1. Molecules with more than one functional group are useful chemical 'building blocks'.

Compound **D**, $CH_3CH(OH)CH_2NH_2$, is an intermediate in the synthesis of a variety of drugs.

Compound **D** can be synthesised from ethanal, CH_3CHO.

Devise a **two-step** synthesis of compound **D** from ethanal.

- Give details of appropriate reagents and relevant conditions.
- Write an equation for each step, showing clearly all organic compounds.

HCN, or H_2SO_4 / KCN → HCN made in situ

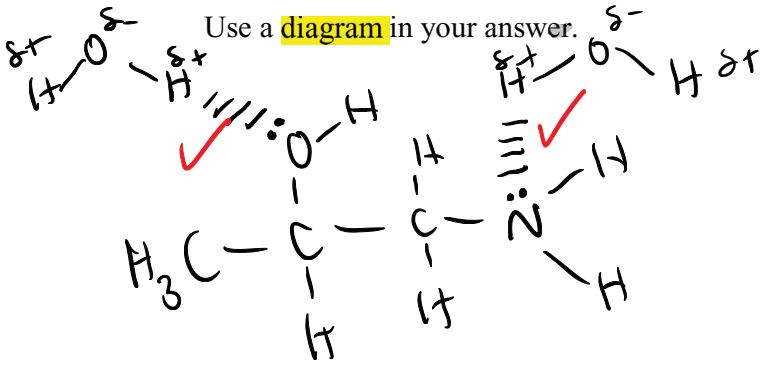
$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$

Reduction:

$CH_3CH(OH)CN + H_2 \xrightarrow{Ni} CH_3CH(OH)CH_2NH_2$ **[4]**

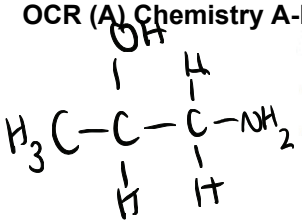
Explain why compound **D** is very soluble in water.

Use a diagram in your answer.



$-NH_2$ and $-OH$ can form H-bonds with water.

we have 2 groups which can form H-bonds with the water. **[3]**



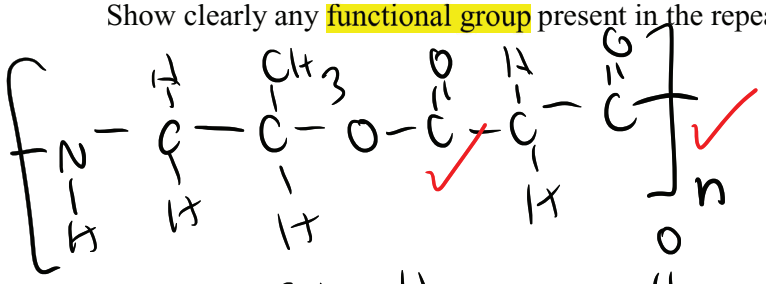
$CH_3CH(OH)CH_2NH_2$

Compound **D** reacts with propanedioic acid, $HOOCCH_2COOH$, to form a condensation polymer.

ester (OH + COOH)
amide (NH_2 + COOH)

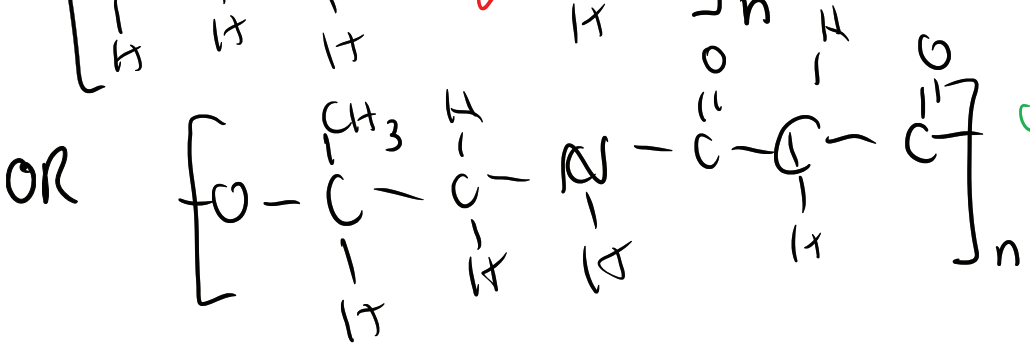
Draw a possible repeat unit of this condensation polymer.

Show clearly any functional group present in the repeat unit.



centred around the ester bond

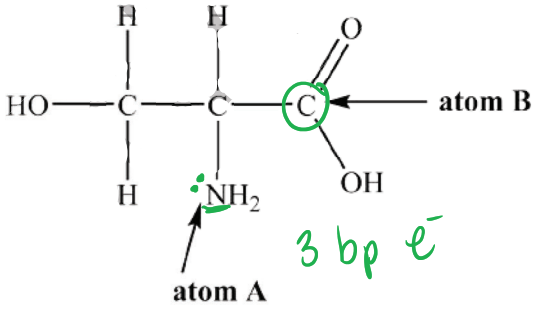
OR



OR centred around the amide bond

[2]

Serine, shown below, is an amino acid.



3 bp e⁻

Use electron repulsion theory to predict the shape of the bonds around atoms **A** and **B**.

Give relevant bond angles around atoms **A** and **B**.

Give reasons for your answers.

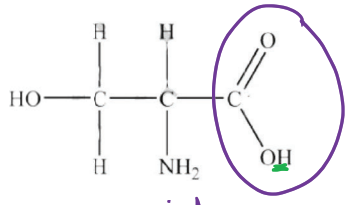
A: 3 bonding pairs of e⁻, 1 lone pair of e⁻ ✓
pyramidal, 107° ✓
B: 3 bonding regions of e⁻, 0 lone pairs of e⁻ ✓
trigonal planar, 120° ✓

[4]

A student adds an excess of aqueous sodium hydroxide to a sample of solid serine.
The student then purifies the resulting reaction mixture to obtain a pure sample of an ionic organic product.

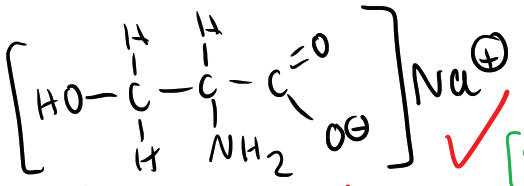
- Draw the structure of the ionic organic compound obtained.
- Outline the steps that the student could carry out to obtain a pure sample of the organic product from the reaction mixture.

NaOH



amino acid

ACID + BASE → SALT + WATER



(+ H_2O)

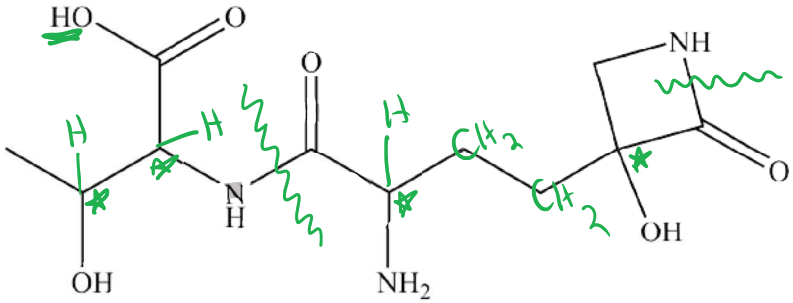
[salt solution]

① Filter the solution ✓

② Recrystallise ✓

[3]

Tabtoxin is a poisonous substance produced by bacteria found in lilac trees.



tabtoxin

C with 4 different groups

Identify the chiral centres present in a molecule of tabtoxin.

On the structure above, mark each chiral centre with an asterisk, *.

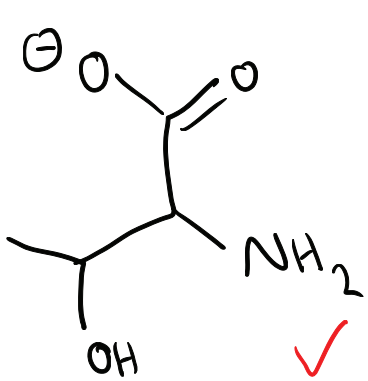
[1]

2 amide bonds

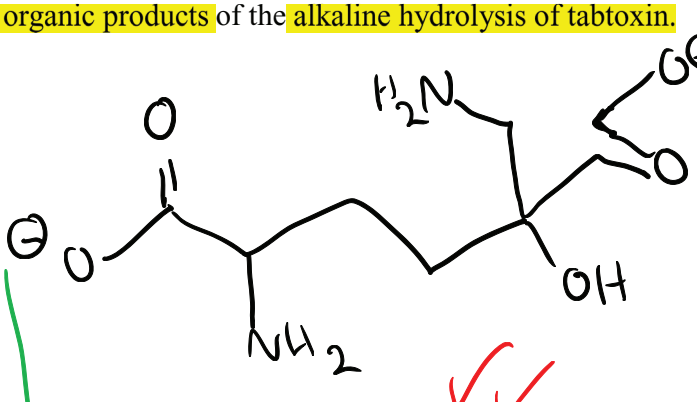
Tabtoxin can be broken down by alkaline hydrolysis.

will hydrolyse ester/amide bonds

Draw the structures of **all** the organic products of the alkaline hydrolysis of tabtoxin.



✓



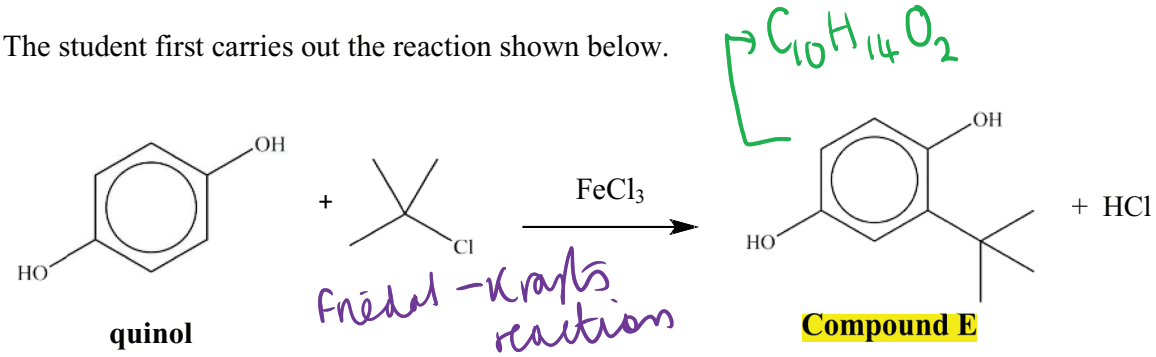
✓ ✓

[4]

⊖ as the proton from the acid reacts with the alkali

2. A student investigates reactions of aromatic compounds.

The student first carries out the reaction shown below.



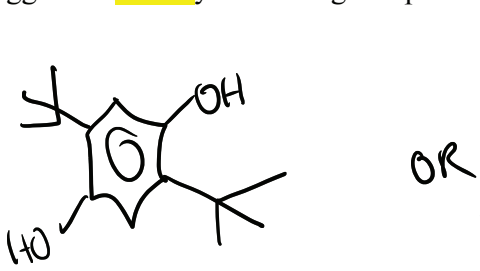
quinol **Compound E**

Friedel-Crafts reaction

$C_{10}H_{14}O_2$

The student obtains a very low yield of compound **E**.
The student obtains a much higher yield of a different organic product with molecular formula $C_{14}H_{22}O_2$.

Suggest an identity for the organic product $C_{14}H_{22}O_2$ and draw its structure below.



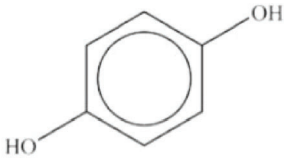
Multiple substitutions → worked out from the difference in molecular formulae.

[1]

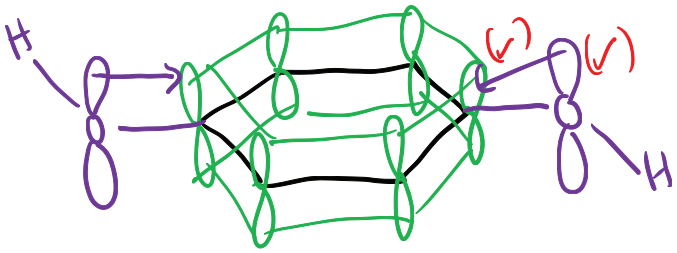
The student is told by a friend that the $FeCl_3$ catalyst is not needed because quinol is more reactive than benzene.

Explain why the student's friend is correct.

You may draw a diagram to support your answer.

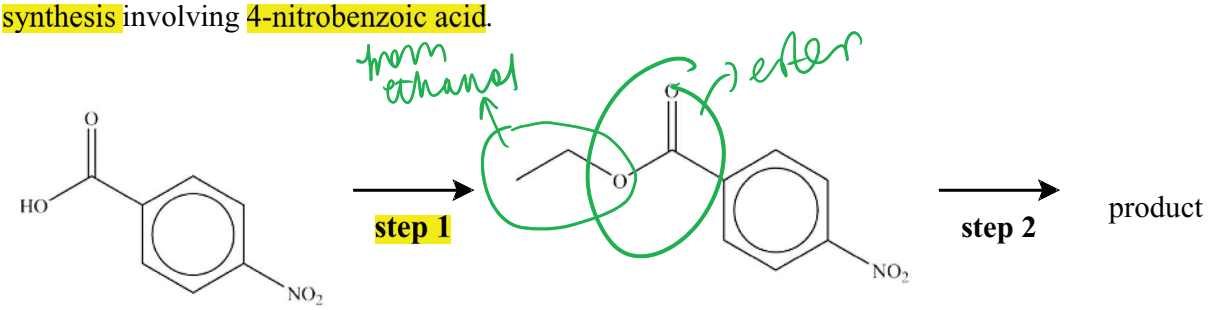


quinol



lone pairs of e⁻ on the oxygen (OH in quinol) → partially delocalise into the ring. Adding e⁻ density to the ring ∴ making it more reactive so no catalyst is needed ∴ quinol more susceptible to attack from an electrophile (⊕). **[3]**

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



Compound F

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

- Esterification (carboxylic acid + alcohol.

conc H_2SO_4 , CH_3CH_2OH .

catalyst + reducing agent.

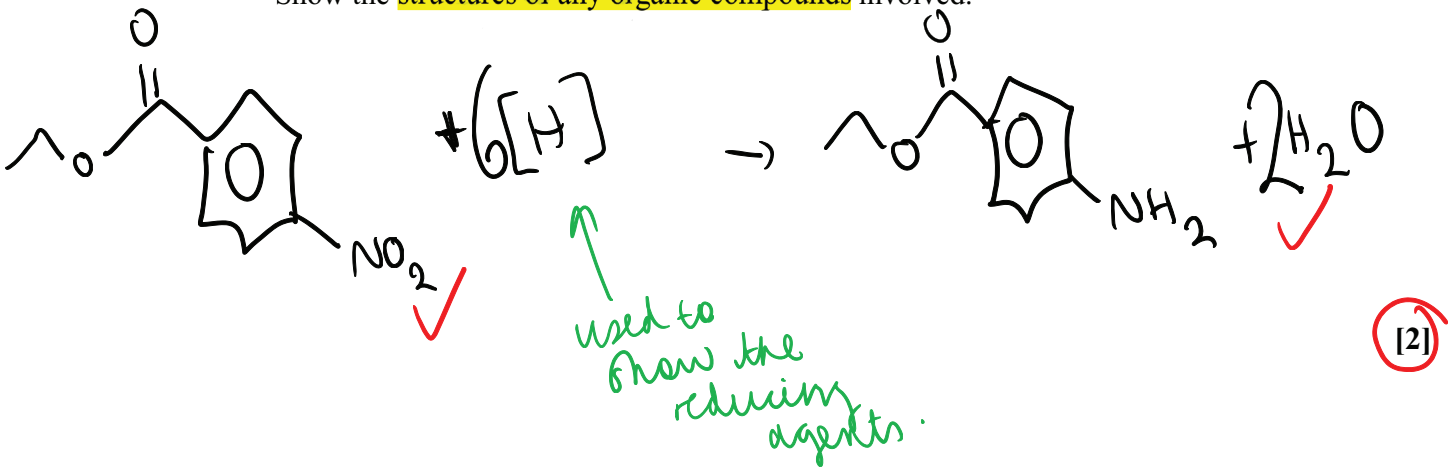
NH_2

[1]

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.

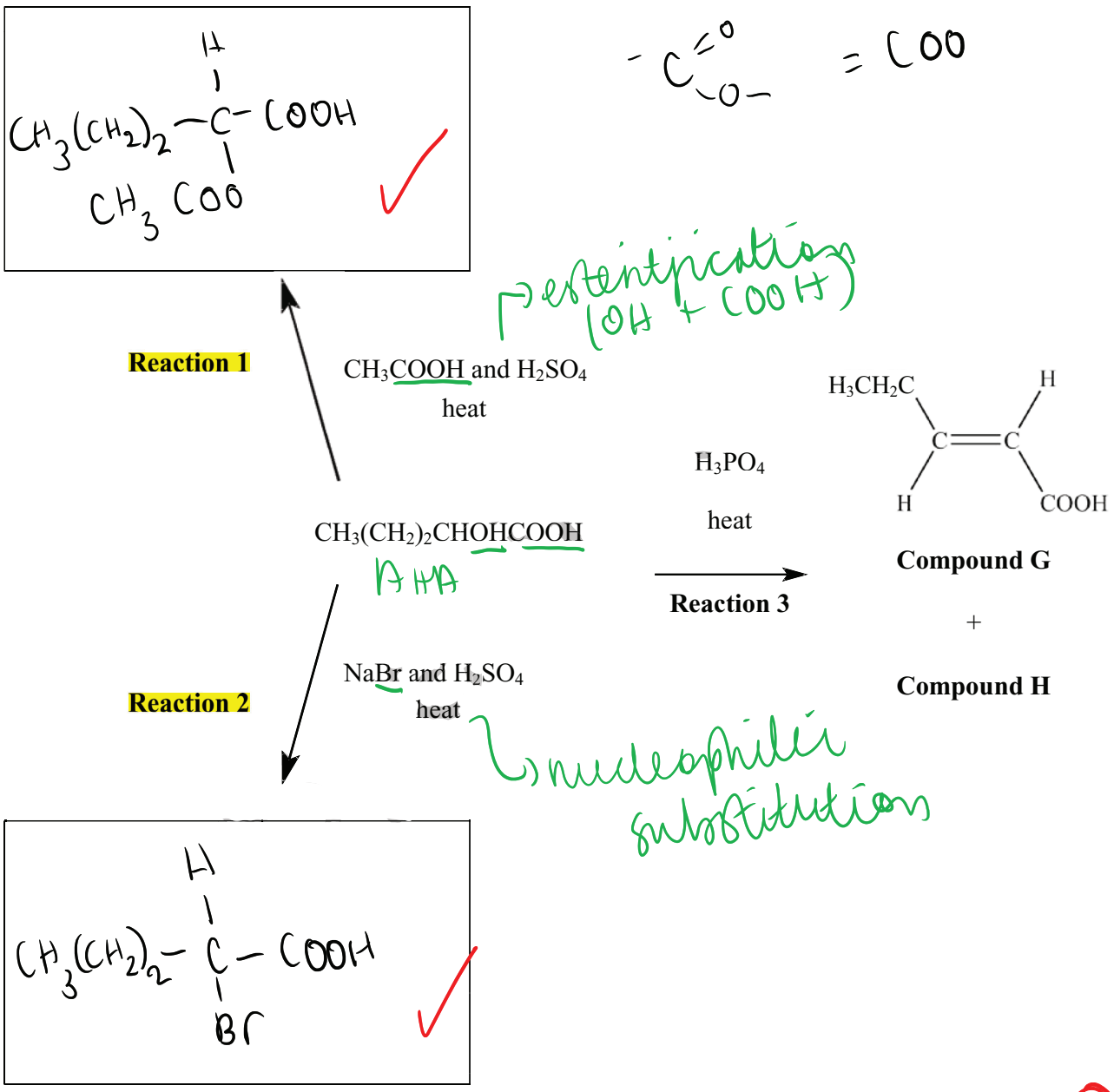


[2]

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

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

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



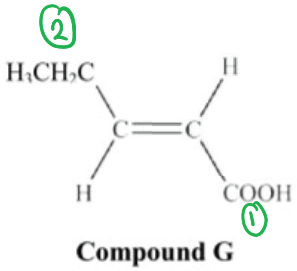
[2]

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

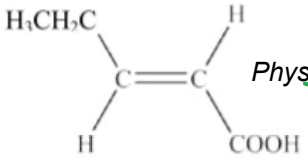
(E)- pent-2-enoic acid

.....

[1]



E-isomer

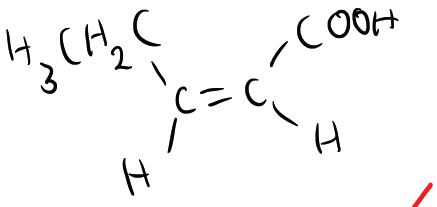


Compound G

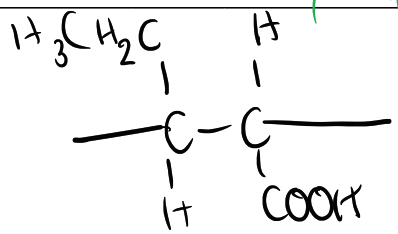
Compound **H** is a stereoisomer of compound **G**.

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

open up the double bond.



Compound H



addition polymer

Z-isomer

[2]

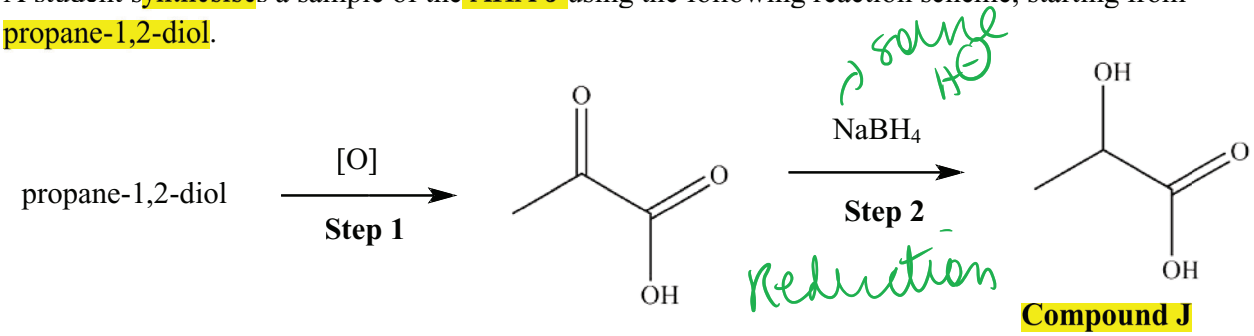
The addition polymer in **(iii)** is used widely in industry. Increasingly, waste polymers are being processed as a more sustainable option than disposal.

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

- combustion for energy production
- use as an organic feedstock for the production of plastics / org. chemicals.

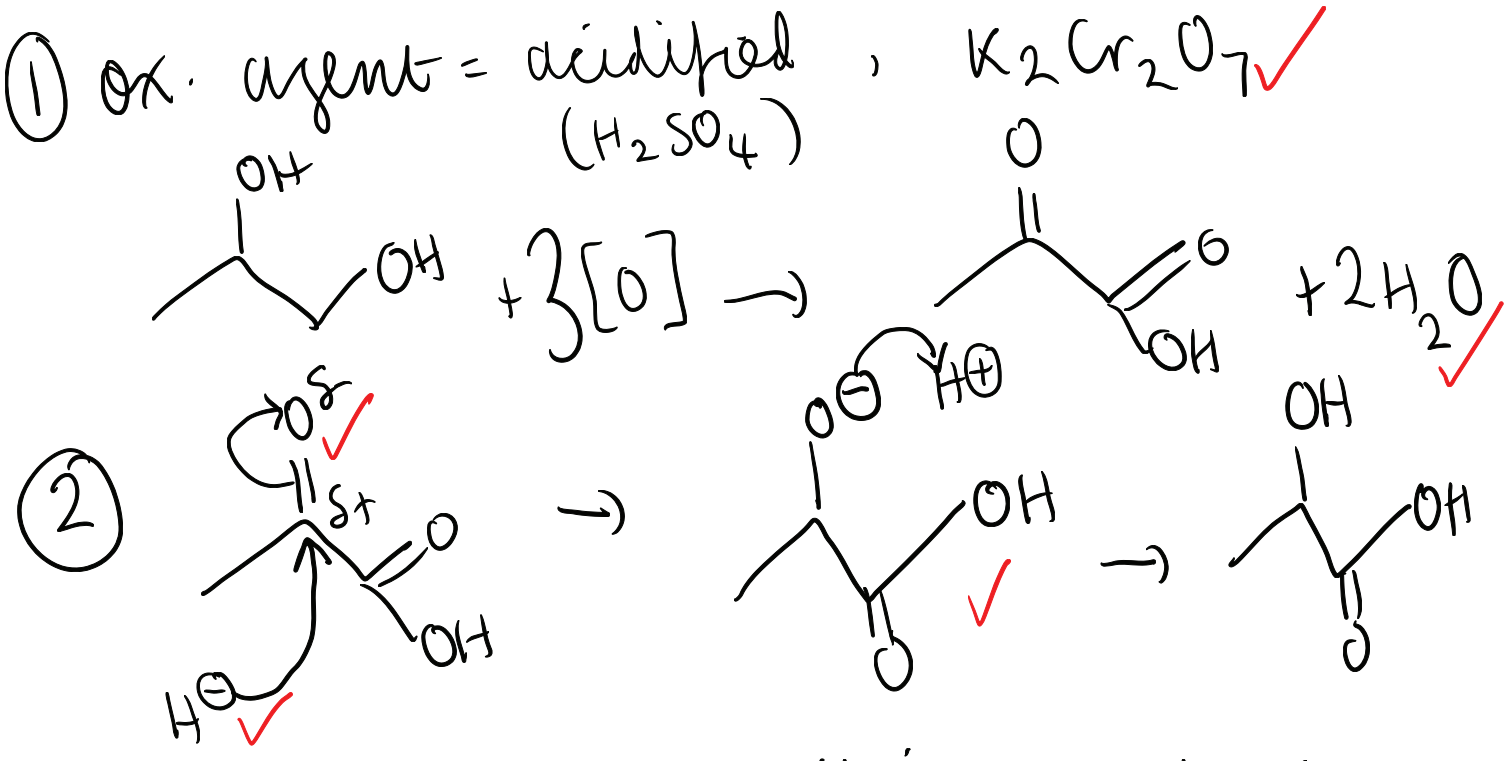
[2]

A student synthesises a sample of the AHA **J** using the following reaction scheme, starting from propane-1,2-diol.



In the space below:

- state a suitable oxidising agent for **Step 1**
- write an equation for **Step 1**
- outline the mechanism for **Step 2**, showing curly arrows and relevant dipoles.



Nucleophilic addition mechanism

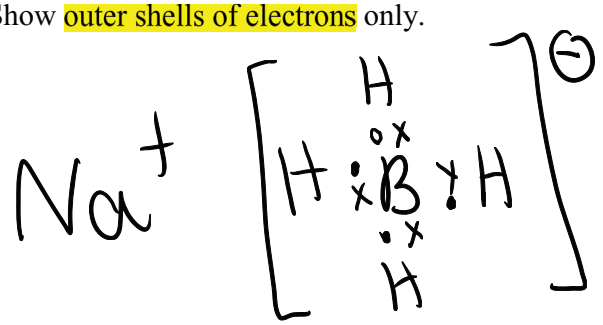
(HO⊖ = nucleophile)

[5]

The reagent used in **Step 2** of the synthesis in **(i)** was $NaBH_4$. $NaBH_4$ contains the ions Na^+ and $[BH_4]^-$.

Draw a '*dot-and-cross*' diagram of $NaBH_4$ and give the **full** electron configuration of Na^+.

Show outer shells of electrons only.



o = e⁻ from Na
x = e⁻ from H
• = e⁻ from B
3 different symbols needed for the mark.

full electronic configuration of Na^+: $1s^2 2s^2 2p^6$ ✓

[2]

Na 11e⁻ : $1s^2 2s^2 2p^6 3s^1$

Compound J

Compound **K** is an AHA that is often used in 'chemical face peels'.

A student wishes to identify compound **K** from the list of compounds below.

glycolic acid	$HOCH_2COOH$
malic acid	$HOOCCH_2CHOHCOOH$
mandelic acid	$C_6H_5CHOHCOOH$
pantoic acid	$HOCH_2C(CH_3)_2CHOHCOOH$

76 g mol⁻¹

Molar mass (K) needed.

The student isolates compound **K** and analyses a sample of the compound by titration.

The student dissolves 1.89 g of compound **K** in water and makes the solution up to 250.0 cm^3 in a volumetric flask. The student titrates 25.0 cm^3 of this solution with 0.150 mol dm^{-3} NaOH(aq).

18.80 cm^3 of NaOH(aq) were required for complete neutralisation.

Use the results of the student's analysis to identify compound **K** from the list above.

Show **all** of your working.

$n(NaOH) = v \times c = \frac{18.80}{1000} \times 0.150 = 0.00282$ mol.

$H^+ : NaOH \rightarrow 1:1 \rightarrow \therefore n(H^+)$ in 25.0 cm^3 = 0.00282 mol.

25 cm^3 ×10 → 250 cm^3

0.00282 × 10 = 0.0282 mol.

$M_r(K) = \frac{m}{n} = \frac{1.89}{0.0282} = 67.0$ g mol⁻¹

×2

134 g mol⁻¹

∴ must be diprotic

$H^+ : NaOH \rightarrow n(H^+) \div 2$

1 : 2

K = Malic acid [5]

Because none of the molar masses of the monoprotic acids are 67.

∴ only one diprotic acid = malic acid.

4. 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.

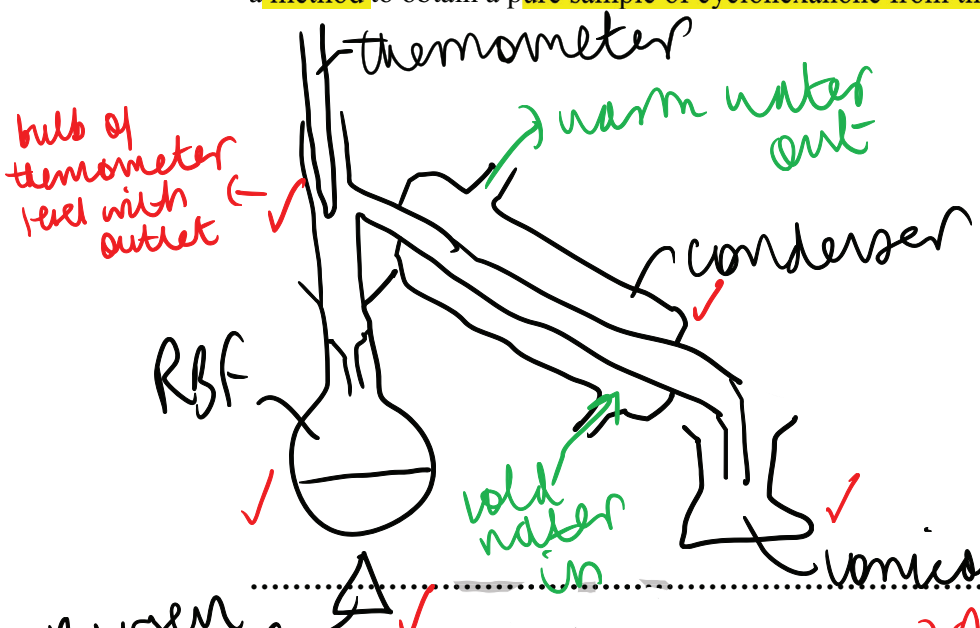
You will need to refer to some or all of the following data to answer these questions.

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

QWC

water

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.



bulb of thermometer level with outlet ✓

OPEN SYSTEM

conical flask.

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 fraction distilling at 156°C. ✓

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

[6]

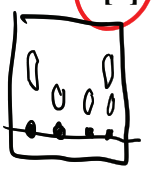
Ethanedioic acid removes excess dichromate ions, $Cr_2O_7^{2-}$, as in the equation below.

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

↳ 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)

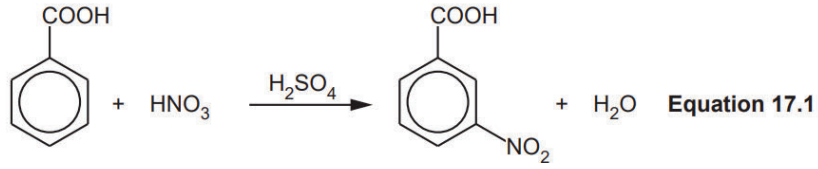
- Reacting our sample 2,4-DNP → orange ppt ✓
- Recrystallise the ppt, determine the melting point ✓ (both points needed for mark)
- Compare the mp to known values for cyclohexanone ✓ [3]

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

5. 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.



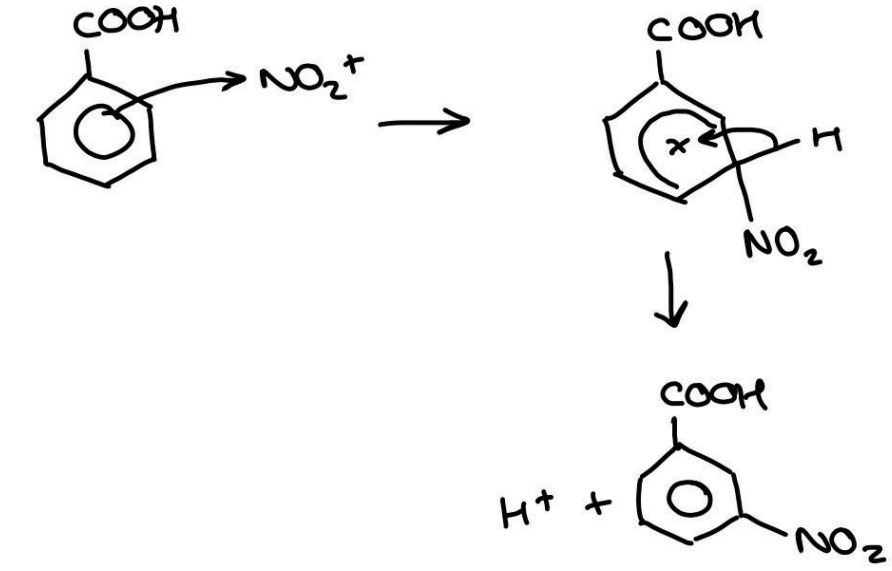
Equation 17.1

benzoic acid **3-nitrobenzoic acid**

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

Show how H_2SO_4 behaves as a catalyst.

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



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

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.

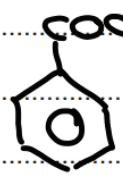
purification:

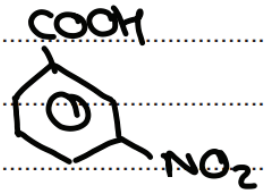
1. recrystalisation

2. dissolve solid in minimal amount of hot solvent

3. cool solution and filter solid

4. wash with cold solvent and dry.

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

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

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

[6]

to check purity conduct a melting point test and compare to known values.

(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.

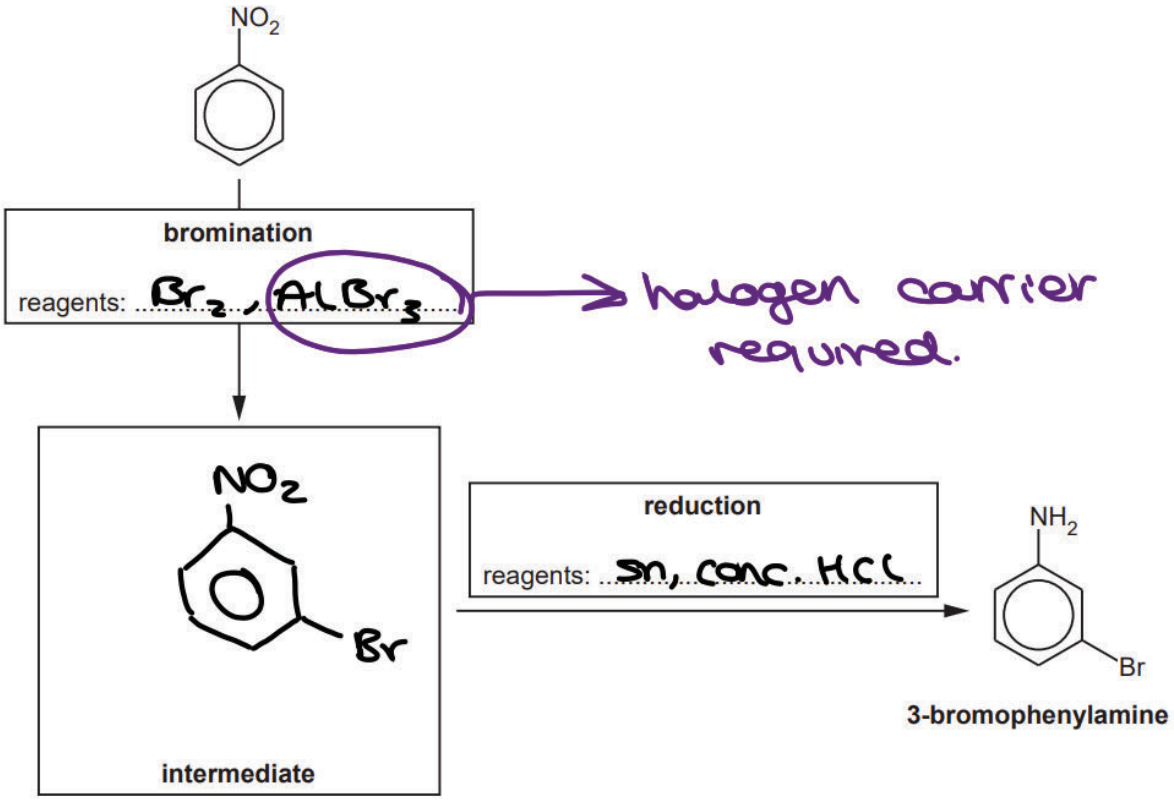
phenol is the easiest to nitrate and benzoic acid is the hardest / least reactive. **[1]**

(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]

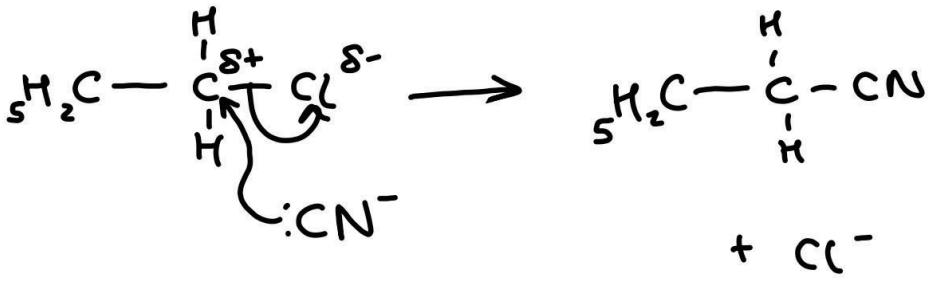
6. This question is about organic compounds containing nitrogen.

(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.

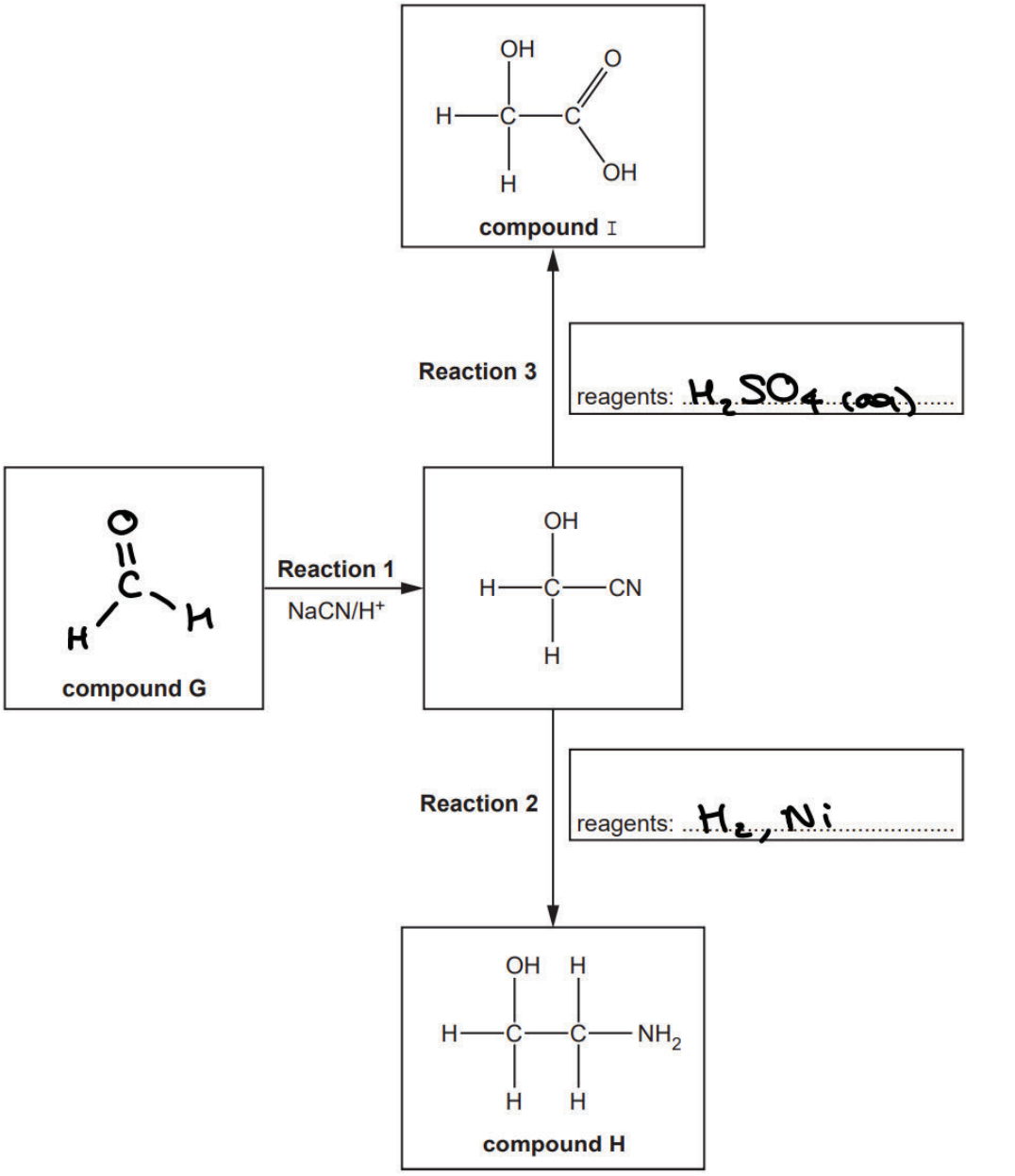
Include curly arrows, relevant dipoles and the structure of the organic product.



[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**.



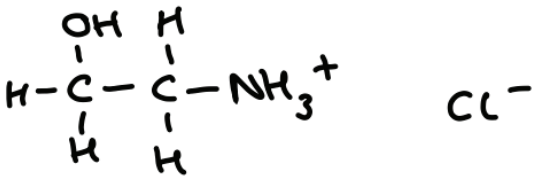
[3]

(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^+)

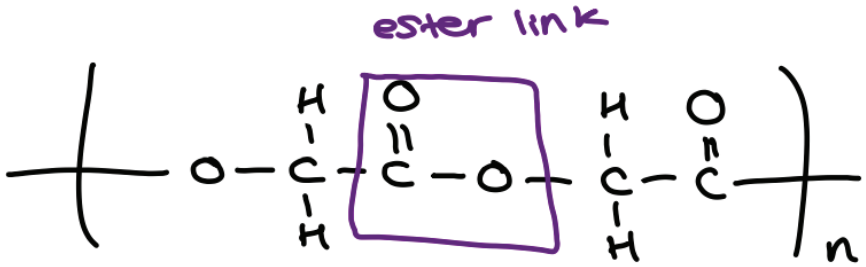
Structure



[2]

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

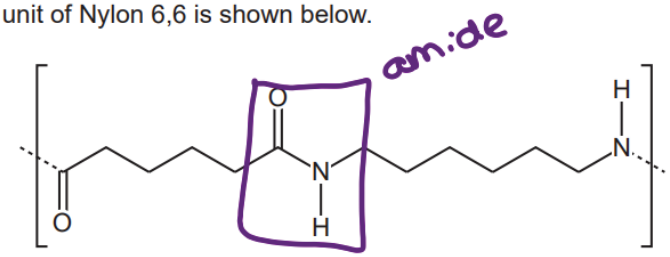
Draw **two** repeat units of polymer **J** and suggest a reason why it is biodegradable.



ester group can undergo hydrolysis

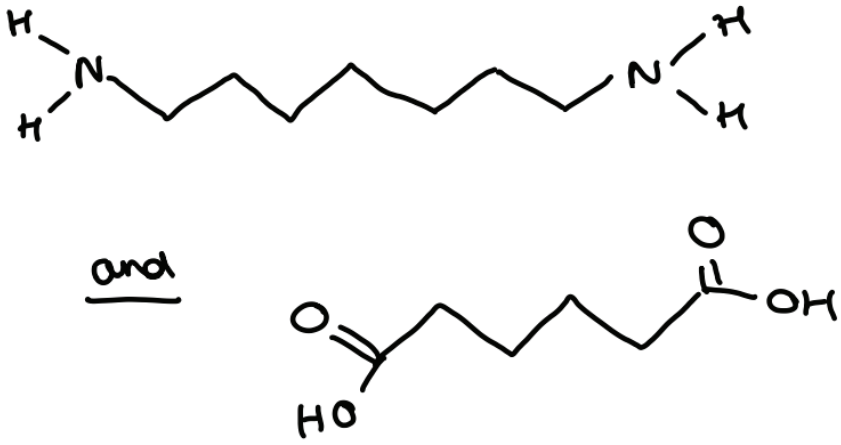
[3]

(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.

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

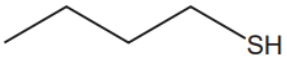
RFM = relative formula mass of repeat unit: $(12\times12)+(6\times2)+(14\times2)+22 = 226$

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

7. 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.

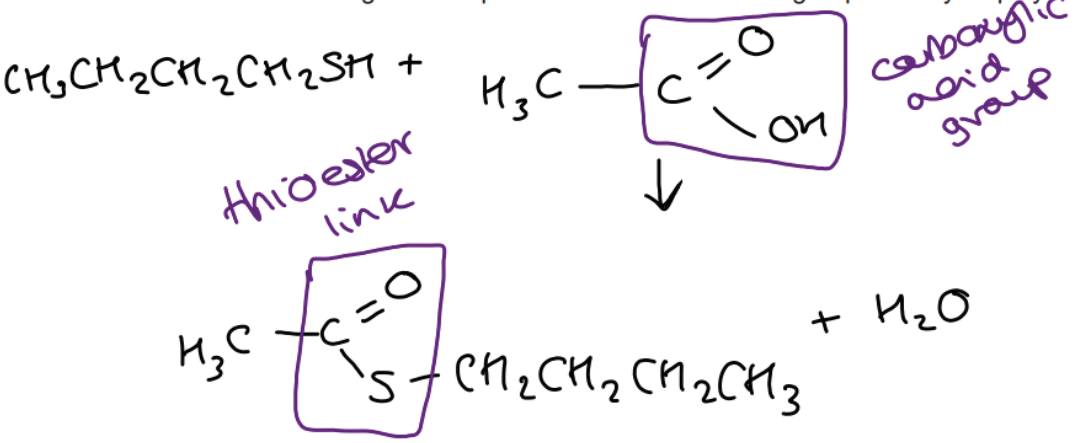
$K_a = \frac{[H^+][C_4H_9S^-]}{[C_4H_9SH]}$

[1]

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

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

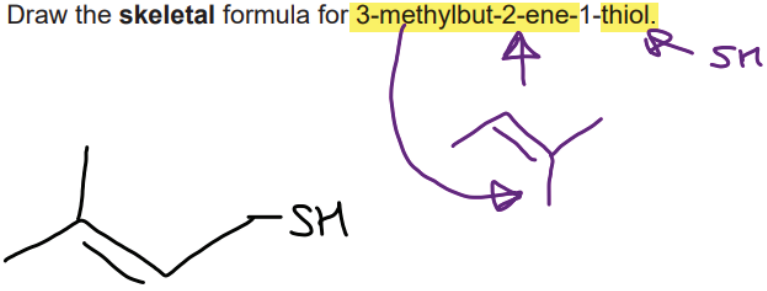
Use structures for all organic compounds with the functional groups clearly displayed.



[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.

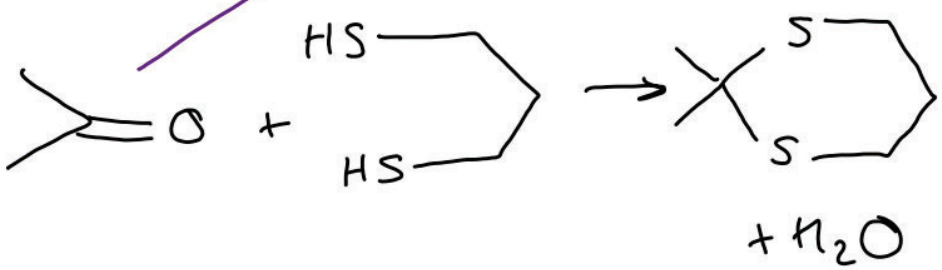


[1]

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

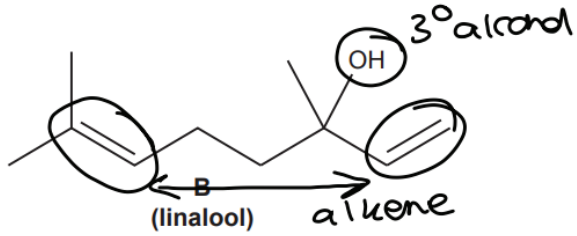
Write an equation for the reaction of propane-1,3-dithiol with propanone.

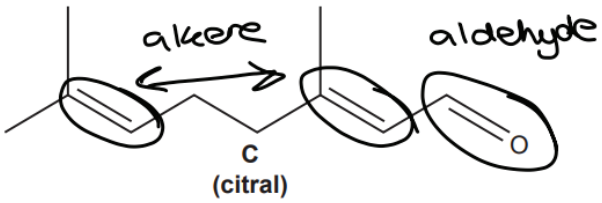
Use structures for organic compounds.

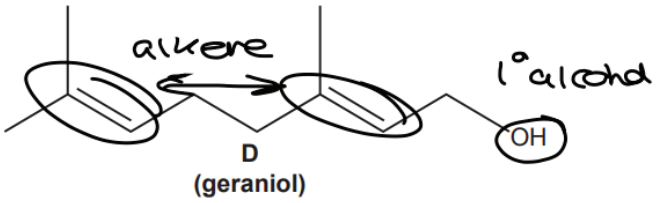


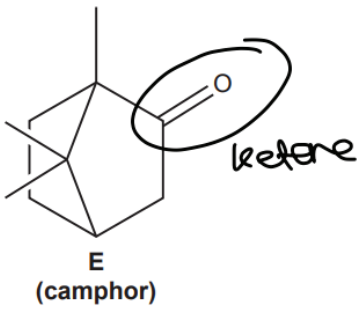
[2]

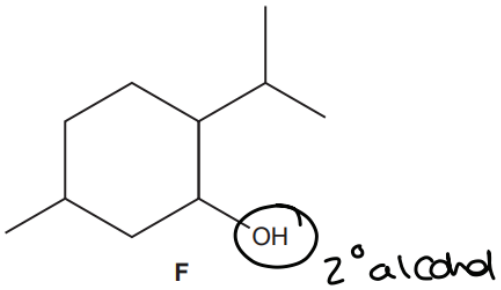
(b)* The structures for six naturally occurring organic compounds with pleasant smells, **B**–**G**, are shown below. The common names in brackets relate to their source and smell.

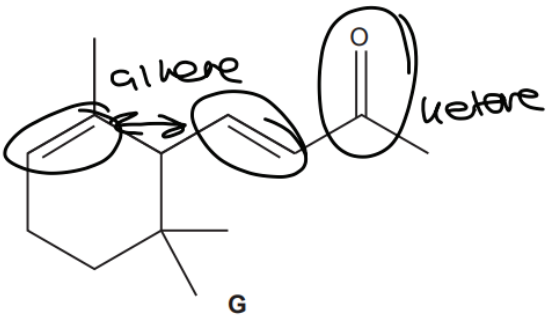












Explain how chemical tests would allow each compound to be distinguished from the other compounds.

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]

8. Which compound does **not** react with nucleophiles?

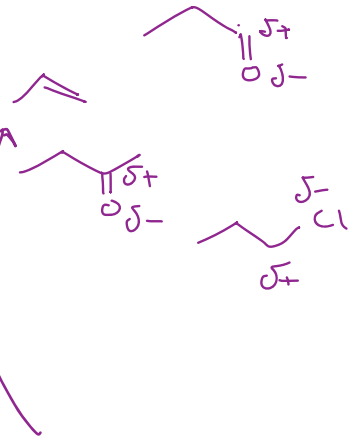
A CH_3CH_2CHO

B CH_3CHCH_2

C $CH_3CH_2COCH_3$

D $CH_3CH_2CH_2Cl$

Your answer B



e⁻ pair donor

e.g. $:OH^-$, $:NH_3$

• all of A, C, and D have δ+ C which is a common site of attack for nucleophiles **[1]**

C=C in propene (B) is highly e⁻ dense and will not elicit attack of e⁻ dense nucleophile.

9. A solid organic compound can be purified by recrystallisation.

Which statement(s) about recrystallisation is/are true?

as T ↑ kinetic E of solvent ↑ ∴ more easily dissolving solid ∴ solubility ↑ as T ↑ True

1 The organic compound is more soluble in hot solvent.

2 The hot solution is cooled before the purified organic compound is collected. True

↳ solution must be cooled to collect solid pure compound.

3 The melting point of the purified organic compound is lower than the impure compound. False.

↳ MP of impure compound is lower than pure compound as impurities interrupt and weaken crystal lattice.

A 1, 2 and 3

B Only 1 and 2

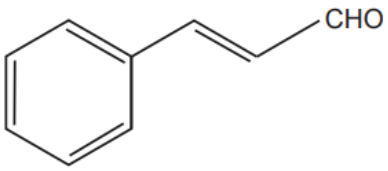
C Only 2 and 3

D Only 1

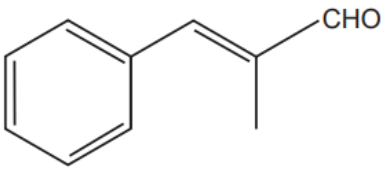
Your answer B

[1]

10. Cinnamaldehyde and methylcinnamaldehyde are naturally occurring organic compounds.



cinnamaldehyde



methylcinnamaldehyde

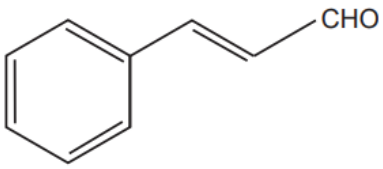
(a) Methylcinnamaldehyde is an *E* stereoisomer.

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

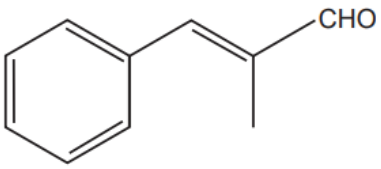
Highest priority groups: C_6H_5, CHO are on opposite sides of the C=C bond.

[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.

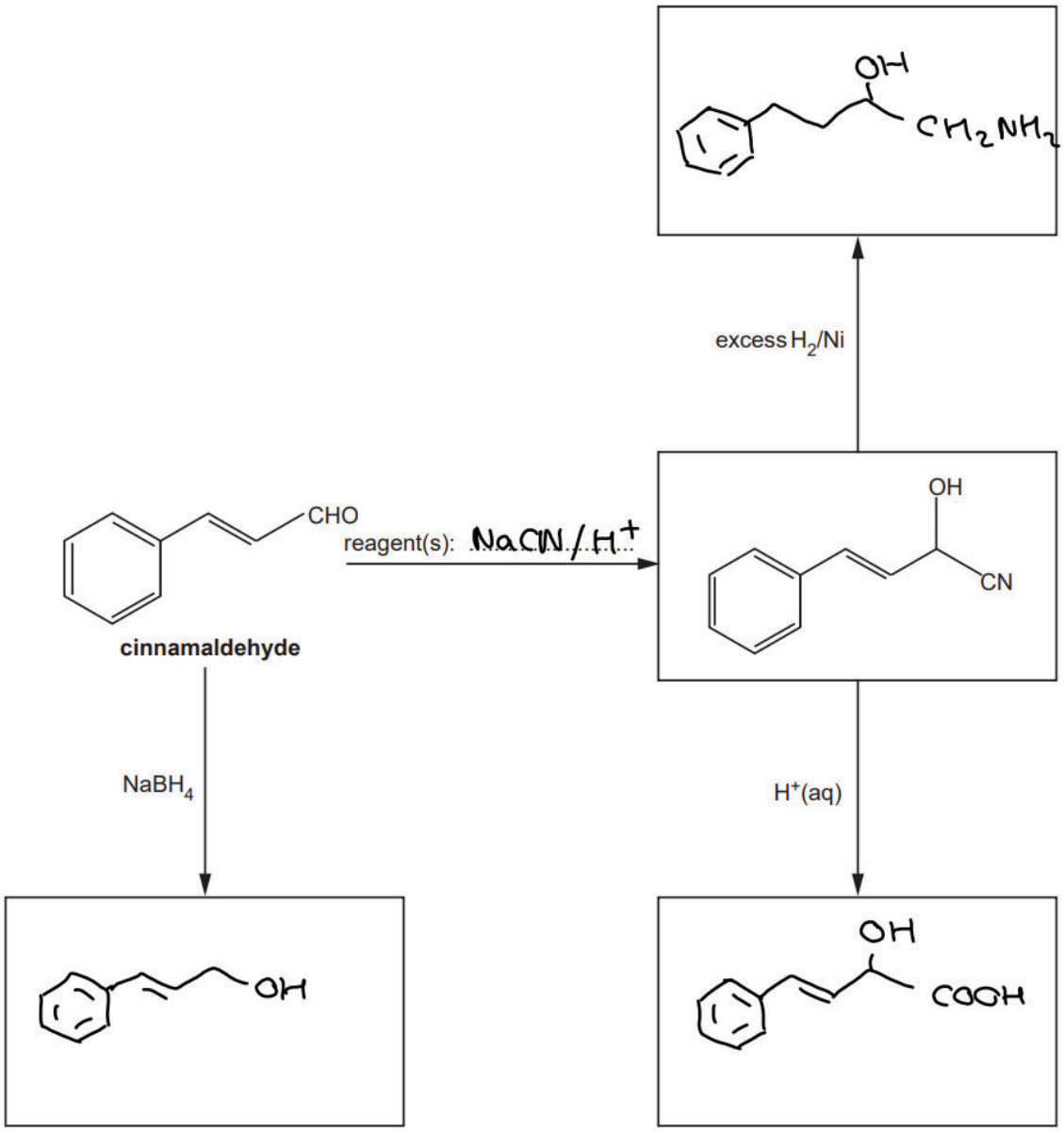
2,4-DNP produces an orange ppt.

Take a melting point and compare to known values.

..... **[3]**

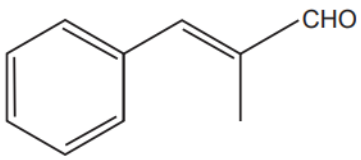
(c) The flowchart below shows some reactions starting with cinnamaldehyde.

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.



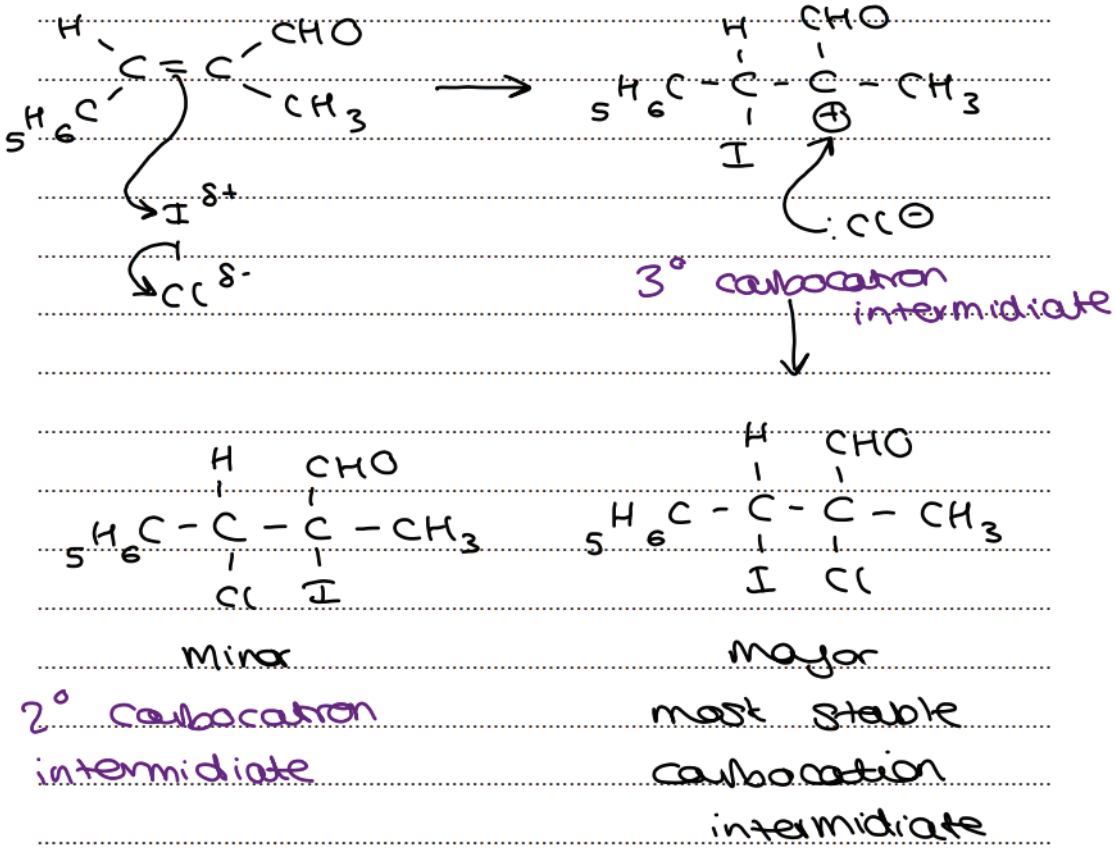
methylcinnamaldehyde

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.

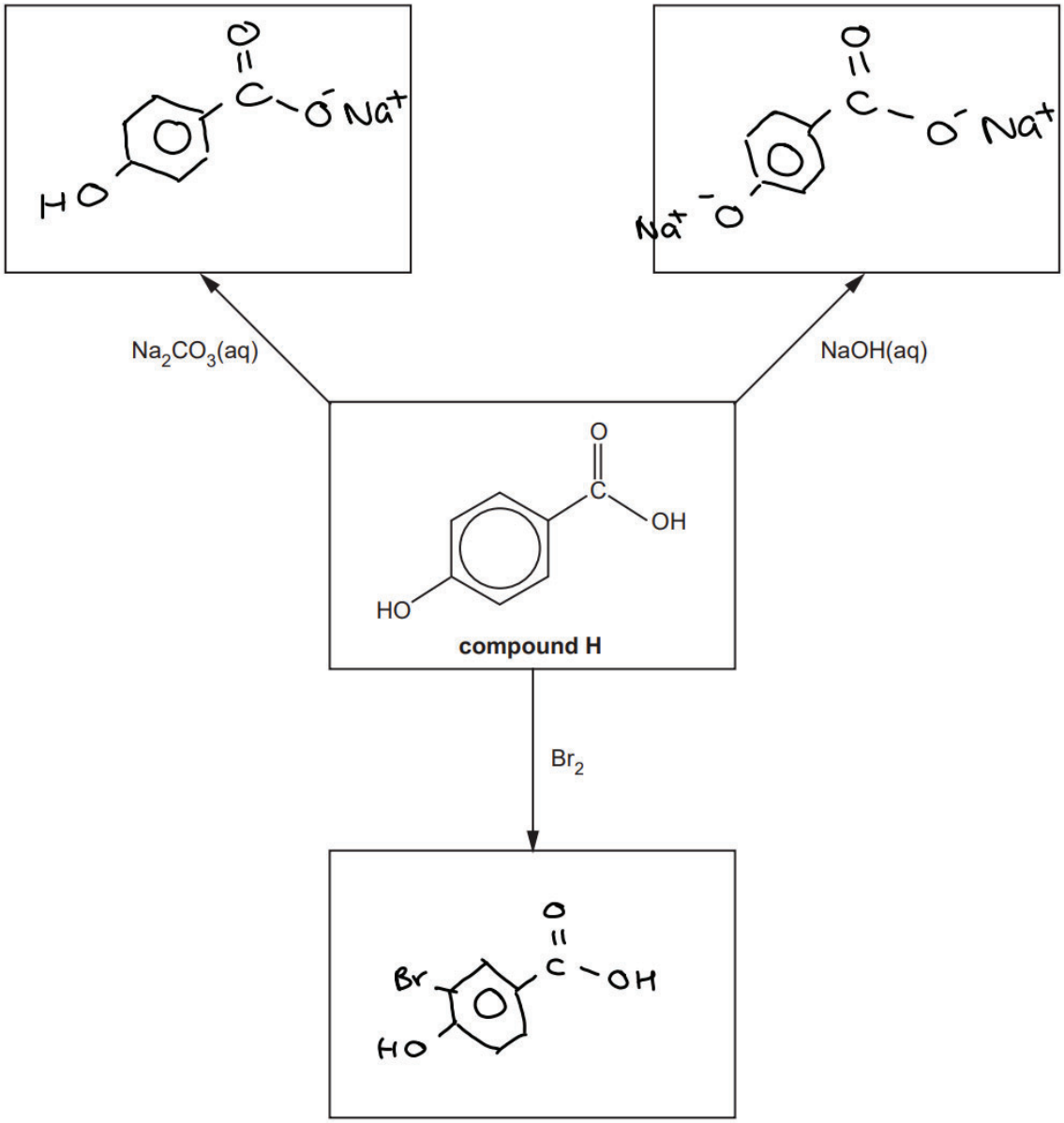
In your mechanism, you can show the phenyl group as C_6H_5. **[6]**



11. This question is about aromatic carboxylic acids and their derivatives.

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

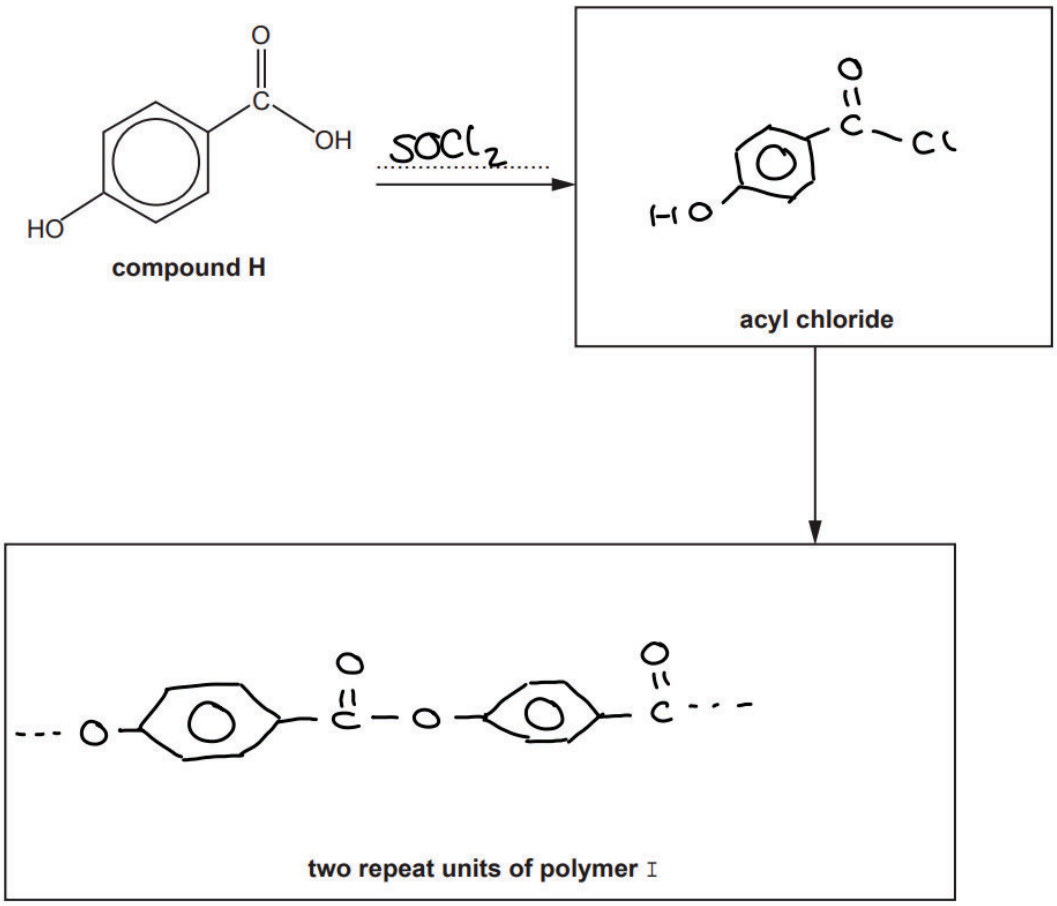
In the boxes, draw the organic products of these reactions.



[3]

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

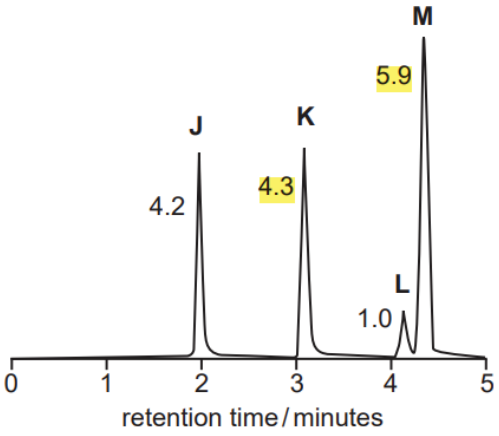
Complete the flowchart by drawing the structure of the acyl chloride and **two** repeat units of polymer I, and stating the **formula** of the reagent(s) required for the first stage on the dotted line.



[4]

(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

$152 - 137 = 15$

$180 - 137 = 43$

$180 - 137 = 43$

$\frac{g\,dm^{-3}}{g\,mol^{-1}} = mol\,dm^{-3}$

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

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

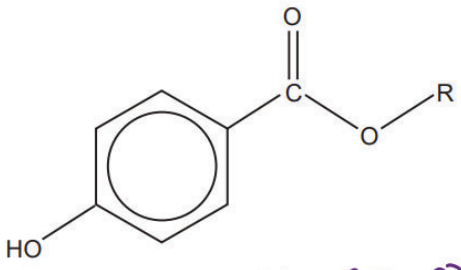
Give your answer to **two** significant figures.

$\frac{9.13 \times 10^{-2}}{166} = 5.50 \times 10^{-4}\ mol\,dm^{-3}$

$5.50 \times 10^{-4} \times \frac{5.9}{4.3} = 7.5 \times 10^{-4}\ mol\,dm^{-3}$

concentration of ester **M** = 7.5×10^{-4} $mol\,dm^{-3}$ **[2]**

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



$1+16+(12\times6)+4+12+(16\times2)$
$= 137$

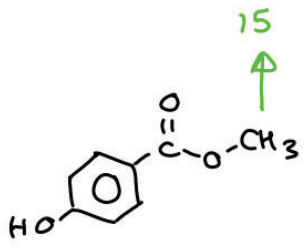
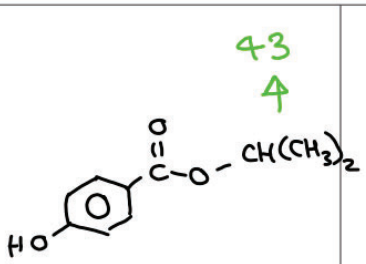
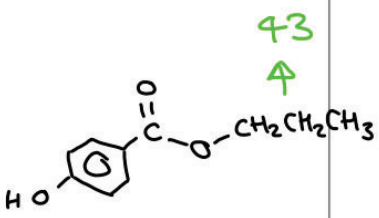
Where 'R' is an alkyl group.

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

$\frac{43}{12} = 3.6$

$12 \times 3 = 36$

$43 - 36 = 7$

 15	 43	 43
J	**L**	**M**

[3]

12. The relative molecular masses and boiling points of some fuels are shown in **Table 22.1**.

Fuel	Relative molecular mass	Boiling point / °C
hexane	86	69
pentan-1-ol	88	138
heptane	100	98

Table 22.1

→ C_nH_{2n+2} = general alkane

(a) Write an equation for the incomplete combustion of heptane.

$C_7H_{16} + 7\frac{1}{2}O_2 \longrightarrow 7CO + 8H_2O$ **[1]**

(b) Explain the difference in the boiling points of the fuels in **Table 22.1**.

- heptane is a longer carbon chain than hexane so has more points of contact
- heptane has stronger induced dipole-dipole interactions
- pentan-1-ol has hydrogen bonds which are stronger than induced dipole-dipole interactions
- more energy is required to break these hydrogen bonds.

[4]

(c) Fuel additives are often used to improve the combustion of a fuel.

(i) Compound **N** is a fuel additive containing carbon, hydrogen and oxygen only.

Complete combustion of 1.71 g of compound **N** produces 2.97 g of CO_2 and 1.62 g of H_2O. The relative molecular mass of compound **N** is 76.0.

Calculate the molecular formula of **N** and suggest a possible structure for the compound.

CO_2 : $\frac{2.97}{12+(16\times2)} = 0.0675$ mol

H_2O: $\frac{1.62}{1+1+16} = 0.0900$ mol

$CO_2 : H_2O$

3 : 4

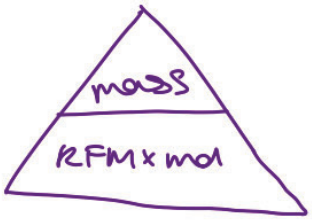
C : H

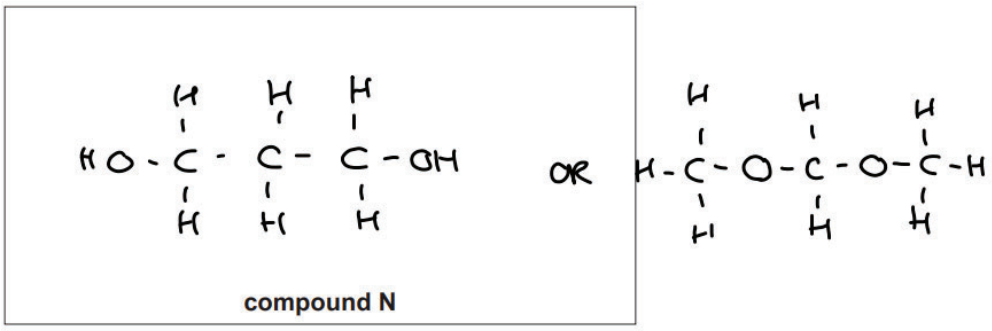
3 : 8

$C_3H_8O_2$

$76 - ((12\times3)+8) = 32$

$\frac{32}{16} = 2 = 2$ O's

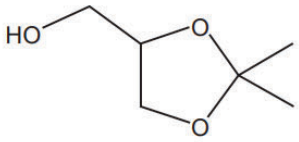




compound N

[5]

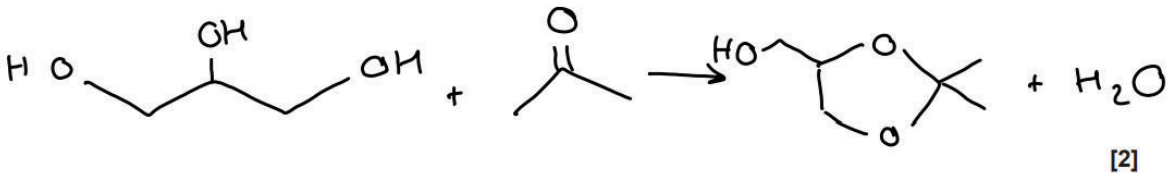
(ii) Solketal has been investigated as a potential fuel additive.



solketal

Solketal is synthesised from propane-1,2,3-triol and a carbonyl compound.

Construct a balanced equation for this synthesis.
Show structures for the organic compounds in your equation.



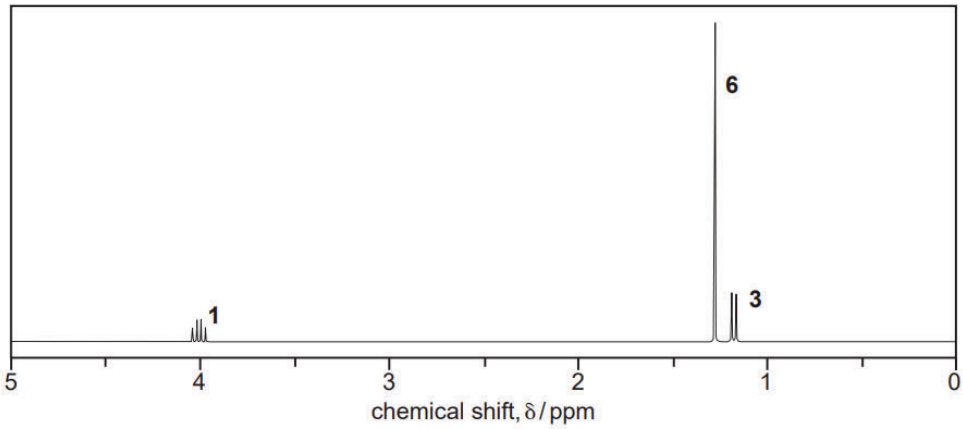
[2]

(d)* A scientist is researching compounds that might be suitable as fuel additives.
One of the compounds gives the analytical results below.

Elemental analysis by mass:
C: 54.54%; H: 9.10%; O: 36.36%

Mass spectrum:
Molecular ion peak at *m*/*z* = 132.0

^{1}H NMR spectrum in D_2O



The numbers by the peaks are the relative peak areas.

When the spectrum is run without D_2O, there are **two** additional peaks with the same relative peak areas at 11.0 ppm and 3.6 ppm.

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

Show **all** your reasoning. **[6]**

$\frac{54.54}{12}$ $\frac{9.10}{1}$ $\frac{36.36}{16}$

$= \frac{4.545}{2.273}$ $= \frac{9.10}{2.273}$ $= \frac{2.273}{2.273}$

$= 2$ $= 4$ $= 1$

empirical formula : C_2H_4O

$(12 \times 2) + 4 + 16 = 44$

$132 \div 44 = 3$

molecular formula : $C_6H_{12}O_3$

$\delta = 4.0$ ppm, quartet, 1 H CH_3-CH-O

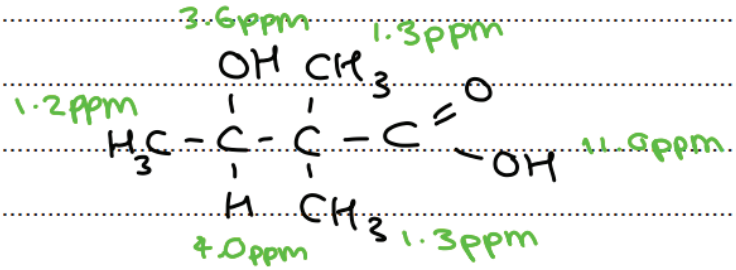
$\delta = 1.3$ ppm, singlet, 6 H $(CH_3)_2-C$

$\delta = 1.2$ ppm, doublet, 3H CH_3-CH

$\delta = 11.0$ ppm = COOH

$\delta = 3.6$ ppm = OH

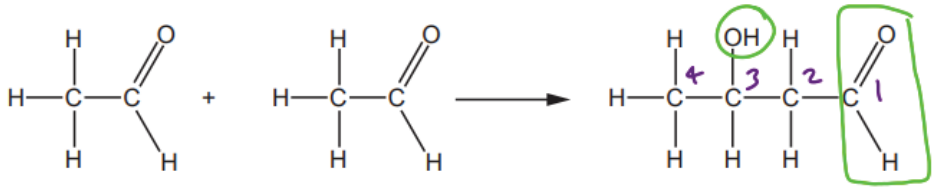
Additional answer space if required.



13. This question is about organic reactions.

(a) Compound **A** is formed when ethanal is mixed with $OH^-(aq)$ ions, which act as a catalyst.

The balanced equation is shown in **reaction 6.1** below.



Reaction 6.1

Compound **A**

(i) Give the systematic name for compound **A**.

3-hydroxybutanal ..... **[1]**

(ii) What type of reaction has taken place?

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

(iii) **Reaction 6.1** takes place in two steps. OH^- ions act as a catalyst.

In **step 1**, ethanal reacts with OH^- ions to set up an acid–base equilibrium.
In **step 2**, compound **A** is formed.

- Complete the equilibrium for **step 1** and label the conjugate acid–base pairs as: **A1**, **B1** and **A2**, **B2**.

CH_3CHO + OH^- $\rightleftharpoons$ CH_3CO^- + H_2O

A1 B2 B1 A2

acids are proton donors

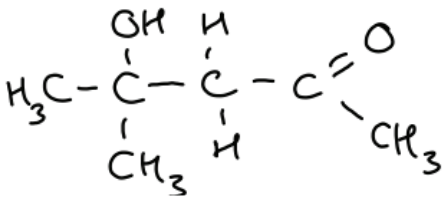
- Suggest the equation for **step 2**.

$CH_3CHO + {}^-CH_2CHO + H_2O \rightarrow CH_3CH(OH)CH_2CHO + OH^-$

[3]

(iv) A similar reaction takes place when propanone, $(CH_3)_2CO$, is mixed with $OH^-(aq)$ ions.

Draw the structure of the organic product of this reaction.



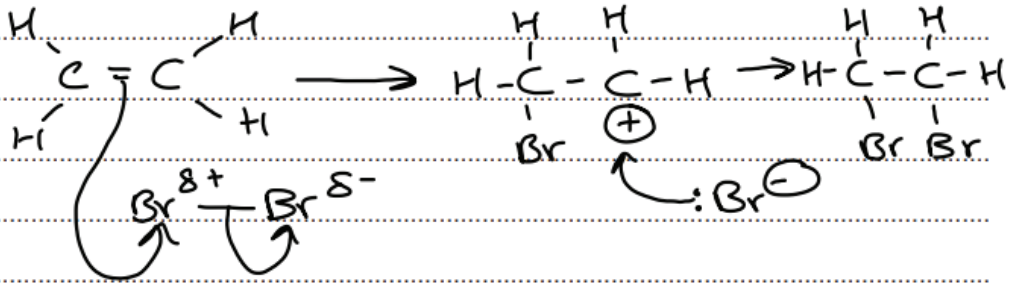
[1]

(b)* Many organic reactions use electrophiles as reagents.

Explain the role of electrophiles in organic chemistry.

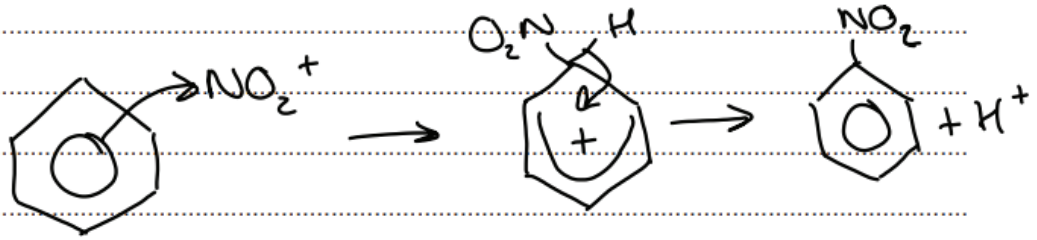
Your answer should include **one** reaction of an aliphatic compound and **one** reaction of an aromatic compound, including relevant mechanisms. **[6]**

electrophilic addition:



electrophilic substitution:

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



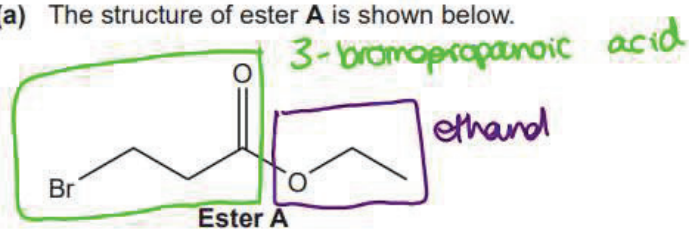
$H^+ + HSO_4^- \rightarrow H_2SO_4$

Additional answer space if required.

electrophiles act as electron pair acceptors.

14. This question is about esters.

(a) The structure of ester **A** is shown below.



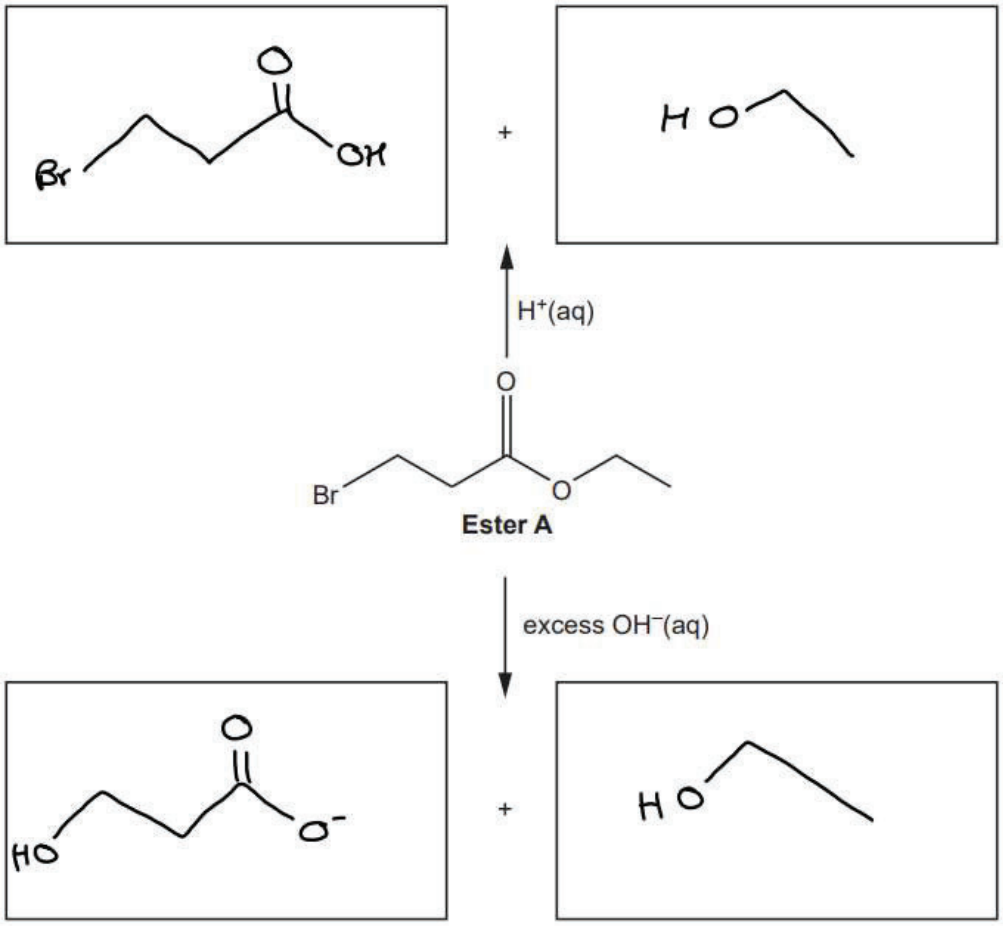
Ester A

(i) What is the systematic name of ester **A**?

ethyl 3-bromopropanoate ..... **[1]**

(ii) In the boxes, draw the organic products for the reactions of the functional groups in ester **A** shown below.

Each reaction forms two organic products.

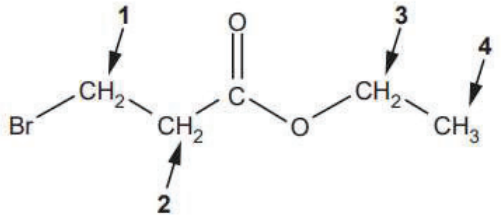


[5]

(iii) Name the type of reactions of ester **A** shown in **(ii)**.

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

(b) The protons in ester **A** are in four different environments, labelled **1–4** on the structure below.



Complete the table to predict the **proton** NMR spectrum of ester **A**.

Proton environment	Chemical shift	Splitting pattern
1	3.0-4.3	triplet
2	2.0-3.0	triplet
3	3.0-4.3	quartet
4	0.5-1.9	triplet

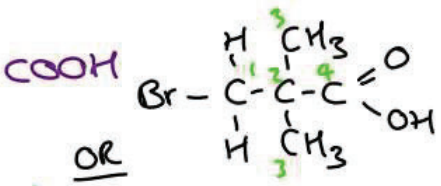
[4]

$C_5H_9O_2Br$

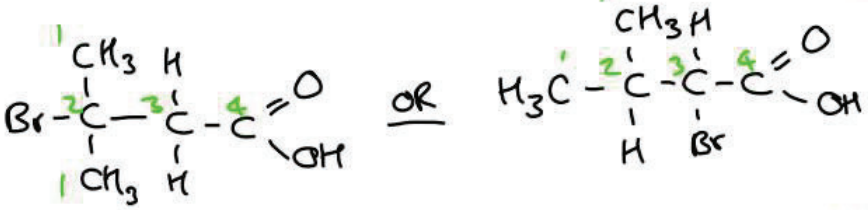
(c) Compound **B** is a structural isomer of ester **A**.

- Compound **B** reacts with aqueous sodium carbonate.
- The ^{13}C NMR spectrum of **B** has 4 peaks.

Draw a possible structure for compound **B**.

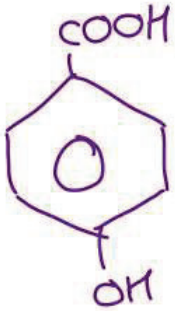


OR



[1]

(d) A polyester is formed from 200 molecules of 4-hydroxybenzoic acid.



What is the relative molecular mass, M_r, of the polyester?

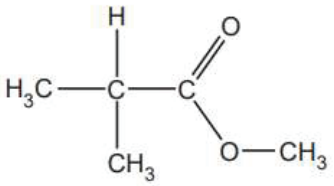
$(12 \times 7) + 6 + ((16 \times 3) = 138 \text{ g mol}^{-1}$

$138 \times 200 = 27600 \text{ g mol}^{-1}$

$27600 - ((99 \times 18) = 24018$

M_r = ... 24018 ..... g mol^{-1} **[2]**

(e)* A student intends to synthesise ester **C**.



Ester C

(i) Plan a two-stage synthesis to prepare 12.75g of ester **C** starting from 2-methylpropanal, $(CH_3)_2CHCHO$. Assume the overall percentage yield of ester **C** from 2-methylpropanal is 40%.

In your answer include the mass of 2-methylpropanal required, reagents, conditions and equations where appropriate.

Purification details are **not** required. **[6]**

$\frac{12.75}{(12\times5)+10+(16\times2)} = 0.125$ mol of ester C

$0.125 \times \frac{100}{40} = 0.3125$ mol of 2methyl-propanal

$((12\times4)+8+16) \times 0.3125 = 22.50$g of 2-methyl propanal

1: $(CH_3)_2CHCHO + [O] \rightarrow (CH_3)_2CHCOOH$

$[O]$: $Cr_2O_7^{2-}/H^+$ and reflux

2: $(CH_3)_2CHCOOH + CH_3OH \xrightarrow[\text{reflux}]{H^+} (CH_3)_2CHCOOCH_3 + H_2O$

Additional answer space if required

.....

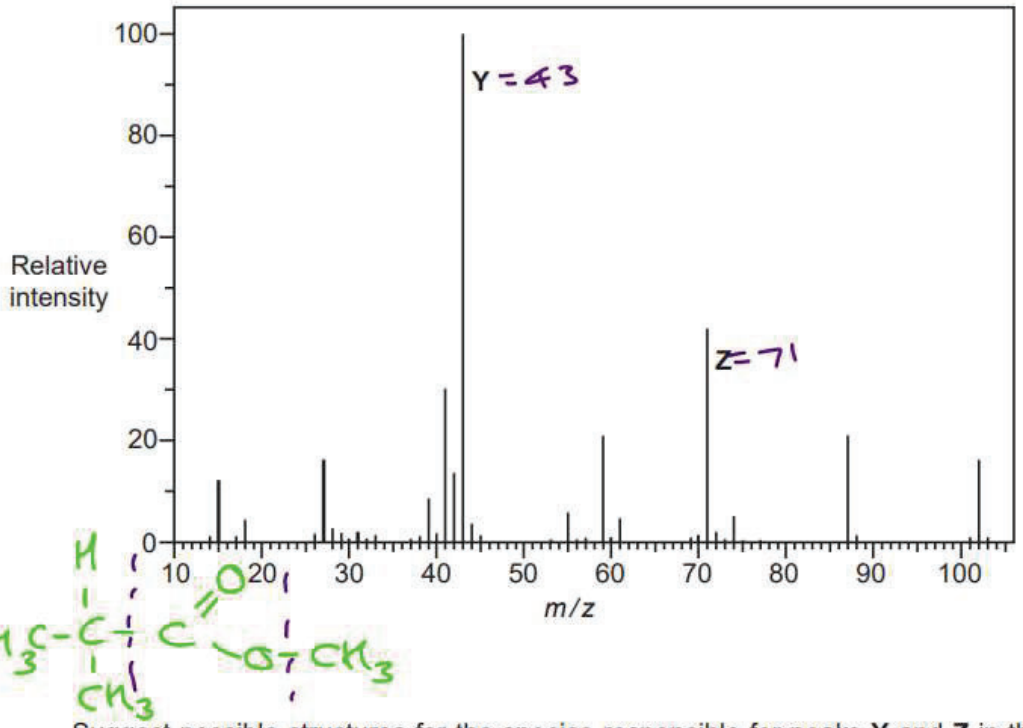
.....

.....

.....

.....

(ii) The mass spectrum of ester **C** is shown below.



Suggest possible structures for the species responsible for peaks **Y** and **Z** in the mass spectrum.

$(CH_3)_2CH^+$	$(CH_3)_2CHCO^+$
Y	**Z**

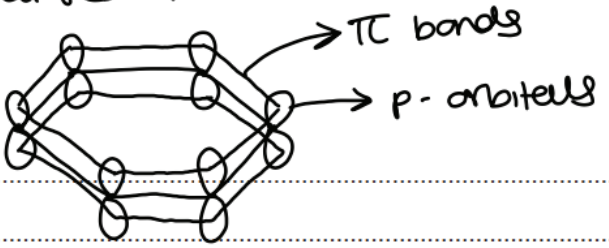
[2]

15. This question is about benzene.

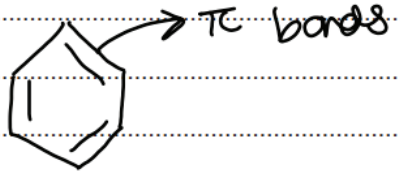
(a) Over time, the Kekulé and delocalised models have been used to describe the bonding and structure of a benzene molecule.

(i) Describe, in terms of orbital overlap, the similarities and differences between the bonding in the Kekulé model and the delocalised model of benzene.

delocalised model:



Kekulé:



differences:

Kekulé has 3 π bonds and the delocalised model has a π ring system

[3]

(ii) Experimental evidence led to the general acceptance of the delocalised model over the Kekulé model.

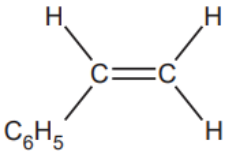
Describe **two** pieces of evidence to support the delocalised model of benzene.

- benzene is less reactive than alkenes
- all C–C bond lengths are the same

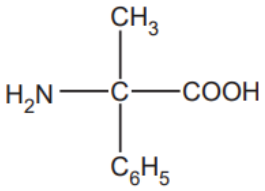
[2]

(b) Benzene can be used as the starting material for the synthesis of compounds **D** and **E**, shown below.

In the diagrams C_6H_5 is a phenyl group.



compound D



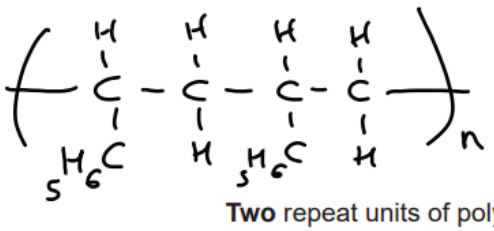
compound E

addition C=C → C-C

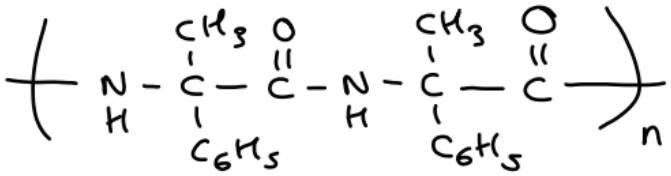
condensation forms $R_2N-\overset{H}{\underset{}{N}}-\overset{O}{\overset{\|}{C}}-R_1$

Compounds **D** and **E** can be converted into polymers. amide

(i) Draw **two** repeat units of these polymers.



Two repeat units of polymer formed from **D**



Two repeat units of polymer formed from **E**

[3]

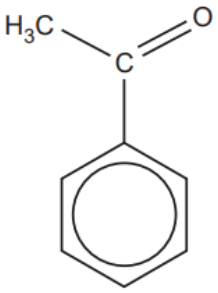
(ii) State the **type** of polymer formed from compounds **D** and **E**.

From compound **D** addition

From compound **E** condensation

[1]

(iii) In the synthesis of compounds **D** and **E**, benzene is first reacted with ethanoyl chloride, CH_3COCl, to form phenylethanone, shown below.



electrophilic substitution

phenylethanone

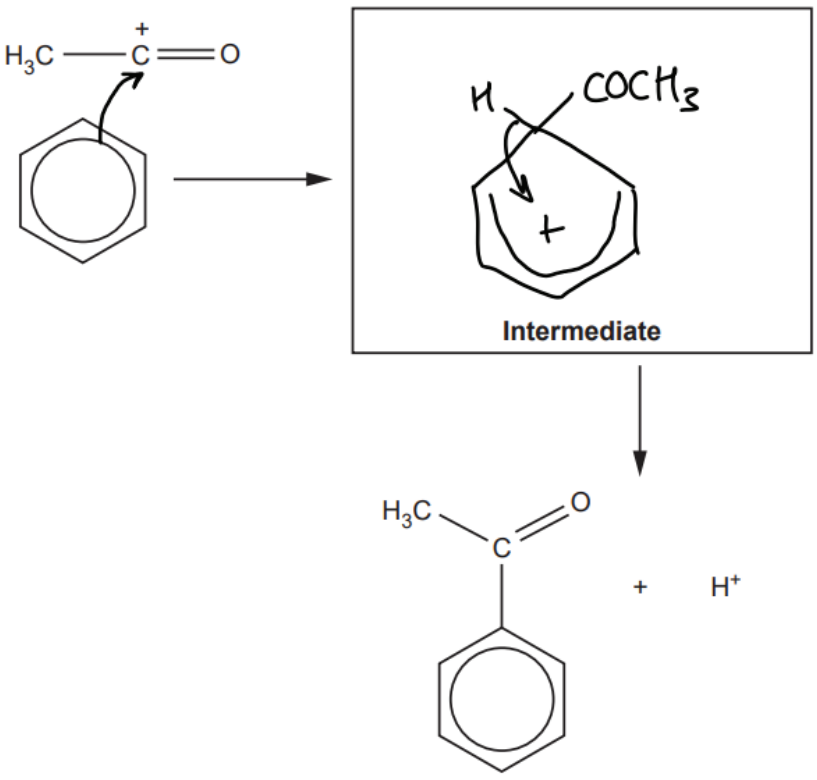
The reaction takes place in the presence of aluminium chloride, $AlCl_3$, which acts as a catalyst.

In the mechanism for this reaction,
- ethanoyl chloride first reacts with aluminium chloride to form the $CH_3–C^+=O$ cation
- the $CH_3–C^+=O$ cation then behaves as an electrophile.

Complete the mechanism for the reaction.

Include equations to show the role of the $AlCl_3$ catalyst, relevant curly arrows and the structure of the intermediate.

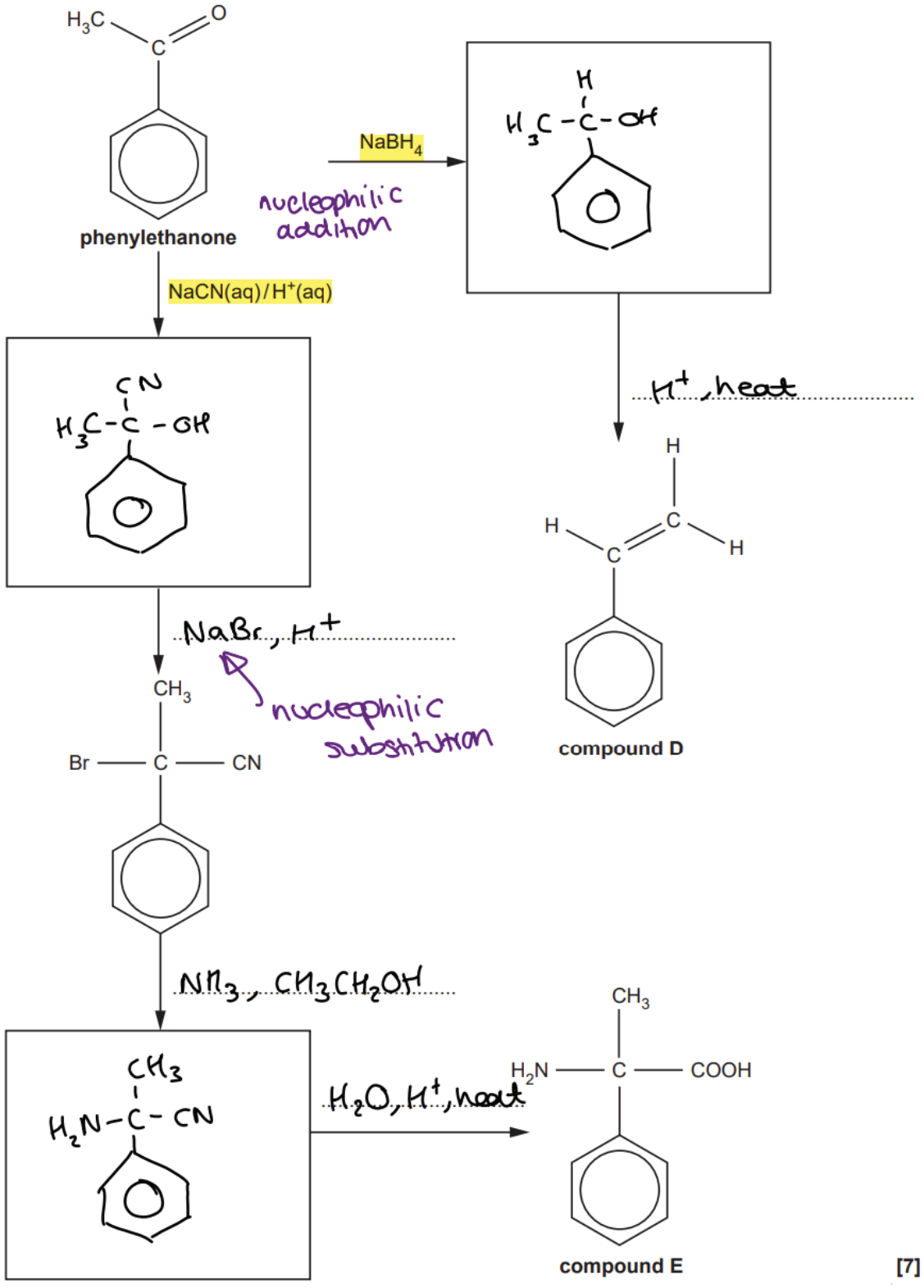
Formation of electrophile $CH_3COCl + AlCl_3 \rightarrow CH_3-C^+=O + AlCl_4^-$



Regeneration of catalyst $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

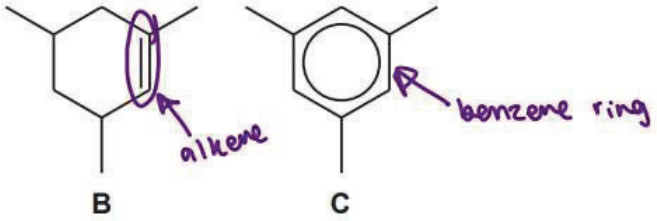
[5]

(iv) Complete the flowchart for the synthesis of compounds **D** and **E** from phenylethanone.



[7]

16. Compounds **B** and **C**, shown below, are unsaturated hydrocarbons containing nine carbon atoms.

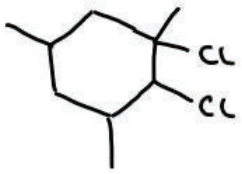
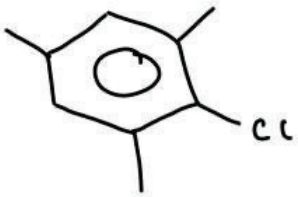


B **C**

(a) Compound **B** reacts with chlorine at room temperature, but compound **C** requires the presence of a halogen carrier.

In both reactions, the organic compound reacts with chlorine in a 1:1 molar ratio.

(i) Draw the structures of the organic product of each reaction.

electrophilic addition	electrophilic substitution
	
Organic product with **B**	Organic product with **C**

[2]

(ii) Explain the relative resistance to chlorination of compound **C** compared with compound **B**.

In B the electrons / π bond is localised

In C the electrons / π ring system is delocalised

In B the electron density is higher so is more susceptible to electrophilic attack / B attracts / accepts the electrophile (CCl_2) more / B polarises the electrophile (CCl_2) more.

[3]

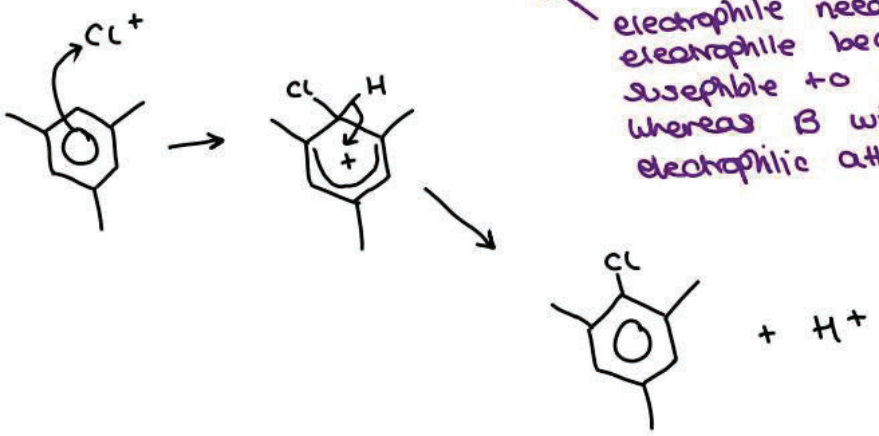
(iii) Outline the mechanism for the reaction of compound **C** with chlorine.

Show the role of the halogen carrier.

forming electrophile

$AlCl_3 + Cl_2 \longrightarrow Cl^+ + AlCl_4^-$

electrophile needs a stronger electrophile because C is less susceptible to electrophilic attack whereas B will undergo electrophilic attack with $Cl^{\delta+}$



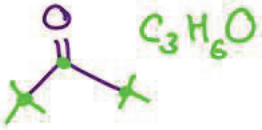
$H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl$

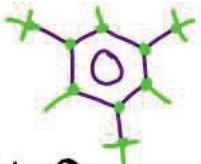
regenerating halogen carrier

[5]

(b) Compound **C** can be prepared by 'trimerisation' of propanone using concentrated sulfuric acid as a catalyst.

Suggest an equation for this reaction, using **molecular** formulae.





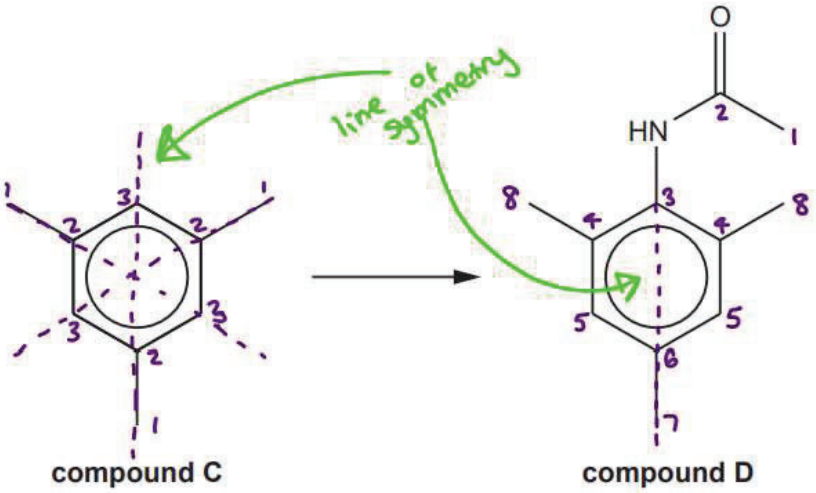
C_9H_{12}

Question confirms 9 carbons in compound C

$3C_3H_6O \longrightarrow C_9H_{12} + 3H_2O$ **[3]**

(c) An organic chemist is investigating compound **D** for possible use as a medicine.

The chemist proposes a synthesis of compound **D** from compound **C**.



compound C **compound D**

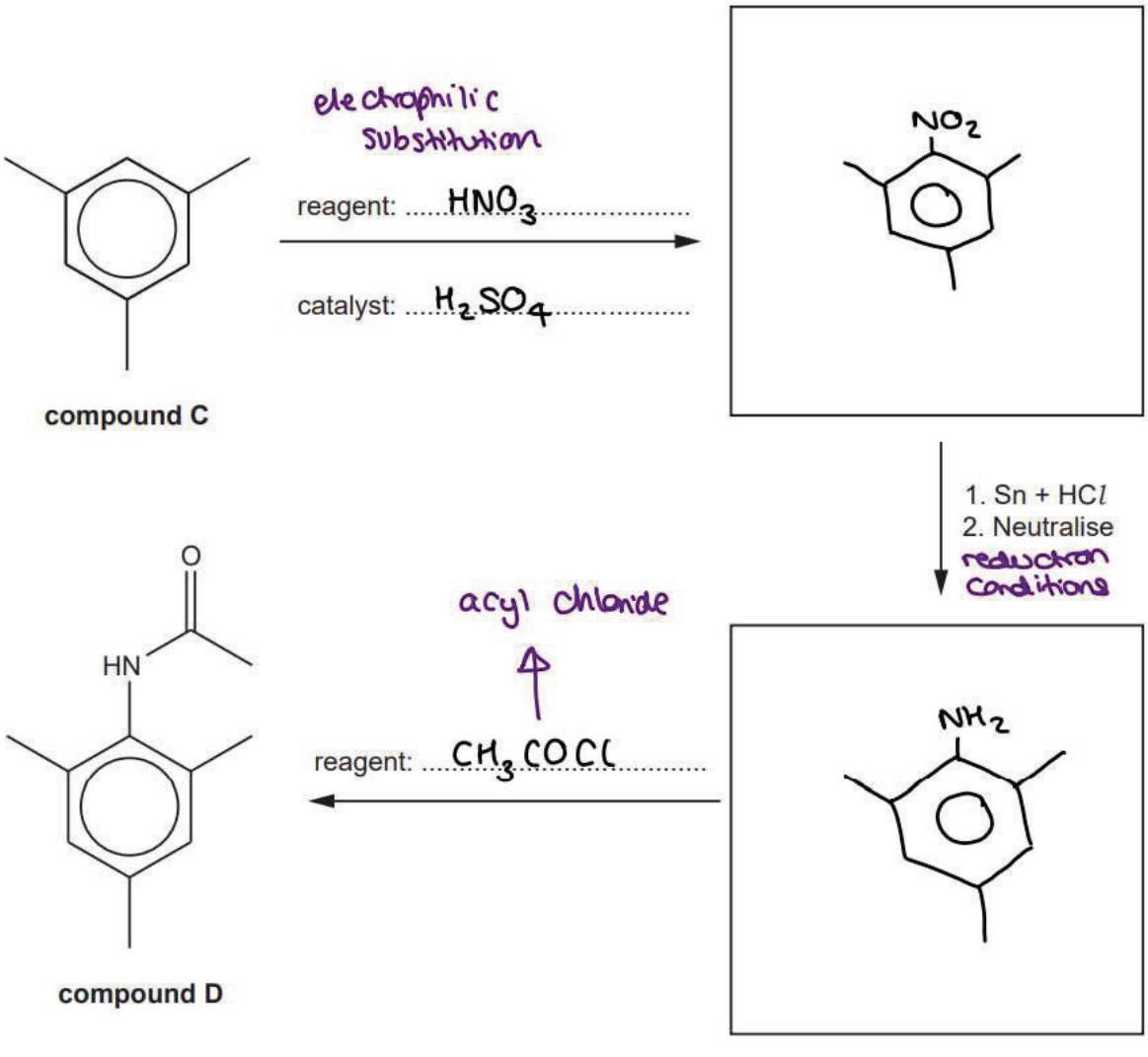
(i) Predict the number of peaks in the ^{13}C NMR spectra of compounds **C** and **D**.

	Compound **C**	Compound **D**
Number of peaks	3	8

[2]

(ii) The chemist develops a three-stage synthesis of compound **D** from compound **C**.

Complete the flowchart.
Show structures for organic compounds.



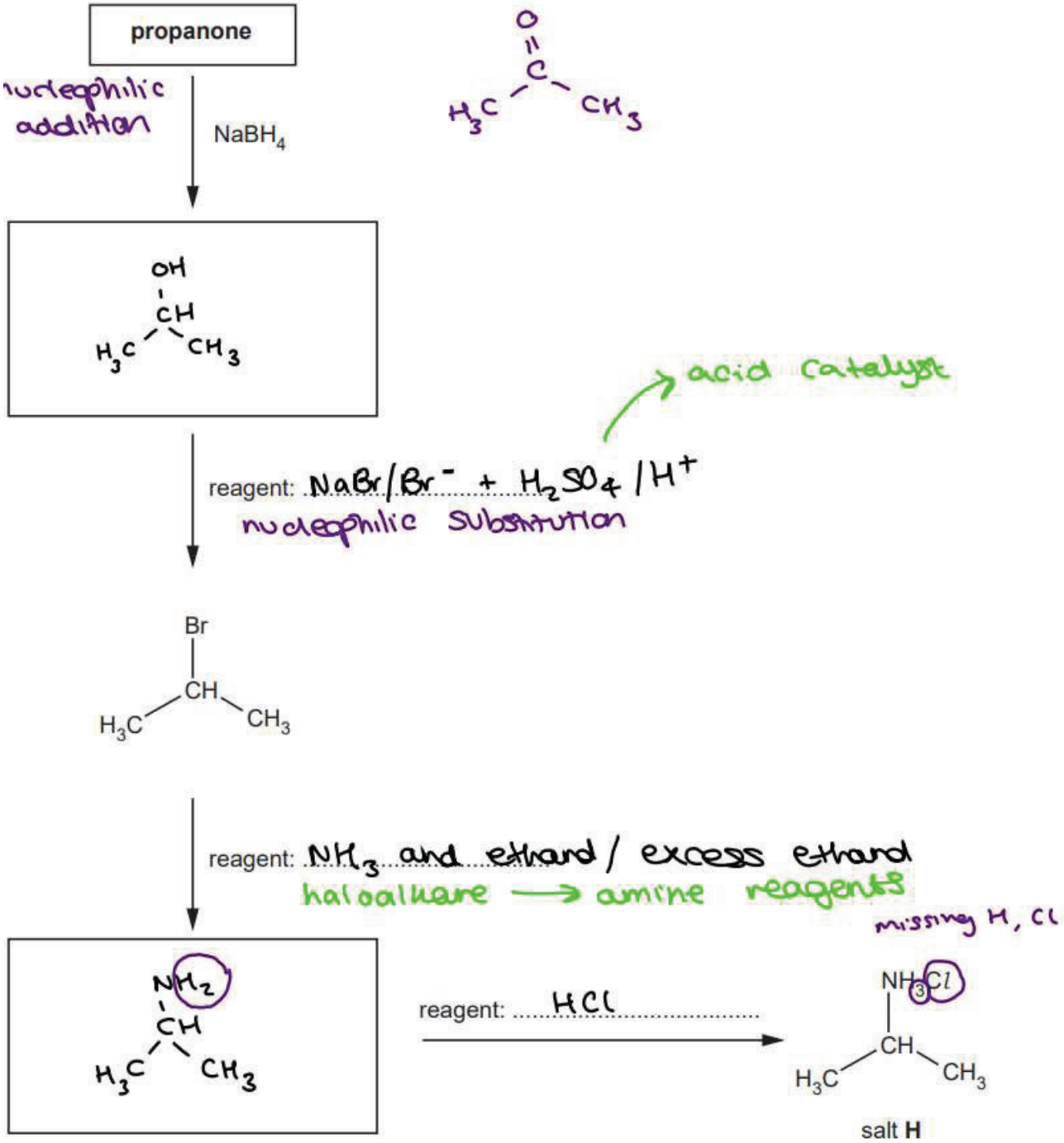
[5]

17. This question is about organic compounds containing nitrogen.

(a) Salt **H**, $(CH_3)_2CHNH_3Cl$, is used in the manufacture of garden weedkillers.

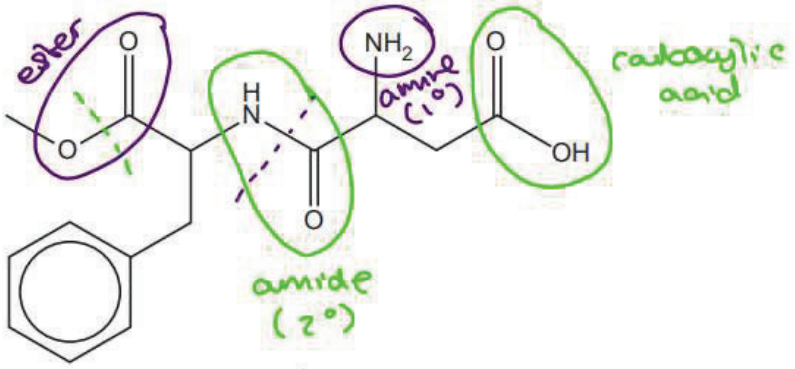
The flowchart shows the synthesis of the salt **H** from propanone.

Complete the flowchart.
Show structures for organic compounds.



[5]

(b) Aspartame, shown below, is an artificial sweetener commonly used as a sugar substitute.



aspartame

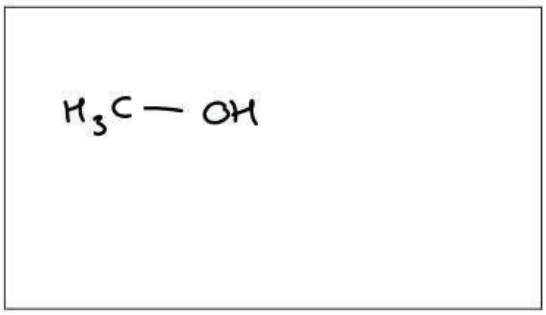
(i) Aspartame contains several functional groups.

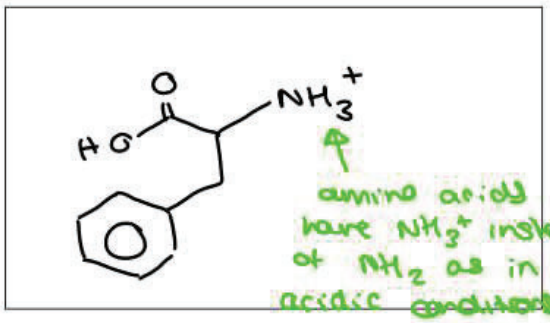
Apart from the benzene ring, name the functional groups in aspartame.

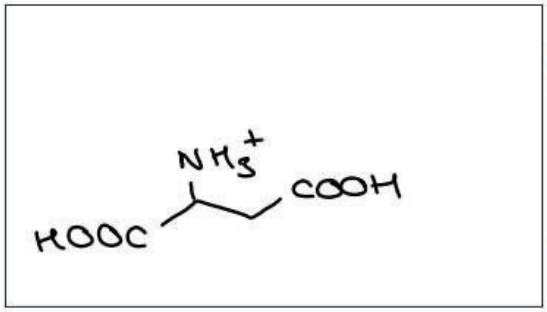
- ester
- amide (2°)
- amine (1°)
- carboxylic acid [3]

(ii) A sample of aspartame is hydrolysed with aqueous acid.

Draw the structures of the **three** organic products of the complete **acid hydrolysis** (H^+) of aspartame.







acid hydrolysis:

ester → alcohol + carboxylic acid

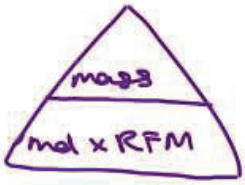
amide → amine + carboxylic acid

[4]

(iii) Some people are concerned that aspartame, $C_{14}H_{18}N_2O_5$, may have adverse health effects.
Research shows that the safe maximum daily intake of aspartame is 1.7×10^{-4} mol kg^{-1}.

- A typical UK adult has a mass of 75 kg.
- A can of a diet drink contains 167 mg of aspartame.

How many cans of this diet drink is it safe for a typical adult to drink in one day?



$(14 \times 12) + 18 + (14 \times 2) + (5 \times 16)$
$= 294$ g mol^{-1}

$\frac{0.167\text{g}}{294} = 5.68 \times 10^{-4}$ mol in 1 can

$1.7 \times 10^{-4} \times 75 = 0.01275$ mol per day

$\frac{0.01275}{5.68 \times 10^{-4}} = 22.4$ cans

Number of cans = 22 **[3]**