1. The functional group in an organic compound, **W**, was identified by carrying out two chemical tests.
The results of the tests are shown below.

Heating with acidified sodium dichromate(VI)(aq)	**Addition of 2,4-dinitrophenylhydrazine(aq)**
orange solution turns green	yellow/orange precipitate formed

Which compound could be **W**?

A $CH_3CH_2CH_2OH$

B CH_3COCH_3

C $CH_3CH(OH)CH_3$

D CH_3CH_2CHO

Your answer D

[1]

2. Cyclohexanone can be prepared in the laboratory by reacting cyclohexanol with concentrated sulfuric acid and sodium dichromate.

Ethanedioic acid is added to the reaction mixture to react with any excess dichromate.

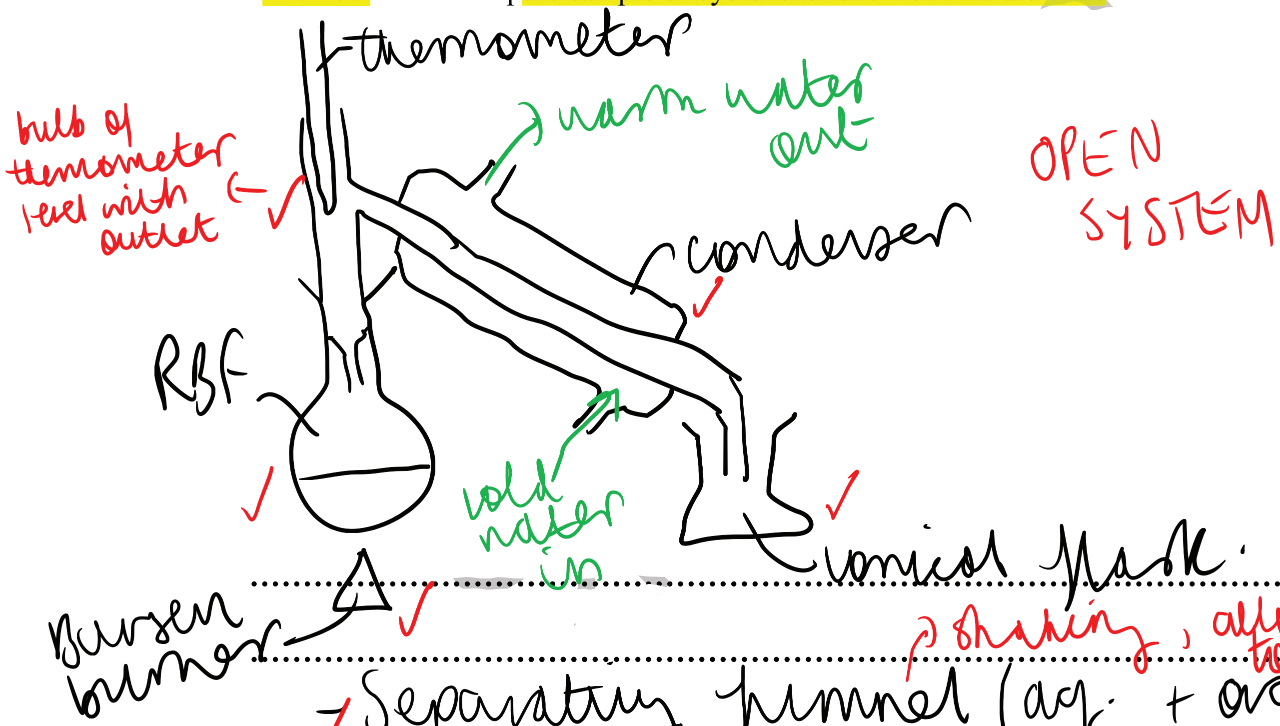
The mixture is then distilled. The impure distillate is a mixture of cyclohexanone and water.

You will need to refer to some or all of the following data to answer these questions.

	Boiling point /°C	Density /g cm^{-3}	M_r
Cyclohexanol	161	0.962	100.0
Cyclohexanone	156	0.948	98.0
water		1	

QWC

Draw a labelled diagram to show how you would safely set up apparatus for distillation and describe a method to obtain a pure sample of cyclohexanone from the distillate.



→ shaking, allow layers to settle

- Separating funnel (aq. + org layer)
  ↳ tap off the layers ✓
- Add a small amount of $MgSO_4$ to our cyclohexanone (drying agent to remove H_2O) ✓
- Re-distil cyclohexanone, collect fractions distilling at 156°C. ✓

[6]

Full marks :- Full, annotated diagrams
- At least two detailed points describing further purification.

Ethanedioic acid removes excess dichromate ions, $Cr_2O_7^{2-}$, as in the equation below.

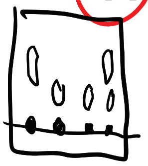
$$3(COOH)_2 + Cr_2O_7^{2-} + 8H^+ \rightarrow 6CO_2 + 2Cr^{3+} + 7H_2O$$

↳ GAS

Suggest how you could tell when the excess dichromate has completely reacted with the ethanedioic acid.

Lack of further effervescence.
(Fizzing / bubbling stops).

[1]



A student monitors the course of this reaction using thin-layer chromatography (TLC).

Outline how TLC could be used to monitor the course of the reaction.

- Take samples from the reaction mixture at regular intervals. ✓
- Spot on a TLC plate, with cyclohexanol + cyclohexanone control. ✓ (Rf values)

[2]

Plan an experiment that would allow the student to confirm the identity of the pure organic product by means of a chemical test.

→ cyclohexanone ↓ KETONE

(Brady's reagent)

- Reacting our sample 2,4-DNP → orange ppt ✓
- Recrystallise the ppt, determine the melting point. ✓ (both points needed for mark)
- Compare the mp to known value for cyclohexanone. ✓

[3]

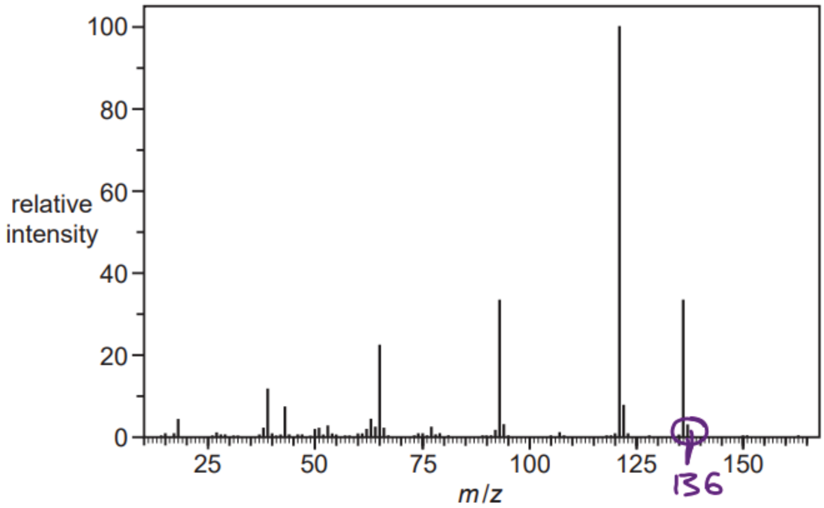
2,4-DNP = 2,4-dinitrophenylhydrazine.

3. 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: $\frac{70.58}{12} = 5.88$, $\frac{5.88}{1.46875} = 4$

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

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

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

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

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

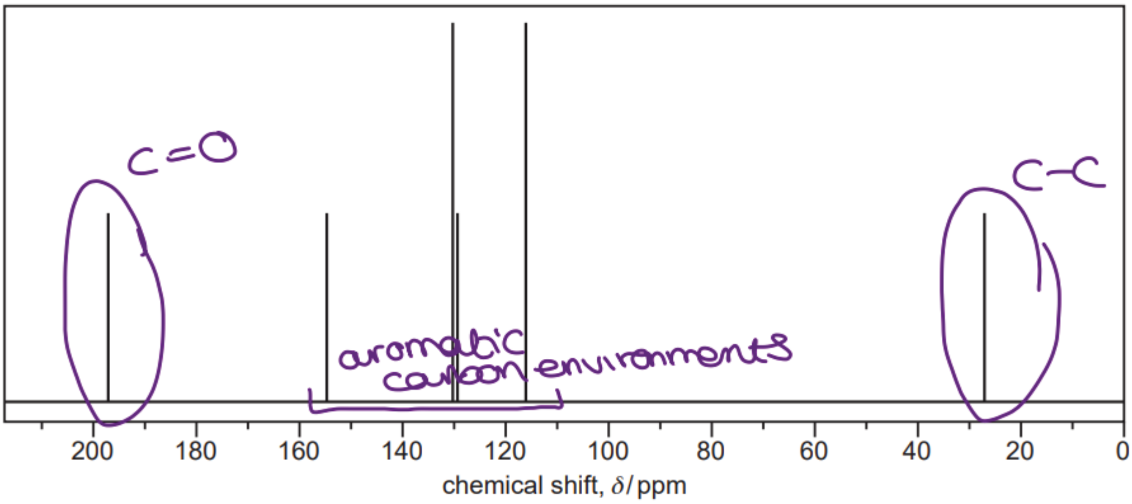
Test	Acidity	$Na_2CO_3(aq)$ test for COOH	2,4-DNP test for C=O	Tollens' reagent test for $-C\frac{=O}{-H}$
Observation	pH = 5 weak acid	No observable change (if present effervesces)	Orange precipitate ✓	No observable change (if present silver mirror)

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

Functional groups ketone, phenol

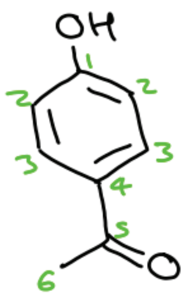
Explanation phenols are weak acids not carboxylic acid as no reaction with Na_2CO_3, but C=O group present as orange ppt in 2,4 DNP but no silver mirror in tollens reagent so not an aldehyde. **[3]**

(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.



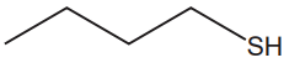
Structure of compound

[3]

4. 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

$$k_a = \frac{[H^+][A^-]}{[HA]}$$

(i) Thiols are weak acids.

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

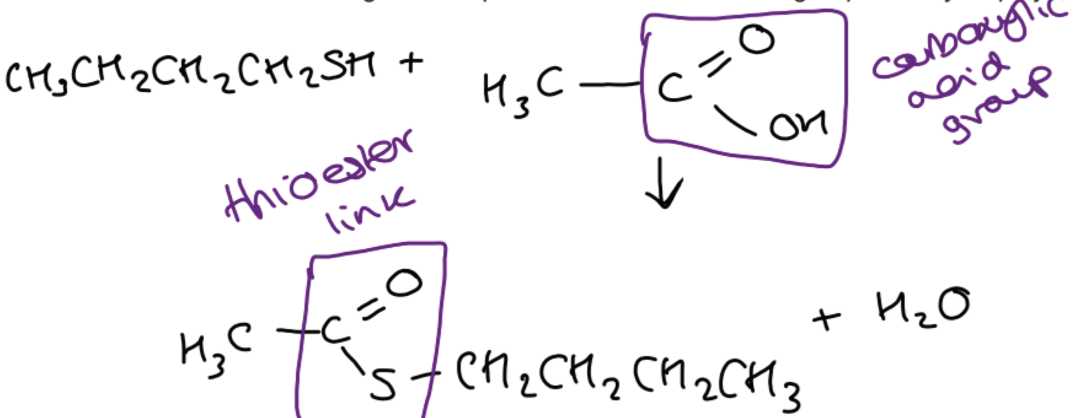
$$k_a = \frac{[H^+][C_4H_9S^-]}{[C_4H_9SH]}$$

[1]

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

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

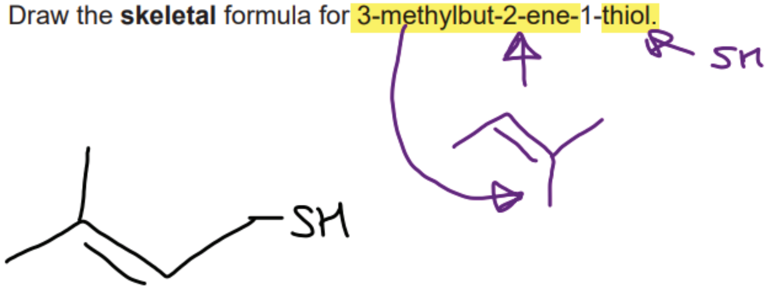
Use structures for all organic compounds with the functional groups clearly displayed.



[2]

(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.

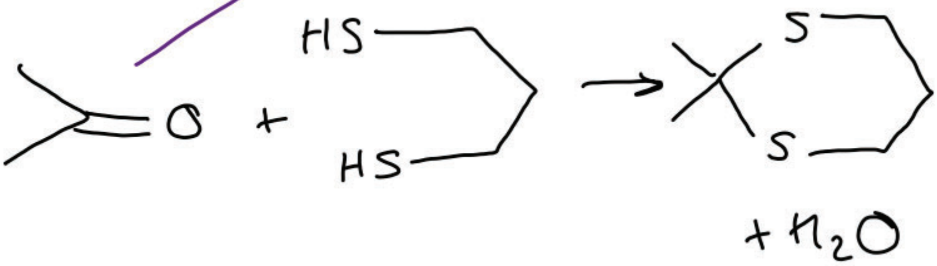


[1]

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

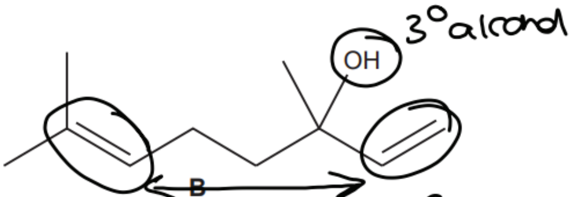
Write an equation for the reaction of propane-1,3-dithiol with propanone.

Use structures for organic compounds.

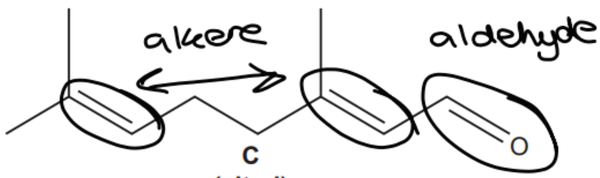


[2]

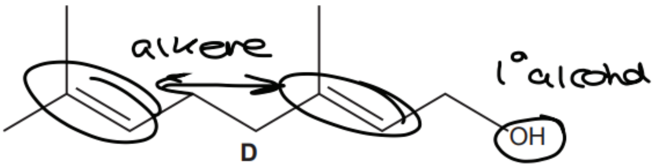
(b)* The structures for six naturally occurring organic compounds with pleasant smells, **B**–**G**, are shown below. The common names in brackets relate to their source and smell.



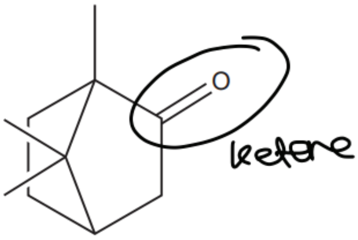
B
(linalool)



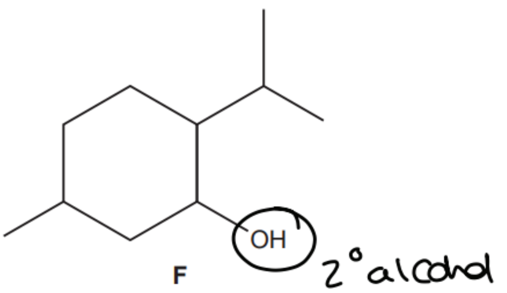
C
(citral)



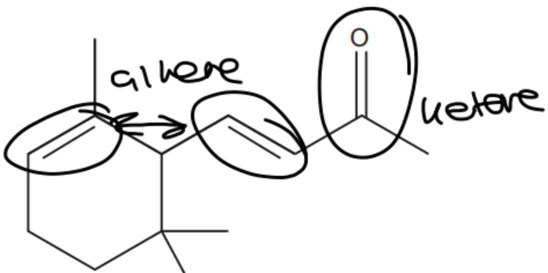
D
(geraniol)



E
(camphor)



F
(menthol)



G
(ionone)

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

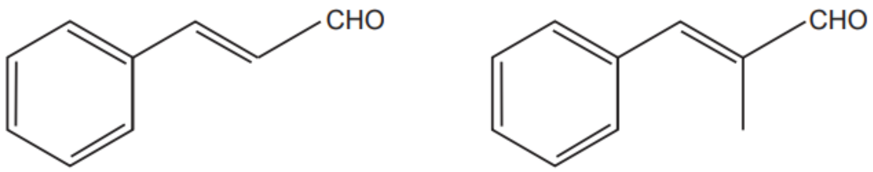
In your answer, include essential details for all test procedures and observations.

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

	B	C	D	E	F	G
decolorizes bromine water alkene	✓	✓	✓			✓
$H^+/Cr_2O_7^{2-}$ orange → green 1°, 2° alcohol, aldehyde		✓	✓		✓	
2,4 DNP orange ppt. C=O		✓		✓		✓
tollens reagent silver mirror aldehyde		✓				

[6]

5. Cinnamaldehyde and methylcinnamaldehyde are naturally occurring organic compounds.



cinnamaldehyde **methylcinnamaldehyde**

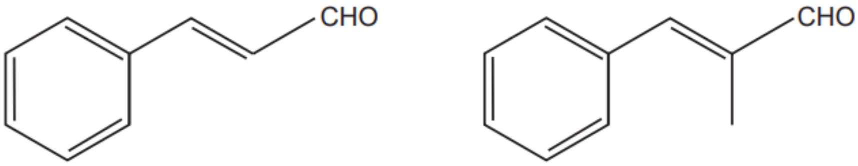
(a) Methylcinnamaldehyde is an *E* stereoisomer.

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

Highest priority groups: C_6H_5, CHO are on opposite sides of the C=C bond.

[2]

(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.

Br_2 goes colourless

[1]

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

Your answer should include the reagent and observations.

Tollen's Reagent produces a silver mirror

[1]

(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.

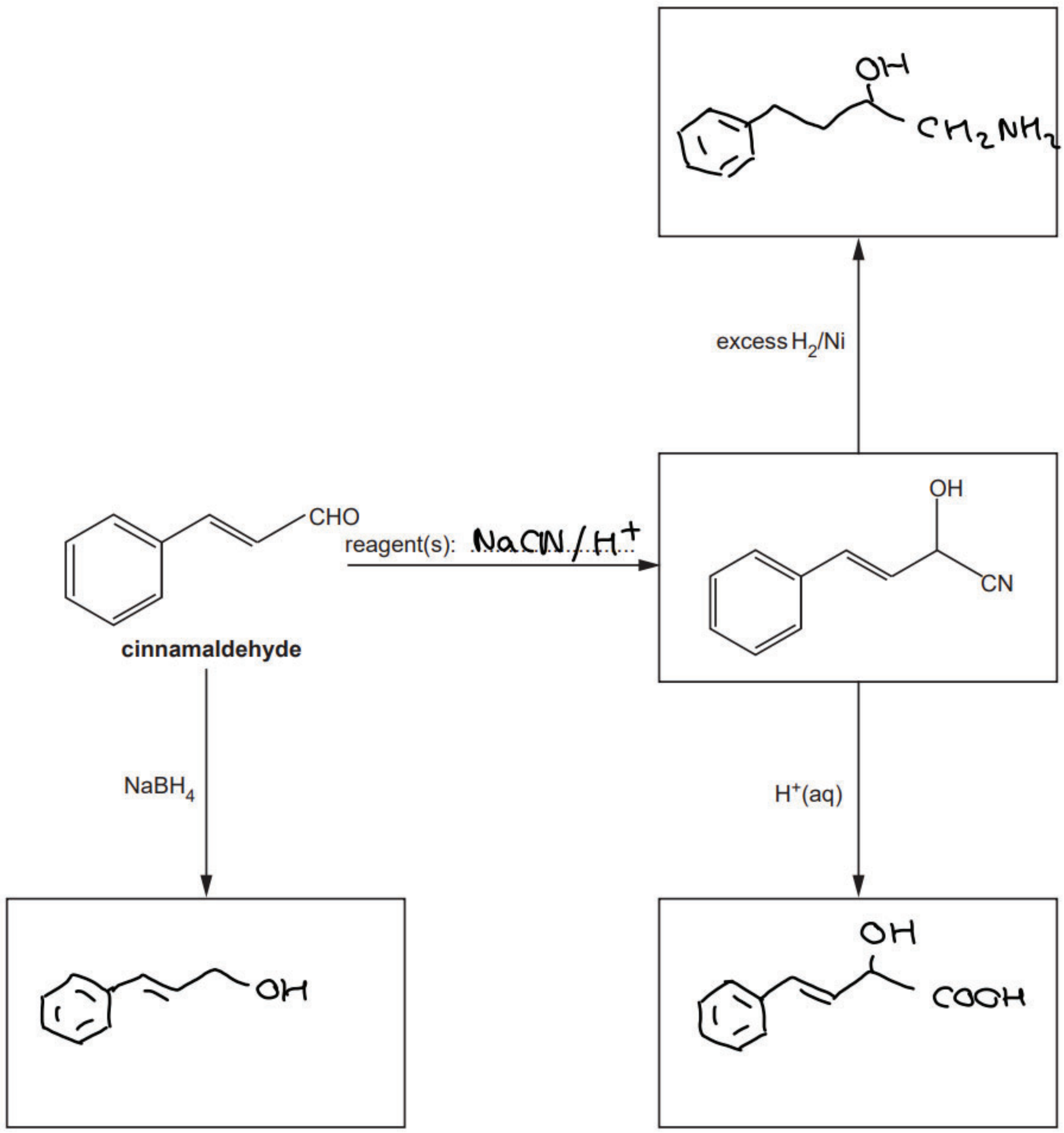
2,4-DNP produces an orange ppt.

Take a melting point and compare to known values.

[3]

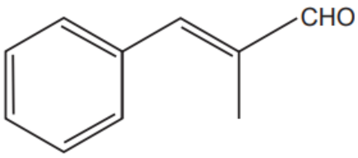
(c) The flowchart below shows some reactions starting with cinnamaldehyde.

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



[5]

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



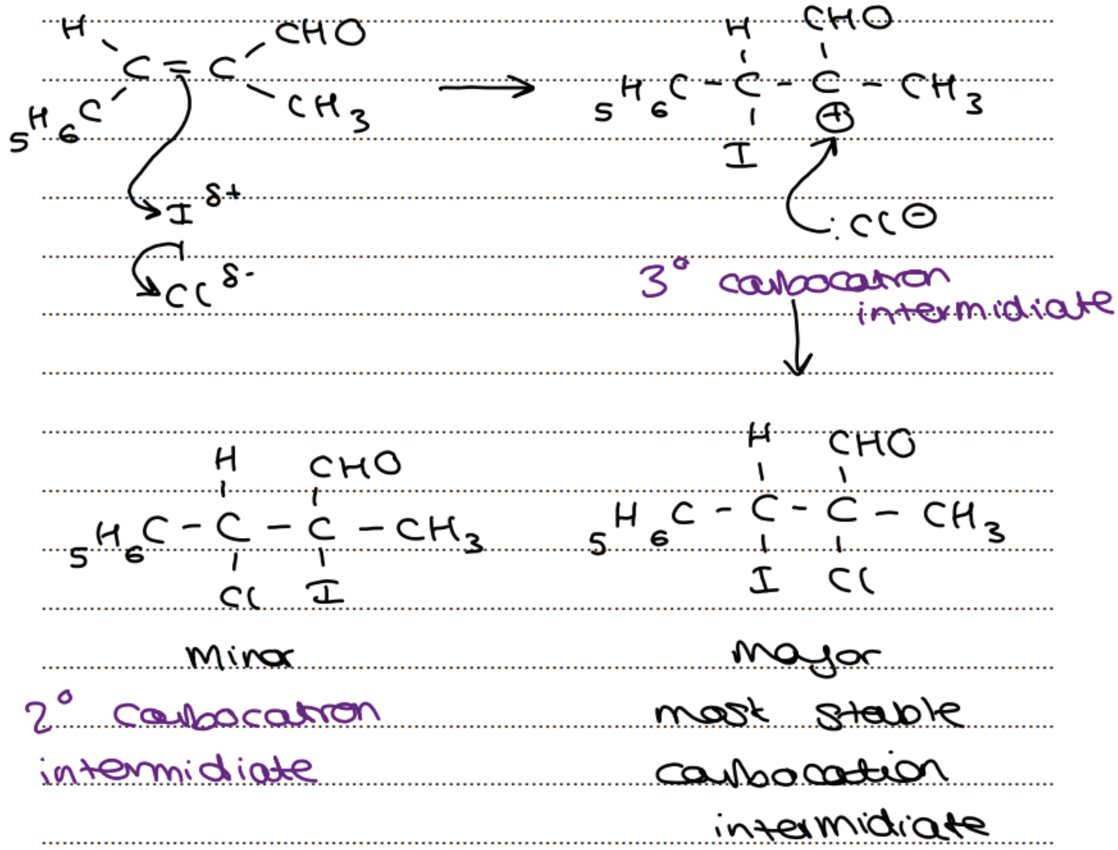
methylcinnamaldehyde

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

	Pauling electronegativity value
Cl	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]**



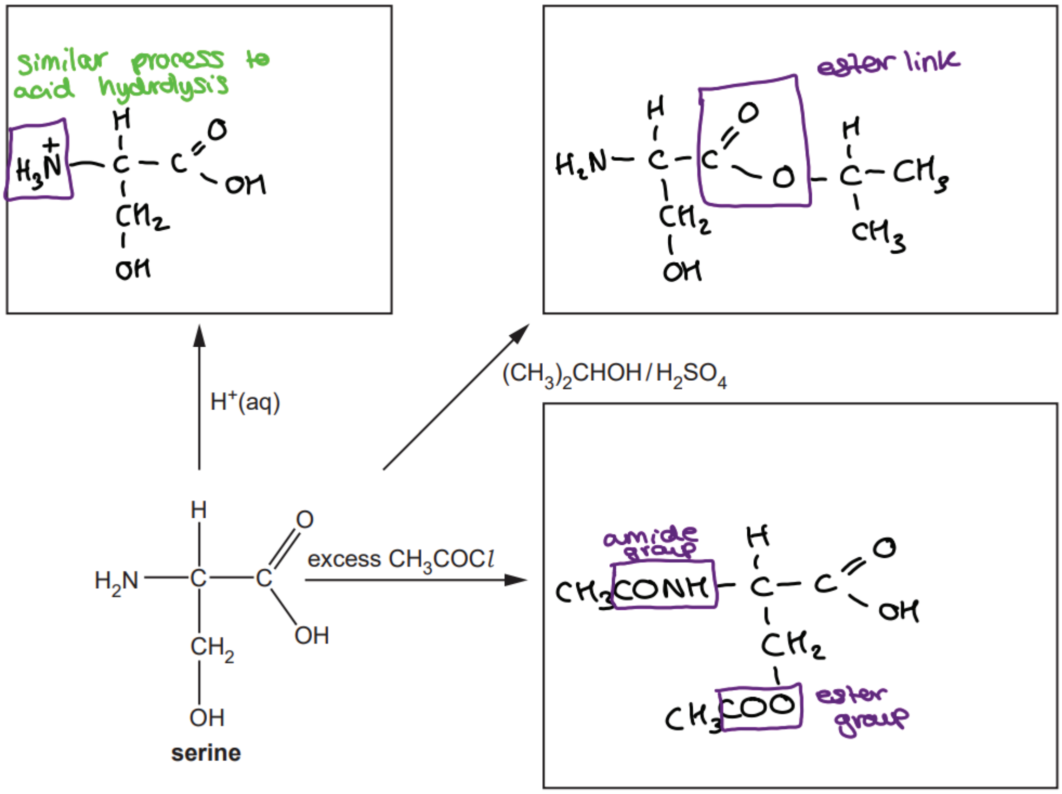
6. This question is about α-amino acids, $RCH(NH_2)COOH$.

(a) **Table 17.1** shows the R groups in four amino acids.

Amino acid	R group
alanine (ala)	CH_3–
serine (ser)	$HOCH_2$–
leucine (leu)	$(CH_3)_2CHCH_2$–
glycine (gly)	H–

Table 17.1

(i) In the boxes, draw the organic products for the reactions of serine shown below.



[4]

(ii) A student is provided with one of the four amino acids in **Table 17.1**.

A student carries out a titration with a standard solution of hydrochloric acid to identify the amino acid. The student's method is outlined below.

- The student dissolves 5.766 g of the amino acid in water and makes the solution up to 250.0 cm^3 in a volumetric flask.
- The student titrates this solution with 25.0 cm^3 of 0.150 $mol\,dm^{-3}$ hydrochloric acid.
- 21.30 cm^3 of the amino acid solution were required for complete neutralisation of the hydrochloric acid.

Determine which amino acid the student used.

$n = V \times C$

$0.15 \times 25 \times 10^{-3} = 3.75 \times 10^{-3}$ mol of HCl

$3.75 \times 10^{-3} \times \frac{250}{21.3} = 0.044$ mol of amino acid

↖ proportion of amino acid volume

$\frac{5.766}{0.044} = 131$ = RFM of amino acid

mass = mol × RFM

$RCH(NH_2)COOH$

$12 + 1 + 14 + 2 + 12 + (16 \times 2) + 1 = 74$

$131 - 74 = 57$

↖ RFM of R group

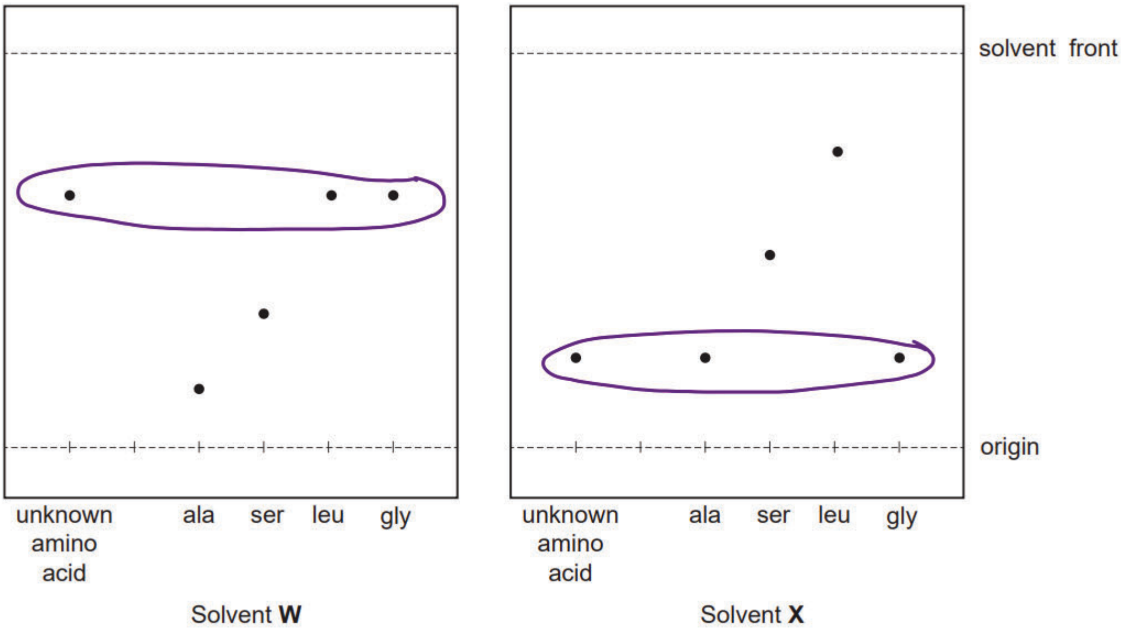
$2(12+3) + 12 + 1 + 12 + 2 = 57$ ⇒ R group of leucine

[4]

(b) The student is provided with another amino acid.

The student attempts to identify the unknown amino acid using chromatography.

The student obtains two TLC chromatograms of the unknown amino acid and the four amino acids in **Table 17.1**, using two different solvents, **W** and **X**.



(i) What is the R_f value of serine (ser) in solvent **W**?

distance travelled by sample / distance travelled by solvent front = 0.9 / 2.6 = 0.35

R_f = 0.35 **[1]**

(ii) Analyse the chromatograms to identify the unknown amino acid.

Explain your reasoning.

Name of unknown amino acid glycine

Explanation matches leu and gly in solvent W and ala and gly in solvent X

[2]

7. Which statement(s) is/are correct for gas chromatography?

   1 The components in a mixture can be identified from their retention time. ✓
   similar to Rf values in TLC

   2 The relative peak areas give the proportions of components in a mixture. ✓
   not height of peak instead area

   3 Calibration curves are used to confirm the concentrations of components in a mixture. ✓
   can plot peak area against concentration

A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer A

[1]