



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

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Candidate number

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First name(s)

Last name

StemUp Model Solution

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.

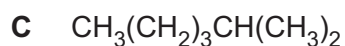
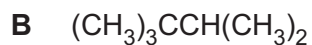
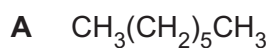
SECTION A

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?



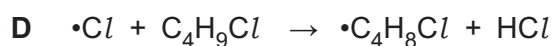
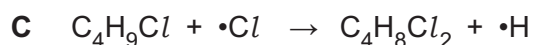
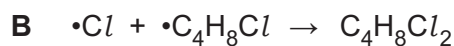
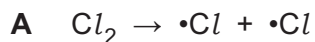
Your answer

A

[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?

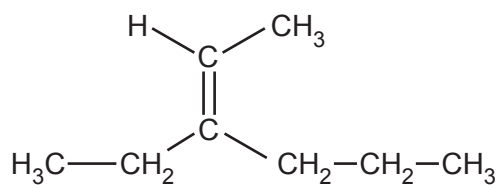


Your answer

D

[1]

3 What is the name of the compound below?



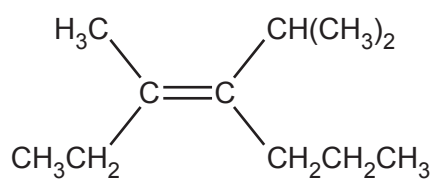
- A 3-Propylpent-2-ene
- B 3-Propylpent-3-ene
- C 3-Ethylhex-2-ene
- D 4-Ethylhex-4-ene

Your answer

C

[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

C

[1]

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

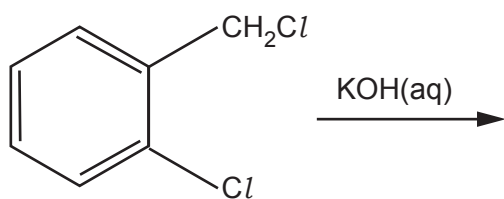
	Types of bond broken	Types of bond formed
A	σ	π
B	π	σ
C	σ and π	π
D	σ and π	σ

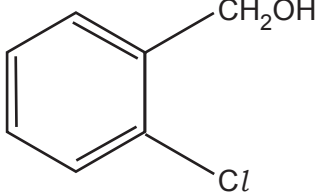
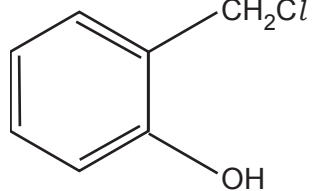
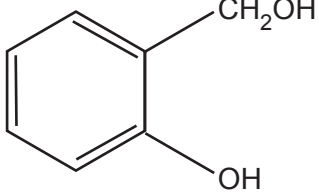
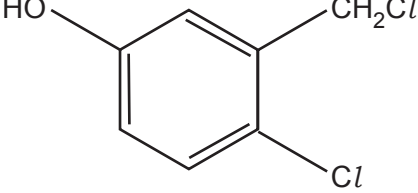
Your answer

D

[1]

6 What is the organic product of the reaction below?



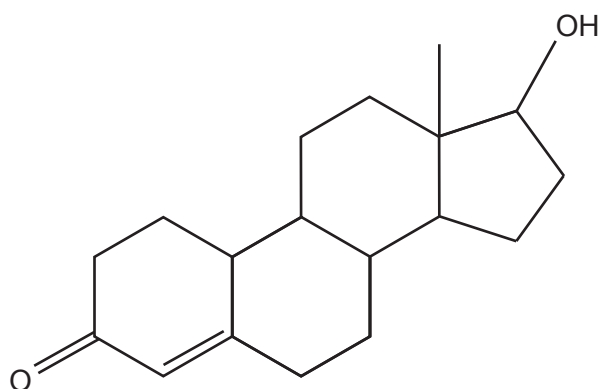
A	
B	
C	
D	

Your answer

A

[1]

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



A 5

B 6

C 7

D 8

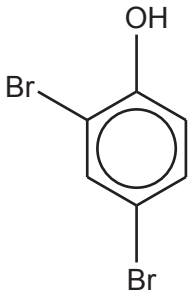
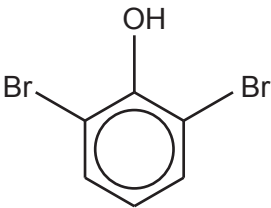
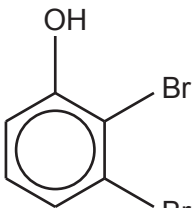
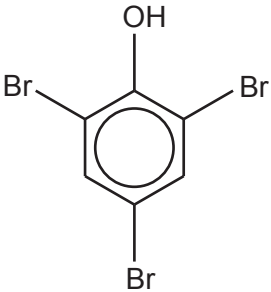
Your answer

B

[1]

8 Phenol reacts with bromine.

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

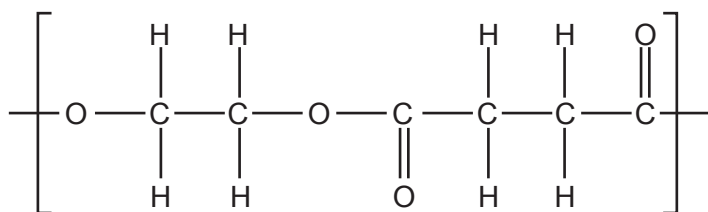
A	
B	
C	
D	

Your answer

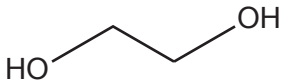
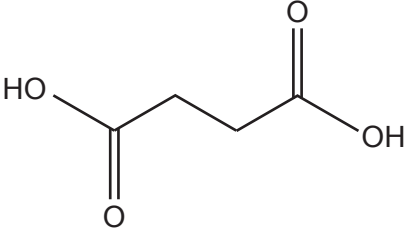
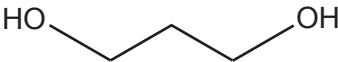
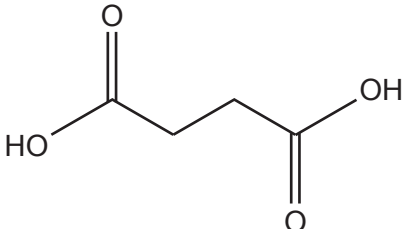
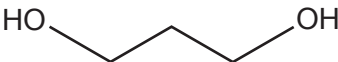
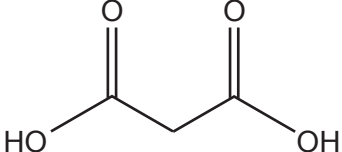
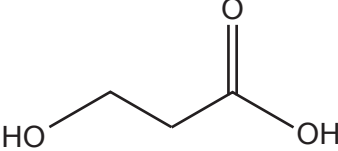
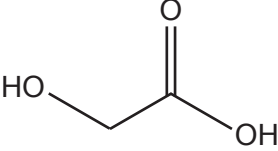
C

[1]

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



Which monomers could form this polymer?

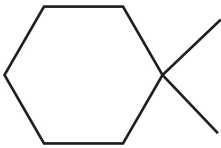
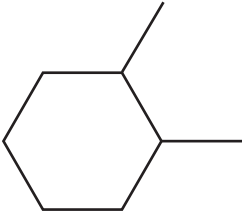
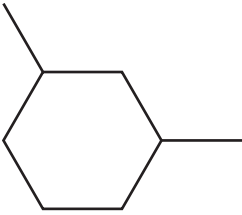
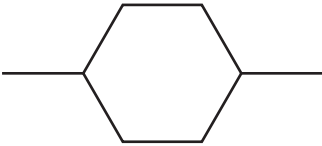
A		
B		
C		
D		

Your answer

A

[1]

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

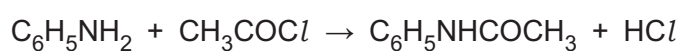
A	
B	
C	
D	

Your answer

B

[1]

11 A student reacts 4.50 g of $\text{C}_6\text{H}_5\text{NH}_2$ with excess CH_3COCl in the reaction below.



$$M_r = 93.0$$

$$M_r = 135.0$$

The reaction produces 3.25 g of $\text{C}_6\text{H}_5\text{NHCOCH}_3$.

What is the percentage yield of $\text{C}_6\text{H}_5\text{NHCOCH}_3$?

A 49.8

B 68.9

C 72.2

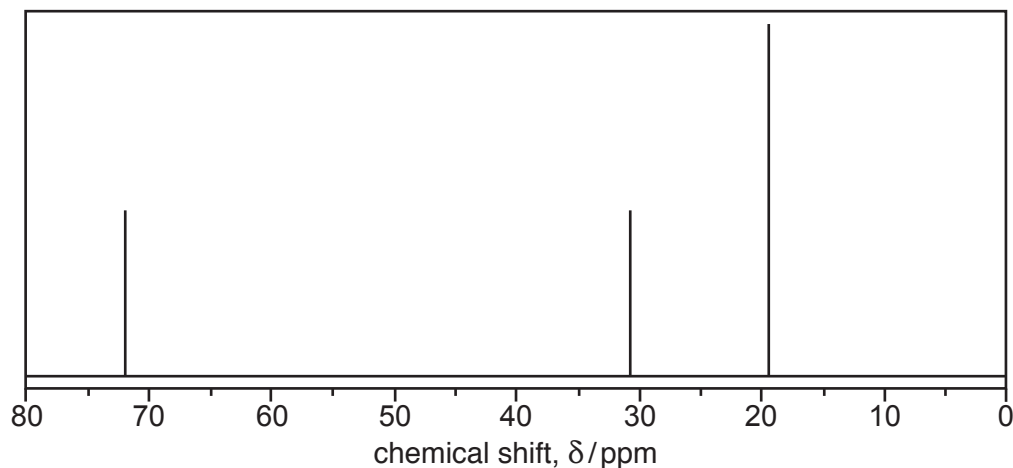
D 95.4

Your answer

A

[1]

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

C

[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

C

[1]

14 Which chemical(s) can react with phenol?

- 1 Potassium hydroxide
- 2 Ethanoyl chloride
- 3 Nitric acid

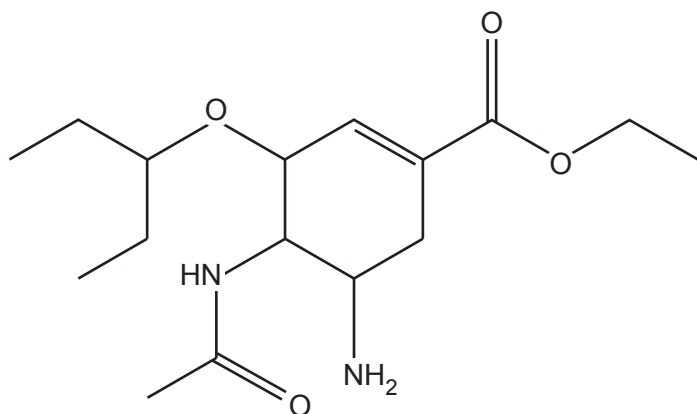
- A** 1, 2 and 3
- B** Only 1 and 2
- C** Only 2 and 3
- D** Only 1

Your answer

A

[1]

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

B

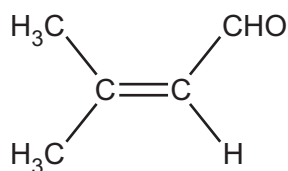
[1]

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.



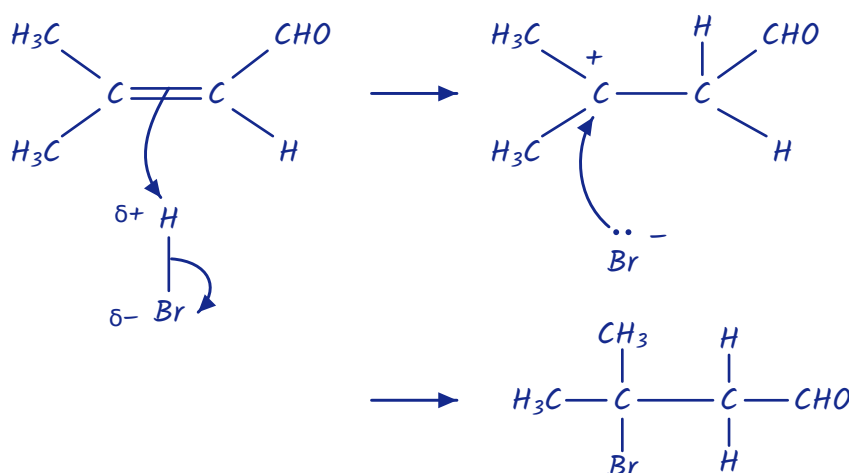
3-methylbut-2-enal

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.



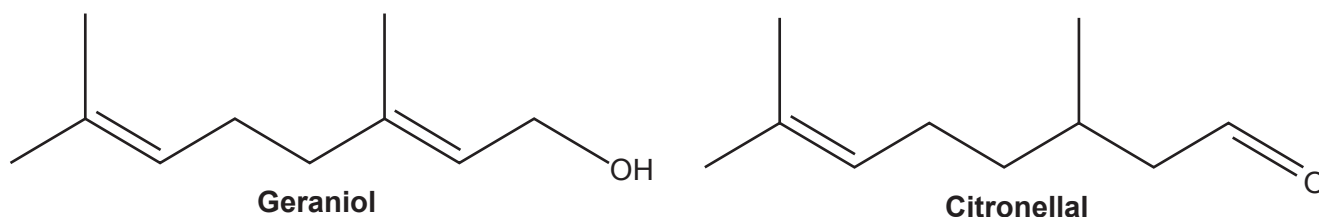
[4]

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

The major product forms from the more stable carbocation intermediate.
This is a tertiary carbocation (the C^+ is bonded to more alkyl groups, i.e.
3 carbon atoms and no H atoms), rather than the less stable secondary
carbocation.

[2]

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



- 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.

Add Tollens' reagent (ammoniacal silver nitrate) to each and warm in a water bath.

Citronellal (the aldehyde) gives a silver mirror; geraniol gives no silver mirror (no change).

[2]

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

C₁₀H₁₈O

[1]

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

Both have the same molecular formula, C₁₀H₁₈O, but different structural formulae.

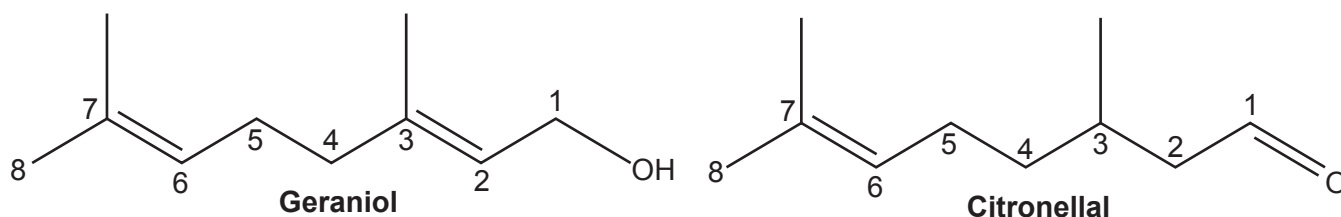
[1]

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

Same structural formula, but a different arrangement of the atoms in space.

[1]

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



Explain the types of stereoisomerism shown by geraniol and citronellal.

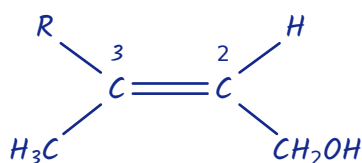
In your answer,

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

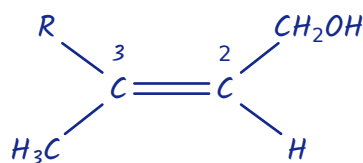
Geraniol shows E/Z isomerism about the C=C bond between carbon-2 and carbon-3; C2 and C3 each have two different groups and there is no rotation about the π bond. The structure shown is the E isomer; the other is Z. (C6=C7 cannot, as C7 has two CH_3 .)

Citronellal shows optical isomerism; carbon-3 is chiral, bonded to 4 different groups, so there are two non-superimposable mirror images.

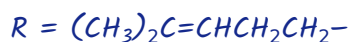
Geraniol stereoisomers



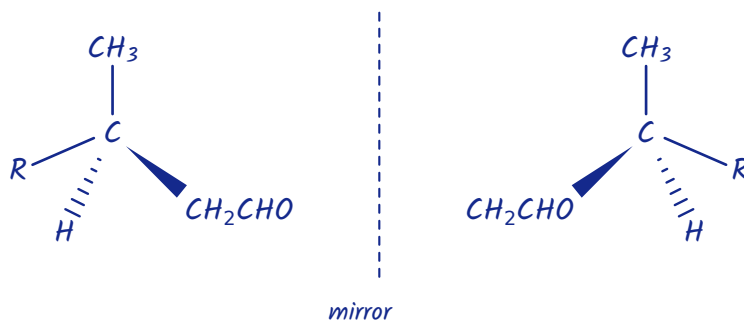
E-geraniol



Z-geraniol



Citronellal stereoisomers



C3 is the chiral carbon ($R = (\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2-$)

[4]

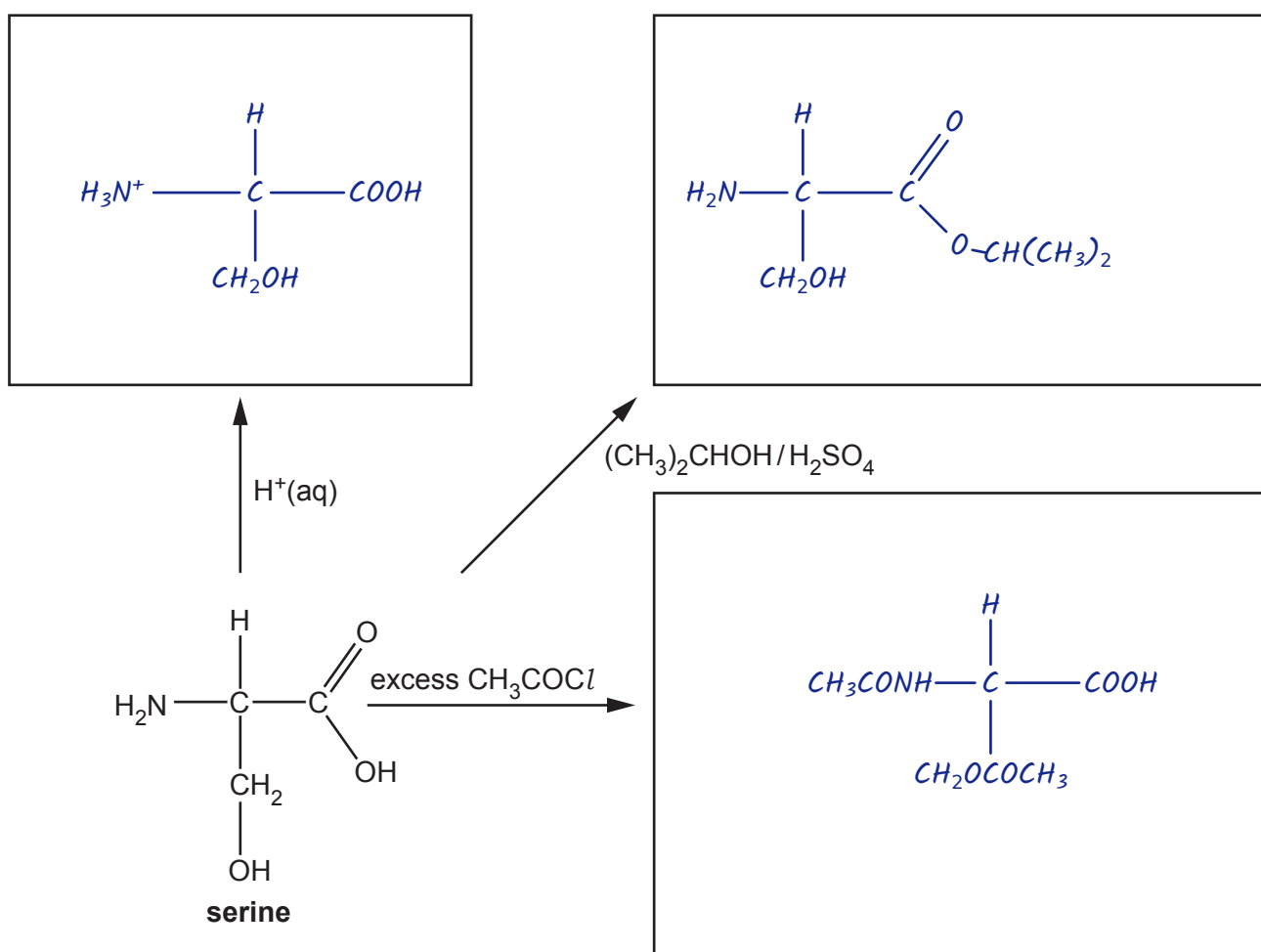
17 This question is about α -amino acids, $\text{RCH}(\text{NH}_2)\text{COOH}$.

(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)	$(\text{CH}_3)_2\text{CHCH}_2-$
glycine (gly)	$\text{H}-$

Table 17.1

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



[4]

- (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 cm³ in a volumetric flask.
- The student titrates this solution with 25.0 cm³ of 0.150 mol dm⁻³ hydrochloric acid.
- 21.30 cm³ of the amino acid solution were required for complete neutralisation of the hydrochloric acid.

Determine which amino acid the student used.

$$n(\text{HCl}) = 0.150 \times 25.0/1000 = 3.75 \times 10^{-3} \text{ mol}$$

amino acid : HCl = 1 : 1 (one NH₂ group), so

$$n(\text{amino acid}) \text{ in } 21.30 \text{ cm}^3 = 3.75 \times 10^{-3} \text{ mol}$$

$$\begin{aligned} n(\text{amino acid}) \text{ in } 250.0 \text{ cm}^3 &= 3.75 \times 10^{-3} \times 250.0/21.30 \\ &= 0.0440 \text{ mol} \end{aligned}$$

$$M(\text{amino acid}) = 5.766/0.0440 = 131 \text{ g mol}^{-1}$$

$$R\text{CH}(\text{NH}_2)\text{COOH}: \text{CH}(\text{NH}_2)\text{COOH} = 74, \text{ so } M(R) = 131 - 74 = 57$$

$$R = \text{C}_4\text{H}_9 = (\text{CH}_3)_2\text{CHCH}_2-$$

(check: leucine C₆H₁₃NO₂, M_r = 131; ala = 89, ser = 105, gly = 75)

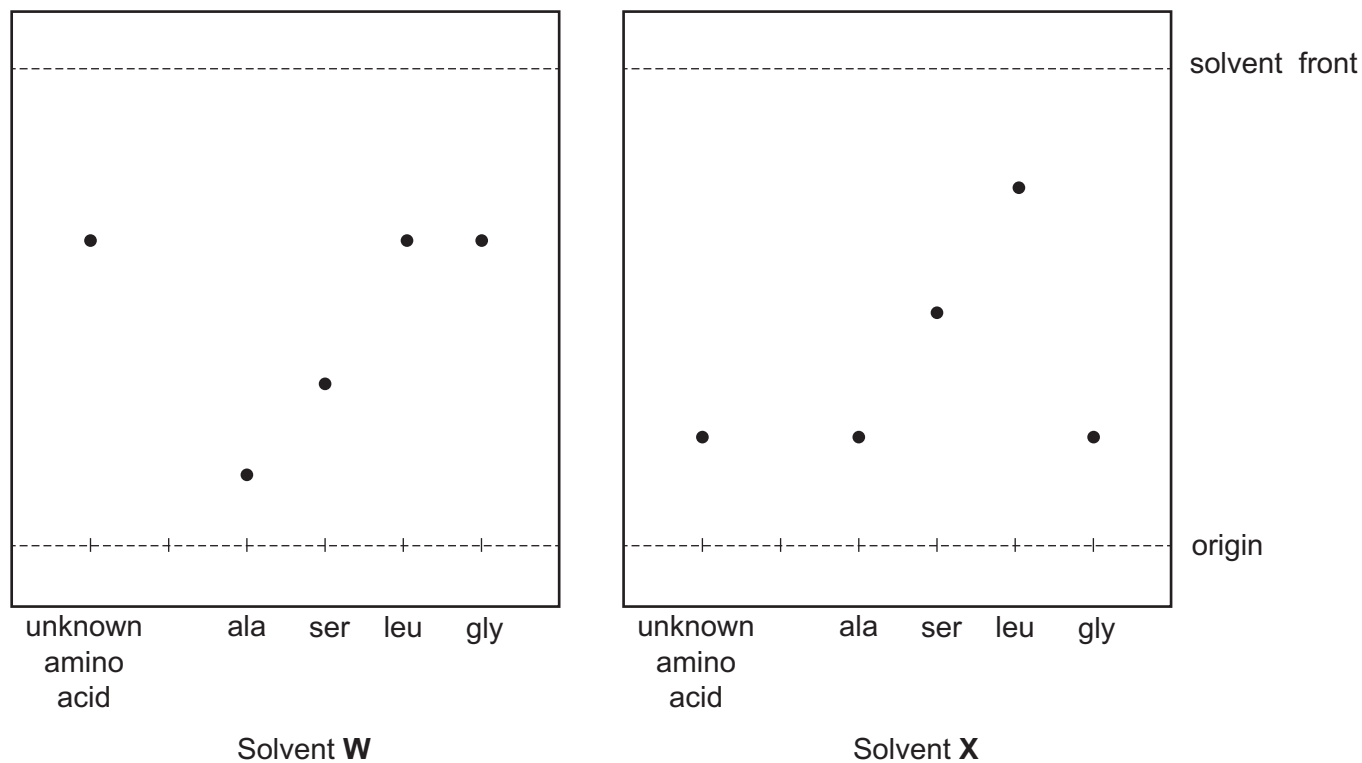
Amino acid = leucine

[4]

- (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**?

$$R_f = \text{distance moved by ser} \div \text{distance moved by solvent}$$

$$= 2.14 \text{ cm} \div 6.31 \text{ cm}$$

$$R_f = 0.34 \quad [1]$$

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

Explain your reasoning.

Name of unknown amino acid glycine

Explanation The unknown has the same R_f value as glycine in both
solvents: in W it matches leucine and glycine, in X it matches alanine
and glycine.

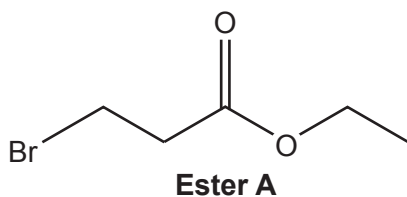
..... [2]

19
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18 This question is about esters.

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

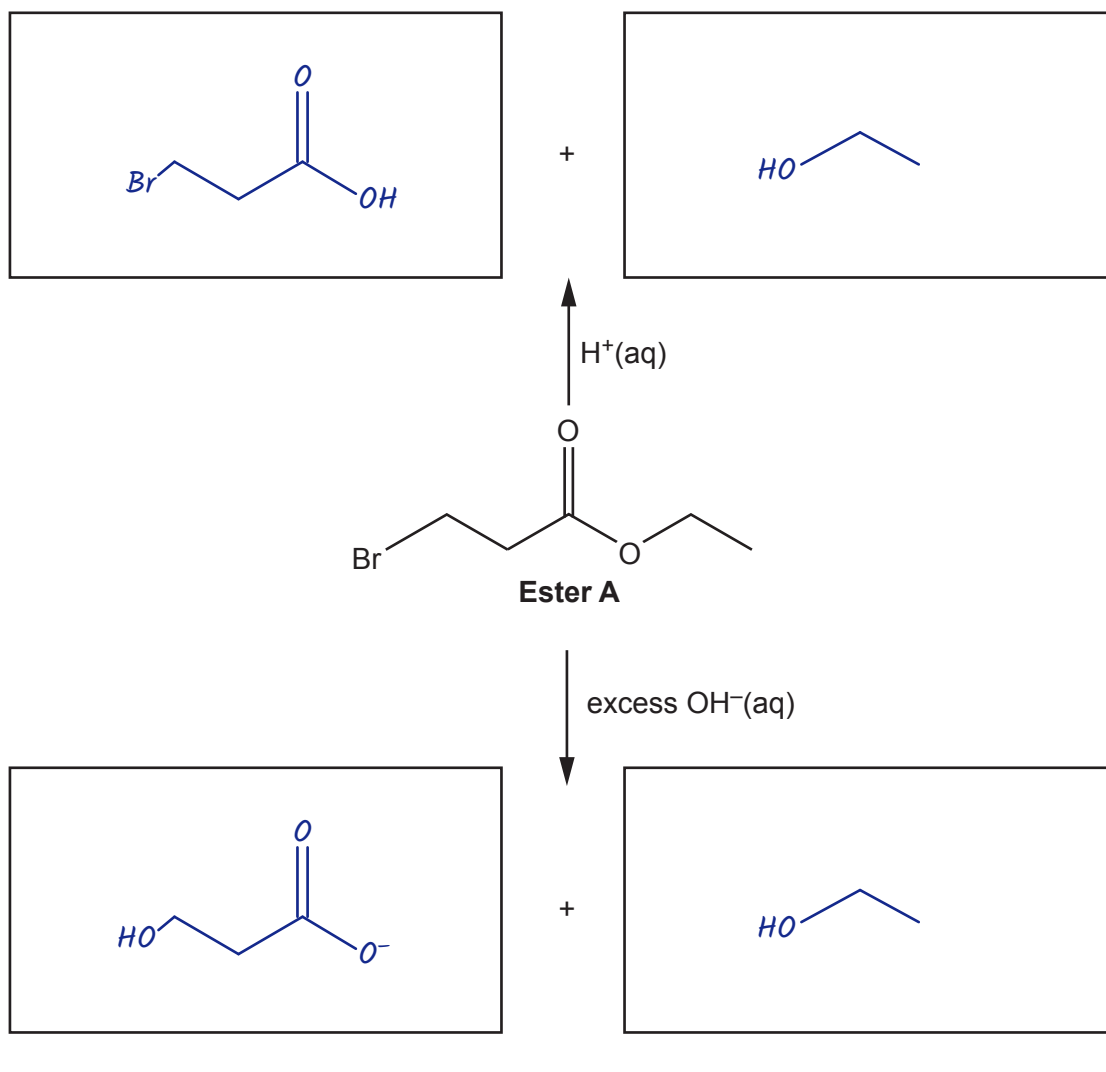


(i) What is the systematic name of ester **A**?

ethyl 3-bromopropanoate..... [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.

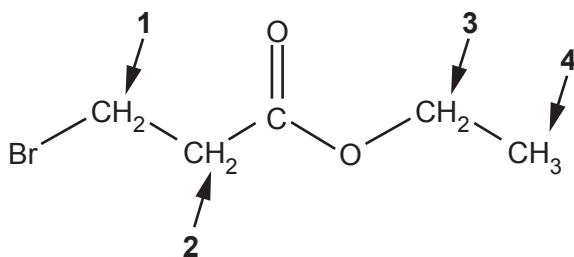


[5]

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

hydrolysis..... [1]

(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**.

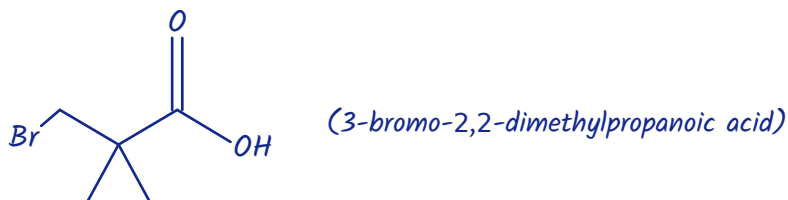
Proton environment	Chemical shift	Splitting pattern
1	3.5 ppm	triplet
2	2.8 ppm	triplet
3	4.1 ppm	quartet
4	1.3 ppm	triplet

[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?

$$M_r(\text{HOC}_6\text{H}_4\text{COOH}) = 138.0$$

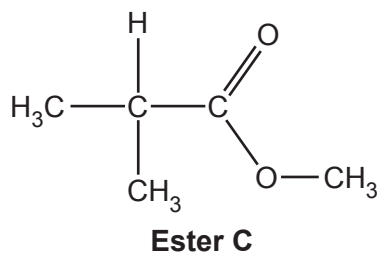
$$200 \times 138.0 = 27600$$

199 ester links form, so 199 H_2O are lost:

$$27600 - 199 \times 18.0 = 24018$$

$$M_r = \dots\dots\dots 24018 \dots\dots\dots \text{g mol}^{-1} \quad [2]$$

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



- (i) Plan a two-stage synthesis to prepare 12.75 g of ester **C** starting from 2-methylpropanal, $(\text{CH}_3)_2\text{CHCHO}$. 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]

$n(\text{ester C}) = 12.75 \div 102.0 = 0.125 \text{ mol}$ (M of $(\text{CH}_3)_2\text{CHCOOCH}_3$, $\text{C}_5\text{H}_{10}\text{O}_2 = 102.0$).

40% overall yield, so $n((\text{CH}_3)_2\text{CHCHO})$ needed $= 0.125 \times 100/40 = 0.3125 \text{ mol}$. $M((\text{CH}_3)_2\text{CHCHO}) = 72.0$, so mass of 2-methylpropanal $= 0.3125 \times 72.0 = 22.5 \text{ g}$.

Stage 1, oxidation of the aldehyde to 2-methylpropanoic acid: reagents $\text{K}_2\text{Cr}_2\text{O}_7$ acidified with dilute H_2SO_4 ($\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$); conditions: heat under reflux (so the acid forms, not the aldehyde distilling off).

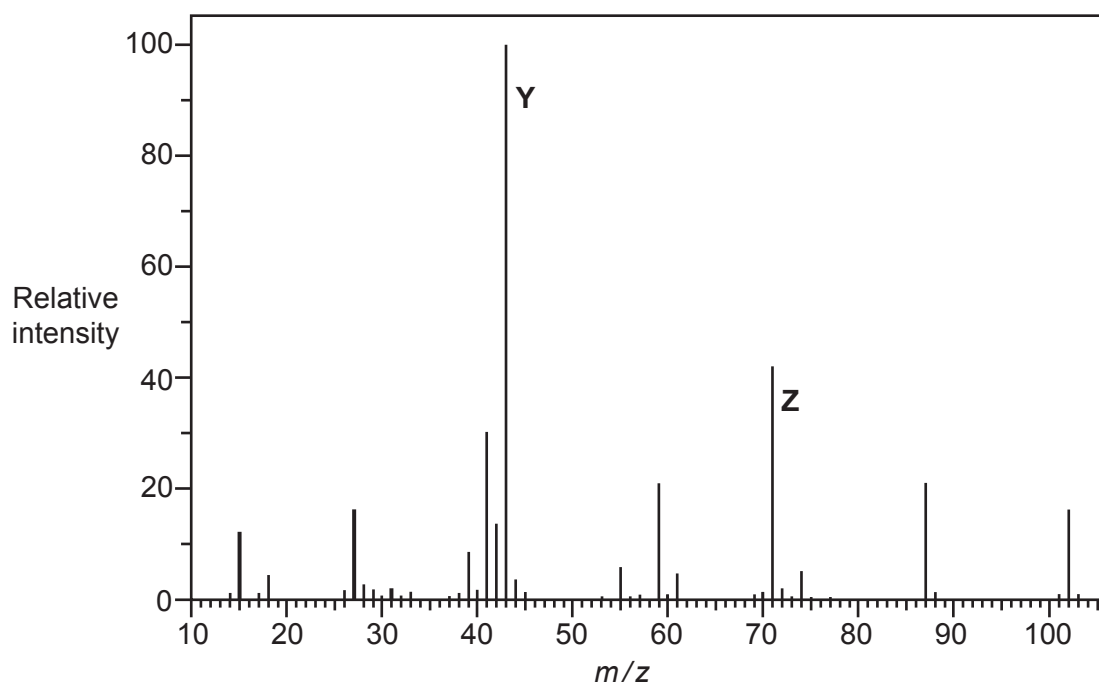
$(\text{CH}_3)_2\text{CHCHO} + [\text{O}] \rightarrow (\text{CH}_3)_2\text{CHCOOH}$

Stage 2, esterification: react the 2-methylpropanoic acid with methanol, CH_3OH ; conditions: concentrated H_2SO_4 as an acid catalyst, heat under reflux.

$(\text{CH}_3)_2\text{CHCOOH} + \text{CH}_3\text{OH} \rightleftharpoons (\text{CH}_3)_2\text{CHCOOCH}_3 + \text{H}_2\text{O}$

Additional answer space if required

(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.

$ \begin{array}{c} + \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{H} \end{array} $ $m/z = 43$	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{C}^+=\text{O} \\ \\ \text{H} \end{array} $ $m/z = 71$
Y	Z

[2]

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.

Similarities: in both models each carbon atom has a p orbital, and p orbitals on adjacent carbon atoms overlap sideways to form π bonds. In both models the π electron density lies above and below the plane of the ring of carbon atoms.

Difference: in the Kekulé model the p orbitals overlap in one direction only (in pairs), giving 3 localised π bonds, i.e. alternating C=C bonds with 2 electrons in each π bond.

In the delocalised model every p orbital overlaps with the p orbitals on both adjacent carbons (both directions), giving a π ring (π system) with 6 electrons spread around the ring.

[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.

Bond lengths: all the C-C bonds in benzene are the same length (0.139 nm), between the lengths of a C-C single bond and a C=C double bond.

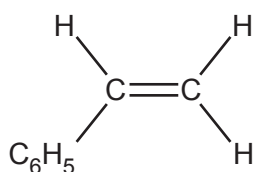
Hydrogenation: ΔH of hydrogenation of benzene (-208 kJ mol^{-1}) is much less exothermic than expected for 3 C=C bonds ($3 \times -120 = -360 \text{ kJ mol}^{-1}$).

Benzene does not decolourise bromine at room temperature; it needs a halogen carrier.

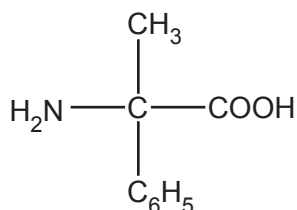
[2]

- (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.



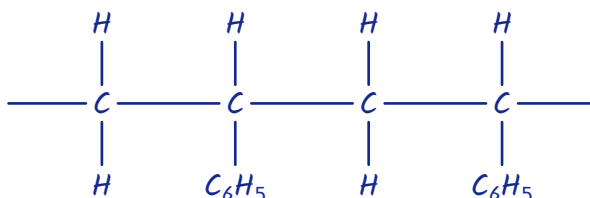
compound D



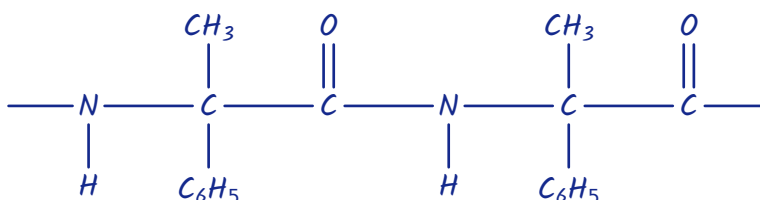
compound E

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]

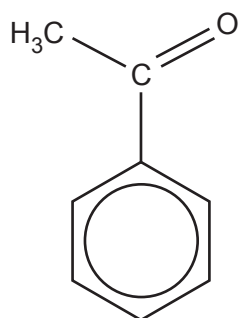
- (ii) State the **type** of polymer formed from compounds **D** and **E**.

From compound **D** ... *addition (polyalkene)*

From compound **E** ... *condensation (polyamide)*

[1]

- (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.

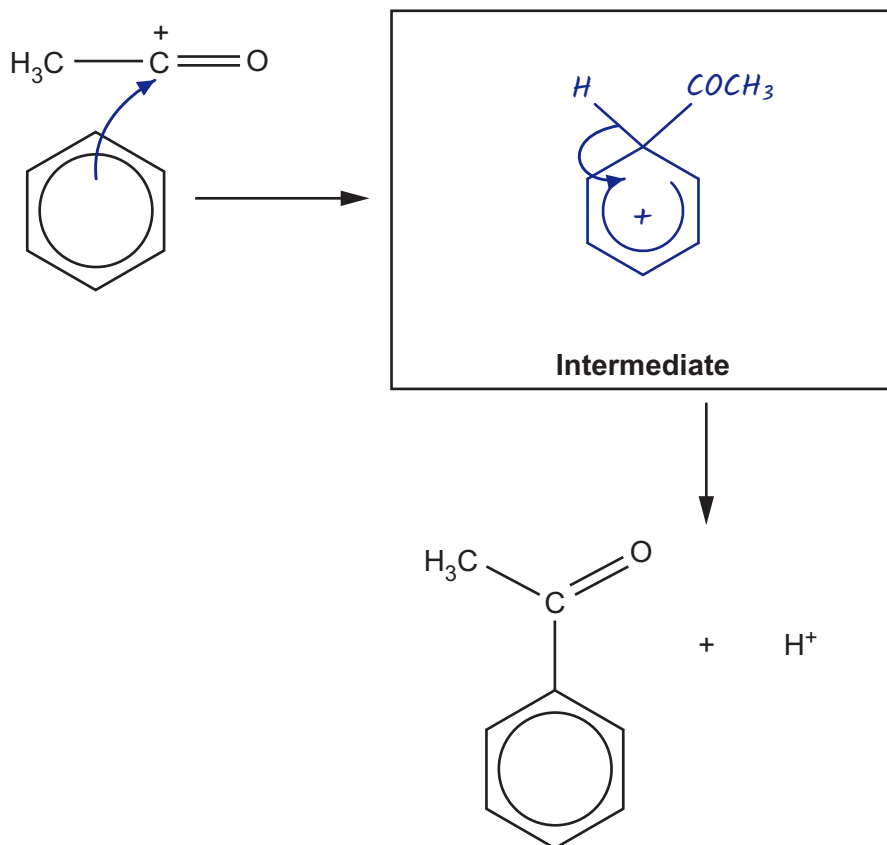
In the mechanism for this reaction,

- ethanoyl chloride first reacts with aluminium chloride to form the $\text{CH}_3\text{-C}^+=\text{O}$ cation
- the $\text{CH}_3\text{-C}^+=\text{O}$ cation then behaves as an electrophile.

Complete the mechanism for the reaction.

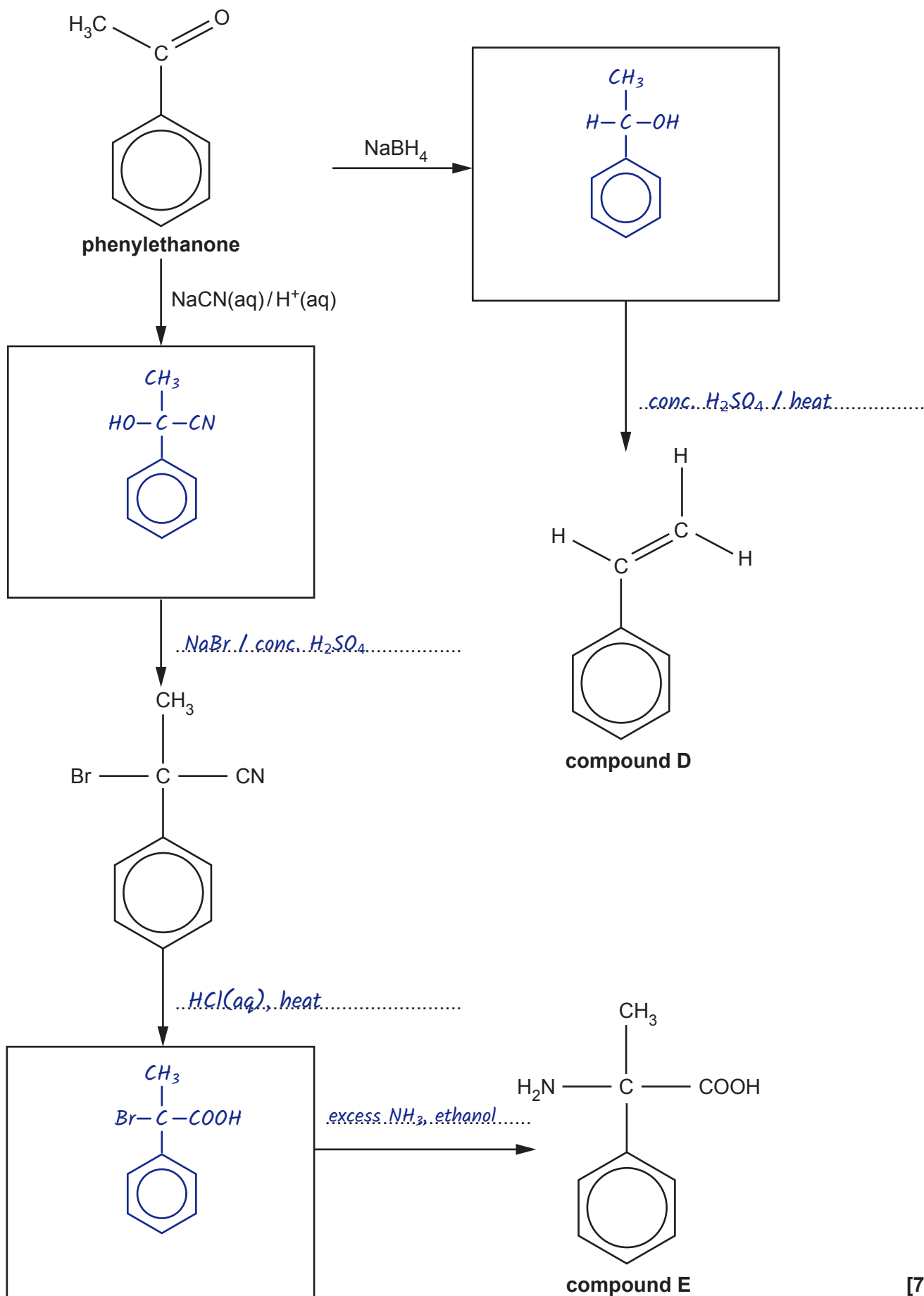
Include equations to show the role of the AlCl_3 catalyst, relevant curly arrows and the structure of the intermediate.

Formation of electrophile $\text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{-C}^+=\text{O} + \text{AlCl}_4^-$



Regeneration of catalyst $\text{H}^+ + \text{AlCl}_4^- \rightarrow \text{AlCl}_3 + \text{HCl}$

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



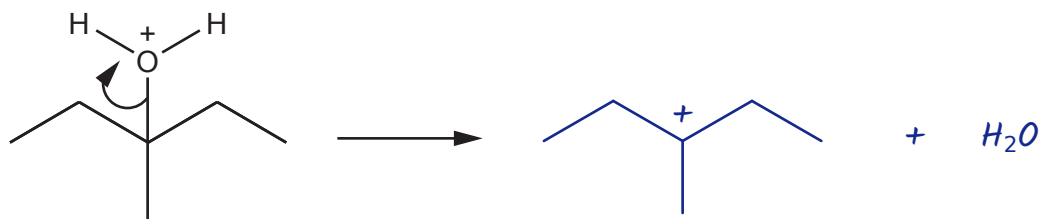
20 This question is about reaction mechanisms.

(a) Chemists use curly arrows in reaction mechanisms.

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

The movement of a pair of electrons (an electron pair).
 [1]

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



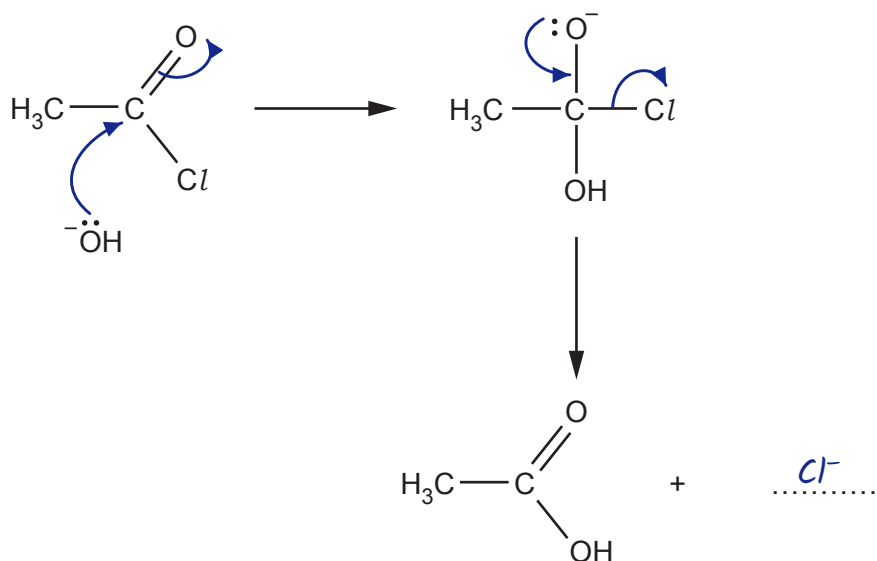
[2]

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

Heterolytic: when the C-O bond breaks, both electrons of the bonding pair go to one atom, the O (forming H_2O and a carbocation).
Fission: breaking of a covalent bond.
 [2]

(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?

A nucleophile: OH^- donates an electron pair (lone pair) to the carbon. [1]

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

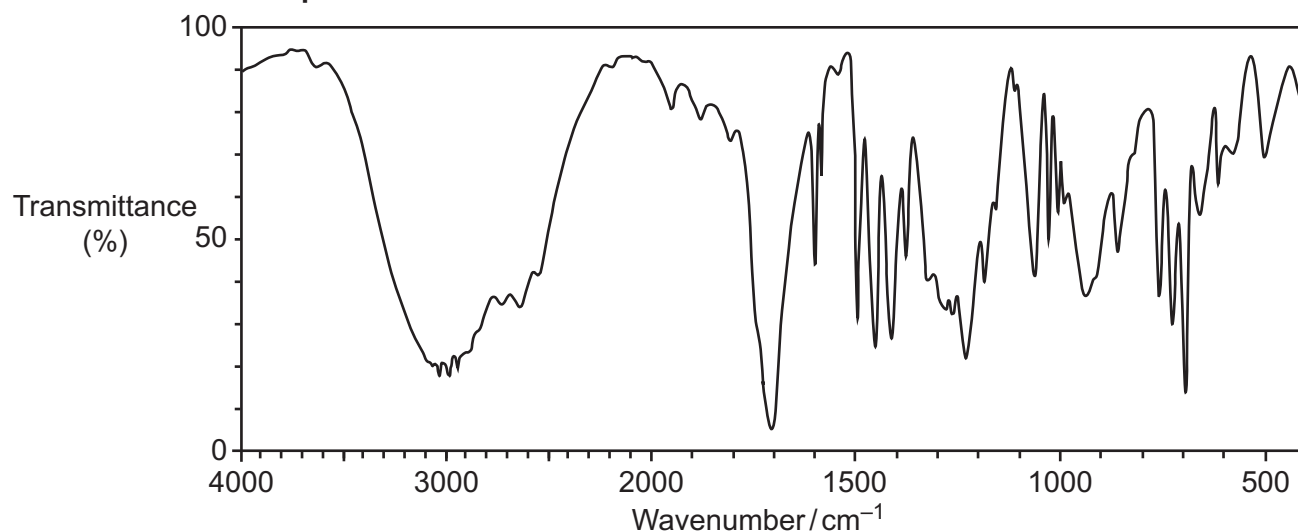
Elemental analysis by mass

C: 73.17%; H: 7.32%; O: 19.51%

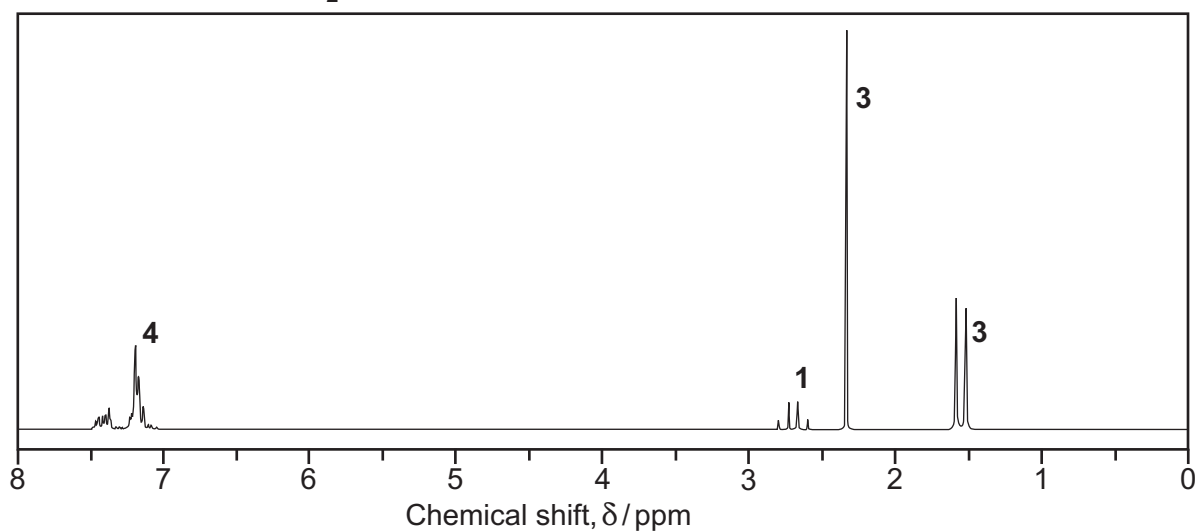
Mass spectrum

Molecular ion peak at $m/z = 164.0$

Infrared spectrum



^1H 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]

$C : H : O = 73.17/12.0 : 7.32/1.0 : 19.51/16.0 = 6.10 : 7.32 : 1.22 = 5 : 6 : 1$, so the empirical formula is $\text{C}_5\text{H}_6\text{O}$ ($M = 82.0$). Molecular ion $m/z = 164.0 = 2 \times 82.0$, so the molecular formula is $\text{C}_{10}\text{H}_{12}\text{O}_2$.

IR: the broad absorption at about 2500 to 3300 cm^{-1} is O-H in a carboxylic acid and the strong peak at about 1710 cm^{-1} is C=O, so the compound contains COOH (a carboxylic acid).

^1H NMR (the COOH proton exchanges with D_2O , so it is not seen):

δ 7.1 to 7.4 ppm, area 4: 4 aromatic H, so a disubstituted benzene ring, C_6H_4 .

δ 2.7 ppm, area 1, quartet: one CH next to a CH_3 (3 adjacent H, $n + 1$ rule):

$\text{Ar}-\text{CH}(\text{CH}_3)-\text{COOH}$.

δ 2.3 ppm, area 3, singlet: CH_3 with no adjacent H, on the benzene ring

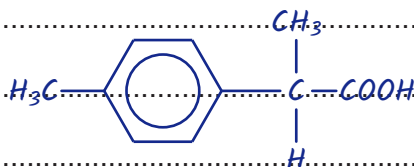
$(\text{Ar}-\text{CH}_3)$.

δ 1.5 ppm, area 3, doublet: CH_3 next to a CH (1 adjacent H), CH_3-CH .

So the compound is $\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{COOH}$, e.g. 2-(4-methylphenyl)propanoic acid ($\text{C}_{10}\text{H}_{12}\text{O}_2$, $M_r = 164.0$):

Additional answer space if required

21



(2-, 3- or 4-substitution of the ring all fit the data)

END OF QUESTION PAPER

[illegible]

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