OCR
Oxford Cambridge and RSA

# Tuesday 11 June 2019 – Afternoon

## A Level Chemistry A

### H432/02 Synthesis and analytical techniques

**Time allowed: 2 hours 15 minutes**

**You must have:**
- the Data Sheet for Chemistry A (sent with general stationery)

**You may use:**
- a scientific or graphical calculator

Please write clearly in black ink. **Do not write in the barcodes.**

Centre number | | | | | | Candidate number | | | | |

First name(s) _____

Last name _____

**INSTRUCTIONS**
- Use black ink. You may use an HB pencil for graphs and diagrams.
- Answer **all** the questions.
- Where appropriate, your answers should be supported with working. Marks may be given for a correct method even if the answer is incorrect.
- 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 (*****).
- This document consists of **32** pages.

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## 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 alkane has the highest boiling point?

**A** $CH_3(CH_2)_5CH_3$

**B** $(CH_3)_3CCH(CH_3)_2$

**C** $CH_3(CH_2)_3CH(CH_3)_2$

**D** $(CH_3)_2CHCH_2CH(CH_3)_2$

Your answer ☐

**[1]**

**2** Butane reacts with chlorine in the presence of ultraviolet radiation to form a mixture of organic products.

Which equation shows a propagation step in the mechanism for this reaction?

**A** $Cl_2 \rightarrow \bullet Cl + \bullet Cl$

**B** $\bullet Cl + \bullet C_4H_8Cl \rightarrow C_4H_8Cl_2$

**C** $C_4H_9Cl + \bullet Cl \rightarrow C_4H_8Cl_2 + \bullet H$

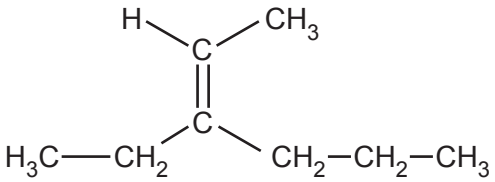
**D** $\bullet Cl + C_4H_9Cl \rightarrow \bullet C_4H_8Cl + HCl$

Your answer ☐

**[1]**

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**3** What is the name of the compound below?



**A** 3-Propylpent-2-ene

**B** 3-Propylpent-3-ene

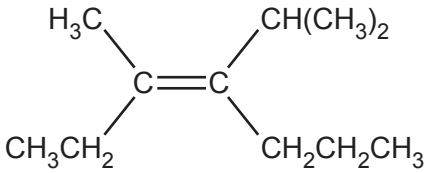
**C** 3-Ethylhex-2-ene

**D** 4-Ethylhex-4-ene

Your answer ☐

**[1]**

**4** The structure of a stereoisomer is shown below.



Which term correctly describes this stereoisomer?

**A** *cis*-

**B** *trans*-

**C** *E*-

**D** *Z*-

Your answer ☐

**[1]**

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**5** Which types of bonds are broken and formed in the reaction of ethene and bromine?

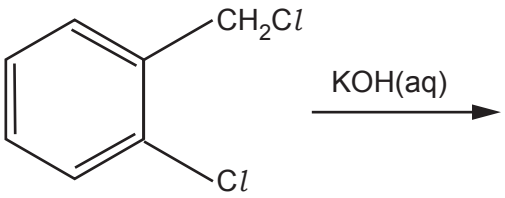
| | Types of bond broken | Types of bond formed |
|---|---|---|
| **A** | σ | π |
| **B** | π | σ |
| **C** | σ and π | π |
| **D** | σ and π | σ |

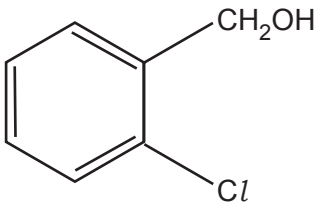
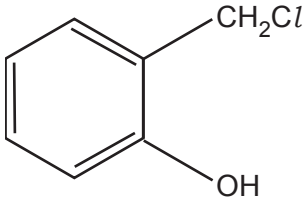
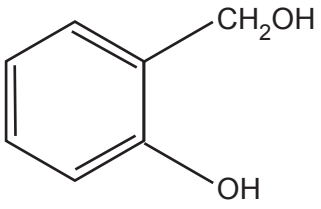
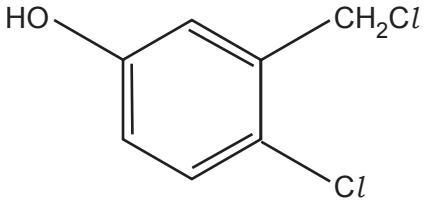
Your answer ☐

**[1]**

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**6** What is the organic product of the reaction below?



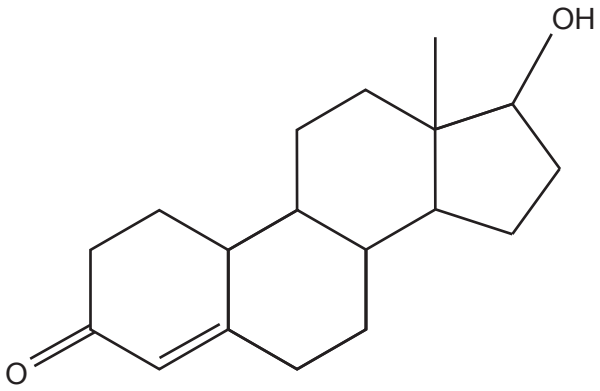

| | |
|---|---|
| **A** |   |
| **B** |   |
| **C** |   |
| **D** |   |

Your answer ☐

**[1]**

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**7** What is the number of chiral carbon atoms in the steroid molecule below?




**A** 5

**B** 6

**C** 7

**D** 8

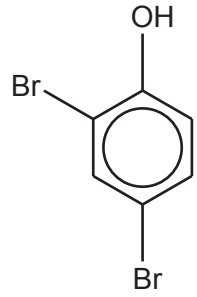
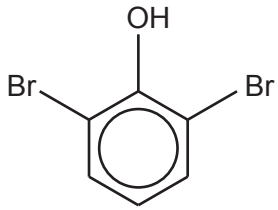
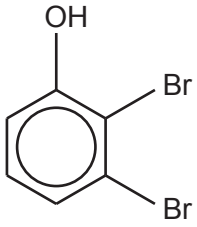
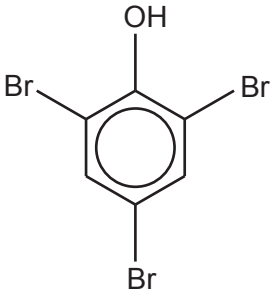
Your answer ☐

**[1]**

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**8** Phenol reacts with bromine.

Which is the **least** likely organic product?

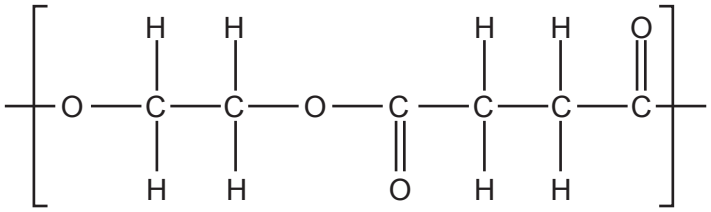
| | |
|---|---|
| **A** |   |
| **B** |   |
| **C** |   |
| **D** |   |

Your answer ☐

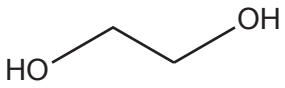
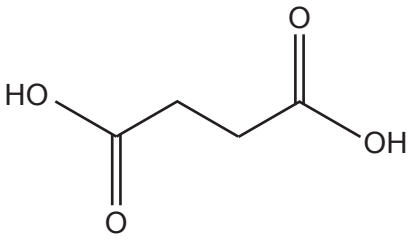
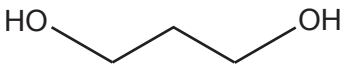
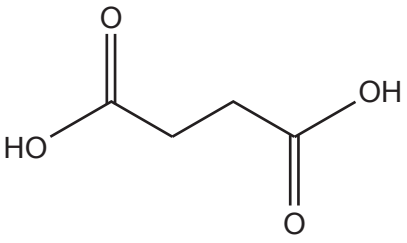
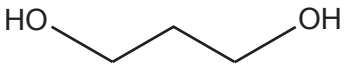
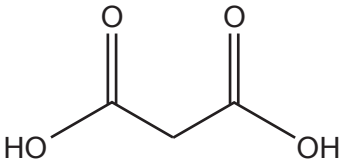
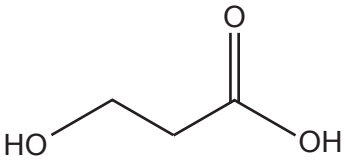
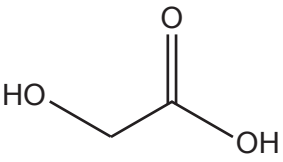
**[1]**

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**9** The repeat unit of a polymer is shown below.



Which monomers could form this polymer?

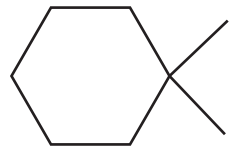
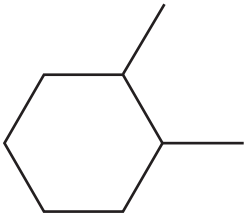
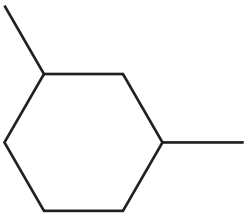
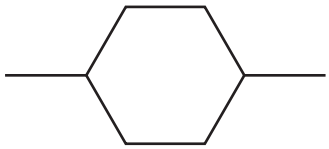
| | | |
|---|---|---|
| **A** |  |  |
| **B** |  |  |
| **C** |  |  |
| **D** |  |  |

Your answer ☐

**[1]**

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**10** Which compound shows 4 peaks in its carbon-13 NMR spectrum?

| | |
|---|---|
| **A** |  |
| **B** |  |
| **C** |  |
| **D** |  |

Your answer ☐

**[1]**

**11** A student reacts 4.50 g of $C_6H_5NH_2$ with excess $CH_3COCl$ in the reaction below.

$$C_6H_5NH_2 + CH_3COCl \rightarrow C_6H_5NHCOCH_3 + HCl$$

$M_r = 93.0$ $M_r = 135.0$

The reaction produces 3.25 g of $C_6H_5NHCOCH_3$.

What is the percentage yield of $C_6H_5NHCOCH_3$?

**A** 49.8

**B** 68.9

**C** 72.2

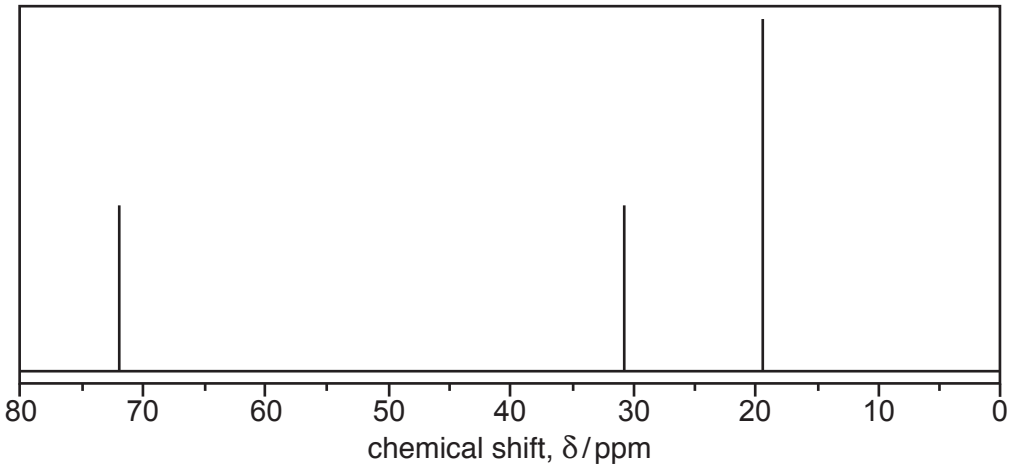
**D** 95.4

Your answer ☐

**[1]**

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**12** A compound produces the $^{13}C$ NMR spectrum below.




Which compound could have produced this spectrum?

**A** Propane

**B** 2-Methylbutane

**C** 2-Methylpropan-1-ol

**D** 2-Methylpropan-2-ol

Your answer ☐

**[1]**

**13** A carbonyl compound is reacted with $NaBH_4$.

Which compound(s) could be formed?

1 2-Methylpentan-2-ol

2 2-Methylpentan-1-ol

3 3-Methylpentan-2-ol

**A** 1, 2 and 3

**B** Only 1 and 2

**C** Only 2 and 3

**D** Only 1

Your answer ☐

**[1]**

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**14** Which chemical(s) can react with phenol?

1 Potassium hydroxide

2 Ethanoyl chloride

3 Nitric acid

**A** 1, 2 and 3

**B** Only 1 and 2

**C** Only 2 and 3

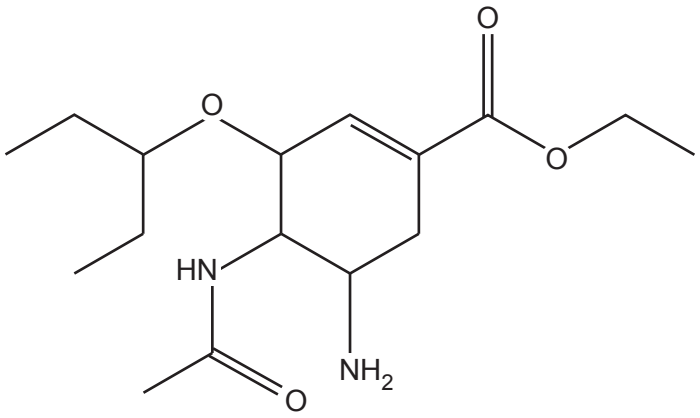
**D** Only 1

Your answer ☐

**[1]**

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**15** The structure of a compound used to treat influenza is shown below.




Which functional group(s) is/are in a molecule of the compound?

1 Ester

2 Secondary amide

3 Ketone

**A** 1, 2 and 3

**B** Only 1 and 2

**C** Only 2 and 3

**D** Only 1

Your answer ☐

**[1]**

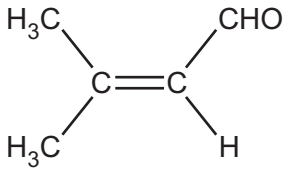
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## SECTION B

Answer **all** the questions.

**16** This question is about unsaturated aldehydes and alcohols.

**(a)** 3-Methylbut-2-enal, shown below, is used as a food flavouring.




**3-methylbut-2-enal**

3-Methylbut-2-enal is reacted with hydrogen bromide, forming a mixture of two organic products.

One of the organic products forms in a much greater quantity than the other organic product.

**(i)** Outline the reaction mechanism for the formation of **one** of the organic products.

Include curly arrows and relevant dipoles.

**[4]**

**(ii)** Explain why one of the organic products forms in a much greater quantity than the other organic product.

.....

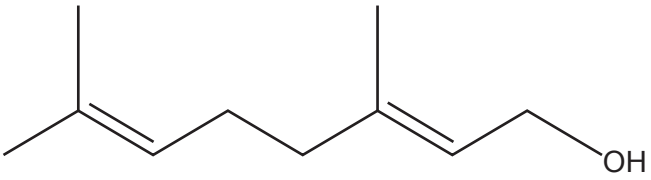
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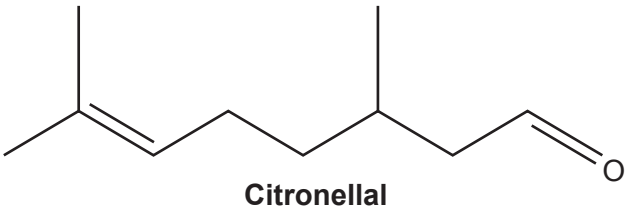
..... **[2]**

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**(b)** Geraniol and citronellal, shown below, are isomers present in 'citronella oil', used as an insect repellent.




**Geraniol**




**Citronellal**

- Geraniol and citronellal are structural isomers of each other.
- They also show stereoisomerism.

**(i)** Describe how the observations from a chemical test would distinguish between geraniol and citronellal.

.....

.....

.....

..... **[2]**

**(ii)** What is the molecular formula of geraniol?

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

**(iii)** Explain why geraniol and citronellal are structural isomers of each other.

.....

.....

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

**(iv)** Explain the term **stereoisomerism**.

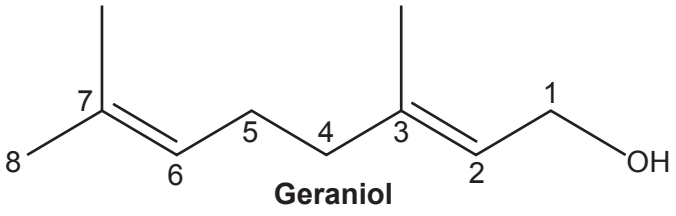
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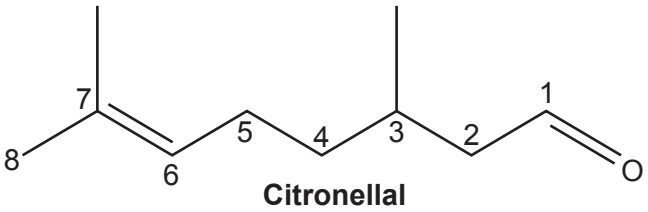
..... **[1]**

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**(v)** The structures of geraniol and citronellal are repeated below with the carbon atoms numbered.




**Geraniol**




**Citronellal**

Explain the types of stereoisomerism shown by geraniol and citronellal.

In your answer,

- refer to the numbered carbon atoms in the structures above
- draw diagrams clearly showing any stereoisomers.

.....

.....

.....

.....

.....

.....

**Geraniol stereoisomers**

**Citronellal stereoisomers**

**[4]**

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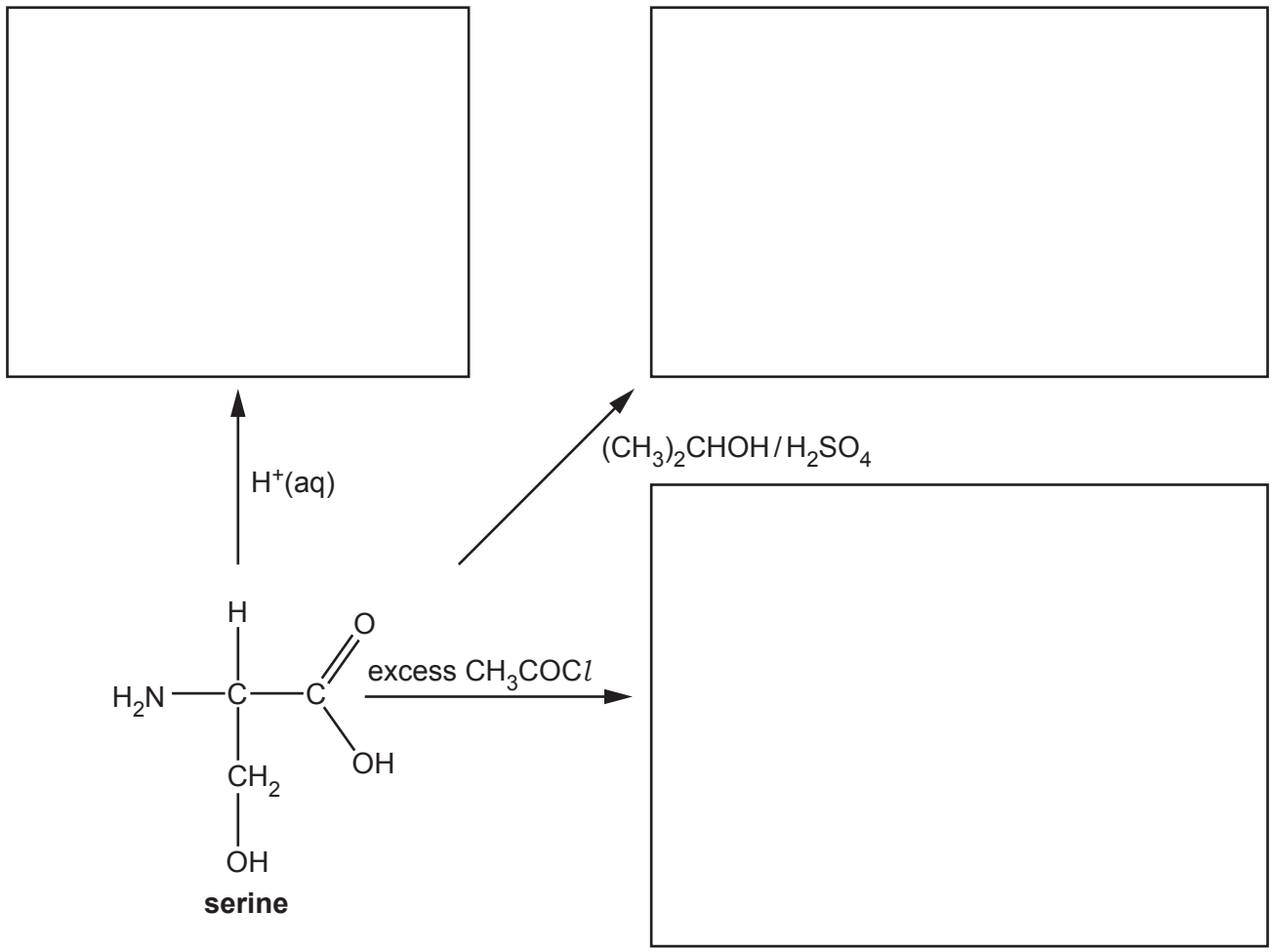
**17** This question is about α-amino acids, $RCH(NH_2)COOH$.

**(a)** **Table 17.1** shows the R groups in four amino acids.

| Amino acid | R group |
|---|---|
| alanine (ala) | $CH_3$– |
| serine (ser) | $HOCH_2$– |
| leucine (leu) | $(CH_3)_2CHCH_2$– |
| glycine (gly) | H– |

**Table 17.1**

**(i)** In the boxes, draw the organic products for the reactions of serine shown below.




**[4]**

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**(ii)** A student is provided with one of the four amino acids in **Table 17.1**.

A student carries out a titration with a standard solution of hydrochloric acid to identify the amino acid. The student's method is outlined below.

- The student dissolves 5.766 g of the amino acid in water and makes the solution up to 250.0 $cm^3$ in a volumetric flask.
- The student titrates this solution with 25.0 $cm^3$ of 0.150 mol $dm^{-3}$ hydrochloric acid.
- 21.30 $cm^3$ of the amino acid solution were required for complete neutralisation of the hydrochloric acid.

Determine which amino acid the student used.

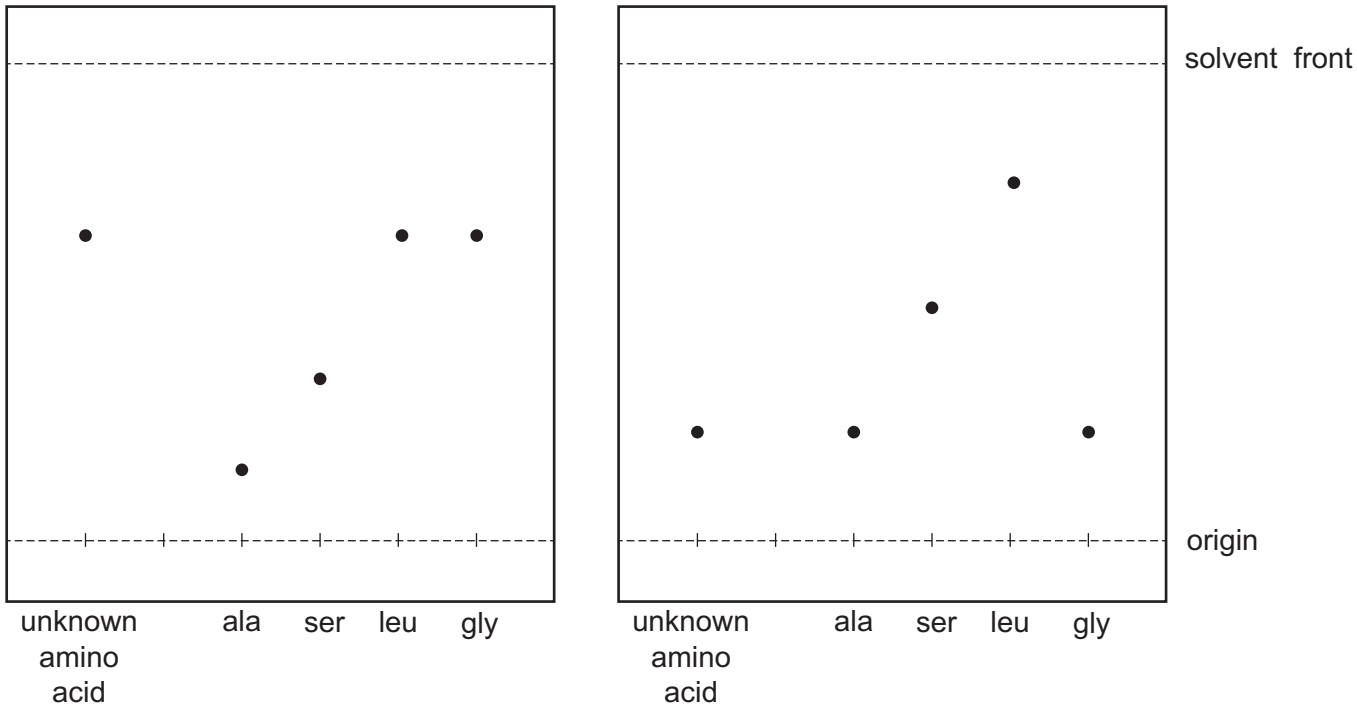
**[4]**

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**(b)** The student is provided with another amino acid.

The student attempts to identify the unknown amino acid using chromatography.

The student obtains two TLC chromatograms of the unknown amino acid and the four amino acids in **Table 17.1**, using two different solvents, **W** and **X**.




**(i)** What is the $R_f$ value of serine (ser) in solvent **W**?

$R_f$ = ..... **[1]**

**(ii)** Analyse the chromatograms to identify the unknown amino acid.

Explain your reasoning.

Name of unknown amino acid .....

Explanation .....

.....

.....

..... **[2]**

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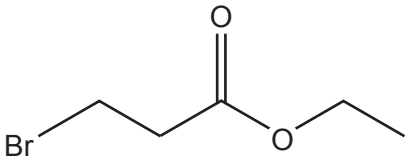
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**18** This question is about esters.

**(a)** The structure of ester **A** is shown below.



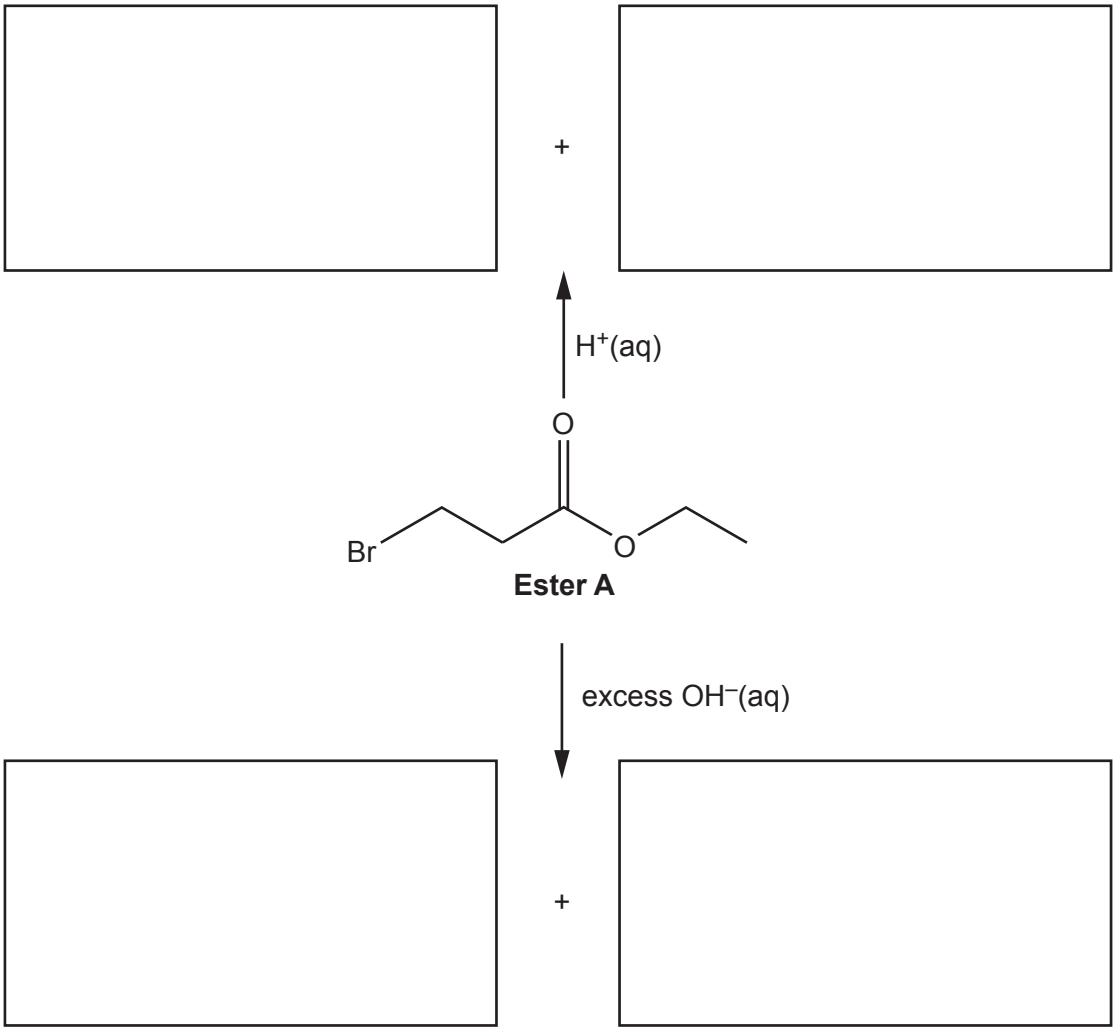

**Ester A**

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

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

**(ii)** In the boxes, draw the organic products for the reactions of the functional groups in ester **A** shown below.

Each reaction forms two organic products.



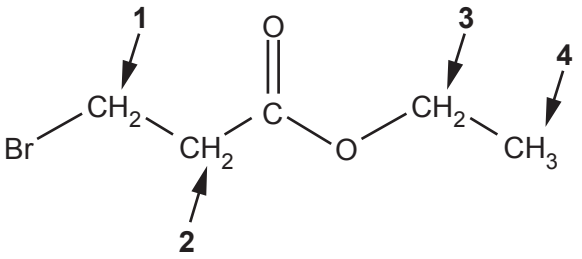

**[5]**

**(iii)** Name the type of reactions of ester **A** shown in **(ii)**.

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

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**(b)** The protons in ester **A** are in four different environments, labelled **1**–**4** on the structure below.




Complete the table to predict the **proton** NMR spectrum of ester **A**.

| Proton environment | Chemical shift | Splitting pattern |
|---|---|---|
| **1** | | |
| **2** | | |
| **3** | | |
| **4** | | |

**[4]**

**(c)** Compound **B** is a structural isomer of ester **A**.

- Compound **B** reacts with aqueous sodium carbonate.
- The $^{13}C$ NMR spectrum of **B** has 4 peaks.

Draw a possible structure for compound **B**.

**[1]**

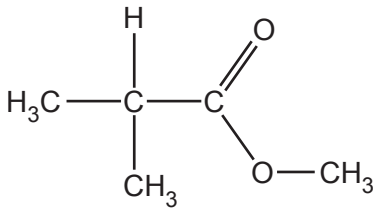
**(d)** A polyester is formed from 200 molecules of 4-hydroxybenzoic acid.

What is the relative molecular mass, $M_r$, of the polyester?

$M_r$ = ..... $g\,mol^{-1}$ **[2]**

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**(e)*** A student intends to synthesise ester **C**.



**Ester C**

**(i)** Plan a two-stage synthesis to prepare 12.75 g of ester **C** starting from 2-methylpropanal, $(CH_3)_2CHCHO$. Assume the overall percentage yield of ester **C** from 2-methylpropanal is 40%.

In your answer include the mass of 2-methylpropanal required, reagents, conditions and equations where appropriate.

Purification details are **not** required. **[6]**

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Additional answer space if required

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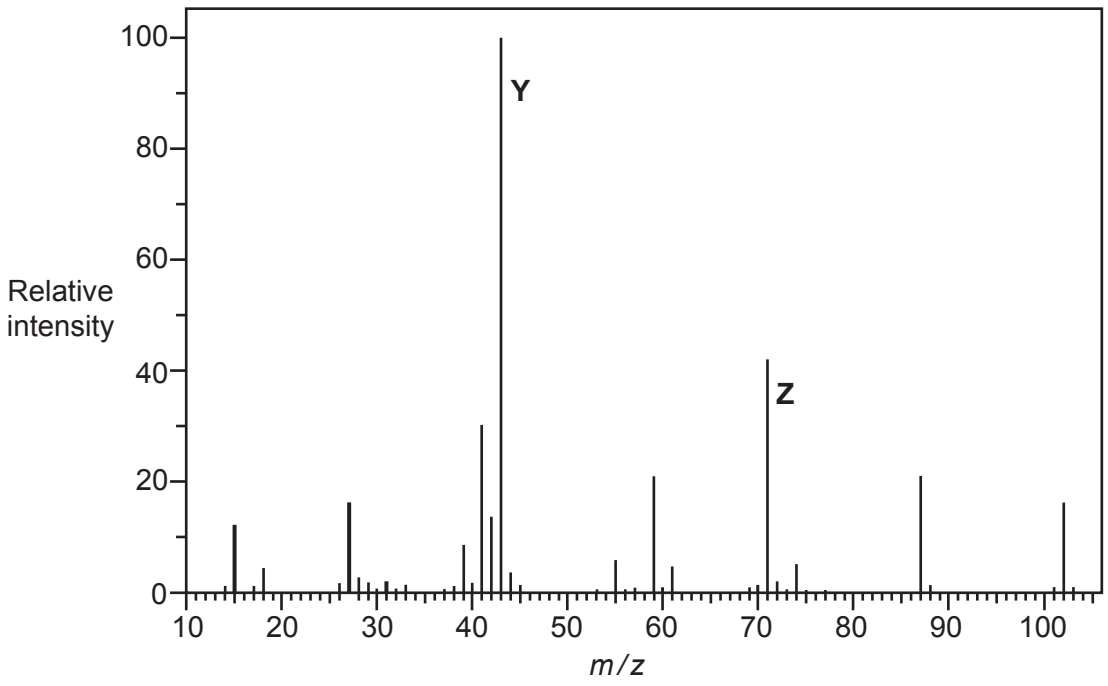
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**(ii)** The mass spectrum of ester **C** is shown below.




Suggest possible structures for the species responsible for peaks **Y** and **Z** in the mass spectrum.

| | |
|---|---|
| | |
| **Y** | **Z** |

**[2]**

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**19** This question is about benzene.

**(a)** Over time, the Kekulé and delocalised models have been used to describe the bonding and structure of a benzene molecule.

**(i)** Describe, in terms of orbital overlap, the similarities and differences between the bonding in the Kekulé model and the delocalised model of benzene.

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

**(ii)** Experimental evidence led to the general acceptance of the delocalised model over the Kekulé model.

Describe **two** pieces of evidence to support the delocalised model of benzene.

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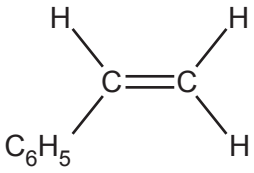
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..... **[2]**

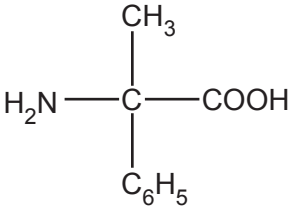
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**(b)** Benzene can be used as the starting material for the synthesis of compounds **D** and **E**, shown below.

In the diagrams $C_6H_5$ is a phenyl group.




**compound D**




**compound E**

Compounds **D** and **E** can be converted into polymers.

**(i)** Draw **two** repeat units of these polymers.

**Two** repeat units of polymer formed from **D**

**Two** repeat units of polymer formed from **E**

**[3]**

**(ii)** State the **type** of polymer formed from compounds **D** and **E**.

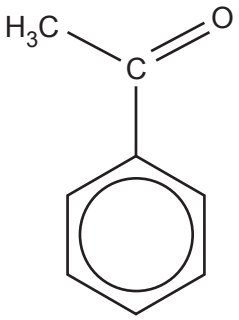
From compound **D** .....

From compound **E** .....

**[1]**

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**(iii)** In the synthesis of compounds **D** and **E**, benzene is first reacted with ethanoyl chloride, $CH_3COCl$, to form phenylethanone, shown below.



**phenylethanone**

The reaction takes place in the presence of aluminium chloride, $AlCl_3$, which acts as a catalyst.

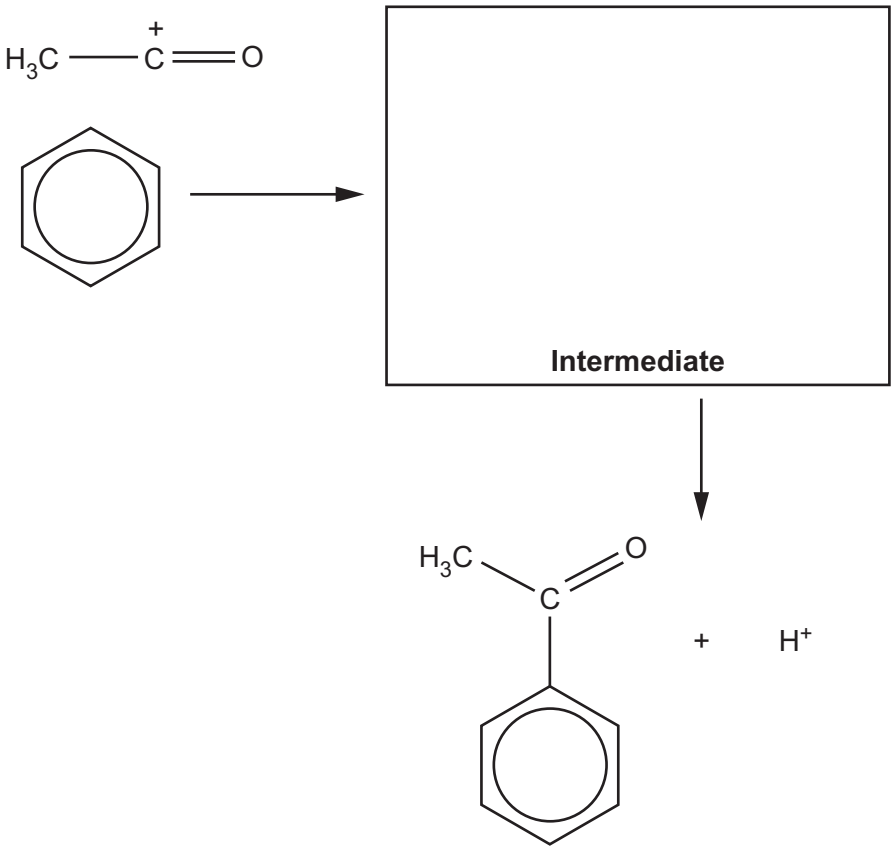
In the mechanism for this reaction,

- ethanoyl chloride first reacts with aluminium chloride to form the $CH_3–C^+=O$ cation
- the $CH_3–C^+=O$ cation then behaves as an electrophile.

Complete the mechanism for the reaction.

Include equations to show the role of the $AlCl_3$ catalyst, relevant curly arrows and the structure of the intermediate.

Formation of electrophile .....

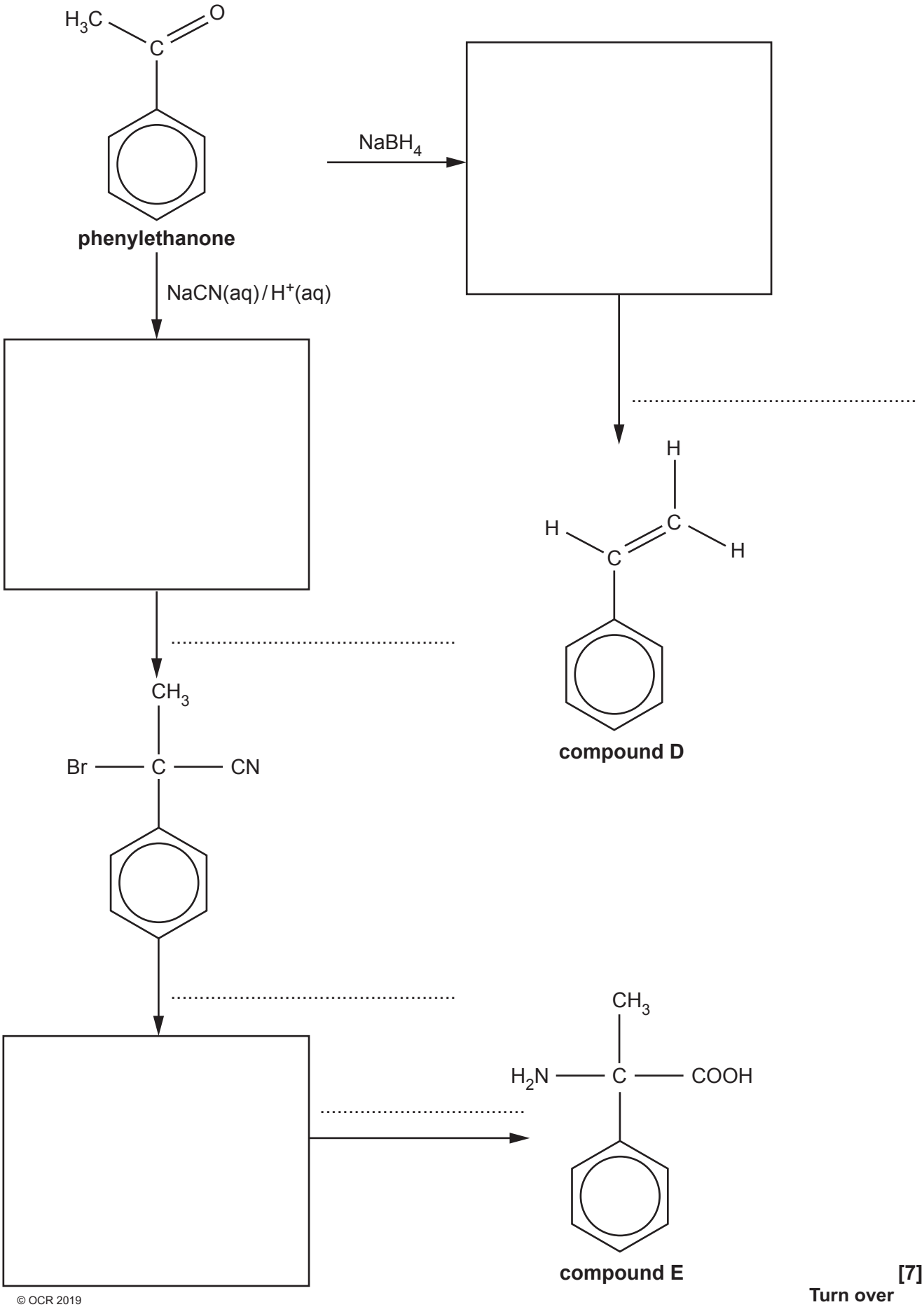



Regeneration of catalyst .....

**[5]**

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**(iv)** Complete the flowchart for the synthesis of compounds **D** and **E** from phenylethanone.




**[7]**

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**20** This question is about reaction mechanisms.

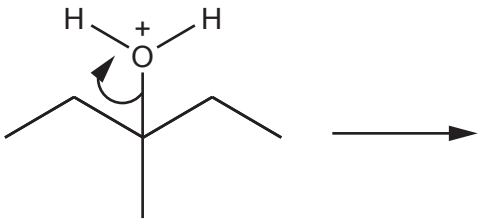
**(a)** Chemists use curly arrows in reaction mechanisms.

**(i)** What does a curly arrow show in a reaction mechanism?

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

**(ii)** Draw structures to show the products in the reaction mechanism below.




**[2]**

**(iii)** Use the mechanism in **(ii)** to explain what is meant by **heterolytic fission**.

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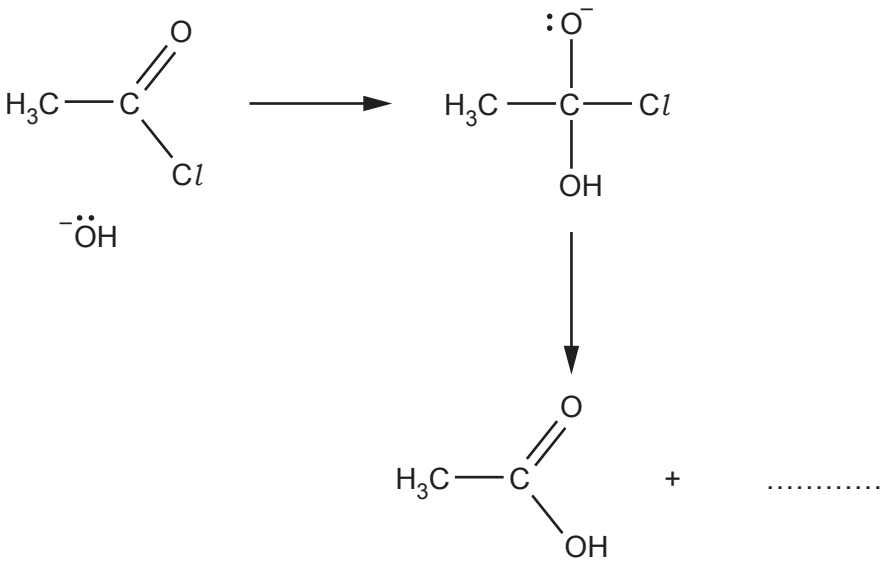
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..... **[2]**

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**(b)** An incomplete reaction mechanism is shown below.

**(i)** Complete the mechanism by adding curly arrows and any missing species.




**[4]**

**(ii)** What is the role of $OH^-$ in this mechanism?

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

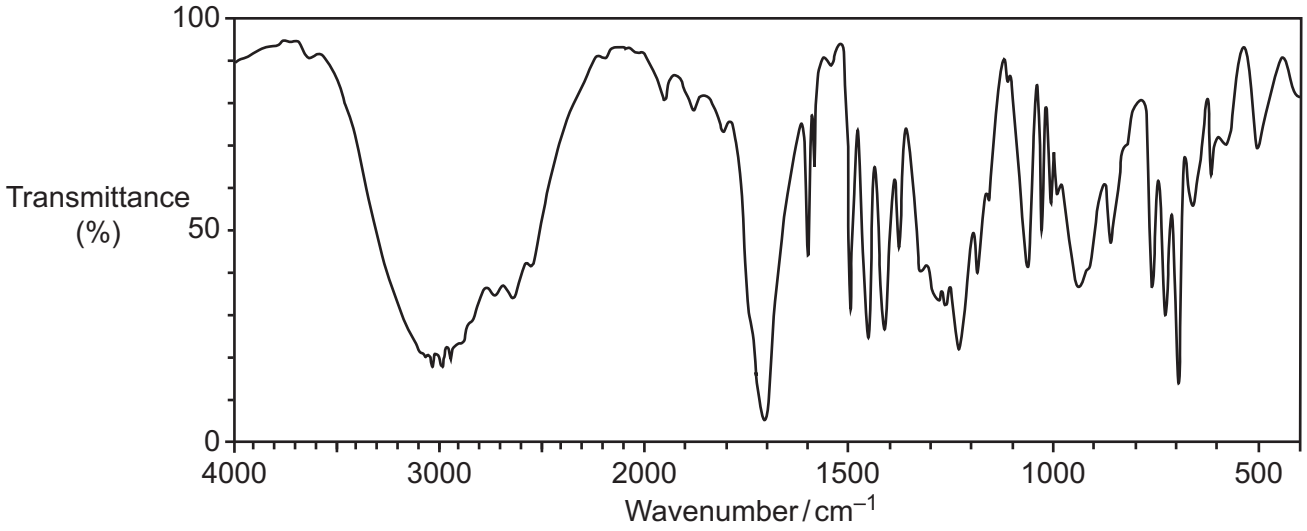
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**21*** Analysis of an unknown organic compound produced the following results.

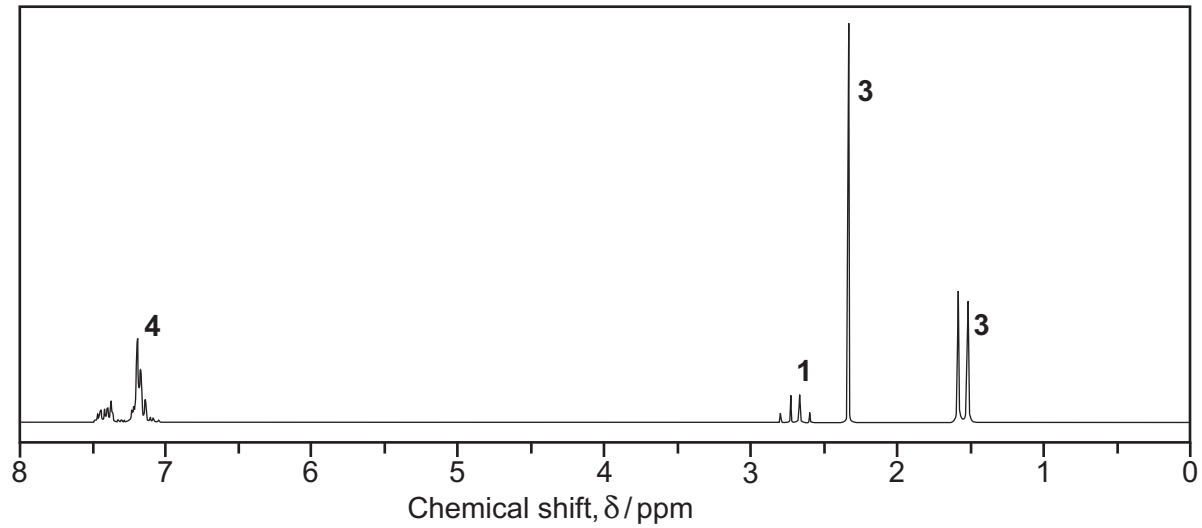
**Elemental analysis by mass**
C: 73.17%; H: 7.32%; O: 19.51%

**Mass spectrum**
Molecular ion peak at $m/z$ = 164.0

**Infrared spectrum**




**$^1$H NMR spectrum in $D_2O$**




The numbers by the peaks are the relative peak areas.

Use the results to suggest **one** possible structure for the unknown compound.

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

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Additional answer space if required

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**END OF QUESTION PAPER**

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## 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).

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