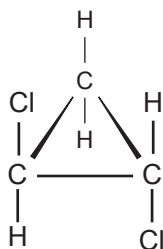


1-phenylbutanone

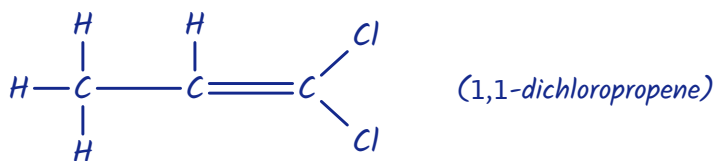
Reagent(s) used *iodine and aqueous sodium hydroxide (I₂/NaOH), warm*

Observations with both compounds *pentan-2-one gives a pale yellow precipitate (of CHI₃); no observable change (no precipitate) with 1-phenylbutanone.*

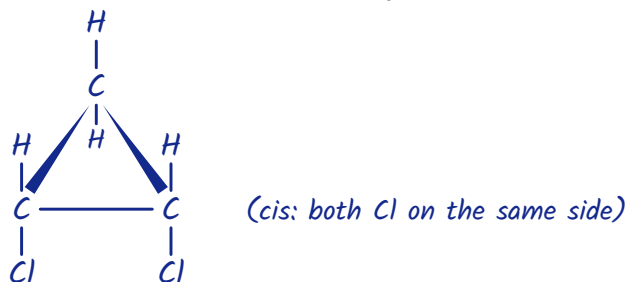
7. The displayed formula of 1,2-dichlorocyclopropane is given below.



- (a) Draw the displayed formula of another structural isomer of formula C₃H₄Cl₂. [1]



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



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.



- (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]

$$n(\text{CH}_3\text{COOH}) = 89.0 \div 60.0 = 1.483 \text{ mol}$$

$$\text{mass of ClCH}_2\text{COOH} = 1.483 \times 94.5 = 140.2 \text{ g}$$

$$\text{increase in mass} = 140.2 - 89.0 = 51.2 \text{ g}$$

Increase in mass = 51.2 g

- II. Chloroethanoic acid reacts with ammonia producing aminoethanoic acid.



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]

$$\text{theoretical mass} = 1.483 \times 75.0 = 111.3 \text{ g}$$

$$\% \text{ yield} = 49.2 \div 111.3 \times 100 = 44.3 \% \text{ (3 sig figs)}$$

Percentage yield = 44.3 %



- 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]

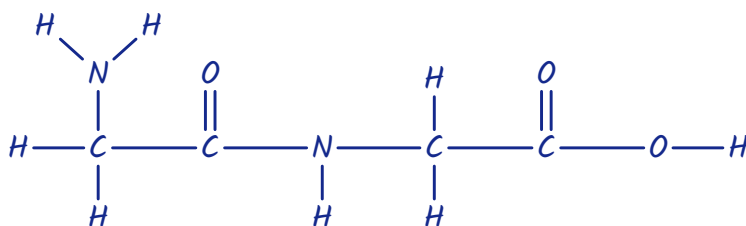
It exists as zwitterions, $^+H_3NCH_2COO^-$, so it is an ionic compound held by strong ionic attractions.

Ionic compounds are not (generally) soluble in covalent solvents such as methanol.

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

It does not contain a chiral centre (asymmetric carbon atom): the central C has two H atoms, so no optical isomers.

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



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



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 dm³. [3]

1 mol aminoethanoic acid gives 1 mol N₂, so $n(\text{N}_2) = 0.300 \text{ mol}$

$pV = nRT$, so $V = nRT \div p$ ($T = 373 \text{ K}$, $p = 98 \times 10^3 \text{ Pa}$)

$V = (0.300 \times 8.31 \times 373) \div (98 \times 10^3) = 9.49 \times 10^{-3} \text{ m}^3$

$V = 9.49 \text{ dm}^3$

Volume produced = 9.49 dm³

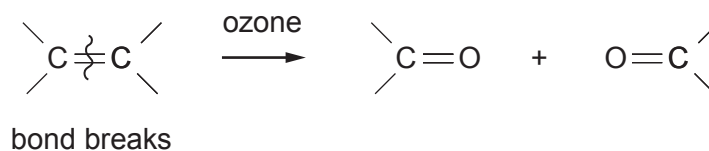
- (e) Hydroxyethanoic acid, CH₂(OH)COOH, can also be prepared by reacting chloroethanoic acid with aqueous sodium hydroxide.

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

With NaOH(aq) the product is the sodium salt, CH₂(OH)COO⁻Na⁺; adding acid protonates the carboxylate ion to give hydroxyethanoic acid.



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]

T is a symmetrical alkene: the groups bonded to each carbon atom of the C=C are the same, so both halves give U.

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

State the colour of this solid derivative.

[1]

orange

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

State what can be deduced from this statement.

[1]

U is not an aldehyde: it has no -CHO group (aldehyde H at 9.8 δ), so U is a ketone.



- 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
$\text{CH}_3(\text{CH}_2)_3\text{C} \begin{array}{l} \text{CH}_3 \\ \text{=O} \end{array}$	106
$\text{CH}_3(\text{CH}_2)_3\text{C} \begin{array}{l} \text{H} \\ \text{=O} \end{array}$	108
$\text{CH}_3\text{CH}_2\text{C} \begin{array}{l} \text{CH}_3 \\ \text{=O} \end{array}$	115
$\text{CH}_3(\text{CH}_2)_2\text{C} \begin{array}{l} \text{H} \\ \text{=O} \end{array}$	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]

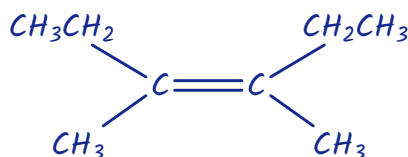
U is not an aldehyde, so it cannot be $\text{CH}_3(\text{CH}_2)_3\text{CHO}$ or

$\text{CH}_3(\text{CH}_2)_2\text{CHO}$; it must be $\text{CH}_3(\text{CH}_2)_3\text{COCH}_3$ or $\text{CH}_3\text{CH}_2\text{COCH}_3$.

An impure solid melts lower than the pure one, so the measured melting temperature (110 to 113 °C) cannot be higher than the literature value: it cannot be $\text{CH}_3(\text{CH}_2)_3\text{COCH}_3$ (106 °C).

So compound U must be butanone, $\text{CH}_3\text{CH}_2\text{COCH}_3$ (115 °C).

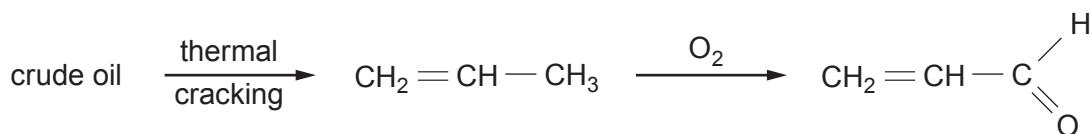
- (iv) Use your answer to part (iii) and other relevant information given in the question to give the structure of alkene **T**. Name alkene **T**. [2]



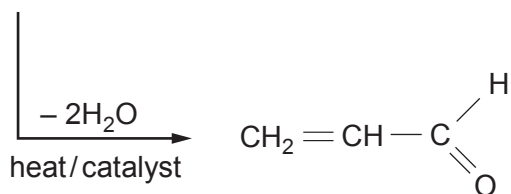
Name *(Z)-3,4-dimethylhex-3-ene*



Method 1 From crude oil



vegetable oil $\xrightarrow{\text{ethanol}}$ propane-1,2,3-triol + biodiesel



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

It uses a renewable raw material (vegetable oil) and does not use crude oil, a finite fossil fuel.

- (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 *the yield of propenal from each method*

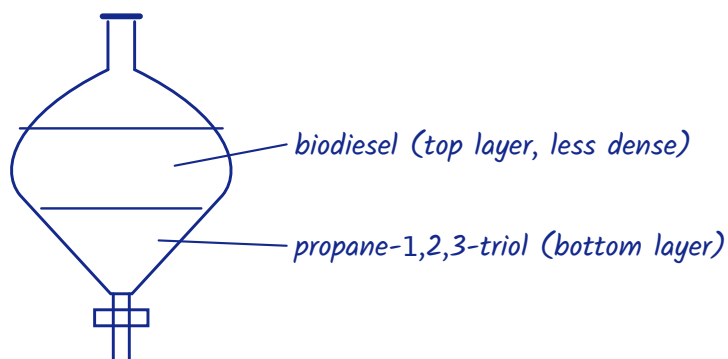
Factor 2 *the temperature conditions needed for each method*



- (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

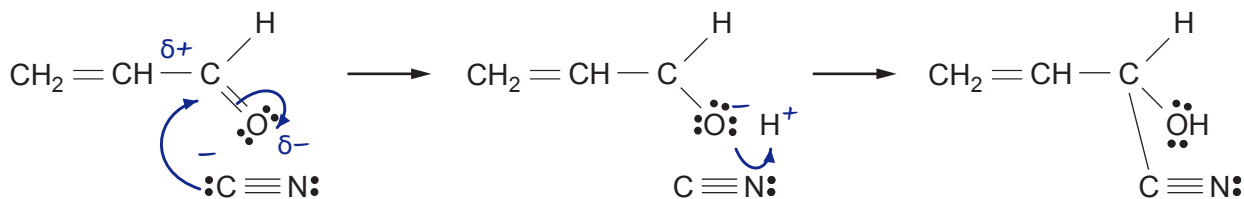
Sketch and name a piece of apparatus that could be used to separate a mixture containing 25 cm³ of each liquid. The two liquids should also be labelled. [2]



Name of apparatus separating funnel

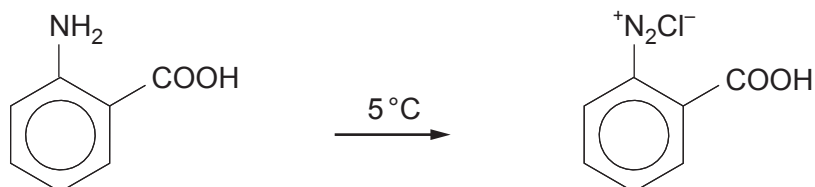
- (iv) Propenal reacts with hydrogen cyanide by a nucleophilic addition reaction.

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



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.

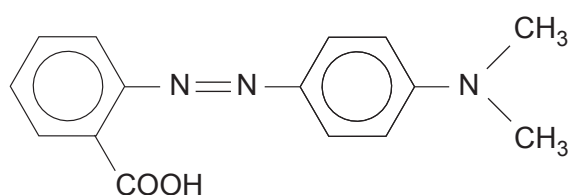


2-aminobenzenecarboxylic acid

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

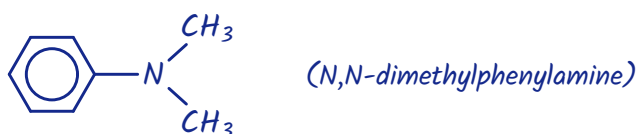
sodium nitrite (NaNO₂) and hydrochloric acid (HCl), i.e. nitrous acid, HNO₂

- (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]

$$f = c \div \lambda = 3.00 \times 10^8 \div (410 \times 10^{-9})$$

$$f = 7.32 \times 10^{14} \text{ Hz}$$

Frequency = 7.32×10^{14} Hz



- (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 $0.0075 \text{ mol dm}^{-3}$. [2]

$$n = 0.0075 \times 250 \div 1000 = 1.875 \times 10^{-3} \text{ mol}$$

$$\text{mass} = 1.875 \times 10^{-3} \times 272 = 0.51 \text{ g}$$

Mass required = 0.51 g

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

$$A = k c \quad \text{where } k \text{ is a constant}$$

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

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

$$k = A \div c = 1.44 \div 0.0096 = 150$$

$$c = A \div k = 1.03 \div 150 = 6.87 \times 10^{-3} \text{ mol dm}^{-3}$$

Concentration = 6.87×10^{-3} 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]

The nitrogen atom has a lone pair of electrons, so it can accept a proton

(H^+): it is a proton acceptor.



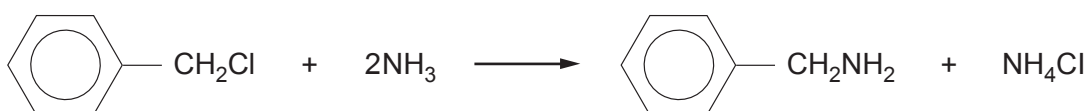
- (iii) When ethanamide is heated with a dehydrating agent the organic product is ethanenitrile.

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]

The amide C=O absorption (1650 to 1750 cm⁻¹) and N-H absorption (3300 to 3500 cm⁻¹) decrease as these bonds are lost.

The C≡N absorption at 2100 to 2250 cm⁻¹ increases (appears) as the nitrile forms.

- (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 phenylmethanamine.

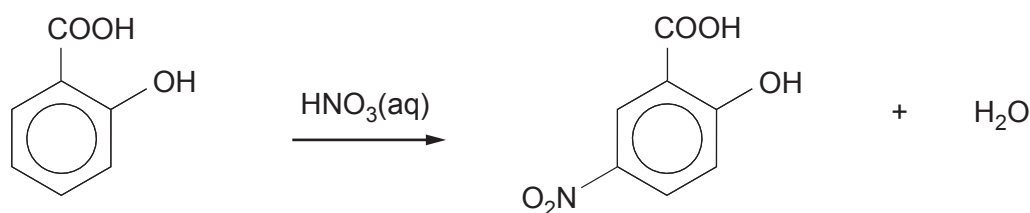


Suggest why phenylamine cannot easily be made by this method from chlorobenzene and ammonia. [1]

The benzene ring's delocalised (negative) electron cloud is not easily attacked by nucleophiles such as NH_3 (it is attacked by electrophiles), and the C-Cl bond in chlorobenzene is stronger than an aliphatic C-Cl bond.



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 cm³ 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 cm³ 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]

Carry out the whole reaction in a fume cupboard because toxic nitrogen

dioxide is given off; wear safety glasses, gloves and a lab coat as nitric acid is corrosive and oxidising.

Weigh 4.00 g of 2-hydroxybenzenecarboxylic acid on a 2 decimal place balance and add it to a 250 cm³ conical flask (or beaker).

Measure 100 cm³ of 2 mol dm⁻³ nitric acid with a 100 cm³ measuring cylinder and add it to the flask.

Stand the flask in a water bath on a hot plate with a thermometer (0 to 110 °C) in the mixture. Heat to 60 °C and keep it at 60 °C by adjusting the heating, stirring with a glass rod (or magnetic stirrer) for 10 minutes.

Measure 300 cm³ of cold water with a measuring cylinder into a 600 cm³ beaker, pour the reaction mixture into it, stir and leave to cool so that the white crystals form.



- (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]

$$n(\text{2-hydroxybenzenecarboxylic acid}) = 4.00 \div 138 = 0.0290 \text{ mol}$$

$$\text{mole ratio } 1 : 1, \text{ so theoretical } n(\text{nitro acid}) = 0.0290 \text{ mol}$$

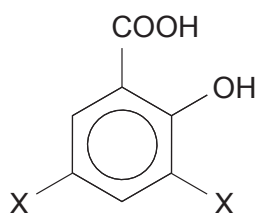
$$\text{theoretical mass} = 0.0290 \times 183 = 5.31 \text{ g}$$

$$\text{mass obtained} = 5.31 \times 41 \div 100 = 2.18 \text{ g}$$

Mass = 2.18 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]

$$M_r \text{ of J with H in place of both X (C}_7\text{H}_6\text{O}_3\text{)} = 138, \text{ so ring part} = 136$$

$$228 - 136 = 92 \text{ for two X groups, so each X has a mass of 46}$$

$$\text{COOH and OH contain 3 O, so the two X groups contain 4 O: 2 O each}$$

$$46 - 32 = 14, \text{ so the other atom is N and X} = \text{NO}_2; \text{ J is}$$

2-hydroxy-3,5-dinitrobenzenecarboxylic acid (NO₂ groups at both X positions).

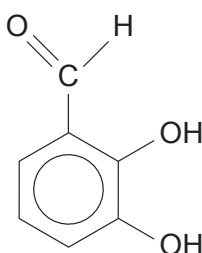


- (iv) The yield of 2-hydroxy-5-nitrobenzenecarboxylic acid in this experiment is low.

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

Use a lower temperature (or more dilute nitric acid, or a shorter heating time) so less further nitration occurs.

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

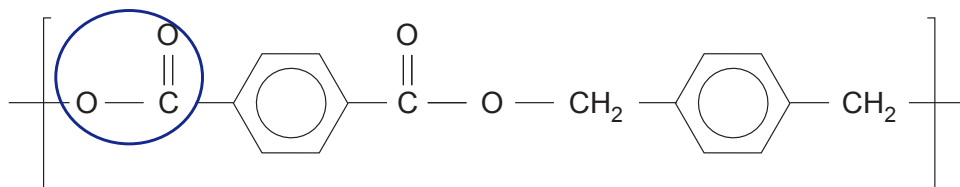


Suggest a simple reaction that will give a positive result for 2-hydroxybenzenecarboxylic acid but **not** for 2,3-dihydroxybenzaldehyde. You should give the reagent(s) used and the result of the test with the acid. [1]

Add sodium hydrogencarbonate solution, $\text{NaHCO}_3(\text{aq})$: the acid gives effervescence (CO_2 gas).

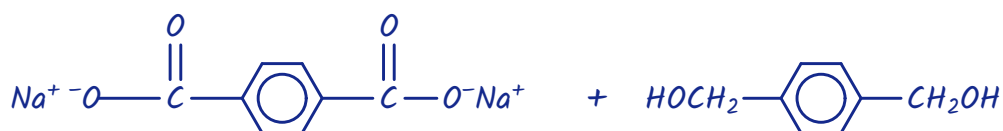
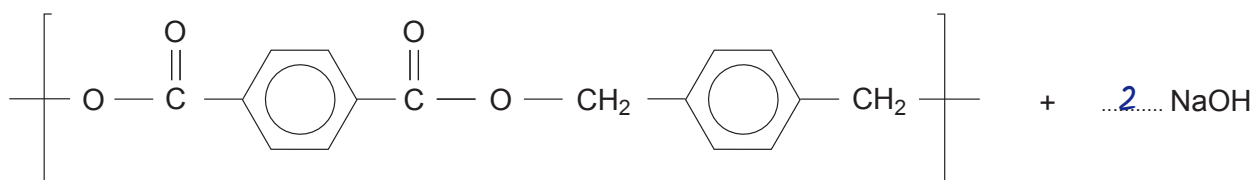


12. (a) A student was given a sample of a polyester **P**. He was told that the repeating unit was as follows.



- (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]

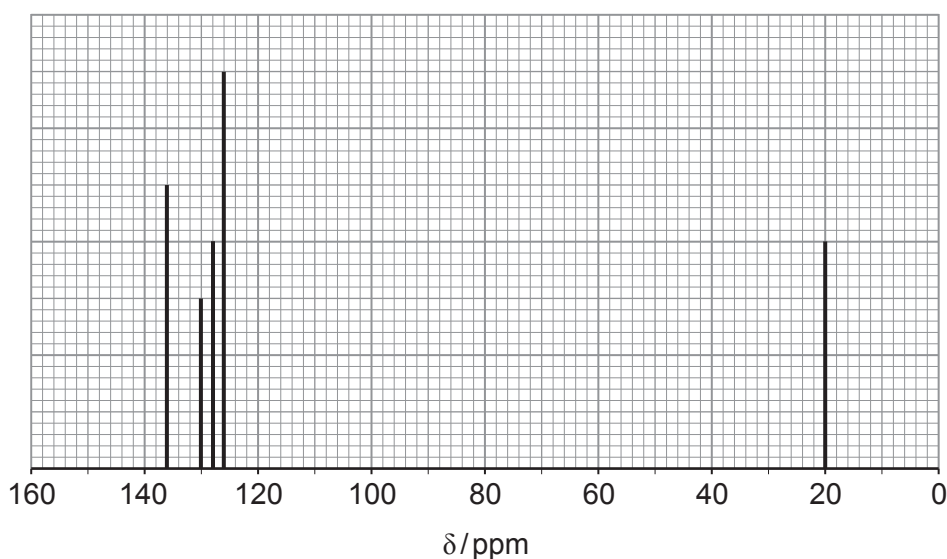
In condensation polymerisation a small molecule (H₂O or HCl) is eliminated as monomers join; in addition polymerisation nothing is eliminated.



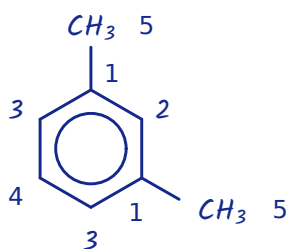
- (iv) One of the raw materials used to make polyester **P** is methylbenzene. Under suitable conditions methylbenzene can be converted to a mixture of dimethylbenzene isomers and benzene.



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]



five carbon environments, 1 to 5

1 to 4 = aromatic C (126 to 138 δ)

5 = CH_3 C (about 21 δ)

1,3-dimethylbenzene has five carbon environments (labelled 1 to 5 above)

and the spectrum shows five peaks.

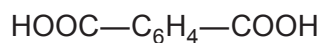
The four peaks between 126 and 138 δ are the aromatic (benzene ring) carbons.

The peak at about 21 δ is the aliphatic CH_3 carbons (both equivalent).

(The 1,2 isomer would give 4 peaks and the 1,4 isomer only 3.)



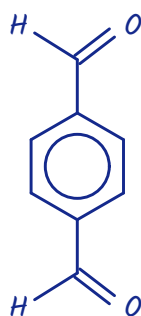
- (v) The isomer of dimethylbenzene used to produce polyester **P** is 1,4-dimethylbenzene. In industry this isomer is oxidised by air to produce benzene-1,4-dicarboxylic acid.



During this reaction a number of other aromatic oxidation products are made. One of these has the empirical formula $\text{C}_4\text{H}_3\text{O}$.

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]



benzene-1,4-dicarbaldehyde, $\text{C}_8\text{H}_6\text{O}_2$

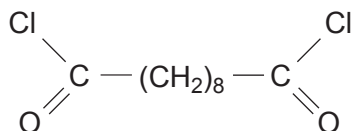
An aromatic compound has at least 6 C atoms, so the molecular formula is likely to be $\text{C}_8\text{H}_6\text{O}_2$ ($2 \times \text{C}_4\text{H}_3\text{O}$).

C_6H_4 plus 2 extra C, 2 H and 2 O: a dialdehyde (an acid-aldehyde, alcohol-aldehyde or acid-alcohol does not fit).

It is made by partial oxidation of each CH_3 group to CHO by O_2 .



- (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]

thionyl chloride (sulfur dichloride oxide), SOCl₂

- (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]

71.0 g of Cl in 239.1 g of decanedioyl dichloride

mass of dichloride = $0.977 \times 239.1 \div 71.0 = 3.29$ g

% purity = $3.29 \div 3.50 \times 100 = 94.0$ %

Percentage purity = *94.0* %

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

Moisture (water vapour) from the air entered the bottle when it was opened before and hydrolysed the decanedioyl dichloride to decanedioic acid (and HCl).

END OF PAPER



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Question number	Additional page, if required. Write the question number(s) in the left-hand margin.
11(a)(i)	<i>Filter off the crystals by suction filtration using a Buchner funnel, filter paper and Buchner flask.</i> <i>Rinse the reaction flask with a little cold water and add the washings to the funnel so no product is lost.</i> <i>Wash the crystals on the filter paper with small portions of cold water until the filtrate is colourless (this removes the yellow solution and the acid).</i> <i>Transfer the crystals to a watch glass and dry them in a warm oven below the melting temperature of the product (or leave them at room temperature in a desiccator) to give dry white crystals.</i>

Examiner only



[illegible]