Carboxylic Acids and Esters

1. Alcohols can be used to prepare organic compounds with different functional groups.

$HO(CH_2)_4OH$ can be oxidised to form $HOOC(CH_2)_2COOH$.

i. State the reagents and conditions and write an equation for this oxidation.

In the equation, use [O] for the oxidising agent.

Reagents and conditions: ---

Equation:

[3]

ii. $HOOC(CH_2)_2COOH$ is soluble in water.

Explain, using a labelled diagram, why $HOOC(CH_2)_2COOH$ is soluble in water.

[2]

2. This question is about two different types of acid found in organic compounds, carboxylic acids and sulfonic acids, as shown in **Fig. 6.1**.

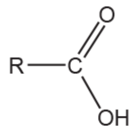
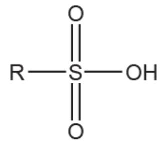
	
Carboxylic acid	Sulfonic acid

Fig. 6.1

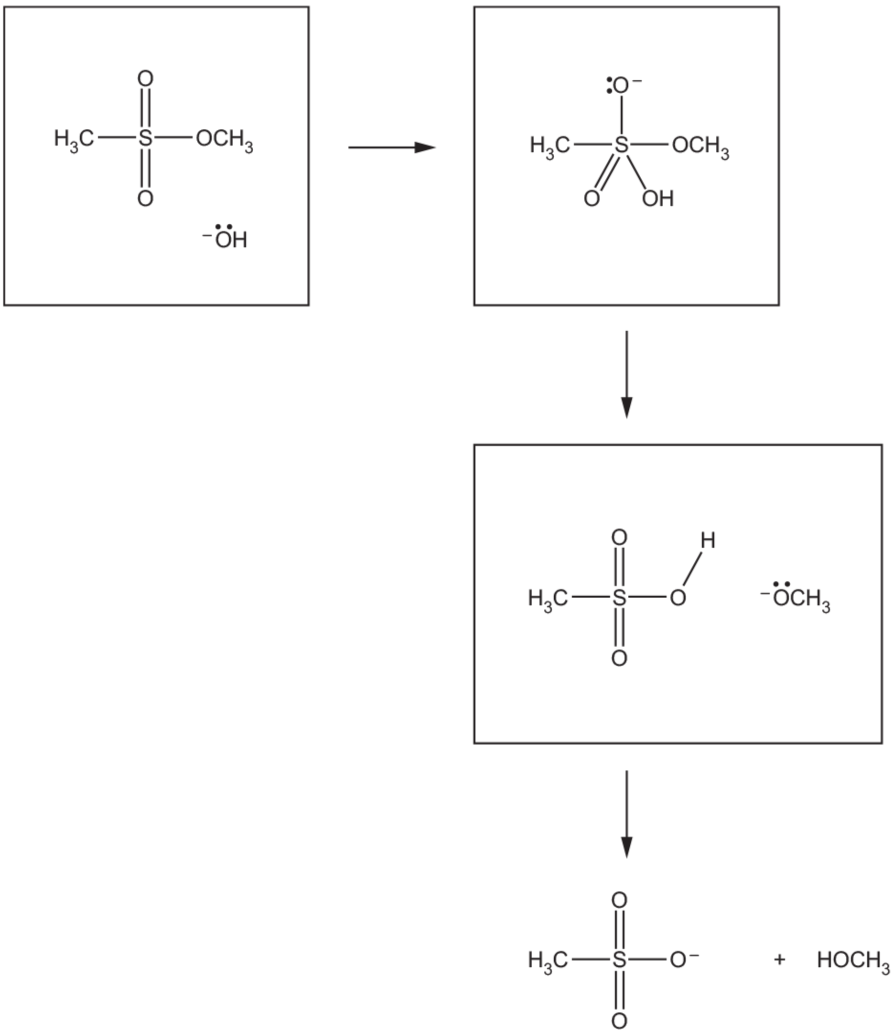
Carboxylic acids and sulfonic acids both form esters.

Sulfonic acid esters can be hydrolysed by aqueous alkali.
The equation shows the alkaline hydrolysis of a sulfonic acid ester.

$CH_3SO_2OCH_3 + OH^- \rightarrow CH_3SO_2O^- + CH_3OH$

In the **3 boxes below**, add curly arrows to show the mechanism for this reaction.

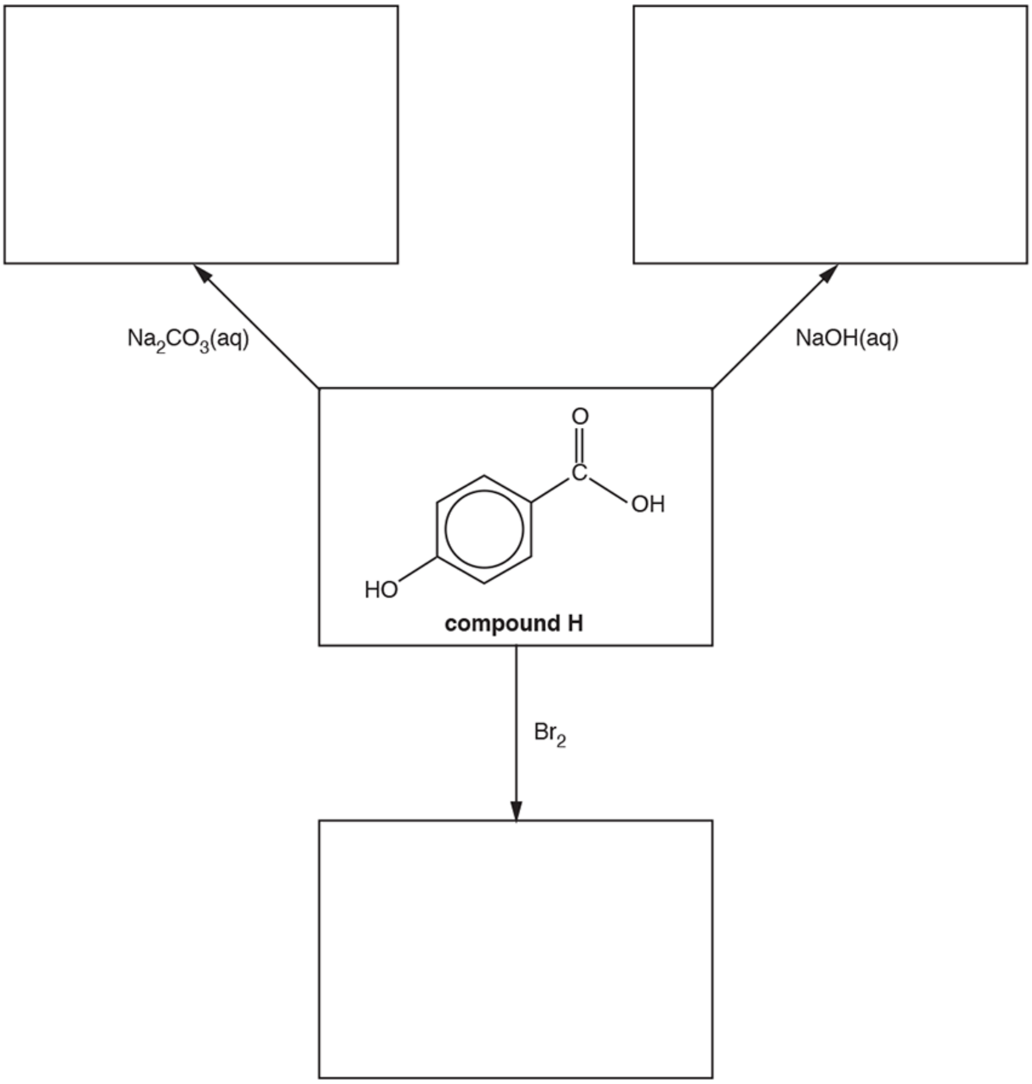
In the first box, the hydroxide ion acts as a nucleophile.



[2]

3(a). This question is about aromatic carboxylic acids and their derivatives.

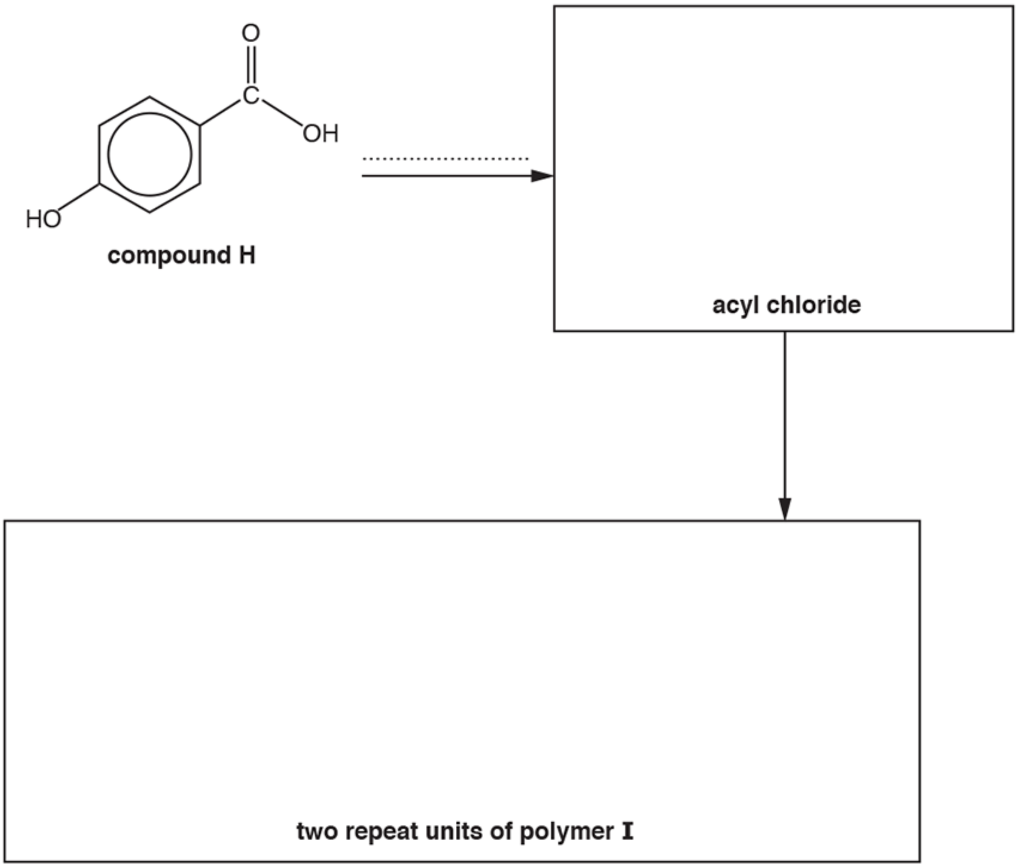
The flowchart below shows some reactions of compound **H**. In the boxes, draw the organic products of these reactions.



[3]

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

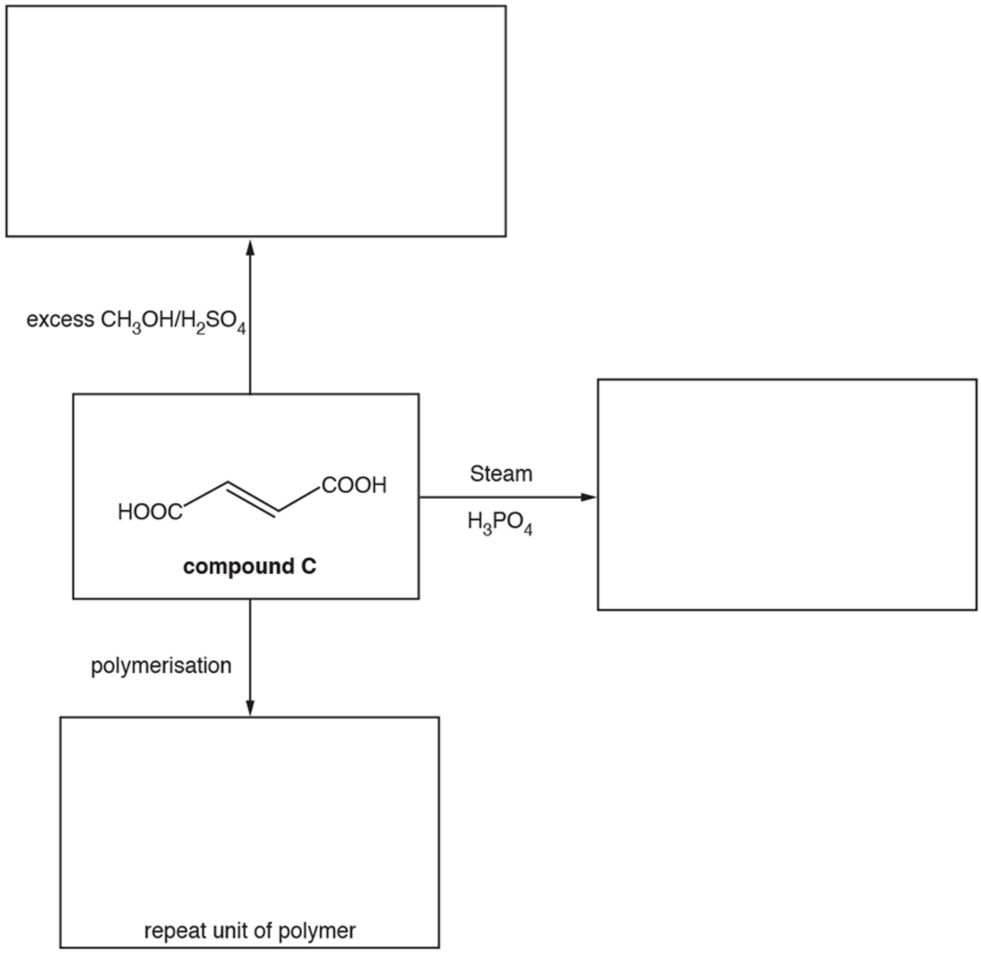
Complete the flowchart by drawing the structure of the acyl chloride and **two** repeat units of polymer **I**, and stating the **formula** of the reagent(s) required for the first stage on the dotted line.



[4]

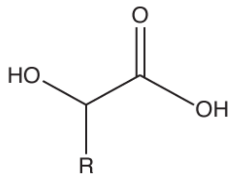
4. The flowchart below shows some reactions of compound **C**.

In the boxes, draw the organic products of these reactions.



[3]

5. The structural formula of compound **A** is shown below.



compound A

Two reactions of compound **A** are carried out.

Suggest an equation for each reaction and state the type of reaction.

In your equations, draw structures for organic compounds.
You can use R for the alkyl group.

i. Magnesium ribbon is added to a solution of compound **A**.
Gas bubbles are seen and the magnesium slowly dissolves.

Equation

Type of reaction ____________________

ii. Compound **A** is heated with a few drops of concentrated sulfuric acid as a catalyst.
A cyclic 'dimer' of compound **A** forms.

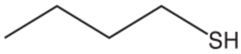
Equation

Type of reaction ____________________

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

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.

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.

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.

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.

7. This question is about weak acids.

Compound **A** is a weak monobasic acid.

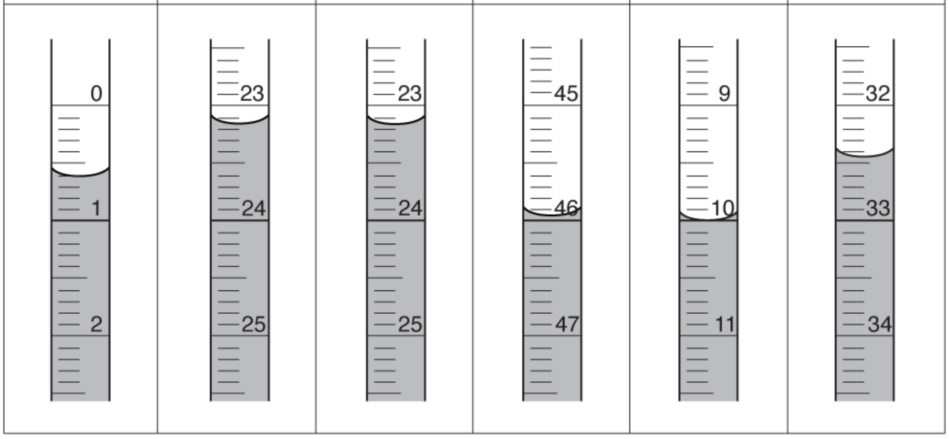
A student is supplied with a 250.0 cm^3 solution prepared from 2.495 g of **A**.

The student titrates 25.0 cm^3 samples of this solution with 0.0840 mol dm^{-3} NaOH in the burette.

The student carries out a trial, followed by the three further titrations. The diagrams show the initial burette readings and the final burette readings for the student's three **further** titrations.

All burette readings are measured to the nearest 0.05 cm^3.

Titration 1		**Titration 2**		**Titration 3**	
Initial reading	Final reading	Initial reading	Final reading	Initial reading	Final reading

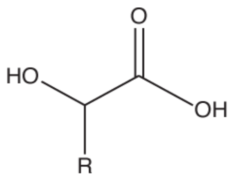


i. Record the student's readings and the titres in an appropriate format.

Calculate the mean titre that the student should use for analysing the results.

mean titre = ------------------------------ cm^3 **[4]**

ii. The structure of compound **A** is shown below.



compound A

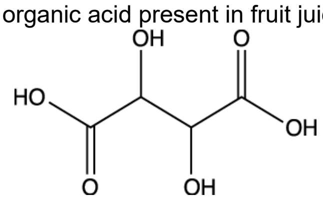
Compound **A** has four optical isomers.

Using this information and the student's results, answer the following.

- Determine the molar mass of **A** and the formula of the alkyl group R.
- Draw the structure of compound **A** and label any chiral carbon atoms with an asterisk*.

Show all your working.

8. Tartaric acid, shown below, is an organic acid present in fruit juice.



i. What is the empirical formula of tartaric acid?

-- **[1]**

ii. Write the systematic name for tartaric acid.

-- **[1]**

iii. Tartaric acid reacts with 1,6-diaminohexane, $H_2N(CH_2)_6NH_2$, to form a polymer.

Draw the structure of **one** repeat unit of this polymer.

[2]

iv. The polymerisation in **(iii)** takes place in two steps.

In the first step, tartaric acid and 1,6-diaminohexane react to form a salt.

Draw the structure of this salt, showing the ions present.

[2]

9(a). A student was provided with five compounds: an aldehyde, a ketone, a carboxylic acid and two esters. The student decides to identify the type of compound by carrying out some chemical tests.

Suggest chemical tests to identify the carboxylic acid and aldehyde.

For each test, include essential reagent(s), observation(s) and a balanced equation.

In your equations, use 'R' for the alkyl group.

i. Test for carboxylic acid.

Reagent(s) ....

Observation(s) ....

Equation

[2]

ii. Test for aldehyde.

Reagent(s) ....

Observation(s) ....

Equation

[2]

(b). Suggest a chemical test to distinguish the ketone from the two esters.

Reagent(s)
....

Observation(s)
....

[1]

(c). The student wants to confirm that the other two compounds are esters. Unfortunately there is no direct test for an ester group.

The esters are $CH_3COOC(CH_3)_3$ and $(CH_3)_3CCOOCH_3$.

The student plans the following:

- hydrolyse the two esters using aqueous sodium hydroxide.
- separate the hydrolysis products.
- carry out tests on the hydrolysis products.

i. Write an equation for the hydrolysis of one of the two esters with aqueous sodium hydroxide.

Show the structures for the organic compounds.

[2]

ii. Suggest a chemical test on the hydrolysis products that would allow the two esters to be identified.

Write an equation for one reaction that takes place.

Show the structures for the organic compounds.

Reagent(s)
....

Observation(s)
....

Equation

[2]

iii. The student thought that NMR spectroscopy could be used to identify the two esters without the need to carry out chemical tests.

The esters are $CH_3COOC(CH_3)_3$ and $(CH_3)_3CCOOCH_3$.

Explain whether the student is correct for ^{13}C and ^{1}H NMR spectroscopy. Your answer should also clearly state any differences between the spectra of the two esters.

---

[3]

(d). The ketone and aldehyde provided to the student both contain five carbon atoms.

The ^{1}H NMR spectrum of the aldehyde contains two singlet peaks only: a large peak at $\delta = 1.2$ ppm and smaller peak at $\delta = 9.6$ ppm.

Suggest **all** possible structures for the ketone and identify the aldehyde.

Show **all** your reasoning.

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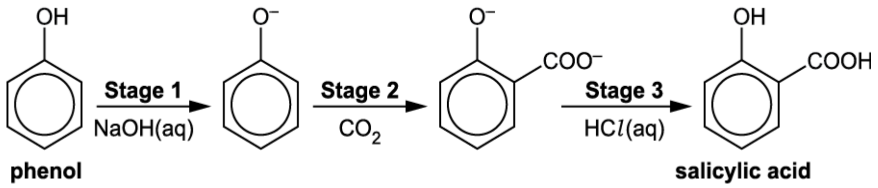
[5]

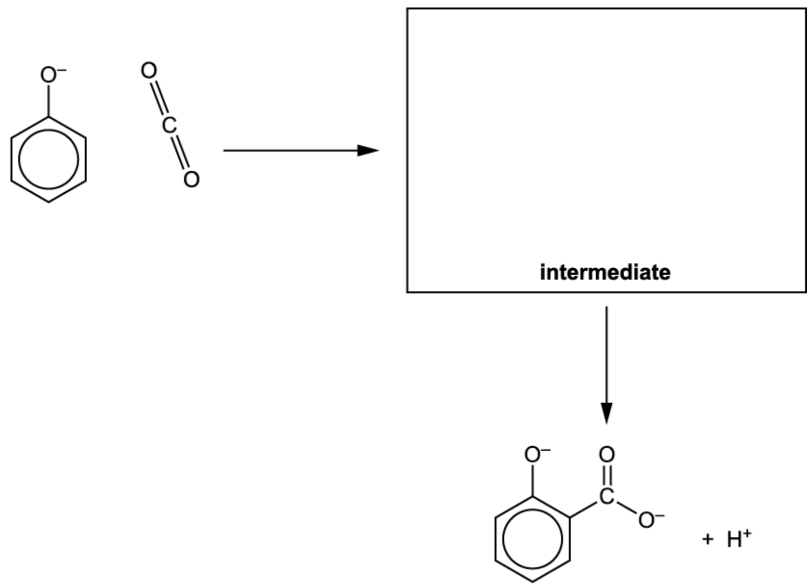
10(a). This question is about medical compounds made from salicylic acid.

Salicylic acid can be made from the reaction of phenol with carbon dioxide as shown below.



i. **Stage 2** takes place by electrophilic substitution and part of the mechanism is shown below.

Complete the mechanism by showing relevant dipoles, curly arrows and the structure of the intermediate.



[3]

ii. What type of reaction takes place during **Stage 1** and **Stage 3**?

Explain your answer.

Type of reaction ....

Explanation ....

--- **[2]**

iii. A chemist prepares 4.83 g of salicylic acid from phenol. The percentage yield of this reaction is 45.0%.

Calculate the mass of phenol that the chemist uses.

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

mass of phenol = ... g **[3]**

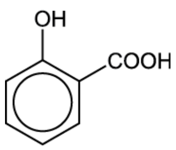
(b). Aspirin is an ester of salicylic acid.

Aspirin can be prepared by reacting salicylic acid with ethanoic anhydride, $(CH_3CO)_2O$. One other organic compound also forms.

Draw **skeletal** formulae for the products of this reaction.

[2]

(c). 'Oil of wintergreen' is used to relieve aching muscles and can be prepared by reacting salicylic acid with methanol.



salicylic acid

i. Suggest the structure of oil of wintergreen and the conditions needed to prepare oil of wintergreen from salicylic acid.

Structure

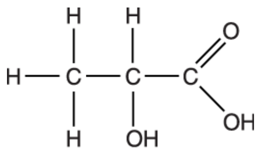
Conditions
.... **[1]**

ii. After its preparation, oil of wintergreen can be purified by distillation.

Draw a **labelled** diagram showing how the apparatus is set up for distillation.

[2]

11. This question is about the preparation, properties and uses of lactic acid.



lactic acid

When heated strongly, lactic acid forms a cyclic 'diester'.
The diester has the molecular formula, $C_6H_8O_4$.

Draw the structure of the cyclic diester.

[1]

12. Stearic acid, oleic acid and linoleic acid are examples of naturally occurring fatty acids.

Traditional name	Structure	Systematic name
Stearic acid	$C_{17}H_{35}COOH$	Octadecanoic acid
Oleic acid	$C_{17}H_{33}COOH$	Octadec-9-enoic acid
Linoleic acid	$C_{17}H_{31}COOH$	Octadeca-9,12-dienoic acid

Sodium stearate is the salt formed when stearic acid reacts with sodium hydroxide solution.

Write an equation for the formation of sodium stearate.

______________________________ **[1]**

13. Aqueous propanoic acid, C_2H_5COOH, reacts with carbonates and alkalis.

i. Write the full equation for the reaction of aqueous propanoic acid with sodium carbonate.

-- **[1]**

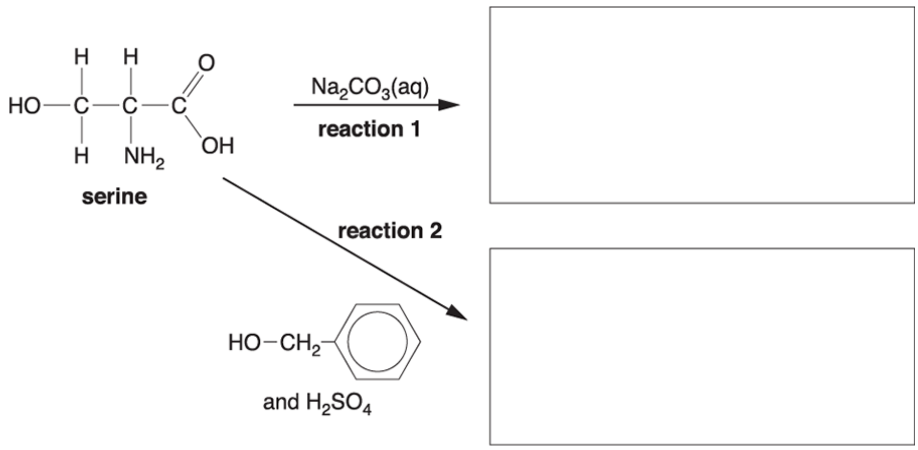
ii. Write the **ionic** equation for the reaction of aqueous propanoic acid with aqueous potassium hydroxide.

-- **[1]**

14. Many α-amino acids have several functional groups.

Serine, shown below, is a naturally occurring α-amino acid.

i. In the boxes below, draw the structure of the organic compounds formed by each reaction.



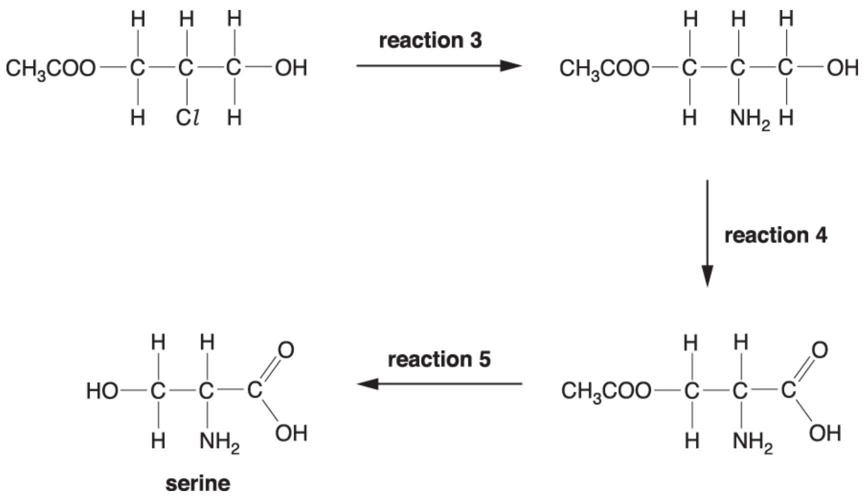
[3]

ii. Suggest a use for the organic compound formed by **reaction 2**.

-- **[1]**

iii. Serine is commonly used in organic synthesis.

One possible method of synthesising serine is shown below.



Complete the following:

Reagent and conditions used for **reaction 3**.

Type of reaction for:

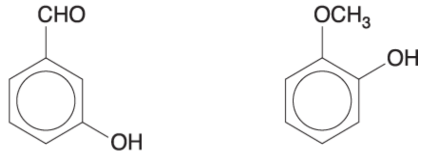
reaction 4 ....

reaction 5 ....

[3]

15. A student analysed a mixture of compounds found in red wine using gas chromatography followed by mass spectrometry (GC-

Two of the compounds found to be present in the mixture are shown below.

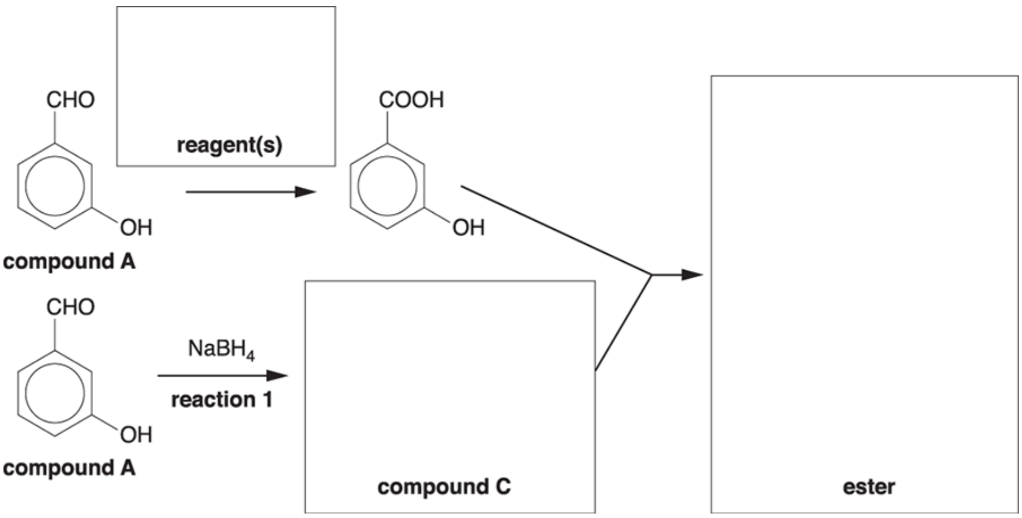


compound A **compound B**

In red wine, compound **A** slowly forms an ester.

The formation of the ester can also be done in the laboratory, as shown in the flowchart below. Separate portions of compound **A** are used in the formation of the ester.

i. Complete the boxes in the flowchart below.

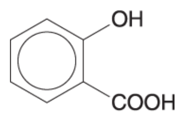


[3]

ii. Give the mechanism to show the formation of compound **C** in **reaction 1**.
Use curly arrows and relevant dipoles.

[3]

16(a). Salicylic acid is a naturally occurring carboxylic acid, widely used in organic synthesis.

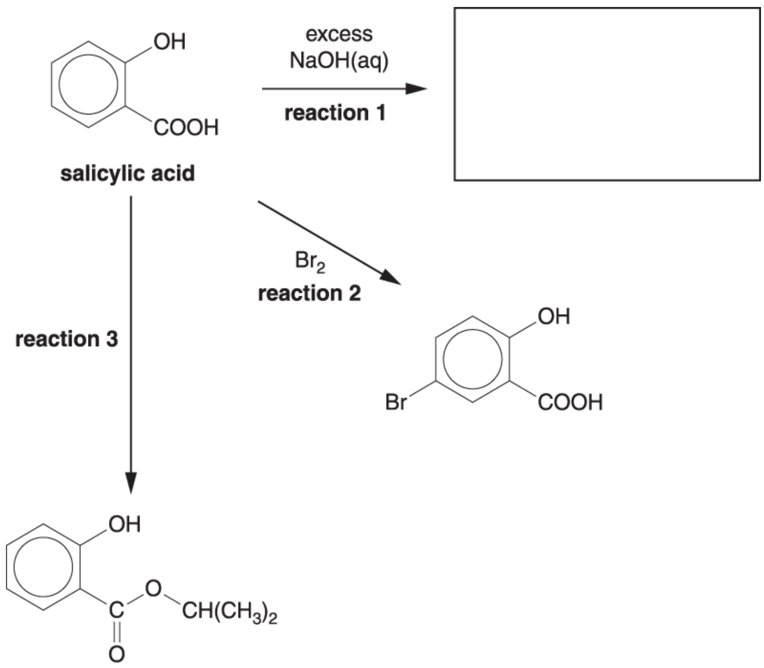


salicylic acid

The flowchart below shows some reactions of salicylic acid.

i. In the box below, draw the structure of the organic compound formed by **reaction 1**.

[1]



ii. Describe what would be **observed** during **reaction 2**.

____

____ **[1]**

iii. Write a chemical equation to represent **reaction 2**.

[1]

iv. State the reagents and conditions in **reaction 3**.

____

____ **[1]**

(b). Bromine reacts more readily with salicylic acid than with benzene.

i. Outline the mechanism for the bromination of salicylic acid shown in **reaction 2** in the flowchart.

A halogen carrier is not required for this reaction.

The electrophile is Br_2.

[4]

ii. Explain why bromine reacts more readily with salicylic acid than with benzene.

In your answer, you should use appropriate technical terms, spelled correctly.

[3]

17. Compound **B**, C_xH_yO, can be oxidised to form a ketone **C**.

0.035 mol of **B** has a mass of 2.59 g.

Compound **B** reacts with compound **D**, $C_3H_6O_2$, in the presence of an acid catalyst to form two compounds **E** and **F**.

- Calculate the molar mass of compound **B**.
- Give the structures of compounds **B**, **C**, **D**, **E** and **F**.

[6]

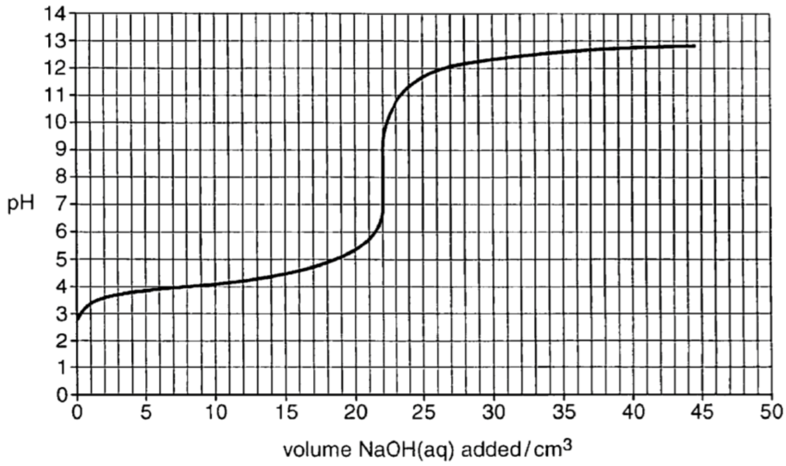
18(a). This question is about different weak acids.

A student carries out a titration to determine the concentration of a solution of ethanoic acid.

The method is outlined below.

- A 25.0 cm^3 sample of $CH_3COOH(aq)$ is pipetted into a conical flask.
- The $CH_3COOH(aq)$ is titrated by adding 0.125 mol dm^{-3} NaOH from a burette.
- The pH of the solution is measured continuously, with stirring, as the NaOH(aq) is added.

The pH titration curve is shown below.



i. How could the student measure the pH continuously as the NaOH(aq) is added?

-- **[1]**

ii. Determine the unknown concentration, in mol dm^{-3}, of the $CH_3COOH(aq)$.
Show your working.

concentration of $CH_3COOH(aq)$ = ...mol dm^{-3} **[2]**

(b). The table shows the pH ranges of four indicators.

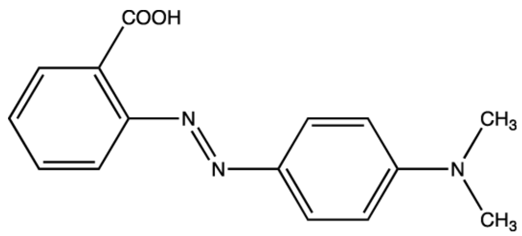
Indicator	congo red	methyl red	brilliant yellow	alizarin yellow R
pH range	3.0−5.0	4.4−6.2	6.6−7.8	10.1−12.0

i. Choose, with a reason, the indicator from the table that is most suitable for the student's titration in **(a)**.

---**[1]**

ii. An indicator is a weak acid, HA, which has a different colour from its conjugate base, A^-.

For methyl red, the HA form is red and the A^- form is yellow.
The structure of methyl red is shown below.



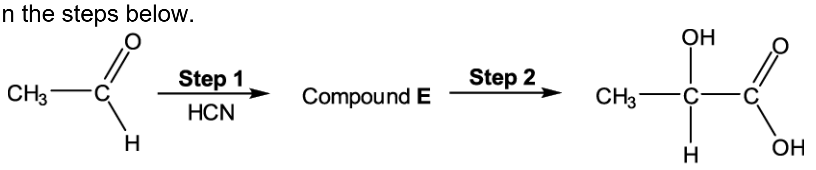
methyl red

Draw the structure of the conjugate base of methyl red and explain, in terms of equilibrium, the colours of methyl red at low pH, at high pH, and at the end point of a titration. You can use HA and A^- in your explanation.

explanation: ---

---**[4]**

19(a). Lactic acid is a naturally occurring chemical, which can be synthesised from ethanal, CH_3CHO, as shown in the steps below.



lactic acid

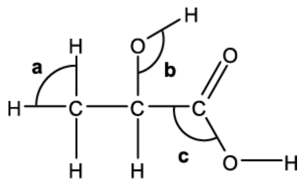
i. Draw the structure for compound **E**.

[1]

ii. Suggest a reagent that could be used for **Step 2**.

-- **[1]**

iii. The displayed formula of lactic acid is shown below.



lactic acid

Suggest a value for each bond angle **a**–**c**.

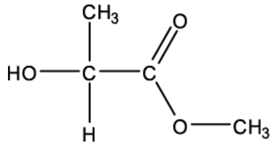
Bond angle **a**: ....

Bond angle **b**: ....

Bond angle **c**: ....

[2]

(b). Methyl lactate is an ester of lactic acid which is used as a solvent.



methyl lactate

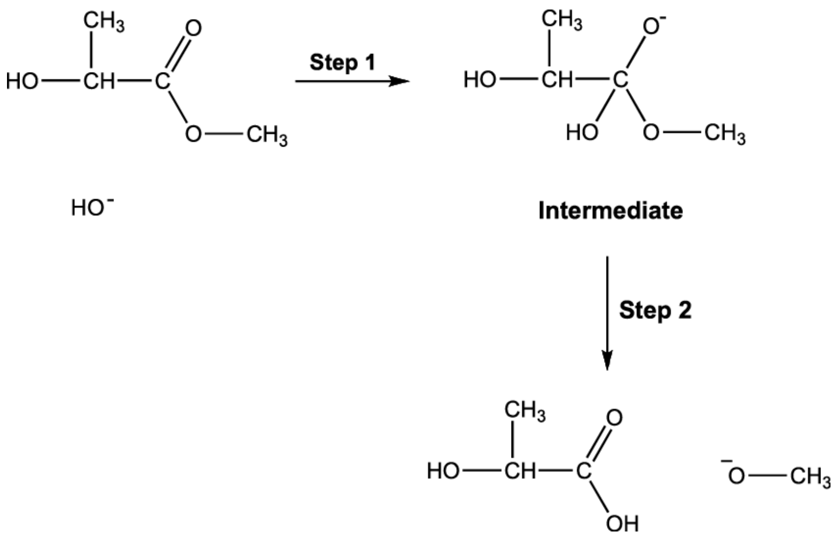
Methyl lactate can be hydrolysed by refluxing with sodium hydroxide solution.

In this reaction the hydroxide ion acts as a nucleophile.

i. Suggest how the hydroxide ion can act as a nucleophile.

-- **[1]**

ii. Part of the mechanism for the hydrolysis is shown below.

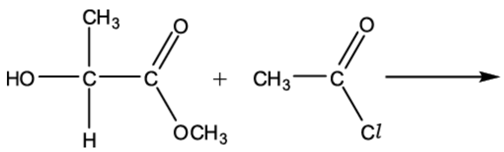


- Add relevant dipoles and curly arrows to show how the intermediate is formed in **Step 1** of the mechanism.
- Add curly arrows to show how the carboxylic acid and $^{-}OCH_3$ ion are formed from the intermediate in **Step 2** of the mechanism.

[4]

iii. Methyl lactate can also react with ethanoyl chloride.

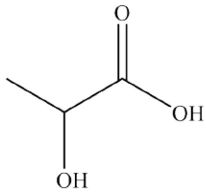
Complete the equation for this reaction.



[2]

20. This question is about organic acids.

Lactic acid, shown below, has two functional groups.



Lactic acid reacts with bases and with many metals.

- An aqueous solution containing 1.125 g of lactic acid is reacted with an excess of magnesium producing hydrogen gas.
- The excess magnesium is removed.
  The water is evaporated, leaving a white solid, **A**.

i. Name the type of reaction of lactic acid with bases and with metals.

reaction with bases:

reaction with metals:

---

[1]

ii. Calculate the volume of H_2(g) produced, measured at room temperature and pressure.

volume of H_2 = ... **[2]**

i. What is the empirical formula of the white solid **A**?

-- **[1]**

ii. Predict **two** reactions of lactic acid, each involving a different functional group.

Do **not** include reactions with bases or metals.

For each reaction,

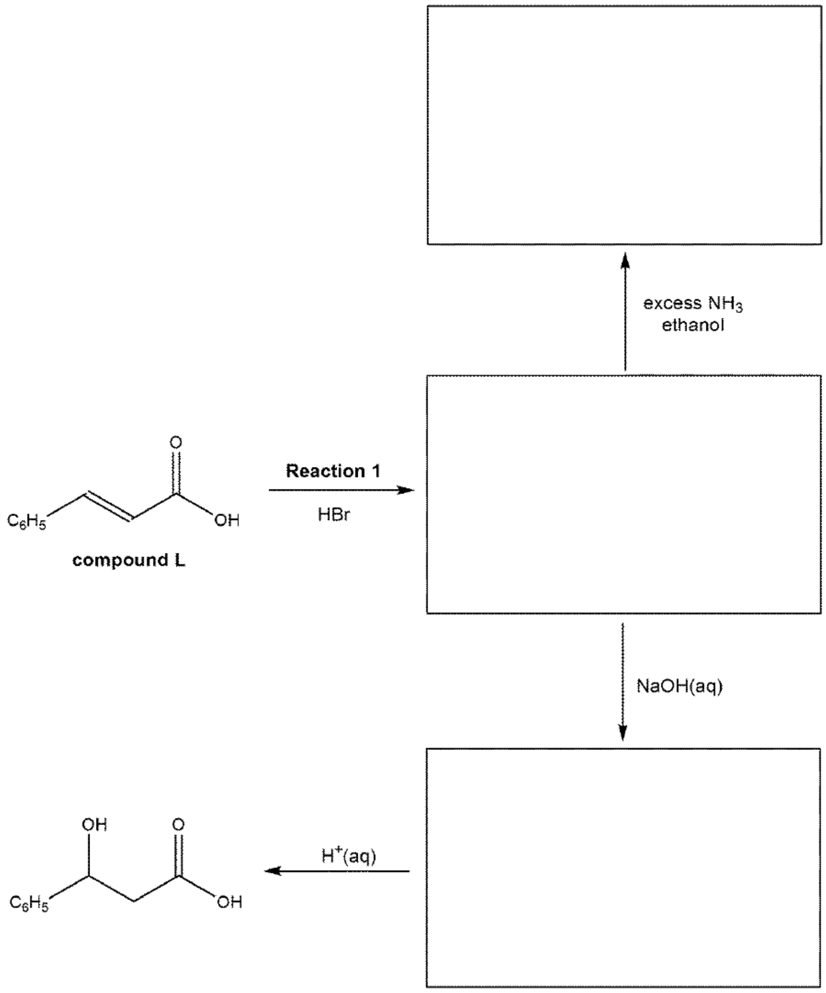
- state the type of reaction, the reagents and conditions
- draw the structures of any organic products formed.

[4]

21(a). This question is about the reactions of compounds with more than one functional group.

A chemist investigates some reactions of compound **L**, as shown in the flowchart below.

Complete the flowchart by showing the missing organic structures in the boxes.

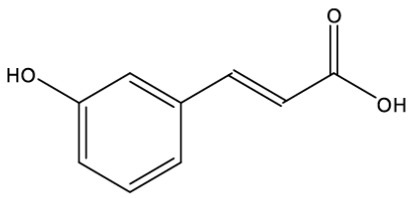


[3]

(b). Outline the mechanism that occurs in **Reaction 1**.
Include curly arrows, relevant dipoles and the name of the mechanism.

name of mechanism .... **[4]**

(c). The chemist synthesises compound **M**, which can undergo both addition and condensation polymerisation.



compound M

i. Draw the repeat unit of the **addition** polymer formed from compound **M**.

[1]

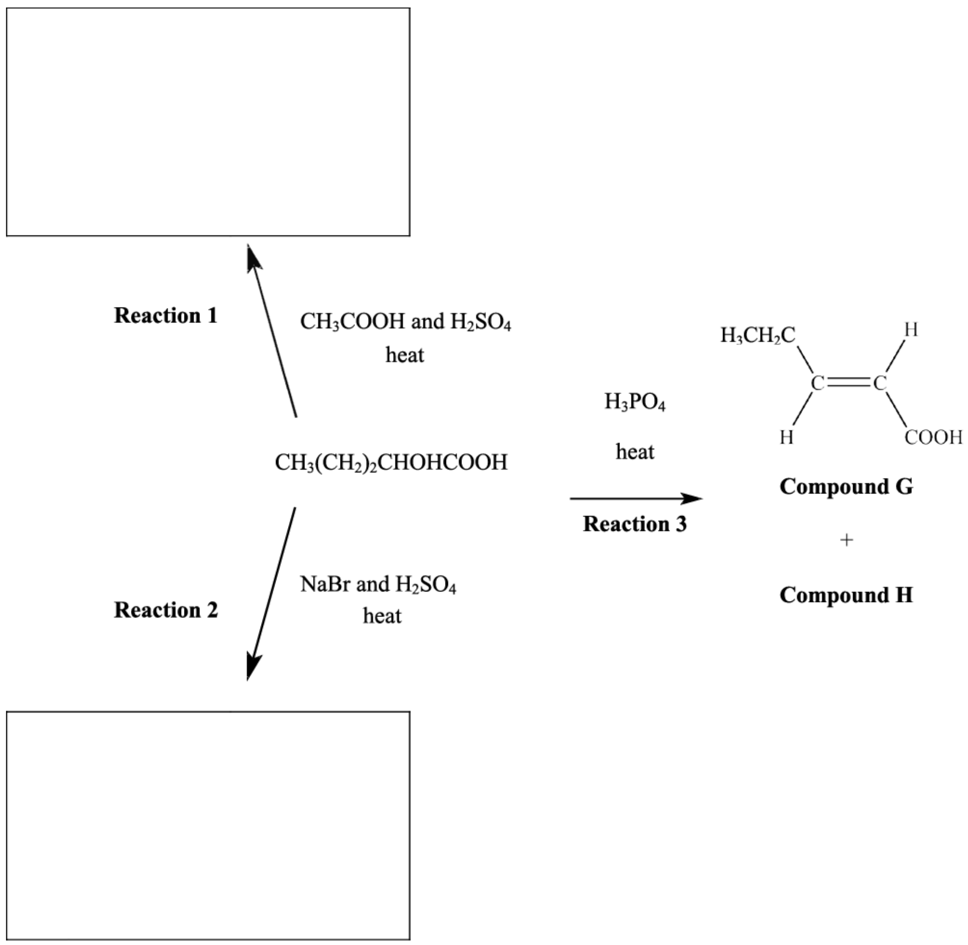
ii. Draw **two** repeat units of the **condensation** polymer formed from compound **M**.

[2]

22. α-Hydroxy acids (AHAs) are naturally occurring acids often used as cosmetics.

The flowchart below shows some reactions of an AHA, $CH_3(CH_2)_2CHOHCOOH$.

i. Fill in the boxes to show the organic products of **Reactions 1** and **2**, clearly showing the relevant functional groups.



[2]

ii. Give the **full** systematic name for compound **G**.

---**[1]**

iii. Compound **H** is a stereoisomer of compound **G**.

- Suggest a structure for compound **H**.
- Draw the repeat unit of the addition polymer that can be formed from compound **H**.

Compound H	**addition polymer**

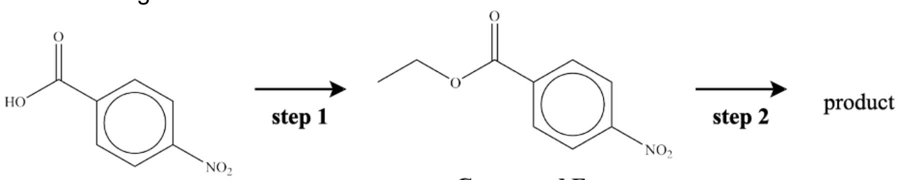
[2]

iv. The addition polymer in (**iii**) is used widely in industry. Increasingly, waste polymers are being processed as a more sustainable option than disposal.

Apart from recycling, state **two** methods for usefully processing waste polymers.

--- **[2]**

23. 4-Nitrobenzoic acid is an important compound in chemical synthesis. The flowchart below shows a synthesis involving 4-nitrobenzoic acid.



Compound F

i. State suitable reactant(s) and conditions for **step 1**.

[1]

ii. In **step 2**, the $-NO_2$ group in compound **F** is reduced by tin and concentrated hydrochloric acid.

Write an equation for the reduction of compound **F**.

Show the structures of any organic compounds involved.

[2]

END OF QUESTION PAPER