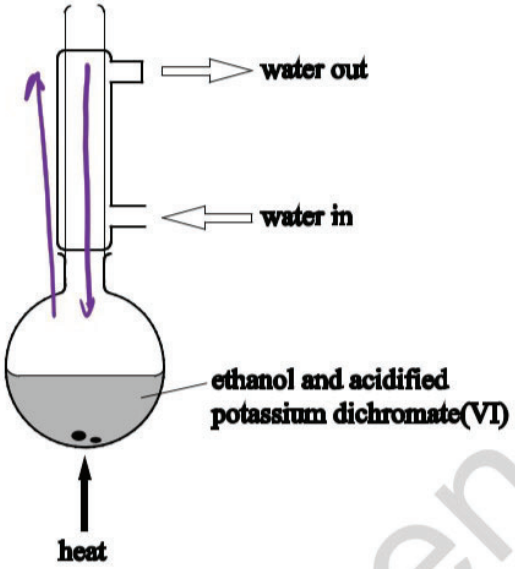
1. Ethanol is oxidised to ethanoic acid using acidified potassium dichromate(IV) solution. The reaction is heated under reflux using the equipment shown in the diagram below.

[O] → aldehyde [O] → ethanoic acid



What is the reason for heating under reflux?

A to ensure even heating

B to prevent any substances escaping → allows full oxidation

C to boil the mixture at a higher temperature

D to allow efficient mixing

Your answer **B**

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.

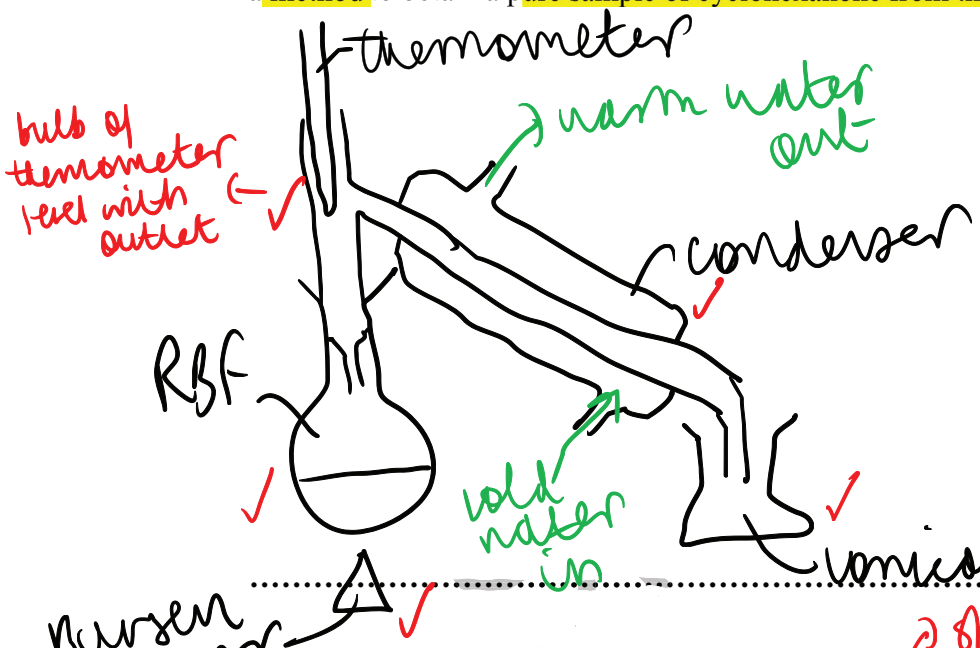
You will need to refer to some or all of the following data to answer these questions.

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

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.



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]

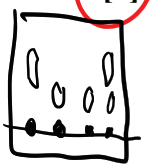
Ethanedioic acid removes excess dichromate ions, $Cr_2O_7^{2-}$, as in the equation below.

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

↳ 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)

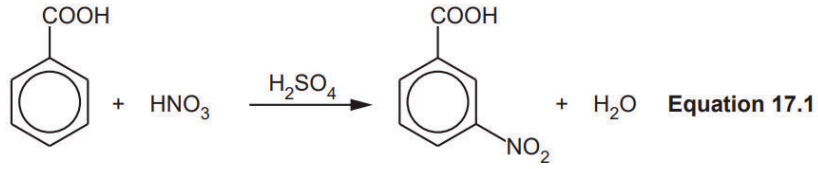
- Reacting our sample 2,4-DNP → orange ppt ✓
- Recrystallise the ppt, determine the melting point ✓ (both points needed for mark)
- Compare the mp to known values for cyclohexanone ✓ **[3]**

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

3. 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.

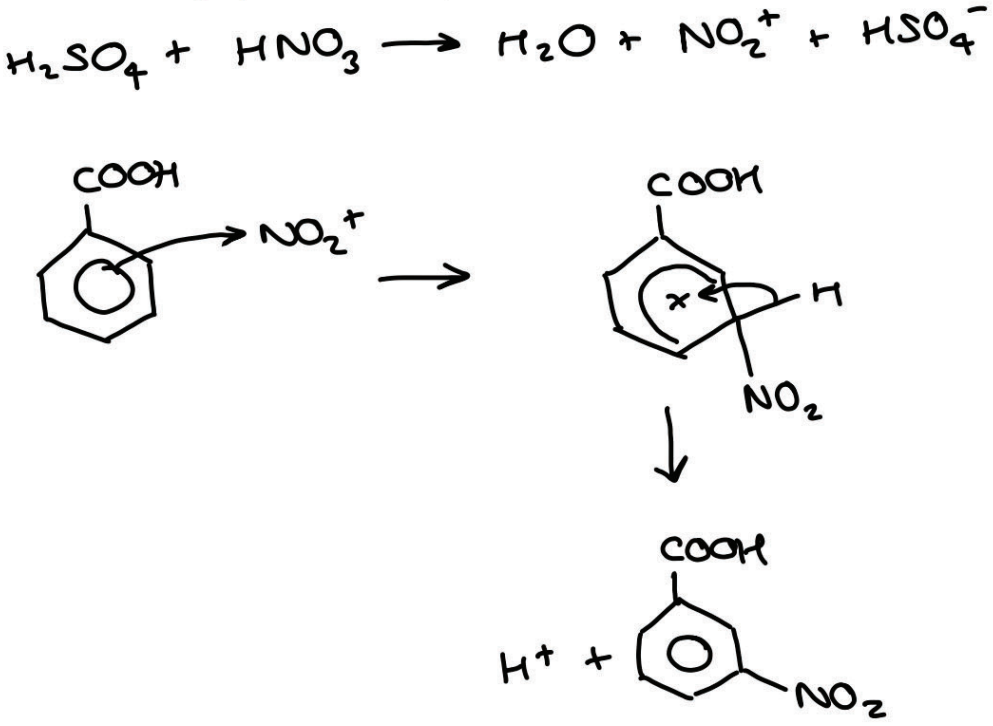


Equation 17.1

benzoic acid **3-nitrobenzoic acid**

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

Show how H_2SO_4 behaves as a catalyst.



[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.

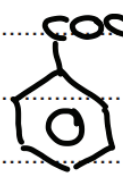
purification:

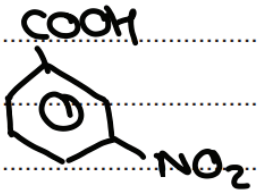
1. recrystalisation

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.

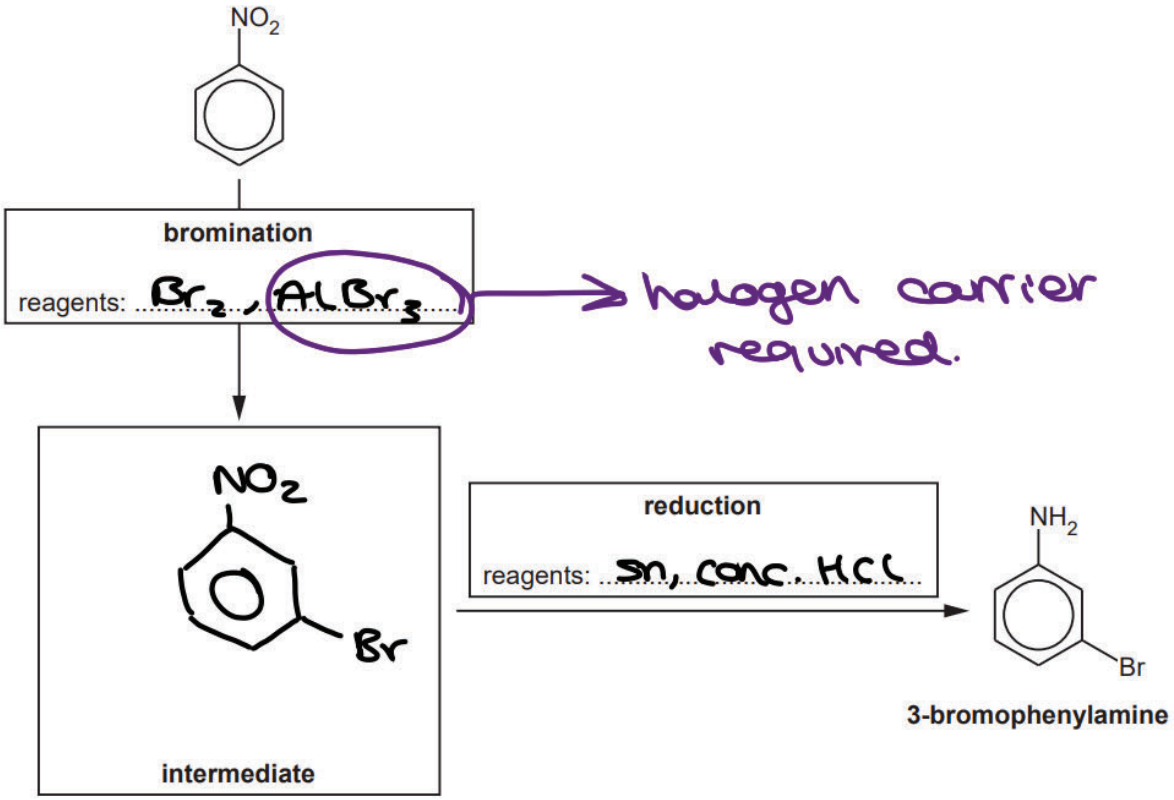
phenol is the easiest to nitrate and benzoic acid is the hardest / least reactive. **[1]**

(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.



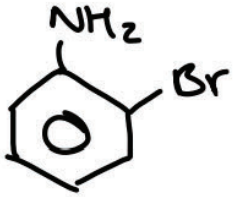
[3]

(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



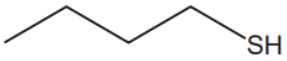
and

[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.

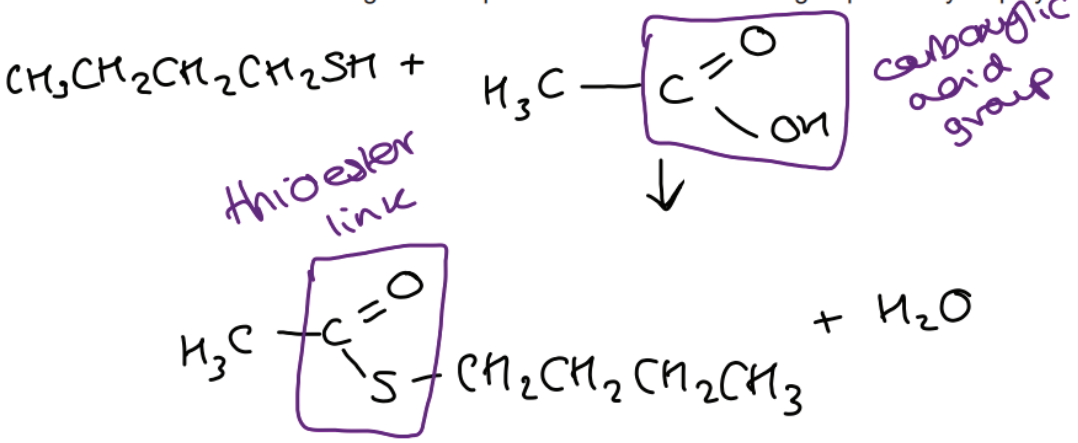
$$K_a = \frac{[H^+][C_4H_9S^-]}{[C_4H_9SH]}$$

[1]

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

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

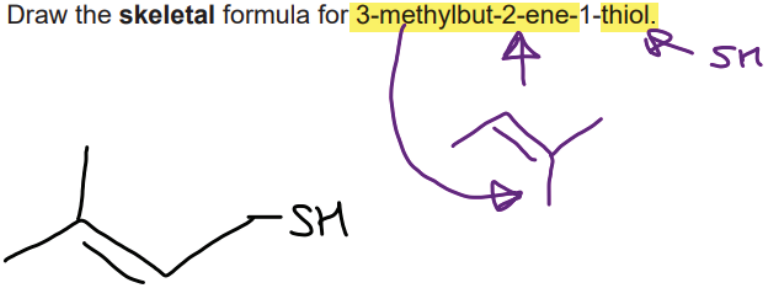
Use structures for all organic compounds with the functional groups clearly displayed.



[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.

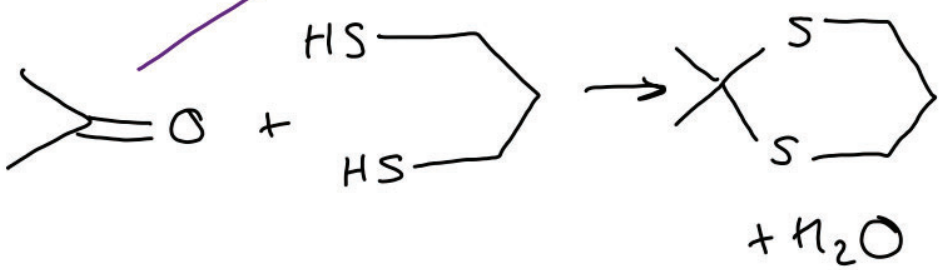


[1]

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

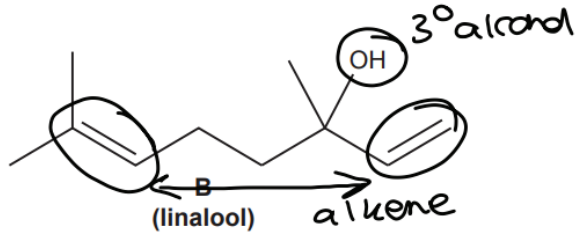
Write an equation for the reaction of propane-1,3-dithiol with propanone.

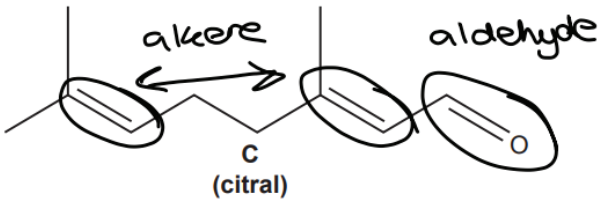
Use structures for organic compounds.

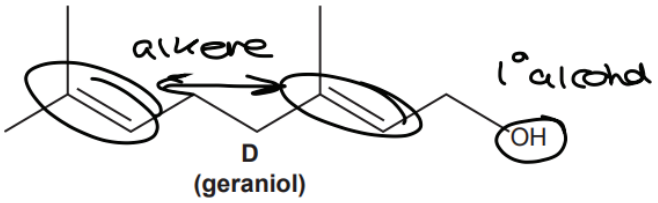


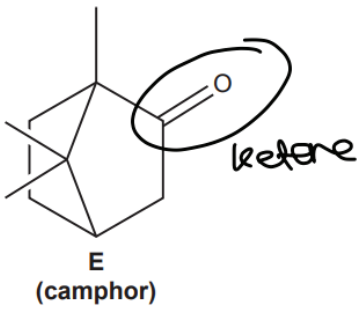
[2]

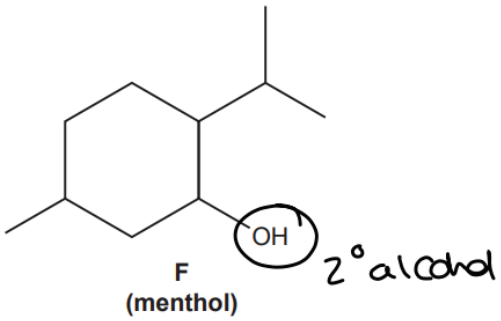
(b)* The structures for six naturally occurring organic compounds with pleasant smells, **B**–**G**, are shown below. The common names in brackets relate to their source and smell.

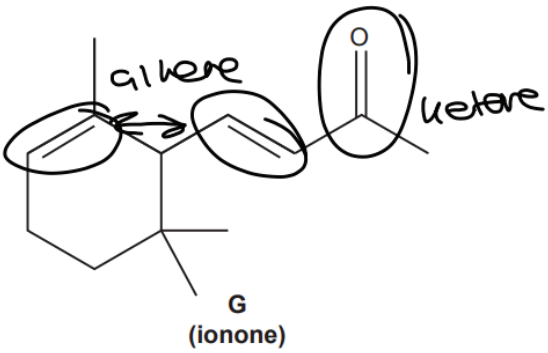












Explain how chemical tests would allow each compound to be distinguished from the other compounds.

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. 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]

6. This question is about two compounds used in medicine.

(a) *Cis*-platin, $PtCl_2(NH_3)_2$, is a complex of platinum which is used in cancer treatment.

(i) What is the oxidation number of platinum in *cis*-platin?

All compounds must have an oxidation number of 0

Pt +2
Cl_2 $-1 \times 2 = -2$
$(NH_3)_2$ $0 \times 2 = 0$

+2 **[1]**

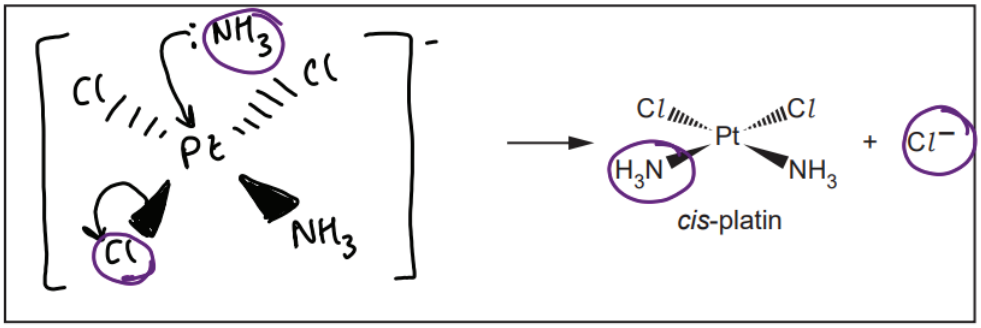
(ii) *Cis*-platin is prepared in a ligand substitution reaction which takes place in multiple steps.

The equation for the final step forming *cis*-platin is shown below.

$$[PtCl_3(NH_3)]^- + NH_3 \rightarrow PtCl_2(NH_3)_2 + Cl^-$$

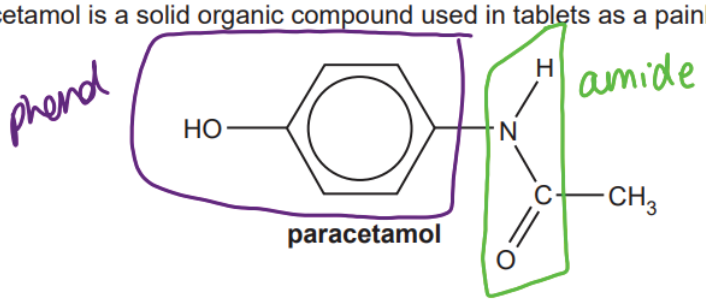
cis-platin

In the box, outline the mechanism for the formation of *cis*-platin from $[PtCl_3(NH_3)]^-$.
Use curly arrows and lone pairs where appropriate.



[2]

(b) Paracetamol is a solid organic compound used in tablets as a painkiller.

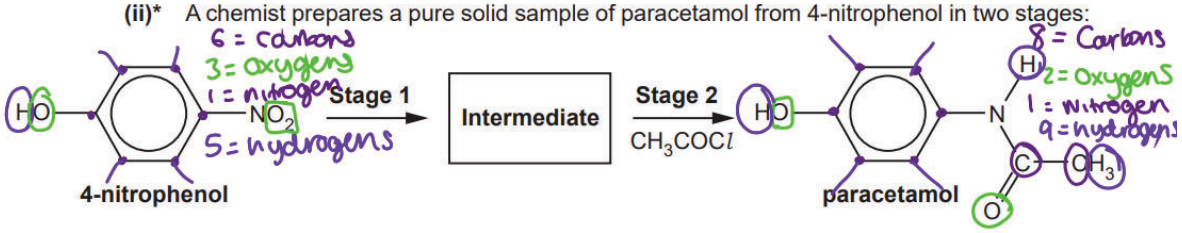


(i) Name the functional groups present in paracetamol.

phenol

amide **[2]**

(ii)* A chemist prepares a pure solid sample of paracetamol from 4-nitrophenol in two stages:



Describe a two-stage synthesis of 5.00 g of pure paracetamol from 4-nitrophenol. The overall percentage yield of paracetamol from 4-nitrophenol is 40.0%.

In your answer, include the mass of 4-nitrophenol required, the reagents and intermediate, and details of the purification of paracetamol. **[6]**

mass of 4-nitrophenol:

mass / mol x RFM

$\frac{5}{(12\times8)+(16\times2)+14+9} = 0.0331$ mol of paracetamol

$0.0331 \times \frac{100}{40} = 0.0828$ mol of 4-nitrophenol

$0.0828 \times ((12\times6)+(16\times3)+14+5) = 11.50\,g$

intermidiate: 4-aminophenol

reagents: Sn, Conc. HCl

- dissolve impure solid in minimum volume of hot solvent
- cool solution and filter solid
- scratch with glass rod

Additional answer space if required.

- wash with cold solvent and dry

7. Benzoic acid, C_6H_5COOH, is added to some foods as a preservative.

A student prepares benzoic acid as outlined below.

Step 1 The student mixes 4.00 cm^3 of phenylmethanol, $C_6H_5CH_2OH$, (density = 1.04 $g\,cm^{-3}$) with sodium carbonate and aqueous potassium manganate(VII), as an oxidising agent. The mixture is heated under reflux.

Step 2 The resulting mixture is cooled and then acidified with concentrated HC*l*. Impure crystals of benzoic acid appear.

Step 3 The student recrystallises the impure crystals to obtain 1.59 g of pure benzoic acid.

(a) In **Step 1**, sodium carbonate, Na_2CO_3, makes the reaction mixture alkaline.

Write an ionic equation to show how carbonate ions form an alkaline solution in water.

$CO_3^{2-} + H_2O \rightarrow OH^- + HCO_3^-$ **[1]**

(b) In **Step 2**, explain why the mixture must be acidified so that crystals of benzoic acid appear.

H^+ reacts with $C_6H_5COO^-$:

$H^+ + C_6H_5COO^- \rightarrow C_6H_5COOH$

[1]

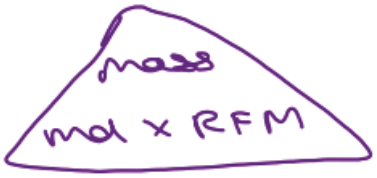
(c) Write the overall equation for the preparation of benzoic acid from phenylmethanol.

Use [O] for the oxidising agent.

$C_6H_5CH_2OH + 2[O] \rightarrow C_6H_5COOH + H_2O$ **[1]**

(d) Calculate the percentage yield of benzoic acid.

Give your answer to **3** significant figures.



$\frac{4 \times 1.04}{((12\times6)+5+12+2+16+1)} = 0.0385$ mol of $C_6H_5CH_2OH$

$\frac{1.59}{((12\times6)+5+12+((16\times2)+1)} = 0.013$ mol of C_6H_5COOH

$\frac{0.013}{0.0385} \times 100 = 33.8\%$ (3sf)

percentage yield = 33.8 % **[3]**

(e) In **Step 3**, describe how the student can recrystallise the impure crystals to obtain pure benzoic acid.

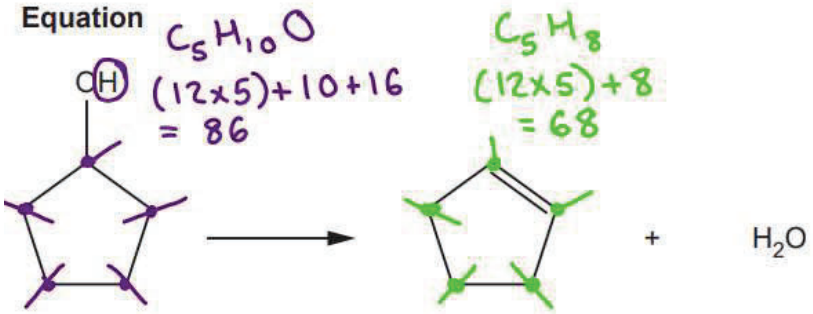
dissolve in a minimal amount of hot solvent. Cool, filter, and leave to dry.

[2]

8. Cyclopentanol can be reacted to form cyclopentene.
Cyclopentene is a liquid with a boiling point of 44 °C and a density of 0.74 g cm^{-3}.
→ temp. to redistill at

A student plans to prepare 4.00 g of cyclopentene by reacting cyclopentanol (boiling point 140 °C) with an acid catalyst.

Equation

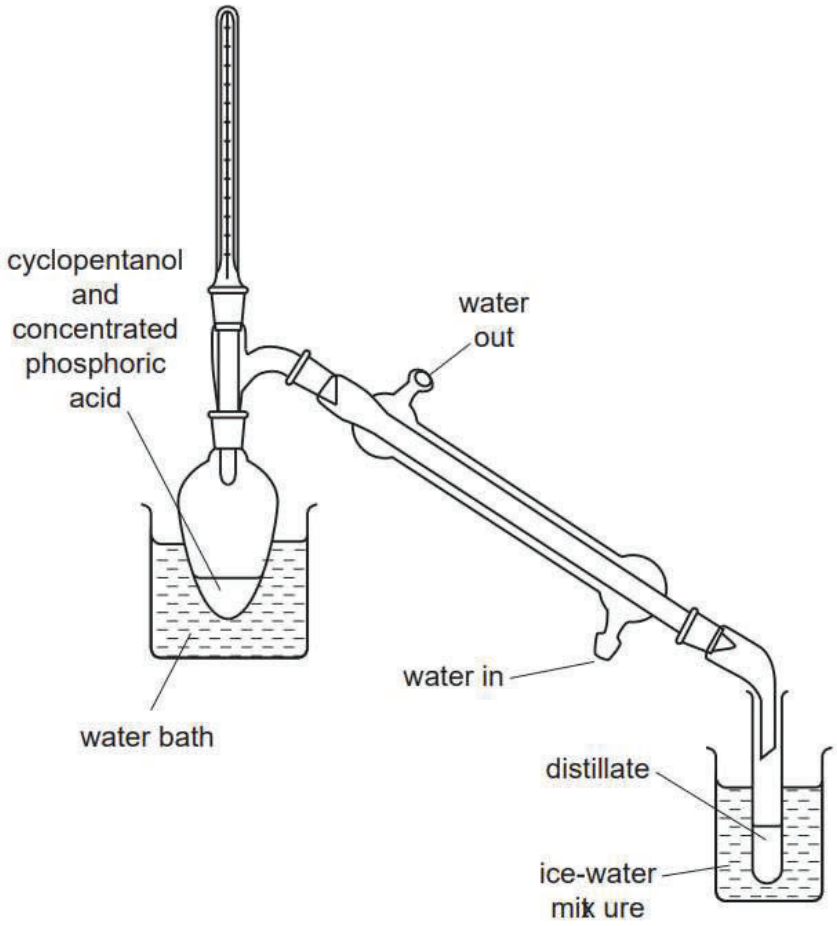


The expected percentage yield of cyclopentene is 64.0%.

Method

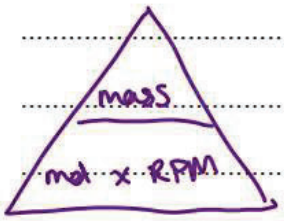
The student carries out the preparation using apparatus set up for distillation, as shown below.

1 The reaction mixture is heated gently, and a distillate containing impure cyclopentene is collected.



2 The distillate has an aqueous layer and an organic layer.
The student purifies the cyclopentene from the distillate.

(a)* Calculate the mass of cyclopentanol that the student should use and explain how pure cyclopentene could be obtained from the distillate. **[6]**



$\frac{4.00}{68} = 0.0588$ mol of cyclopentene

$0.0588 \times \frac{100}{64} = 0.0919$ mol of cyclopentanol

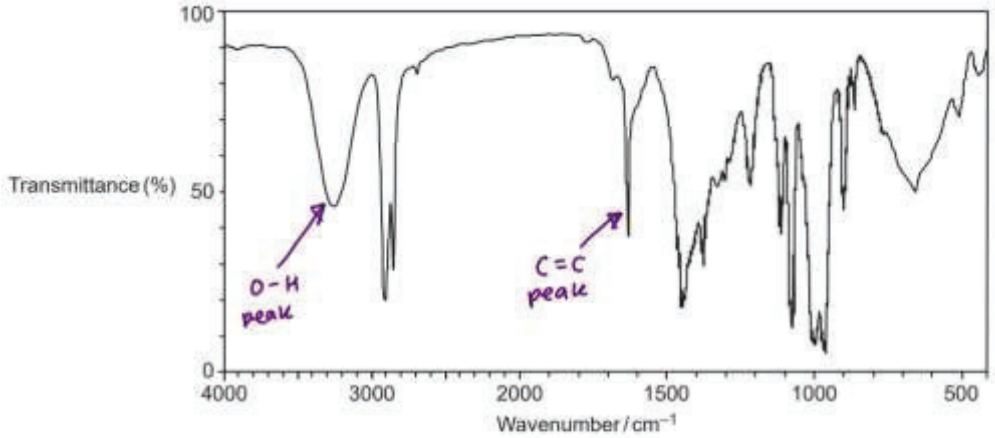
$0.0919 \times 86 = 7.90\text{g}$ (2dp.)

purification:

- Add a neutralising agent such as Na_2CO_3
- In a separating funnel the organic layer is on top (cyclopentene is less dense so on top)
- Drying with anhydrous salt such as, $MgSO_4$ / Na_2SO_4 / $CaCl_2$ (removes traces of water)
- Redistill at approx. 44 °C

Additional answer space if required

(b) The organic layer in the distillate was analysed by IR spectroscopy.
The IR spectrum is shown below.



Explain how the IR spectrum of the organic layer suggests that cyclopentene has been formed and that the reaction is incomplete. ← Same Cyclopentanol and cyclopentene present in IR

O-H / alcohol peak in region 3200 - 3600 cm⁻¹

C=C / alkene peak in region 1620 - 1680 cm⁻¹

.....

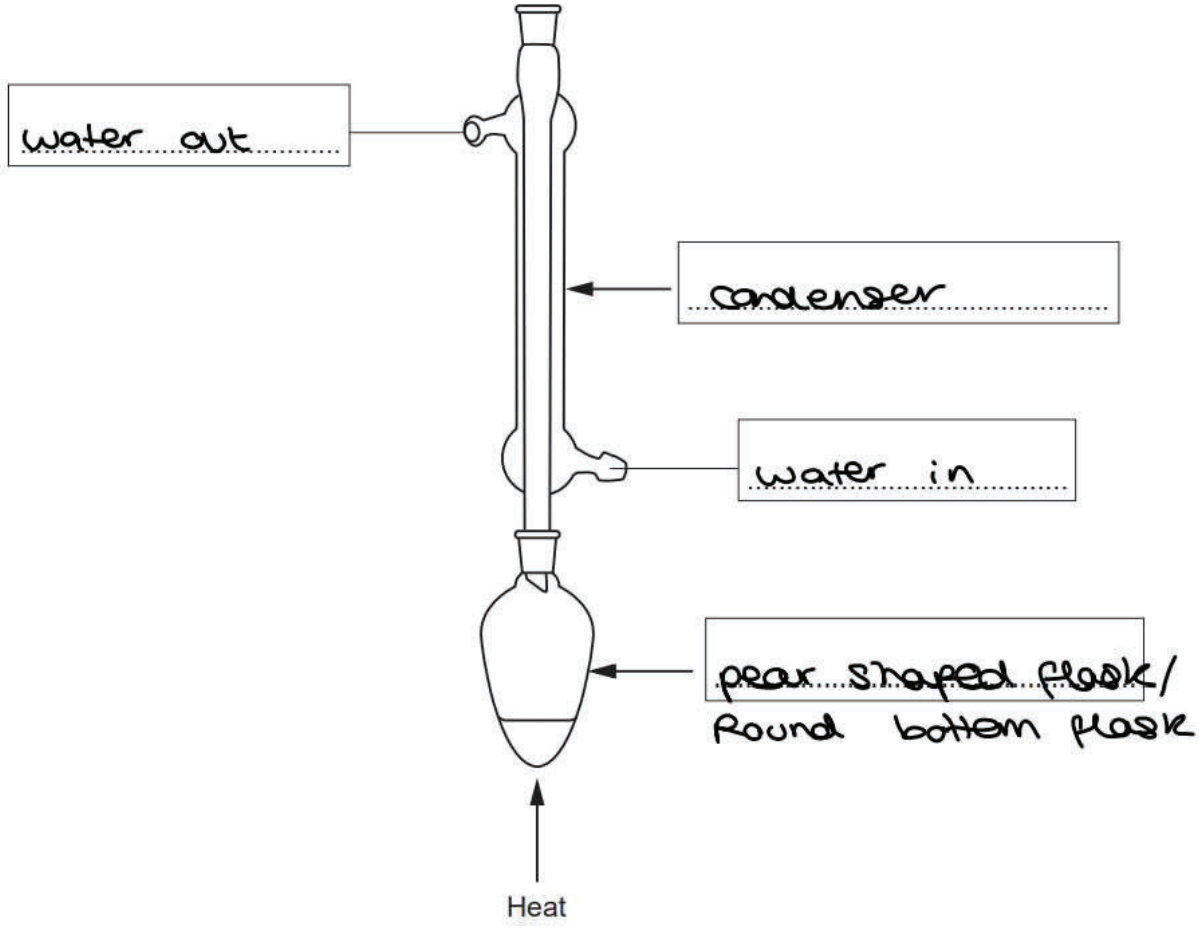
.....

..... [2]

9. This question is about organic chemistry.

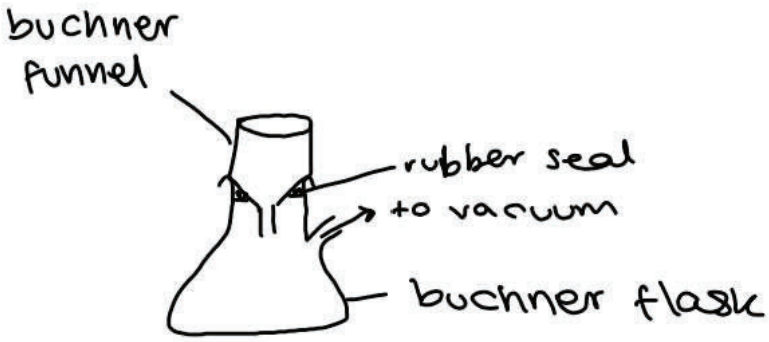
(a) This part is about two practical techniques used in organic preparations.

(i) Complete the missing labels on the diagram and name the technique.



Name of technique: Reflux ..... **[2]**

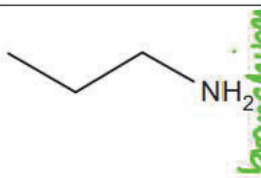
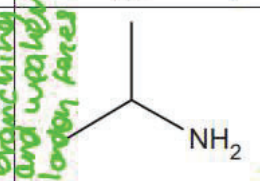
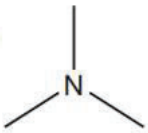
(ii) Draw a labelled diagram to show apparatus set up for filtration under reduced pressure (vacuum filtration).



[2]

(b) This part is about amines.

(i) The table shows the structures and boiling points of three amines, which are structural isomers of C_3H_9N.

Amine	$CH_3CH_2CH_2NH_2$	$(CH_3)_2CHNH_2$	$(CH_3)_3N$
Skeletal formula			
Boiling point/°C	48–49 °C	33–34 °C	3–4 °C

branching and weaker London forces

hydrogen bonds

Explain the difference in the boiling points of the three amines.

NH_2 no branches / longer chain, more points of contact / more surface interactions so stronger induced dipole - dipole interactions (London forces)

non-hindered N lone pairs

$\ddot{N}H_2$ and $\ddot{N}H_2$ can form hydrogen bonds

N can't form H bonds

H bonds are stronger than London forces so more energy is needed to break H bonds. [4]

(ii) Amine **A** is a liquid at room temperature and pressure.

When vaporised, 0.202 g of the amine produces 72.0 cm^3 of gas at 1.00×10^5 Pa and 100 °C. The ^{13}C NMR spectrum of amine **A** has 3 peaks.

Determine the molecular formula of **A** and suggest a possible structure for amine **A**.

$n = \frac{PV}{RT}$

$R = 8.314$

$V = 72 \times 10^{-6}\ m^3$

$T = 373\ K$

$P = 1 \times 10^5\ Pa$

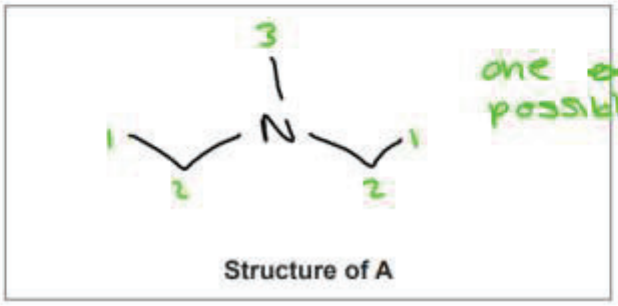
$n = \frac{1 \times 10^5 \times 72 \times 10^{-6}}{8.314 \times 373} = 2.32 \times 10^{-3}\ mol$

$\frac{0.202}{2.32 \times 10^{-3}} = 87$

$C_5H_{13}N$

mass / mol × RFM

Molecular formula of **A** $C_5H_{13}N$



one example of possible structure

Structure of A

[6]

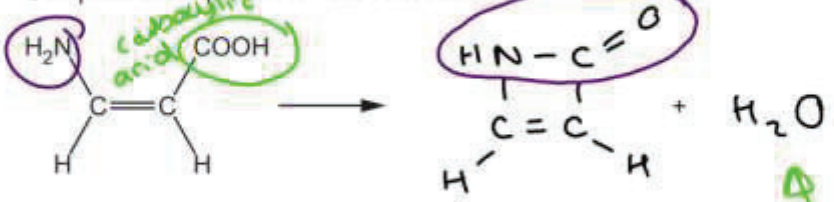
(c) The amino acid Z-$H_2NCH{=}CHCOOH$ can react to form a cyclic compound with the molecular formula C_3H_3NO and one other product.

Complete the equation for this reaction.

amide

amine

carboxylic acid



look at what is missing from reactant

[2]