Answer **all** the questions.

1 Methylbenzene, $C_6H_5CH_3$, is an aromatic hydrocarbon and is used widely as a solvent. It is readily nitrated and it can form mono-, di-, or tri-nitromethylbenzenes.

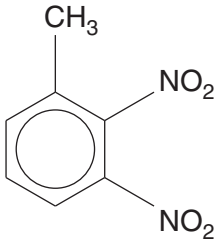
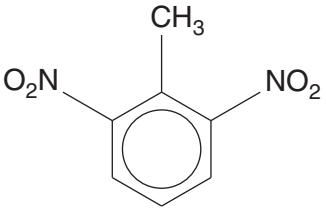
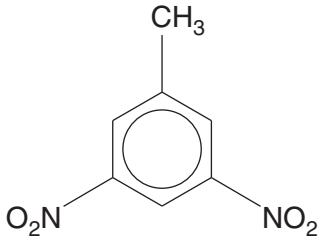
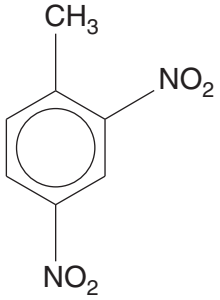
(a) 4-Nitromethylbenzene can be formed by the nitration of methylbenzene.

Outline the mechanism for the formation of 4-nitromethylbenzene from methylbenzene using NO_2^+ as the electrophile.

[4]

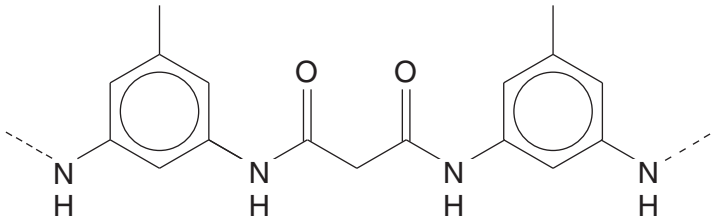
(b) There are six possible structural isomers of $CH_3C_6H_3(NO_2)_2$ that are dinitromethylbenzenes. Four of the isomers are shown below.

Draw the structures of the other two isomers in the boxes provided.

 **isomer 1**	 **isomer 2**	 **isomer 3**
 **isomer 4**	**isomer 5**	**isomer 6**

[2]

(c) A research chemist investigated whether dinitromethylbenzenes could be used in the manufacture of fibres.
The chemist devised a **two**-stage synthesis of the condensation polymer below, starting from one of the isomers in part **(b)**.



For the **first** stage of the synthesis,

- Which of the isomers **1**, **2**, **3** or **4** could be used?
- Identify the product formed and state suitable reagents.
- Write an equation.

For the **second** stage of the synthesis,

- Suggest an organic compound that could react with the organic product from the **first** stage to form the polymer.
- State the type of condensation polymer formed.

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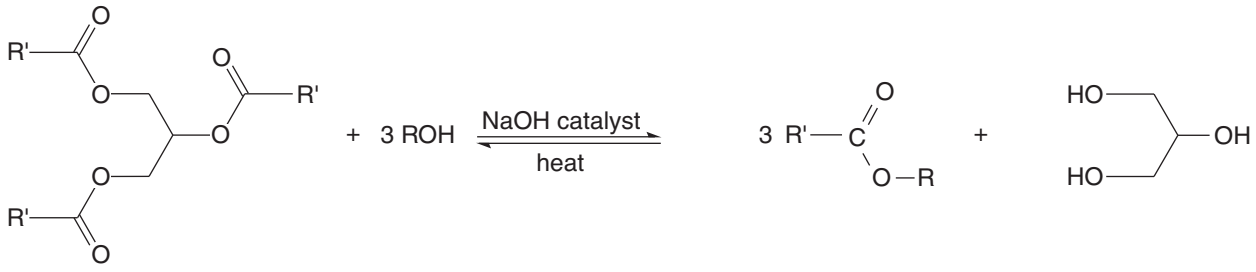
..... **[6]**

[Total: 12]

2 Esters of fatty acids are used as biodiesels. These esters can be produced from triglycerides by the transesterification process below.



triglyceride **biodiesel** **glycerol**

(a) Give the systematic name of glycerol.

..... **[1]**

(b) **(i)** Suggest a suitable alcohol, ROH, that could be used industrially to make biodiesel.

Justify your answer.

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..... **[1]**

(ii) The alcohol, ROH, is added in excess.

Suggest why the alcohol has to be in excess.

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..... **[1]**

(c) Esters can also be made by reacting an alcohol with either a carboxylic acid or with an acid anhydride.

Write equations for the formation of ethyl propanoate, $CH_3CH_2COOCH_2CH_3$, starting from:

- a carboxylic acid and an alcohol,

- an acid anhydride and an alcohol.

[2]

(d) Compound **A**, $C_4H_8O_3$, can lose water to form either:

compound **B**, a cyclic ester
OR
compound **C**, a polyester.

Identify compounds **A**, **B** and **C**.

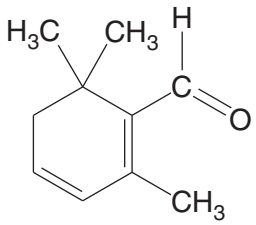
compound **A**	compound **B**
compound **C**	

[3]

[Total: 8]

Turn over

3 Safranal, shown below, is an aldehyde which contributes to the aroma of saffron.



safranal

An undergraduate chemist investigated some reactions of safranal.

(a) She prepared a solution of Tollens' reagent and added a few drops of safranal. She then warmed the mixture for about 5 minutes in a water bath.

Describe what you would expect the chemist to see.

State the type of reaction that the safranal undergoes.

Draw the structure of the organic product formed in this reaction.

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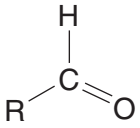
[3]

(b) The chemist then reduced safranal using an aqueous solution of $NaBH_4$.

Outline the mechanism for this reaction.

Use curly arrows and show any relevant dipoles.



can be used to represent safranal.

[4]

(c) Suggest one reaction of safranal that does **not** involve the aldehyde group.

State the reagent, observation (if any) and draw the organic product.

reagent .....

observation .....

organic product

[3]

[Total: 10]

4 Read the passage below and answer the questions that follow.

α-Amino acids can be synthesised in the laboratory by the two synthetic routes below.

Synthesis 1

An α-chlorocarboxylic acid is reacted with an excess of concentrated ammonia solution. The resulting solution is neutralised to produce an α-amino acid.

$$C\ell CH(R)COOH \xrightarrow[\text{concentrated ammonia solution}]{\textbf{step 1}} H_2NCH(R)COO^- \xrightarrow[\text{neutralisation}]{\textbf{step 2}} H_2NCH(R)COOH$$

Synthesis 2

An aldehyde is reacted with an aqueous solution of potassium cyanide and ammonium chloride. The resulting product is hydrolysed with aqueous acid and then neutralised to produce an α-amino acid.

$$RCHO \xrightarrow{KCN(aq)/NH_4C\ell(aq)} H_2NCH(R)CN \xrightarrow[\text{followed by neutralisation}]{\text{aqueous acid}} H_2NCH(R)COOH$$

(a) A chemist attempted the synthesis of the α-amino acid alanine (where R is CH_3) using **synthesis 1**.

(i) Write the equation for the reaction of $C\ell CH(CH_3)COOH$ with excess concentrated ammonia solution, $NH_3(aq)$, in **step 1** of **synthesis 1**.

[1]

(ii) A disadvantage of **synthesis 1** is that the α-amino acid can react further. For example, in the synthesis of alanine, an impurity with molecular formula $C_6H_{11}NO_4$ is also formed.

Draw the structure of this impurity.

[1]

(b) A chemist attempted the synthesis of the α-amino acid aspartic acid (where R is CH_2COOH) using **synthesis 2**.

(i) Draw the **skeletal** formula of the organic compound that could be used to synthesise aspartic acid using **synthesis 2**.

[1]

(ii) Draw **3D** diagrams of the optical isomers of aspartic acid.

[2]

(c) Many pharmaceuticals also have a chiral centre.

Discuss two possible **disadvantages** of producing a chiral drug as a mixture of stereoisomers.

State **two** ways in which a single optical isomer might be synthesised.

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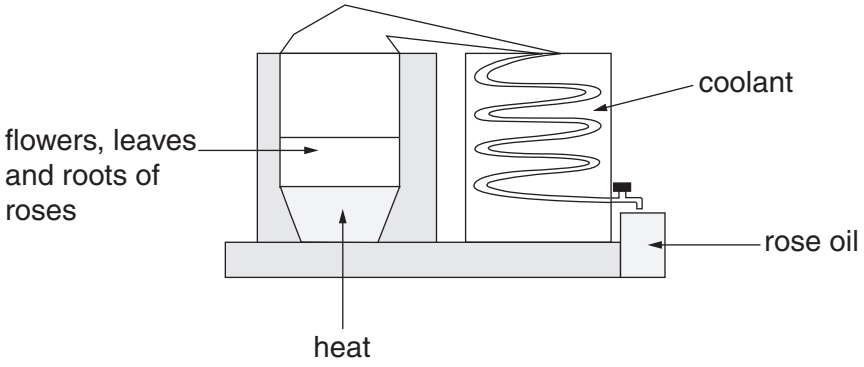
..... **[4]**

[Total: 9]

Turn over

5 Rose oil can be extracted from the flowers, leaves and roots of roses using the apparatus below.



(a) The rose oil contains a mixture of compounds, some of which can be separated by using thin-layer chromatography (TLC). The chromatogram obtained is shown below.

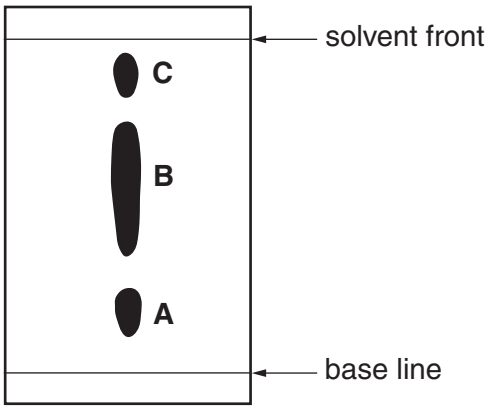


Fig. 5.1

(i) Explain how TLC separates compounds in the mixture.

In your answer, you should use appropriate technical terms, spelled correctly.

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..... **[1]**

(ii) Estimate the R_f value of **A**.

[1]

(iii) Using the chromatogram in **Fig. 5.1**, suggest why it is **not** possible to conclude that the rose oil contains **only** three different compounds.

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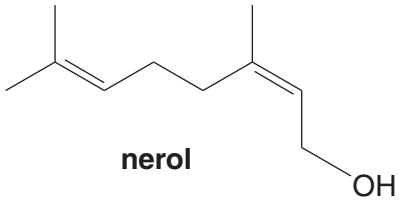
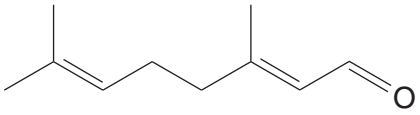
..... **[1]**

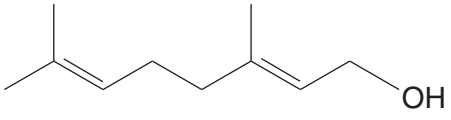
(b) GC–MS was used to identify the compounds present in the rose oil as nerol, geraniol, citral and menthol, shown below. These compounds all have stereoisomers.



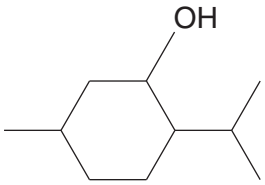
nerol



citral



geraniol



menthol

(i) Explain how GC–MS can be used to identify these compounds in the rose oil.

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..... **[1]**

(ii) Suggest, with a reason, which two compounds might be present in **B** in **Fig. 5.1**.

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..... **[1]**

(iii) Explain what is meant by the term *stereoisomers*.

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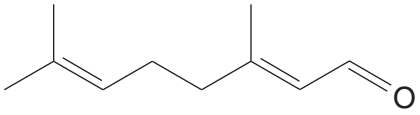
..... **[1]**

Turn over

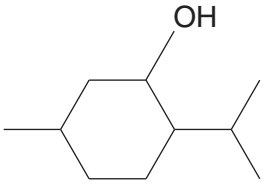
(iv) Draw a circle around the feature in citral that causes the stereoisomerism.



citral

[1]

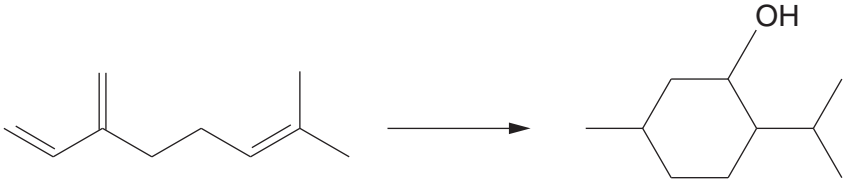
(v) Identify with asterisks (*) **all** the chiral centres in menthol that cause the stereoisomerism.



menthol

[2]

(c) Menthol is used in a wide range of products including lip balms, cough medicines and perfumery. The demand for menthol exceeds the supply from natural sources. Menthol is manufactured, using a chiral synthesis, from myrcene, a readily available starting material.



myrcene **menthol**

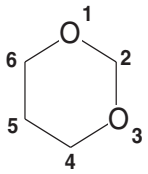
Calculate the mass of menthol that can be synthesised from 34.0 g of myrcene.
The percentage yield is 60%. M_r (Myrcene) = 136.

mass of menthol = ... g **[3]**

[Total: 12]

6 A company was planning to build a power station that will burn plastic waste. The local residents were concerned about possible emission of pollutants such as dioxanes and aromatic hydrocarbons. The residents employed an independent chemical engineer to advise about possible emissions.

Some scientists suspect that dioxanes, such as 1,3-dioxane, and aromatic hydrocarbons may be linked to some types of cancer.



1,3-dioxane

(a) Predict the splitting patterns in the proton NMR spectrum of 1,3-dioxane.

Identify which protons are responsible for each splitting pattern.

In your answer, you should use appropriate technical terms, spelled correctly.

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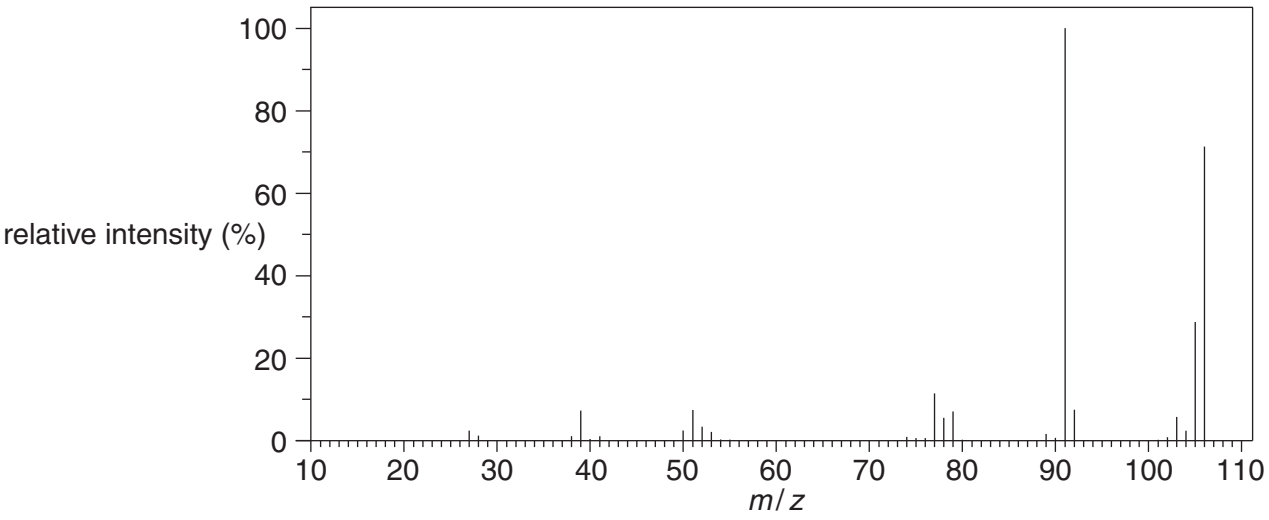
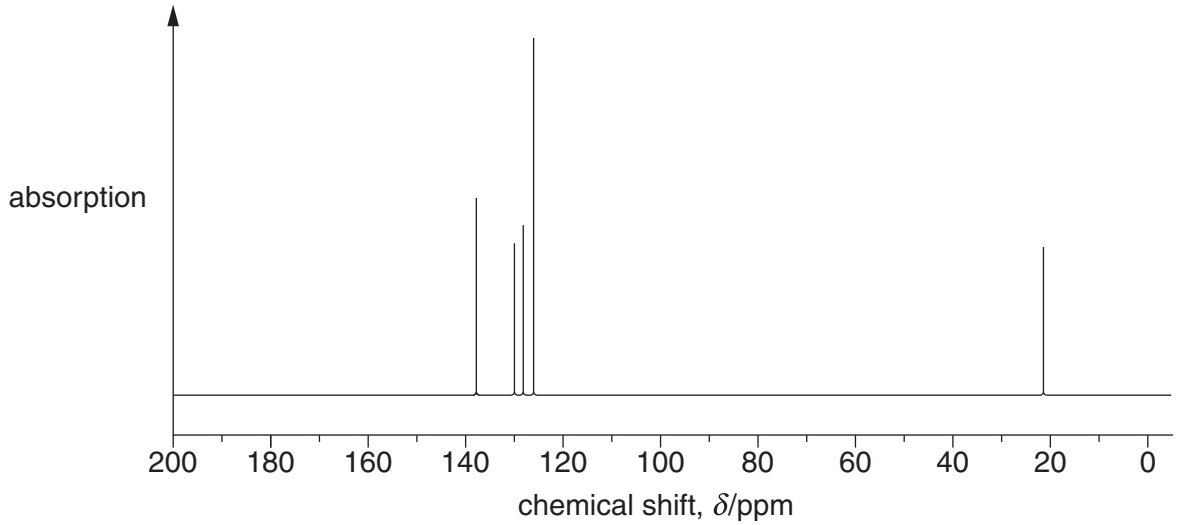
..... **[3]**

TURN OVER FOR QUESTION 6 (b)

(b) The independent chemical engineer investigated an unknown aromatic hydrocarbon.
He obtained the mass spectrum and the ^{13}C NMR spectrum of the aromatic hydrocarbon, which are shown below.





The aromatic hydrocarbon is one of **four** possible isomers.

Use the spectra to identify the aromatic hydrocarbon.

Show **all** of your working and explain how you ruled out the other three isomers.

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aromatic hydrocarbon is:

[6]

[Total: 9]

END OF QUESTION PAPER