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)

H432/02

First name	
Last name	
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.

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

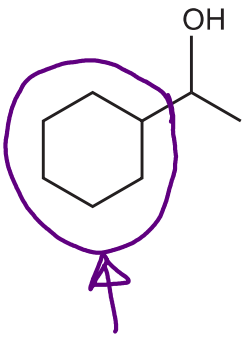
D Potassium nitrate

Your answer [B]

white ppt cream ppt. in $AgNO_3$

[1]

2 How can the molecule below be described?



Saturated: no C=C bonds

Alicyclic

A Aromatic and alicyclic

B Aliphatic and unsaturated

C Aromatic and unsaturated

D Alicyclic and saturated

Your answer [D]

[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 $+5O_2 \rightarrow 3CO_2 + 4H_2O$

B C_2H_2O $+2O_2 \rightarrow 2CO_2 + H_2O$

C C_2H_4O $+2\frac{1}{2}O_2 \rightarrow 2CO_2 + 2H_2O$

D C_2H_3N $+1\frac{1}{2}O_2 \rightarrow 2CO_2 + \frac{3}{2}H_2O + NO_2$

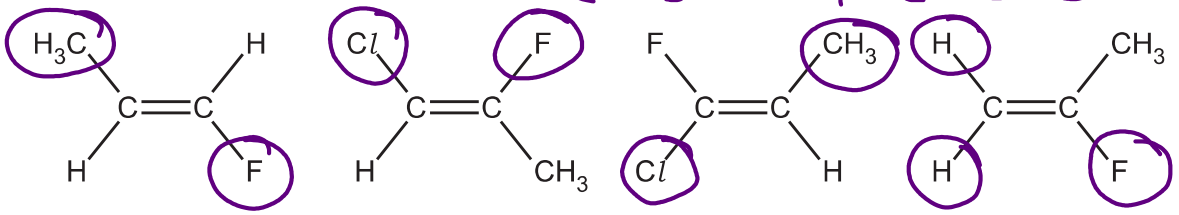
same molar ratio

Your answer C

[1]

4 Which molecule is a Z-isomer?

highest priority groups on same side of C=C bond



same priority no E-Z isomerism

Your answer B

[1]

5 Which type of reaction has the greatest atom economy?

A Substitution

B Hydrolysis

C Elimination

D Addition

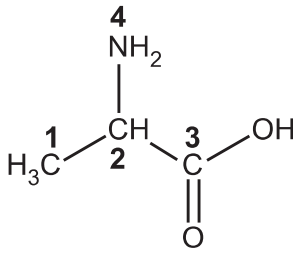
$$\frac{\text{RFM of desired product}}{\text{RFM of reactants}} \times 100$$

100% atom economy as no by-products created

Your answer D

[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 4bp 0lp

B Atom 2 4bp 0lp

C Atom 3 3bp 0lp

D Atom 4 3bp 1lp

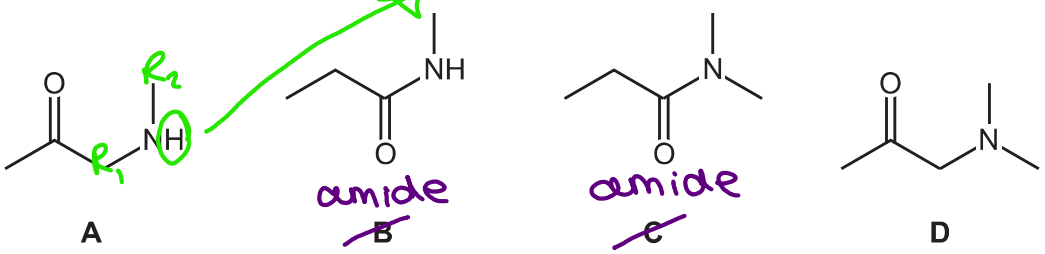
3 bonded pairs (bp) with no lone pairs (lp)

Your answer C

[1]

7 Which molecule is a secondary amine?

2 R groups and 1 H group

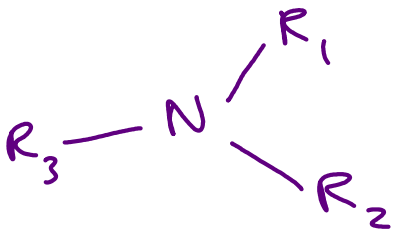


A **B** amide **C** amide **D**

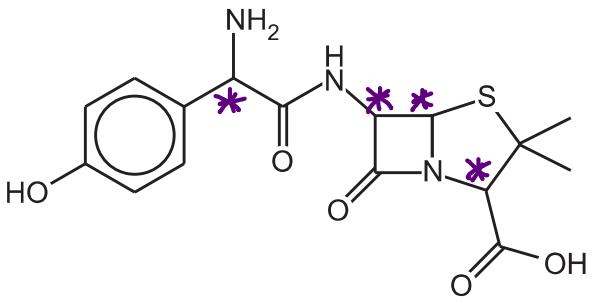
Your answer A

[1]

general formula of an amine:



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



A 2

B 3

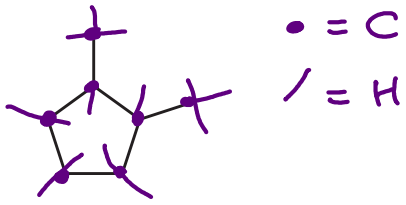
C 4

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}

C_7H_{14}

Your answer C

[1]

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

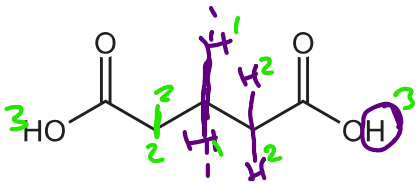
D CH_3COCl $+H_2O \longrightarrow CH_3COOH + HCl$

both acids

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

3 unique environments

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}

1 : 1 molar ratio

$0.1 \times 6.023 \times 10^{23}$

$= 6.023 \times 10^{22}$

Your answer A

[1]

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

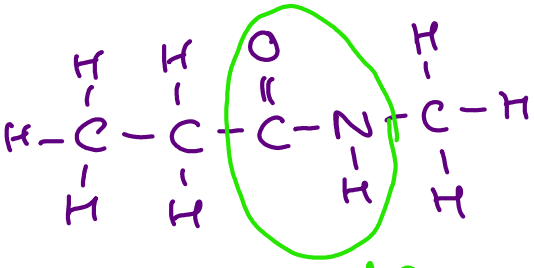
A $CH_3CH_2COCl + CH_3NH_2$

B $CH_3CH_2CONH_2 + CH_3Br$

C $CH_3CH_2COONa + CH_3NH_2$

D $CH_3CH_2COCH_3 + NH_3$

Your answer **A**



amide and 2 R groups (2°)

[1]

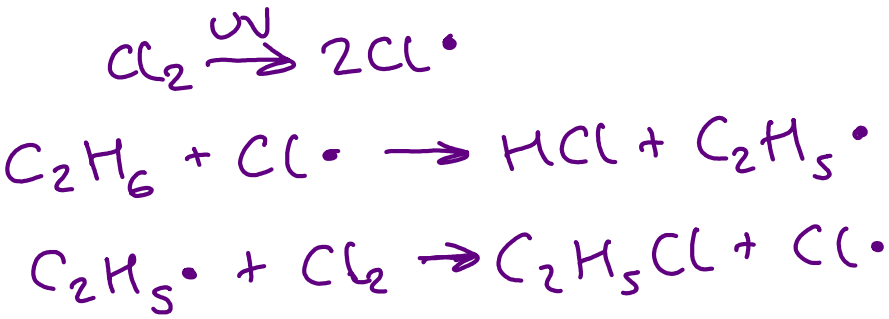
14 Ethane reacts with chlorine by radical substitution to form chloroethane.

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**

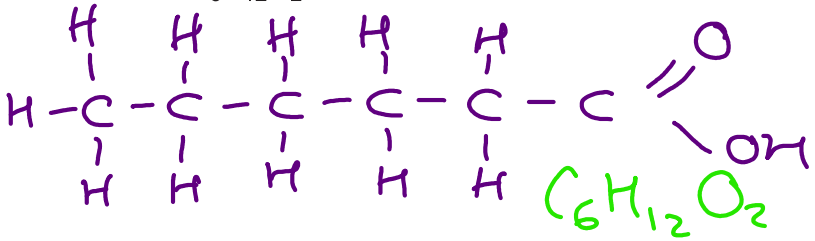
[1]

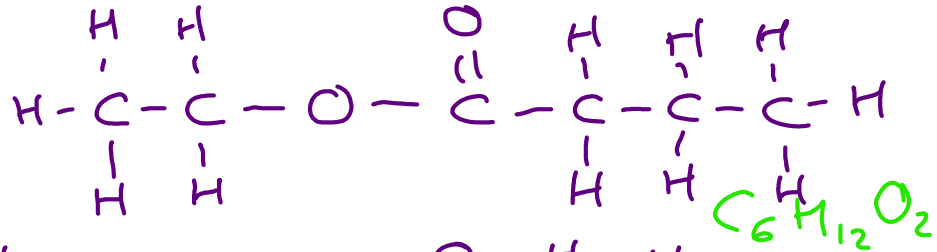
15 Which compound(s) is a/are structural isomer(s) of $C_6H_{12}O_2$?

1 hexanoic acid

2 ethyl butanoate

3 propyl propanoate





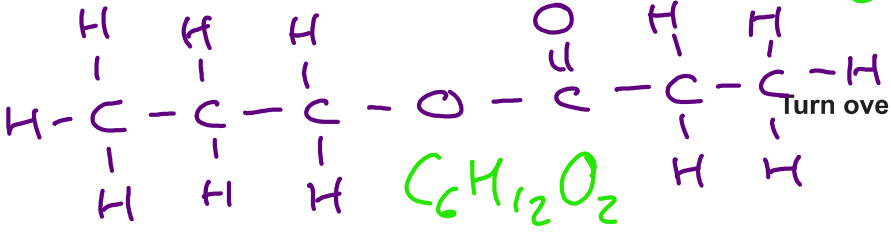
A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer **A**



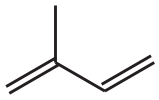
[1]

SECTION B

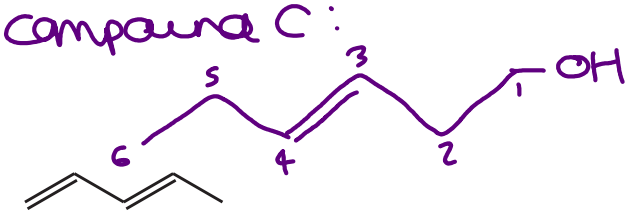
Answer **all** the questions.

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 meaning it has fewer points of contact and weaker london forces which require less energy to break.

[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

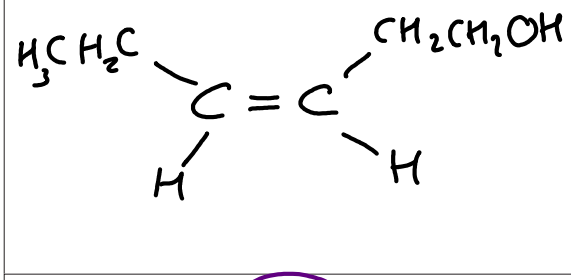
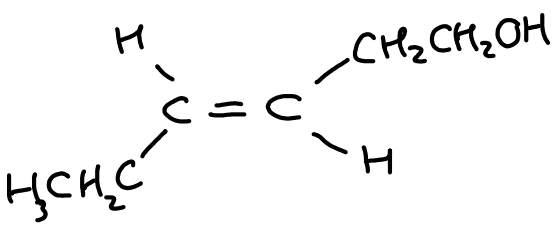
[1]

(ii) Define the term *stereoisomers*.

same structural formula but a different spatial arrangement of atoms.

[1]

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

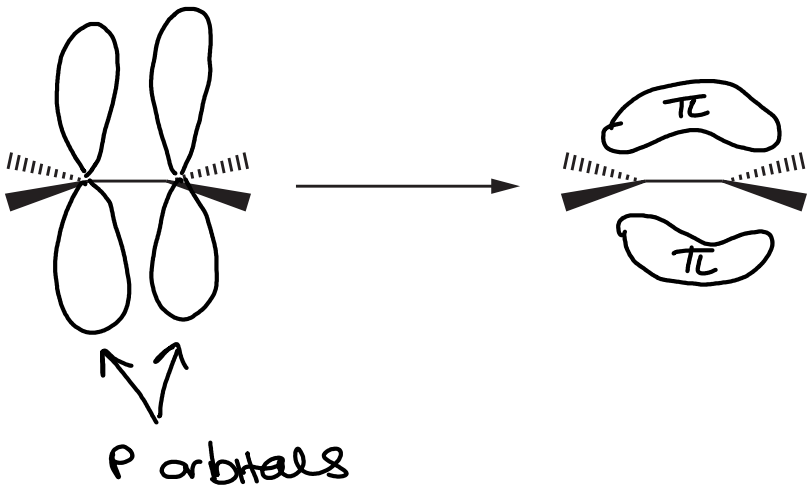
	
cis	*trans*

H on same side of C=C

[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]

a π bond is the sideways overlap of p orbitals.

(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

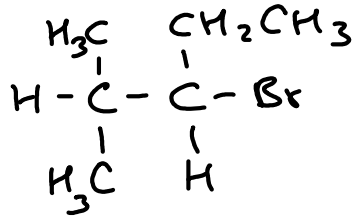
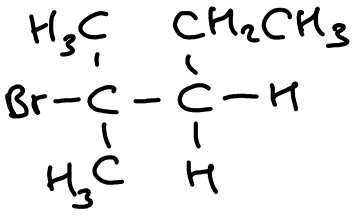
(i) Suggest how an HBr molecule can act as an electrophile.

electron pair acceptor

HBr accepts a pair of electrons

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

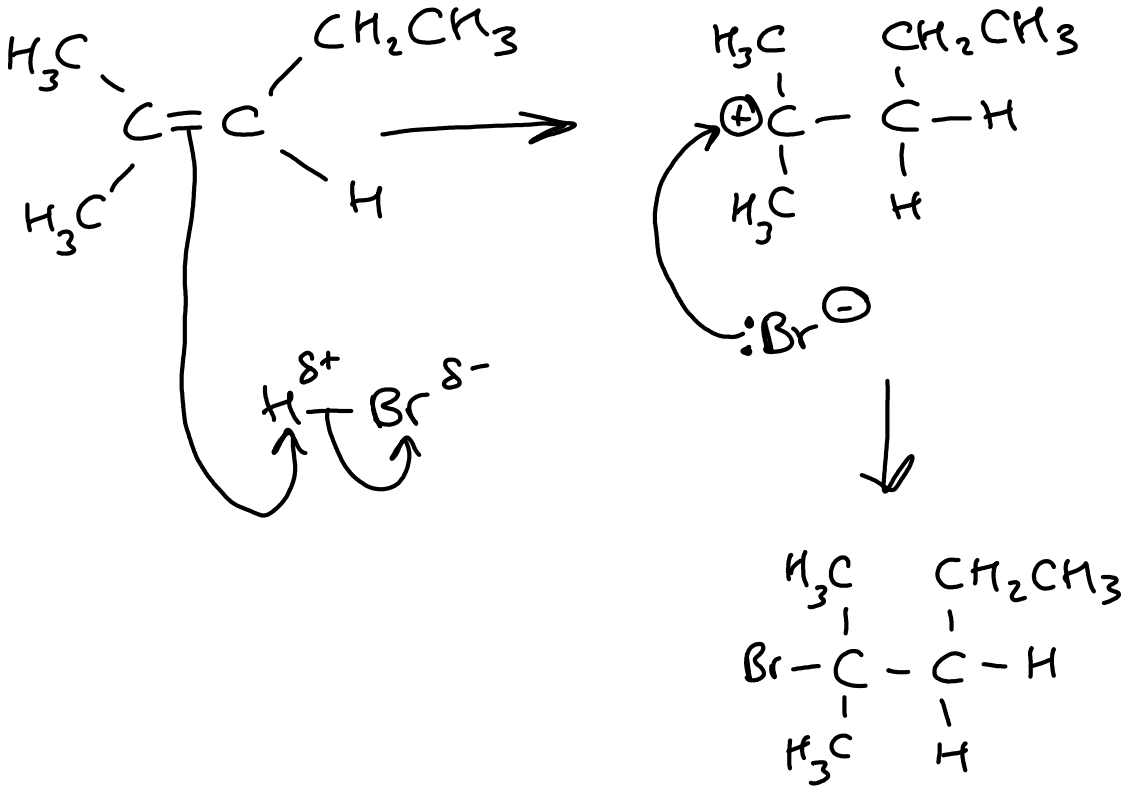
(ii) Draw the structures of the two organic compounds **E** and **F**.

	
E	**F**

[2]

(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 ..... F .....

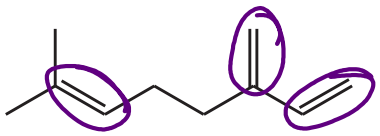
Explanation ..... reaction goes via the most stable carbocation intermidiate .....

.....

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

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

mol = vol (cm^3) / 24000 cm^3



myrcene

3 double bonds so 1:3 molar ratio needed

(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.

moles of myrcene = $\frac{204 \times 10^{-3}}{((12 \times 10) + 16)} = 1.5 \times 10^{-3}$ mol

$1.5 \times 10^{-3} \times 3 = 4.5 \times 10^{-3}$ mol

$4.5 \times 10^{-3} \times 24000 = 108\ cm^3$

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.

$\frac{5.28}{24} = 0.22$ mol of H_2

$\frac{0.22}{0.02} = 11$ → 11 double bonds

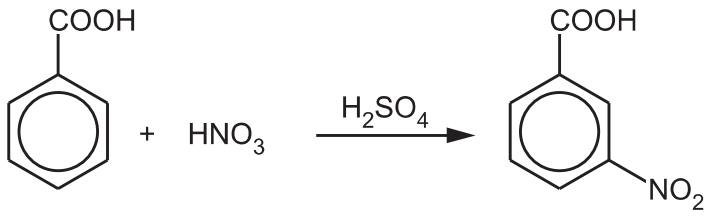
$C_{40}H_{78}$

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



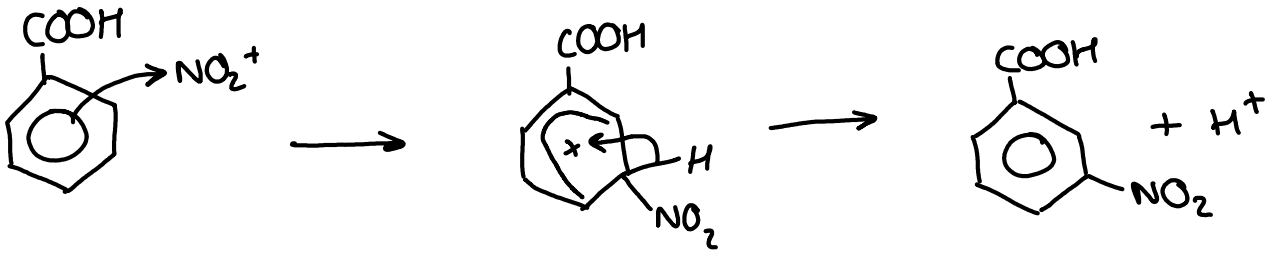
Equation 17.1

benzoic acid **3-nitrobenzoic acid**

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

Show how H_2SO_4 behaves as a catalyst.

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



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

reformation of the catalyst

[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.

Purification:

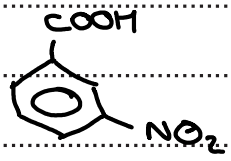
1. Recrystallisation

2. Dissolve solid in minimal amount of hot solvent

3. Cool solution and filter solid

4. wash with cool solvent and dry

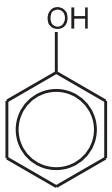
$\frac{4.97}{122}$ = 0.0407 mol of 

$\frac{4.85}{167}$ = 0.0290 mol of 

$\frac{0.0290}{0.0407} \times 100 = 71.3\%$

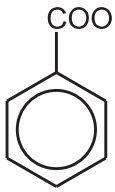
To check purity conduct a melting point test and compare to known values [6]

(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.**

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.

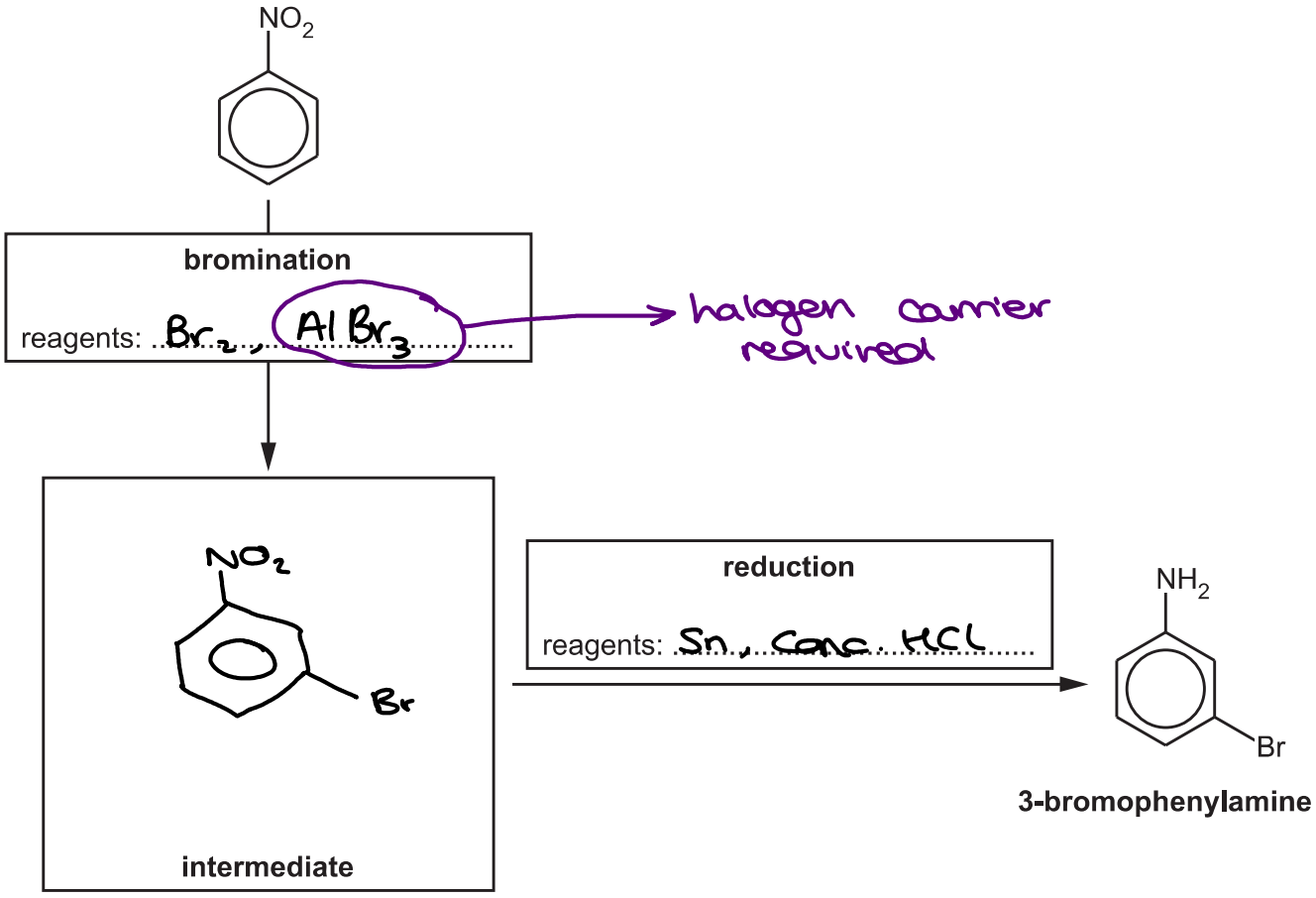
phenol is the easiest to nitrate and benzoic acid is the hardest / least reactive. **[1]**

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

Phenol: the lone pair of electrons on O is partially delocalised into the π ring system.
Benzoic acid: COOH is an electron withdrawing group
Overall in phenol the electron density is greater so is more susceptible to attack. **[3]**

(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.



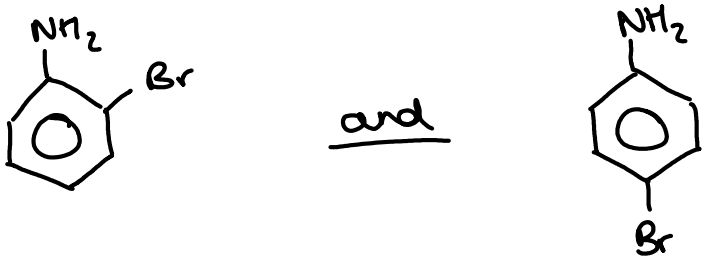
[3]

(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 NH_2 is a 2,4 directing group so Br groups would be arranged differently on the benzene ring.

Structures



[3]

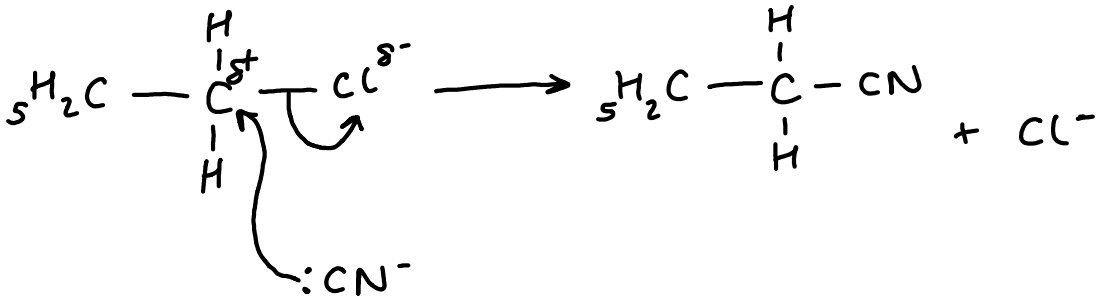
18 This question is about organic compounds containing nitrogen.

(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.

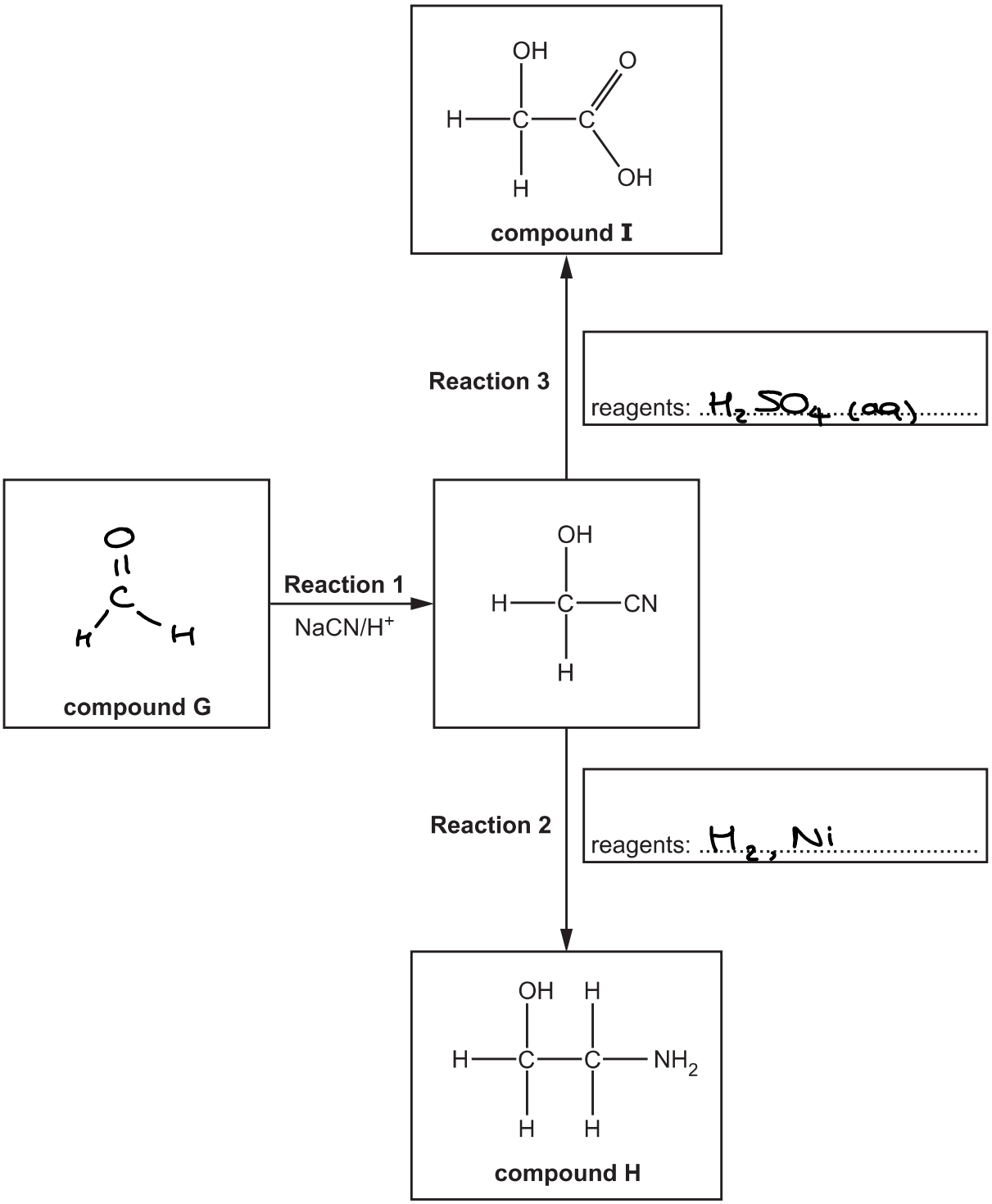
Include curly arrows, relevant dipoles and the structure of the organic product.



[3]

(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.**



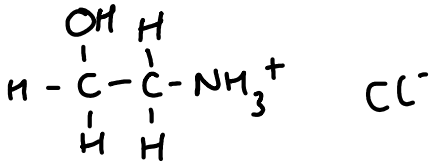
[3]

(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 Nitrogen lone pair accepts a proton (H^+)

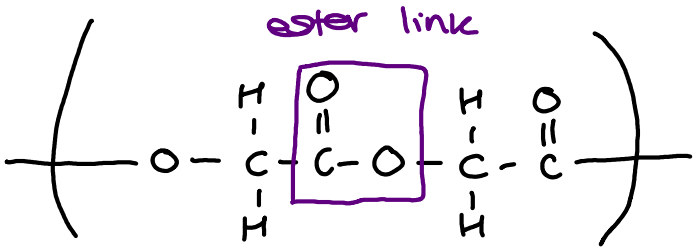
Structure



[2]

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

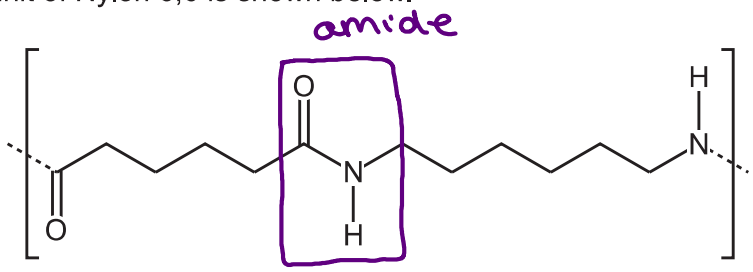
Draw **two** repeat units of polymer **J** and suggest a reason why it is biodegradable.



ester group can undergo hydrolysis

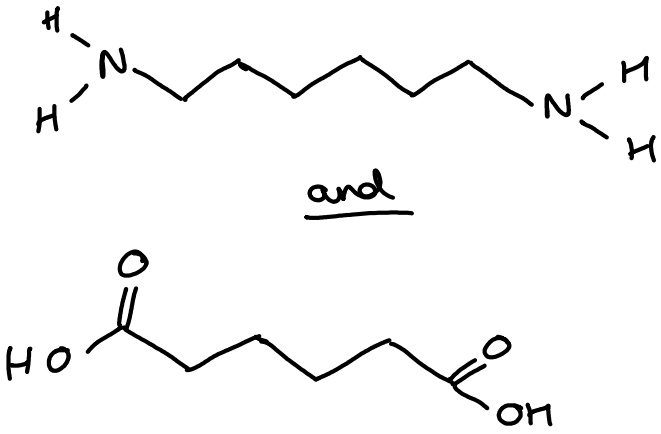
[3]

(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.



[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.

$\frac{21500}{226} = 95.1$

RFM = relative formula mass of repeat unit:
$(12 \times 12) + (16 \times 2) + (14 \times 2) + 22 = 226$

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

19 This question is about alcohols.

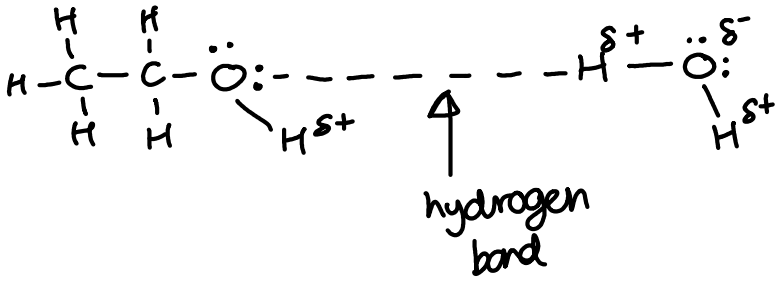
(a) Construct an equation for the complete combustion of an unsaturated alcohol with 5 carbon atoms.

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



[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

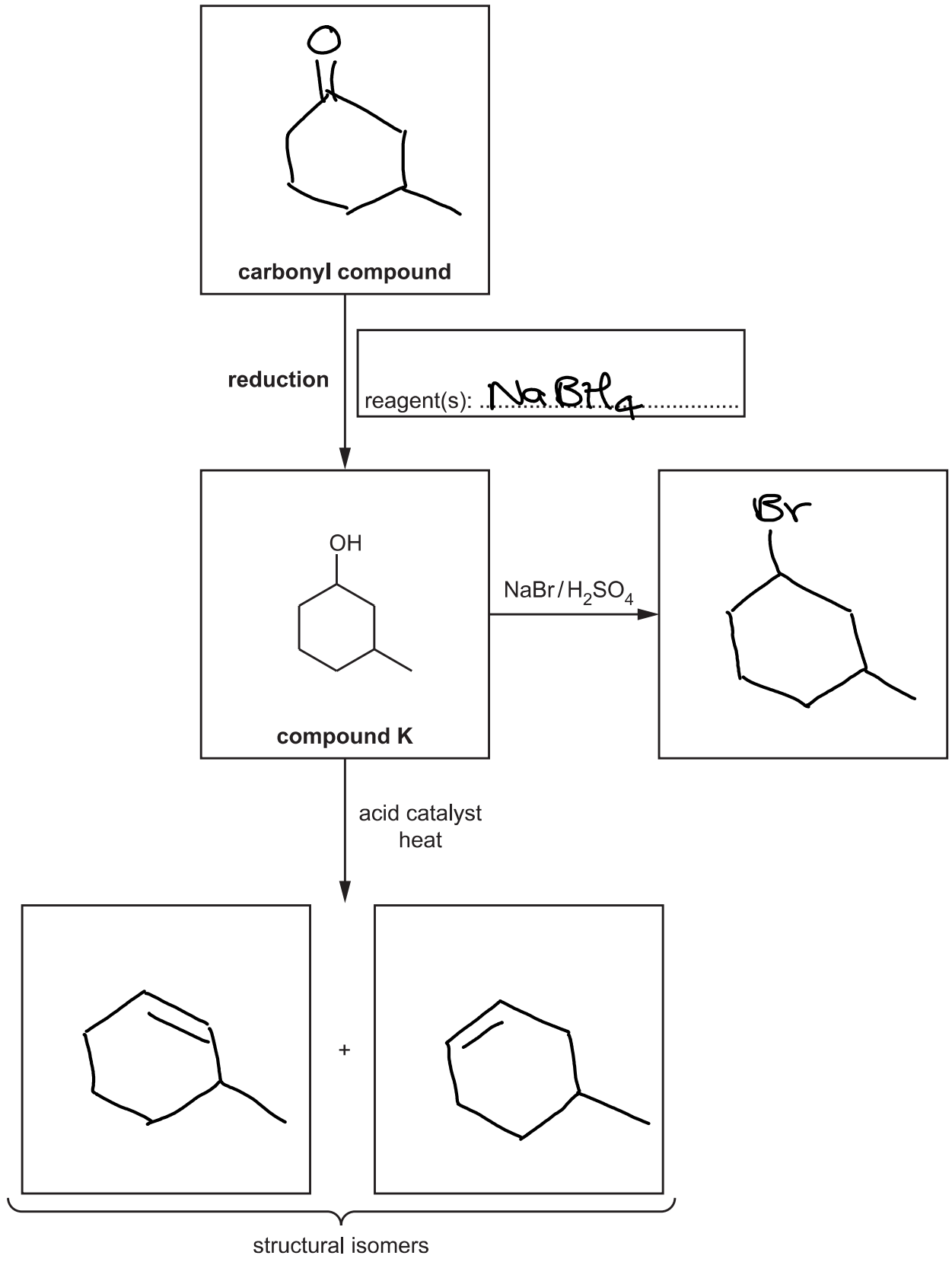
Explain the difference in solubility of hexan-1-ol and hexane-1,6-diol.

hexane-1,6-diol has more OH groups therefore can form more hydrogen bonds in water.

[1]

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

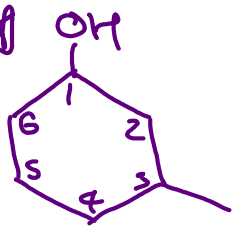
(i) Complete the flowchart by filling in each box.



[5]

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

3-methylcyclohexanol [1]



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

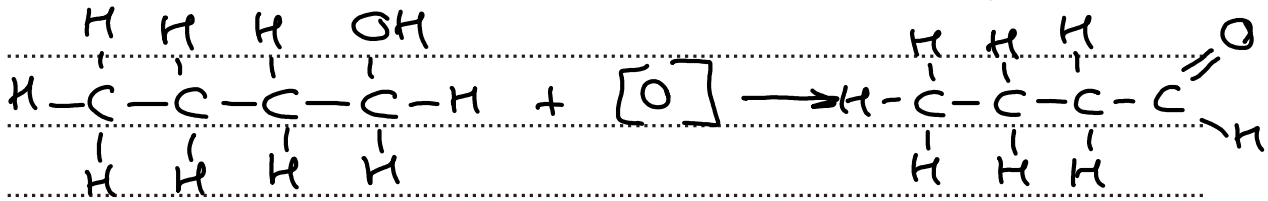
Describe both oxidation reactions of butan-1-ol.

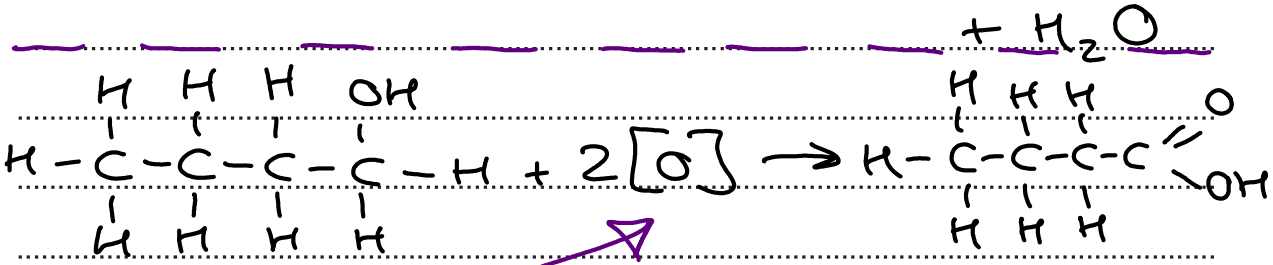
For each reaction include

- 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.

distillation : H^+, $Cr_2O_7^{2-}$





reflux : H^+, $Cr_2O_7^{2-}$

balanced equation with different ratio of [O] compared to aldehydes

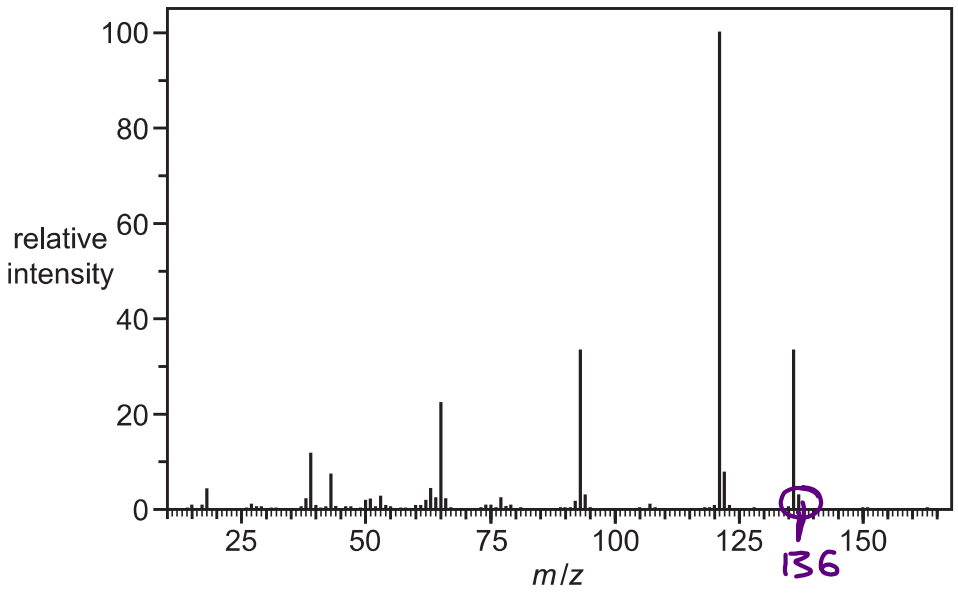
[5]

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.

C_4H_4O has an RFM of: $(12\times4)+4+16 = 68$ so multiply by 2

C: $\frac{70.58}{12} = \frac{5.88}{1.46875} = 4$

H: $\frac{5.92}{1} = \frac{5.92}{1.46875} = 4$

O: $\frac{23.50}{16} = \frac{1.46875}{1.46875} = 1$

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

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

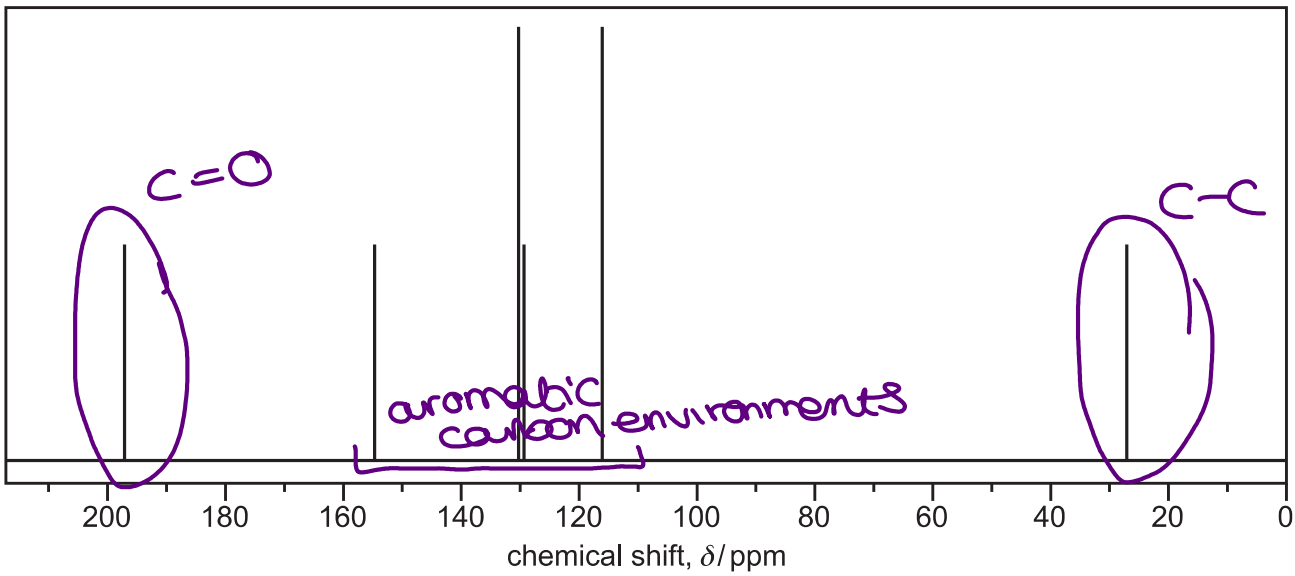
Test	Acidity	Na_2CO_3(aq)	2,4-DNP	Tollens' reagent
		test for COOH	test for C=O	test for $-C\overset{O}{\underset{H}{}}$
Observation	pH = 5 weak acid	No observable change if present effervesces	Orange precipitate ✓	No observable change if present silver mirror

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

Functional groups ketone, phenol

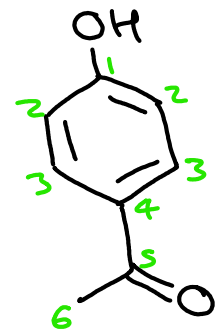
Explanation phenols are weak acids not carboxylic acid as no reaction with Na_2CO_3, but C=O group present as orange ppt in 2,4 DNP but no silver mirror in tollens reagent so not an aldehyde. **[3]**

(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.

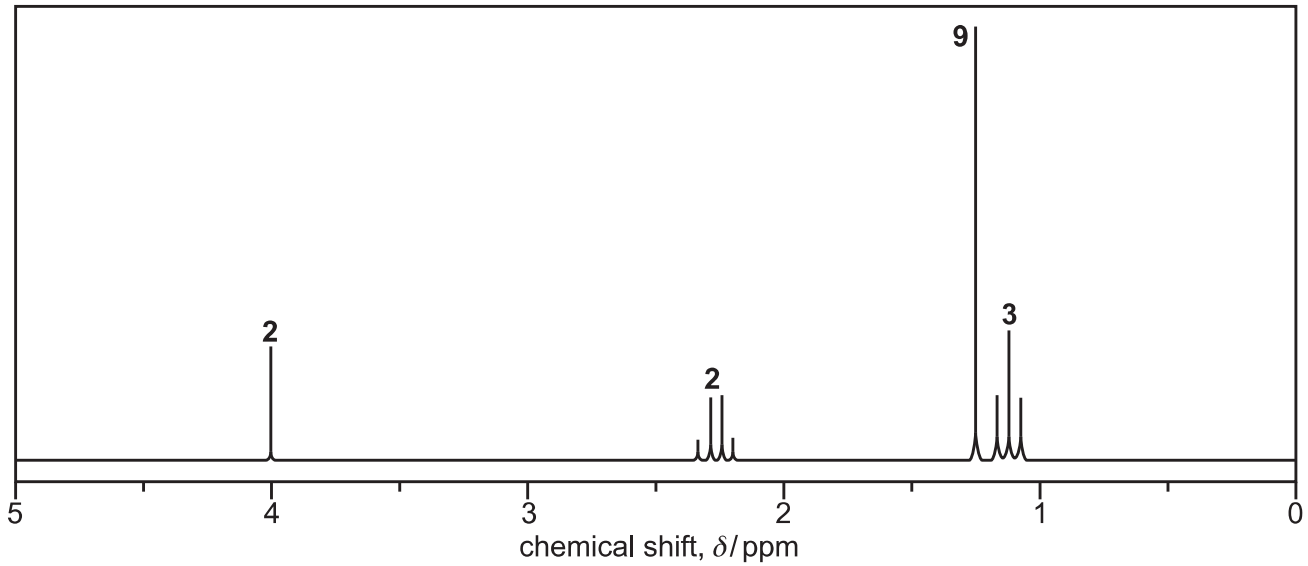
peaks between 110 - 160 ppm are the 4 aromatic carbon environments. Peaks between 190 - 200 ppm is a C=O peak between 20 - 30 ppm is C-C.



Structure of compound

[3]

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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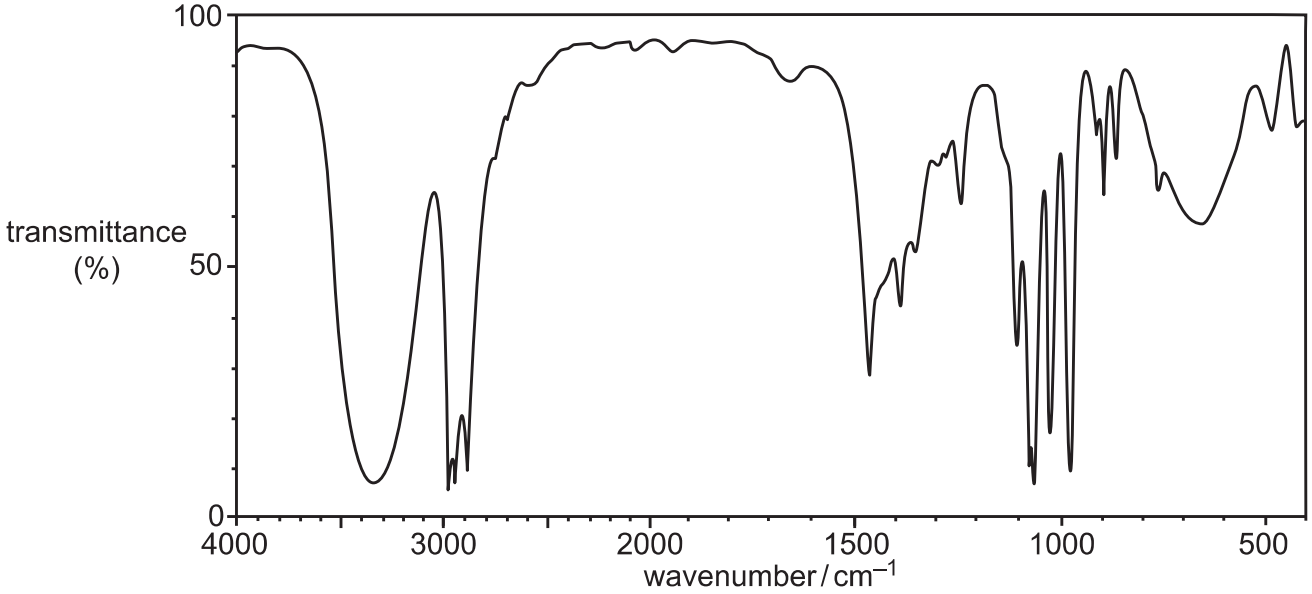
Infrared spectrum of N



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

Show **all** of your reasoning.

Solution unavailable due to copyright issue.

[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).