Surname	Centre Number	Candidate Number
First name(s)		2

GCE A LEVEL

1410U40-1

Z22-1410U40-1

MONDAY, 20 JUNE 2022 – MORNING

CHEMISTRY – A2 unit 4
Organic Chemistry and Analysis

1 hour 45 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1. to 7.**	**10**	
Section B	**8.**	**14**	
	9.	**17**	
	10.	**13**	
	11.	**12**	
	12.	**14**	
	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. You may use a pencil for graphs and diagrams only.

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

Section A Answer **all** questions.
Section B Answer **all** questions.

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

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.10**(a).

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SECTION A

Answer **all** questions.

1. A hydrocarbon is either cyclopentane or pent-1-ene.

Use the **Data Booklet** to choose a characteristic infrared absorption that will positively identify the compound as pent-1-ene. [1]

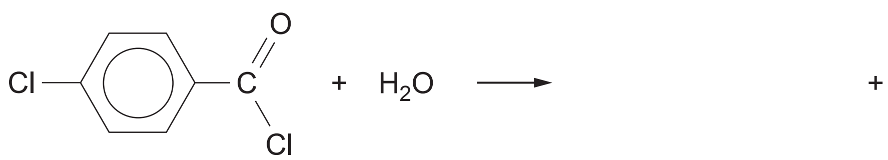
....

....

2. Give the **name** of a compound of formula C_4H_8 that will decolourise acidified potassium manganate(VII). [1]

....

3. Complete the equation for the reaction shown below. [1]



4. Give the structure of a compound of molecular formula $C_4H_8Br_2$ whose low resolution ^1H NMR spectrum consists of three peaks. [1]

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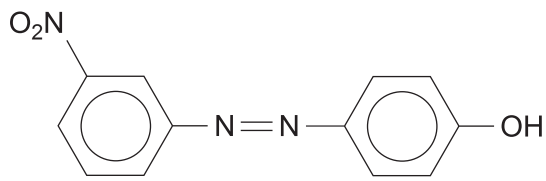
5. The formula of an azo dye, produced by reacting a diazonium compound with phenol, is shown below.



Write the formula of the amine that is used to produce this diazonium compound. [1]

6. Ethanal reacts with hydrogen cyanide to give 2-hydroxypropanenitrile, $CH_3CH(OH)(CN)$.

(a) State the type of mechanism occurring during this reaction. [1]

....

(b) Draw the structures of the two enantiomers of 2-hydroxypropanenitrile. [1]

1410U401 03

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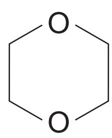
7. Three isomers have the molecular formula $C_4H_8O_2$.

(a) (i) Give the structure of an isomer that gives bubbles of carbon dioxide when tested with aqueous sodium hydrogencarbonate. [1]

(ii) Give the structure of an isomer that is both a ketone and a secondary alcohol. [1]

(b) Describe and explain the high resolution ^{1}H NMR spectrum of 1,4-dioxane.

The position of the signal(s) is **not** required. [1]



1,4-dioxane

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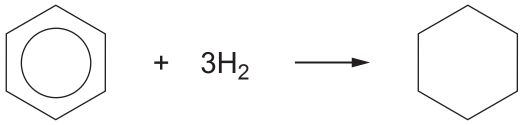
SECTION B

Answer **all** questions.

8. (a) The starting material for making polyamides is often benzene, obtained from petroleum.

(i) The first stage in the production of a particular polyamide is the hydrogenation of benzene at increased temperature and pressure.



Suggest the name of a catalyst that can be used for the hydrogenation of alkenes and an arene, such as benzene. [1]

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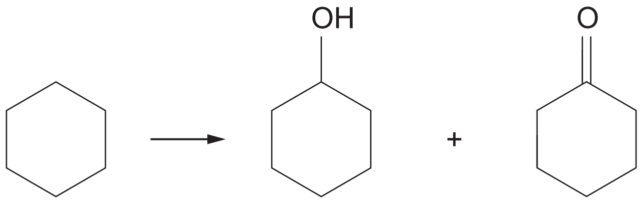
(ii) Cyclohexane, the product from the first stage, is then catalytically oxidised using air. This results in KA (a mixture of cyclohexanol and cyclohexanone). The mixture typically contains around 60% of cyclohexanone.



I. Using characteristic infrared values, describe how you could identify both cyclohexanol and cyclohexanone in KA. You should identify the bonds and their absorption frequencies in your answer. [2]

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II. A student suggested that you could find the proportion of cyclohexanol and cyclohexanone in KA by comparing the percentage of oxygen in each compound.

Calculate the percentage of oxygen in each compound. Use your answers to explain why this method would probably not give an accurate answer for the proportion of each compound present in KA. [3]

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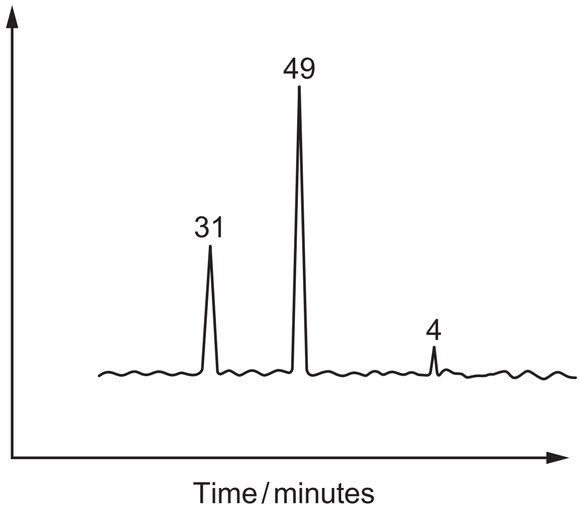
III. The proportions present in KA can be found more effectively by using gas chromatography.

A typical chromatogram of a sample of KA is shown below. The largest peak is due to cyclohexanone.



Calculate the percentage by volume of cyclohexanone in the mixture. [1]

Percentage of cyclohexanone = ... %

(iii) A sample of the cyclohexanol in KA is oxidised in the laboratory by refluxing with a suitable reagent.

State a suitable oxidising agent that can be used. [1]

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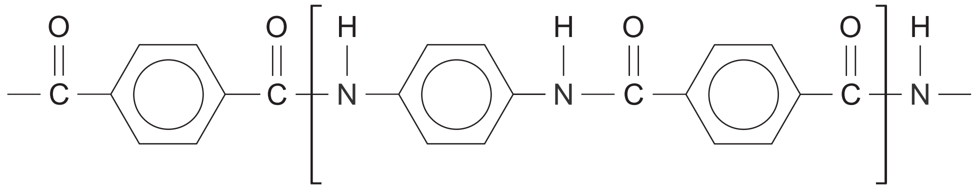
(b) The formula of the polyamide 'Kevlar' is shown below.



Give the structures of two starting materials that can react together to produce this polymer. [2]

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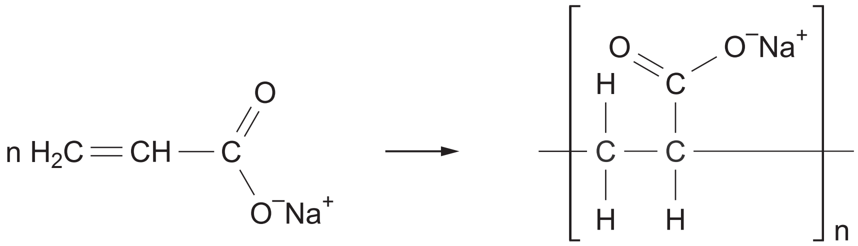
(c) The polymer poly(sodiumacrylate) is an example of a super absorbing polymer.



(i) Explain why this polymer is described as an addition polymer and not as a polyester. [2]

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(ii) Poly(sodiumacrylate) is capable of absorbing several hundred times its own mass of water, whilst remaining as a solid material.

In an experiment, 4.0×10^{-6} mol of the polymer absorbed 150 g of water. This mass of water is 300 times the mass of the polymer used.

Calculate the relative molecular mass of the polymer. [2]

M_r = ...

14

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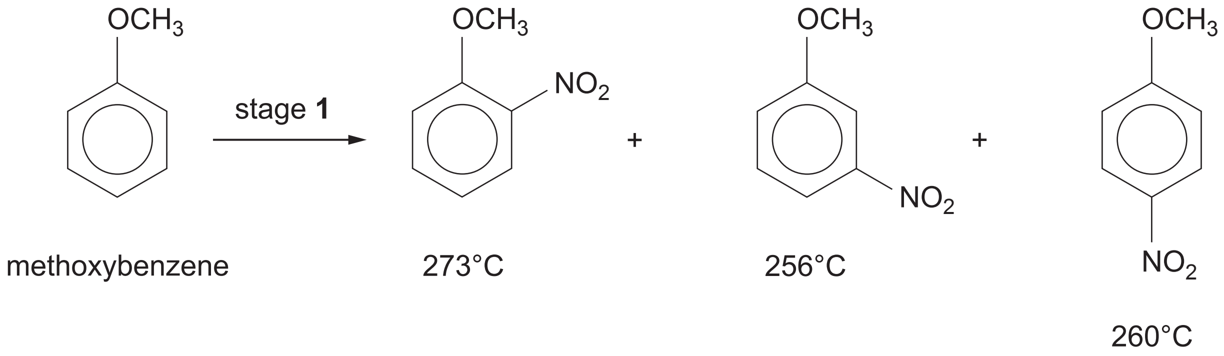
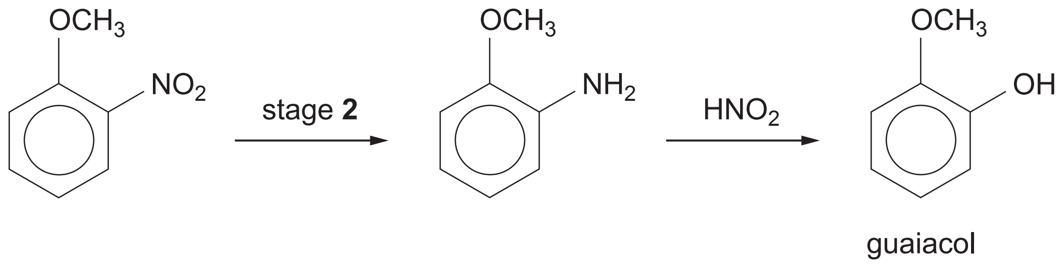
9. (a) Guaiacol (2-methoxyphenol) can be produced in a three-stage method from anisole (methoxybenzene). The boiling temperature of each product of stage **1** is shown.





Use your knowledge of a similar reaction, using benzene as the starting material, to answer parts (i)-(iii).

(i) Suggest a reagent(s) for stage **1**. [1]

....

(ii) Suggest a reagent(s) for stage **2**. [1]

....

(iii) Suggest and explain a practical problem that might occur at the end of stage **1**, before proceeding to stage **2**. [1]

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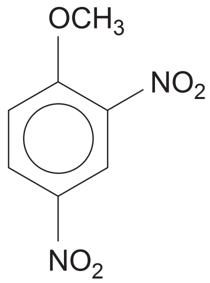
(iv) Complete the table below, indicating what is observed (if anything) when guaiacol reacts with aqueous solutions of these reagents. [2]

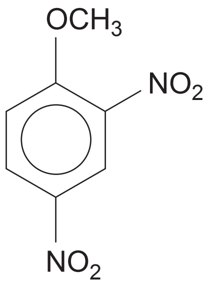
Reagent	$FeCl_3$	$NaHCO_3$
Observation		

(b) 2,4-Dinitroanisole can also be made by the nitration of anisole.



This compound has been used as an explosive. On detonation, it gives carbon, carbon monoxide, nitrogen and steam.

Balance the equation for this reaction. [1]



$\longrightarrow$ .... C + ... CO + ... N_2 + ... H_2O

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11

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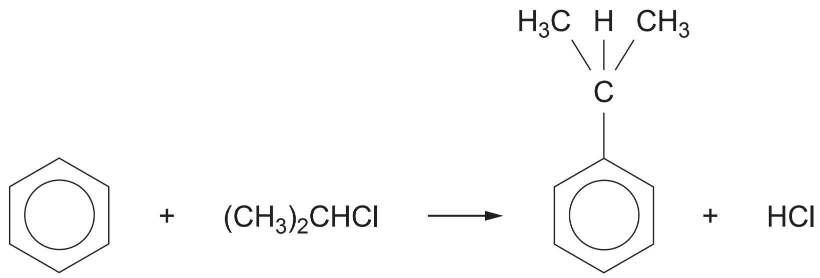
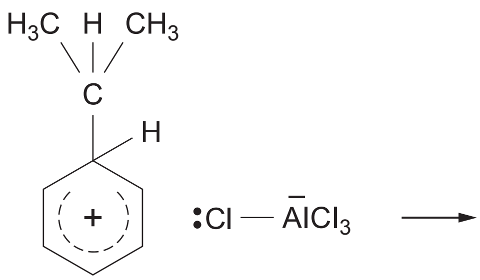
(c) (1-Methylethyl)benzene (commonly called cumene) can be prepared from benzene by a Friedel-Crafts reaction.



cumene

The products of the first step of the reaction are given below.

Complete the mechanism, showing how cumene, hydrogen chloride and the catalyst are formed from the intermediate product. [2]



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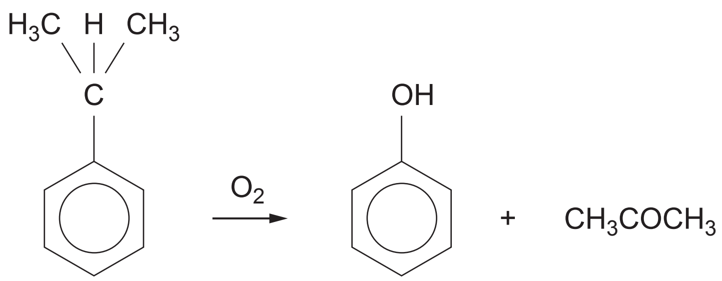
(d) Cumene is an important material in the industrial preparation of phenol and propanone.



(i) The yield of phenol (M_r 94) in this process is 86% with benzene (M_r 78) as the starting material.

Calculate the mass of phenol produced from 234 kg of benzene. [2]

Mass of phenol = ... kg

(ii) During this reaction a cumene radical is produced.

State what is meant by the term 'radical'. [1]

....

....

(iii) Give the formula of a radical formed during the reaction of methane with chlorine. [1]

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(e) Phenol reacts with aqueous bromine to give 2,4,6-tribromophenol.

If aqueous bromine is added slowly to an aqueous solution of phenol, describe how you would know when the reaction is just complete. [1]

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(f) Phenol reacts with benzoyl chloride, to give the ester phenyl benzoate and hydrogen chloride.

(i) Write the equation for this reaction. [1]

(ii) The reaction in part (i) is carried out in the presence of aqueous sodium hydroxide, which removes HCl as it is formed.

Explain why this method would not be suitable for a similar reaction, using ethanoyl chloride in place of benzoyl chloride. [1]

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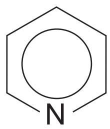
(iii) Esterification reactions, such as those in part (i), are sometimes carried out using pyridine in place of sodium hydroxide.

Explain the feature present in the structure of pyridine that enables it to react in this way. [2]



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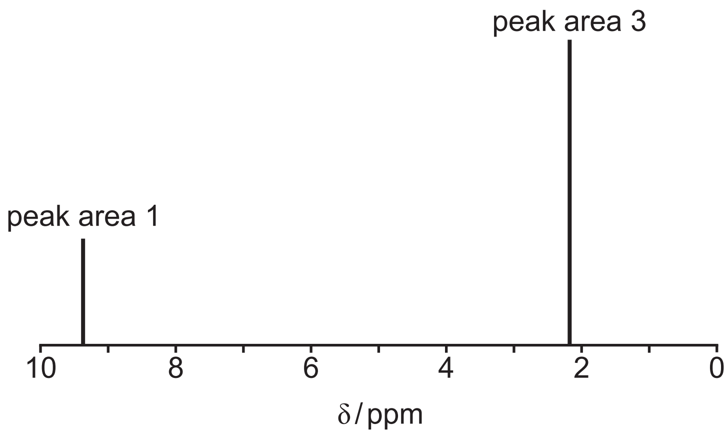
10. (a) Compound **G** contains only carbon, hydrogen and oxygen.

It has a molar mass of 72 g mol^{-1} of which 50.0% is carbon. The compound reacts positively with Tollens' reagent and gives a yellow solid when treated with alkaline iodine solution. It reacts with sodium tetrahydridoborate(III) to give a new compound which has a molar mass of 76 g mol^{-1}.

The high resolution ^{1}H NMR spectrum of compound **G** is shown below.



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

You should comment on how each piece of data has helped you to deduce the structure.
[6 QER]

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(b) The absorption spectrum of compound **G** shows a maximum absorption at 450 nm.

Light energy measured in kJ mol^{-1} (E) is related to wavelength (λ) by the equation

$$E = \frac{\text{constant}}{\lambda}$$

The energy of light of wavelength 656 nm is 183 kJ mol^{-1}.

Calculate the energy of the maximum absorption of compound **G** at 450 nm. [2]

Energy = ... kJ mol^{-1}

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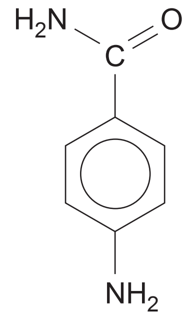
(c) The formula of 4-aminobenzamide is



(i) When this compound is warmed with excess aqueous sodium hydroxide, only the amide group reacts.

I. Give the structure of the organic product. [1]

II. State the nature of the attacking reagent and explain why the NH_2 group bonded to the benzene ring is not removed. [2]

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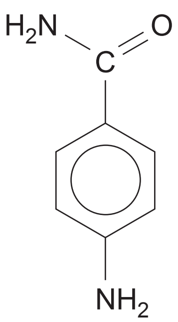
(ii) Both the functional groups in 4-aminobenzamide are attacked by nitric(III) acid at room temperature, giving 4-hydroxybenzoic acid, nitrogen gas and water as the products.

Complete the equation for this reaction. [2]

 + ... HNO_2 $\longrightarrow$ + ... N_2 + ... H_2O

13

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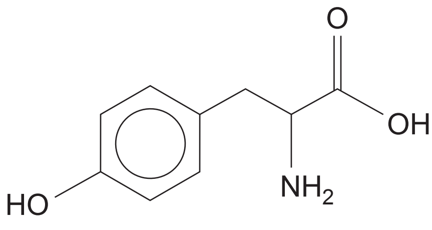
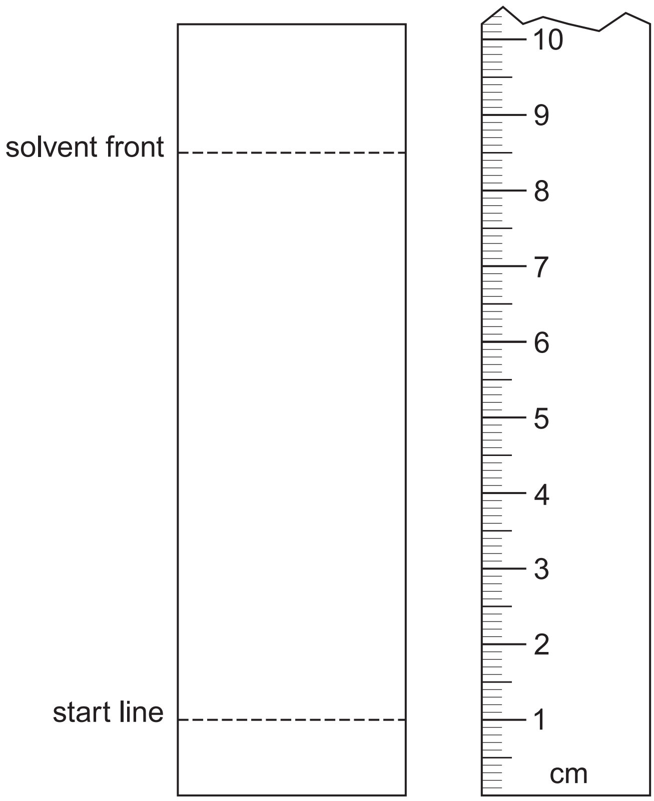
11. (a) Tyrosine is one of the amino acids making up casein, the protein in milk.



tyrosine

(i) Using a particular solvent tyrosine has an R_f value of 0.67.

On the chromatogram below show the spot given by tyrosine. [1]



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(ii) Write the formula for the zwitterion of tyrosine. [1]

(iii) Tyrosine is described as a hydrophobic amino acid, as its solubility in water is very low.

Use the formula of tyrosine to give a reason for this low solubility. [1]

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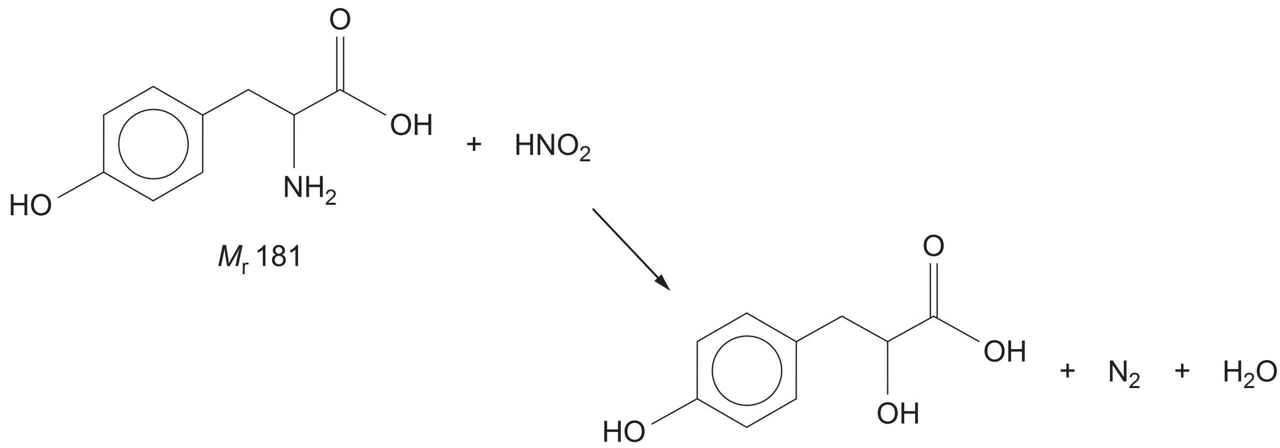
(iv) Amino acids, such as tyrosine, react with nitric(III) acid to give the corresponding hydroxy acid and nitrogen gas.



I. A sample of tyrosine was treated with an excess of nitric(III) acid and produced 147 cm^3 of nitrogen, measured at 298 K and 1 atm pressure.

Show that this volume of nitrogen will be produced from 1.09 g of tyrosine. [2]

II. The experiment was repeated with a sample of tyrosine from a different batch.
This time the same starting mass gave 132 cm^3 of nitrogen under the same conditions.

Suggest **one** reason for this different result. [1]

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....

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(b) There is increasing interest in the production of important chemicals by biotechnology, rather than from the use of fossil fuels.

One of these compounds is butane-1,4-dioic acid, which can be made from glucose.

$$\underset{\substack{\text{glucose} \\ M_r\ 180}}{C_6H_{12}O_6} \xrightarrow{\text{anaerobic bacteria}} \underset{\substack{\text{butane-1,4-dioic acid} \\ M_r\ 118}}{HOOC(CH_2)_2COOH} + \text{other products}$$

In practice, a constant pH is maintained by the addition of calcium hydroxide.
As butane-1,4-dioate ions are produced they react with calcium hydroxide to give insoluble calcium butane-1,4-dioate, which is then filtered from the mixture.

$$\underset{\substack{\text{glucose} \\ M_r\ 180}}{C_6H_{12}O_6} + \underset{M_r\ 74}{Ca(OH)_2} \longrightarrow \underset{\text{calcium butane-1,4-dioate}}{(CH_2)_2(COO)_2Ca} + \text{other products}$$

(i) Calculate the atom economy for the production of calcium butane-1,4-dioate. [2]

Atom economy = ... %

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(ii) In an experiment, 54.0 g of glucose produced 41.2 g of calcium butane-1,4-dioate.

Calculate the minimum volume of sulfuric acid, of concentration 2.5 mol dm^{-3}, necessary to convert all the calcium butane-1,4-dioate into butane-1,4-dioic acid. [2]

$$(CH_2)_2(COO)_2Ca \quad + \quad H_2SO_4 \longrightarrow HOOC(CH_2)_2COOH \quad + \quad CaSO_4$$

Volume of sulfuric acid = ... cm^3

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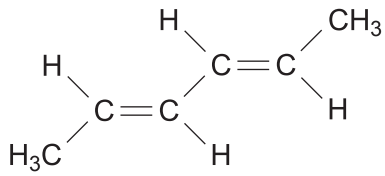
(c) Hexa-2,4-diene is one of the important products that can be produced from butane-1,4-dioic acid.



hexa-2,4-diene

Use the formula to help you to describe the ^{13}C NMR spectrum of this compound.

Your answer should include the number of peaks seen and your reasoning.
The position and size of the peaks is not required. [2]

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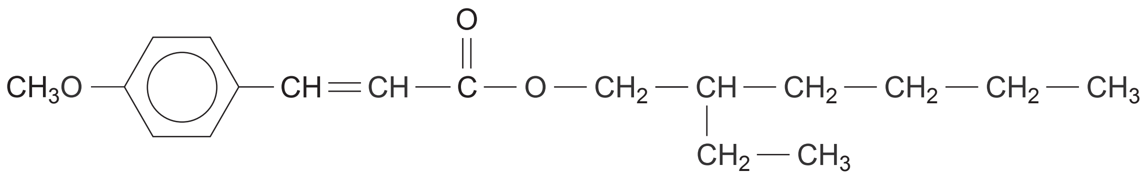
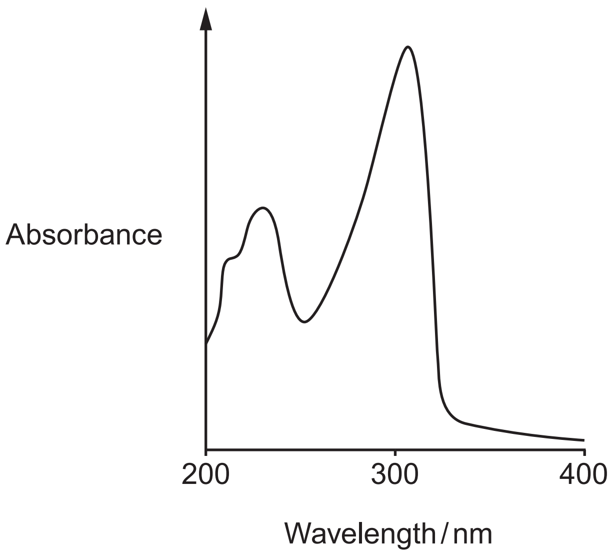
12. (a) People are increasingly concerned about the effect of the Sun's ultraviolet rays on the skin. A number of compounds have been developed for use as sunscreens. One of these compounds is compound **A**.



compound **A**

(i) The ultraviolet absorption spectrum of compound **A** is shown below.



Ultraviolet radiation is divided into three regions.

Region	Wavelength / nm
UVA	320-400
UVB	290-320
UVC	200-290

Use this information to explain why it may be necessary to use another sunscreen compound, together with compound **A**, when producing a commercial sunscreen. [1]

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(ii) Compound **A** is an ester that is made by reacting together 2-ethylhexanol and the appropriate acid, in the presence of a catalyst.

Give the molecular formula of the acid used in this reaction. [1]

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(iii) Compound **A** displays both forms of stereoisomerism.

I. State how structural isomerism differs from stereoisomerism. [2]

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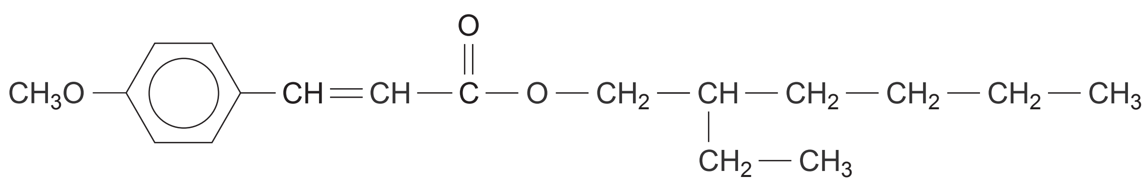
II. Indicate the position of a chiral centre on the formula of compound **A** below. [1]



III. When compound **A** is made by the method described in part (ii) above, an equimolar mixture of both enantiomers is produced.

State how a solution of this mixture affects the plane of plane polarised light. [1]

....

IV. Exposure of a mixture of both *E*- and *Z*- forms of compound **A** to UV radiation results in the *E*- form gradually changing to the *Z*- form.

Using the general formula of compound **A** as R—CH═CH—R', draw and label these two forms of compound **A**. [2]

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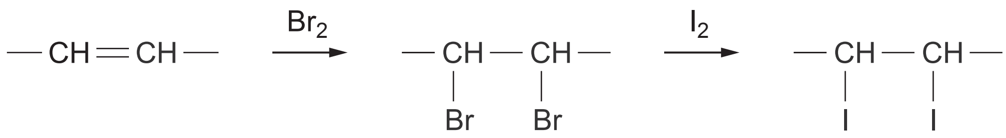
(b) Palm oil contains around 40% of unsaturated oil and 60% of saturated oil. The amount of unsaturation in an oil can be measured indirectly in a reaction with iodine.

(i) In the first stage of this method bromine adds across the C$=$C double bonds present.

State the type of mechanism occurring when bromine adds across these double bonds. [1]

....

(ii) The overall reaction with iodine can be represented by the following equation.



In palm oil, most of the unsaturated oils are present as glyceryl trioleate (M_r 885). This compound contains three C$=$C double bonds per molecule.

An 8.41 g sample of palm oil reacted indirectly with 0.0128 mol of iodine (I_2).

Calculate the percentage of unsaturated oil (as glyceryl trioleate) present in the palm oil. [2]

Percentage of unsaturated oil = ... %

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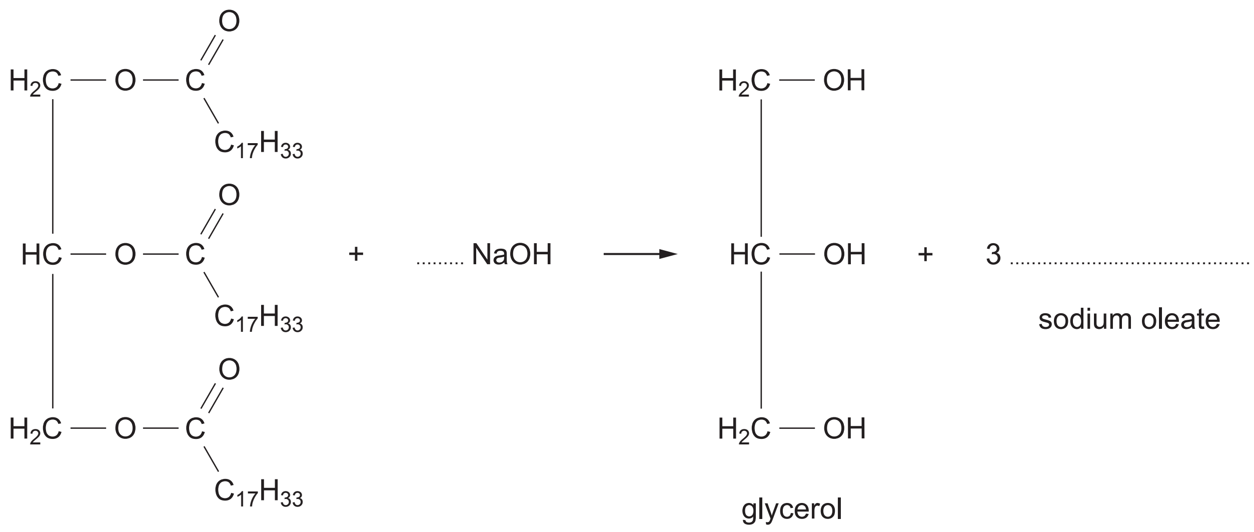
(iii) Oils such as palm oil can be refined and used to make soaps such as sodium oleate.

Complete the equation below, which represents the alkaline hydrolysis of the unsaturated oil. [2]



(iv) Fats and oils are esters of carboxylic acids and glycerol.

Give the systematic name of glycerol (seen in part (iii) above). [1]

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14

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