

**OXFORD CAMBRIDGE AND RSA EXAMINATIONS**  
**A LEVEL**  
**H432/02**  
**CHEMISTRY A**

**Synthesis and analytical techniques**

**TUESDAY 12 JUNE 2018: Afternoon**

**TIME ALLOWED: 2 hours 15 minutes**  
**plus your additional time allowance**

**MODIFIED ENLARGED 36pt**

<b>First name</b>						<b>Last name</b>					
<b>Centre number</b>						<b>Candidate number</b>					

**YOU MUST HAVE:**  
**the Data Sheet for Chemistry A**

**YOU MAY USE:**  
**a scientific or graphical calculator**

**READ INSTRUCTIONS OVERLEAF**



# **INSTRUCTIONS**

**Use black ink. You may use an HB pencil for graphs and diagrams.**

**Complete the boxes on the front page with your name, centre number and candidate number.**

**Answer ALL the questions.**

**Write your answer to each question in the space provided. If additional space is required, use the lined page(s) at the end of this booklet. The question number(s) must be clearly shown.**

# **INFORMATION**

**The total mark for this paper is 100.**

**The marks for each question are shown in brackets [ ].**

**Quality of extended responses will be assessed in questions marked with an asterisk (\*).**

## SECTION A

You should spend a maximum of 20 minutes on this section.

Write your answer to each question in the box provided.

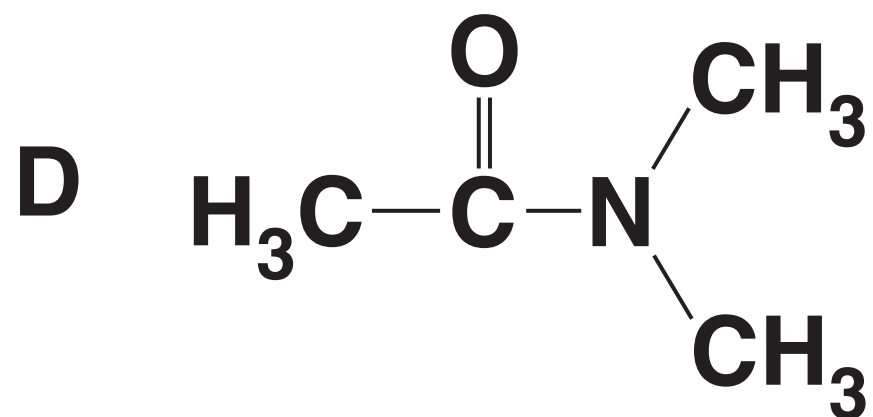
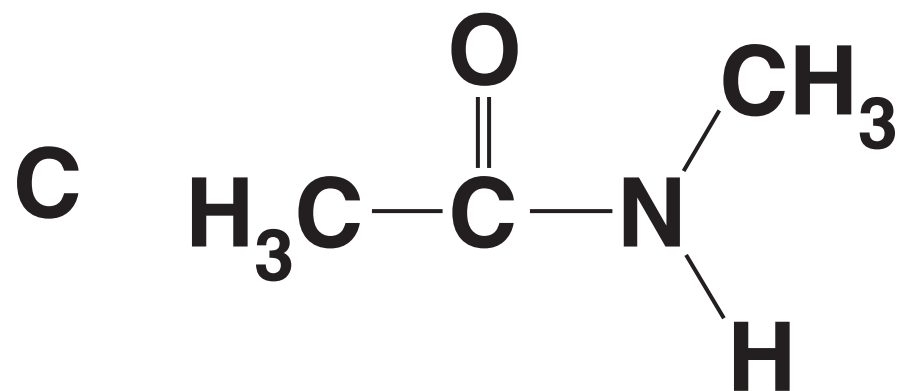
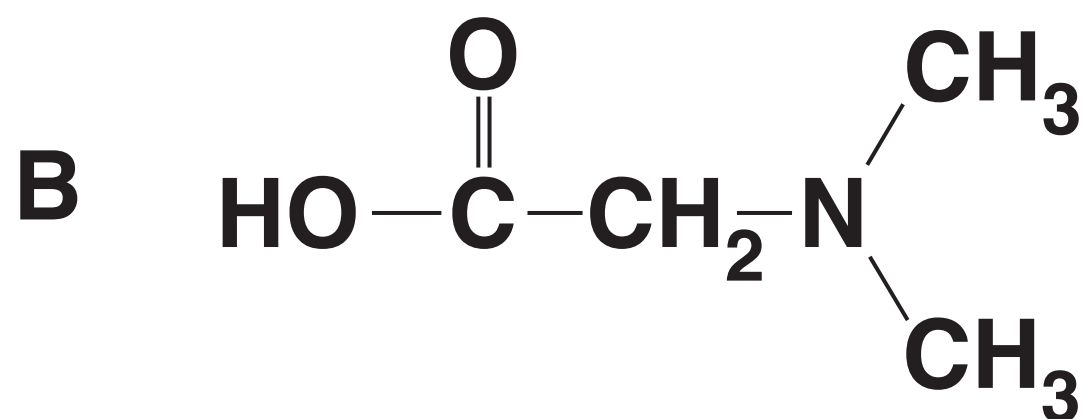
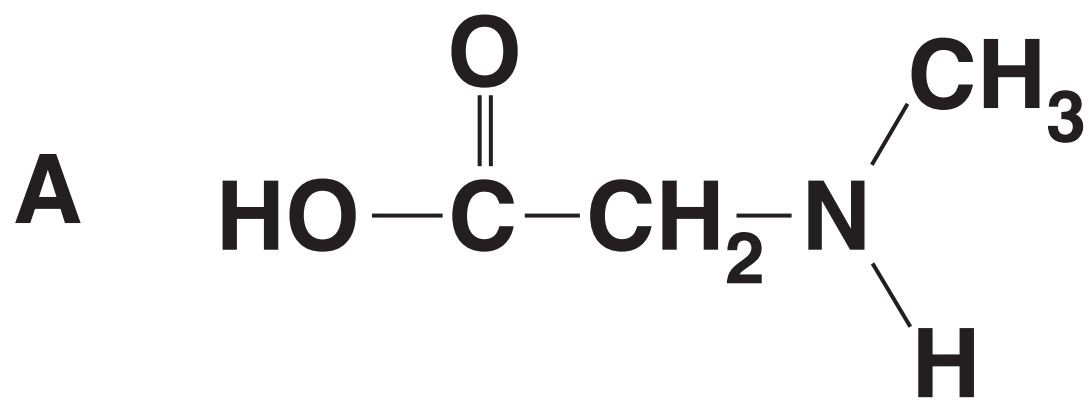
Answer ALL the questions.

- 1 Which compound is used as a standard for NMR chemical shift measurements? [1]



Your answer

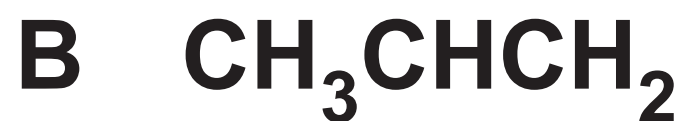
**2 Which compound is a secondary amide? [1]**



**Your answer**

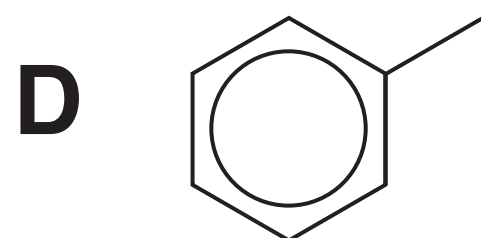
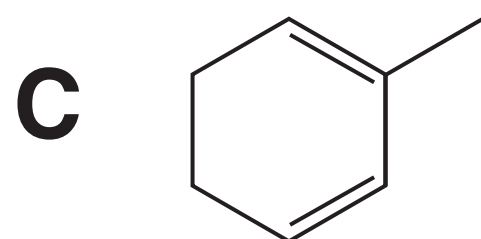
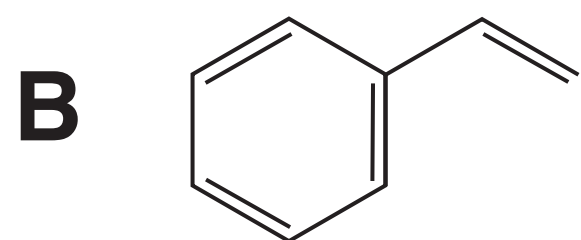
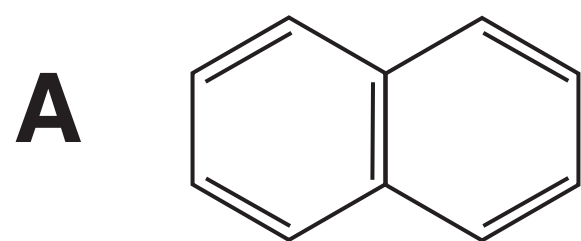


**3 Which compound does NOT react with nucleophiles? [1]**



**Your answer**

4 Which structure represents an alicyclic compound? [1]



Your answer

**5 Which molecule is NOT planar? [1]**



**Your answer**

**6 What is the number of peaks in the  $^1\text{H}$  NMR spectrum of  $\text{HOOCCH}_2\text{CHOHCH}_2\text{COOH}$ ? [1]**

**A 3**

**B 4**

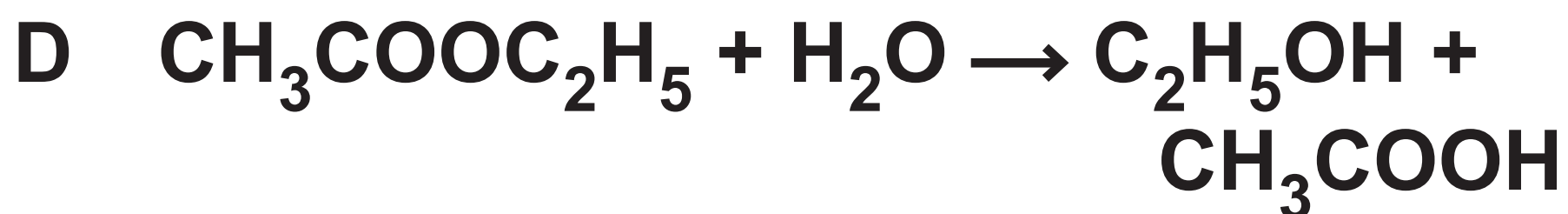
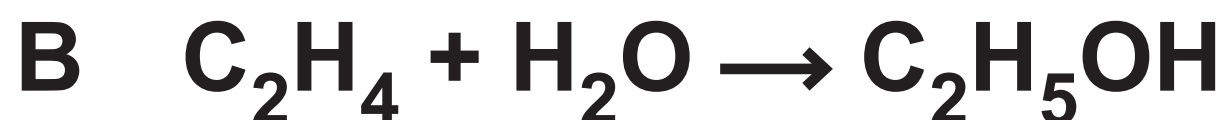
**C 5**

**D 6**

**Your answer**

**7 Ethanol can be prepared by different reactions.**

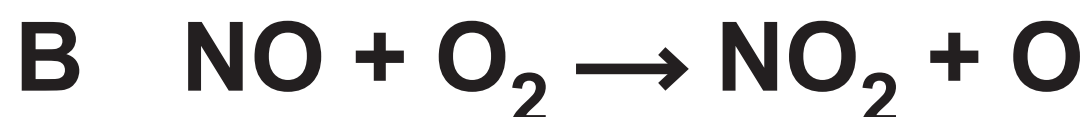
**Which reaction has the lowest atom economy? [1]**



**Your answer**

**8 The breakdown of ozone is catalysed by NO radicals.**

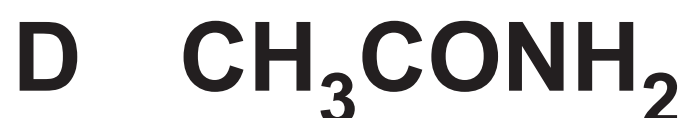
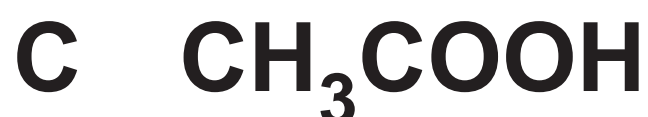
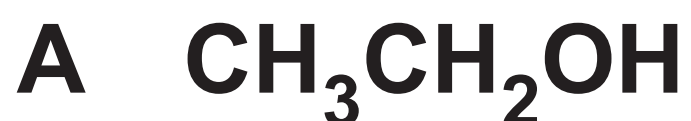
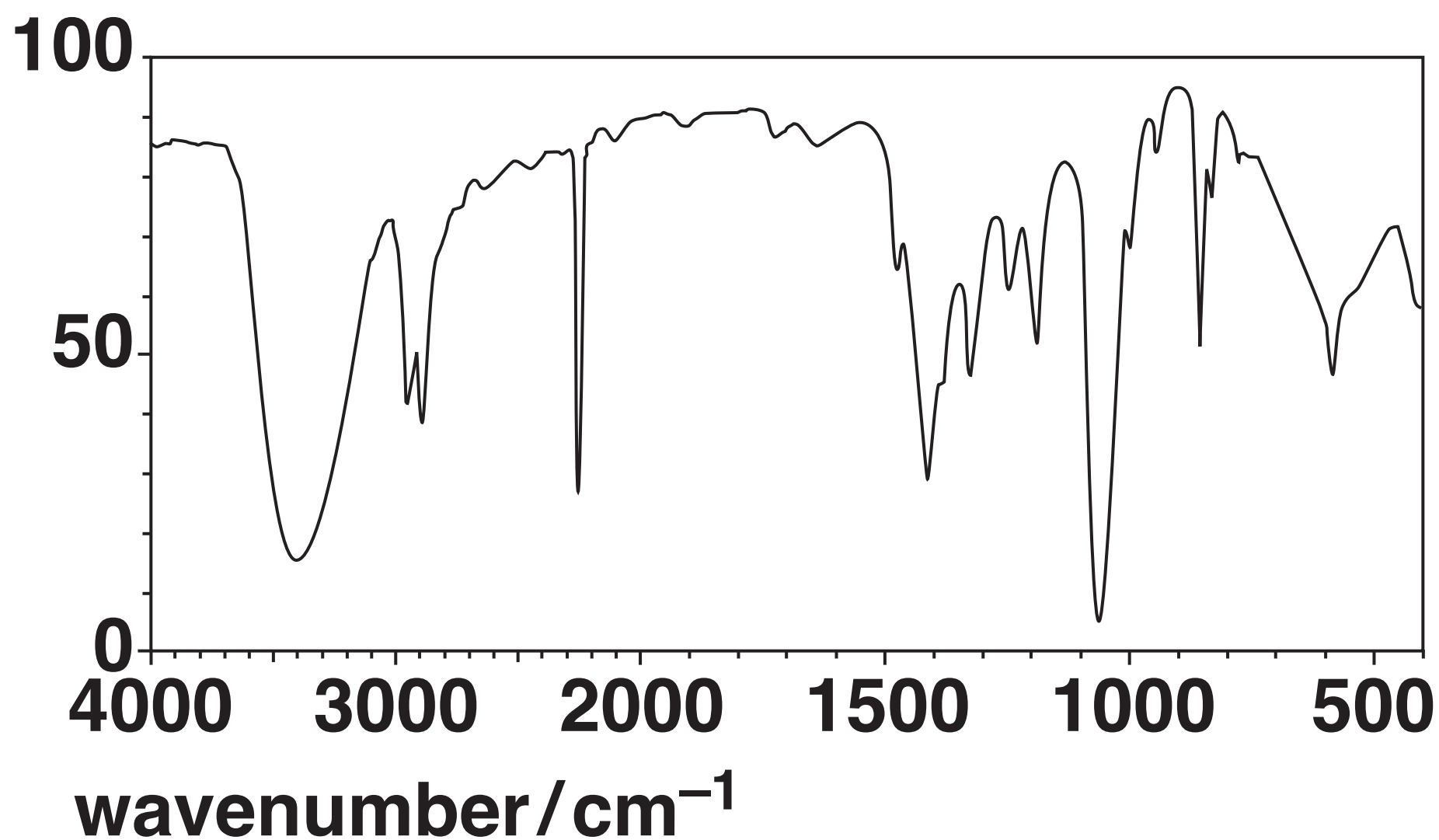
**Which equation is a propagation step in the mechanism for this process? [1]**



**Your answer**

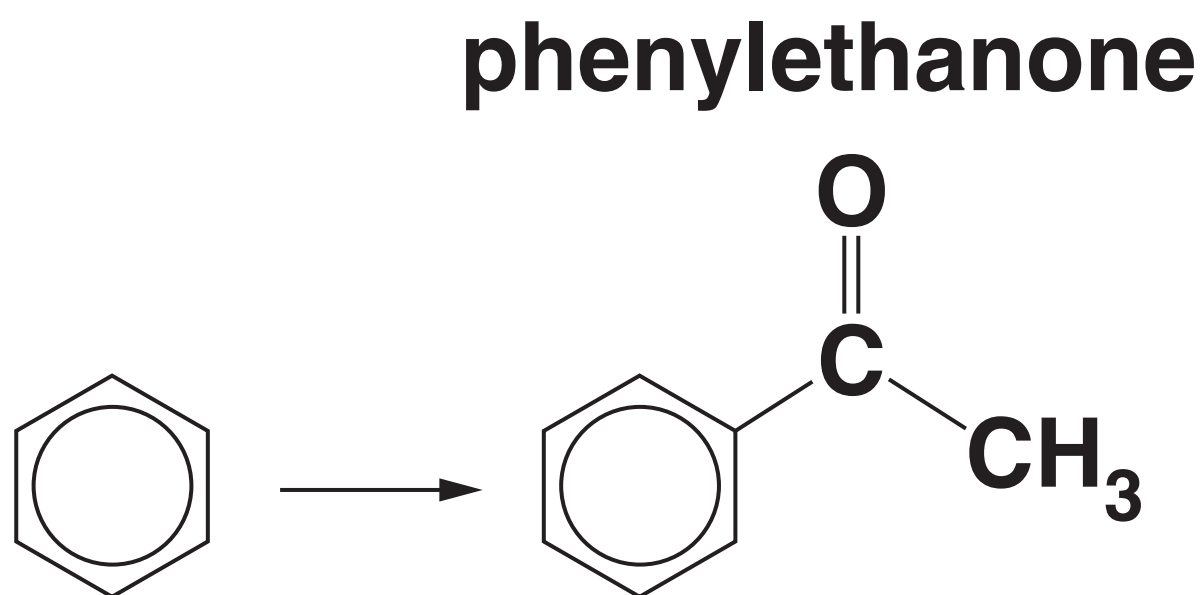
9 Which compound could have produced the IR spectrum below? [1]

transmittance (%)



Your answer

**10 Benzene reacts with an organic reagent in the presence of a halogen carrier to form phenylethanone.**



**Which organic reagent is required? [1]**

**A CH<sub>3</sub>CH<sub>2</sub>OH**

**B CH<sub>3</sub>CHO**

**C CH<sub>3</sub>COC*l***

**D CH<sub>3</sub>COOH**

**Your answer**

**11 How many straight-chain structural isomers of  $C_7H_{15}Cl$  contain a chiral carbon atom? [1]**

**A 1**

**B 2**

**C 3**

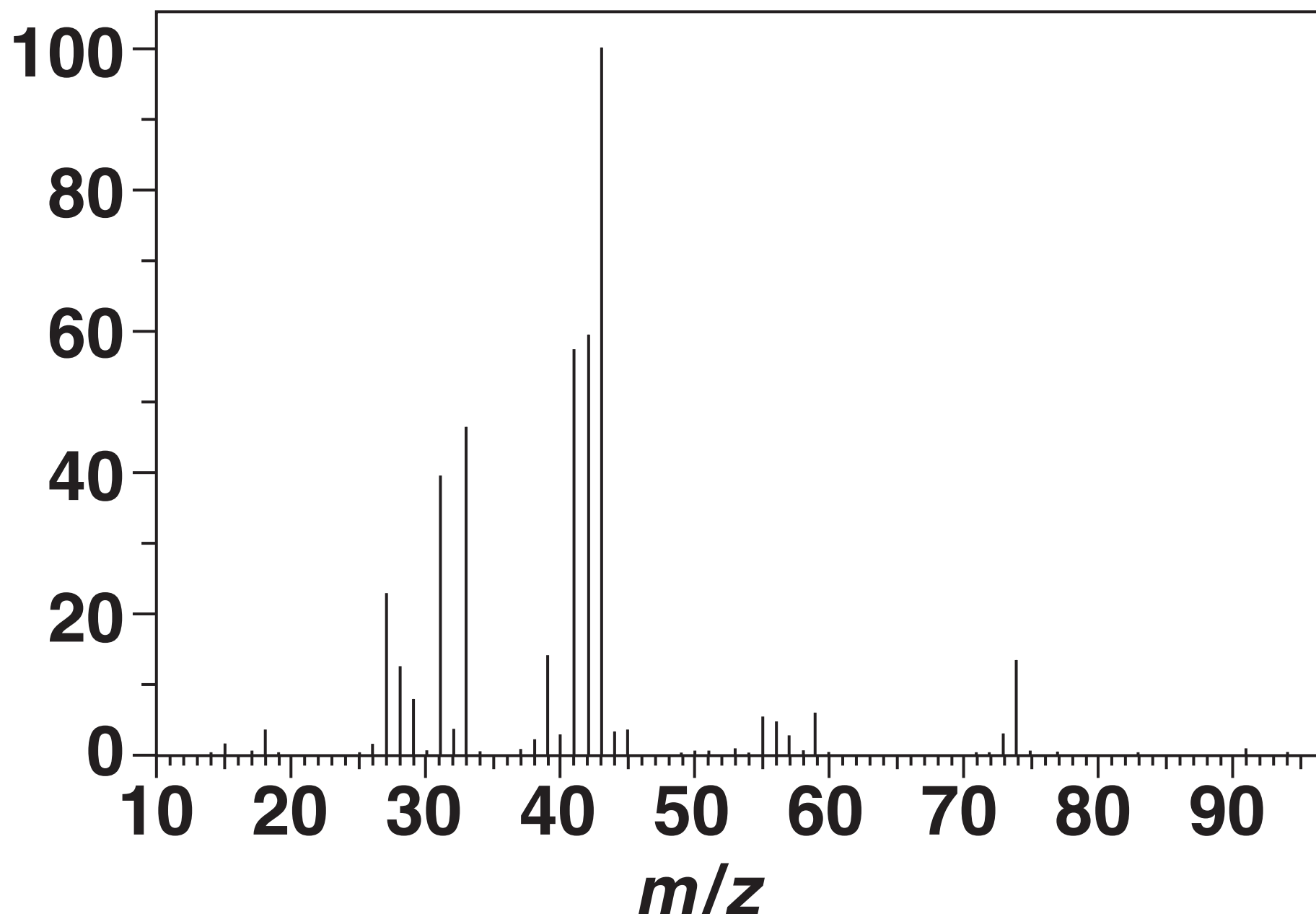
**D 4**

**Your answer**



12 The mass spectrum of  $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$  is shown below.

relative intensity



Which ion is responsible for the peak with the greatest relative intensity? [1]

- A  $\text{CHCH}_2\text{OH}^+$
- B  $\text{CH}_3\text{CH}_2\text{CH}^+$
- C  $(\text{CH}_3)_2\text{CH}^+$
- D  $\text{CH}_3\text{CO}^+$

Your answer

**13 Which statement(s) support(s) the delocalised model for the structure of benzene? [1]**

- 1 All carbon–carbon bonds have the same length.**
- 2 The enthalpy change of hydrogenation of benzene is less exothermic than expected.**
- 3 Bromine reacts with benzene less readily than with cyclohexene.**

- A 1, 2 and 3**
- B Only 1 and 2**
- C Only 2 and 3**
- D Only 1**

**Your answer**

**14 A solid organic compound can be purified by recrystallisation.**

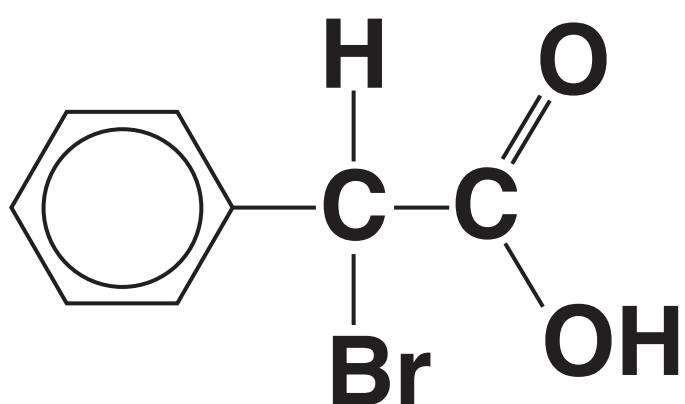
**Which statement(s) about recrystallisation is/are true? [1]**

- 1 The organic compound is more soluble in hot solvent.**
- 2 The hot solution is cooled before the purified organic compound is collected.**
- 3 The melting point of the purified organic compound is lower than the impure compound.**

- A 1, 2 and 3**
- B Only 1 and 2**
- C Only 2 and 3**
- D Only 1**

**Your answer**

**15 Which of the following could react with the compound below to form a carbon–carbon bond? [1]**



- 1     $\text{CH}_3\text{Cl}$  and  $\text{AlCl}_3$**
- 2    KCN in ethanol**
- 3     $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{SO}_4$**

- A    1, 2 and 3**
- B    Only 1 and 2**
- C    Only 2 and 3**
- D    Only 1**

**Your answer**

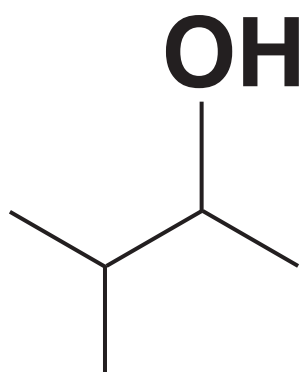
## SECTION B

Answer ALL the questions.

**16 This question is about reactions of organic compounds containing carbon, hydrogen and oxygen.**

**(a) A chemist investigates two reactions of alcohol A, shown below.**

**ALCOHOL A**



**(i) What is the systematic name of alcohol A?**

\_\_\_\_\_ [1]

**(ii) What is the structural formula of alcohol A?**

\_\_\_\_\_ **[1]**

**(iii) The chemist heats alcohol A with an acid catalyst to form a mixture containing TWO alkenes.**

**Draw the structures of the TWO alkenes formed in this reaction.**  
**[2]**

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- (iv) The chemist heats alcohol A with sodium chloride and sulfuric acid.**

**Construct a balanced equation for this reaction.**

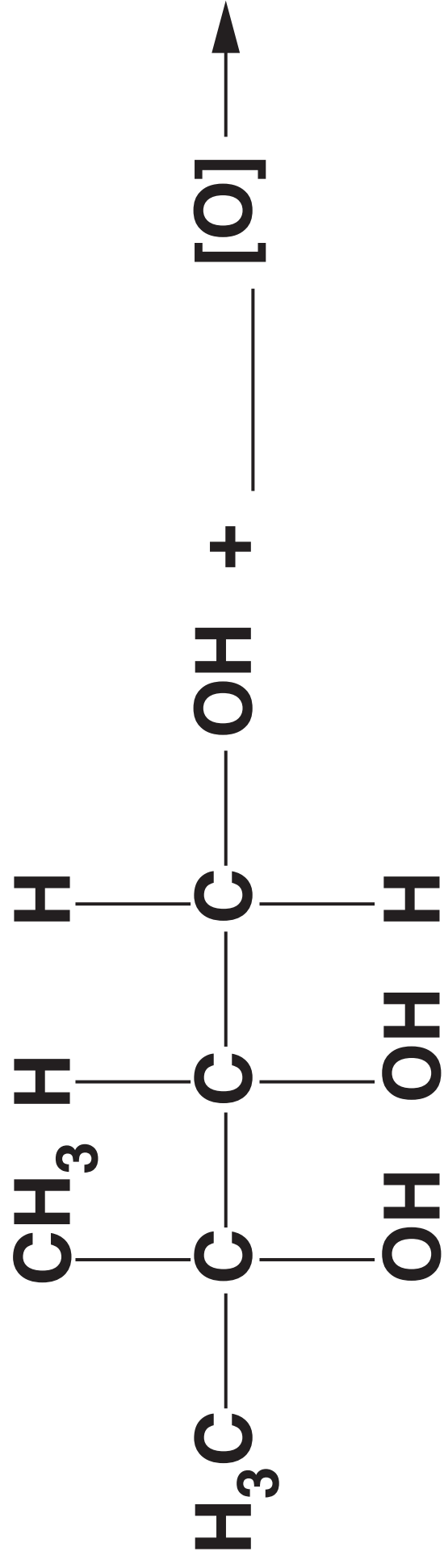
**Show structures for the organic compounds in your equation. Use the space below. [2]**

**(b) Compound B, shown opposite, is refluxed with excess acidified potassium dichromate(VI) to form a single organic product.**

**Complete the equation for this reaction. [2]**

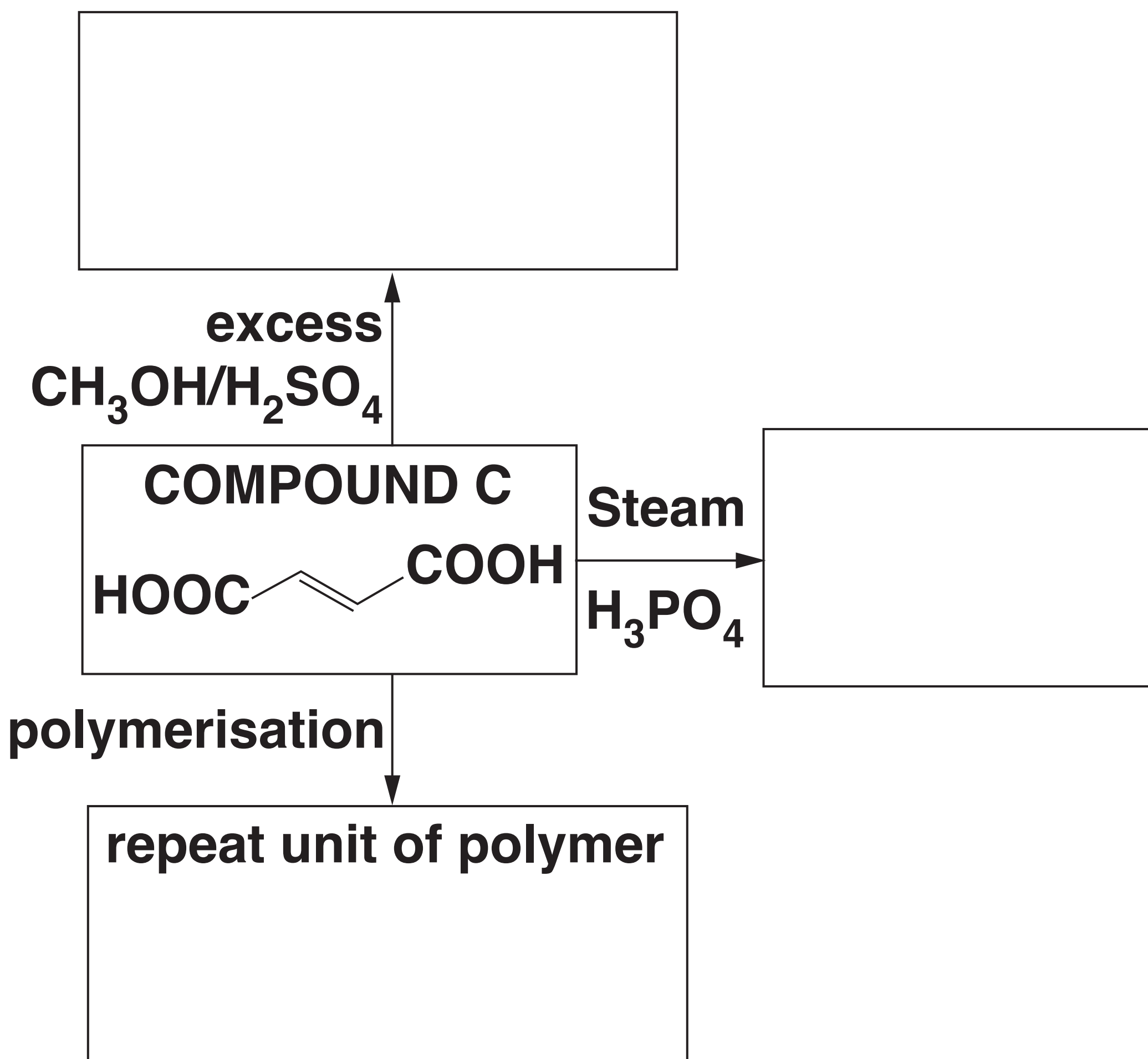


## COMPOUND B



(c) The flowchart below shows some reactions of compound C.

In the boxes, draw the organic products of these reactions. [3]



**17 The general formula of an  $\alpha$ -amino acid is  $\text{RCH}(\text{NH}_2)\text{COOH}$ .**

**(a) The  $\alpha$ -amino acid cysteine ( $\text{R} = \text{CH}_2\text{SH}$ ) shows optical isomerism.**

**Draw 3-D diagrams to show the optical isomers of cysteine. Use the space below. [2]**

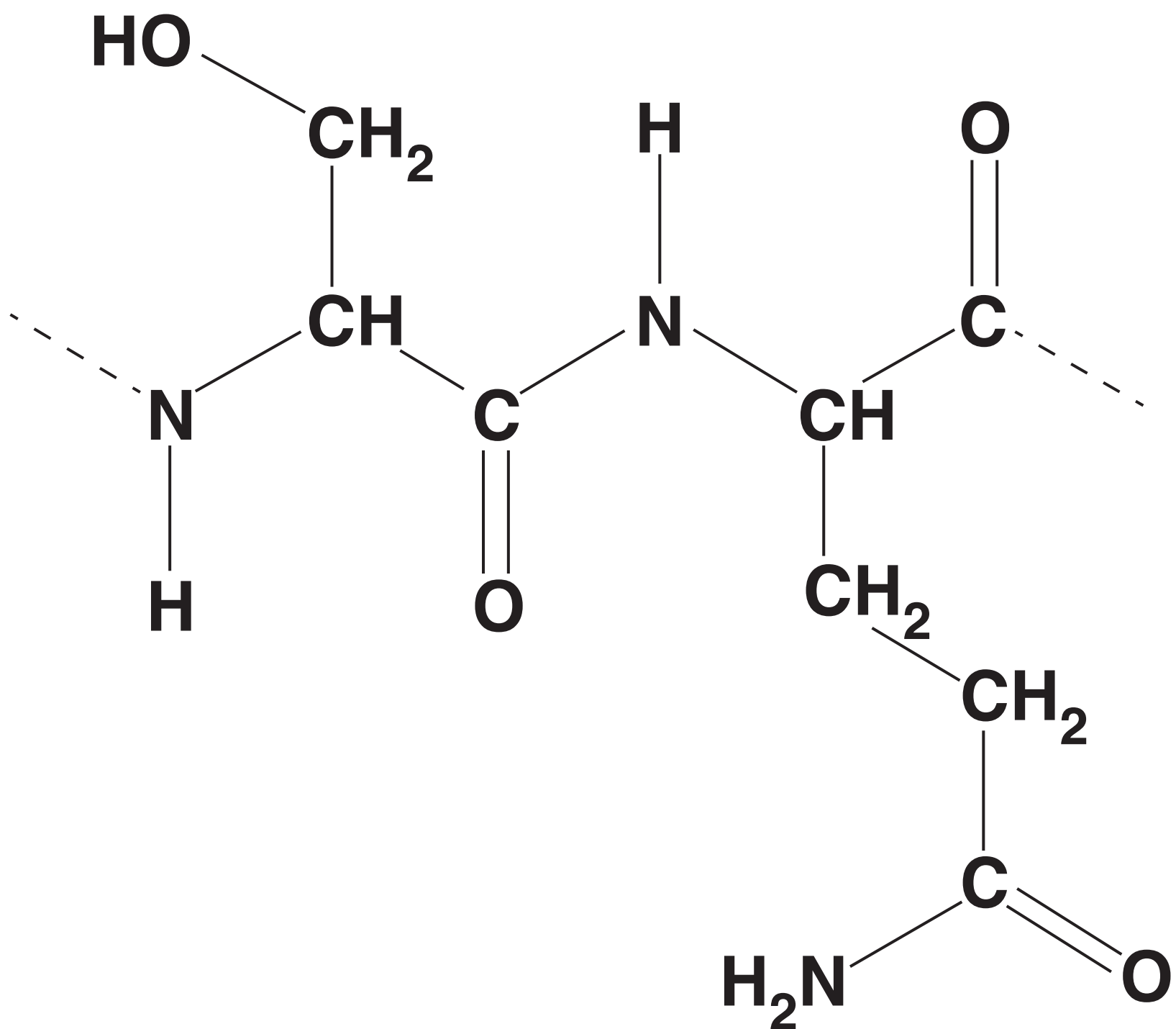
**(b) The  $\alpha$ -amino acid lysine  
( $R = (CH_2)_4NH_2$ ) reacts with an  
excess of dilute hydrochloric acid  
to form a salt.**

**Draw the structure of the salt  
formed in this reaction. Use the  
space below. [2]**

**Question 17 part (c) begins on page 26**

**(c)  $\alpha$ -Amino acids can react to form proteins.**

**A short section of a protein chain is shown below.**



**A student hydrolyses the protein with hot NaOH(aq).**

**Draw the structures of the organic products formed from this section of the protein. Use the space below.**

**[3]**

**18 This question is about aromatic compounds.**

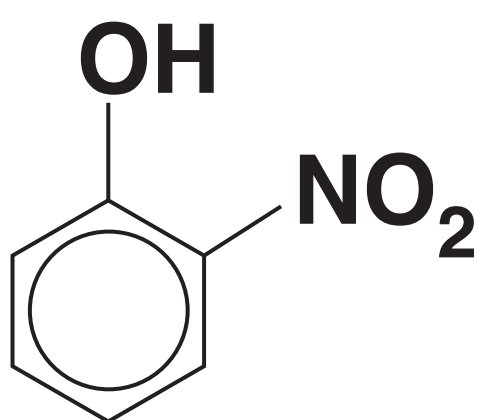
**(a) Phenol undergoes nitration more readily than benzene.**

**(i) A student carries out the nitration of phenol with dilute nitric acid to produce 2-nitrophenol and 4-nitrophenol.**

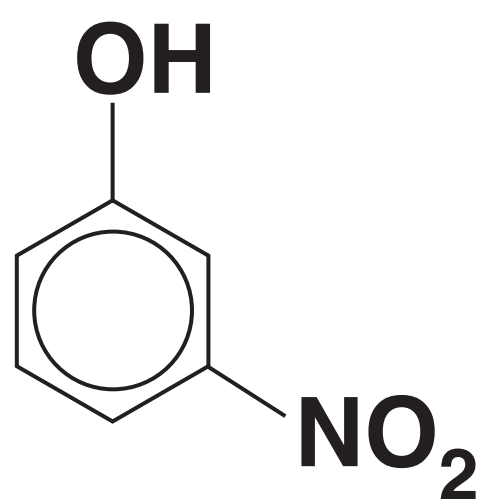
**A small amount of 3-nitrophenol is also produced.**



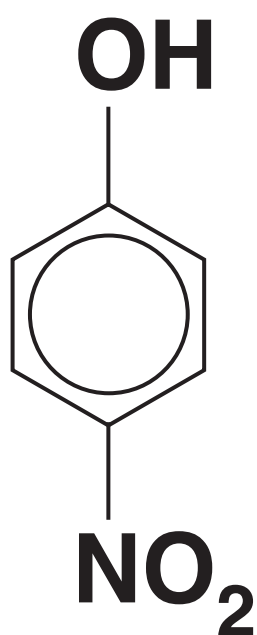
## 2-NITROPHENOL



## 3-NITROPHENOL



## 4-NITROPHENOL



**The student thought that  $^{13}\text{C}$  NMR spectroscopy could be used to distinguish between these three nitrophenols.**

**Explain whether the student is correct.**

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**[3]**

**(ii) Explain why phenol is nitrated more readily than benzene.**

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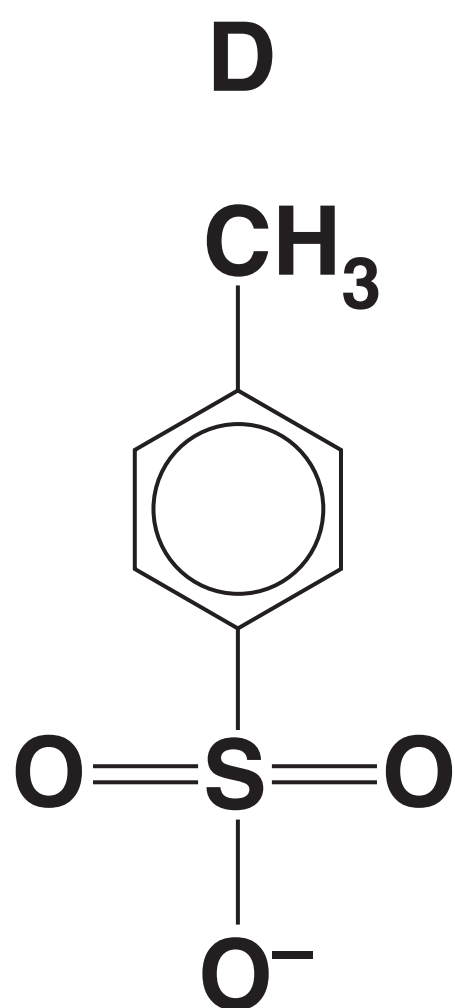
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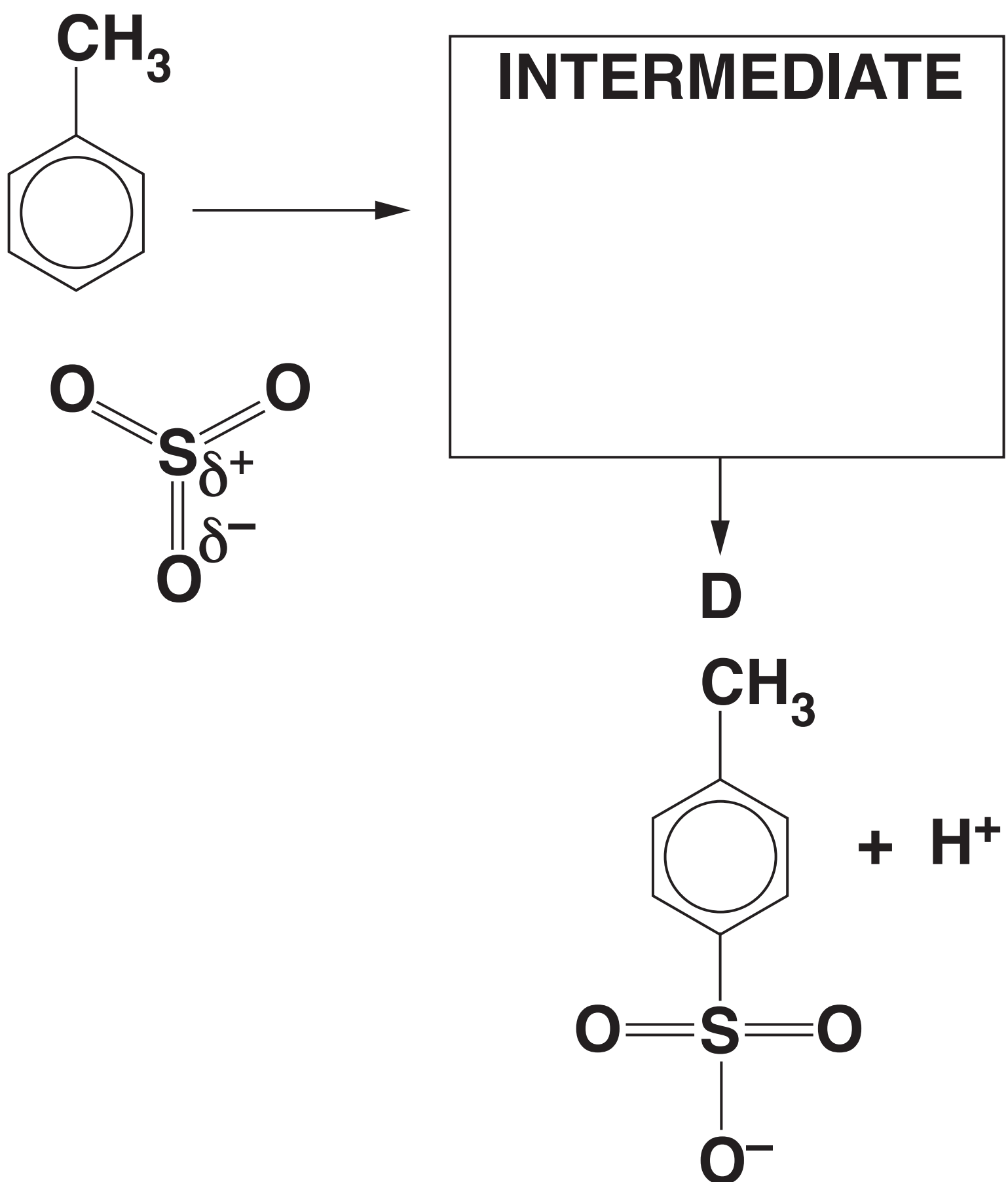
**[3]**

**(b) Methylbenzene reacts with sulfur trioxide,  $\text{SO}_3$ , to form D, shown below.**



**The electrophile in this reaction is  $\text{SO}_3$ .**

Complete the mechanism for the formation of D.  
Show curly arrows and the structure of the intermediate. [3]



**19 This question is about the hydrolysis of haloalkanes.**

**(a) The rate of hydrolysis of a haloalkane depends on the halogen present.**

**State and explain how the halogen in the haloalkane affects the rate of hydrolysis.**

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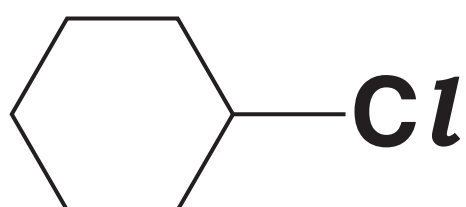
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**[2]**

**(b) Chlorocyclohexane is hydrolysed with aqueous sodium hydroxide.**

**Outline the mechanism for this reaction.**

**Show curly arrows, relevant dipoles and the products. [3]**



**(c) A student hydrolyses a haloalkane, E, using the following method.**

**0.0100 mol of haloalkane E is refluxed with excess NaOH(aq) to form a reaction mixture containing an organic product F.**

**The reaction mixture is neutralised with dilute nitric acid.**

**Excess AgNO<sub>3</sub>(aq) is added to the reaction mixture. 1.88 g of a precipitate G forms.**

**Organic product, F, has a molar mass of 74.0 g mol<sup>-1</sup> and has a chiral carbon atom.**



- (i) Draw a LABELLED diagram to show how the student would carry out the hydrolysis of haloalkane E. Use the space below. [2]**

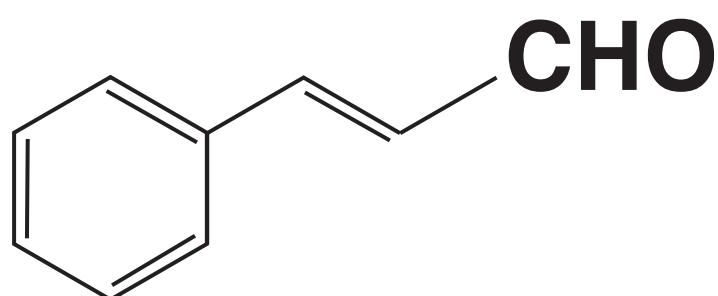
**(ii) Analyse the information to identify E, F and G.**

**Show your working. Use the space below. [3]**

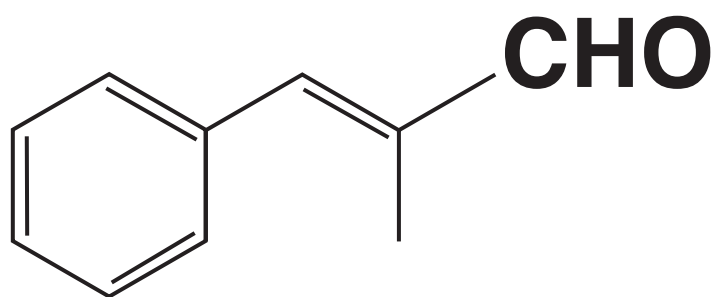
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**20 Cinnamaldehyde and methylcinnamaldehyde are naturally occurring organic compounds.**

## **CINNAMALDEHYDE**



## **METHYLCINNAMALDEHYDE**



**(a) Methylcinnamaldehyde is an *E* stereoisomer.**

**Explain this statement in terms of the Cahn-Ingold-Prelog (CIP) rules.**

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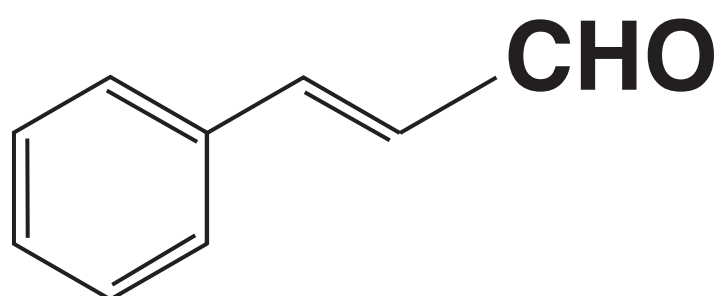
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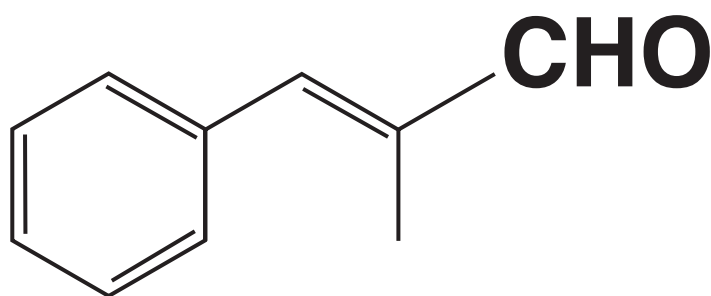
[2]

**(b) A student plans to carry out some chemical tests on both cinnamaldehyde and methylcinnamaldehyde.**

### **CINNAMALDEHYDE**



### **METHYLCINNAMALDEHYDE**



- (i) Suggest a suitable chemical test to confirm that both compounds contain an unsaturated carbon chain.**

**Your answer should include the reagent and observations.**

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**[1]**

- (ii) Describe a chemical test to confirm that both compounds contain an aldehyde functional group.**

**Your answer should include the reagent and observations.**

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**[1]**

**(iii) Describe a chemical test to confirm that cinnamaldehyde and methylcinnamaldehyde contain a carbonyl group.**

**How could the products of this test be used to distinguish between the two compounds?**

**Your answer should NOT include spectroscopy.**

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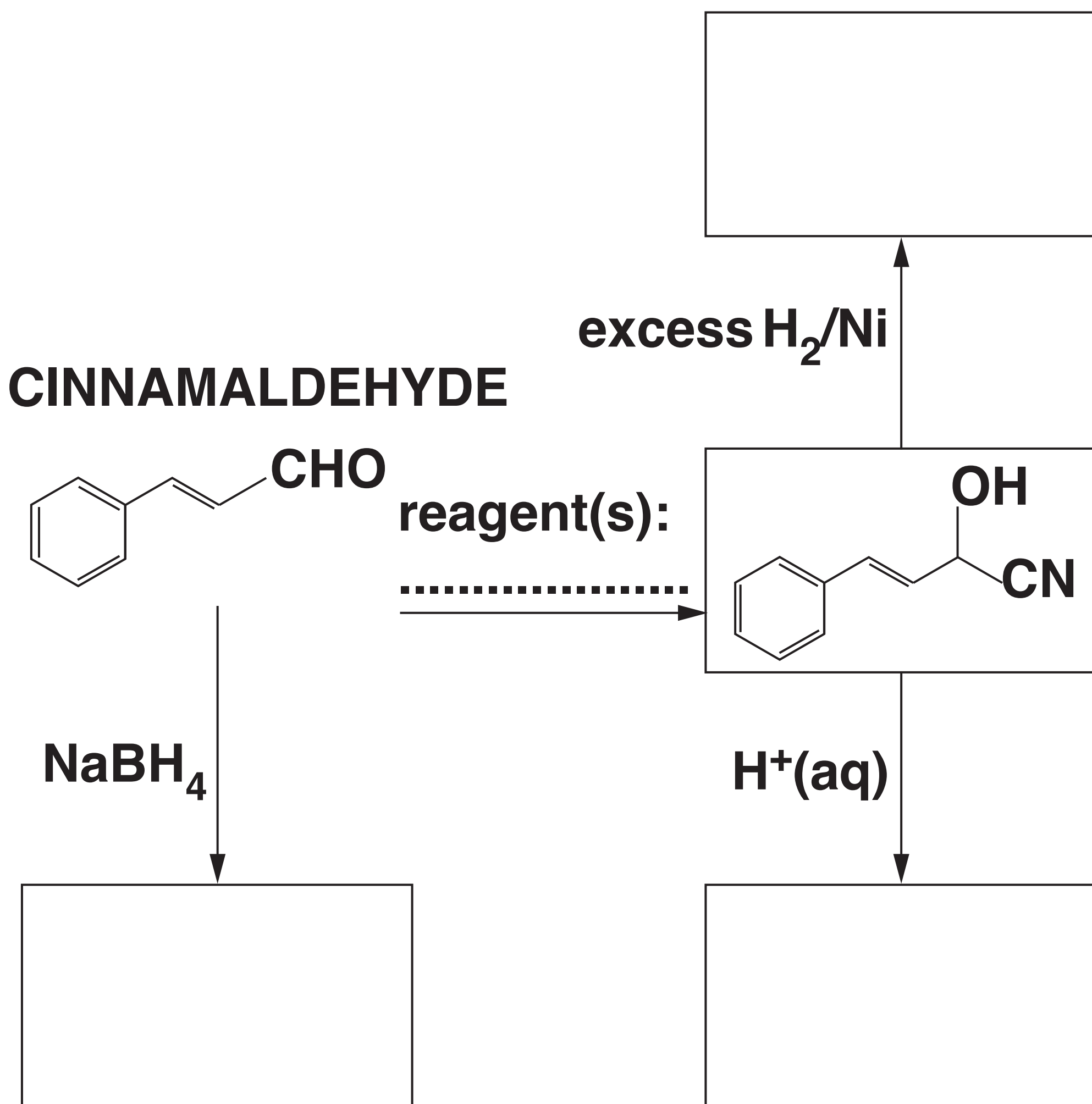
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**[3]**



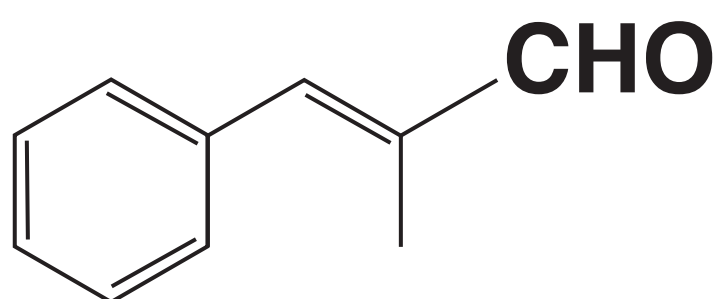
(c) The flowchart below shows some reactions starting with cinnamaldehyde.

Draw the structures of the missing organic compounds in the boxes and add the missing reagent(s) on the dotted line. [5]



**(d)\* Methylcinnamaldehyde reacts with iodine monochloride,  $\text{ICl}$ , by electrophilic addition. The reaction produces a mixture containing two different organic products.**

## **METHYLCINNAMALDEHYDE**



**The electronegativity values of chlorine and iodine are given in the table below.**

	<b>Pauling electronegativity value</b>
<b><math>\text{Cl}</math></b>	<b>3.0</b>
<b><math>\text{I}</math></b>	<b>2.5</b>

**Outline the mechanism, using the ‘curly arrow’ model, for the formation of ONE of the organic products and explain which of the two possible organic products is more likely to be formed.**

[illegible]

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**Additional answer space if required.**

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**21 This question is about aromatic carboxylic acids and their derivatives.**

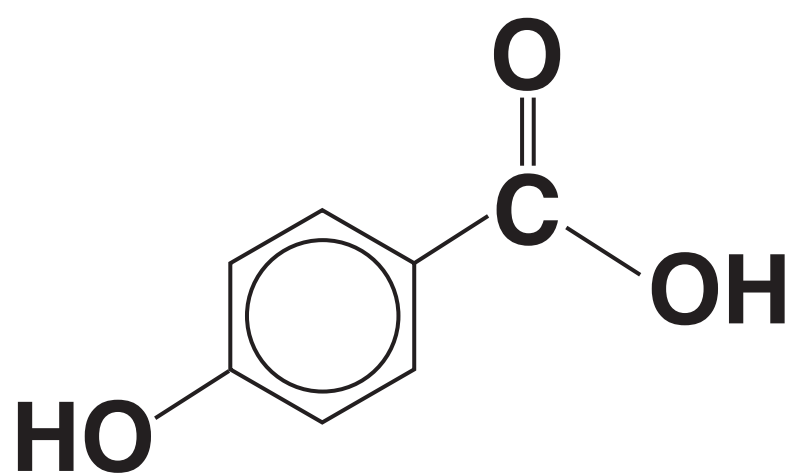
**(a) The flowchart on page 51 shows some reactions of compound H.**

**In the boxes, draw the organic products of these reactions. [3]**

**Na<sub>2</sub>CO<sub>3</sub>(aq)**

**NaOH(aq)**

**COMPOUND H**

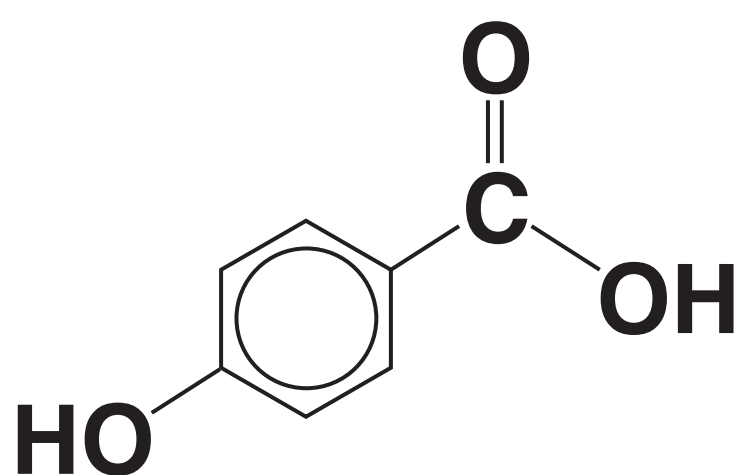


**Br<sub>2</sub>**

(b) Compound H is used in the synthesis of polymer I, as shown in the flowchart below.

Complete the flowchart by drawing the structure of the acyl chloride and TWO repeat units of polymer I, and stating the FORMULA of the reagent(s) required for the first stage on the dotted line. [4]

COMPOUND H



ACYL CHLORIDE

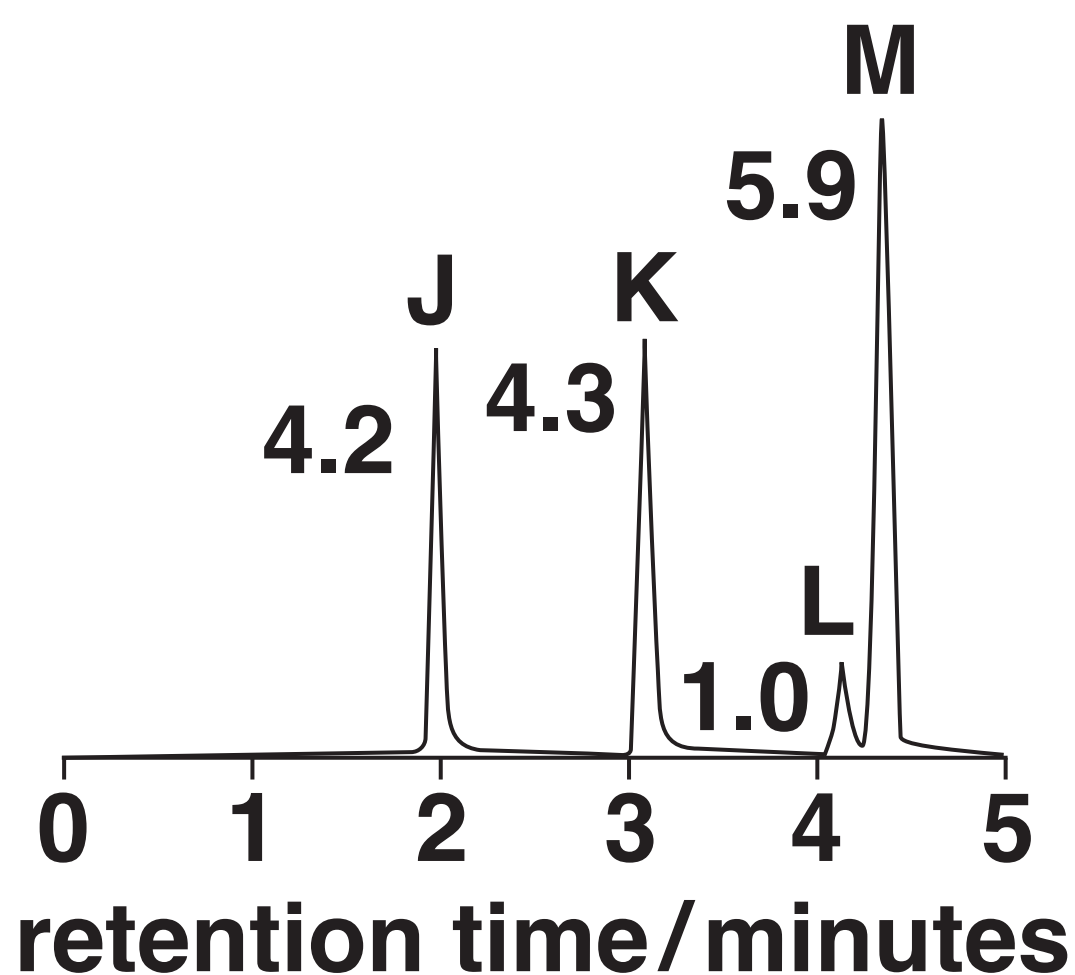


TWO REPEAT UNITS OF POLYMER I



- (c) A cosmetic product containing four esters, J, K, L and M, is analysed by gas chromatography and mass spectrometry. The results are shown below.

## **GAS CHROMATOGRAM**



The numbers by the peaks are the relative molar proportions of the compounds in the mixture.

# MASS SPECTROMETRY

<b>ester</b>	<b><i>m/z</i> of molecular ion peak</b>
<b>J</b>	<b>152</b>
<b>K</b>	<b>166</b>
<b>L</b>	<b>180</b>
<b>M</b>	<b>180</b>

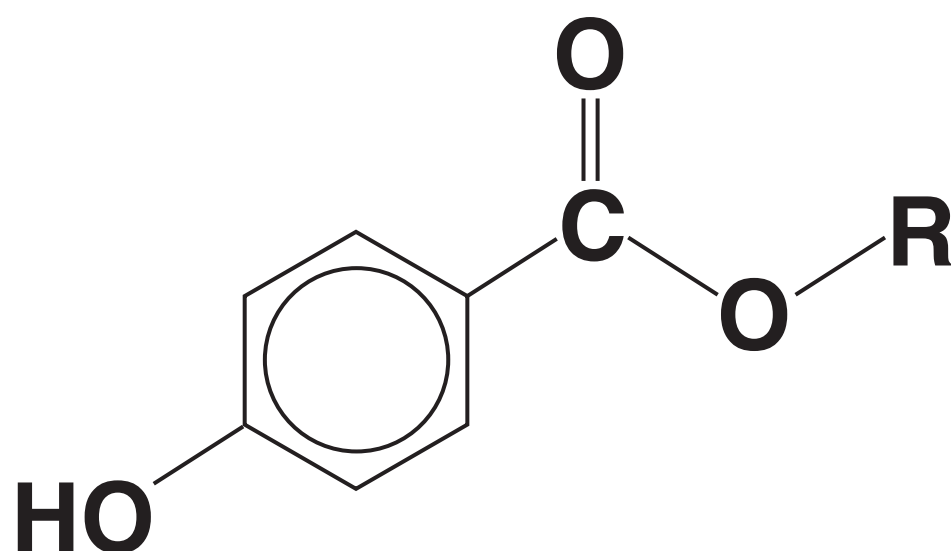
- (i) The concentration of ester K in the cosmetic product is  $9.13 \times 10^{-2} \text{ g dm}^{-3}$ .

Using the results, calculate the concentration, in  $\text{mol dm}^{-3}$ , of ester M in the cosmetic product.

Give your answer to TWO significant figures.

concentration of ester M = \_\_\_\_\_  $\text{mol dm}^{-3}$   
[2]

**(ii) A general structure for esters J, L and M is shown below.**



**Where 'R' is an alkyl group.**

**Use the mass spectrometry results to deduce possible structures for esters J, L and M.**

**[3]**

<b>J</b>	<b>L</b>	<b>M</b>
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**22 The relative molecular masses and boiling points of some fuels are shown in TABLE 22.1.**

**TABLE 22.1**

<b>Fuel</b>	<b>Relative molecular mass</b>	<b>Boiling point/°C</b>
<b>hexane</b>	<b>86</b>	<b>69</b>
<b>pentan-1-ol</b>	<b>88</b>	<b>138</b>
<b>heptane</b>	<b>100</b>	<b>98</b>

**(a) Write an equation for the incomplete combustion of heptane.**

**\_\_\_\_\_ [1]**

[illegible]

**(c) Fuel additives are often used to improve the combustion of a fuel.**

**(i) Compound N is a fuel additive containing carbon, hydrogen and oxygen only.**

**Complete combustion of 1.71 g of compound N produces 2.97 g of  $\text{CO}_2$  and 1.62 g of  $\text{H}_2\text{O}$ . The relative molecular mass of compound N is 76.0.**

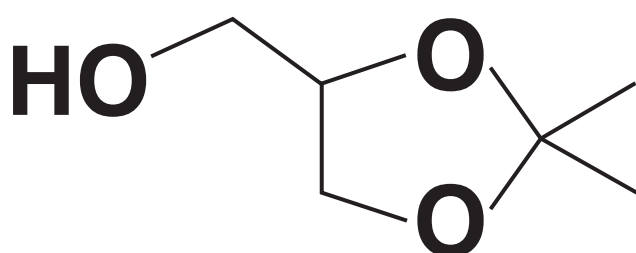
**Calculate the molecular formula of N and suggest a possible structure for the compound. [5]**



**compound N**

- (ii) Solketal has been investigated as a potential fuel additive.**

**solketal**



**Solketal is synthesised from propane-1,2,3-triol and a carbonyl compound.**

**Construct a balanced equation for this synthesis.**

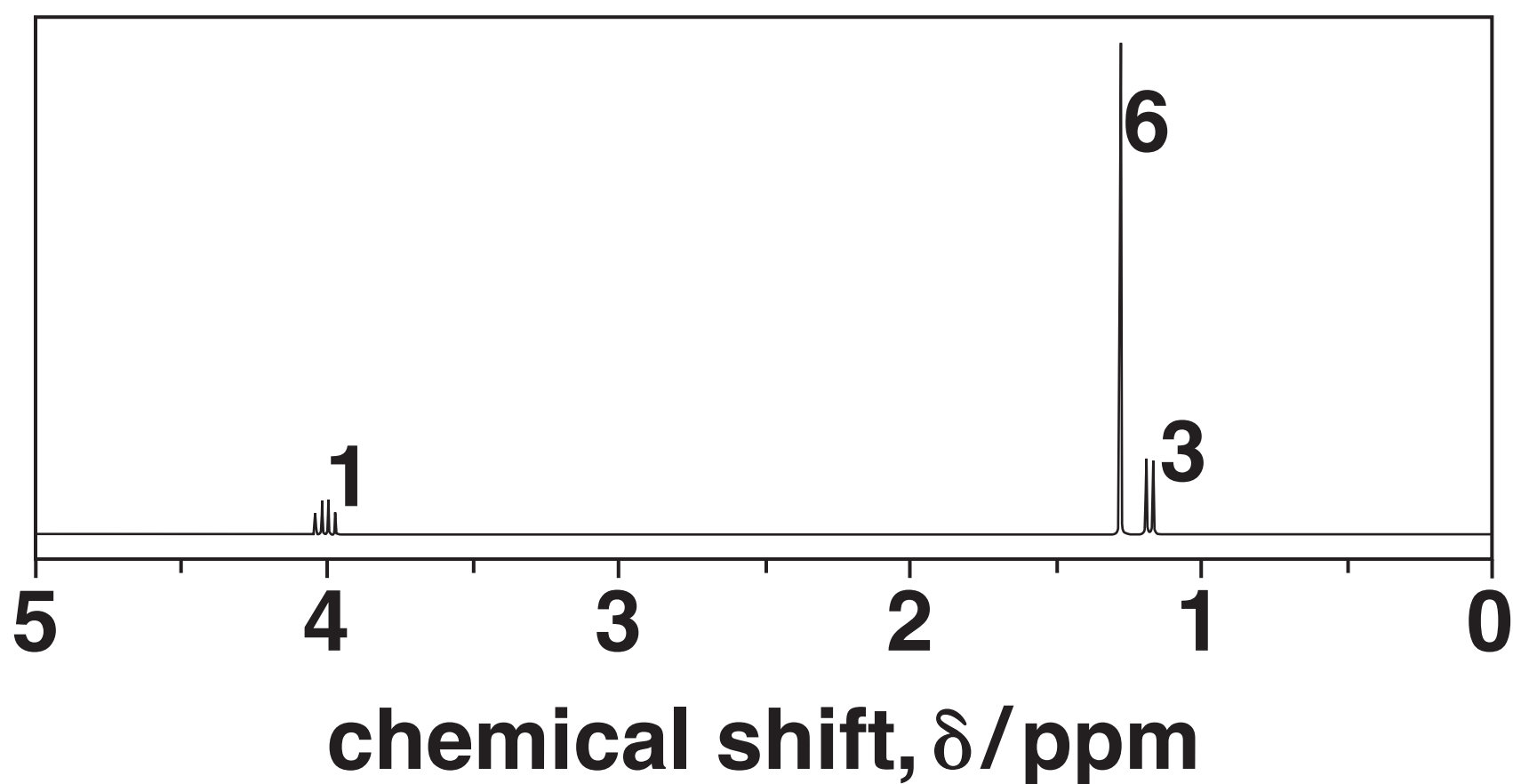
**Show structures for the organic compounds in your equation.  
Use the space below. [2]**

**(d)\* A scientist is researching compounds that might be suitable as fuel additives. One of the compounds gives the analytical results below.**

**ELEMENTAL ANALYSIS BY MASS:  
C: 54.54%; H: 9.10%; O: 36.36%**

**MASS SPECTRUM:  
Molecular ion peak at  $m/z = 132.0$**

**$^1\text{H}$  NMR SPECTRUM IN  $\text{D}_2\text{O}$**



**The numbers by the peaks are the relative peak areas.**

**When the spectrum is run without  $D_2O$ , there are TWO additional peaks with the same relative peak areas at 11.0 ppm and 3.6 ppm.**

**Use the information provided to suggest a structure for the compound.**

**Show ALL your reasoning. [6]**

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**Additional answer space if required.**

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**END OF QUESTION PAPER**

## ADDITIONAL ANSWER SPACE

**If additional space is required, you should use the following lined page(s). The question number(s) must be clearly shown in the margin(s).**

[illegible]

