

**OXFORD CAMBRIDGE AND RSA EXAMINATIONS
A LEVEL**

H432/02

CHEMISTRY A

Synthesis and analytical techniques

MONDAY 19 JUNE 2017: Morning

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

MODIFIED ENLARGED

First name		Last name	
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Centre number						Candidate number				
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YOU MUST HAVE:

the Data Sheet for Chemistry A

YOU MAY USE:

a scientific or graphical calculator

a ruler (cm/mm)

READ INSTRUCTIONS OVERLEAF



INSTRUCTIONS

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

Complete the boxes on the first 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 (*).

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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.

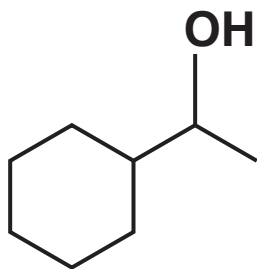
- 1 A chemist compares the rates of hydrolysis of 1-chloropropane and 1-bromopropane in ethanol.

Which reagent in aqueous solution should be used?

- A Silver chloride
- B Silver nitrate
- C Potassium chloride
- D Potassium nitrate

Your answer [1]

2 How can the molecule below be described?



- A Aromatic and alicyclic**
- B Aliphatic and unsaturated**
- C Aromatic and unsaturated**
- D Alicyclic and saturated**

Your answer

[1]

- 3 Complete combustion of an organic compound forms 40 cm^3 of carbon dioxide and 40 cm^3 of water vapour, under the same conditions of temperature and pressure.

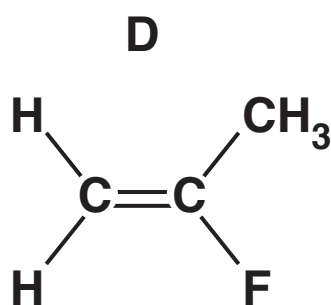
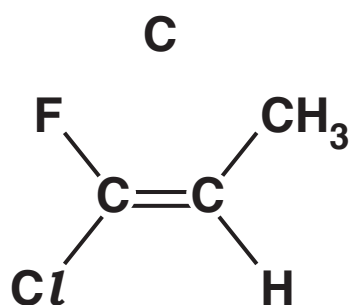
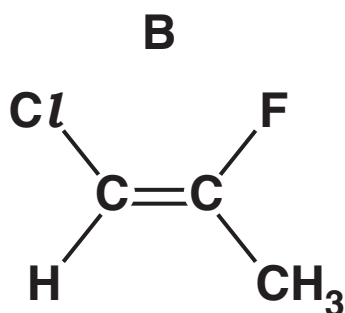
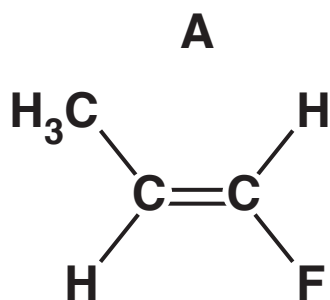
Which molecular formula could the organic compound have?

- A C_3H_8
- B $\text{C}_2\text{H}_2\text{O}$
- C $\text{C}_2\text{H}_4\text{O}$
- D $\text{C}_2\text{H}_3\text{N}$

Your answer

[1]

4 Which molecule is a Z-isomer?



Your answer

[1]

5 Which type of reaction has the greatest atom economy?

A Substitution

B Hydrolysis

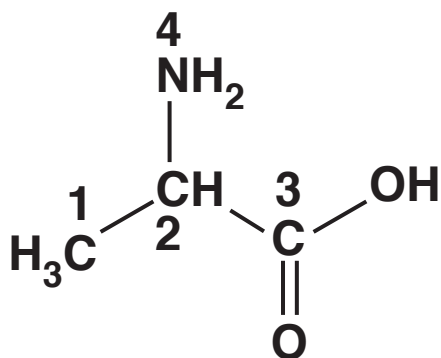
C Elimination

D Addition

Your answer

[1]

6 Four atoms, 1–4, are labelled in the structure below.



Which atom has a trigonal planar arrangement of bonds around it?

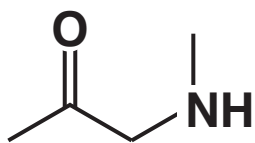
- A Atom 1
- B Atom 2
- C Atom 3
- D Atom 4

Your answer

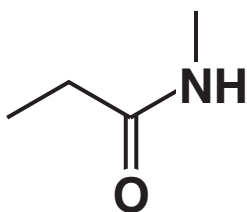
[1]

7 Which molecule is a secondary amine?

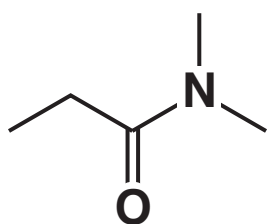
A



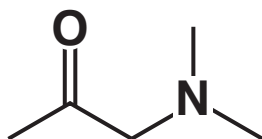
B



C



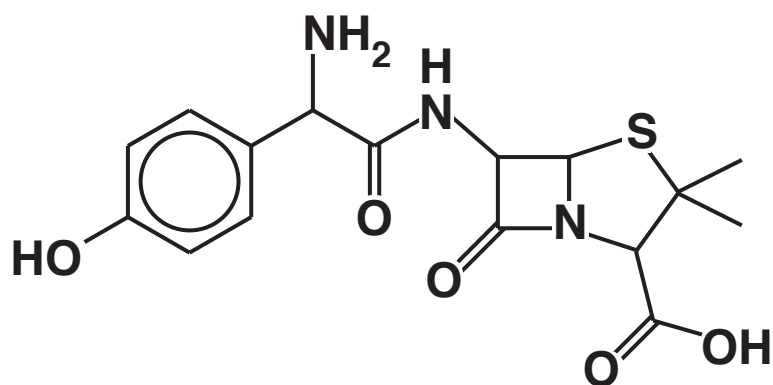
D



Your answer

[1]

8 What is the number of chiral centres in the molecule below?



A 2

B 3

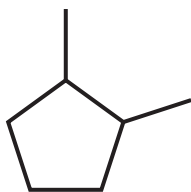
C 4

D 5

Your answer

[1]

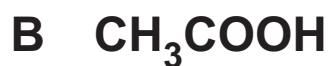
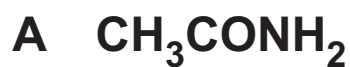
- 9 What is the molecular formula of the compound below?



Your answer [1]

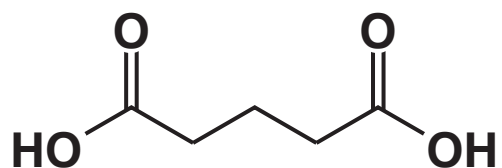
- 10 Equal amounts of the four compounds are added to the same volume of water.

Which compound would produce the most acidic solution?



Your answer [1]

11 The compound below is analysed by ^1H NMR spectroscopy.



How many peaks are observed in the ^1H NMR spectrum?

A 5

B 4

C 3

D 2

Your answer

[1]

12 0.1 mol of $\text{HOOCCH}_2\text{COOH}$ are reacted with 0.1 mol of aqueous NaOH .

How many molecules of water are formed?

A 6.02×10^{22}

B 3.01×10^{22}

C 6.02×10^{23}

D 3.01×10^{23}

Your answer [1]

13 Which reagents could be used to prepare $\text{CH}_3\text{CH}_2\text{CONHCH}_3$?



Your answer [1]

14 Ethane reacts with chlorine by radical substitution to form chloroethane.

Which radical(s) is/are present in the mechanism?

1 $\text{H}\cdot$

2 $\text{Cl}\cdot$

3 $\text{C}_2\text{H}_5\cdot$

A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer

[1]

15 Which compound(s) is a/are structural isomer(s) of $C_6H_{12}O_2$?

1 hexanoic acid

2 ethyl butanoate

3 propyl propanoate

A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer

[1]

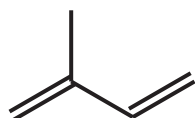
SECTION B

Answer ALL the questions.

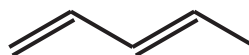
16 This question is about unsaturated hydrocarbons.

(a) Compound A and compound B are isomers.

COMPOUND A



COMPOUND B



Compound A has a lower melting point than compound B.

Suggest why.

[2]

(b) Compound C, $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{OH}$, exists as *cis* and *trans* stereoisomers.

(i) Name compound C.

_____ [1]

(ii) Define the term 'stereoisomers'.

_____ [1]

(iii) Draw the structures of the 'cis' and 'trans' stereoisomers of compound C. [2]

'cis'	'trans'

(c) The C=C group in an alkene contains a π -bond.

Complete the diagram below to show how p-orbitals are involved in the formation of a π -bond. [1]



- (d) Compound D, shown below, reacts with hydrogen bromide by electrophilic addition. A mixture of two organic compounds, E and F, is formed.

COMPOUND D



- (i) Suggest how an HBr molecule can act as an electrophile.

[1]

- (ii) Draw the structures of the two organic compounds E and F below. [2]

E	F

- (iii) Outline the mechanism of the reaction between compound D and hydrogen bromide to form EITHER compound E OR compound F. Use the space below.**

Include curly arrows and relevant dipoles. [3]

(iv) Which of E or F is the major organic product?

Explain your answer.

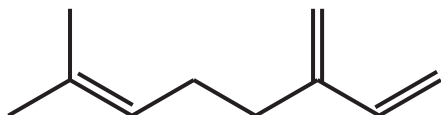
Major organic product _____

Explanation _____

_____ **[1]**

- (e) Myrcene, $C_{10}H_{16}$, is a naturally occurring hydrocarbon containing more than one carbon-carbon double bond.

MYRCENE



- (i) Reaction of 204 mg of myrcene with hydrogen gas produces a saturated alkane.

Calculate the volume of hydrogen gas, in cm^3 and measured at RTP, needed for this reaction.

Show your working.

volume = _____ cm^3 [2]

- (ii) β -Carotene is a naturally occurring unsaturated hydrocarbon found in carrots. A β -carotene molecule contains 40 carbon atoms, has two rings, and a branched chain.

0.0200 mol of β -carotene reacts with 5.28 dm³ of hydrogen gas to form a saturated hydrocarbon.

Using molecular formulae, construct a balanced equation for this reaction.

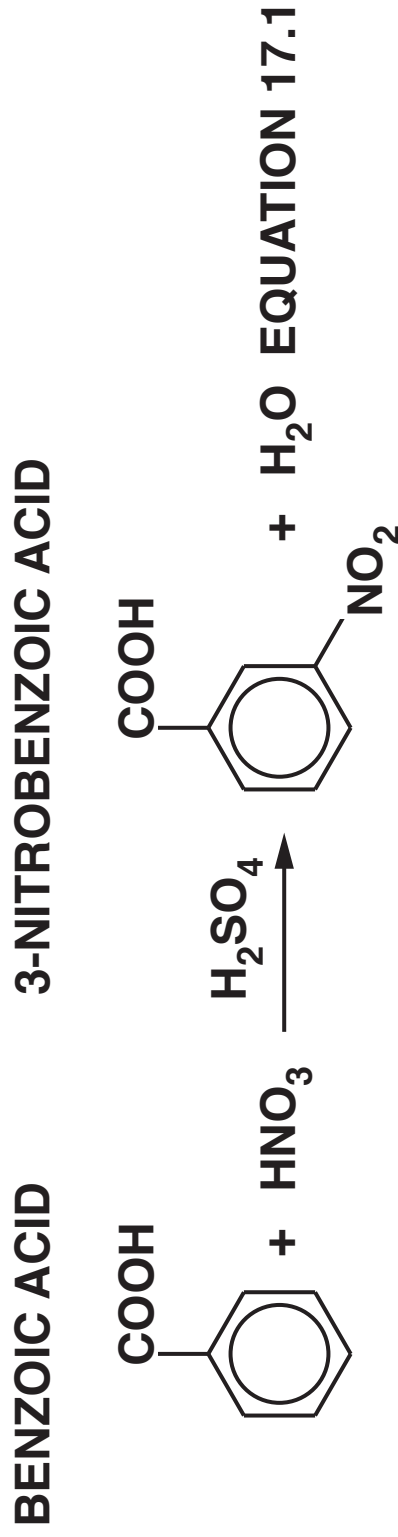
Include relevant calculations and reasoning.

Equation _____ [4]

17 This question is about the chemistry of aromatic compounds.

- (a) Benzoic acid can be nitrated by concentrated nitric acid in the presence of concentrated sulfuric acid as a catalyst, as shown in EQUATION 17.1.

The organic product of this reaction is 3-nitrobenzoic acid.



- (i) Outline the mechanism for this nitration of benzoic acid.

Show how H_2SO_4 behaves as a catalyst. Use the space opposite. [5]

(ii)* A chemist carries out the reaction in EQUATION 17.1 using 4.97 g of benzoic acid.

The chemist obtains 3-nitrobenzoic acid as an impure solid.

The chemist purifies the solid to obtain 4.85 g of 3-nitrobenzoic acid.

Describe a method to obtain a pure sample of 3-nitrobenzoic acid from the impure solid, determine the percentage yield and check its purity. [6]

(b) A student investigates the relative ease of nitration of phenol, benzene, and benzoic acid.

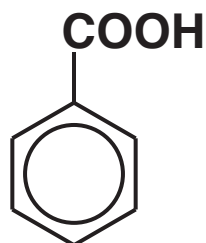
PHENOL



BENZENE



**BENZOIC
ACID**



The student finds that the conditions required for the nitration of each compound are different, as shown in TABLE 17.1.

TABLE 17.1

Compound	phenol	benzene	benzoic acid
Conditions required for nitration	<p>Dilute HNO_3</p> <p>20°C</p> <p>No catalyst</p>	<p>Concentrated HNO_3</p> <p>55°C</p> <p>H_2SO_4 catalyst</p>	<p>Concentrated HNO_3</p> <p>100°C</p> <p>H_2SO_4 catalyst</p>

(i) State the trend in the relative ease of nitration of phenol, benzene, and benzoic acid.

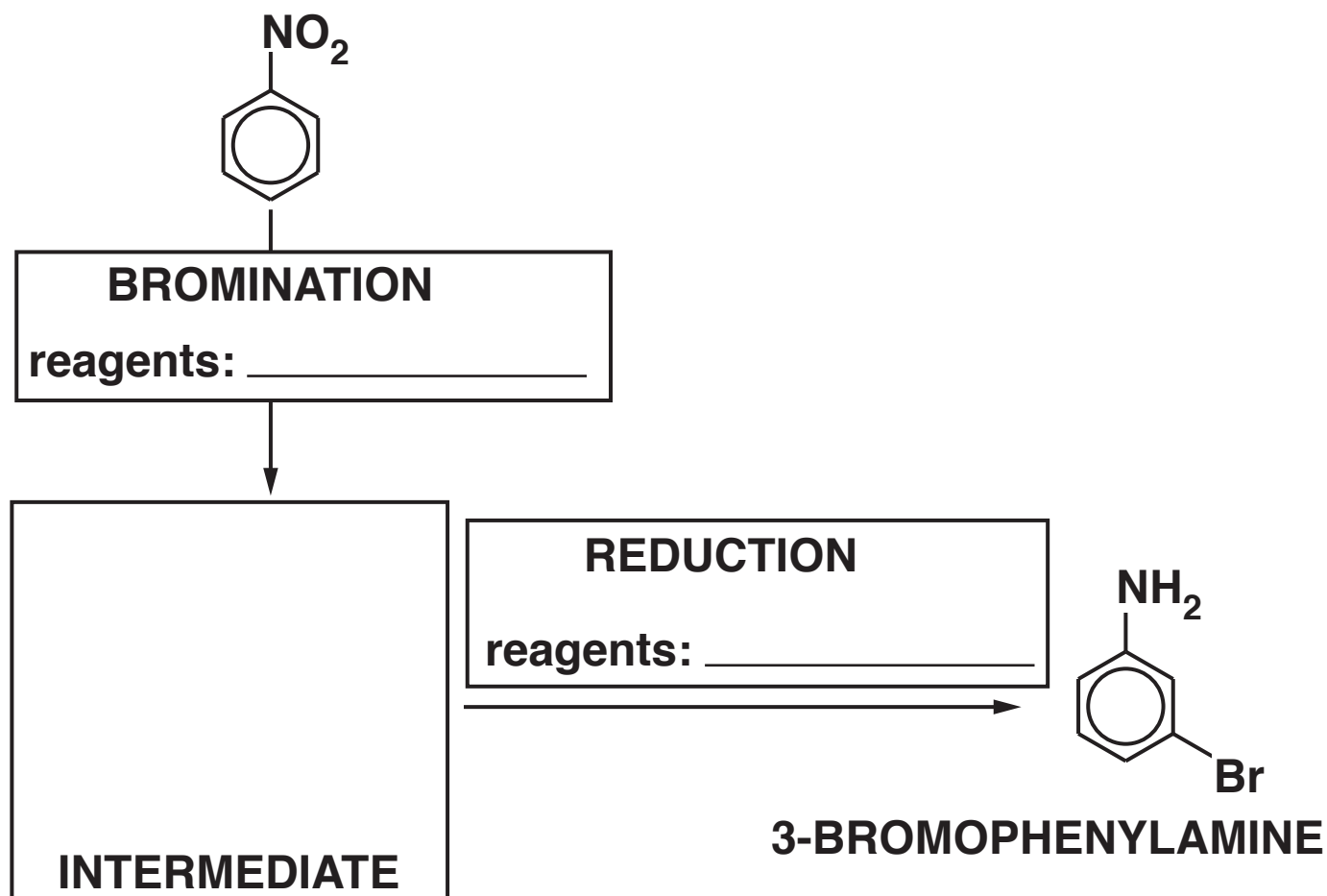
[1]

(ii) Apply your knowledge of the bonding in arenes to explain the trend in part (b)(i).

[3]

(c) A student synthesises 3-bromophenylamine, shown below, starting from nitrobenzene.

- (i) Complete the flowchart below showing the structure of the intermediate and the FORMULAE of the reagents for each stage. [3]



- (ii) Another student attempts the same synthesis but carries out reduction **BEFORE** bromination. The student was surprised to find that two structural isomers of 3-bromophenylamine had been formed instead of the desired organic product.

Explain this result and suggest the structures of the two isomers that formed. [3]

Explanation

Structures

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18 This question is about organic compounds containing nitrogen.

(a) Sodium cyanide, NaCN, can be reacted with many organic compounds to increase the length of a carbon chain.

(i) 1-Chloropropane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$, reacts with ethanolic sodium cyanide by nucleophilic substitution.

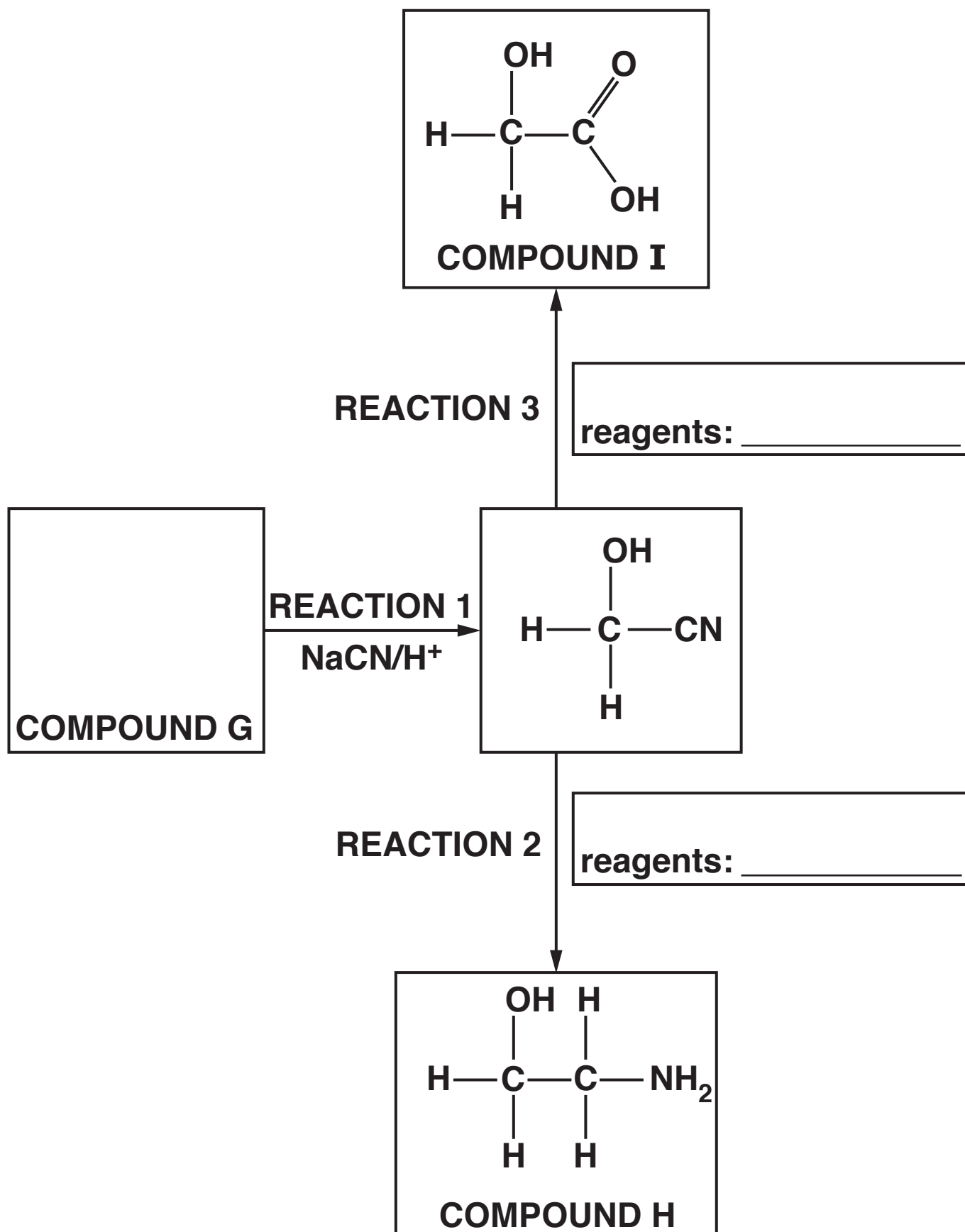
Outline the mechanism for this reaction in the space below.

Include curly arrows, relevant dipoles and the structure of the organic product. [3]

- (ii) Compound G is used to synthesise compounds H and I as shown in the flowchart opposite.

Complete the flowchart showing the structure of compound G and the FORMULAE of the reagents for REACTION 2 and REACTION 3.

[3]



- (iii) Compound H reacts with dilute hydrochloric acid to form a salt.

Explain why compound H can react with dilute hydrochloric acid and suggest a structure for the salt formed. [2]

Explanation _____

Structure

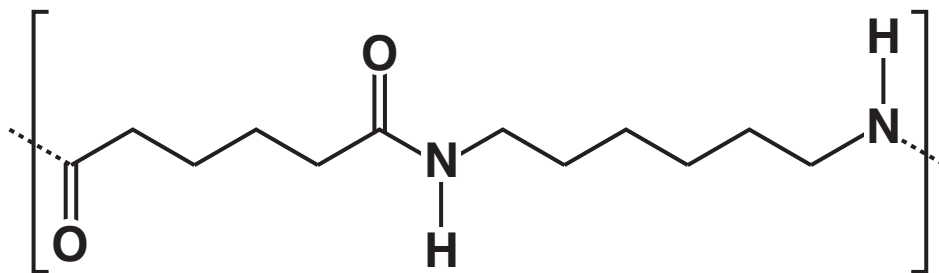
- (iv) Compound **I** is the monomer for the biodegradable polymer J.

Draw **TWO** repeat units of polymer J and suggest a reason why it is biodegradable.

[3]

(b) The repeat unit of Nylon 6,6 is shown below.

NYLON 6,6



(i) Draw the structures of TWO monomers that can be used to form Nylon 6,6 in the space below. [2]

- (ii) A sample of Nylon 6,6 has a relative molecular mass of 21500.

Estimate the number of repeat units in the sample.

Give your answer as a WHOLE number.

number of repeat units = _____ [1]

19 This question is about alcohols.

- (a) Construct an equation for the complete combustion of an unsaturated alcohol with 5 carbon atoms.**

_____ **[1]**

- (b) Many alcohols, including ethanol, are soluble in water.**

- (i) Explain, with the aid of a diagram, why ethanol is soluble in water.**

Include relevant dipoles and lone pairs.

_____ **[2]**

- (ii) The solubility of hexan-1-ol and hexane-1,6-diol in water is shown below in TABLE 19.1.

TABLE 19.1

Alcohol	Solubility in water / g dm⁻³
hexan-1-ol	5.9
hexane-1,6-diol	500

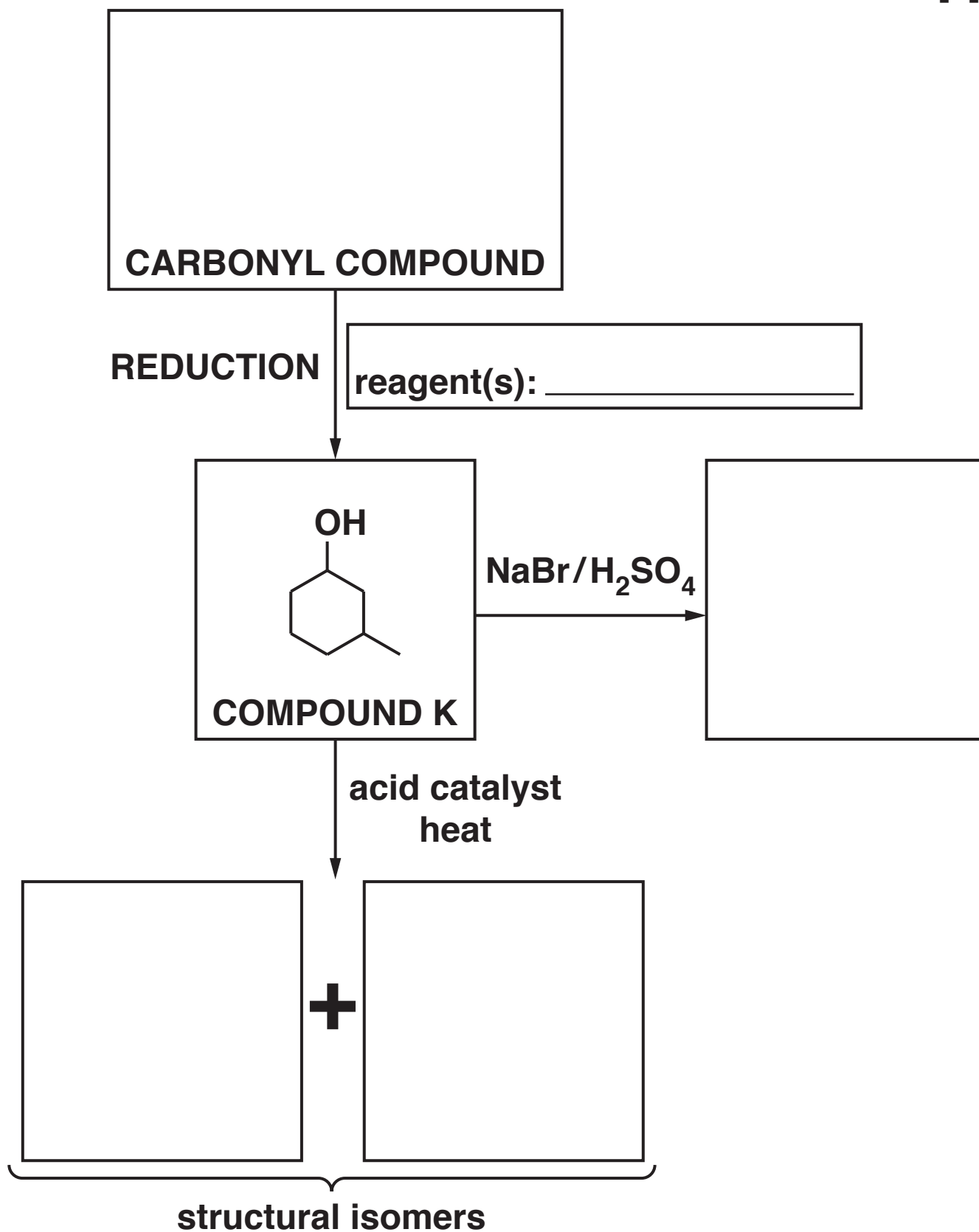
Explain the difference in solubility of hexan-1-ol and hexane-1,6-diol.

[1]

(c) Alcohols are important in organic synthesis and can be formed by the reduction of carbonyl compounds.

(i) Complete the flowchart by filling in each box.

[5]



(ii) What is the name of compound K?

_____ **[1]**

- (d) Butan-1-ol can be oxidised to form two different organic products, depending on the reaction conditions used.

Describe both oxidation reactions of butan-1-ol.

For each reaction include
the structure of the organic product

a balanced equation

the essential reaction conditions.

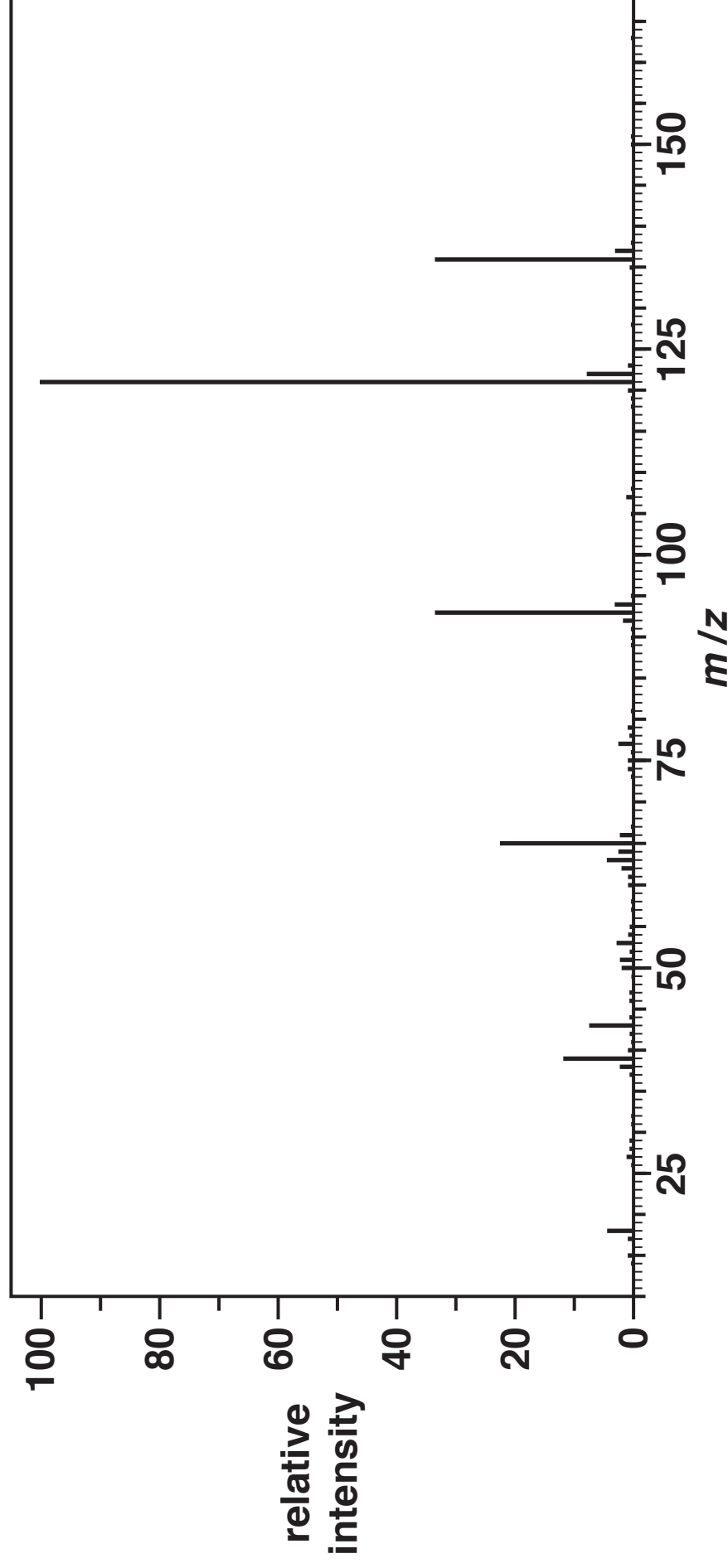
In your equations you may use [O] to represent
the oxidising agent. [5]

20 A chemist analyses a naturally occurring aromatic compound.

(a) The percentage composition and mass spectrum of the compound are shown below.

Percentage composition by mass: C, 70.58%; H, 5.92%; O, 23.50%.

Mass spectrum



Determine the molecular formula of the compound.

Show your working.

molecular formula = _____ [3]

(b) Qualitative tests are carried out on the aromatic compound. The results are shown opposite.

**Determine the functional groups in the compound.
Explain your reasoning.**

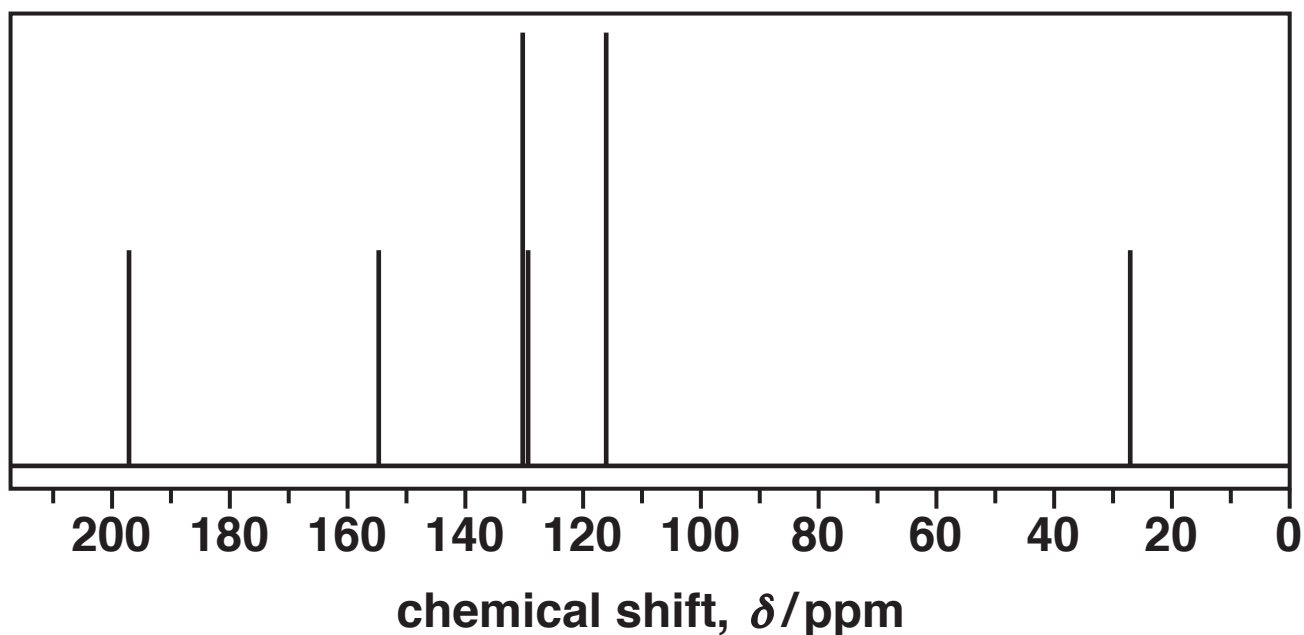
Functional groups _____

Explanation _____

_____ **[3]**

Test	Acidity	Na₂CO₃(aq)	2,4-DNP	Tollens' reagent
Observation	pH = 5	No observable change	Orange precipitate	No observable change

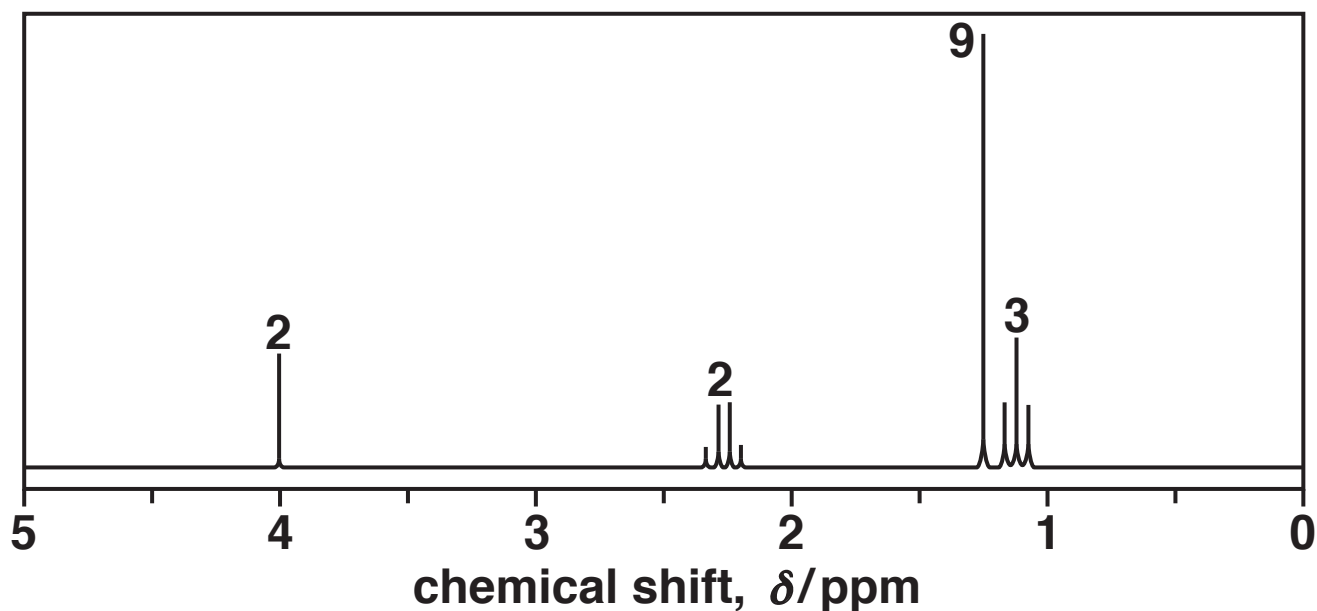
(c) The carbon-13 NMR spectrum of the compound is shown below.



Using the spectrum and the results from (a) and (b), determine the structure of the compound. Explain your reasoning. [3]

STRUCTURE OF COMPOUND

21* Compound L is an organic compound containing carbon, hydrogen and oxygen only.
The ^1H NMR spectrum of compound L is shown below.
The numbers by the peaks are the relative peak areas.



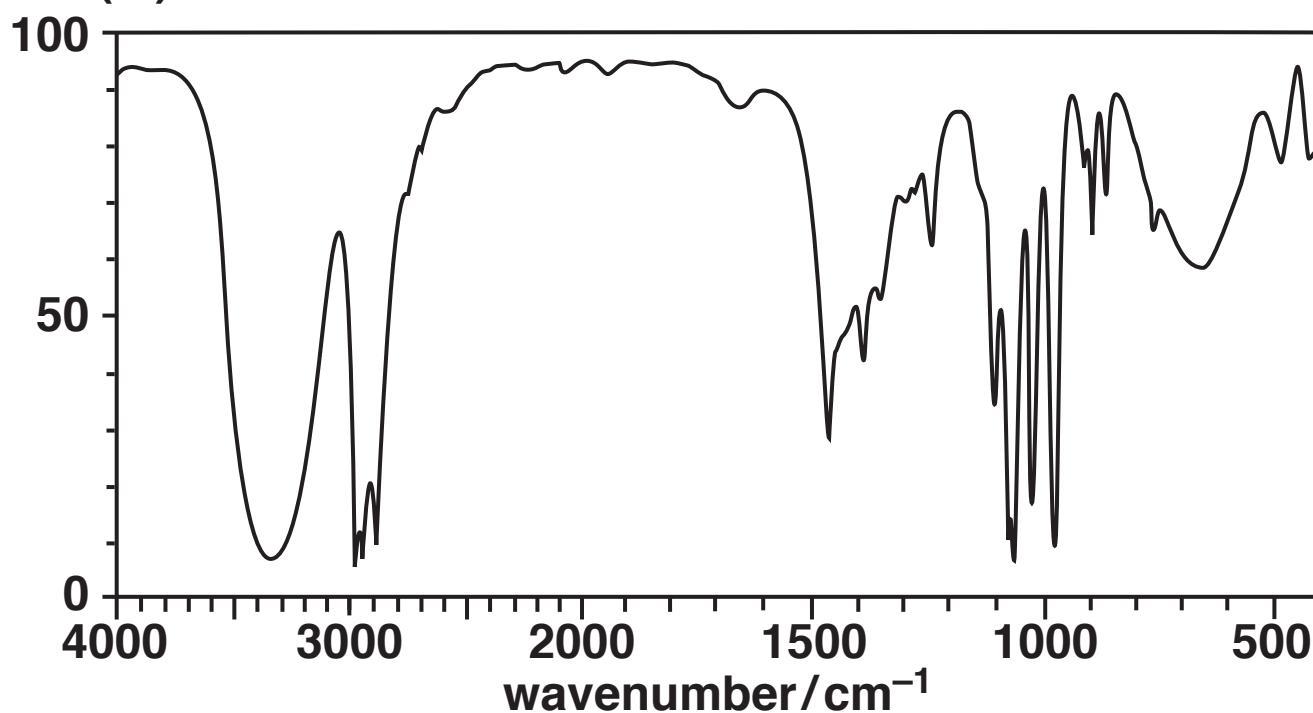
Compound L is refluxed with aqueous hydrochloric acid, forming two organic compounds M and N. The infrared spectra of M and N are shown below.

Infrared spectrum of M

Item removed due to third party copyright restrictions.

Infrared spectrum of N

transmittance
(%)



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

Show ALL of your reasoning. [6]

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).

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