Carbonyl Compounds, Carboxylic Acids, Esters & Polyesters AS & A Level

Model Answers 3

Level	A Level
Subject	Chemistry
Exam Board	OCR
Module	Organic Chemistry & Analysis
Topic	Carbonyl Compounds, Carboxylic Acids, Esters & Polyesters
Paper	AS & A Level
Booklet	Model Answers 3

Time allowed: **57 minutes**

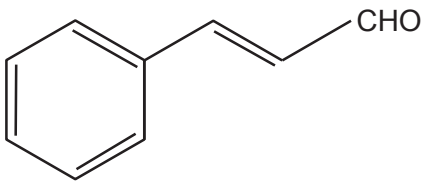
Score: **/42**

Percentage: **/100**

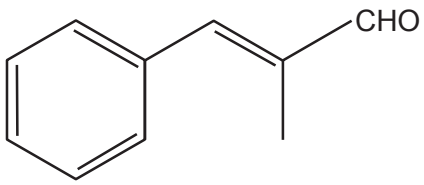
Grade Boundaries:

A*	A	B	C	D	E
>85%	73%	60%	47%	34%	21%

Cinnamaldehyde and methylcinnamaldehyde are naturally occurring organic compounds.



cinnamaldehyde



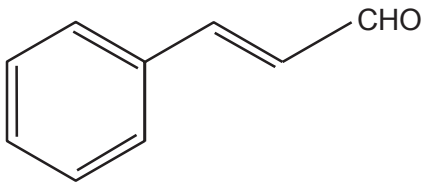
methylcinnamaldehyde

(a) Methylcinnamaldehyde is an *E* stereoisomer.

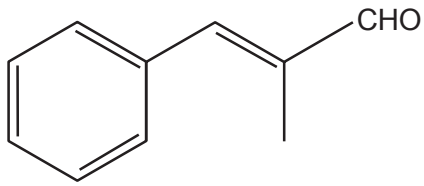
Explain this statement in terms of the Cahn-Ingold-Prelog (CIP) rules. **[2]**

In the Cahn-Ingold-Prelog system groups are assigned priority based on their atomic number, with the groups of higher atomic number thus having higher priority. If the higher priority groups/atoms are on different/opposite sides of the double bond then the compound is the *E* isomer. The high(est) priority groups in the molecule are C_6H_5 **AND** CHO and the lowest priority groups are H and CH_3.

(b) A student plans to carry out some chemical tests on both cinnamaldehyde and methylcinnamaldehyde.



cinnamaldehyde



methylcinnamaldehyde

(i) Suggest a suitable chemical test to confirm that both compounds contain an unsaturated carbon chain.

Your answer should include the reagent and observations. **[1]**

Bromine/ Br_2 **AND** goes colourless/decolourised as the bromine atoms add across the carbon carbon double bond.

(ii) Describe a chemical test to confirm that both compounds contain an aldehyde functional group.

Your answer should include the reagent and observations. **[1]**

Tollens' (reagent) **AND** Silver (mirror/precipitate/ppt/solid) which is a solution of silver nitrate in aqueous ammonia. It oxidises an aldehyde to its corresponding carboxylic acid, producing elemental silver in the reduction process, hence the name silver mirror test.

(iii) Describe a chemical test to confirm that cinnamaldehyde and methylcinnamaldehyde contain a carbonyl group.

How could the products of this test be used to distinguish between the two compounds?

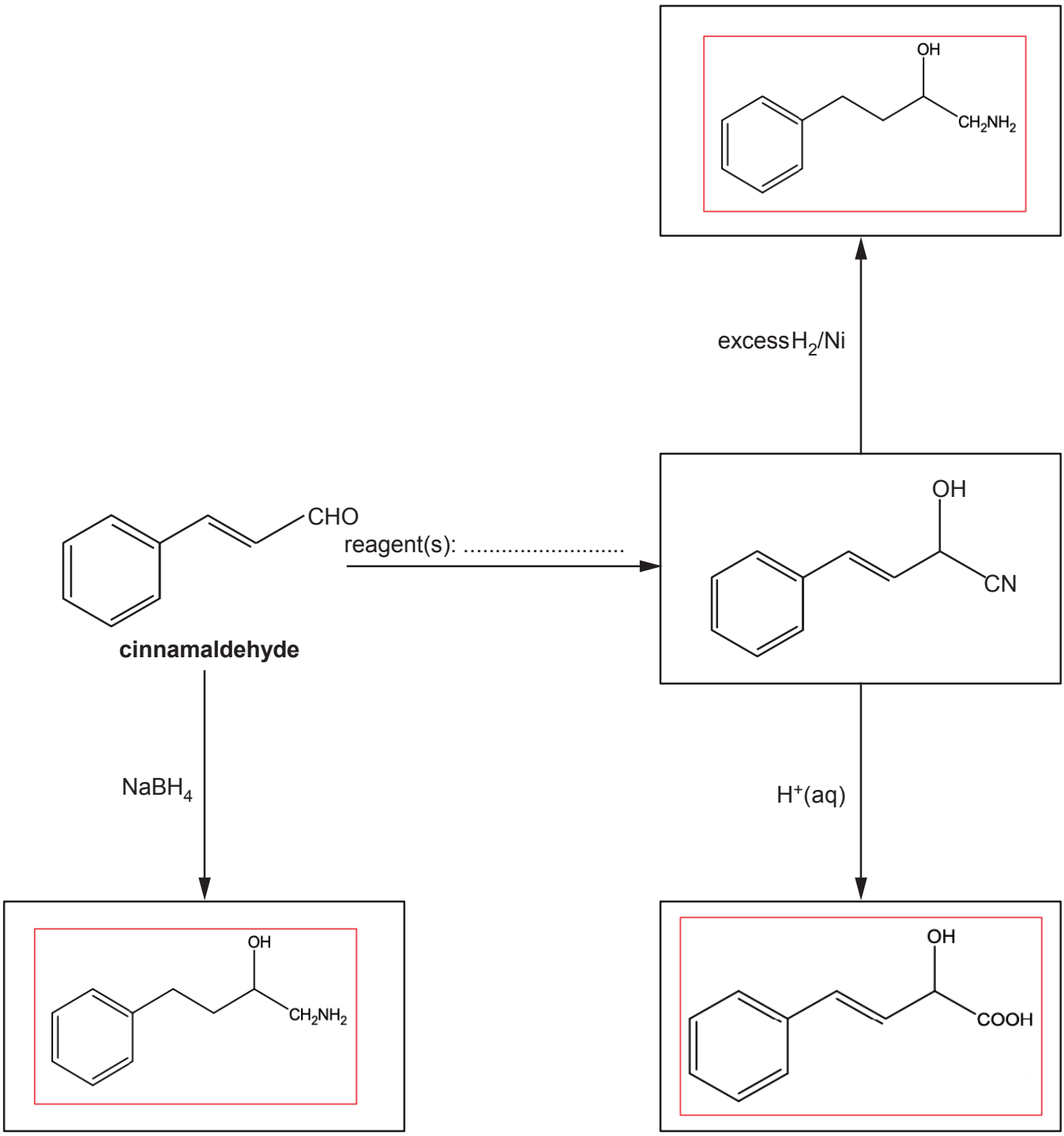
Your answer should **not** include spectroscopy. **[3]**

(Add) 2,4-dinitrophenylhydrazine **AND** orange/yellow/red precipitate forms which is 2,4-dinitrophenylhydrazone. This is known as Brady's test in which the NH_2 group of 2,4-DNP adds across the C=O group, which is followed by the removal of a water molecule. 2,4-DNP is usually stored in acid and alcohol as in the solid state it is explosive and extremely dangerous.

To distinguish between the two compounds, obtain the melting point (of crystals) using appropriate apparatus and compare to known values/database.

(c) The flowchart below shows some reactions starting with cinnamaldehyde.

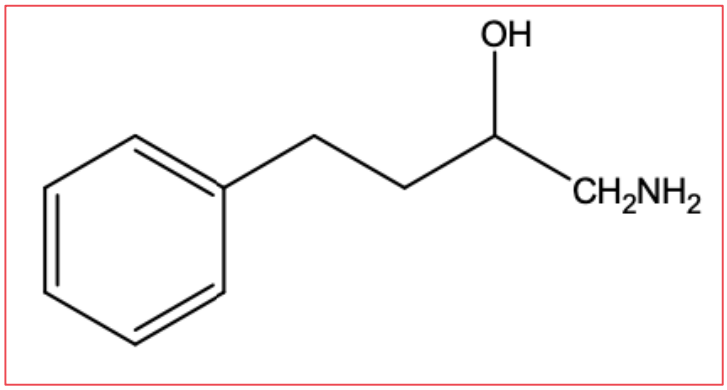
Draw the structures of the missing organic compounds in the boxes and add the missing reagent(s) on the dotted line.



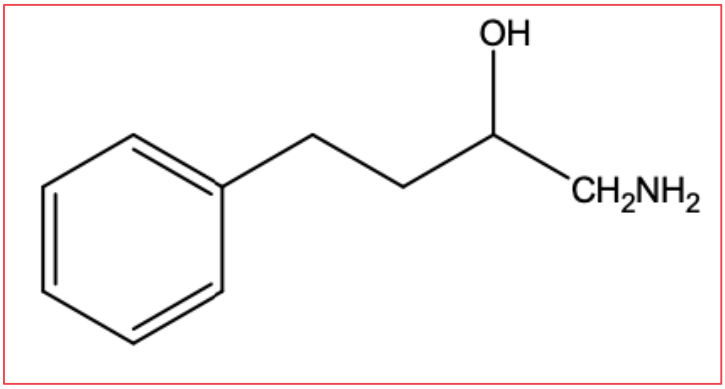
[5]

In the first step the reagent required is NaCN/H^+ to produce the **hydroxynitrile product** in a nucleophilic substitution reaction.

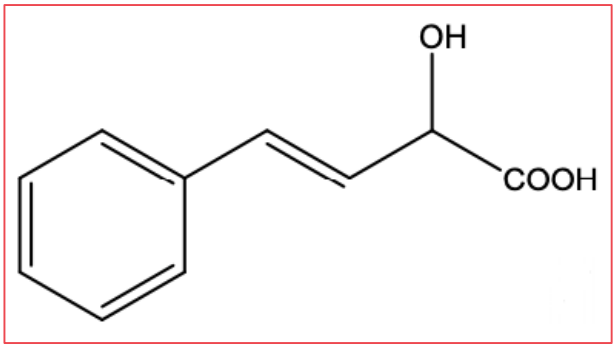
For the reaction in excess H_2/Ni , the nitrile compound is reduced to an **amine**:



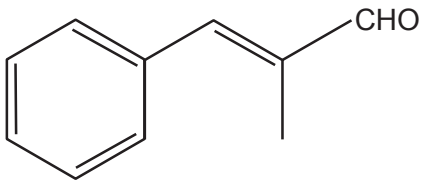
For the reaction of cinnamaldehyde in $NaBH_4$, it is reduced to form a **primary alcohol**:



For the reaction in H^+(aq), the hydroxyl nitrile is hydrolysed to a **carboxylic acid** in acidic conditions:



(d)* Methylcinnamaldehyde reacts with iodine monochloride, IC*l*, by electrophilic addition. The reaction produces a mixture containing two different organic products.



methylcinnamaldehyde

The electronegativity values of chlorine and iodine are given in the table below.

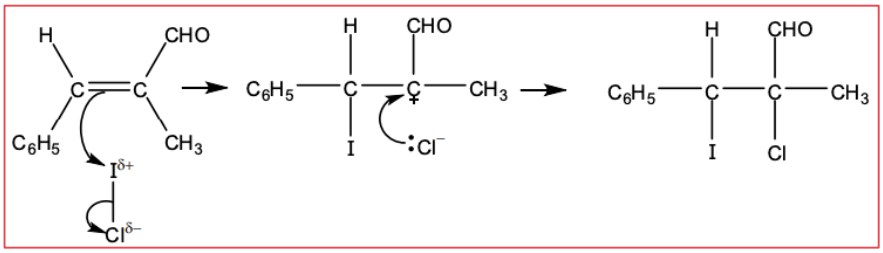
	Pauling electronegativity value
C*l*	3.0
I	2.5

Outline the mechanism, using the 'curly arrow' model, for the formation of **one** of the organic products and explain which of the two possible organic products is more likely to be formed.

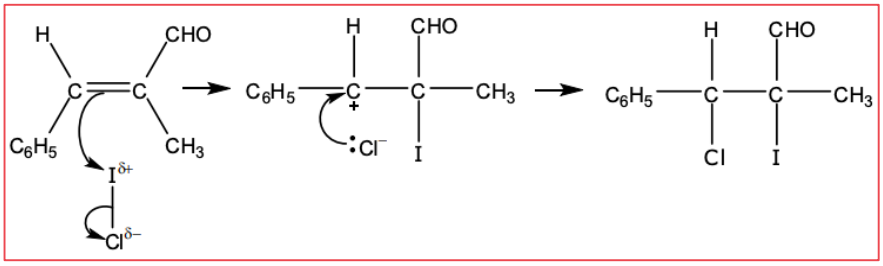
In your mechanism, you can show the phenyl group as C_6H_5. **[6]**

Mechanism for formation of either product

- Curly arrow from C=C to attack the I atom of the I-C*l* making sure the curly arrow begins in the centre of the C=C bond and ends at the second I atom.
- Correct dipole on I-C*l* with the
- Curly arrow from I-C*l* bond to C*l* with the δ+ sign on the less electronegative iodine atom.
- Carbocation with full positive charge on carbon atom as the carbocation does not have a partial charge, hence it must have a + sign only and not a δ sign.
- Curly arrow from negative charge on Cl^- or lone pair on Cl^- to carbon atom with positive charge making sure the base of the arrow begins in the **middle** of the **lone pair** and ends at the **positive side** of the carbon atom.

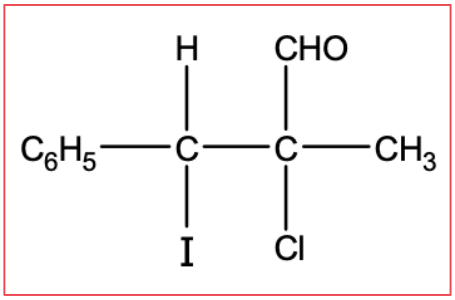


OR

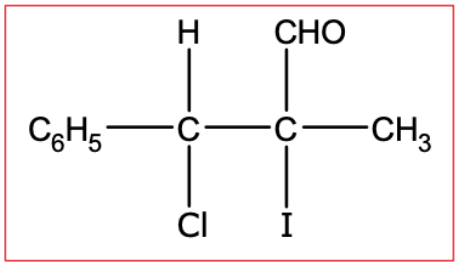


Organic products

- Major/most likely product as the chlorine atom bonds to the carbocation that has the most alkyl groups attached. Cl has a higher Pauling electronegativity value, hence it is acting as the electrophile here while I is the nucleophile.



- Minor/least likely product as the electrophile bonds to the most less stable primary carbon atom.



Major/most likely product is formed from the most stable carbocation intermediate

OR – C*l* is attached to carbon atom with the least hydrogens attached

OR the carbon with the most –C atoms attached

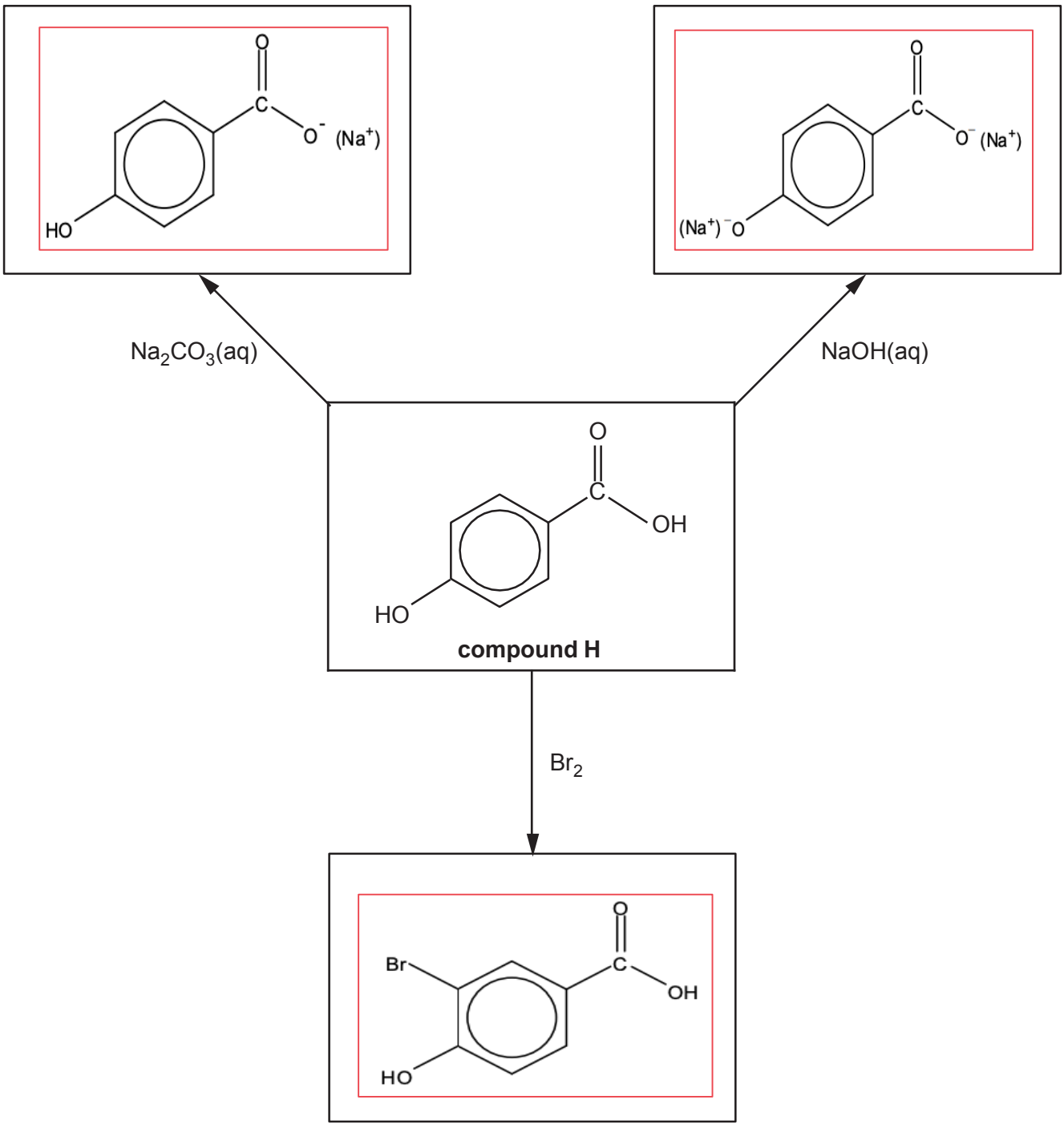
OR the – I is attached to the carbon atom with most hydrogens attached

(Total 18 marks)

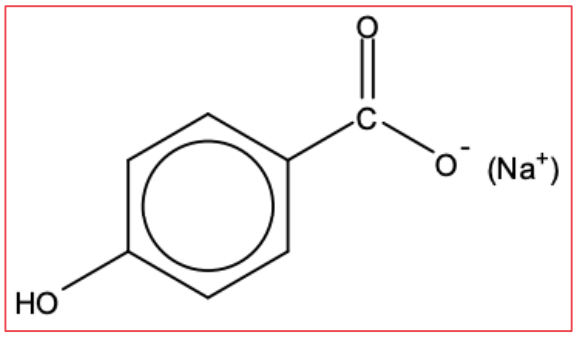
This question is about aromatic carboxylic acids and their derivatives.

(a) The flowchart below shows some reactions of compound **H**.

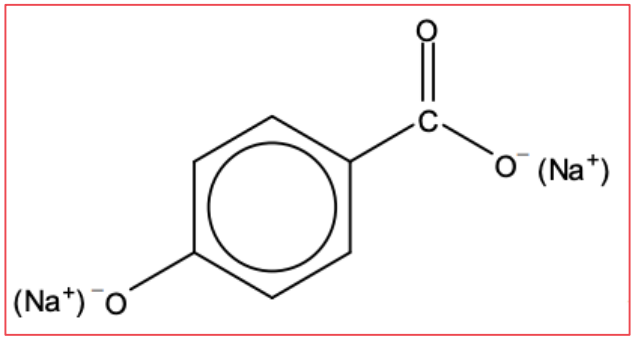
In the boxes, draw the organic products of these reactions. **[3]**



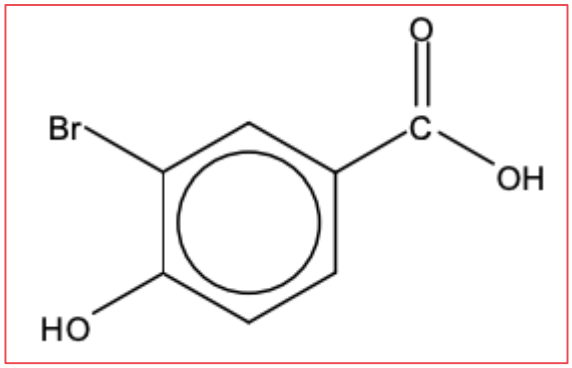
The product from reaction with Na_2CO_3 produces the sodium ethanoate molecule, salt and water.



The product from reaction with NaOH (which is a stronger base) produces the ethanoate molecule, salt and water. The sodium atom also replaces the hydrogen on the hydroxyl group.

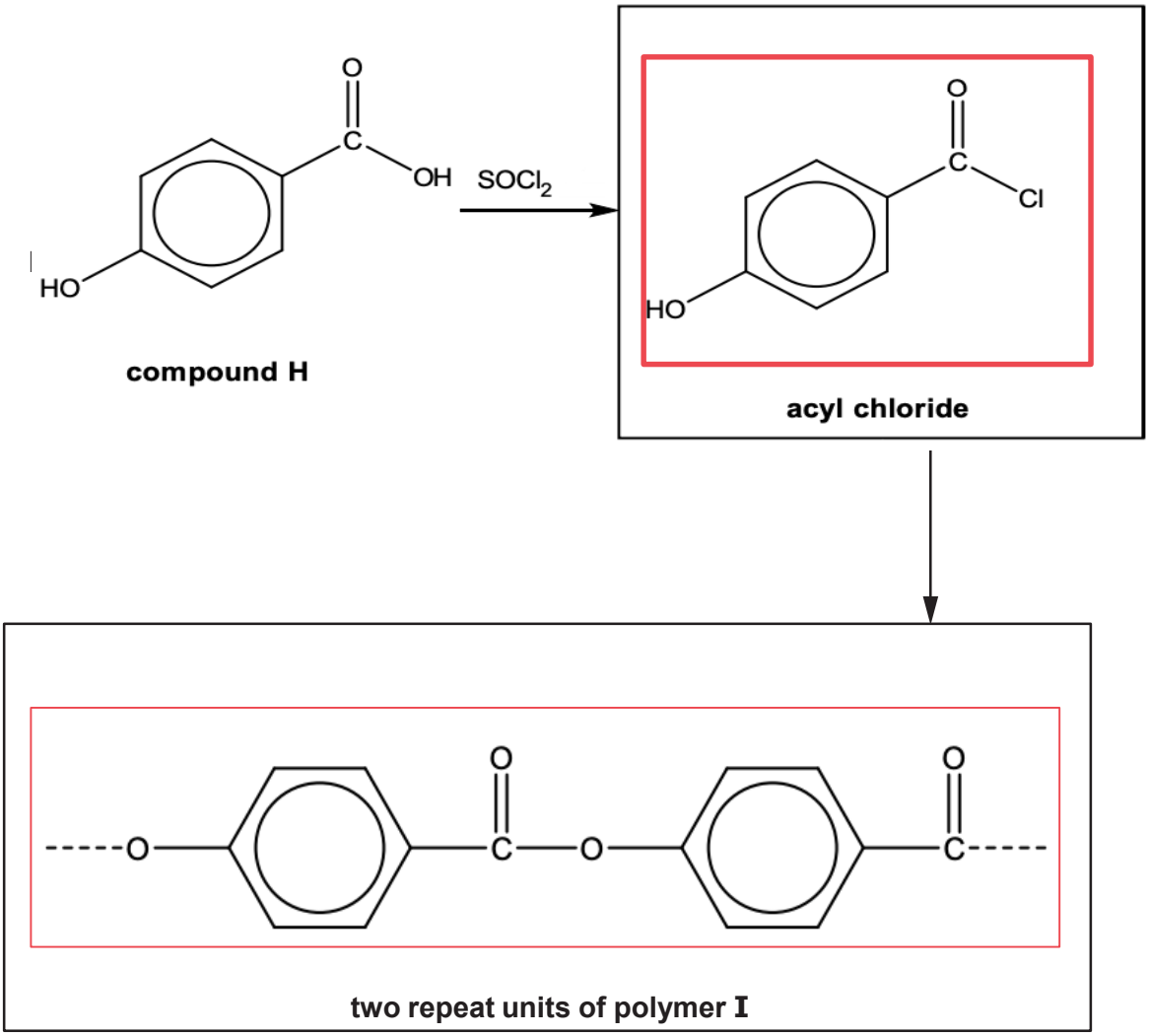


Product from Br_2 in which a bromine atom substitutes a hydrogen atom on the benzene ring.



(b) Compound **H** is used in the synthesis of polymer **I**, as shown in the flowchart below.

Complete the flowchart by drawing the structure of the acyl chloride and **two** repeat units of polymer **I**, and stating the **formula** of the reagent(s) required for the first stage on the dotted line.



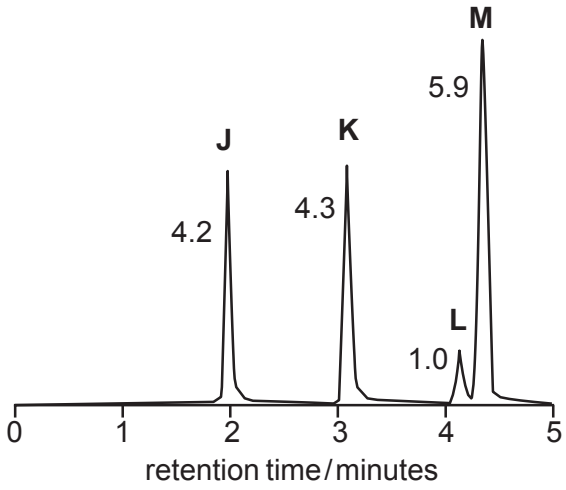
[4]

Carboxylic acids produce acyl chlorides in reaction with thionyl chloride.

The diagram of the polymer must include the ester link as well as the rest of the structure.

(c) A cosmetic product containing four esters, **J**, **K**, **L** and **M**, is analysed by gas chromatography and mass spectrometry. The results are shown below.

Gas chromatogram



The numbers by the peaks are the relative molar proportions of the compounds in the mixture.

Mass spectrometry

ester	*m/z* of molecular ion peak
J	152
K	166
L	180
M	180

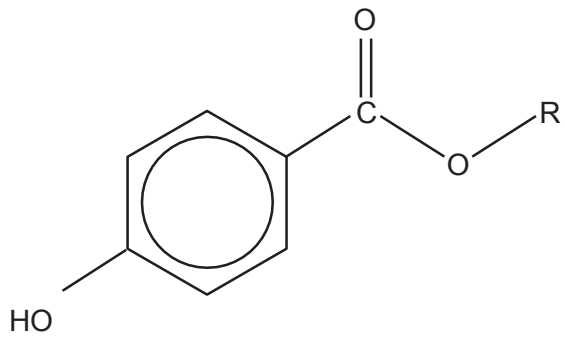
(i) The concentration of ester **K** in the cosmetic product is 9.13×10^{-2} g dm^{-3}.

Using the results, calculate the concentration, in mol dm^{-3}, of ester **M** in the cosmetic product.

Give your answer to **two** significant figures. **[2]**

Step	Working out
1. Calculate the concentration of ester K in mol dm^{-3}.	$[K] = \frac{913 \; x \; 10}{166} = 5.50 \times 10^{-4}$ (mol dm^{-3})
2. Use the molar ratio given in the question to calculate the concentration of ester M.	$[M] = \frac{5.9}{4.3} \times 5.50 \times 10^{-4} = 7.50 \times 10^{-4}$ (mol dm^{-3})

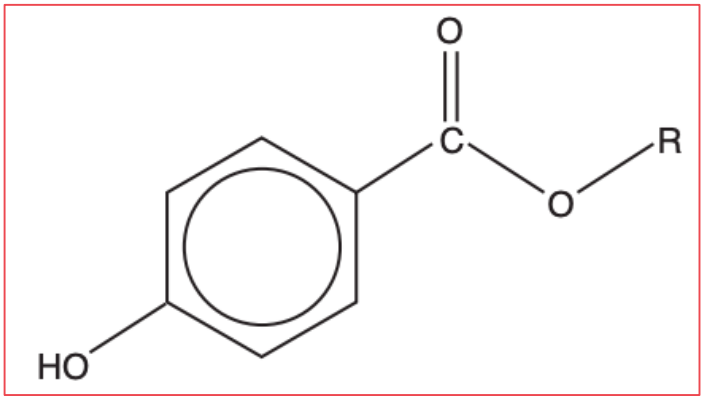
(ii) A general structure for esters **J**, **L** and **M** is shown below.

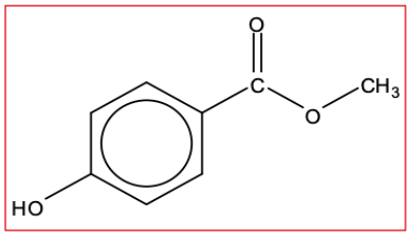
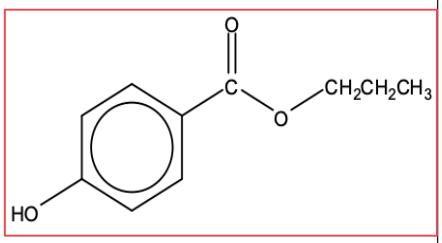
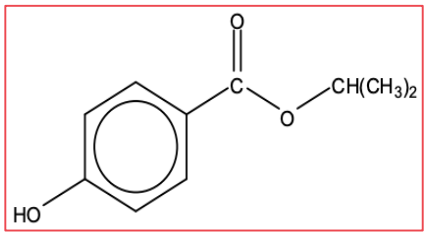


Where 'R' is an alkyl group.

Use the mass spectrometry results to deduce possible structures for esters **J**, **L** and **M**. **[3]**

The molecular mass for the general structure (below) is 137. To this number add on the number of appropriate methyl groups to arrive at the m/z ratio given for each ester.



J	L	M
		

Ester J:

M_r = 137 + 12 + 3 = 142

Ester L:

M_r = 137 + 14 + 14 + 15 = 180

Ester M:

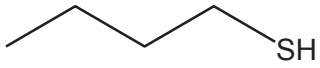
M_r = 137 + 13 + (2 x 15) = 180

(Total 12 marks)

This question is about organic molecules that have a strong smell.

(a) Thiols are foul-smelling, organic sulfur compounds with the functional group –SH.

Butane-1-thiol, shown below, contributes to the strong smell of skunks.



butane-1-thiol

(i) Thiols are weak acids.

Write the expression for the acid dissociation constant, K_a, for butane-1-thiol.

[1]

Write the equilibrium expression before writing the expression for K_a:

$C_4H_9SH \rightleftharpoons H^+ + C_4H_9S^-$

$K_a = \frac{[H+][C_4H_9S^-]}{[C_4H_9SH]}$

Square brackets required

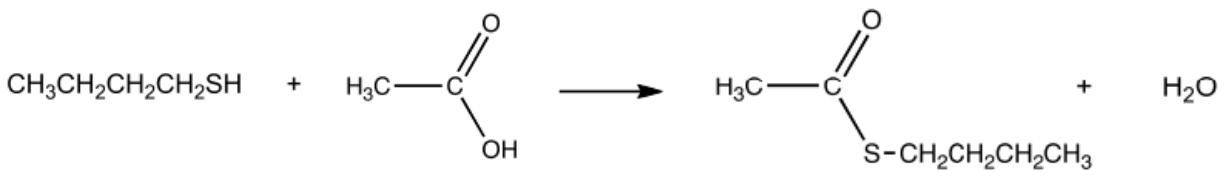
(ii) Thiols react with carboxylic acids to form thioesters.

Write an equation for the reaction of butane-1-thiol with ethanoic acid.

Use structures for all organic compounds with the functional groups clearly displayed.

[2]

The reaction is shown below:

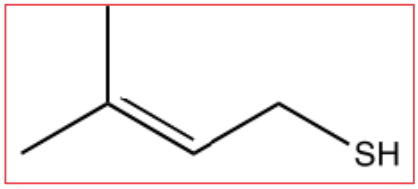


Clearly draw the **carbonyl** and **alcohol** groups as well as the sulfur atom.

(iii) When beer is exposed to light, 3-methylbut-2-ene-1-thiol is formed, which gives an unpleasant smell and flavour to the beer.

Draw the **skeletal** formula for 3-methylbut-2-ene-1-thiol.

[1]



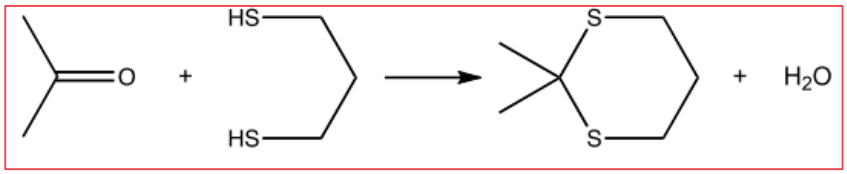
Draw a 4 carbon chain, add on the thiol group on one end and the alkene and methyl groups on carbons 2 and 3 respectively.

(iv) Propane-1,3-dithiol reacts with carbonyl compounds in a condensation reaction to form a cyclic organic sulfur product.

Write an equation for the reaction of propane-1,3-dithiol with propanone.

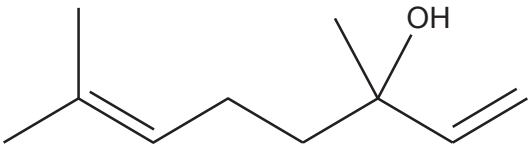
Use structures for organic compounds.

[2]

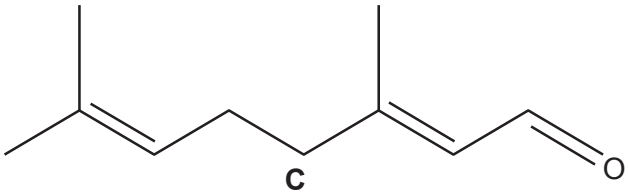


Include the water molecule at the end as a product of condensation.

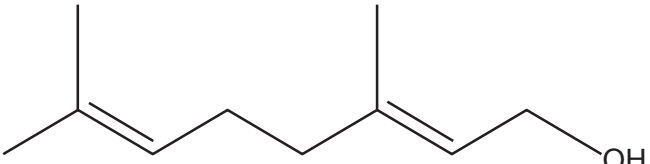
(b)* The structures for six naturally occurring organic compounds with pleasant smells, **B**–**G**, are shown below. The common names in brackets relate to their source and smell.



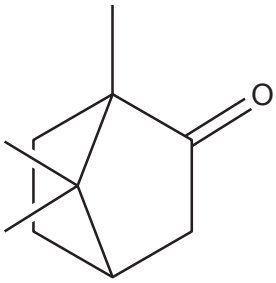
B
(linalool)



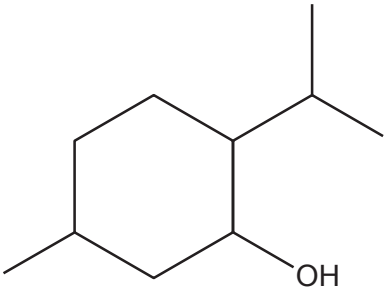
C
(citral)



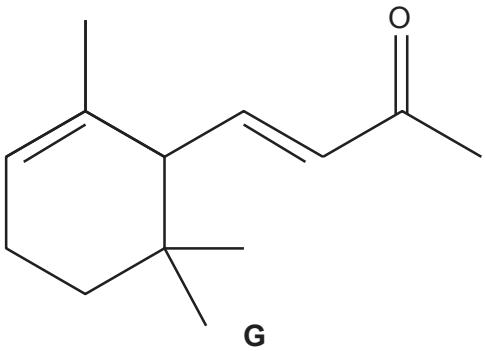
D
(geraniol)



E
(camphor)



F
(menthol)



G
(ionone)

Explain how chemical tests would allow each compound to be distinguished from the other compounds.

In your answer, include essential details for all test procedures and observations.

Details of apparatus and quantities are **not** required.

[6]

Indicative scientific points may include:

Start this question by identifying the functional groups on each molecule and writing them down.

Functional groups

- B alkene and tertiary alcohol
- C alkene and aldehyde
- D alkene and primary alcohol
- E ketone
- F secondary alcohol
- G alkene and ketone

Then list the tests used to identify each functional group.

Tests

- B, C, D and G Bromine decolourises
- C, D and F $(H^+ /)Cr_2O_7^{2-}$ green
- C, E and G 2,4-DNP orange precipitate
- C Tollens silver mirror

For Tollens' **ALLOW** alternative: Fehling's solution produces a 'brown/brick red/orange precipitate

For 2,4-DNP, **ALLOW** 2,4-DNPH and Brady's

Once the functional groups and tests have been written down, tabulate the expected results as shown below. Then use the table and a process of elimination to distinguish between each compound.

For example: Compound C reacts produces a positive result in **all tests** but it is the only one that does so, hence it can be distinguished in this way. No two samples produce the same column of results, hence the compounds can be distinguished.

	B	C	D	E	F	G
Bromine	✓	✓	✓			✓
$(H^+/)Cr_2O_7^{2-}$		✓	✓		✓	
2,4-DNP		✓		✓		✓
Tollens		✓				

(Total 12 marks)