Haloalkanes
AS & A Level

Model Answers 3

Level	A Level
Subject	Chemistry
Exam Board	OCR
Module	Core Organic Chemistry
Topic	Haloalkanes
Paper	AS & A Level
Booklet	Model Answers 3

Time allowed: **50 minutes**

Score: **/37**

Percentage: **/100**

Grade Boundaries:

A*	A	B	C	D	E
>85%	73%	60%	47%	34%	21%

This question is about the hydrolysis of haloalkanes.

(a) 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]**

Links rate of reaction to strength of bond/bond enthalpy eg:

The weaker the bond the faster the reaction and the stronger the bond then it takes longer to break and so a lower bond enthalpy reacts faster than a higher bond enthalpy. The strength of the halogen-carbon bond decreases as we move down Group 7 due to **increasing** atomic distances, hence those haloalkanes from further down the group will react faster.

Correct comparison of rate of reaction for at least **two** C–Hal bonds eg:

C–F bond is hydrolysed slow**est**

C–I bond is hydrolysed faster than C–Br

C–Br has shorter reaction time than C–Cl

Hence a fluoroalkane reacts **slower** than a chloroalkane which in turn reacts **slower** than a bromoalkane etc. as the bond enthalpy decreases **moving down** the group.

OR

Correct comparison of C–Hal bond strength/enthalpy of at least **two** of C–Hal bonds

e.g.

C–I bond is the weak**est**

C–I has lower bond enthalpy than C–Br

C–Br is broken more easily/readily than C–Cl

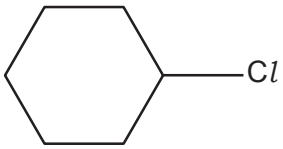
C–Hal bond strength decreases down group (7)

(b) Chlorocyclohexane is hydrolysed with aqueous sodium hydroxide.

Outline the mechanism for this reaction.

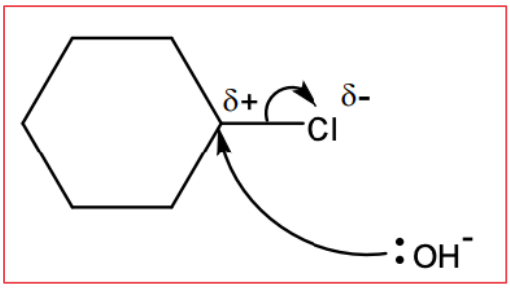
Show curly arrows, relevant dipoles and the products.

[3]

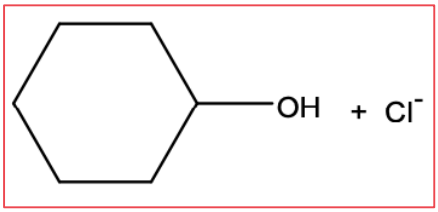


Curly arrow from the lone pair of electrons on the HO^- (OH^-) to carbon atom of C–Cl bond

Dipole shown on C–Cl bond as represented by $C^{\delta+}$ and $Cl^{\delta-}$ **AND** curly arrow from the middle of the C–Cl bond to Cl atom.



Correct organic product **AND** Cl^- as shown below.



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

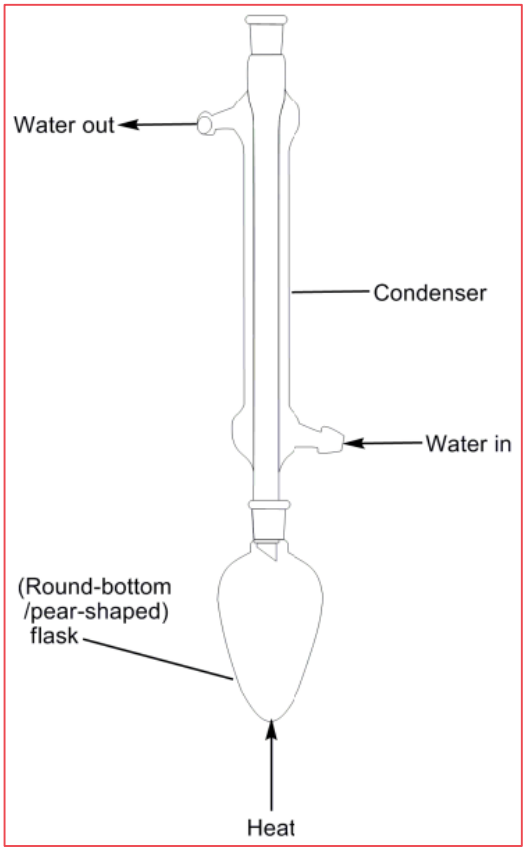
- 0.0100 mol of haloalkane **E** is refluxed with excess NaOH(aq) to form a reaction mixture containing an organic product **F**.
- The reaction mixture is neutralised with dilute nitric acid.
- Excess $AgNO_3$(aq) is added to the reaction mixture. 1.88 g of a precipitate **G** forms.

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]

Diagram showing round bottom/pear shaped flask **AND** upright condenser as reflux is required because the reaction occurs only very slowly at room temperature.



Labels

(Round-bottom/pear-shaped) flask which are the preferred glassware for reflux due to their resistance to high temperatures and shape which allows for small volumes to react.

AND condenser **AND** water in at bottom and out at the top as this ensures that there is always cold water in the condenser.

AND heat (source) which must be positioned right below the pear shaped flask.

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

Show your working. **[3]**

Start with **precipitate G**

Silver bromide/AgBr **AND**

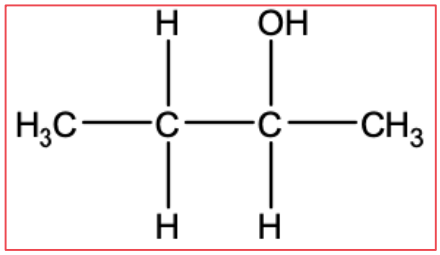
$M = \frac{1.88}{0.01} = 188$ (g mol^{-1})

188 – 107.9 (A_r of silver) = 80.1 (so halide is Br$^-$)

Alcohol F and Haloalkane E

In the hydrolysis of haloalkanes the halogen atom is substituted by an -OH group in a nucleophilic substitution reaction.

F/alcohol: butan-2-ol with the second carbon from the left being the chiral carbon. The -OH group has attached to where the bromine atom was positioned.



E/haloalkane:

E is haloalkane of C_4H_9X with

- same halogen as **G** which is bromine.

AND

- same carbon chain as **F** as in the hydrolysis of haloalkanes the halogen atom is substituted by an -OH group, with the carbon chain remaining intact.

(Total 10 marks)

(a) 1-Bromobutane is an organic liquid with a boiling point of 102 °C.

A student prepares 1-bromobutane by reacting butan-1-ol with sulfuric acid and sodium bromide. The student boils the mixture for one hour.

The equation is shown below.

$$CH_3CH_2CH_2CH_2OH + H^+ + Br^- \rightarrow CH_3CH_2CH_2CH_2Br + H_2O$$

The student obtains a reaction mixture containing an organic layer (density = 1.27 g cm^{-3}) and an aqueous layer (density = 1.00 g cm^{-3}).

(i)* Draw a labelled diagram to show how you would safely set up apparatus for the preparation. Outline a method to obtain a pure sample of 1-bromobutane from the reaction mixture. **[6]**

Correctly labelled diagram of reflux apparatus that works, with no safety problems and an appreciation of most of the purification steps required to gain a pure sample.

Apparatus set up for reflux:

- round-bottom/pear shaped flask
- heat source
- condenser

Detail: water flow in condenser bottom to top; open system.

Safety precautions for using a reflux

- Use of a **heating mantel** rather than a naked flame to avoid exposing flammable vapours to a naked flame in the event of a leak.
- The flask should be clamped at the **neck** and not higher up on the condenser.
- Anti-bumping granules to prevent excessive shaking of the apparatus.
- Use of **grease** on the ground glass joint of the condenser to ensure a tight seal and avoid loss of vapour.
- Make sure the top of the condenser is **open** and unblocked.

Purification

- Use of a **separating funnel** to separate
- organic and aqueous layers

Detail: Collect lower organic layer density greater

The lower layer is the most dense of the two and is removed first using a separating funnel.

- **Drying** with an anhydrous salt,

Detail: e.g. $MgSO_4$, $CaCl_2$, etc.

This step removes the water. Dry organic liquids should be clear.

- **Redistillation**

Detail: Collect fraction distilling at 102ºC.

The narrower the boiling point range then the purer the product. The distillation apparatus should be thoroughly clean and dry before redistilling.

(ii) The student used 0.150 mol of butan-1-ol. The student obtained a 61.4% percentage yield of 1-bromobutane.

Calculate the mass of 1-bromobutane obtained.

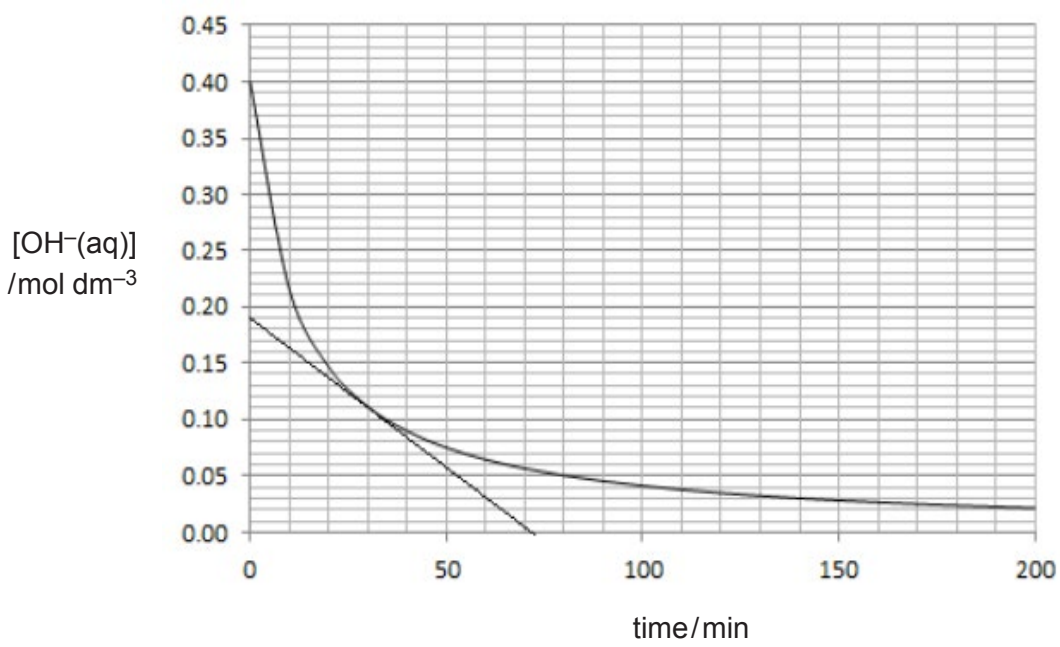
Give your answer to **three** significant figures.

[2]

Step	**Working out**
1. Calculate the moles of 1-bromobutane.	n(1-bromobutane) = 0.150 x $\frac{61.4}{100}$= 0.0921 (mol)
2. Convert to mass and express correct to 3 significant figures.	Mass 1-bromobutane = 0.0921 x 136.9 = 12.6 (g)

(b) A student investigates the rate of reaction of 1-bromobutane with aqueous hydroxide ions.

The graph shows how the hydroxide ion concentration, $[OH^-(aq)]$, changes during the reaction.



Using the graph, calculate the rate of reaction, in mol dm^{-3} min^{-1}, at 30 minutes.

Show your working on the graph and in the space below.

[2]

Tangent on graph drawn at approximately t = 30 min (± 10 mins)

Exam Tip

Draw tangents very carefully and placing the ruler right up against the curve. The tangent is correctly positioned when the **angles** between the curve and the tangent on either side of the point that touches the curve are the **same**.

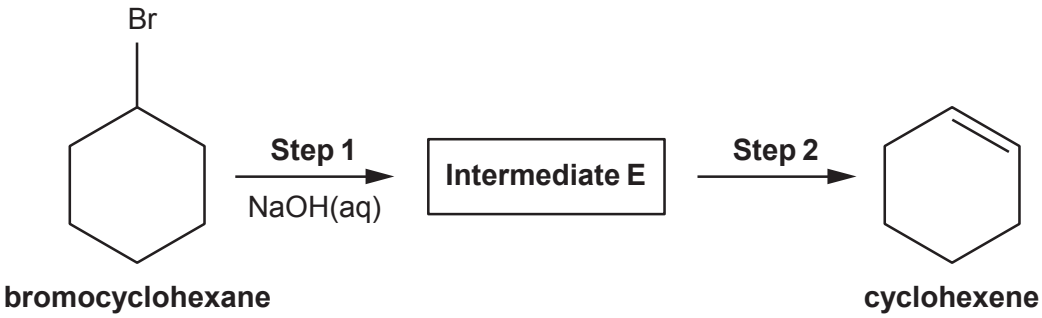
Calculation of rate = Gradient (y/x) of tangent drawn e.g. $\frac{0.19}{72}$ = 2.64 x 10^{-3} / 0.00264 (mol dm^{-3} min^{-1})

Make sure you use the correct units for the rate of reaction.

(Total 10 marks)

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

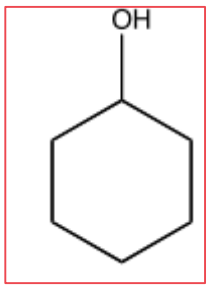
(a) A student devises a two-stage synthesis of cyclohexene from bromocyclohexane.



bromocyclohexane **cyclohexene**

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

[2]



Acid (catalyst) **AND** heat usually under reflux to obtain a good yield. This is a nucleophilic substitution reaction.

(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. **[3]**

Step	Working out
1. First calculate the moles of cyclohexene by dividing the mass by the relative molecular mass (82).	$n(C_6H_{10}) = \frac{1.23}{82}$ **OR** 0.0150 mol
2. Then calculate the moles of bromocyclohexane by dividing the mass by the relative molecular mass (162.9).	$n(C_6H_{10}) = \frac{5.50}{162.9}$ **OR** 0.0338 mol
3. Once the molar quantities are calculated we can then calculate the percentage yield using the equation % yield = $\frac{actual\ yield}{theoretical\ yield}$ x 100.	Percentage yield = $\frac{0.0150}{0.0338}$ = 44.4(%) Final answer **must** be to 3 significant figures

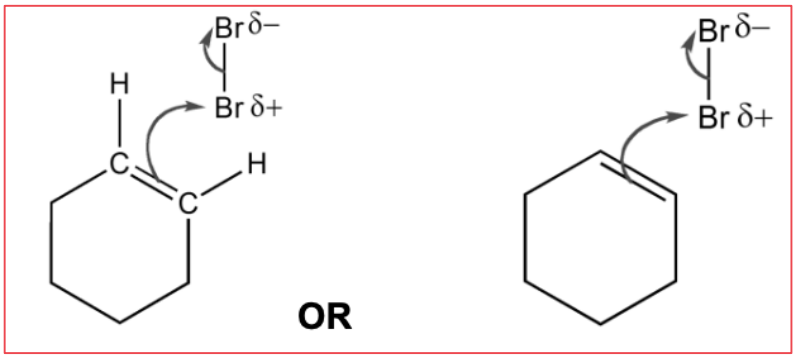
(b) Cyclohexene is reacted with bromine to prepare the organic compound **F**.

Give the structure of compound **F** and outline the mechanism for this reaction.

Include curly arrows, charges and relevant dipoles. **[4]**

Curly arrow from double bond to Br of Br–Br making sure that the arrow starts in the middle of the C=C bond and ends up at one of the Br atoms.

Correct dipole shown on Br–Br **AND** curly arrow showing breaking of Br–Br bond which again must begin in the middle of the bond and end at an atom.

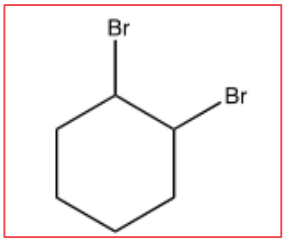


Exam Tip

Curly Arrows

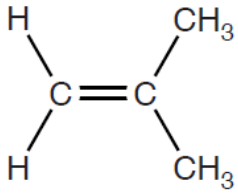
Curly arrows must be drawn clearly and accurately and should always start at either the bond or electron lone pair. The head of the arrow always goes at the atom to which the electron pair transfers.

Correct product



(Total 9 marks)

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



Compound B

(a) **(i)** Compound **B** is a member of a homologous series.

Name the homologous series and state its general formula.

Homologous series Alkene

General formula C_nH_{2n} **[1]**

If unsure about the general formula you can always substitute the numbers from the given molecule and check that the formula gives the correct amount of C and H atoms.

(ii) What reagents and conditions are needed to convert compound **B** into a saturated hydrocarbon? **[1]**

Hydrogen/H_2 AND Ni (catalyst)

In hydrogenation reactions, alkenes are converted to alkanes through the addition of **hydrogen** across the double bonds via π bond rupture. The reaction occurs at high temperatures (around 425K) and pressures, and a **nickel** catalyst is used. Platinum, palladium or rhodium could also be used.

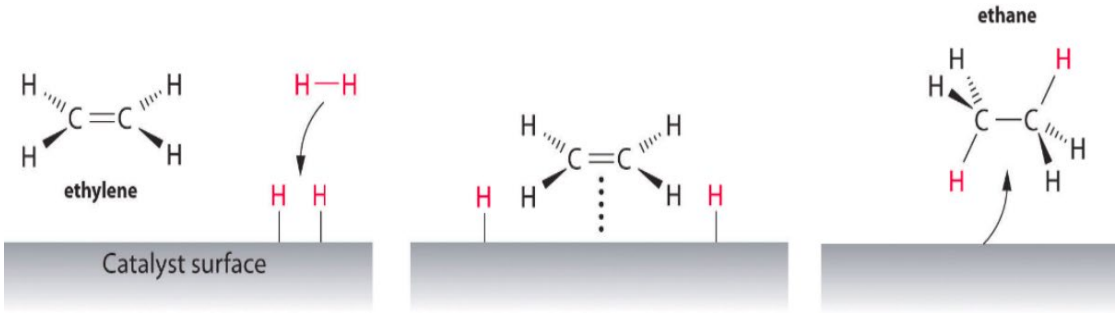
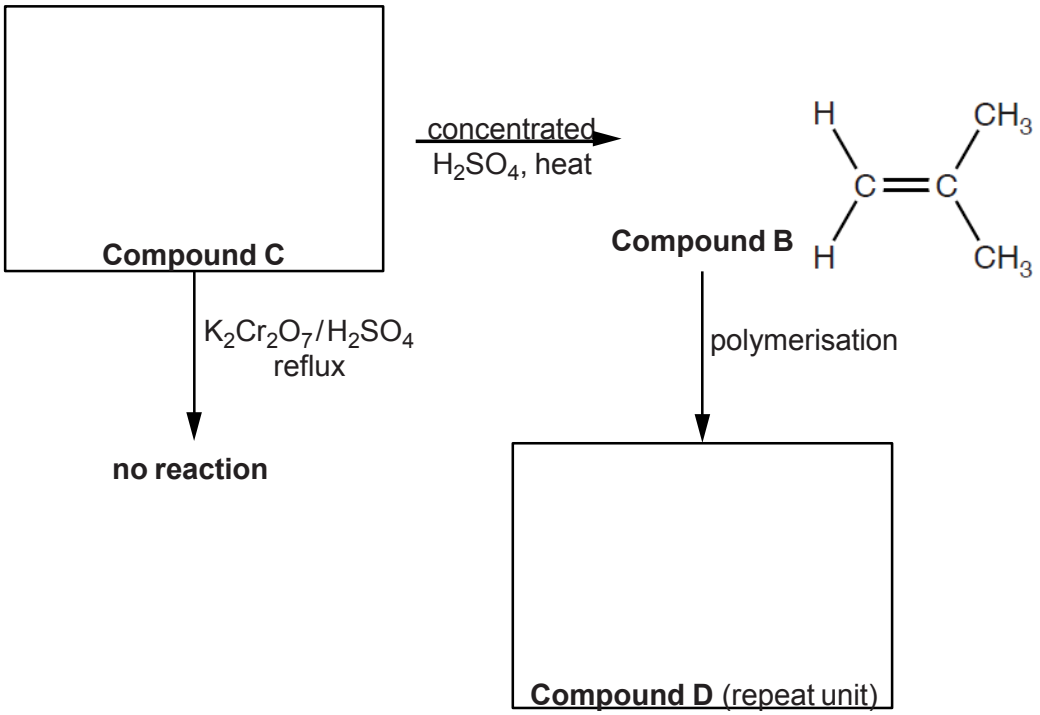


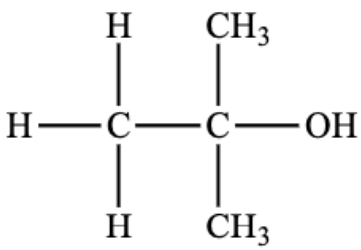
Image showing the catalytic hydrogenation of ethene (ethylene) to ethane

(b) Some reactions involving compound **B** are shown in the flowchart below.

Complete the flowchart, showing the structures of organic compounds **C** and **D**.



[2]



Compound C is a **tertiary alcohol** which do not undergo oxidation reactions, hence there is no reaction with acidified potassium dichromate. Alcohols are dehydrated by heating under reflux in concentrated acidic catalytic conditions which produces an alkene.

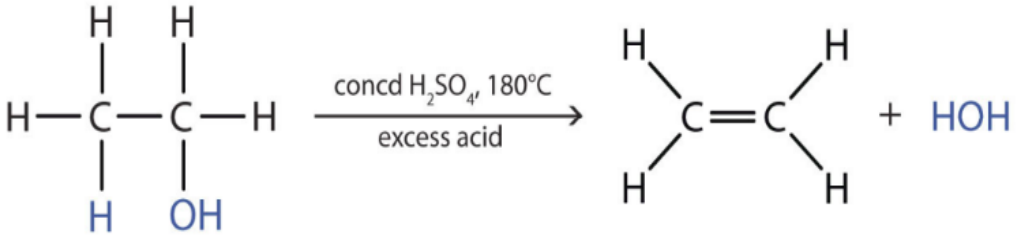
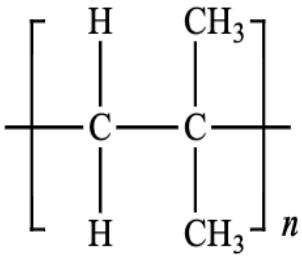


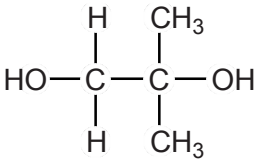
Image showing the dehydration of ethanol producing ethene and a water molecule



Alkenes undergo polymerisation reactions which are shown using notation as shown in compound D. When drawing the repeat units make sure you:

- Replace the C=C with a single bond and add on the side atoms / groups correctly.
- Add the square brackets and the continuation bonds which **extend** through the brackets on either side.
- Add small subscript n on the right hand side which indicates there is a large number of repeat units.

(c) The structure of compound **F** is shown below.



Compound F

(i) What is the empirical formula of compound **F**? **[1]**

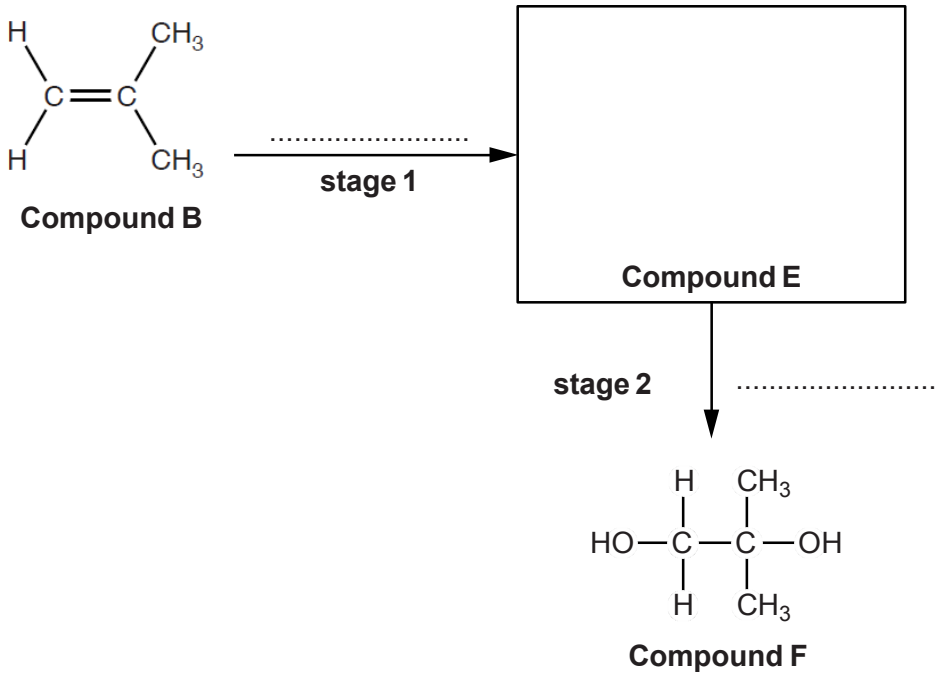
C_2H_5O

Count the number of C, H and O atoms to get the **molecular formula**, $C_4H_{10}O_2$. Then divide across by 2 to find the lowest whole number ratio which is the **empirical formula**.

(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.

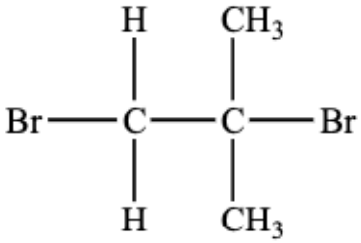
Draw the structure of compound **E** in the box and state the reagents for each stage on the dotted lines.



Compound B

Compound F

[3]



Stage 1: Compound E: Bromine/Br_2

Halogenation of alkenes involves the rapid addition of halogen across the C=C double bond which occurs at room temperature.

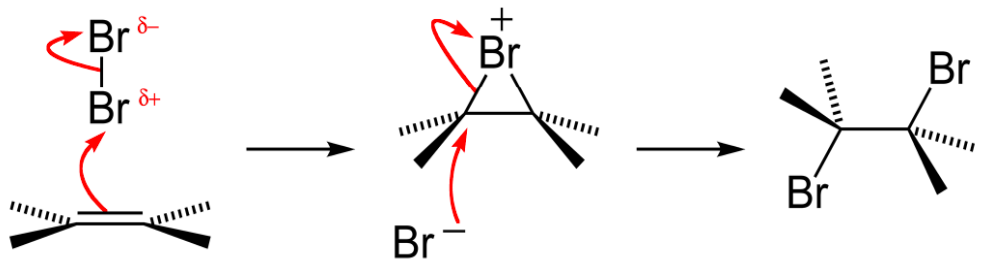


Image showing the mechanism for the bromination of ethene

Stage 2: NaOH/KOH **OR** OH^- Only award if intermediate contains at least one halogen atom

Compound E is a haloalkane which undergoes hydrolysis via a nucleophilic substitution reaction. The halogen atoms are replaced by the nucleophilic OH^- groups. Alcohols are formed in this process which is performed at high temperatures and under reflux.

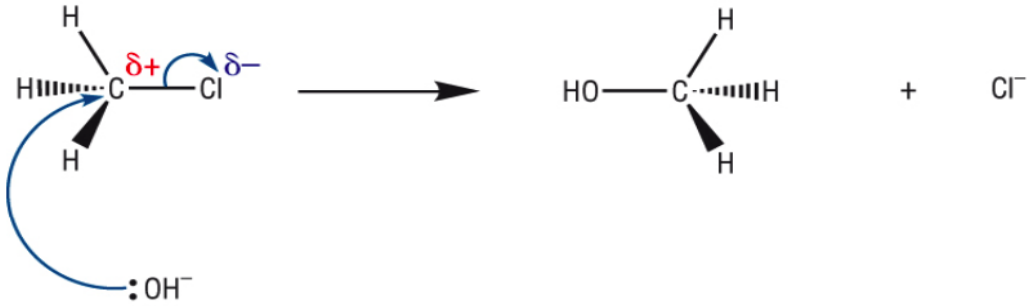


Image showing the nucleophilic substitution mechanism for the hydrolysis of chloromethane

(Total 8 marks)