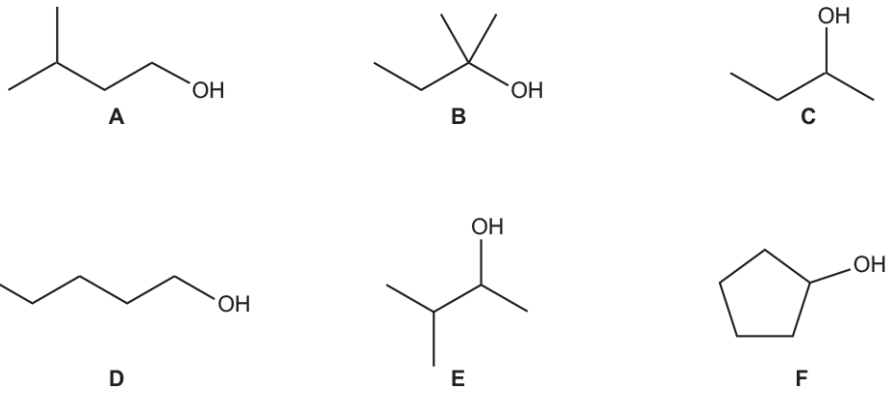
Haloalkanes

1(a). This question is about the alcohols **A–F** shown below.



Alcohol **A** can be prepared by the alkaline hydrolysis of the bromoalkane, $(CH_3)_2CHCH_2CH_2Br$. The hydrolysis with aqueous NaOH is shown in **equation 5.1**.

$(CH_3)_2CHCH_2CH_2Br + NaOH \rightarrow (CH_3)_2CHCH_2CH_2OH + NaBr$ **equation 5.1**
alcohol A

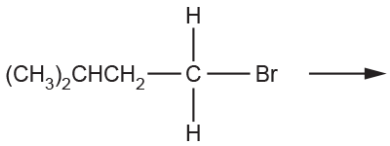
A student gently heats a mixture of $(CH_3)_2CHCH_2CH_2Br$ and NaOH(aq) for 25 minutes.

i. Calculate the atom economy for the preparation of alcohol **A** in **equation 5.1.**

atom economy = ... % **[2]**

ii. Outline the mechanism for the alkaline hydrolysis of $(CH_3)_2CHCH_2CH_2Br$.
The structure of $(CH_3)_2CHCH_2CH_2Br$ has been provided.

Show curly arrows, relevant lone pairs and dipoles, and the products.



[3]

iii. Name this type of mechanism.

[1]

(b). The student decides to prepare alcohol **A** using the same method as in the part above but using the chloroalkane $(CH_3)_2CHCH_2CH_2Cl$ instead of the bromoalkane, $(CH_3)_2CHCH_2CH_2Br$.

State and explain how the rates of hydrolysis of the chloroalkane and the bromoalkane would differ.

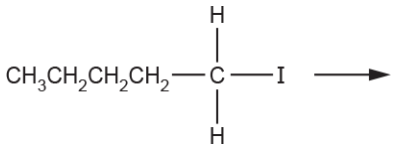
---**[2]**

2. This question is about 1-iodopentane, $CH_3CH_2CH_2CH_2CH_2I$.

1-Iodopentane can be hydrolysed by aqueous sodium hydroxide.

i. Outline the mechanism for this reaction.

Include curly arrows, relevant dipoles and the final product(s).



[3]

ii. 1-Iodopentane can also be hydrolysed by water using aqueous silver nitrate, with ethanol as the solvent.

A student uses this method to compare the rates of hydrolysis of 1-iodopentane and 1-bromopentane.

What measurement and observation would allow the student to compare the rates of hydrolysis?

---**[1]**

iii. 1-Iodopentane was found to react faster than 1-bromopentane.

Explain why.

---**[2]**

3. An alcohol can be prepared by hydrolysing the haloalkane $C_2H_5CHBrCH_3$ with aqueous sodium hydroxide.

i. Outline the mechanism for this reaction.

Show curly arrows and relevant dipoles.

[3]

ii. The infrared (IR) spectrum for $C_2H_5CHBrCH_3$ is shown in **Fig. 25.2**.
The C–Br bond absorption is labelled.

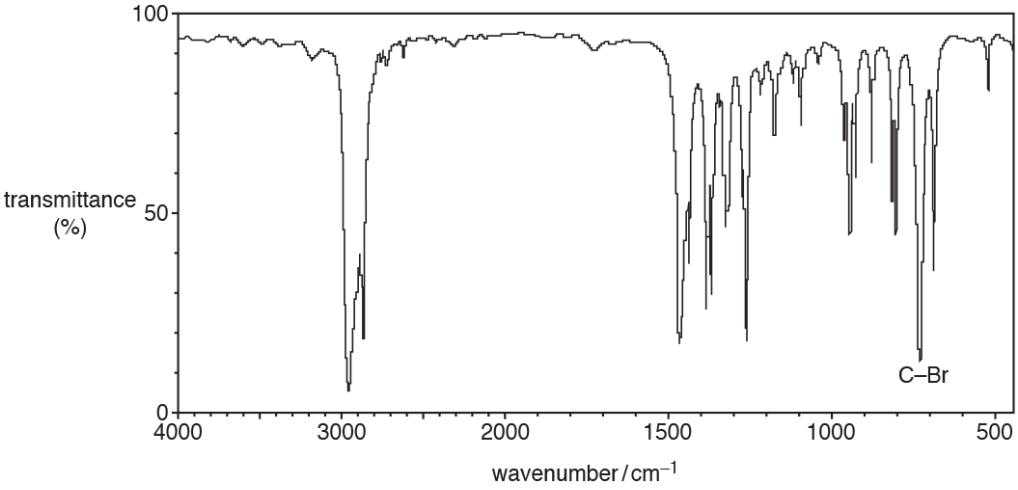


Fig. 25.2

Outline how IR spectroscopy could be used to show that the bromoalkane functional group has reacted and that the alcohol functional group has formed.

---

[2]

4(a). This question is about the hydrolysis of haloalkanes.

The rate of hydrolysis of a haloalkane depends on the halogen present.

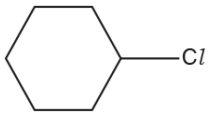
State and explain how the halogen in the haloalkane affects the rate of hydrolysis.

---**[2]**

(b). Chlorocyclohexane is hydrolysed with aqueous sodium hydroxide.

Outline the mechanism for this reaction.

Show curly arrows, relevant dipoles and the products.



[3]

(c). A student hydrolyses a haloalkane, **E**, using the following method.

- 0.0100 mol of haloalkane **E** is refluxed with excess NaOH(aq) to form a reaction mixture containing an organic product **F**.
- The reaction mixture is neutralised with dilute nitric acid.
- Excess $AgNO_3$(aq) is added to the reaction mixture. 1.88 g of a precipitate **G** forms.

Organic product, **F**, has a molar mass of 74.0 g mol^{-1} and has a chiral carbon atom.

i. Draw a **labelled** diagram to show how the student would carry out the hydrolysis of haloalkane **E**.

[2]

ii. Analyse the information to identify **E**, **F** and **G**.

Show your working.

[3]

5. Alcohols are used in organic synthesis.

Pentan-2-ol can be prepared by the alkaline hydrolysis of 2-iodopentane.

$$CH_3CH(I)CH_2CH_2CH_3 + NaOH \rightarrow CH_3CH(OH)CH_2CH_2CH_3 + NaI$$

The reaction mixture is boiled for 20 minutes.

i. State the most appropriate technique that could be used to boil the reaction mixture for 20 minutes.

[1]

ii. Describe the mechanism for the alkaline hydrolysis of 2-iodopentane.

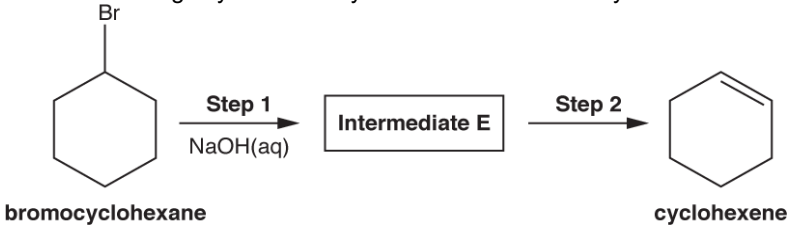
In your answer, include the name of the mechanism, curly arrows and relevant dipoles.

name of mechanism: .....

[4]

6. Organic compounds can be prepared in the laboratory using synthetic routes with two or more stages.

A student devises a two-stage synthesis of cyclohexene from bromocyclohexane.



i. Suggest the structure of **intermediate E** and the reagent(s) and conditions for **step 2**.

reagent(s) and conditions ----------

ii. The student carries out this synthesis and obtains 1.23 g of pure cyclohexene from 5.50 g of bromocyclohexane.

Calculate the percentage yield of cyclohexene.

Give your final answer to an **appropriate** number of significant figures.

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

7(a). Haloalkanes are hydrolysed by aqueous sodium hydroxide.

i. Outline the mechanism of the reaction of 1-bromobutane with aqueous sodium hydroxide.

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

[3]

ii. Name the type of mechanism in **(i)**.

---

[1]

iii. The organic product in **(i)** can be formed faster using a different haloalkane than 1-bromobutane.

Identify this haloalkane.

Explain your answer.

Haloalkane

.....

Explanation

.....

---

[1]

(b). The use of some haloalkanes, such as chlorotrifluoromethane, has been banned as they form C*l* • radicals which break down ozone.

i. Construct an equation to show the formation of C*l* • radicals from chlorotrifluoromethane.

---

[1]

ii. Ozone is broken down by C*l* • radicals in a two-step process.

Write the equations for the two steps and the overall equation for this process.

Step 1

.....

Step 2

.....

Overall equation

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

iii. A research chemist found that 1.00 g of C*l* • radicals can breakdown 135 kg of O_3.

Calculate the number of O_3 molecules removed by one C*l* • radical.

Give your answer in **standard form** and to **three** significant figures.

number of O_3 molecules = ... **[3]**

8(a). A student was provided with a mixture of two structural isomers. Each isomer has the percentage composition by mass C, 29.29%; H, 5.70%; Br, 65.01%. The relative molecular mass of each isomer is less than 150.

Determine the structures of the two structural isomers.

Show your working.

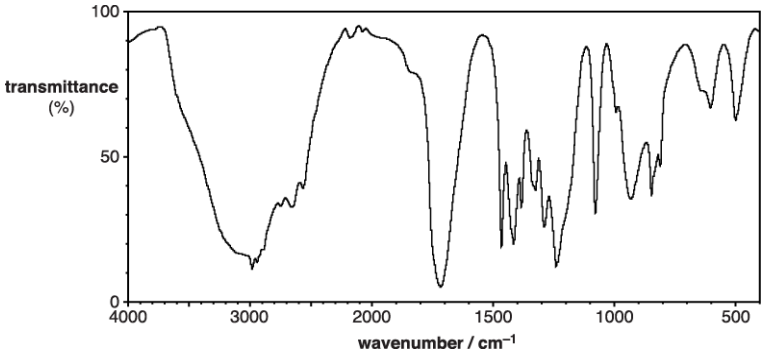
In your answer you should link the evidence with your explanation.

---

[5]

(b). The student heats the mixture of the two structural isomers from **(a)** under reflux with aqueous sodium hydroxide to form two compounds, **E** and **F**. The student separates the two compounds.

Compound **E** is heated under reflux with acidified potassium dichromate(VI) to form compound **G**, which gives the infrared spectrum below.



i. Analyse the information and spectrum to determine the structures of **E**, **F** and **G**.

Include an equation for the formation of **G** from **E**.

In your answer you should link the evidence with your explanation.

_____

_____

_____

_____

_____

_____ **[6]**

ii. Compound **G** is heated with compound **F** in the presence of a small amount of concentrated sulfuric acid to form organic compound **H**.

Draw the structure of the organic compound **H**.

[2]

9. In the stratosphere, nitrogen oxides can catalyse the breakdown of ozone.

i. State **two** sources of nitrogen oxides in the stratosphere.

_____

_____ **[1]**

ii. Write equations to show how nitrogen monoxide catalyses the breakdown of ozone.

_____

_____

_____ **[2]**

10. Alcohols can be prepared from halogenoalkanes. 2,2-dimethylpropan-1-ol can be prepared by hydrolysis of a chloroalkane with aqueous sodium hydroxide.

i. Write the equation for this reaction.

Use structures for the organic compounds.

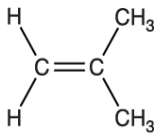
[1]

ii. Outline the mechanism for this reaction.

Show curly arrows and relevant dipoles.

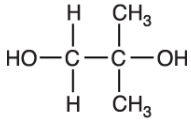
[2]

11. Compound **B**, shown below, can be used to synthesise organic compounds with different functional groups.



Compound B

The structure of compound **F** is shown below.



Compound F

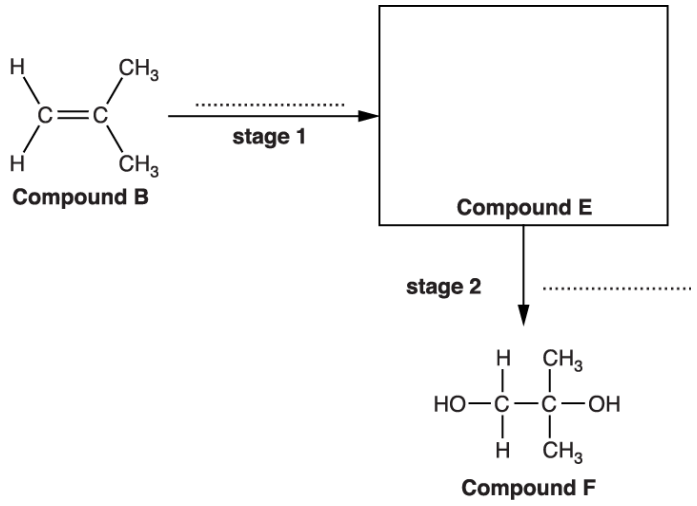
i. What is the empirical formula of compound **F**?

[2]

ii. A student plans a two-stage synthesis for preparing compound **F** from compound **B.**

The synthesis first prepares compound **E**, as shown in the flowchart.

Draw the structure of compound **E** in the box and state the reagents for each stage on the dotted lines.



[3]

12. Nitrogen forms several different oxides.

N_2O is a useful anaesthetic and NO has been linked to the depletion of ozone in the stratosphere.

NO radicals catalyse the breakdown of ozone in the stratosphere.

Write **two** equations to show how NO radicals catalyse this breakdown.

---

[2]

13(a). Reaction mechanisms use curly arrows and can involve electrophiles and nucleophiles.

i. What does a *curly arrow* represent in mechanisms?

---

[1]

ii. What is meant by the term *nucleophile*?

---

[1]

(b). Allyl bromide, $CH_2=CHCH_2Br$, reacts with aqueous sodium hydroxide.

i. Outline the mechanism of this reaction.

Include curly arrows, relevant dipoles and final product(s).

[3]

ii. Name the type of mechanism.

---

[1]

(c). Allyl bromide, $CH_2=CHCH_2Br$, is used in the production of polymers.

Allyl bromide is reacted as shown below.

$$CH_2=CHCH_2Br \xrightarrow{\textbf{step 1}} \underset{\textbf{1-bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[Cl_2]{\textbf{step 2}} \text{mixture of organic products}$$

i. State the reagents and conditions for **step 1**.

---

[1]

ii. In **step 2**, 1-bromopropane reacts with chlorine by radical substitution.

Outline the mechanism for the monochlorination of 1-bromopropane.
In your mechanism, you can show the formula of 1-bromopropane as C_3H_7Br.

Include the names of the three stages in this mechanism, state the essential conditions and all termination steps.

---

[5]

iii. Radical substitution produces a mixture of organic products.

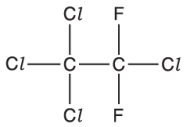
Suggest **two** reasons why.

---

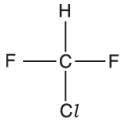
[2]

14. This question is about the compounds shown below.

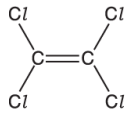
B



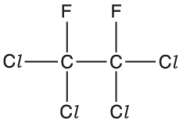
C



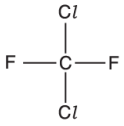
D



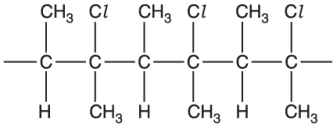
E



F



G



H

Compound **G** was once used as a propellant in aerosols. Compound **G** has been linked with depletion of the ozone layer in the stratosphere.

i. State **two** properties that made compound **G** suitable for use as an aerosol.

1

2

---

[1]

ii. Explain the following statements, using equations where appropriate.
- Life on Earth benefits from the presence of an ozone layer.
- The concentration of ozone is maintained in the ozone layer.
- Compound **G** produces radicals which catalyse the breakdown of ozone.

[5]

iii. Alternative 'ozone-friendly' compounds are now used as propellants instead of compound **G**.

Which compound, **B** to **H**, might be suitable as an 'ozone-friendly' propellant?

[1]

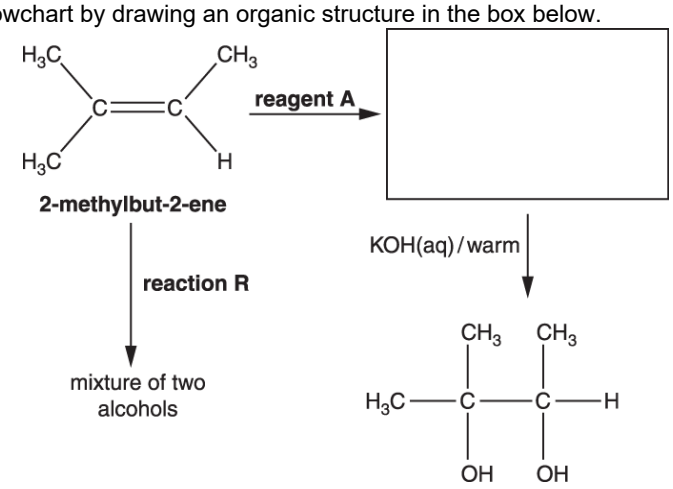
15. Give chemical explanations for the following statements.

The rate of hydrolysis of 1-bromobutane is faster than that of 1-chlorobutane.

[1]

16(a). The flowchart shows how 2-methylbut-2-ene can be converted into a number of organic products.

Complete the flowchart by drawing an organic structure in the box below.



[1]

(b). Identify reagent **A**.

_____ **[1]**

(c). In the flowchart, **reaction R** forms a mixture of two alcohols that are structural isomers of $C_5H_{12}O$.

i. State the reagents and conditions needed for **reaction R**.

_____ **[1]**

ii. What is meant by the term *structural isomers*?

_____

_____ **[1]**

iii. Draw the two structural isomers of $C_5H_{12}O$ formed in **reaction R**.

[2]

iv. Suggest why 2-methylbut-2-ene is less soluble in water than either of the structural isomers formed.

_____

_____

_____ **[2]**

17(a). 1-Bromobutane, $CH_3CH_2CH_2CH_2Br$, reacts with methoxide ions, CH_3O^-, by nucleophilic substitution.

Suggest how the methoxide ion can act as a nucleophile.

---

[1]

(b). Using the 'curly arrow' model, suggest the mechanism for this reaction.

Show any relevant dipoles.

[3]

(c). 1-Iodobutane also reacts with methoxide ions.

Indicate, by placing a tick in one of the boxes, how the use of 1-iodobutane would affect the rate of reaction compared with that of 1-bromobutane.

1-Iodobutane does not change the rate	
1-Iodobutane increases the rate	
1-Iodobutane decreases the rate	

Explain your answer.

---

[1]

(d). The ethanoate ion, CH_3COO^- acts as a nucleophile when reacting with 1-bromobutane in a substitution reaction.

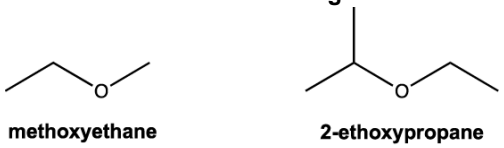
Draw the skeletal formula and give the name of the organic product formed in this reaction.

skeletal formula

name of product ..... **[2]**

18(a). Ethers are a homologous series of organic compounds containing the R−O−R functional group.

The structures and names of two ethers are shown in **Fig. 4.1.**



methoxyethane **2-ethoxypropane**

Fig. 4.1

Draw the **skeletal** formula of the ether, 2-ethoxy-3-methylbutane.

[1]

(b). Ethers can be prepared by nucleophilic substitution of haloalkanes with alkoxide ions, RO^-.

i. Alkoxide ions can be prepared by reacting sodium with an alcohol. A gas is also formed.

Write an equation for the formation of methoxide ions from sodium and an alcohol.

---

[1]

ii. Methoxyethane, shown in **Fig. 4.1**, can be prepared by reacting bromoethane, CH_3CH_2Br, with methoxide ions, CH_3O^-.

Suggest the mechanism for the nucleophilic substitution of CH_3CH_2Br with CH_3O^-.

Show curly arrows, charges, relevant dipoles, and products.

[3]

iii. In this mechanism, explain how CH_3O^- ions have acted as a nucleophile.

State the type of bond fission that takes place.

---

[1]

(c). 2-Ethoxypropane, shown in **Fig. 4.1**, is analysed by ^{1}H NMR spectroscopy.

Complete the table to predict the ^{1}H NMR spectrum of 2-ethoxypropane.
You may **not** need to use all the rows.

Chemical shift, δ/ppm	Relative peak area	Splitting pattern

[4]

(d). In organic reactions, alkoxide ions can also act as a base.

The diagram below shows an incomplete mechanism for the reaction of a diester with methoxide ions, CH_3O^- (**Step 1**), followed by reaction of the intermediate with bromoethane (**Step 2**).

i. For **Step 1**, add curly arrows to show how CH_3O^- reacts with the diester to form the intermediate.
In the box, draw the structure of the organic product formed in **Step 2**.

[3]

ii. Explain how CH_3O^- ions have acted as a base in this mechanism.

---

[1]

19. Haloalkanes can undergo hydrolysis.

A student carries out an experiment to find the relative rate of hydrolysis of 1-chloropropane, C_3H_7Cl, 1-bromopropane, C_3H_7Br, and 1-iodopropane, C_3H_7I.

The student adds 2 cm^3 of ethanol to 2 cm^3 of aqueous silver nitrate to three test tubes labelled **A**, **B** and **C**.

The student adds 5 drops of a different haloalkane to each test-tube in rapid succession and shakes each tube. The student measures the time for a precipitate to form in each test-tube.

The results are shown below.

Test tube	Haloalkane	Time taken for reaction to take place
A	C_3H_7Cl	about half an hour
B	C_3H_7Br	a few minutes
C	C_3H_7I	a few seconds

i. Write an **ionic** equation involving aqueous silver nitrate for formation of **one** of the precipitates.

---

[1]

ii. What do the experimental results tell you about the carbon–halogen bond enthalpies?

---

[1]

iii. How could the student modify their experiment so that it could be completed in less time?

---

[1]

END OF QUESTION PAPER