



Oxford Cambridge and RSA

Tuesday 12 October 2021 – Morning

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

You can use:

- a scientific or graphical calculator
- an HB pencil



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

Centre number

--	--	--	--	--

Candidate number

--	--	--	--

First name(s)

Last name

StemUp Model Solution

INSTRUCTIONS

- Use black ink. You can use an HB pencil, but only for graphs and diagrams.
- Write your answer to each question in the space provided. If you need extra space use the lined pages at the end of this booklet. The question numbers must be clearly shown.
- Answer **all** the questions.
- Where appropriate, your answer should be supported with working. Marks might be given for using a correct method, even if your answer is wrong.

INFORMATION

- The total mark for this paper is **100**.
- The marks for each question are shown in brackets [].
- Quality of extended response will be assessed in questions marked with an asterisk (*).
- This document has **32** pages.

ADVICE

- Read each question carefully before you start your answer.

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 2-Methylbutane is reacted with chlorine by radical substitution.

What is the number of structural isomers with the molecular formula $C_5H_{11}Cl$ that could be formed?

- A 2
- B 3
- C 4
- D 5

Your answer

C

[1]

- 2 Which type(s) of stereoisomerism is/are shown by 2,4-dimethylhex-2-ene?

- A *E/Z* isomerism only.
- B Optical isomerism only.
- C Both *E/Z* isomerism and optical isomerism.
- D Neither *E/Z* isomerism nor optical isomerism.

Your answer

B

[1]

- 3 Which sample contains the greatest number of carbon atoms?

- A 20.0g C_6H_5OH
- B 30.0g C_2H_5COOH
- C 40.0g CH_3CHO
- D 50.0g CH_3OH

Your answer

C

[1]

4 What is the correct equation for the incomplete combustion of butan-1-ol?

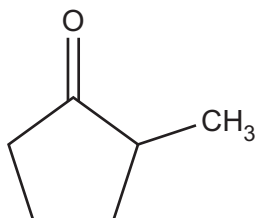
- A $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + 1\frac{1}{2}\text{O}_2 \rightarrow 4\text{CO} + 5\text{H}_2$
- B $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + 2\text{O}_2 \rightarrow 4\text{CO} + 5\text{H}_2$
- C $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + 4\text{O}_2 \rightarrow 4\text{CO} + 5\text{H}_2\text{O}$
- D $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + 4\frac{1}{2}\text{O}_2 \rightarrow 4\text{CO} + 5\text{H}_2\text{O}$

Your answer

C

[1]

5 2-Methylcyclopentanone, shown below, is reacted with $\text{NaCN(aq)/H}^+(\text{aq})$ to form an organic product.



2-methylcyclopentanone

Which statement is correct?

- A In the mechanism, a CN^- ion accepts an electron pair.
- B The mechanism is electrophilic addition.
- C The organic product has one chiral centre.
- D The organic product has the molecular formula $\text{C}_7\text{H}_{11}\text{NO}$.

Your answer

D

[1]

- 6 $\text{CH}_3\text{CH}_2\text{COOCH}_3$ is heated with aqueous sodium hydroxide to produce two organic products.

What are the two organic products?

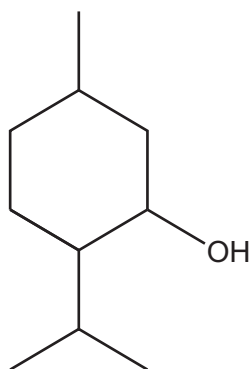
- A** $\text{CH}_3\text{CH}_2\text{COOH}$ and CH_3OH
B $\text{CH}_3\text{CH}_2\text{COONa}$ and CH_3OH
C $\text{CH}_3\text{CH}_2\text{COOH}$ and CH_3ONa
D $\text{CH}_3\text{CH}_2\text{COONa}$ and CH_3ONa

Your answer

B

[1]

- 7 Menthol, shown below, is heated with an acid catalyst.



menthol

Which structure could be formed?

A	B	C	D

Your answer

A

[1]

8 Which compound contains a bond angle of approximately 120° ?

- A $\text{CH}_3\text{CH}_2\text{CN}$
- B $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$
- C $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$
- D $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$

Your answer

C

[1]

9 Which reaction is **not** a reduction?

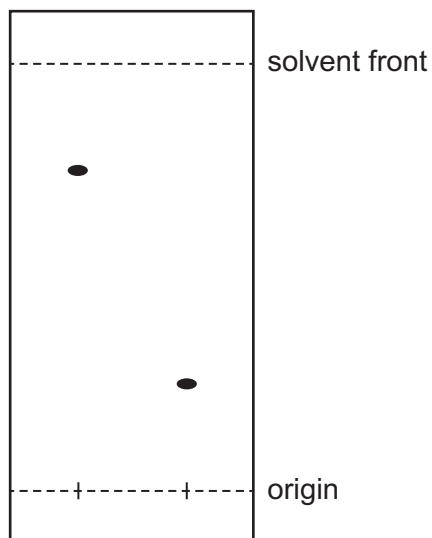
- A $\text{C}_6\text{H}_5\text{NO}_2 \rightarrow \text{C}_6\text{H}_5\text{NH}_2$
- B $\text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2$
- C $\text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2$
- D $\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_3\text{CHOHCH}_3$

Your answer

C

[1]

10 A TLC chromatogram for two compounds is shown below.



What is the R_f value for the compound that is most strongly adsorbed onto the stationary phase?

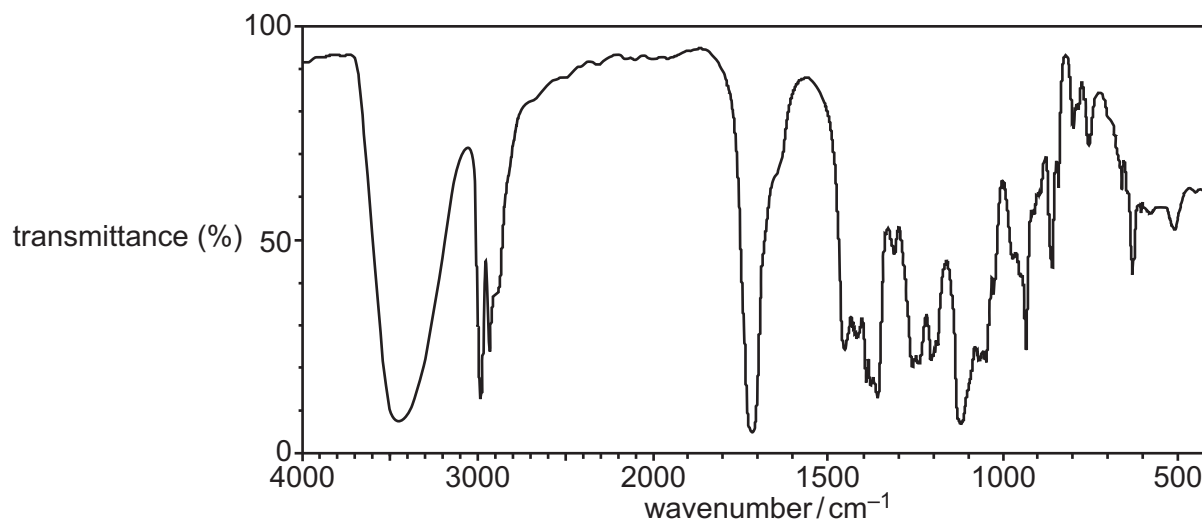
- A 0.25
- B 0.33
- C 0.69
- D 0.78

Your answer

A

[1]

11 Which compound could have produced the IR spectrum below?



- A $(\text{CH}_3)_2\text{CHCHO}$
- B $(\text{CH}_3)_2\text{CHCOOH}$
- C $\text{CH}_3\text{CH}(\text{OH})\text{CH}=\text{CH}_2$
- D $\text{CH}_3\text{COCH}(\text{OH})\text{CH}_3$

Your answer

D

[1]

12 Which peak would be in the mass spectrum of propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, but **not** in the mass spectrum of propanone, CH_3COCH_3 ?

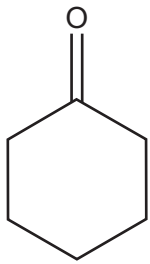
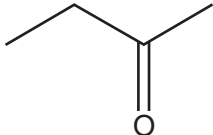
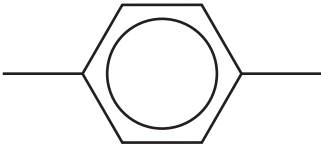
- A $m/z = 15$
- B $m/z = 29$
- C $m/z = 43$
- D $m/z = 58$

Your answer

B

[1]

13 Which compound(s) has/have four peaks in a ^{13}C NMR spectrum?

1	
2	
3	

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

Your answer

B

[1]

14 Which of the following statement(s) provide(s) evidence for the delocalised model of benzene rather than the Kekulé model?

- 1** The enthalpy change of hydrogenation is more exothermic than expected.
- 2** Benzene only reacts with bromine in the presence of a halogen carrier.
- 3** The carbon-carbon bonds all have the same length.

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

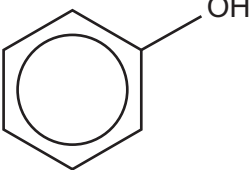
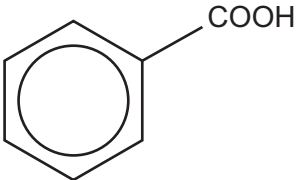
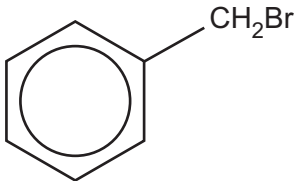
Your answer

C

[1]

15 Compounds **1**, **2** and **3** are heated with NaOH(aq).

Which compound(s) react(s)?

1	
2	
3	

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

Your answer

A

[1]

SECTION B

Answer **all** the questions.

- 16 But-1-ene, $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_3$, and buta-1,3-diene, $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$, are unsaturated compounds used to make many organic products.

(a) But-1-ene and buta-1,3-diene have σ -bonds and π -bonds.

(i) Explain what is meant by the terms **σ -bond** and **π -bond**.

σ -bond: *Head-on overlap of orbitals directly between the two bonding atoms.*

π -bond: *Sideways overlap of adjacent p-orbitals, above and below the bond axis.*

[2]

(ii) How many σ - and π -bonds are in one molecule of buta-1,3-diene?

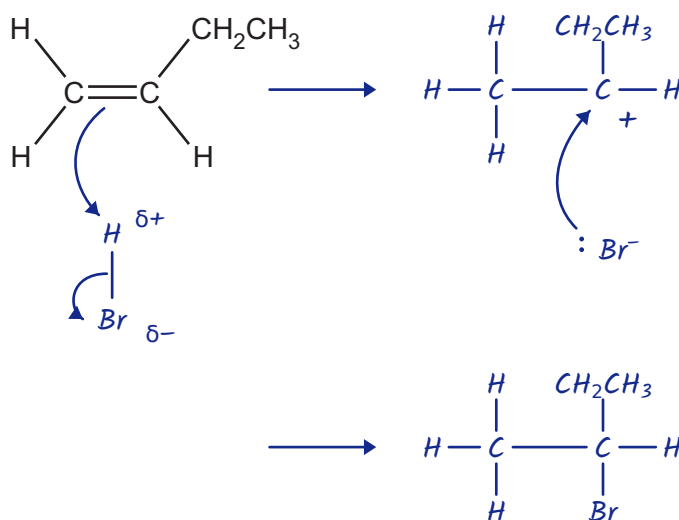
σ -bonds: *9* π -bonds: *2* [2]

(b) But-1-ene is reacted with hydrogen bromide, forming a mixture of two saturated organic products.

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

(i) Outline the reaction mechanism for the formation of this **major** organic product. The structure of but-1-ene has been provided.

Include curly arrows and relevant dipoles.



[4]

- (ii) Explain why one organic product is formed in a much greater quantity than the other organic product.

The major product (2-bromobutane) forms from the more stable carbocation intermediate: a secondary carbocation (C^+ bonded to more alkyl groups / more C atoms). The minor product forms from the less stable primary carbocation. [2]

- (iii) Buta-1,3-diene is reacted with an excess of hydrogen bromide, forming a mixture of saturated organic products.

How many saturated organic products could be present in this mixture?

3 [1]

- (c) A student thought that buta-1,3-diene can show stereoisomerism.

The student drew out skeletal formulae for the stereoisomers of buta-1,3-diene:



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

Compounds with the same structural formula but a different arrangement of the atoms in space. [1]

- (ii) Explain, with a reason, whether the student is correct or incorrect.

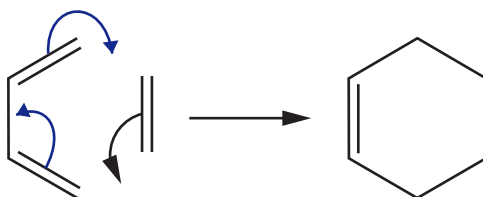
The student is incorrect: there is no E/Z isomerism because each end carbon of the $C=C$ bonds has two identical groups (2 H atoms) attached. The two drawings are the same molecule, interconverted by rotation about the $C-C$ single bond. [1]

(d) 'Diels-Alder' reactions are used in the synthesis of many important organic compounds.

The Diels-Alder reaction of buta-1,3-diene with ethene is shown below.



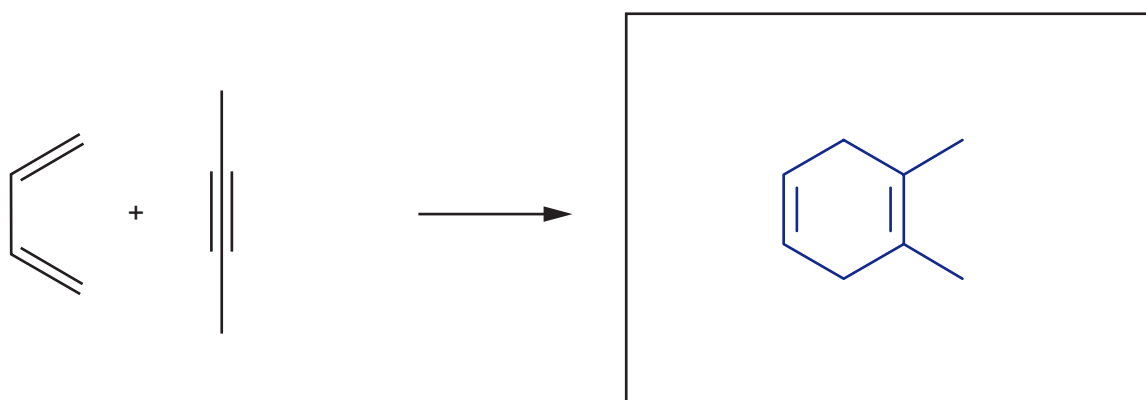
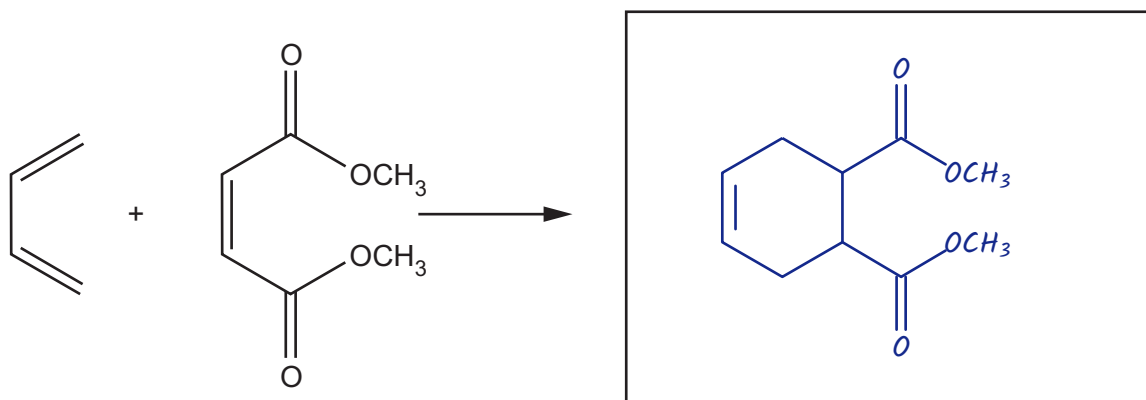
(i) Add curly arrows to the diagram below to complete the mechanism for this Diels-Alder reaction.



[2]

(ii) Two more Diels-Alder reactions of buta-1,3-diene are shown below.

In the boxes, draw the organic product of each reaction.



[2]

13
BLANK PAGE

PLEASE DO NOT WRITE ON THIS PAGE

17 This question is about haloalkanes and polymers.

- (a) Freon-13, is a CFC with the molecular formula CClF_3 .
In the upper atmosphere, the presence of Freon-13 can lead to ozone depletion.

Explain, with the aid of equations, how Freon-13 can lead to this ozone depletion.

Use 'dots' ($\bullet$) to show the position of unpaired electrons.

UV breaks the C-Cl bond homolytically: $\text{CClF}_3 \rightarrow \text{CF}_3\bullet + \text{Cl}\bullet$

$\text{Cl}\bullet + \text{O}_3 \rightarrow \bullet\text{ClO} + \text{O}_2$

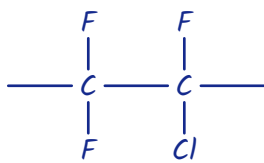
$\bullet\text{ClO} + \text{O} \rightarrow \text{Cl}\bullet + \text{O}_2$

$\text{Cl}\bullet$ is regenerated (catalyst), so one $\text{Cl}\bullet$ breaks down many O_3 . [3]

- (b) An oligomer is a polymer with a low molecular mass and a small number of repeat units.

An oligomer made from 2-chloro-1,1,2-trifluoroethene is used as a lubricating oil.

- (i) Draw the repeat unit of this oligomer.



[1]

- (ii) The boiling point of the lubricating oil can be increased by increasing the number of repeat units.

Explain this statement.

Longer chains have more electrons and more points of contact between

molecules, so stronger London forces and more permanent dipole-dipole

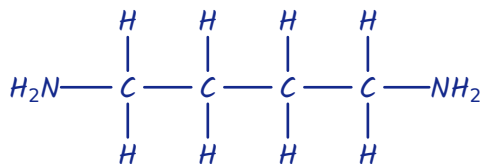
interactions. More energy is needed to break these intermolecular forces.

[2]

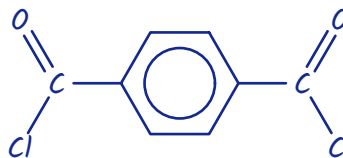
(c) A polymer can be made from the monomers:

- 1,4-diaminobutane
- benzene-1,4-diacyl dichloride.

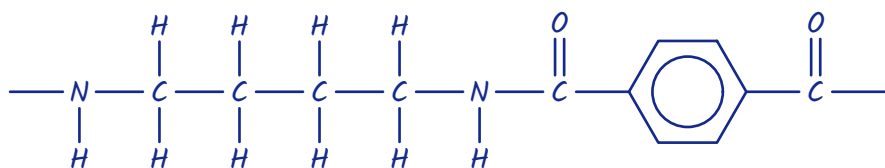
Draw the structures of these monomers and **one** repeat unit of the polymer.



1,4-diaminobutane



benzene-1,4-diacyl dichloride



one repeat unit of polymer

[4]

18 This question is about organic acids.

(a) Table 18.1 shows the R groups in four amino acids.

Amino acid	R group
alanine	CH_3-
valine	$(\text{CH}_3)_2\text{CH}-$
threonine	$\text{CH}_3\text{CH}(\text{OH})-$
lysine	$\text{H}_2\text{N}(\text{CH}_2)_4-$

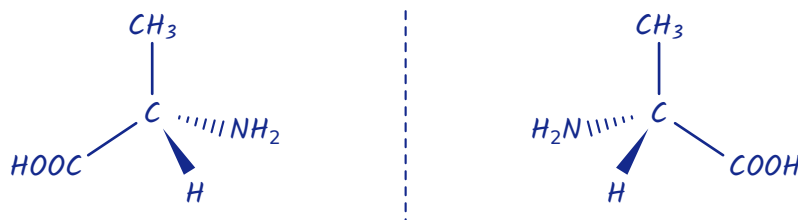
Table 18.1

Most amino acids show optical isomerism.

(i) Explain the term **optical isomerism**.

Stereoisomers that are non-superimposable mirror images of each other
(about a chiral centre).
 [1]

(ii) Draw 3-D diagrams to show the optical isomers of alanine.

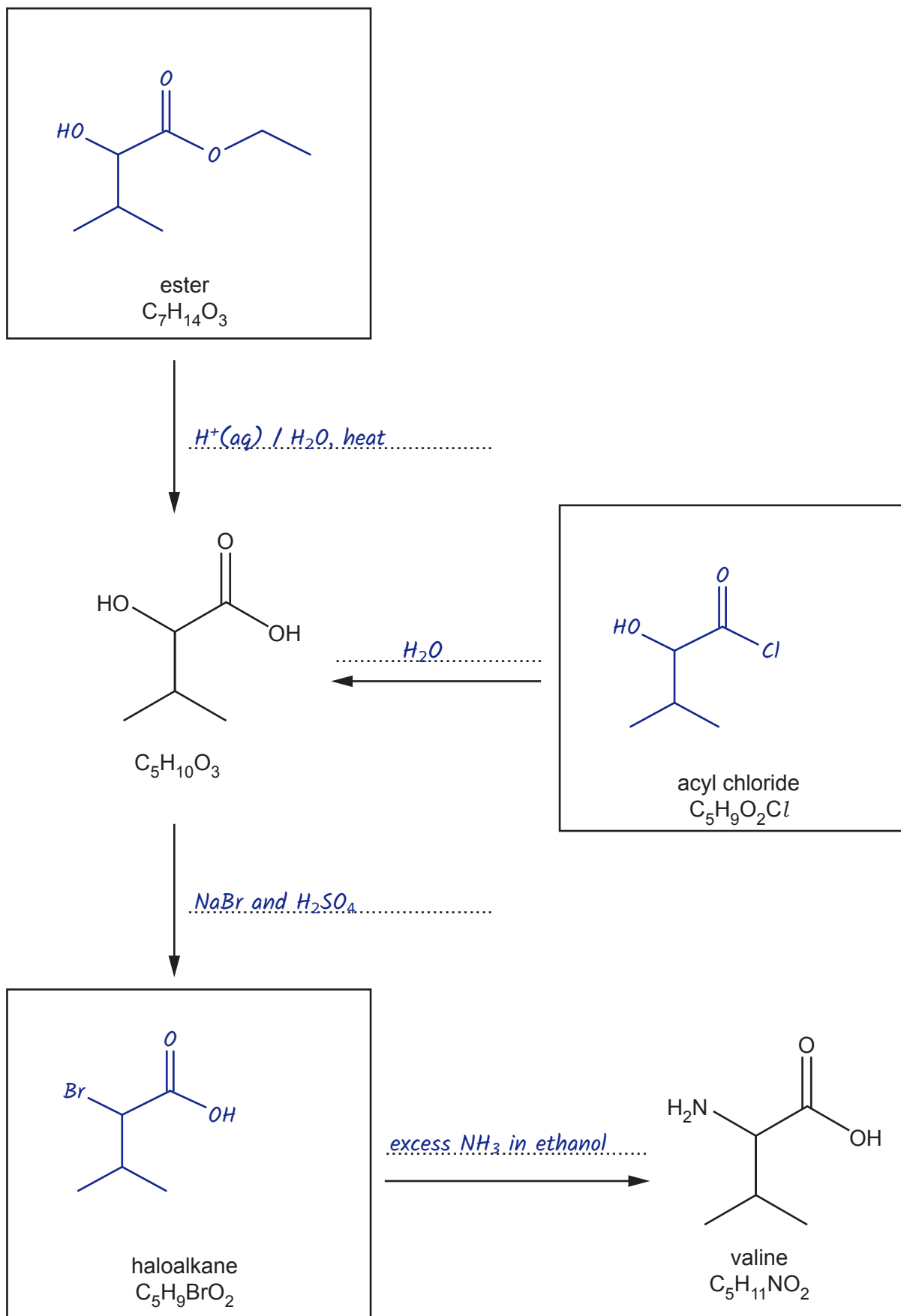


[2]

(iii) How many optical isomers does threonine have?

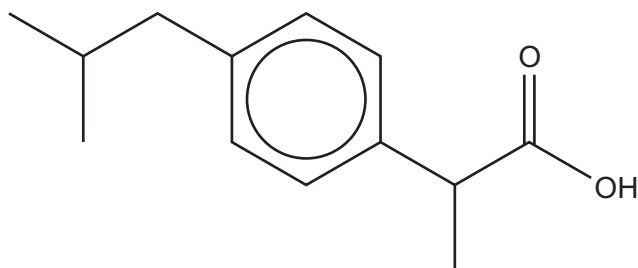
4
 [1]

(b) Complete the flowchart for two synthetic routes to the amino acid valine.



[7]

(c) Ibuprofen, shown below, is used as a painkiller.



ibuprofen

(i) What is the molecular formula of ibuprofen?

$C_{13}H_{18}O_2$ [1]

(ii) One ibuprofen tablet contains 400 mg of ibuprofen.

Calculate the number of ibuprofen molecules in one ibuprofen tablet.

Give your answer to **3** significant figures.

$$M(C_{13}H_{18}O_2) = (13 \times 12.0) + (18 \times 1.0) + (2 \times 16.0) = 206.0 \text{ g mol}^{-1}$$

$$n(\text{ibuprofen}) = (400 \div 1000) \div 206.0 = 1.94 \times 10^{-3} \text{ mol}$$

$$\text{number of molecules} = 1.94 \times 10^{-3} \times 6.02 \times 10^{23} = 1.17 \times 10^{21}$$

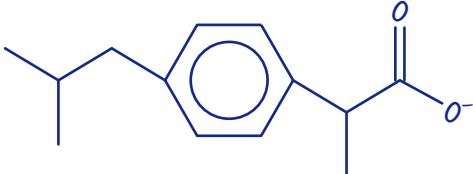
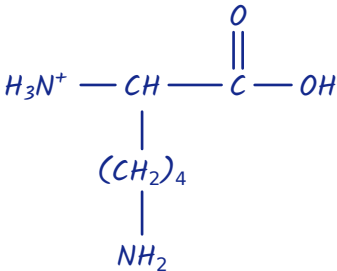
number of ibuprofen molecules = 1.17×10^{21} [3]

- (d) Tablets based on ibuprofen and lysine are now available from pharmacies.

These tablets are claimed to act faster than ibuprofen by being absorbed into the body more quickly than ibuprofen alone.

One type of these tablets contains a salt of ibuprofen and the amino acid lysine ($R = -(\text{CH}_2)_4\text{NH}_2$) in a 1:1 molar proportion.

- (i) Suggest the structure of each ion in this lysine salt of ibuprofen, including the position of any charges.

	
- ion	+ ion

[2]

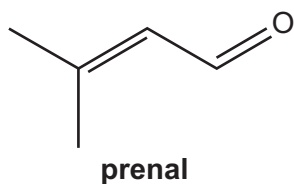
- (ii) Suggest why tablets based on a salt of ibuprofen should act faster in the body than ibuprofen.

*The salt is ionic, so it is more soluble in water than ibuprofen and
dissolves faster in the body.*

[1]

19 This question is about organic synthesis.

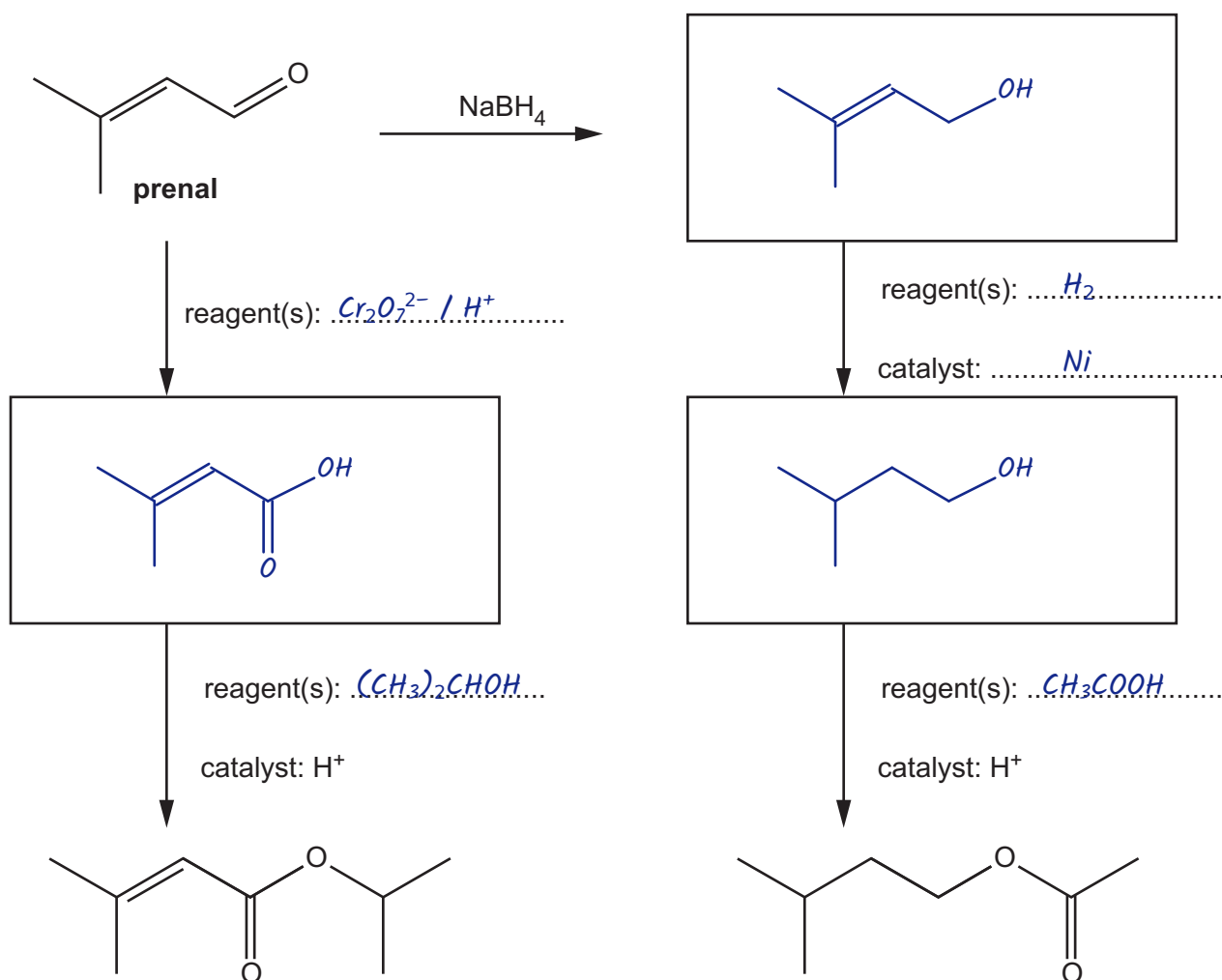
(a) Prenal, shown below, is used in the synthesis of some pharmaceuticals.



(i) What is the systematic name for prenal?

3-methylbut-2-enal..... [1]

(ii) Complete the flowchart below for the synthesis of two compounds starting from prenal.



[7]

21
BLANK PAGE

PLEASE DO NOT WRITE ON THIS PAGE

(b)* A student intends to synthesise compound **A** using the two-stage route below.



Plan a two-stage synthesis to prepare 5.44 g of compound **A** starting from (chloromethyl)benzene, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$. Assume that the overall percentage yield of compound **A** from (chloromethyl)benzene is 25%.

In your answer, include the mass of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ required, reagents, and equations where appropriate.

Purification details are **not** required.

[6]

Calculation: $M(\text{compound A, } \text{C}_6\text{H}_5\text{CH}_2\text{COOH}) = 136.0 \text{ g mol}^{-1}$

$n(\text{A}) = 5.44 \div 136.0 = 0.0400 \text{ mol}$

Overall yield is 25%, so $n(\text{C}_6\text{H}_5\text{CH}_2\text{Cl})$ needed = $0.0400 \times 100 \div 25 = 0.160 \text{ mol}$

$M(\text{C}_6\text{H}_5\text{CH}_2\text{Cl}) = 126.5 \text{ g mol}^{-1}$, so mass of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ required = $0.160 \times 126.5 = 20.24 \text{ g} = 20.2 \text{ g}$

Stage 1: nucleophilic substitution to form the nitrile intermediate $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$.

Heat (chloromethyl)benzene under reflux with NaCN (or KCN) in ethanol; the CN^- ion replaces Cl and adds one carbon to the chain:

$\text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{CN}^- \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CN} + \text{Cl}^-$

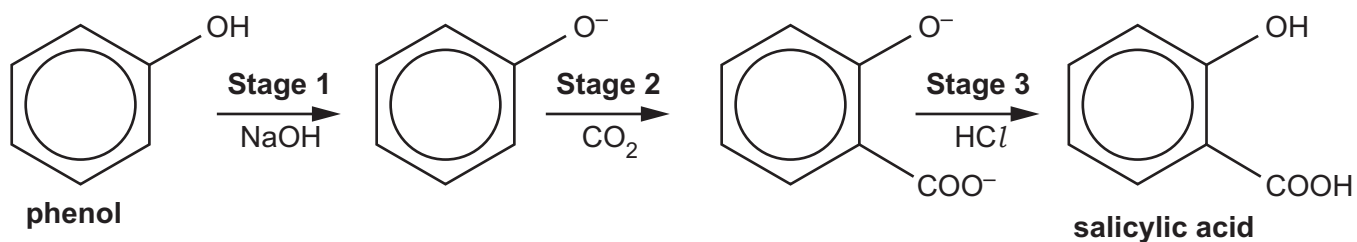
Stage 2: acid hydrolysis of the nitrile. Heat the intermediate $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$ under reflux with dilute hydrochloric acid, HCl(aq) ($\text{H}^+/\text{H}_2\text{O}$), to form compound A:

$\text{C}_6\text{H}_5\text{CH}_2\text{CN} + 2\text{H}_2\text{O} + \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{COOH} + \text{NH}_4\text{Cl}$

Additional answer space if required.

20 This question is about reactions of phenol.

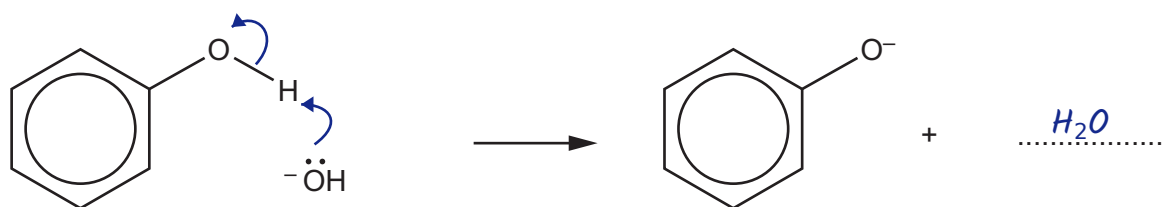
(a) Salicylic acid can be prepared from phenol as shown below.



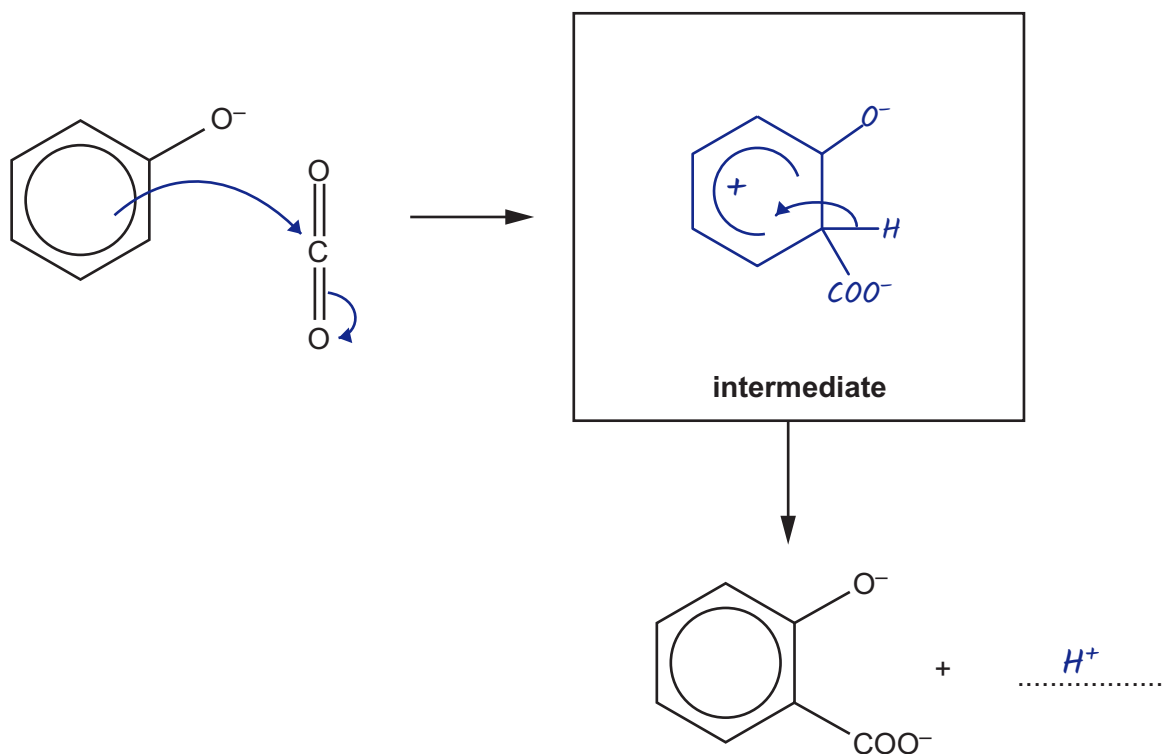
(i) Complete the mechanism below for **Stage 1** and **Stage 2**.

Show curly arrows, the structure of the intermediate and the missing formulae on the dotted lines.

Stage 1



Stage 2



[6]

- (ii) What are the roles of ^-OH and CO_2 in the mechanism?

^-OH *base (it removes H^+ from the OH group)*

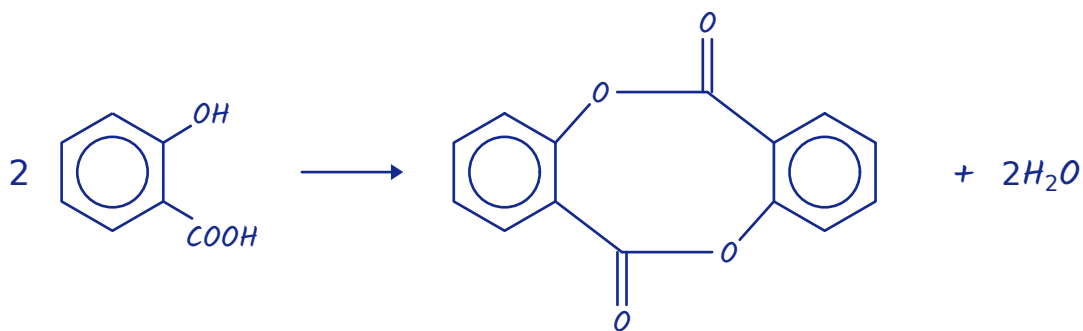
CO_2 *electrophile (electron pair acceptor)*

[2]

- (iii) Two molecules of salicylic acid can react together in the presence of an acid catalyst to form compound **B**.

Compound **B** has three rings and a molecular formula of $\text{C}_{14}\text{H}_8\text{O}_4$.

Write the equation for this reaction showing the structures of organic compounds.



[3]

(b) A student reacts phenol with nitric acid and sulfuric acid at 100 °C to form impure crystals of an organic compound, **C**. The student purifies the crystals by recrystallisation.

- (i) Describe how the student could recrystallise the impure crystals to obtain a pure sample of **C**.

Dissolve the impure crystals in the minimum volume of hot solvent (e.g. hot water). Cool the solution so that crystals of C form; soluble impurities stay in solution. Filter off the crystals (under reduced pressure), wash with a little cold solvent and leave to dry.

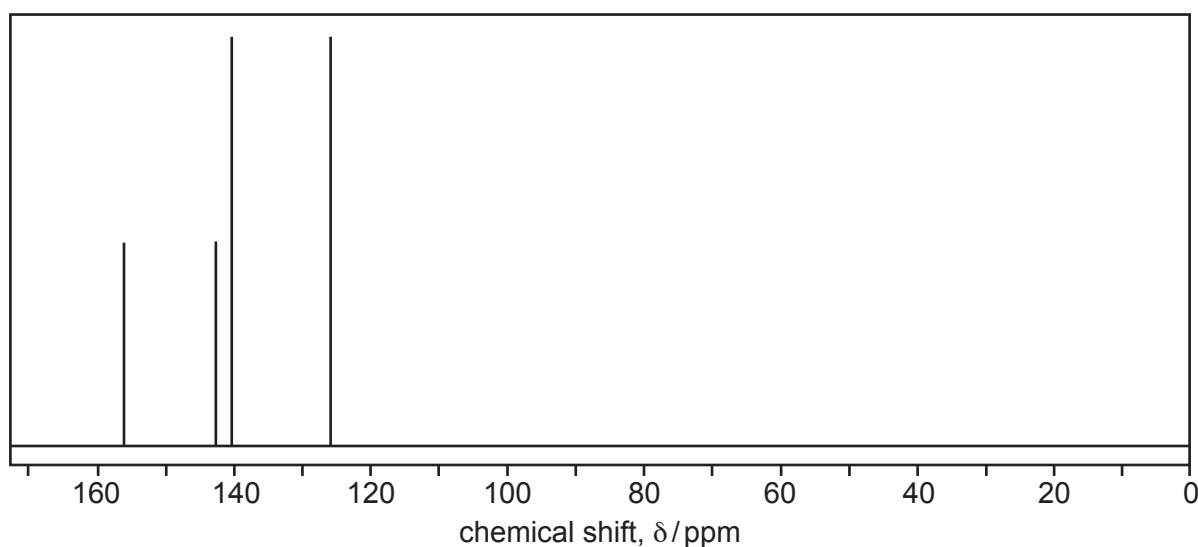
[3]

- (ii) The pure sample of **C** is analysed to give the following results.

Percentage composition by mass: C, 31.44%; H, 1.31%; N, 18.34%; O, 48.91%.

The mass spectrum of **C** shows a molecular ion peak at $m/z = 229.0$

The ^{13}C NMR spectrum of **C** is shown below.



The table shows directing effects for different groups in the electrophilic substitution of aromatic compounds.

Directing effect	2- and 4- directing	3-directing
Group	-OH	-NO ₂
	-NH ₂	

Analyse all the information to suggest the structure for **C**.

Show all your reasoning.

$$C : H : N : O = 31.44/12.0 : 1.31/1.0 : 18.34/14.0 : 48.91/16.0$$

$$= 2.62 : 1.31 : 1.31 : 3.06 = 6 : 3 : 3 : 7, \text{ so the empirical formula is}$$



$M(C_6H_3N_3O_7) = 72.0 + 3.0 + 42.0 + 112.0 = 229.0$, which matches the molecular ion peak at $m/z = 229.0$, so the molecular formula is



This is phenol, C_6H_5OH , with three ring H atoms replaced by $-NO_2$

groups: $C_6H_2(OH)(NO_2)_3$, a trinitrophenol, formed by nitration

(electrophilic substitution).

The ^{13}C NMR spectrum has 4 peaks, so there are 4 carbon environments:

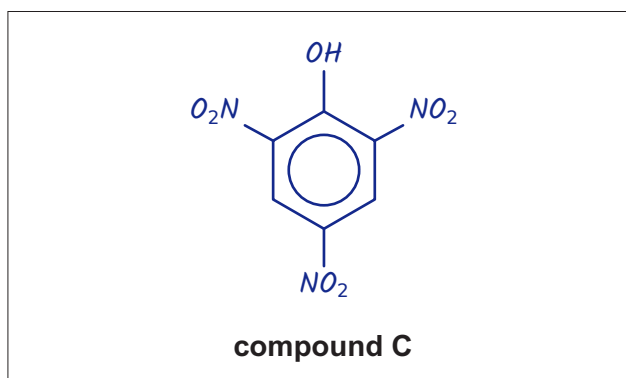
the molecule is symmetrical, so it is 2,4,6- or 3,4,5-trinitrophenol. Peaks:

about 155 ppm C-OH; about 142 and 140 ppm C- NO_2 ; about 126 ppm

C-H (aromatic C).

The $-OH$ group is 2- and 4-directing, so the $-NO_2$ groups substitute at positions 2, 4 and 6, not 3, 4 and 5.

So **C** is 2,4,6-trinitrophenol:



[6]

- 21* Compounds **D**, **E** and **F** are isomers with the molecular formula $C_5H_{10}O$.
One of the compounds is alicyclic.

A student carries out test-tube tests on the compounds.
The observations are shown below.

Compound	2,4-DNP	$H^+/Cr_2O_7^{2-}$, reflux	Bromine water
D	No change	Green solution	No colour change
E	Orange precipitate	No colour change	No colour change
F	Orange precipitate	No colour change	No colour change

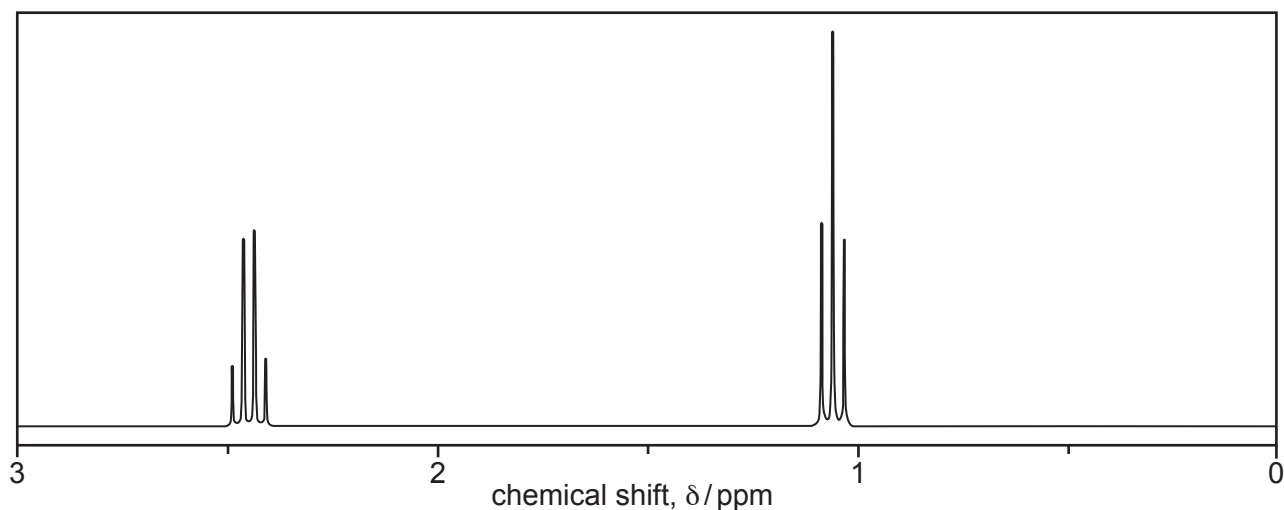
^{13}C NMR spectrum of **D**

Compound **D** has 3 peaks at δ /ppm: 24, 36, 73.

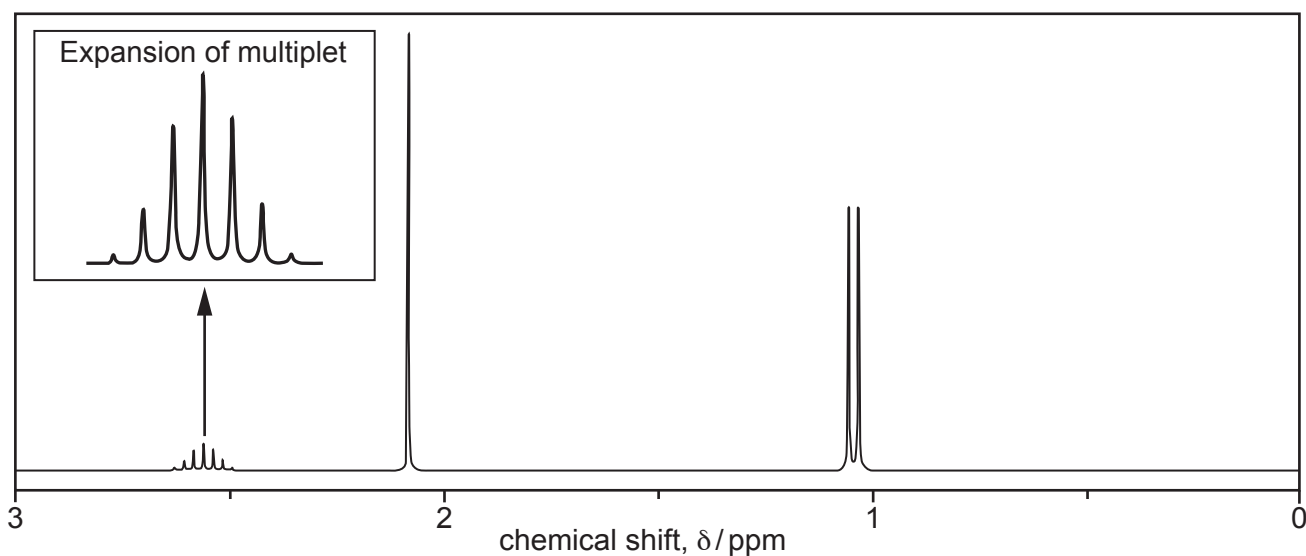
^1H NMR spectra of **E** and **F**

The integration data has been omitted.

Compound E



Compound F



Analyse the observations and results to identify the structures of **D**, **E** and **F**.

Explain your reasoning.

[6]

2,4-DNP: E and F give an orange precipitate, so they contain a carbonyl group ($C=O$); D does not.

$H^+/Cr_2O_7^{2-}$: D turns the solution green (orange to green), so D is a primary or secondary alcohol. E and F do not react, so they are not aldehydes; E and F are ketones.

Bromine water: none decolourise it, so D, E and F have no $C=C$ and are saturated. As D ($C_5H_{10}O$) has no $C=C$ and no $C=O$ it must contain a ring; D is the alicyclic compound.

D: ^{13}C NMR has 3 peaks, so 3 carbon environments; $\delta = 73$ ppm is $C-O$ and $\delta = 24$ and 36 ppm are $C-C$. D is cyclopentanol (C_5H_9OH), which is symmetrical.

E: $\delta = 2.4$ ppm, quartet: $CH_3-CH_2-C=O$ (CH_2 next to $C=O$, split by 3 H). $\delta = 1.1$ ppm, triplet: CH_3-CH_2- (split by 2 H). Only 2 H environments, so E is symmetrical: E is pentan-3-one, $CH_3CH_2COCH_2CH_3$.

F: $\delta = 2.6$ ppm, heptet (multiplet): $(CH_3)_2-CH-C=O$, split by 6 H. $\delta = 2.1$ ppm, singlet: $CH_3-C=O$, no H on adjacent C. $\delta = 1.1$ ppm, doublet: two equivalent CH_3-CH- , split by 1 H.

F is 3-methylbutan-2-one, $CH_3COCH(CH_3)_2$.

Additional answer space if required.

END OF QUESTION PAPER

This image shows a blank sheet of white paper designed for handwriting practice. It features a solid black vertical line on the left side, creating a narrow margin. The rest of the page is filled with evenly spaced, horizontal dashed lines for writing. There are no other markings or text on the page.

Oxford Cambridge and RSA

Copyright Information

OCR is committed to seeking permission to reproduce all third-party content that it uses in its assessment materials. OCR has attempted to identify and contact all copyright holders whose work is used in this paper. To avoid the issue of disclosure of answer-related information to candidates, all copyright acknowledgements are reproduced in the OCR Copyright Acknowledgements Booklet. This is produced for each series of examinations and is freely available to download from our public website (www.ocr.org.uk) after the live examination series.

If OCR has unwittingly failed to correctly acknowledge or clear any third-party content in this assessment material, OCR will be happy to correct its mistake at the earliest possible opportunity.

For queries or further information please contact The OCR Copyright Team, The Triangle Building, Shaftesbury Road, Cambridge CB2 8EA.

OCR is part of the Cambridge Assessment Group; Cambridge Assessment is the brand name of University of Cambridge Local Examinations Syndicate (UCLES), which is itself a department of the University of Cambridge.