OCR
Oxford Cambridge and RSA

A Level Chemistry A

H432/02 Synthesis and analytical techniques

Monday 19 June 2017 – Morning

Time allowed: 2 hours 15 minutes

6826116453

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

You may use:
- a scientific or graphical calculator
- a ruler (cm/mm)

H43202

First name	
Last name	StemUp Model Solution

Centre number						Candidate number				

INSTRUCTIONS
- Use black ink. You may use an HB pencil for graphs and diagrams.
- Complete the boxes above 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.
- Do **not** write in the barcodes.

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 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

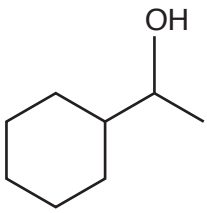
C Potassium chloride

D Potassium nitrate

Your answer B

[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 D

[1]

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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 C_2H_2O

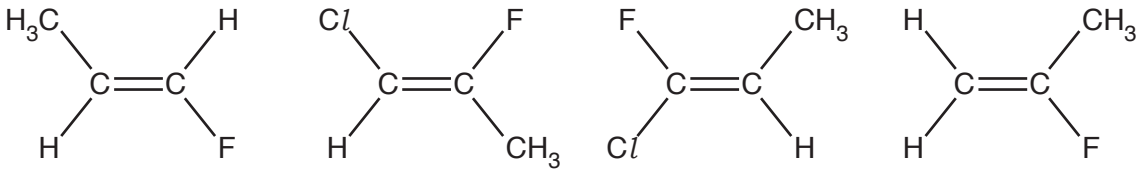
C C_2H_4O

D C_2H_3N

Your answer C

[1]

4 Which molecule is a *Z*-isomer?



A **B** **C** **D**

Your answer B

[1]

5 Which type of reaction has the greatest atom economy?

A Substitution

B Hydrolysis

C Elimination

D Addition

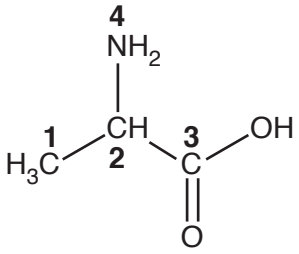
Your answer D

[1]

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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

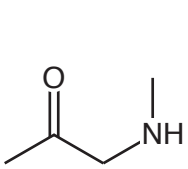
C Atom 3

D Atom 4

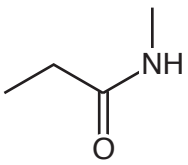
Your answer C

[1]

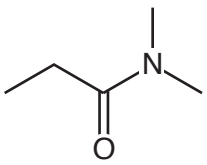
7 Which molecule is a secondary amine?



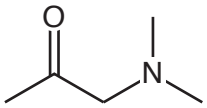
A



B



C



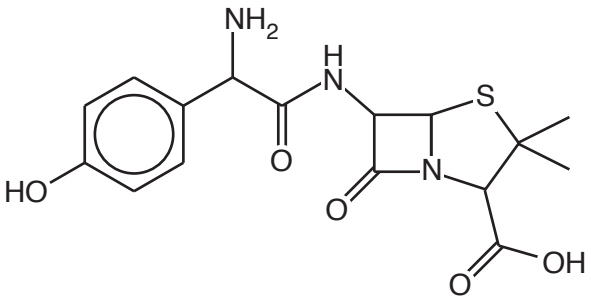
D

Your answer A

[1]

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



A 2

B 3

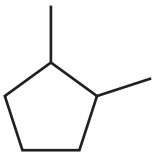
C 4

D 5

Your answer C

[1]

9 What is the molecular formula of the compound below?



A C_7H_{10}

B C_7H_{12}

C C_7H_{14}

D C_7H_{16}

Your answer C

[1]

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

Which compound would produce the most acidic solution?

A CH_3CONH_2

B CH_3COOH

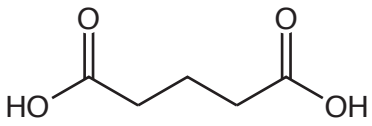
C CH_3COOCH_3

D CH_3COCl

Your answer D

[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 C

[1]

12 0.1 mol of $HOOCCH_2COOH$ 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 A

[1]

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13 Which reagents could be used to prepare $CH_3CH_2CONHCH_3$?

A $CH_3CH_2COCl + CH_3NH_2$

B $CH_3CH_2CONH_2 + CH_3Br$

C $CH_3CH_2COONa + CH_3NH_2$

D $CH_3CH_2COCH_3 + NH_3$

Your answer A

[1]

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

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

1 $H^{\bullet}$

2 $Cl^{\bullet}$

3 $C_2H_5^{\bullet}$

A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer C

[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 A

[1]

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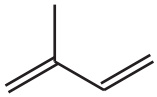
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SECTION B

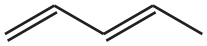
Answer **all** the questions.

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.

Compound A is branched, so its molecules have fewer points of contact (less surface interaction) between molecules than the straight-chain compound B. So A has weaker induced dipole-dipole interactions (London forces) between its molecules, and less energy is required to break these interactions.

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

(b) Compound **C**, $CH_3CH_2CH{=}CHCH_2CH_2OH$, exists as *cis* and *trans* stereoisomers.

(i) Name compound **C**.

hex-3-en-1-ol ..... **[1]**

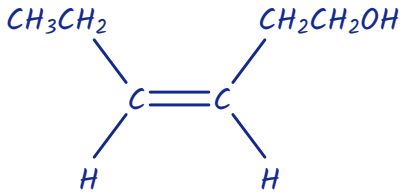
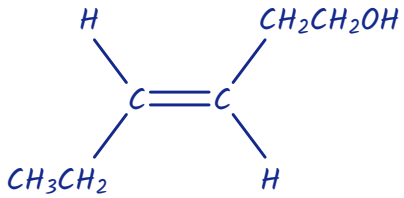
(ii) Define the term *stereoisomers*.

Stereoisomers have the same structural formula but a different arrangement of their atoms in space.

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

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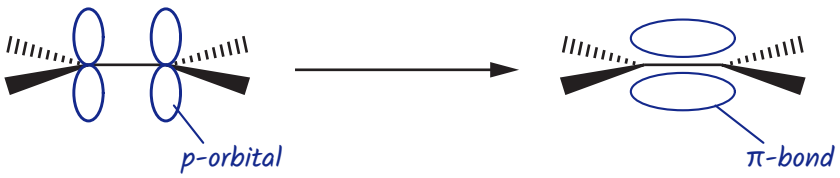
(iii) Draw the structures of the *cis* and *trans* stereoisomers of compound **C**.

	
cis	*trans*

[2]

(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]

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



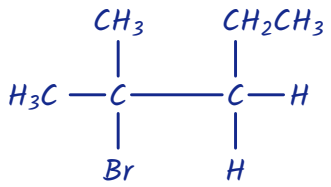
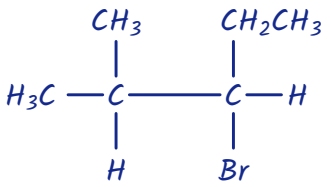
compound D

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

The H-Br bond is polar ($H^{\delta+}$-$Br^{\delta-}$), so the δ+ H atom accepts a pair of electrons from the C=C bond.

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

(ii) Draw the structures of the two organic compounds **E** and **F**.

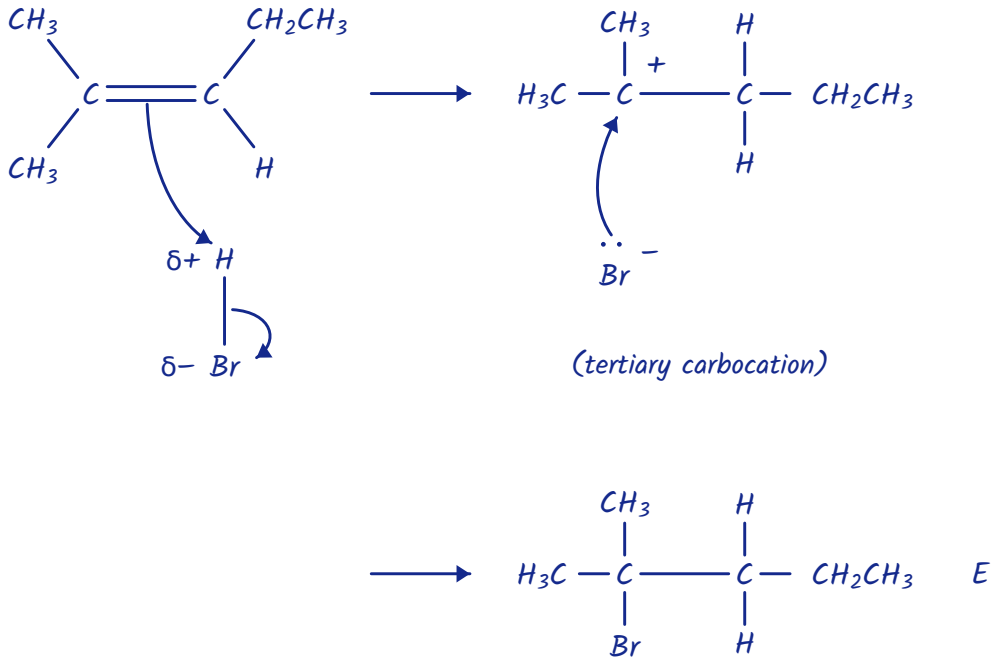
	
E	**F**

[2]

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(iii) Outline the mechanism of the reaction between compound **D** and hydrogen bromide to form **either** compound **E or** compound **F**.

Include curly arrows and relevant dipoles.



[3]

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

Explain your answer.

Major organic product *E (2-bromo-2-methylpentane)*

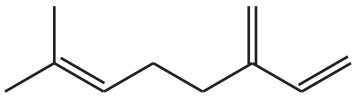
Explanation *E forms via a tertiary carbocation, which is more stable than the secondary carbocation that would form F, because more electron-donating alkyl groups are attached to the C^+.*

[1]

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(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.

$n(myrcene) = 0.204 \div 136.0 = 1.50 \times 10^{-3}$ mol

3 C=C bonds, so $n(H_2) = 3 \times 1.50 \times 10^{-3} = 4.50 \times 10^{-3}$ mol

$V(H_2) = 4.50 \times 10^{-3} \times 24\,000 = 108\ cm^3$

volume = ... 108 ..... 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 dm^3 of hydrogen gas to form a saturated hydrocarbon.

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

Include relevant calculations and reasoning.

$n(H_2) = 5.28 \div 24.0 = 0.220$ mol

ratio H_2 : β-carotene = $0.220 \div 0.0200 = 11$, so 1 mol of β-carotene reacts with 11 mol of H_2: it has 11 C=C double bonds.

A saturated chain alkane with 40 C would be $C_{40}H_{82}$; each ring removes 2 H, so the saturated product with two rings is $C_{40}H_{78}$.

β-carotene has 22 fewer H than this (11 C=C), so it is $C_{40}H_{56}$.

Equation ..... $C_{40}H_{56} + 11H_2 \rightarrow C_{40}H_{78}$ ..... **[4]**

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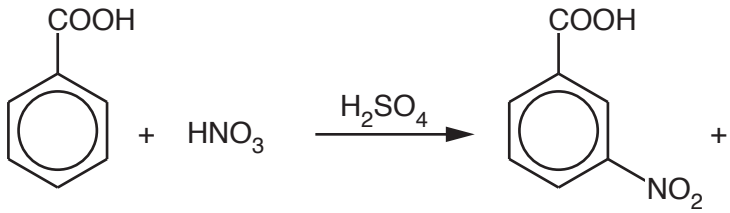
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17 This question is about the chemistry of aromatic compounds.

(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.



Equation 17.1

benzoic acid **3-nitrobenzoic acid**

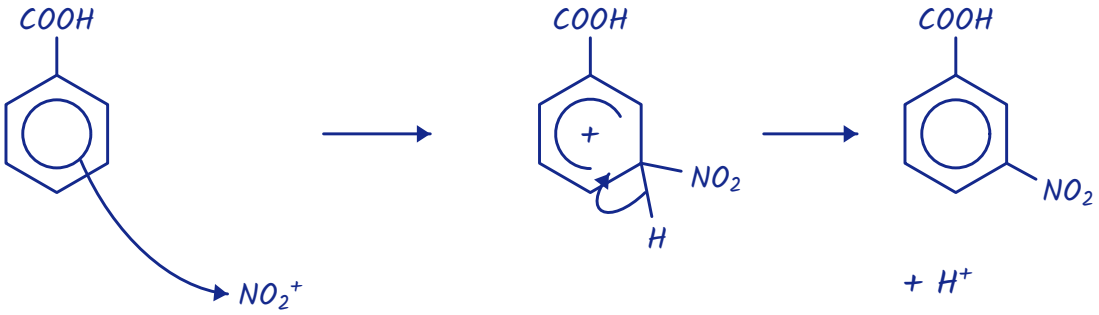
(i) Outline the mechanism for this nitration of benzoic acid.

Show how H_2SO_4 behaves as a catalyst.

Generation of the electrophile:

$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$

Electrophilic substitution:



Regeneration of the catalyst:

$H^+ + HSO_4^- \rightarrow H_2SO_4$

H_2SO_4 reacts in the first step but is regenerated at the end, so it acts as a catalyst.

[5]

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(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.

Recrystallisation: dissolve the impure solid in the minimum volume of hot water (solvent).

Filter the hot solution to remove insoluble impurities, then cool it so that 3-nitrobenzoic acid crystallises; soluble impurities stay in solution.

Filter the crystals under reduced pressure, wash with a little cold water and leave to dry.

Yield: n(benzoic acid) = 4.97 ÷ 122.0 = 0.0407 mol

n(3-nitrobenzoic acid) = 4.85 ÷ 167.0 = 0.0290 mol (1 : 1 ratio)

percentage yield = 0.0290 ÷ 0.0407 × 100 = 71.3%

Purity: measure the melting point of the dry crystals and compare it with the data book value. A pure sample melts sharply, very close to the data book value; impurities lower the melting point and make it melt over a range.

[6]

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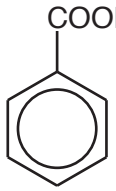
(b) A student investigates the relative ease of nitration of phenol, benzene, and benzoic acid.



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**.

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

Table 17.1

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

Ease of nitration decreases from phenol to benzene to benzoic acid; phenol is nitrated most easily and benzoic acid least easily.

[1]

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

In phenol a lone pair of electrons on the O atom is (partially) delocalised into the π-system of the ring, so the electron density of the ring is higher and the ring is more susceptible to attack; it attracts (polarises) the electrophile NO_2^+ more.

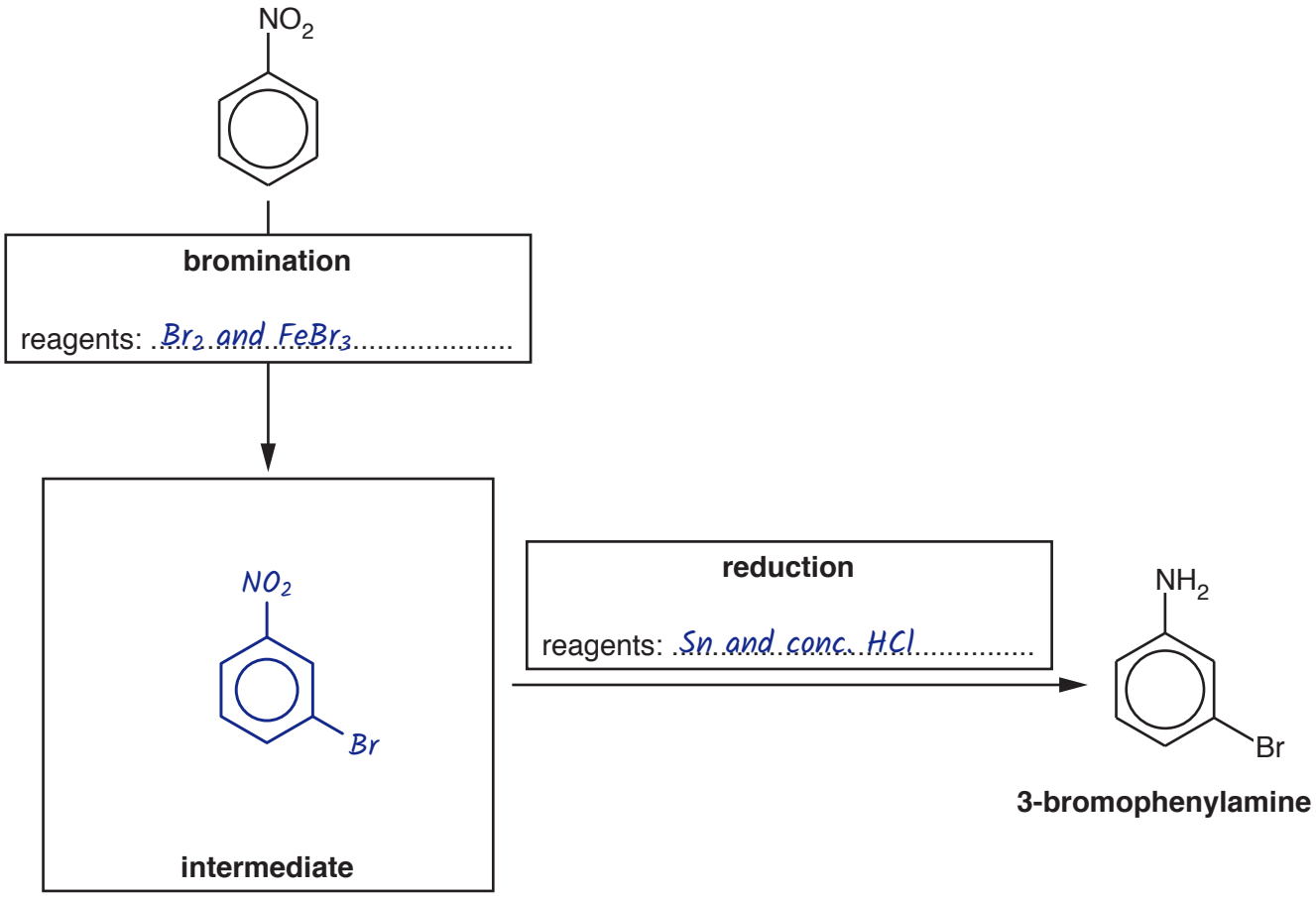
In benzoic acid the -COOH group is electron withdrawing, so the electron density of the ring is lower and the ring is less susceptible to attack; it attracts NO_2^+ less.

[3]

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

(i) Complete the flowchart showing the structure of the intermediate and the **formulae** of the reagents for each stage.



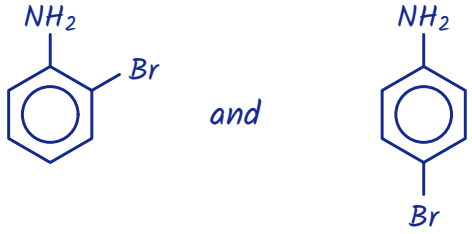
[3]

(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.

Explanation The $-NH_2$ group is 2,4-directing (ortho/para directing), so after reduction the Br substitutes at the 2- or 4-position, not at the 3-position.

Structures



[3]

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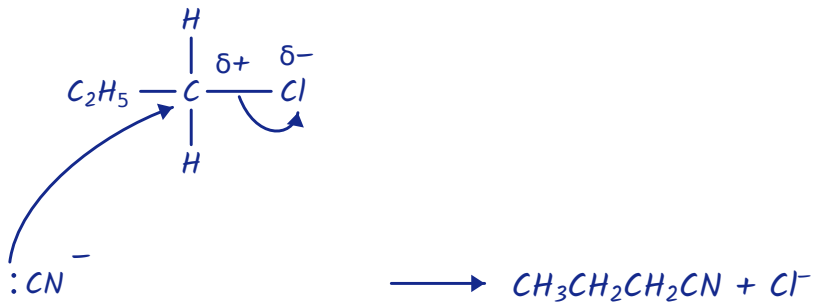
18 This question is about organic compounds containing nitrogen.

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

(i) 1-Chloropropane, $CH_3CH_2CH_2Cl$, reacts with ethanolic sodium cyanide by nucleophilic substitution.

Outline the mechanism for this reaction.

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



[3]

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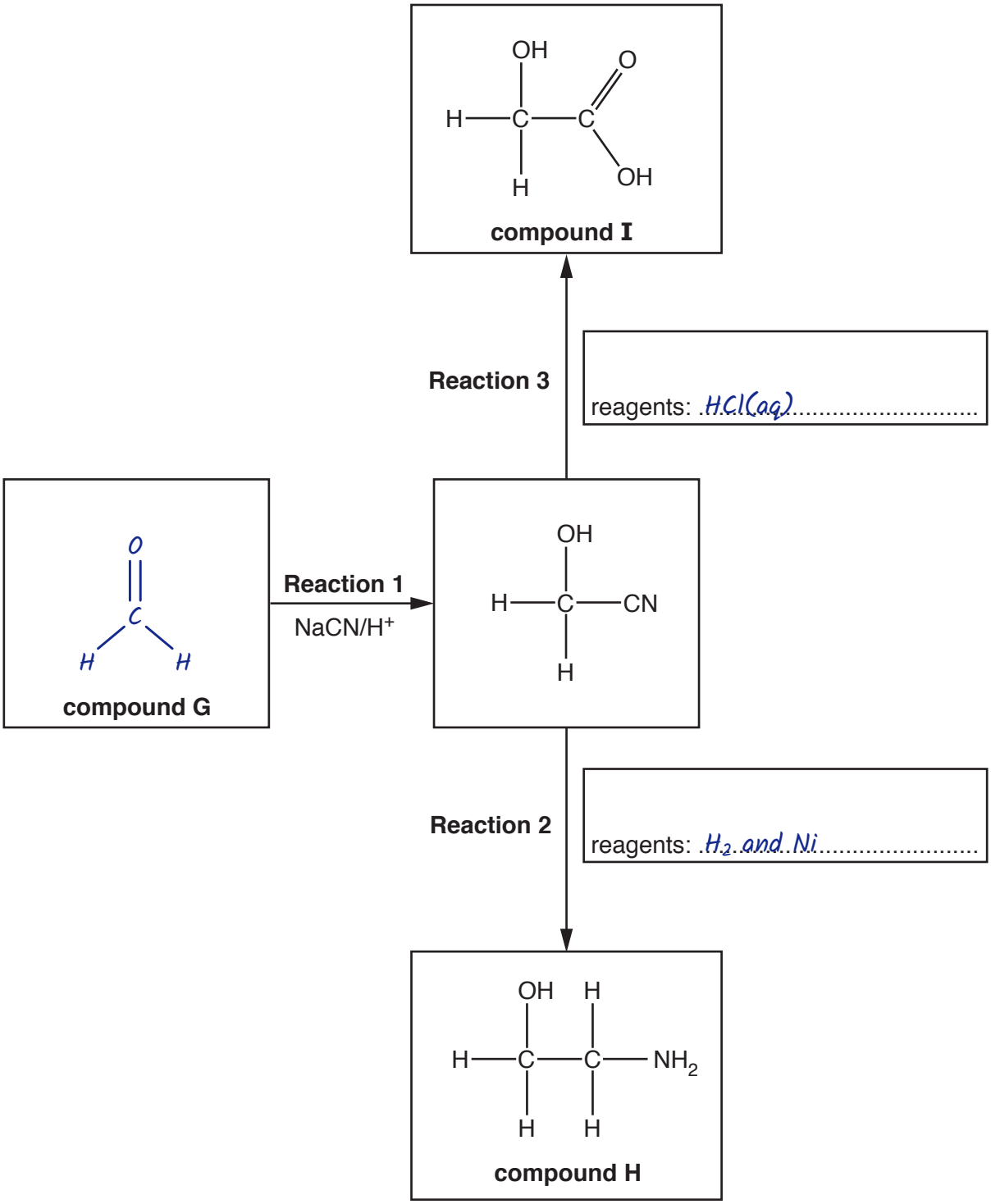
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(ii) Compound **G** is used to synthesise compounds **H** and **I** as shown in the flowchart below.

Complete the flowchart showing the structure of compound **G** and the **formulae** of the reagents for **Reaction 2** and **Reaction 3**.



[3]

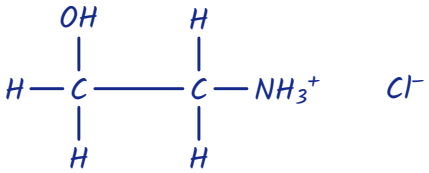
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(iii) Compound **H** reacts with dilute hydrochloric acid to form a salt.

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

Explanation *The lone pair of electrons on the N atom of the $-NH_2$ group accepts a proton (H^+) from the acid, so compound H acts as a base.*

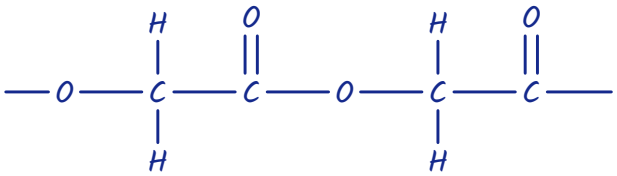
Structure



[2]

(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.



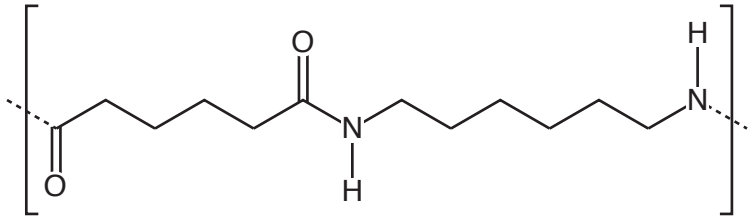
Polymer J is a polyester: its ester groups (ester bonds) can be hydrolysed, so the polymer is broken down into small molecules.

[3]

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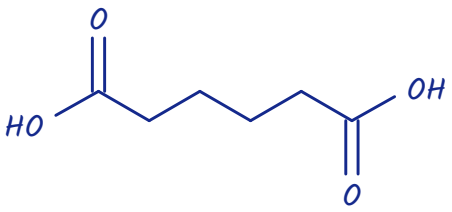
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(b) The repeat unit of Nylon 6,6 is shown below.

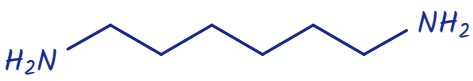


Nylon 6,6

(i) Draw the structures of **two** monomers that can be used to form Nylon 6,6.



hexanedioic acid



hexane-1,6-diamine

[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.

repeat unit $C_{12}H_{22}N_2O_2$, $M = 226.0$

$21\,500 \div 226.0 = 95.1$

number of repeat units = ... *95* ..... **[1]**

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19 This question is about alcohols.

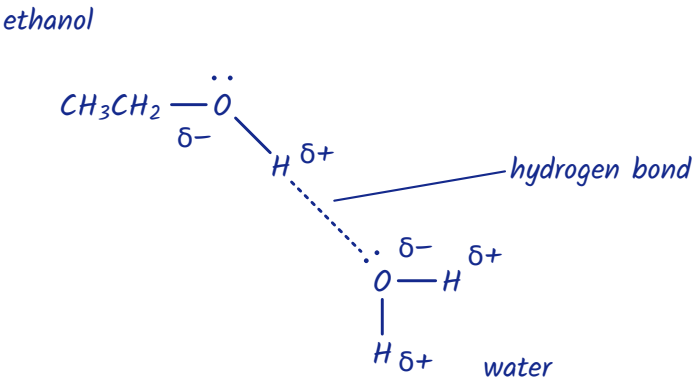
(a) Construct an equation for the complete combustion of an unsaturated alcohol with 5 carbon atoms.

$C_5H_{10}O + 7O_2 \rightarrow 5CO_2 + 5H_2O$ **[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.



Ethanol forms hydrogen bonds with water: the polar O-H bond gives a δ+ H, which is attracted to a lone pair on the δ− O atom of another molecule. **[2]**

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

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

Table 19.1

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

Hexane-1,6-diol has two -OH groups whereas hexan-1-ol has only one, so hexane-1,6-diol forms more hydrogen bonds with water molecules, so it is far more soluble.

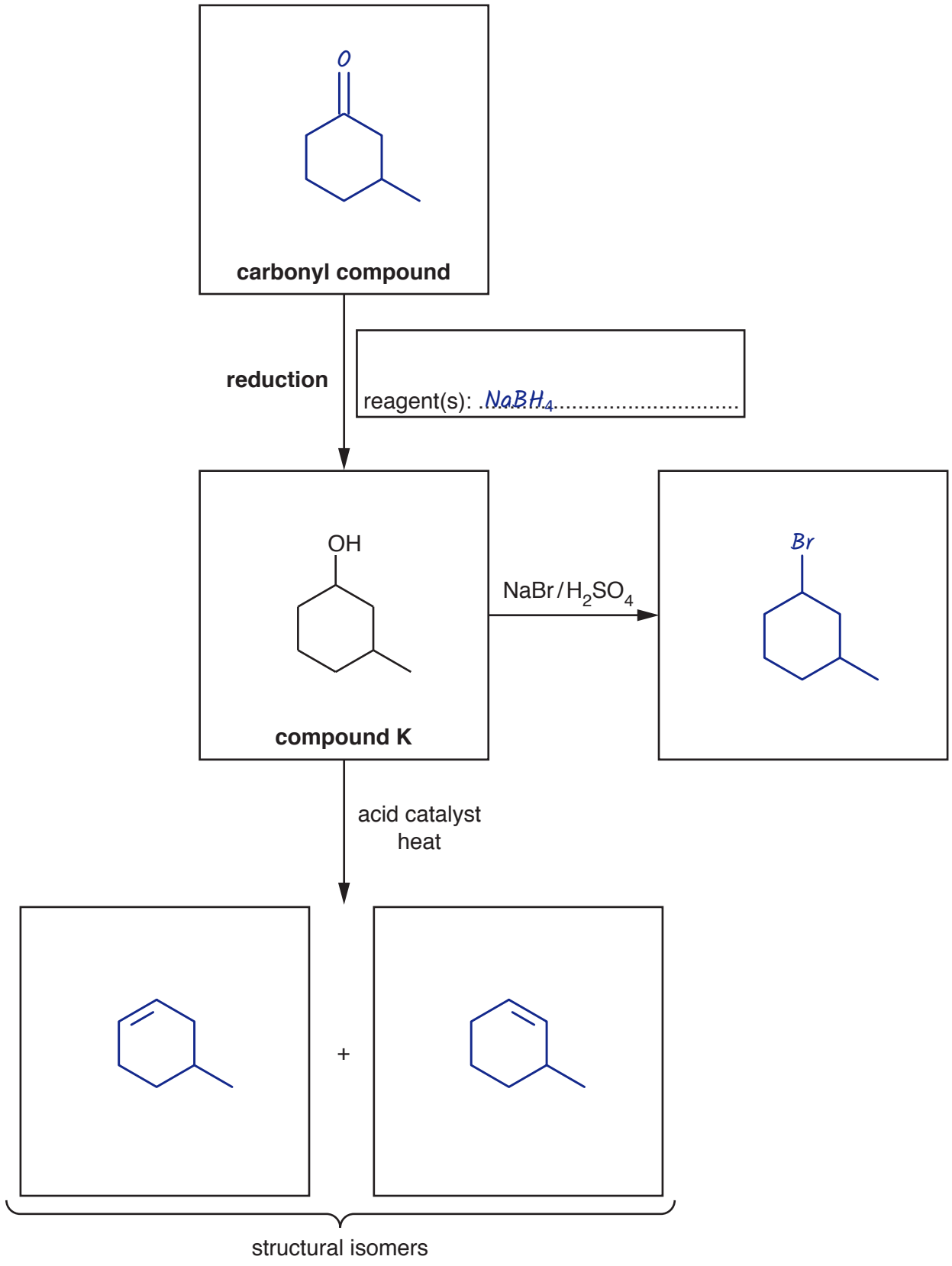
[1]

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(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]

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(ii) What is the name of compound **K**?

3-methylcyclohexanol ..... **[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.

Both use acidified potassium dichromate(VI), $K_2Cr_2O_7/H_2SO_4$, as the oxidising agent (orange to green).

1: heat and distil the product off as it forms, giving the aldehyde butanal, $CH_3CH_2CH_2CHO$:

$CH_3CH_2CH_2CH_2OH + [O] \rightarrow CH_3CH_2CH_2CHO + H_2O$

2: heat under reflux with excess oxidising agent, giving the carboxylic acid butanoic acid, $CH_3CH_2CH_2COOH$:

$CH_3CH_2CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2CH_2COOH + H_2O$

..... **[5]**

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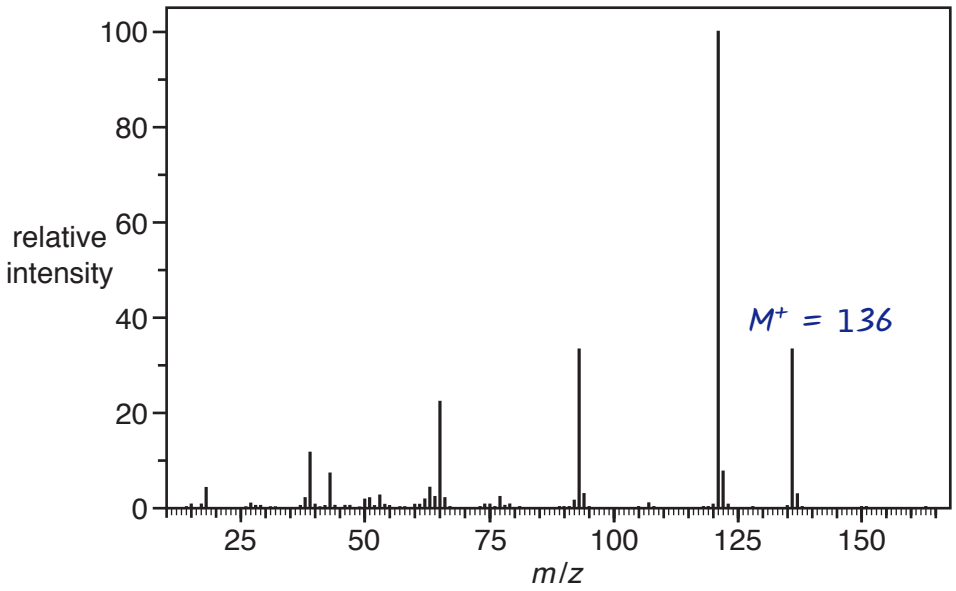
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20 A chemist analyses a naturally occurring aromatic compound.

(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.

C : H : O = 70.58/12.0 : 5.92/1.0 : 23.50/16.0 = 5.88 : 5.92 : 1.47

÷ 1.47 gives 4 : 4 : 1, so empirical formula = C_4H_4O (68.0)

molecular ion peak M^+ at m/z = 136, and 136 ÷ 68.0 = 2

molecular formula = ... $C_8H_8O_2$ ..... **[3]**

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

Test	**Acidity**	**Na_2CO_3(aq)**	**2,4-DNP**	**Tollens' reagent**
Observation	pH = 5	No observable change	Orange precipitate	No observable change

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

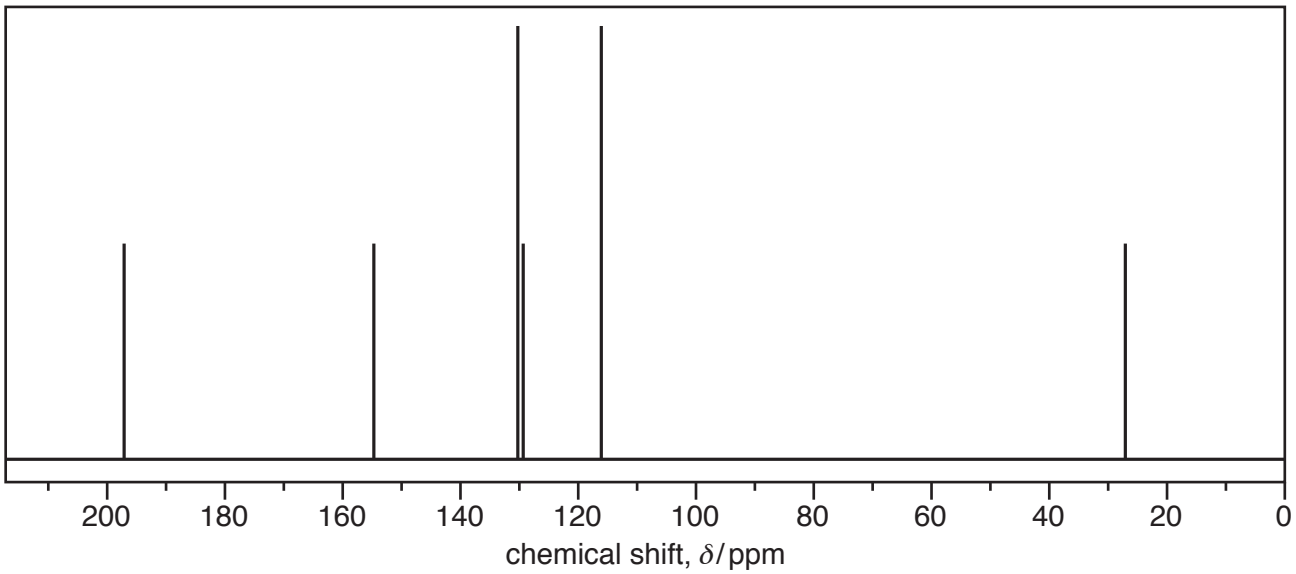
Functional groups ..... phenol and ketone .....

Explanation ..... pH = 5, so it is weakly acidic, but no reaction with Na_2CO_3, so it is a phenol, not a carboxylic acid. .....

Orange precipitate with 2,4-DNP, so it has a carbonyl group (aldehyde or ketone); no change with Tollens', so not an aldehyde; a ketone. ..... **[3]**

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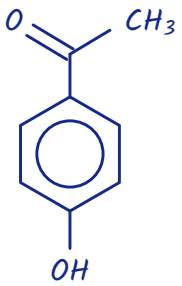
(c) The carbon-13 NMR spectrum of the compound is shown below.



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

Four peaks at 115 to 160 ppm are the four aromatic C environments (1,4-disubstituted ring).

Peak at about 197 ppm is the ketone C=O (190 to 200 ppm) and the peak at about 27 ppm is C-C, the CH_3 next to C=O (20 to 30 ppm).



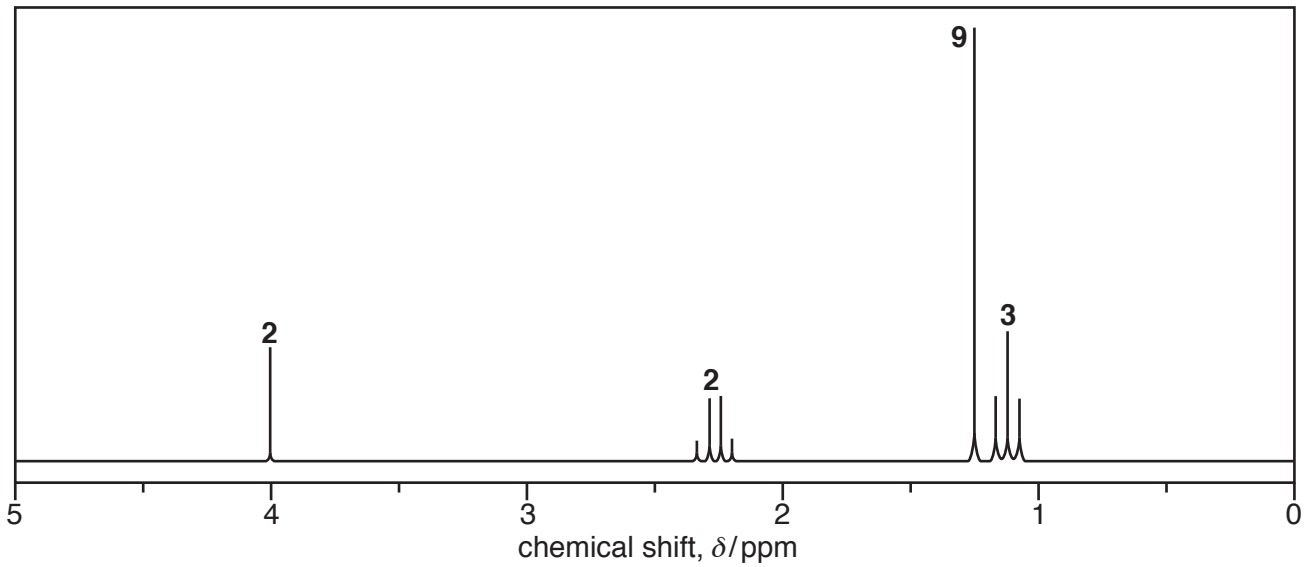
Structure of compound

[3]

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



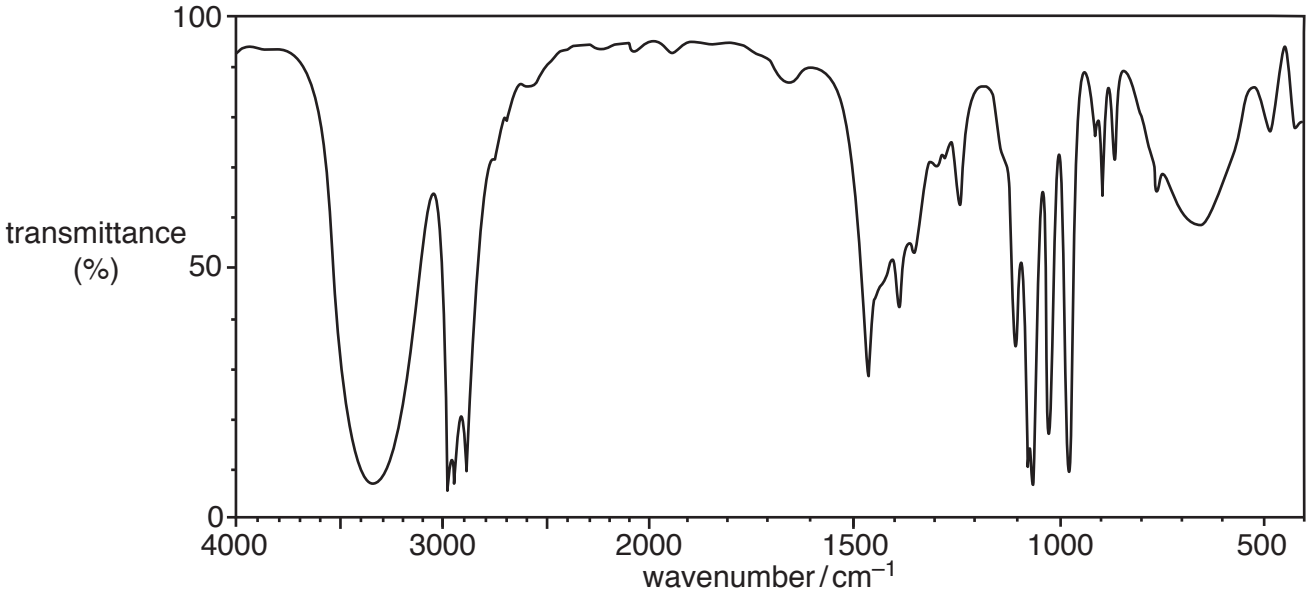
Compound **L** is refluxed with aqueous hydrochloric acid, forming two organic compounds **M** and **N**. The infrared spectra of **M** and **N** are shown below.

Infrared spectrum of M

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Infrared spectrum of N



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

Show **all** of your reasoning.

L is an ester: refluxing with HCl(aq) hydrolyses it into a carboxylic acid (M) and an alcohol (N).

IR of M: broad O-H peak at 2500 to 3300 cm^{-1} and C=O peak at about 1720 cm^{-1}, so M is a carboxylic acid.

IR of N: broad O-H peak at about 3300 cm^{-1} and no C=O peak near 1700 cm^{-1}, so N is an alcohol.

^1H NMR of L: four H environments.

δ 1.1 ppm, triplet, 3H: CH_3 next to a CH_2 (CH_3CH_2-).

δ 1.2 ppm, singlet, 9H: $(CH_3)_3C$-, adjacent C has no H.

δ 2.3 ppm, quartet, 2H: CH_2 next to CH_3 and to C=O (CH_3CH_2COO-).

δ 4.0 ppm, singlet, 2H: -CH_2-O- next to the ester O, adjacent C has no H.

So L is $CH_3CH_2COOCH_2C(CH_3)_3$, 2,2-dimethylpropyl propanoate ($C_8H_{16}O_2$); M is CH_3CH_2COOH and N is $(CH_3)_3CCH_2OH$.

..... **[6]**

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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