OCR
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

8245761543

H432/02

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

Centre number | | | | | | Candidate number | | | | |

First name(s) _____

Last name _____

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.

2

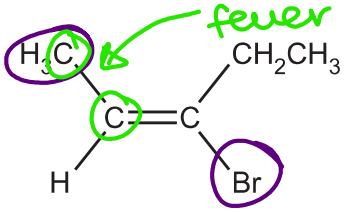
SECTION A

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?



fewer C's before C=C
Highest priority groups on opposite sides of C=C
E

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 [–]

[1]

2 Which statement about bonds is correct?

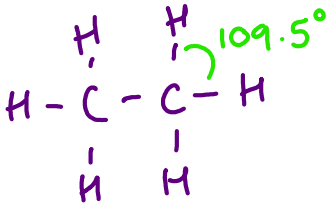
A The C=C bond in ethene is ~~more~~ less polar than the C−C bond in ethane.

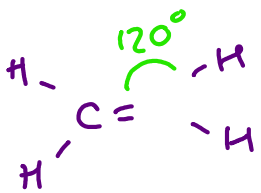
B A σ-bond is stronger than a π-bond. ✓ greater + stronger lateral overlap

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~~ direct overlap of p orbitals.

Your answer [B]





120° > 109.5°

[1]

3 Which of these reagent(s) will **not** react with $HOCH_2CH_2CH_2COOH$?

A NaCN in ethanol

B C_2H_5OH in the presence of an acid catalyst

C $(CH_3CO)_2O$

D concentrated H_2SO_4

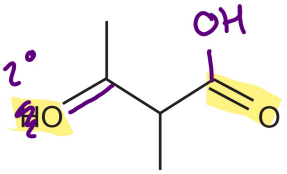
Your answer A

[1]

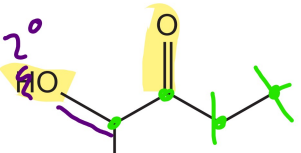
4 Which compound can be refluxed with acidified potassium dichromate(VI) to form an organic product with molecular formula $C_5H_8O_2$?

A

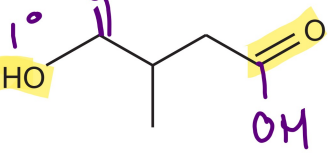
B



C



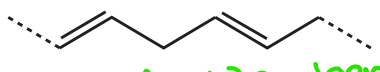
D



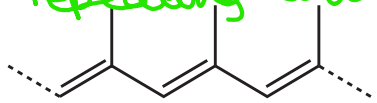
Your answer C

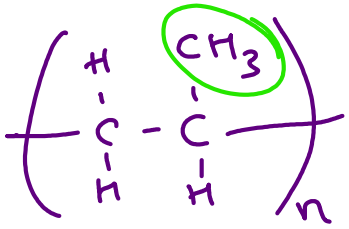
[1]

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

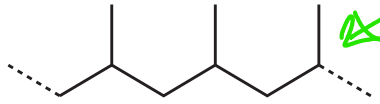
A 

no double bond in repeating unit

B 



C 

D 

CH_3 Side chain

Your answer D

[1]

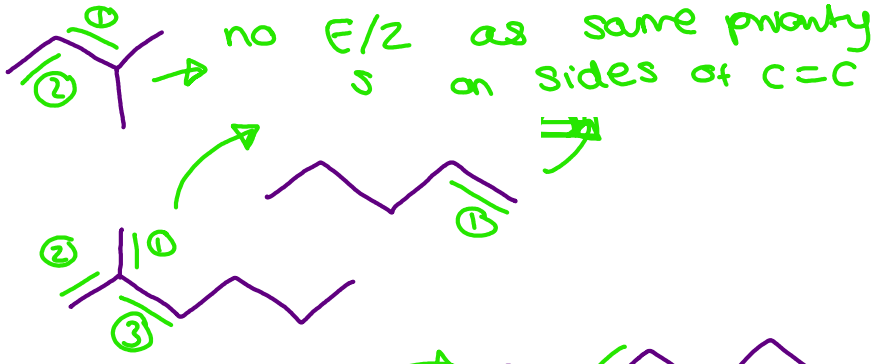
6 Which alcohol reacts with an acid catalyst to form a mixture of stereoisomers?

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?

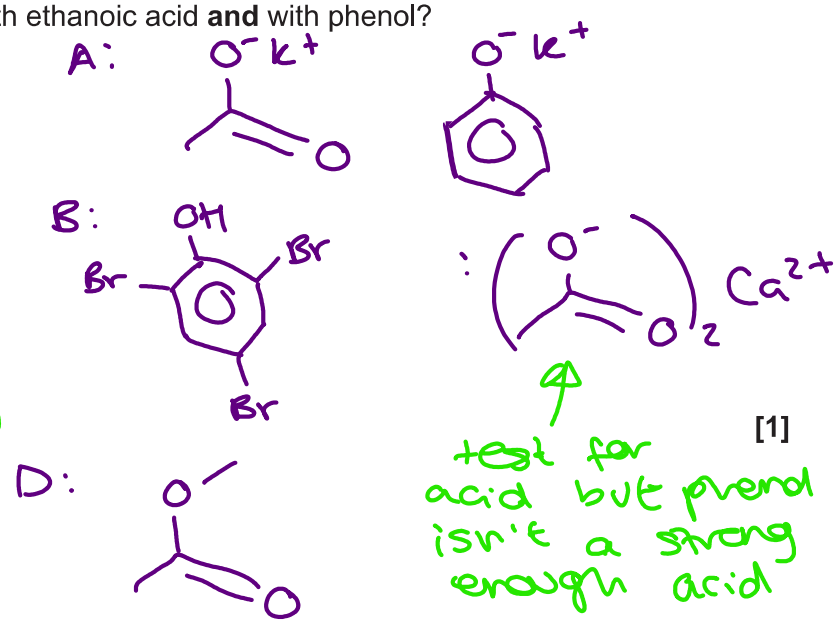
A Aqueous potassium hydroxide

B Bromine only reacts with phenol

C Calcium carbonate only reacts with CH_3COOH

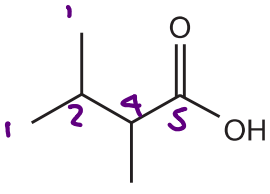
D Methanol and an acid catalyst only reacts with ethanoic acid (CH_3COOH)

Your answer A

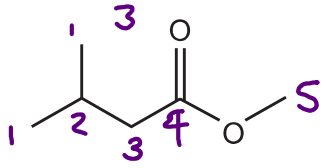


[1]

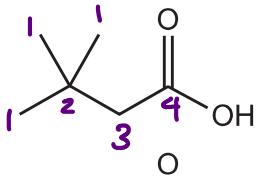
8 Which isomer of $C_6H_{12}O_2$ produces the smallest number of peaks in its ^{13}C NMR spectrum?

A 

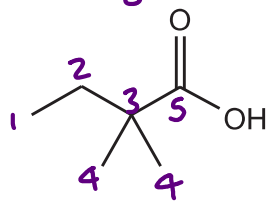
5 peaks

B 

5 peaks

C 

4 peaks

D 

5 peaks

Your answer C

[1]

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

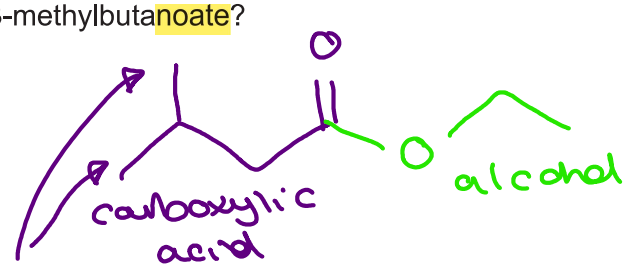
ester

A $CH_3CH_2COOCH_2CH_2CH(CH_3)_2$

B $CH_3CH_2COOCH(CH_3)CH_2CH_3$

C $CH_3CH_2CH(CH_3)COOCH_2CH_3$

D $(CH_3)_2CHCH_2COOCH_2CH_3$



2 CH_3 groups at beginning

Your answer D

[1]

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

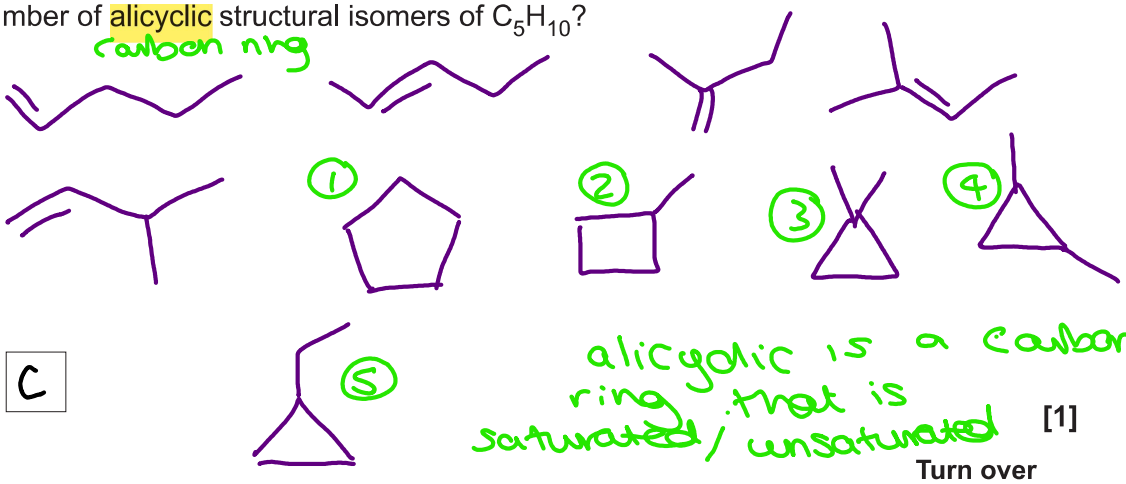
carbon ring

A 3

B 4

C 5

D 6



Your answer C

alicyclic is a carbon ring that is saturated / unsaturated

[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 CH_2

C C_2H_5

D C_3H_8

$\frac{3.38}{12+(16\times2)} = 0.0768$ mol of CO_2

mass / mol × RFM

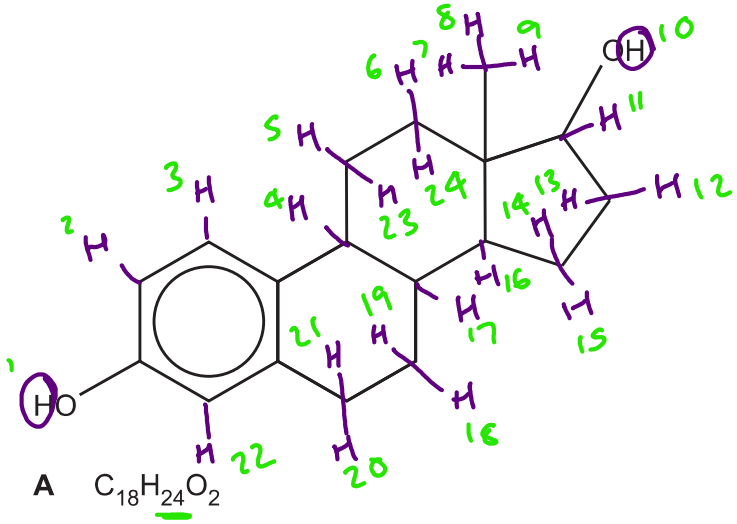
$\frac{1}{0.0768} = 13$ = RFM of hydrocarbon

$13 - 12 = 1$ ∴ CH

Your answer A

[1]

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



A $C_{18}H_{24}O_2$

B $C_{18}H_{26}O_2$

C $C_{18}H_{28}O_2$

D $C_{18}H_{30}O_2$

only H changes

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. ✓
similar to R_f values in TLC

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

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

A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer [A]

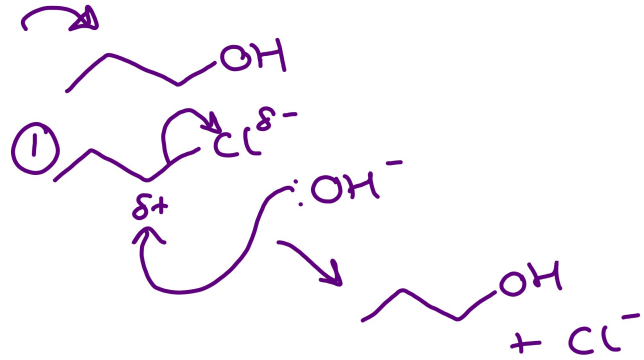
[1]

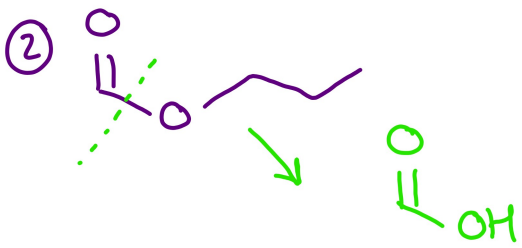
14 Which of the following reactions produce propan-1-ol?

✓ 1 The alkaline hydrolysis of 1-chloropropane.

✓ 2 The acid hydrolysis of propyl methanoate.

~~3~~ The acid hydrolysis of propanenitrile.





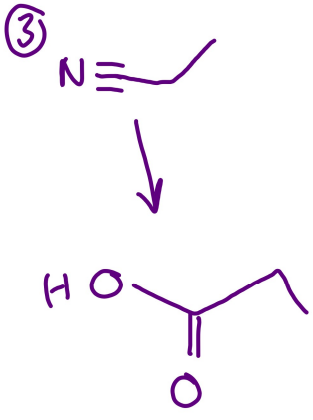
A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

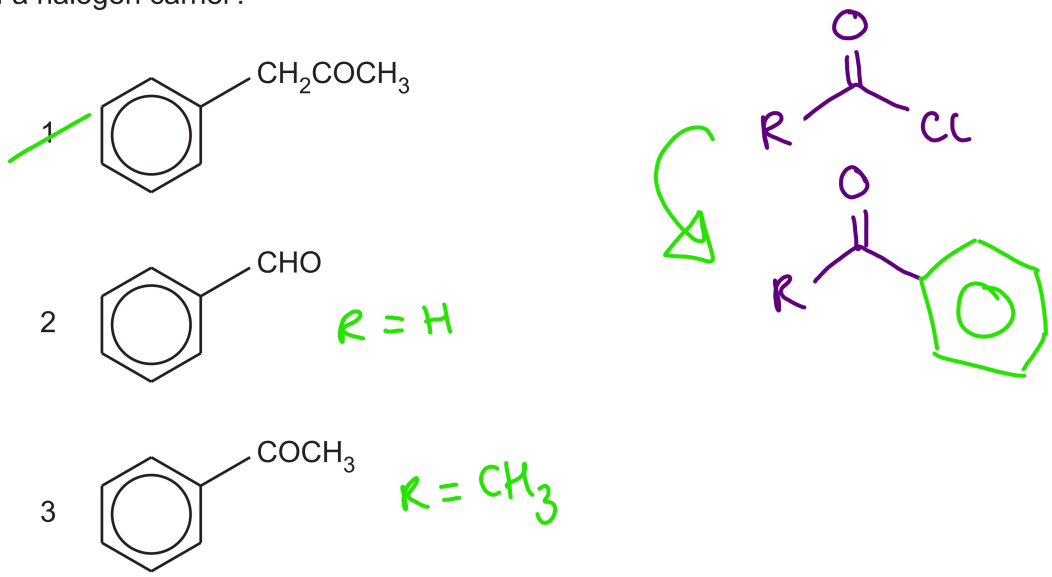
D Only 1

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

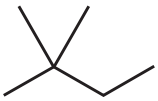
Your answer C

[1]

SECTION B

Answer **all** the questions.

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



A

(a) Hydrocarbon **A** can be reacted with bromine in the presence of ultraviolet radiation to prepare $(CH_3)_3CCHBrCH_3$.

What is the systematic name for $(CH_3)_3CCHBrCH_3$?

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

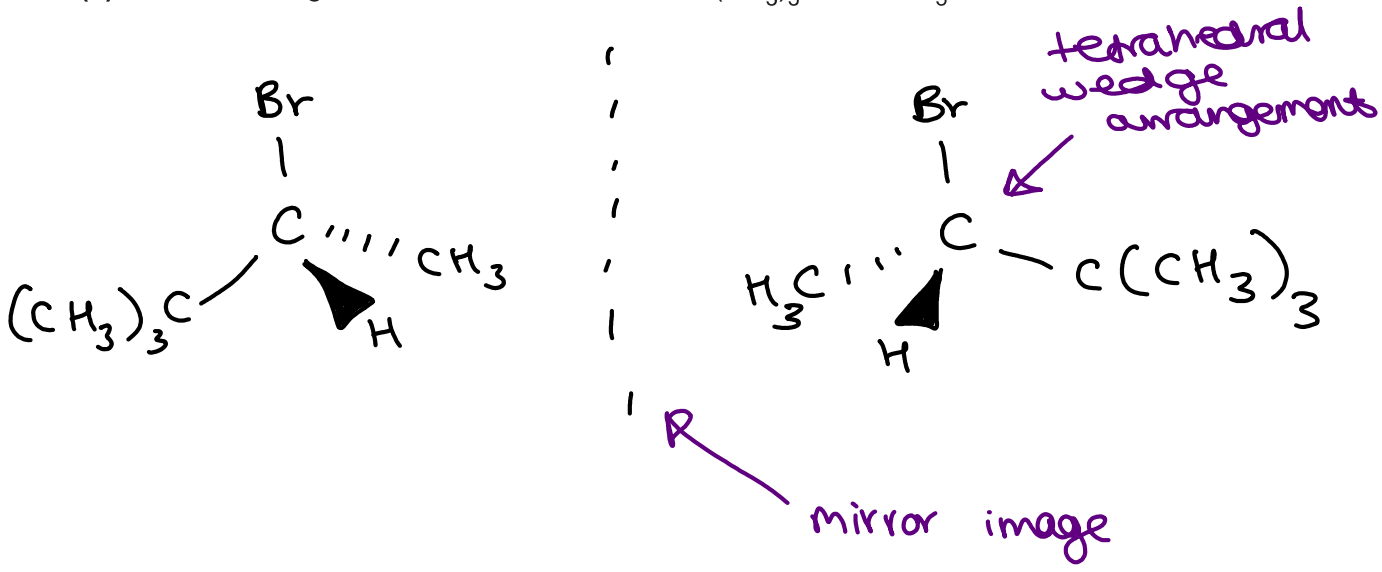
(b) $(CH_3)_3CCHBrCH_3$ has stereoisomers.

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

Explanation: Same structural formula but a different spatial arrangement of atoms .....

Type of stereoisomerism: optical ..... **[1]**

(ii) Draw 3D diagrams for the stereoisomers of $(CH_3)_3CCHBrCH_3$.



[2]

11

(c) Complete the table to show the mechanism for the reaction of hydrocarbon **A** with Br_2 to form $(CH_3)_3CCHBrCH_3$.

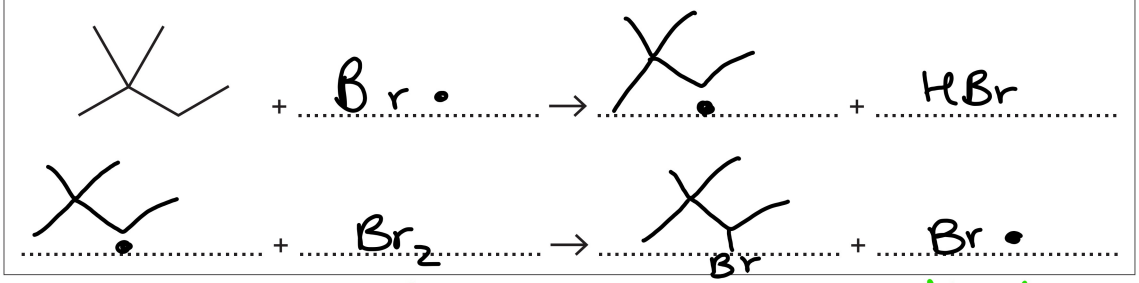
free - radical substitution common example with Cl_2

Use skeletal formulae for all organic compounds.
Use 'dots' (•) to show the position of unpaired electrons.

Initiation

$Br_2 \xrightarrow{UV} 2Br\bullet$

Propagation



Termination: 2 radicals → a non-radical

[3]

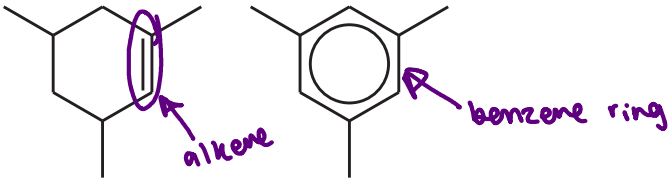
(d) State **two** limitations of using radical substitution in organic synthesis.

1 further substitution(s) / produces different termination products / more than one termination step / mixture of products formed.

2 substitution at different positions along chain

[2]

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

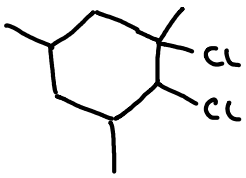
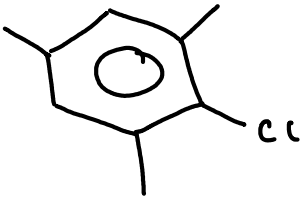


B **C**

(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]

13

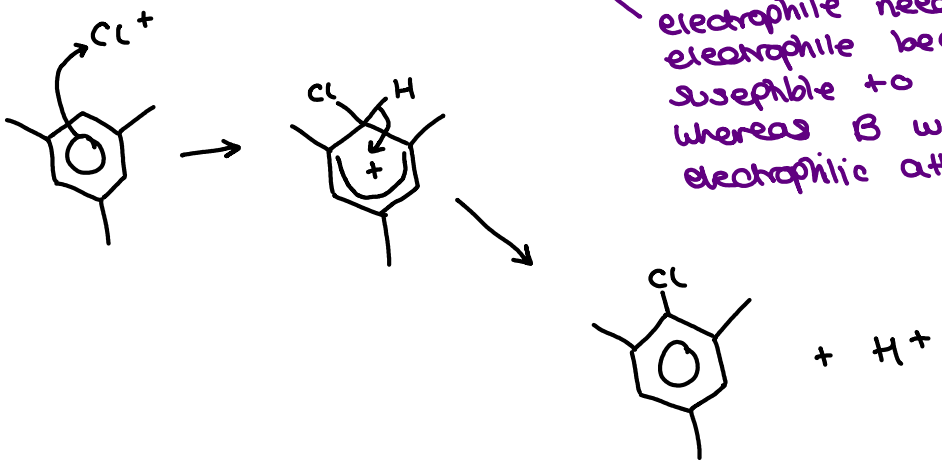
(iii) Outline the mechanism for the reaction of compound **C** with chlorine.

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 $Cl^{\delta+}$



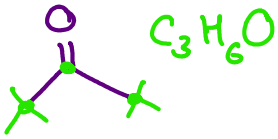
$H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl$

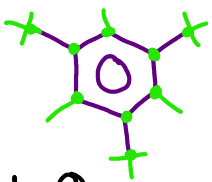
regenerating halogen carrier

[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.





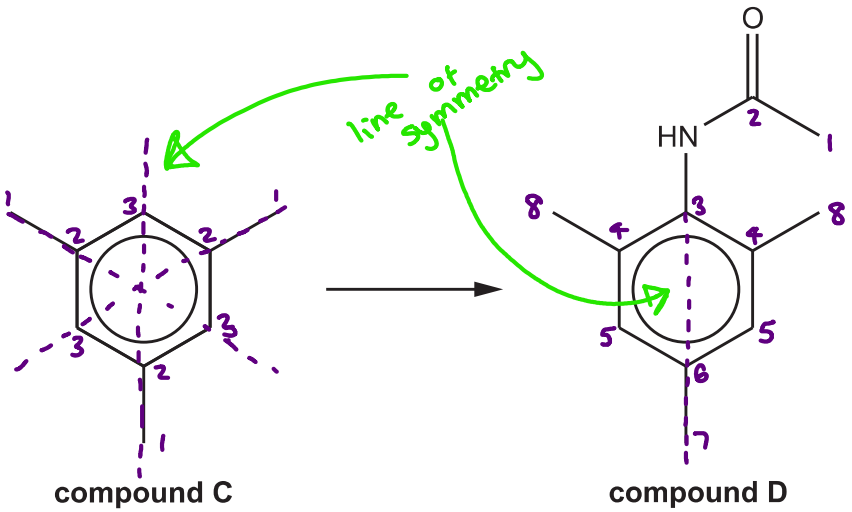
C_9H_{12}

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**.



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

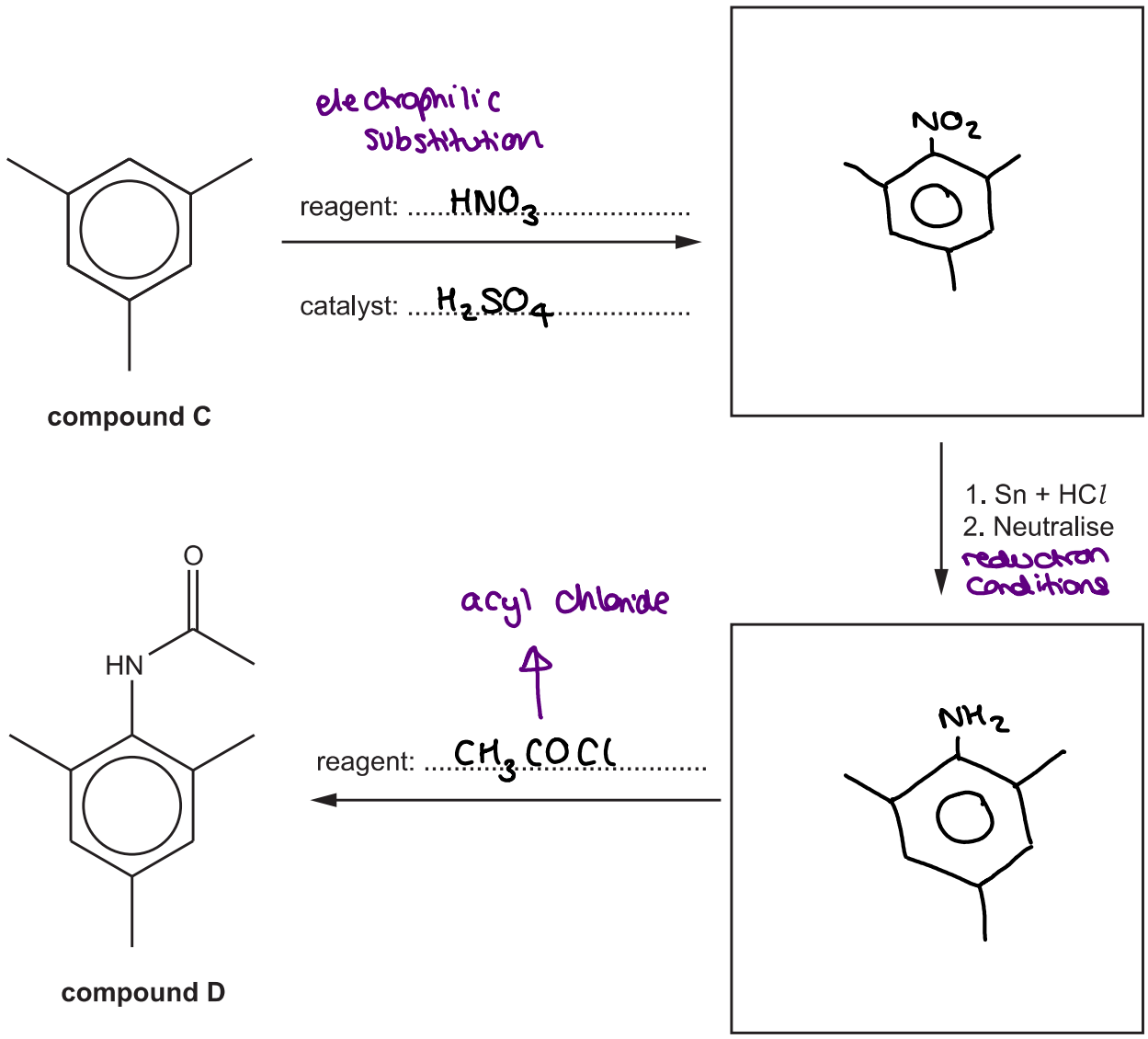
	Compound **C**	Compound **D**
Number of peaks	3	8

[2]

15

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

Complete the flowchart.
Show structures for organic compounds.



compound C

compound D

[5]

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

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

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

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

Reagents and conditions: $K_2Cr_2O_7$, H^+ (acidified) and reflux distillation would form an aldehyde

Equation:

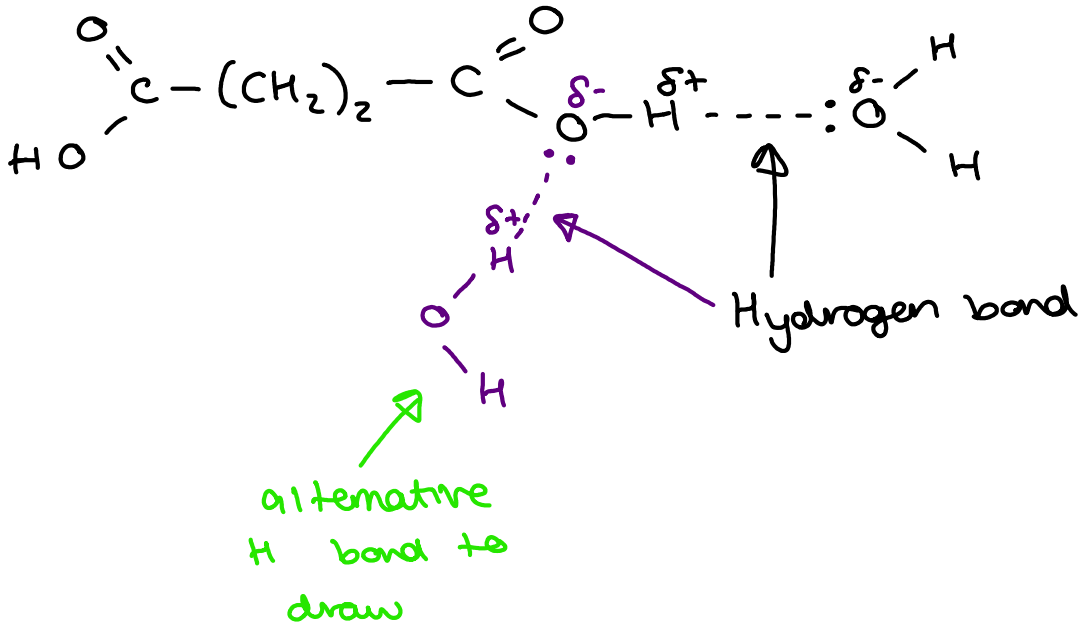
$$HO(CH_2)_4OH + 4[O] \longrightarrow HOOC(CH_2)_2COOH + 2H_2O$$

balance the lost H's in H_2O

[3]

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

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



[2]

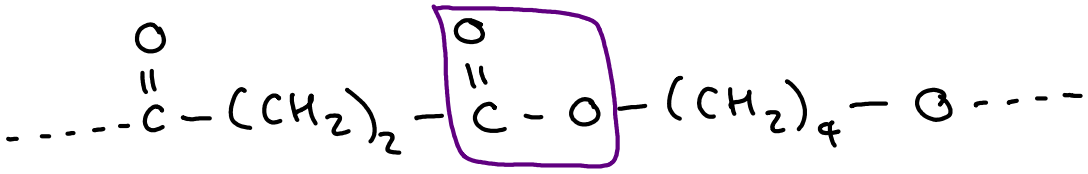
17

(b) $HOOC(CH_2)_2COOH$ and $HO(CH_2)_4OH$ react together to form polymer **E**.

alcohol + carboxylic acid → ester + water

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

The functional groups should be clearly displayed.



ester link (one repeat unit = one ester link)

[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.

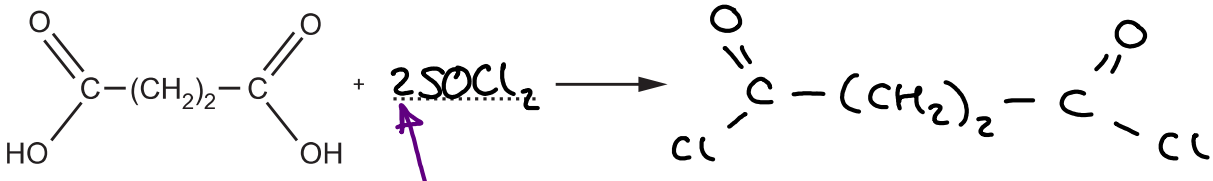
ester group can be broken down via hydrolysis **[1]**

(iii) A large yield of polymer **E** can be obtained by reacting a diacyl dichloride with $HO(CH_2)_4OH$.

The diacyl dichloride is prepared from $HOOC(CH_2)_2COOH$.

reaction map shows this

Complete the equation for the formation of a diacyl dichloride from $HOOC(CH_2)_2COOH$.



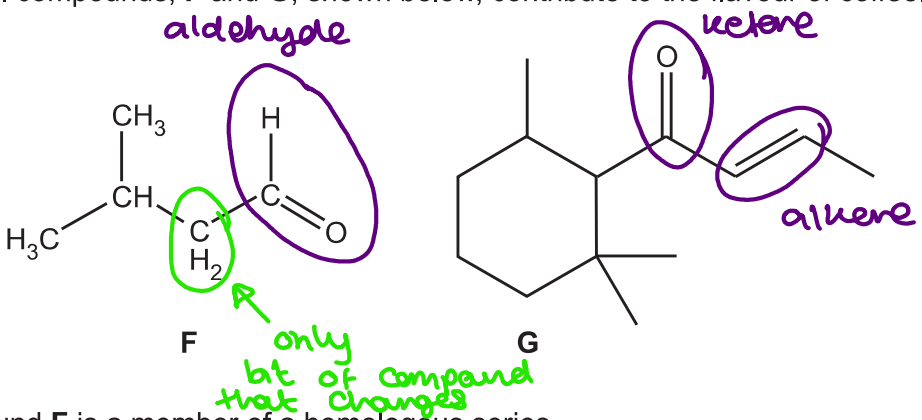
because diacyl dichloride

$+ 2SO_2 + 2HCl$

OH's lost from carboxylic acid and balanced here

[3]

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



C_4H_8O + $C_{20}H_{40}$ ($CH_2 \times 20$)

only bit of compound that changes

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

(i) Explain the term homologous series.

Same functional group / similar chemical properties / reactions each successive / subsequent member differs by CH_2

[2]

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

$C_{24}H_{48}O$ **[1]**

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

F / aldehyde tollen's reagent, silver mirror

test for aldehyde

G / alkene Br_2 goes colourless

test for alkene

test for C=O group

G / ketone 2,4 DNP orange ppt.

tollen's reagent no silver mirror

need to confirm that C=O is a ketone not an aldehyde

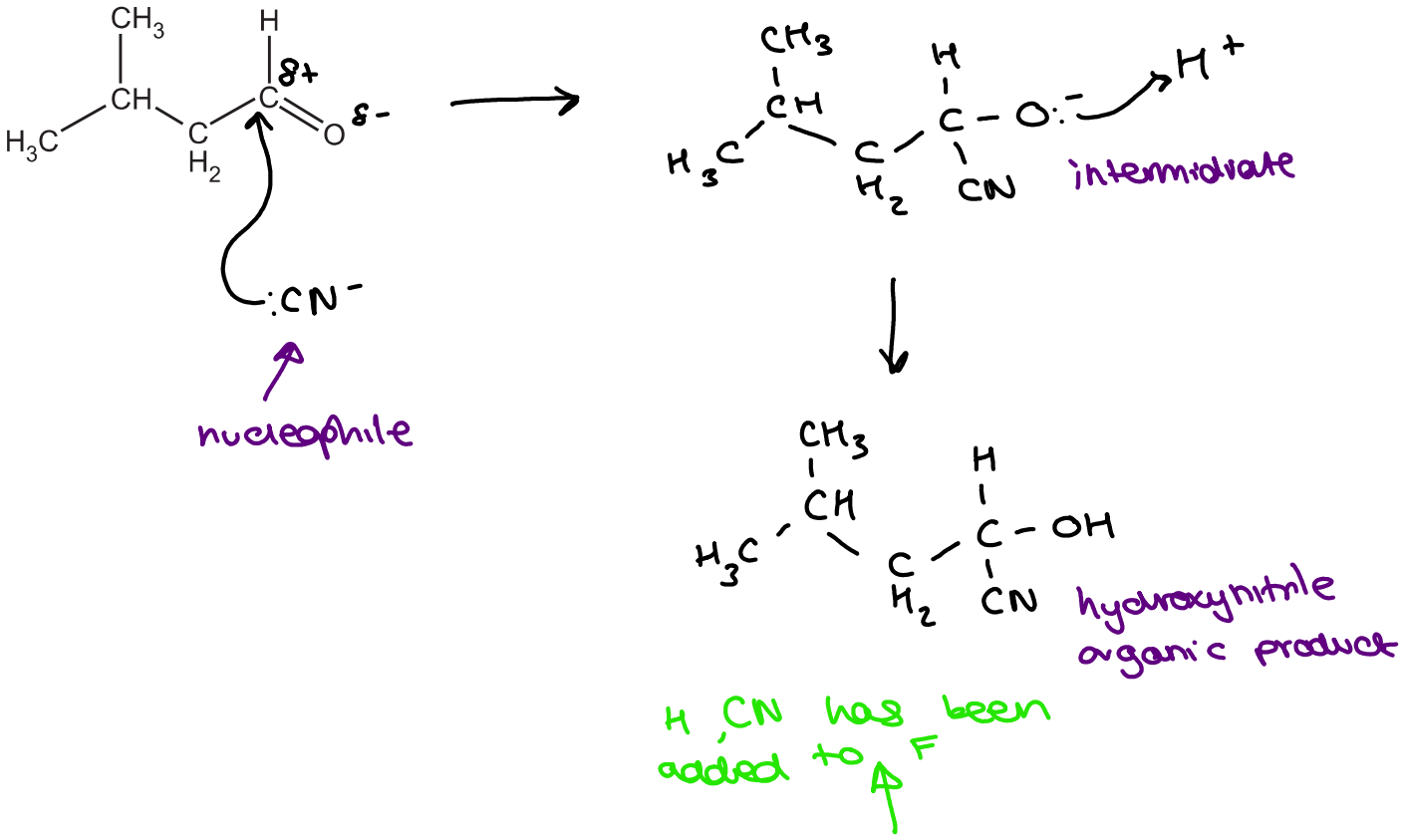
[4]

19

(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.

Heterolytic: one atom receives 2 electrons

Fission: breaking of a covalent bond

..... **[2]**

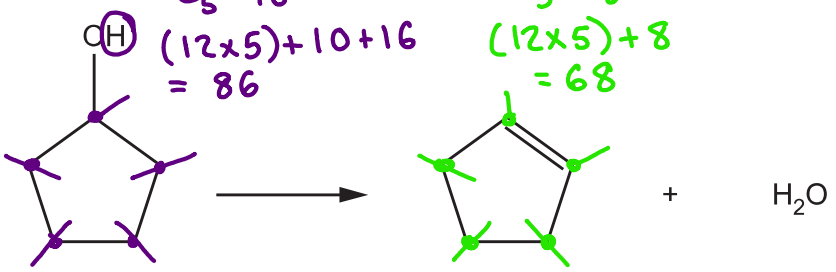
20 Cyclopentanol can be reacted to form cyclopentene.
Cyclopentene is a liquid with a boiling point of 44 °C and a density of 0.74 g cm^{-3}.

→ 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

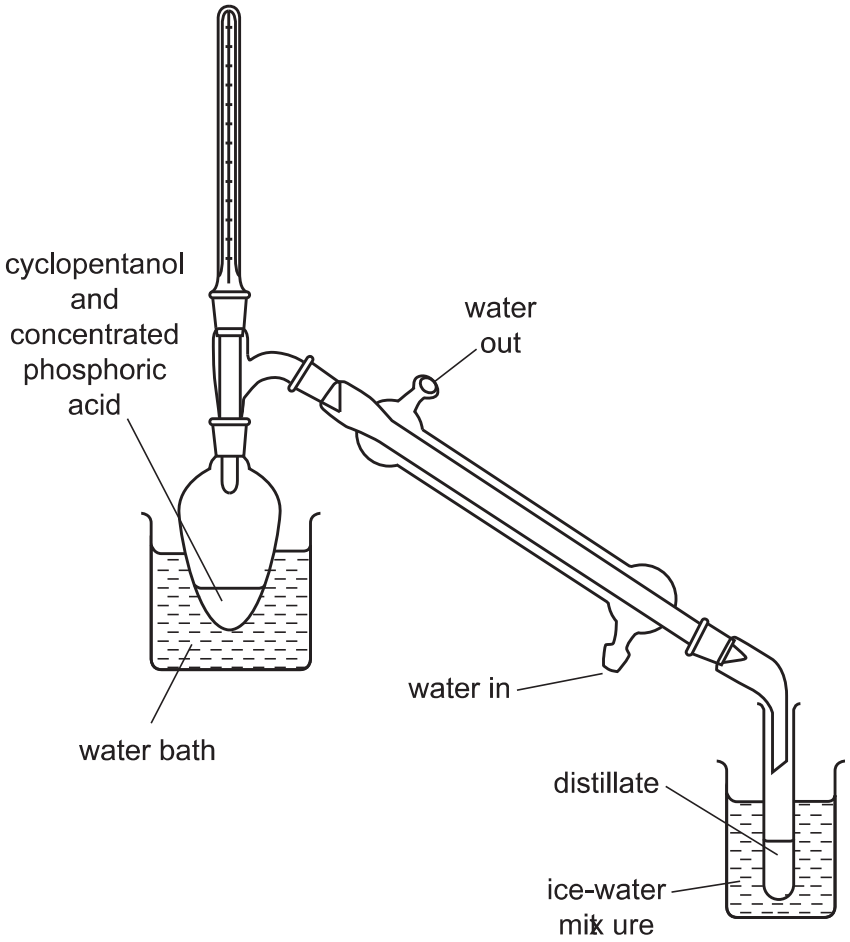
$C_5H_{10}O$ $(12\times5)+10+16 = 86$ C_5H_8 $(12\times5)+8 = 68$



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.

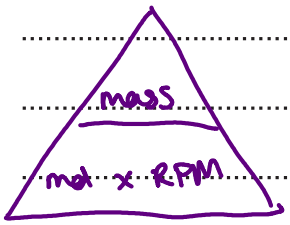
1 The reaction mixture is heated gently, and a distillate containing impure cyclopentene is collected.



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

21

(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

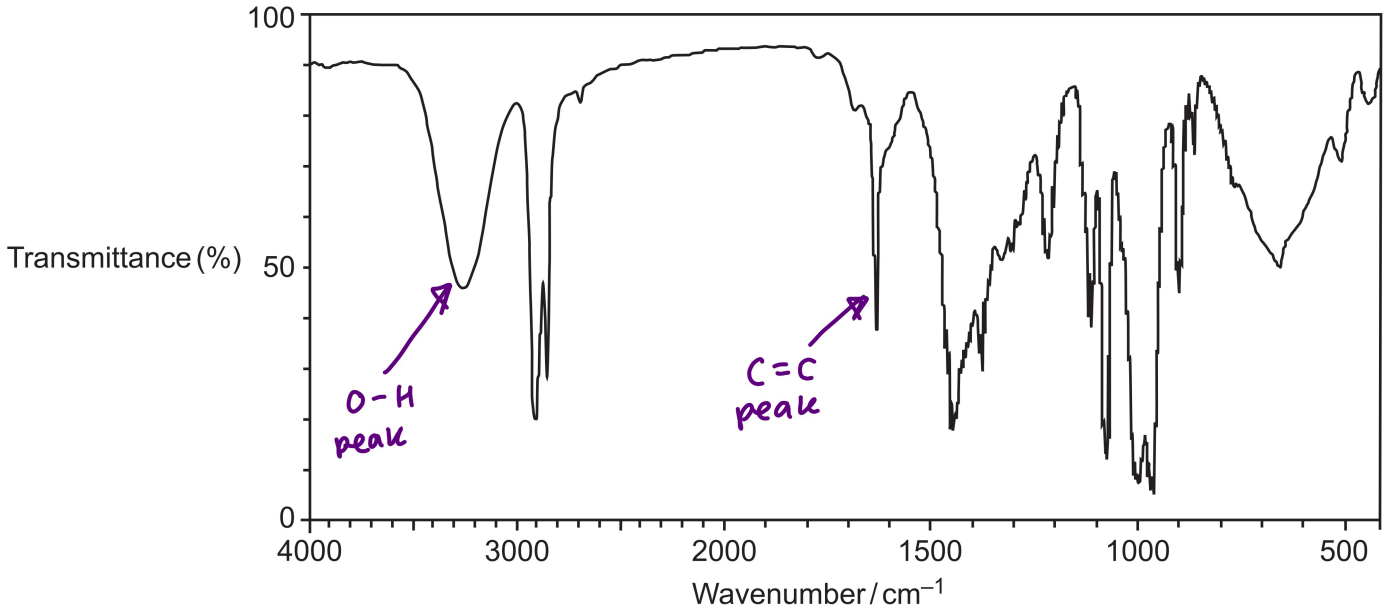
$0.0919 \times 86 = 7.90\text{g}$ (2dp.)

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 cyclopentene and cyclopentanol present in IR

O-H / alcohol peak in region 3200-3600 cm^{-1}

C=C / alkene peak in region 1620-1680 cm^{-1}

.....

.....

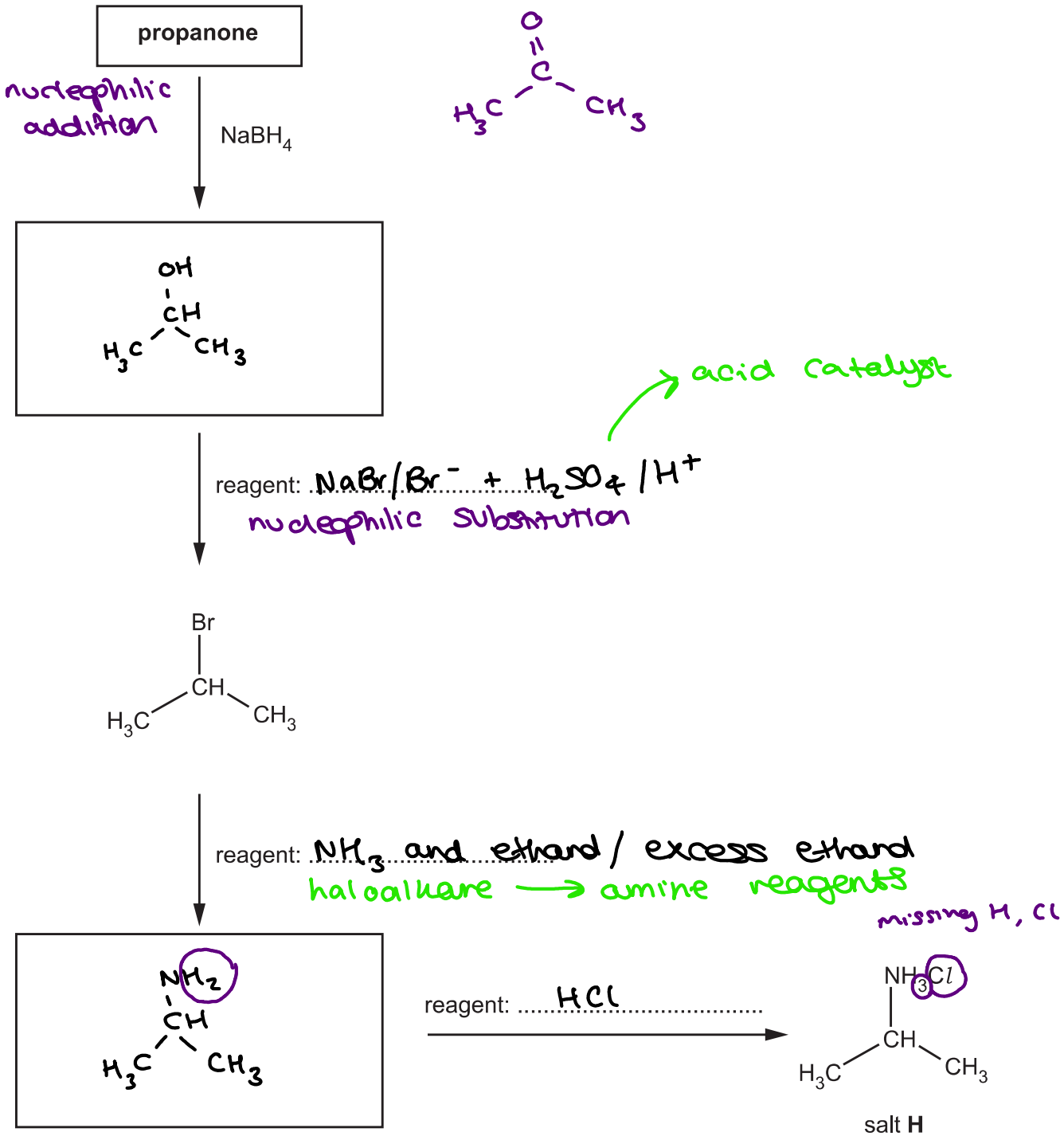
..... **[2]**

21 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.

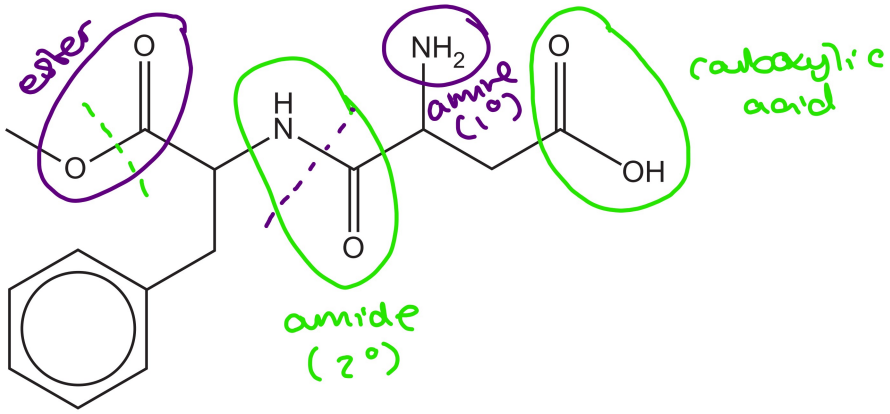
Complete the flowchart.
Show structures for organic compounds.



[5]

24

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



aspartame

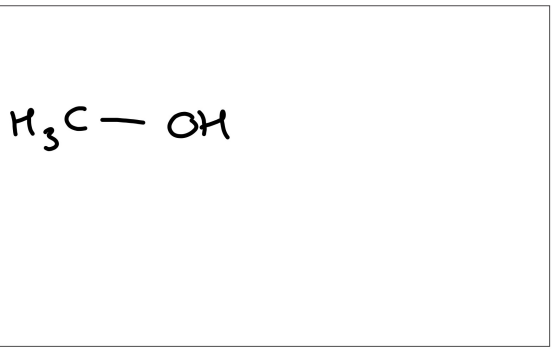
(i) Aspartame contains several functional groups.

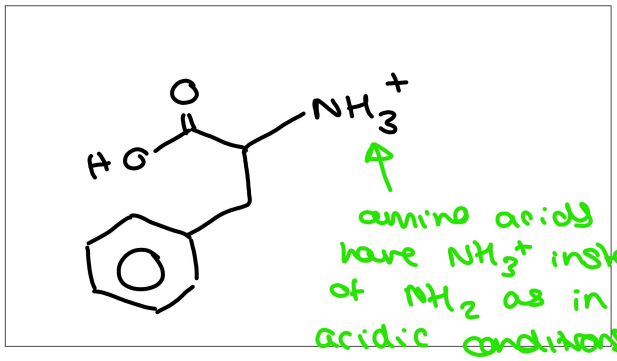
Apart from the benzene ring, name the functional groups in aspartame.

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

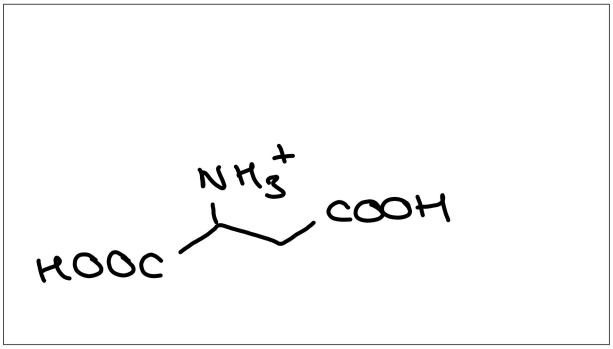
(ii) A sample of aspartame is hydrolysed with aqueous acid.

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





amino acids have NH_3^+ instead of NH_2 as in acidic conditions (H^+)



acid hydrolysis:

ester → alcohol + carboxylic acid

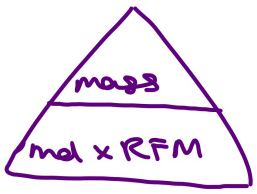
amide → amine + carboxylic acid

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

- 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?



$(14 \times 12) + 18 + (14 \times 2) + (5 \times 16)$

$= 294\ g\,mol^{-1}$

$\frac{0.167\,g}{294} = 5.68 \times 10^{-4}$ 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]**

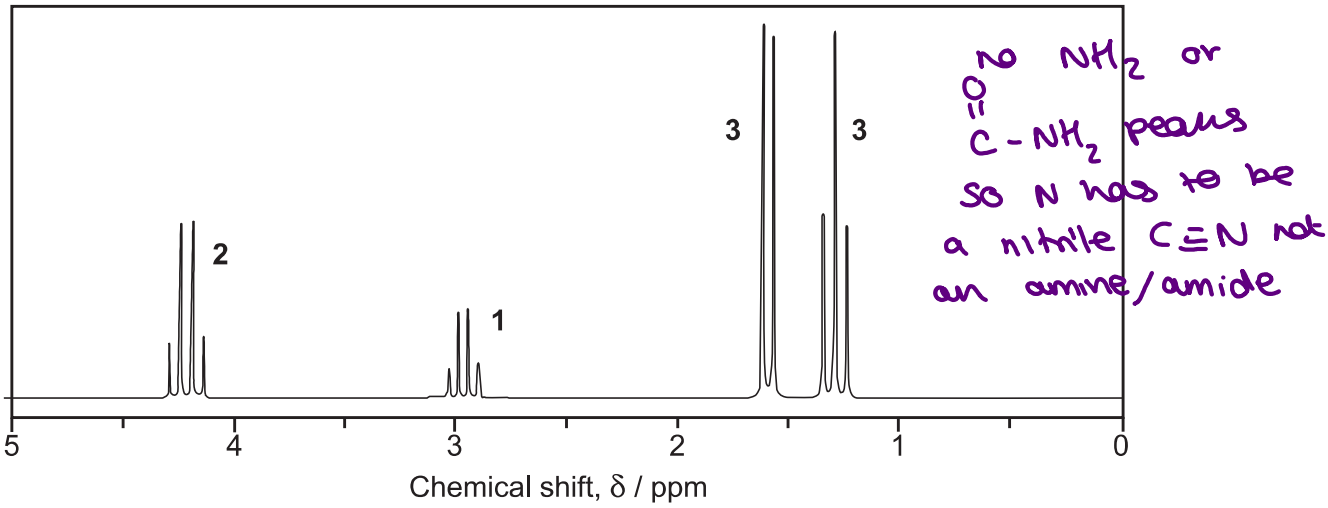
22 An organic compound **I** is analysed, using a combination of techniques. The analytical data is shown below.

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

Proton NMR spectrum



no NH_2 or $C(=O)-NH_2$ peaks so N has to be a nitrile C≡N not an amine/amide

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

→ chloroform-d
$CDCl_3$ used as a solvent

D_2O used to identify OH or NH peaks

→ when D_2O used the OH or NH peaks disappear but when D_2O not used OH or NH peaks are present **[2]**

27

(b)* Determine the structure of compound **I**, showing **all** your reasoning. **[6]**

$\frac{56.69}{12}$ $\frac{7.09}{1}$ $\frac{11.02}{14}$ $\frac{25.2}{16}$

$\frac{=4.72}{0.787}$ $\frac{=7.09}{0.787}$ $\frac{=0.787}{0.787}$ $\frac{=1.575}{0.787}$

$= 6$ $= 9$ $= 1$ $= 2$

$C_6H_9NO_2$ empirical formula and molecular formula

$(6\times12) + 9 + 14 + (16\times2) = 127.0$

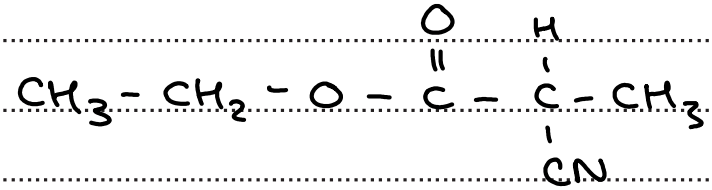
$\delta = 4.2$ ppm quartet, 2H $CH_3-\underline{CH_2}-O$

$\delta = 2.9$ ppm quartet, 1H $\underset{\underset{O}{\|}}{C}-\underline{CH}-CH_3$

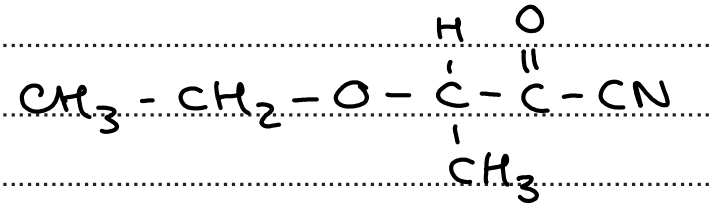
$\delta = 1.7$ ppm doublet, 3H $CH-\underline{CH_3}$

$\delta = 1.3$ ppm triplet $\underline{CH_3}-CH_2$

Additional answer space if required



ester
nitrile



ketone
nitrile
ether

functional groups in the compounds

END OF QUESTION PAPER