



Oxford Cambridge and RSA

Tuesday 13 October 2020 – Morning

A Level Chemistry A

H432/02 Synthesis and analytical techniques

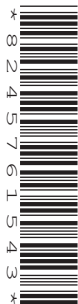
Time allowed: 2 hours 15 minutes

You must have:

- the Data Sheet for Chemistry A

You can use:

- a scientific or graphical calculator
- an HB pencil



Please write clearly in black ink. **Do not write in the barcodes.**

Centre number

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Candidate number

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First name(s)

Last name

StemUp Model Solution

INSTRUCTIONS

- Use black ink. You can use an HB pencil, but only for graphs and diagrams.
- Write your answer to each question in the space provided. If you need extra space use the lined pages at the end of this booklet. The question numbers must be clearly shown.
- Answer **all** the questions.
- Where appropriate, your answer should be supported with working. Marks might be given for using a correct method, even if your answer is wrong.

INFORMATION

- The total mark for this paper is **100**.
- The marks for each question are shown in brackets [].
- Quality of extended response will be assessed in questions marked with an asterisk (*).
- This document has **28** pages.

ADVICE

- Read each question carefully before you start your answer.

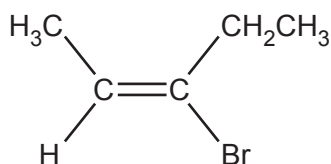
SECTION A

You should spend a maximum of 20 minutes on this section.

Write your answer to each question in the box provided.

Answer **all** the questions.

- 1 What is the name of the compound below?



- A *E*-3-bromopent-2-ene
B *E*-3-bromopent-3-ene
C *Z*-3-bromopent-2-ene
D *Z*-3-bromopent-3-ene

Your answer

A

[1]

- 2 Which statement about bonds is correct?

- A The C=C bond in ethene is more polar than the C–C bond in ethane.
B A σ -bond is stronger than a π -bond.
C The H–C–H bond angle in ethane is greater than the H–C–H bond angle in ethene.
D A σ -bond is formed from sideways overlap of p orbitals.

Your answer

B

[1]

3 Which of these reagent(s) will **not** react with $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{COOH}$?

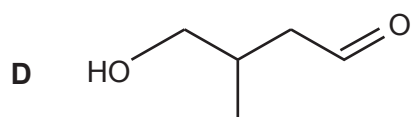
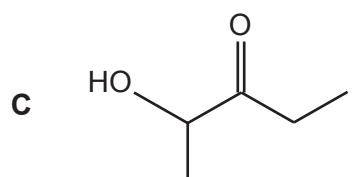
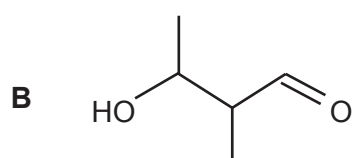
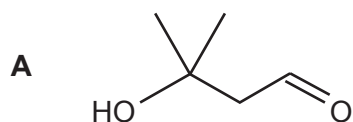
- A NaCN in ethanol
- B $\text{C}_2\text{H}_5\text{OH}$ in the presence of an acid catalyst
- C $(\text{CH}_3\text{CO})_2\text{O}$
- D concentrated H_2SO_4

Your answer

A

[1]

4 Which compound can be refluxed with acidified potassium dichromate(VI) to form an organic product with molecular formula $\text{C}_5\text{H}_8\text{O}_2$?

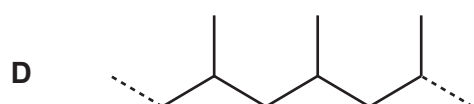
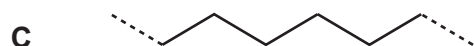
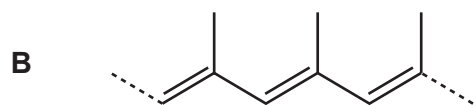


Your answer

C

[1]

5 Which structure shows a section of poly(propene)?



Your answer

D

[1]

6 Which alcohol reacts with an acid catalyst to form a mixture of stereoisomers?

A 3-methylbutan-2-ol

B pentan-1-ol

C 2-methylhexan-2-ol

D heptan-4-ol

Your answer

D

[1]

7 Which one of the following reacts with ethanoic acid **and** with phenol?

A Aqueous potassium hydroxide

B Bromine

C Calcium carbonate

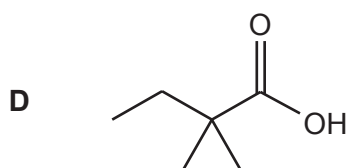
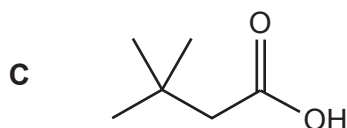
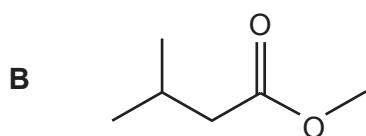
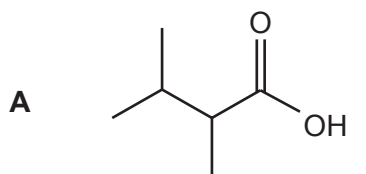
D Methanol and an acid catalyst

Your answer

A

[1]

8 Which isomer of $C_6H_{12}O_2$ produces the smallest number of peaks in its ^{13}C NMR spectrum?

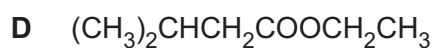
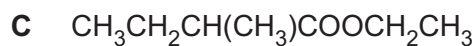


Your answer

C

[1]

9 What is the structural formula of ethyl 3-methylbutanoate?



Your answer

D

[1]

10 What is the number of alicyclic structural isomers of C_5H_{10} ?

A 3

B 4

C 5

D 6

Your answer

C

[1]

- 11 Complete combustion of 1.00 g of a hydrocarbon gives 3.38 g carbon dioxide.

What is the empirical formula of the hydrocarbon?

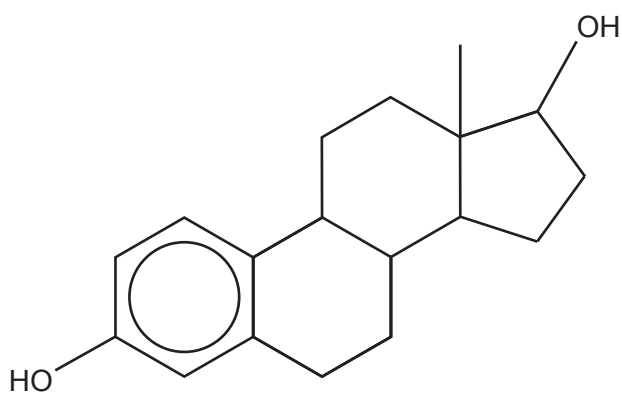
- A CH
- B CH₂
- C C₂H₅
- D C₃H₈

Your answer

A

[1]

- 12 What is the molecular formula of the steroid molecule below?



- A C₁₈H₂₄O₂
- B C₁₈H₂₆O₂
- C C₁₈H₂₈O₂
- D C₁₈H₃₀O₂

Your answer

A

[1]

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

- 1 The components in a mixture can be identified from their retention time.
- 2 The relative peak areas give the proportions of components in a mixture.
- 3 Calibration curves are used to confirm the concentrations of components in a mixture.

- A** 1, 2 and 3
B Only 1 and 2
C Only 2 and 3
D Only 1

Your answer

A

[1]

14 Which of the following reactions produce propan-1-ol?

- 1 The alkaline hydrolysis of 1-chloropropane.
- 2 The acid hydrolysis of propyl methanoate.
- 3 The acid hydrolysis of propanenitrile.

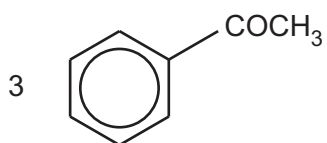
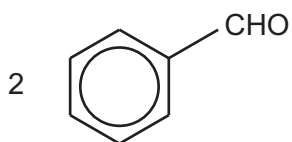
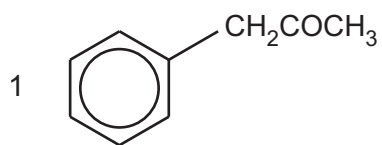
- A** 1, 2 and 3
B Only 1 and 2
C Only 2 and 3
D Only 1

Your answer

B

[1]

- 15 Which compound(s) could be prepared by reacting benzene with an acyl chloride in the presence of a halogen carrier?



- A** 1, 2 and 3
B Only 1 and 2
C Only 2 and 3
D Only 1

Your answer

C

[1]

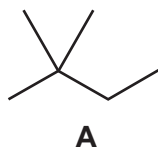
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SECTION B

Answer **all** the questions.

- 16 The structure of hydrocarbon **A** is shown below.



- (a) Hydrocarbon **A** can be reacted with bromine in the presence of ultraviolet radiation to prepare $(\text{CH}_3)_3\text{CCHBrCH}_3$.

What is the systematic name for $(\text{CH}_3)_3\text{CCHBrCH}_3$?

2-bromo-3,3-dimethylbutane [1]

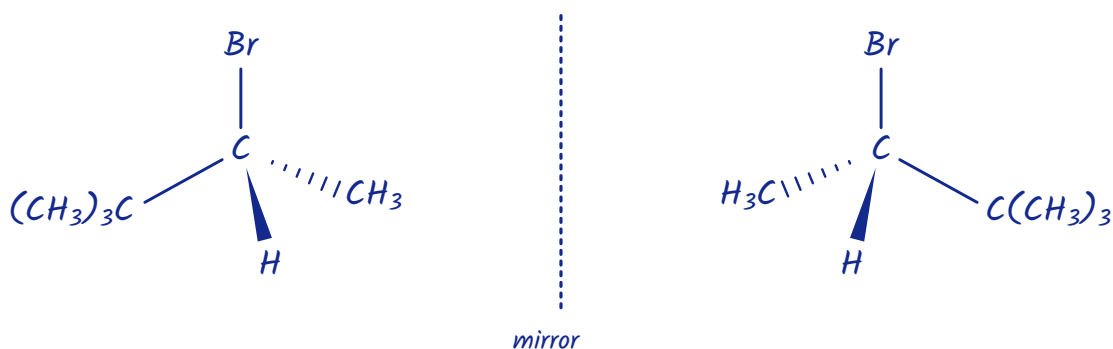
- (b) $(\text{CH}_3)_3\text{CCHBrCH}_3$ has stereoisomers.

- (i) Explain the term stereoisomers and name this type of stereoisomerism.

Explanation: Same structural formula but a different arrangement of the
atoms in space.

Type of stereoisomerism: optical [1]

- (ii) Draw 3D diagrams for the stereoisomers of $(\text{CH}_3)_3\text{CCHBrCH}_3$.

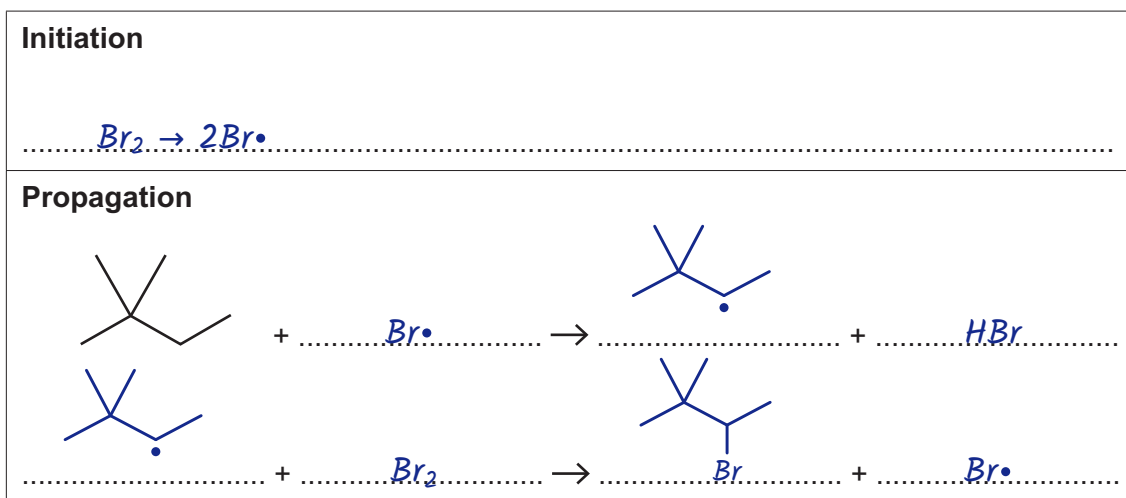


[2]

- (c) Complete the table to show the mechanism for the reaction of hydrocarbon **A** with Br_2 to form $(\text{CH}_3)_3\text{CCHBrCH}_3$.

Use skeletal formulae for all organic compounds.

Use 'dots' (•) to show the position of unpaired electrons.



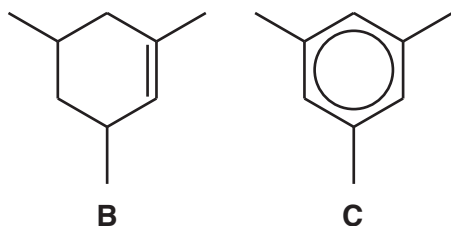
[3]

- (d) State **two** limitations of using radical substitution in organic synthesis.

- 1 Further substitution occurs: more than one H atom is replaced, so a mixture of dibromo and multibromo products forms.
- 2 Substitution can occur at different positions along the chain (H atoms on other carbon atoms are replaced).

[2]

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



- (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.

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 π -bond electrons are localised between the two carbon atoms of the C=C bond.

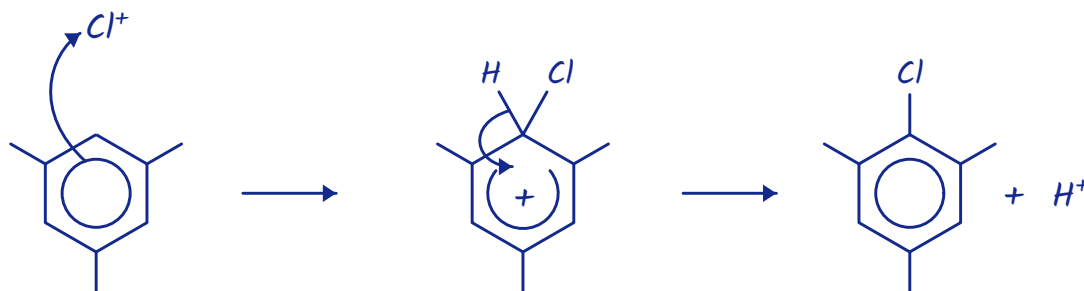
In C, the π -electrons are delocalised around the ring (delocalised π -system), which is more stable.

So B has a higher electron density in its C=C bond than C. B can polarise Cl_2 more and is more susceptible to electrophilic attack, so C is more resistant and needs a halogen carrier.

[3]

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

Show the role of the halogen carrier.



AlCl_3 (the halogen carrier) accepts a lone pair from Cl_2 to generate the Cl^+ electrophile and is regenerated at the end, so it acts as a catalyst.

Mechanism: electrophilic substitution.

[5]

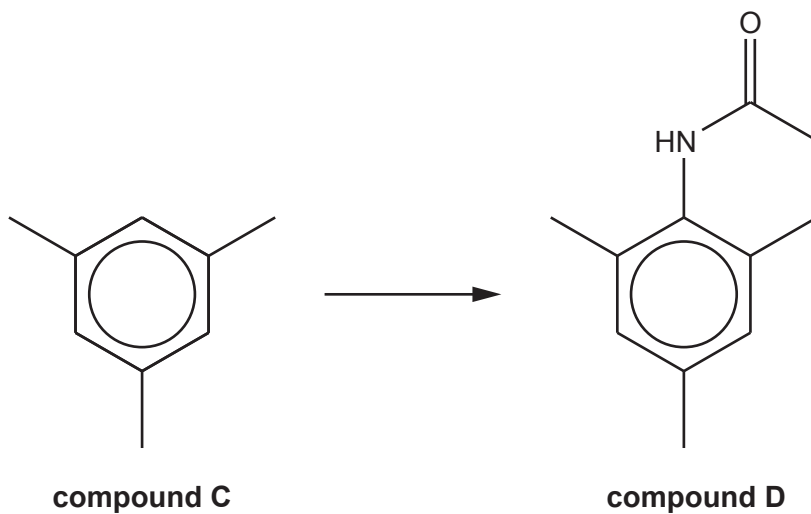
(b) Compound **C** can be prepared by 'trimerisation' of propanone using concentrated sulfuric acid as a catalyst.

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



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

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



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

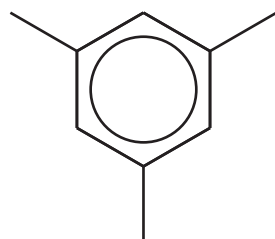
	Compound C	Compound D
Number of peaks	3.....	8.....

[2]

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

Complete the flowchart.

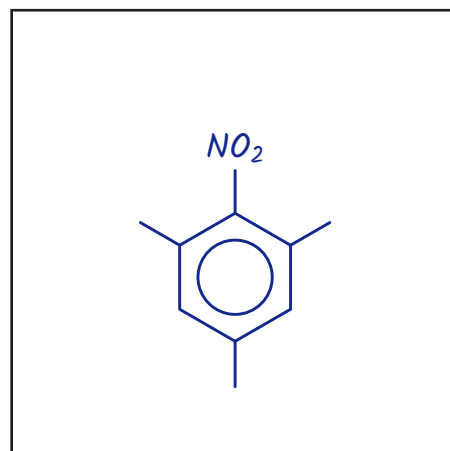
Show structures for organic compounds.



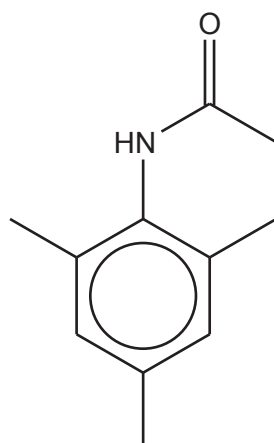
compound **C**

reagent: ...*conc. HNO₃*.....

catalyst: ...*conc. H₂SO₄*.....

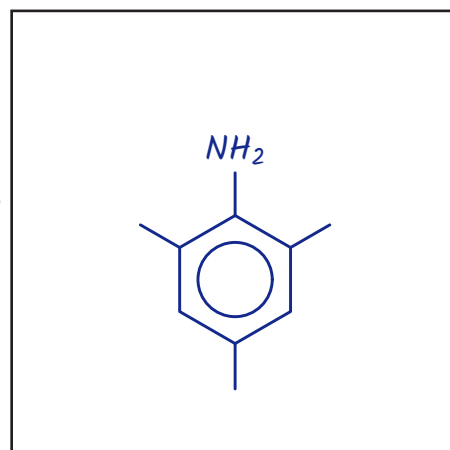


1. Sn + HCl
2. Neutralise



compound **D**

reagent: ...*CH₃COCl*.....



[5]

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

(a) $\text{HO}(\text{CH}_2)_4\text{OH}$ can be oxidised to form $\text{HOOC}(\text{CH}_2)_2\text{COOH}$.

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

In the equation, use $[\text{O}]$ for the oxidising agent.

Reagents and conditions: $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 (acidified dichromate)

heat under reflux

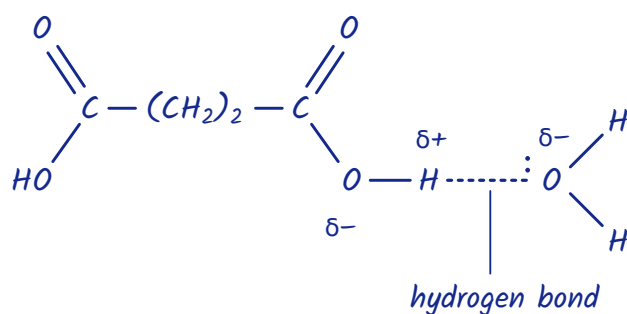
Equation:



[3]

(ii) $\text{HOOC}(\text{CH}_2)_2\text{COOH}$ is soluble in water.

Explain, using a labelled diagram, why $\text{HOOC}(\text{CH}_2)_2\text{COOH}$ is soluble in water.



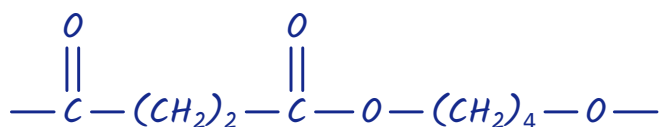
The δ^+ H of each O-H group forms a hydrogen bond with a lone pair on the δ^- O atom of a water molecule, so $\text{HOOC}(\text{CH}_2)_2\text{COOH}$ dissolves in water.

[2]

(b) $\text{HOOC}(\text{CH}_2)_2\text{COOH}$ and $\text{HO}(\text{CH}_2)_4\text{OH}$ react together to form polymer **E**.

(i) Draw **one** repeat unit of polymer **E**.

The functional groups should be clearly displayed.



[2]

(ii) Governments are encouraging the development of biodegradable polymers to reduce dependency on persistent plastic waste derived from fossil fuels.

Polymer **E** is a biodegradable polymer.

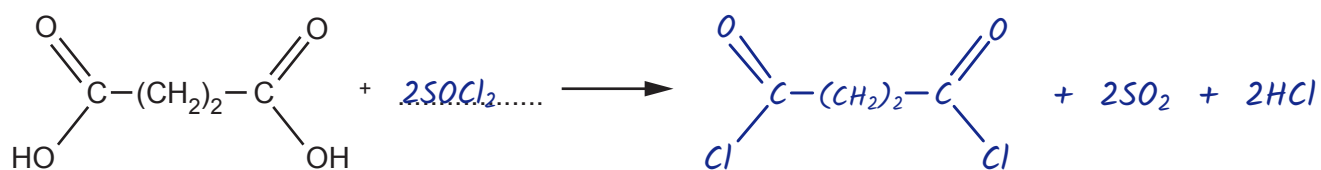
Suggest why polymer **E** is able to biodegrade.

The ester bonds in polymer E can be hydrolysed (broken down), so the polymer breaks down. [1]

(iii) A large yield of polymer **E** can be obtained by reacting a diacyl dichloride with $\text{HO}(\text{CH}_2)_4\text{OH}$.

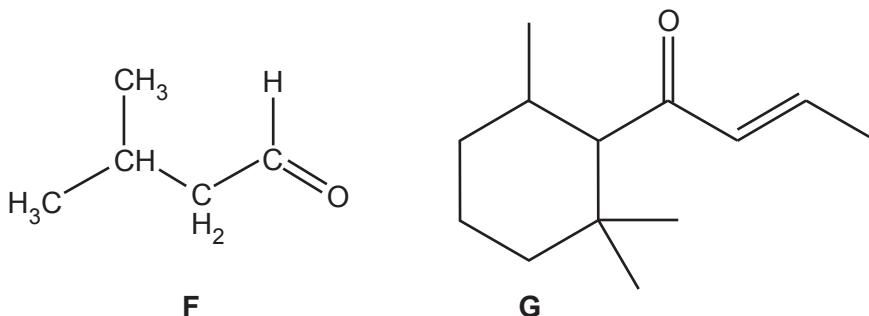
The diacyl dichloride is prepared from $\text{HOOC}(\text{CH}_2)_2\text{COOH}$.

Complete the equation for the formation of a diacyl dichloride from $\text{HOOC}(\text{CH}_2)_2\text{COOH}$.



[3]

19 The carbonyl compounds, **F** and **G**, shown below, contribute to the flavour of coffee.



(a) Compound **F** is a member of a homologous series.

(i) Explain the term homologous series.

A series of organic compounds with the same functional group (similar chemical reactions), in which each successive member differs by CH_2 .

[2]

(ii) Predict the molecular formula for the member of this homologous series containing 24 carbon atoms.

$\text{C}_{24}\text{H}_{48}\text{O}$

[1]

(b) Describe suitable chemical tests, with observations, that would confirm the presence of the functional groups in **F** and **G**.

F (aldehyde): add Tollens' reagent (ammoniacal silver nitrate) and warm: a silver mirror forms.

G (alkene, $\text{C}=\text{C}$): add bromine water: it is decolourised (orange to colourless).

G (ketone, $\text{C}=\text{O}$): add 2,4-dinitrophenylhydrazine (2,4-DNP): an orange precipitate forms.

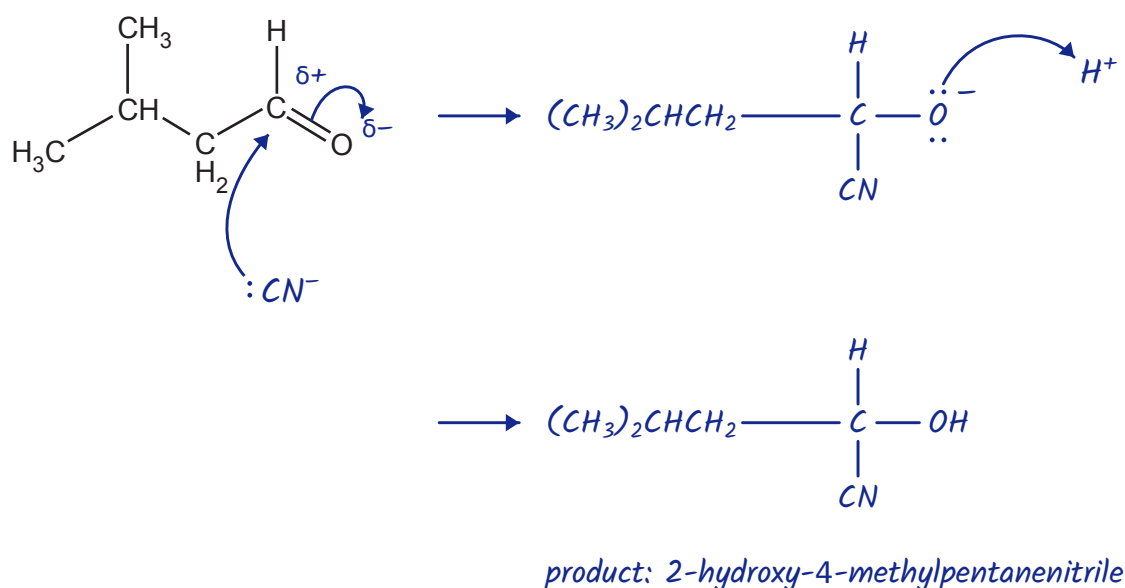
G with Tollens' reagent: no silver mirror (no change), so G is a ketone, not an aldehyde.

[4]

(c) Compound **F** reacts with HCN using NaCN(aq) and H⁺(aq).

- (i) Outline the mechanism for the reaction of **F** with NaCN(aq) and H⁺(aq) and state the name of the mechanism. The structure of **F** has been provided.

Include relevant dipoles, lone pairs and the structure of the organic product.



Name of mechanism: nucleophilic addition [5]

- (ii) Explain why the mechanism in (c)(i) involves heterolytic fission.

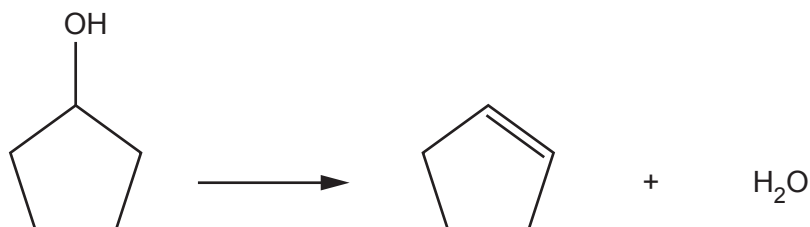
The π -bond of $\text{C}=\text{O}$ breaks by heterolytic fission: one bonded atom,
the O atom, receives both electrons of the covalent bond, forming O^- .

[2]

- 20 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.

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

Equation

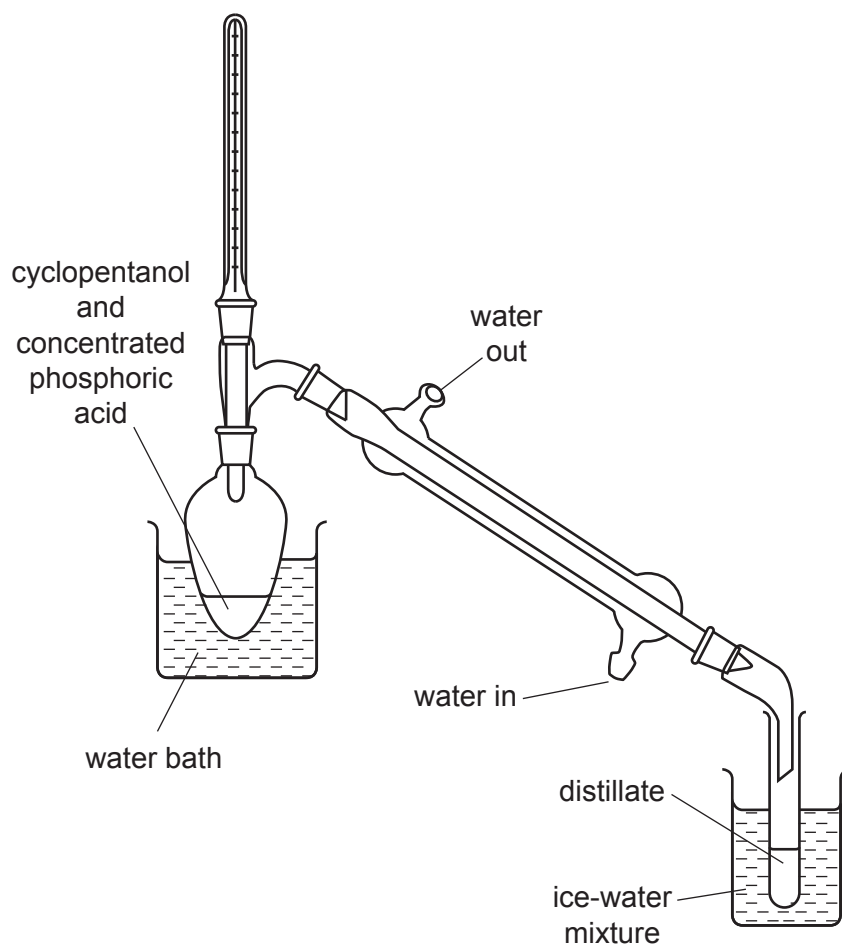


The expected percentage yield of cyclopentene is 64.0%.

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]

Mass of cyclopentanol: $M_r(\text{cyclopentene}, \text{C}_5\text{H}_8) = 68.0$ and $M_r(\text{cyclopentanol}, \text{C}_5\text{H}_9\text{OH}) = 86.0$

$n(\text{cyclopentene}) \text{ needed} = 4.00 \div 68.0 = 0.0588 \text{ mol}$

The yield is 64.0%, so $n(\text{cyclopentanol}) = 0.0588 \times 100 \div 64.0 = 0.0919 \text{ mol}$

Mass of cyclopentanol = $0.0919 \times 86.0 = 7.90 \text{ g}$

Purification: pour the distillate into a separating funnel and add aqueous sodium carbonate, $\text{Na}_2\text{CO}_3(\text{aq})$, to neutralise any acid (releasing the CO_2 pressure).

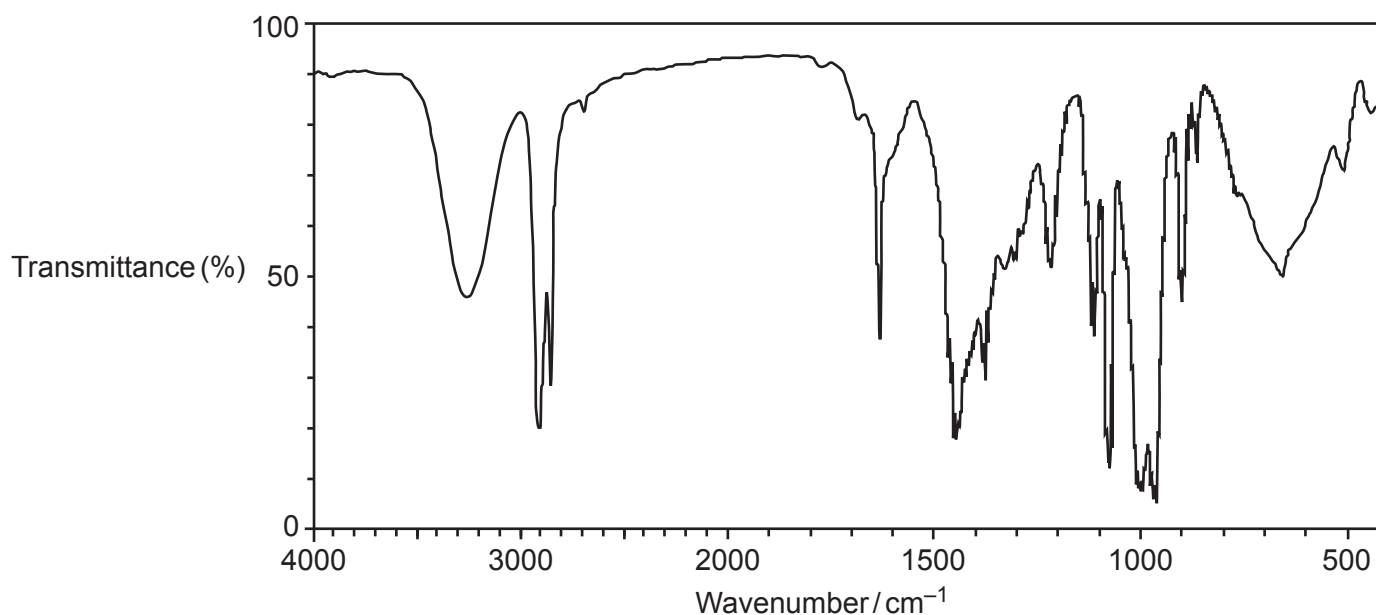
Shake and allow the layers to separate. Cyclopentene (density 0.74 g cm^{-3}) is less dense than water, so the organic layer is on top; run off and discard the lower aqueous layer.

Transfer the organic layer to a dry flask and add an anhydrous salt as a drying agent, e.g. anhydrous MgSO_4 or CaCl_2 , and swirl until the liquid is clear. Decant or filter off the drying agent.

Additional answer space if required

Redistil the dried liquid and collect the pure cyclopentene that distils at about 44°C (its boiling point).

- (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.

The absorption at about 1650 cm^{-1} ($1620\text{ to }1680\text{ cm}^{-1}$) is due to the $\text{C}=\text{C}$ bond of an alkene, so cyclopentene has formed.

The broad absorption at about 3300 cm^{-1} ($3200\text{ to }3600\text{ cm}^{-1}$) is due to the O-H of an alcohol, so cyclopentanol is still present and the reaction is incomplete.

[2]

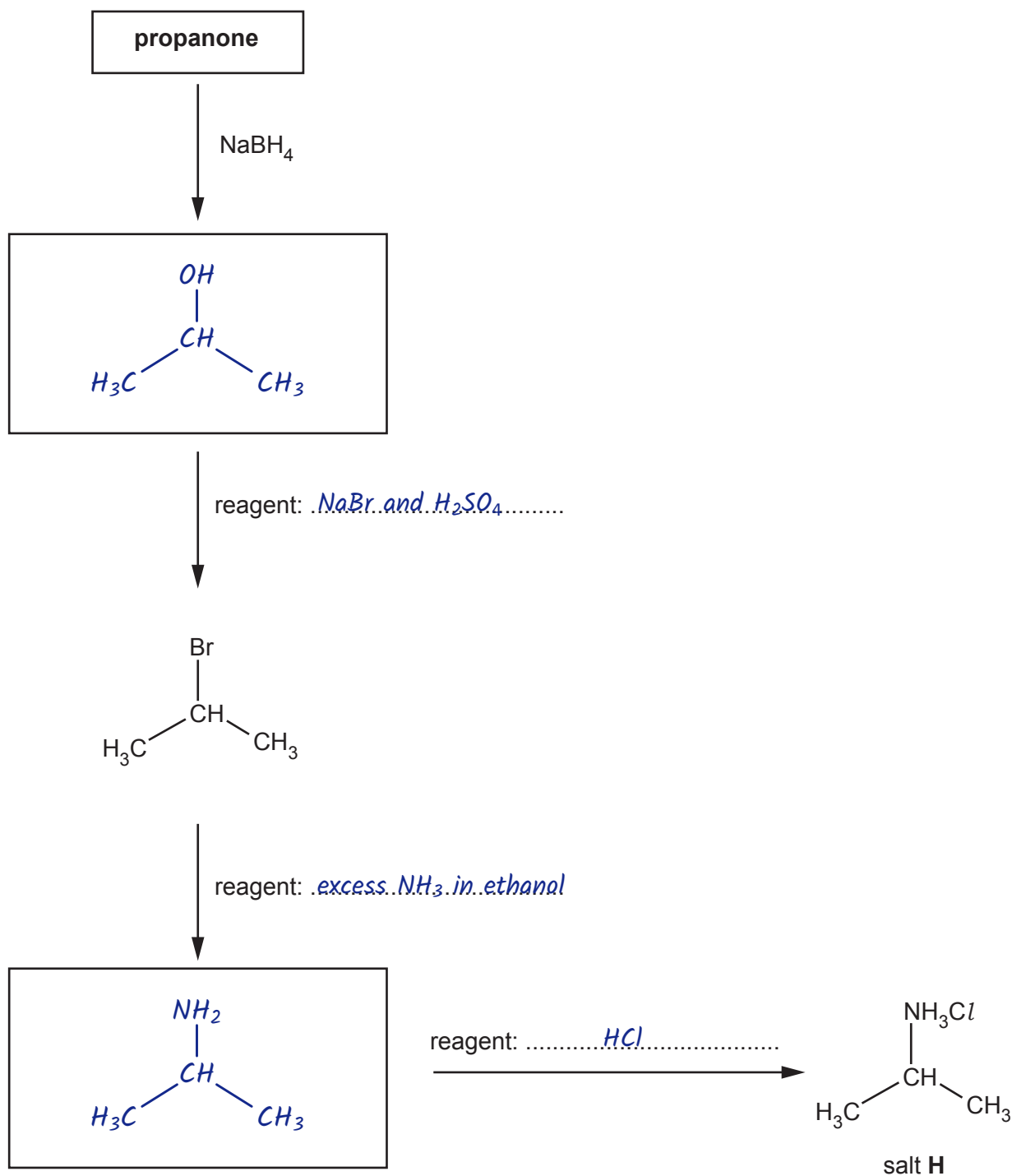
21 This question is about organic compounds containing nitrogen.

(a) Salt **H**, $(\text{CH}_3)_2\text{CHNH}_3\text{Cl}$, is used in the manufacture of garden weedkillers.

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

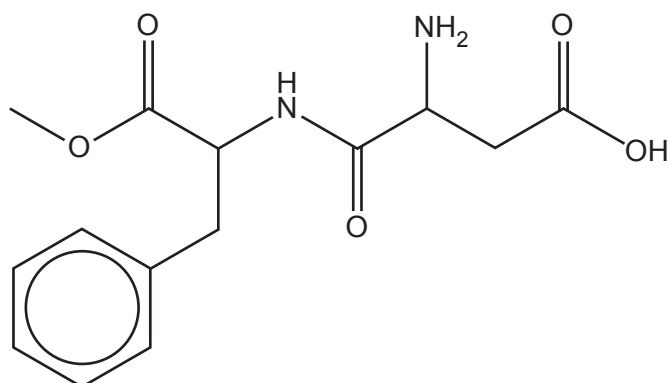
Complete the flowchart.

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

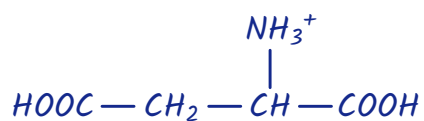
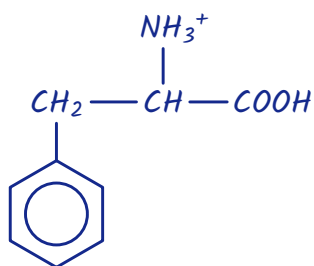
amine

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** of aspartame.



[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 $1.7 \times 10^{-4} \text{ mol kg}^{-1}$.

- 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?

$$M_r(C_{14}H_{18}N_2O_5) = 294.0$$

$$n(\text{aspartame}) \text{ in one can} = 0.167 \div 294.0 = 5.68 \times 10^{-4} \text{ mol}$$

$$\text{maximum } n(\text{aspartame}) \text{ per day} = 1.7 \times 10^{-4} \times 75 = 1.275 \times 10^{-2} \text{ mol}$$

$$\text{number of cans} = 1.275 \times 10^{-2} \div 5.68 \times 10^{-4} = 22.4$$

Number of cans = ...22.4 (22 whole cans)..... [3]

- 22 An organic compound **I** is analysed, using a combination of techniques. The analytical data is shown below.

Elemental analysis by mass

C, 56.69%; H, 7.09%; N, 11.02%; O, 25.20%

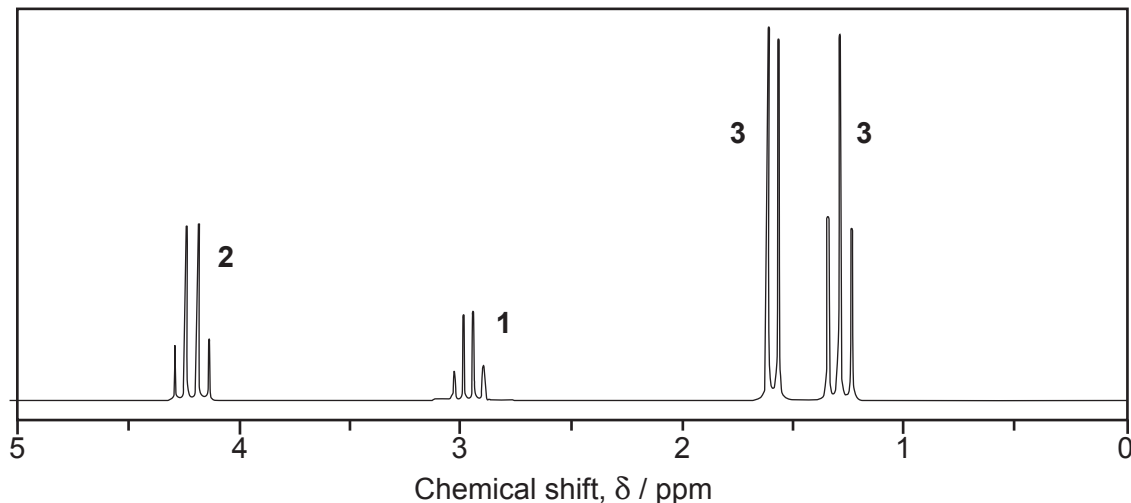
Mass spectrum

Molecular ion peak at $m/z = 127.0$

IR spectrum

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Proton NMR spectrum



- (a) Explain the use of two deuterated compounds in NMR spectroscopy.

CDCl₃ is used as the solvent: it has no ¹H atoms, so it gives no peak in the proton NMR spectrum.

D₂O is added to identify O-H or N-H protons: they exchange with D, so their peak disappears.

[2]

(b)* Determine the structure of compound **I**, showing **all** your reasoning.

[6]

$C : H : N : O = 56.69/12.0 : 7.09/1.0 : 11.02/14.0 : 25.20/16.0 = 4.72 :$

$7.09 : 0.787 : 1.575 = 6 : 9 : 1 : 2$, so the empirical formula is $C_6H_9NO_2$

(mass 127.0).

The molecular ion peak at $m/z = 127.0$ equals the empirical formula mass,

so the molecular formula is $C_6H_9NO_2$.

IR: the absorption at about 1750 cm^{-1} is $C=O$ (ester) and the absorption

at about 2280 cm^{-1} is $C\equiv N$ (nitrile).

Proton NMR: 4 environments, ratio 2 : 1 : 3 : 3.

$\delta = 4.2\text{ ppm}$, quartet, 2H: $O-CH_2-CH_3$, a CH_2 next to the ester O and next to a CH_3 .

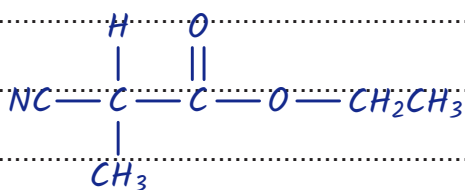
$\delta = 2.9\text{ ppm}$, quartet, 1H: $CO-CH(CN)-CH_3$, a CH next to a CH_3 .

$\delta = 1.6\text{ ppm}$, doublet, 3H: CH_3 next to the CH ($CH-CH_3$).

$\delta = 1.3\text{ ppm}$, triplet, 3H: CH_3 next to the CH_2 (CH_2-CH_3).

So **I** is ethyl 2-cyanopropionate, $CH_3CH(CN)COOCH_2CH_3$.

Additional answer space if required



END OF QUESTION PAPER

[illegible]

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