Cambridge Assessment International Education

Cambridge Pre-U

CANDIDATE NAME									
CENTRE NUMBER						CANDIDATE NUMBER			

3603257366

CHEMISTRY **9791/03**

Paper 3 Part B Written **May/June 2023**

2 hours 15 minutes

You must answer on the question paper.

You will need: Data booklet

INSTRUCTIONS

- Answer **all** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working, use appropriate units and use an appropriate number of significant figures.

INFORMATION

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [ ].

This syllabus is regulated for use in England, Wales and Northern Ireland as a Cambridge International Level 3 Pre-U Certificate.

This document has **20** pages. Any blank pages are indicated.

DC (PQ/CT) 324831

1 Iodine gas and hydrogen gas react at 800 K to form hydrogen iodide.

(a) Write an equation for the reaction of iodine gas with hydrogen gas.

..... [1]

(b) Iodine gas is less ideal than hydrogen gas.

(i) State the conditions of temperature and pressure under which gases behave most like an ideal gas.

.....

..... [1]

(ii) Suggest why iodine is a less ideal gas than hydrogen at 800 K.

Explain your answer.

.....

..... [2]

(c) A series of experiments is carried out to investigate the kinetics of the reaction between iodine gas and hydrogen gas. The results are shown in the table.

experiment	$[H_2]$ / mol dm^{-3}	$[I_2]$ / mol dm^{-3}	rate of reaction / mol dm^{-3} s^{-1}
1	0.100	0.100	1.28×10^{-3}
2	0.100	0.200	2.56×10^{-3}
3	0.500	0.300	1.92×10^{-2}
4	0.500	0.500	

(i) Calculate the order of reaction with respect to $[I_2]$.
Explain your answer.

order of reaction with respect to $[I_2]$ .....

explanation .....

.....
[1]

(ii) Calculate the order of reaction with respect to $[H_2]$.
Explain your answer.

order of reaction with respect to $[H_2]$ .....

explanation .....

.....
[1]

(iii) State the rate equation for the reaction of iodine gas with hydrogen gas.

rate = [1]

(iv) Use the data from **experiment 2** to calculate the rate constant, k, at 800 K.

k = ... units ..... [1]

(v) Calculate the rate of reaction for **experiment 4**.

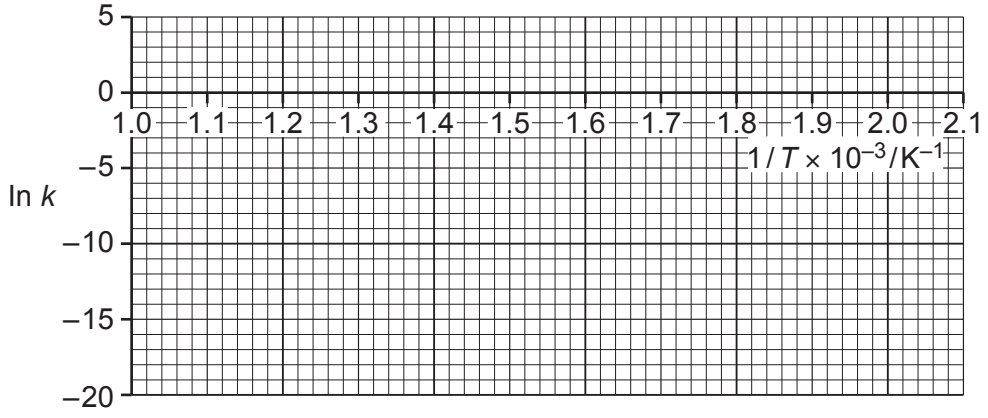
rate of reaction = ... $mol\,dm^{-3}\,s^{-1}$ [1]

(d) A further series of experiments is conducted at different temperatures with the same concentrations as those used in experiment 1. The value of k at each temperature is given.

experiment	k (units not given)	temperature T / K	$1/T$ in K^{-1}	ln k
5	2.08×10^{-7}	500	2.00×10^{-3}	–15.39
6	3.10×10^{-2}	700		
7	2.31×10^{1}	900		

(i) Complete the table. [1]

(ii) Plot ln k against $1/T \times 10^{-3}$ on the axes provided only using the values in the table for experiments 5, 6 and 7. Draw a line of best fit. [2]



(iii) Use the relevant equation in the *Data Booklet* and the line of best fit to calculate the activation energy, E_a, for the reaction.
Show your working.

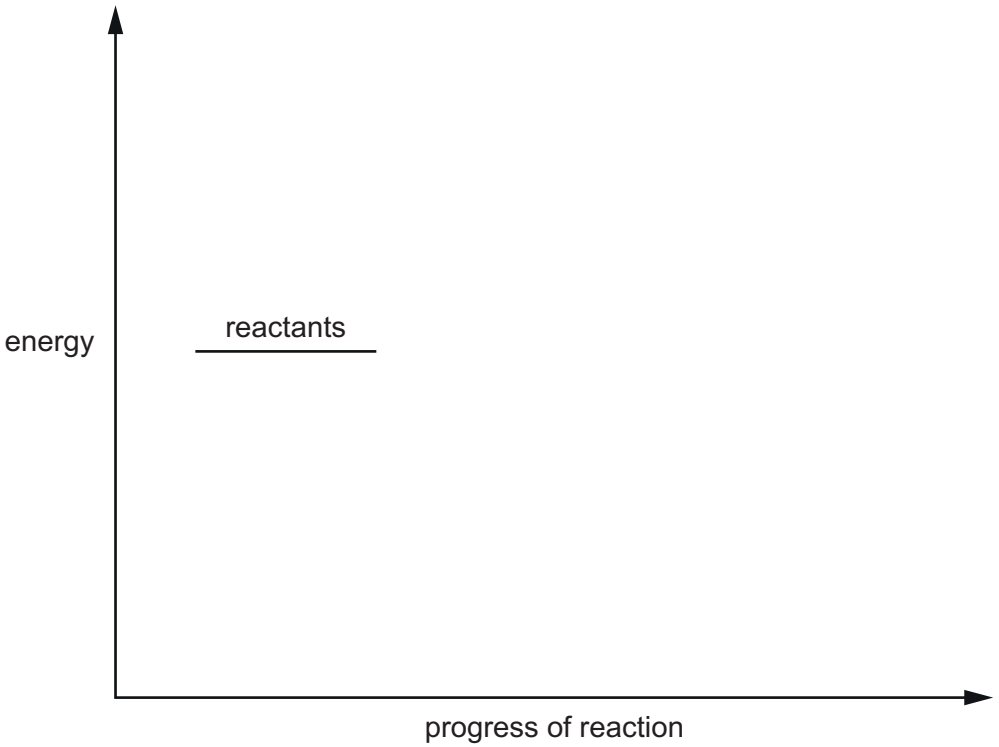
E_a = ... $kJ\,mol^{-1}$ [3]

(e) One data source gives the activation energy of the iodine gas and hydrogen gas forward reaction as +170.2 kJ mol^{-1} and the activation energy of the reverse reaction as +182.8 kJ mol^{-1}.

Use these values from the data source to calculate a value for ΔH for the forward reaction and to complete a sketch of the reaction profile energy diagram. Assume it is a one-step reaction.

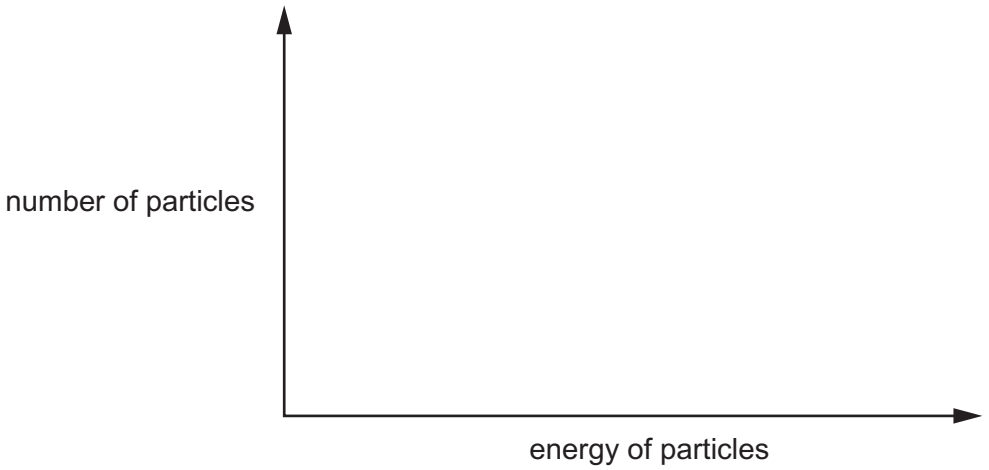
Add labels for:
- E_a(forward) for the activation energy of the forward reaction
- E_a(reverse) for the activation energy of the reverse reaction
- ΔH for the forward reaction.

ΔH for the forward reaction = ... kJ mol^{-1}



[4]

(f) The axes for a Maxwell–Boltzmann distribution are shown in the diagram.



(i) Sketch Maxwell–Boltzmann distributions for the reactions at 500 K and 900 K on the diagram, clearly labelling each line. [3]

(ii) Explain why the reaction is slower at 500 K than at 900 K. Annotate the diagram to illustrate your answer.

.....

.....

.....

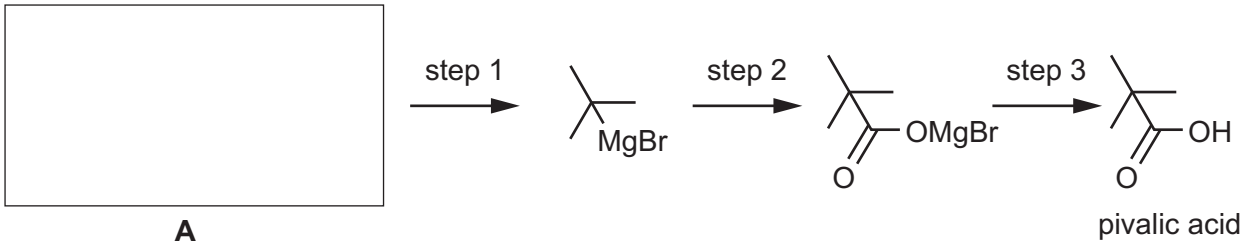
.....

..... [3]

[Total: 25]

2 Dimethylpropanoic acid, $CH_3C(CH_3)_2COOH$, is known as pivalic acid. It is used in industry as its esters are resistant to hydrolysis.

(a) Pivalic acid is made in a three-step process starting from **A**.



A

pivalic acid

(i) Draw the structure of **A** in the box. Name **A**.

name of **A** ..... [2]

(ii) State what reacts with the Grignard reagent in step 2.

..... [1]

(b) Pivalic acid has a pK_a value of 5.03.
Calculate the pH of the solution formed when 0.40 g of pivalic acid is dissolved in 200 cm^3 of water.
Show your working.

pH = ... [4]

(c) Pivalic acid and pentanoic acid are isomers. Pentanoic acid has a pK_a value of 4.82.

- Suggest what the pK_a values of these two acids indicate about their acidic strength.
- Explain how the different inductive effects of the alkyl groups lead to different acid strengths.

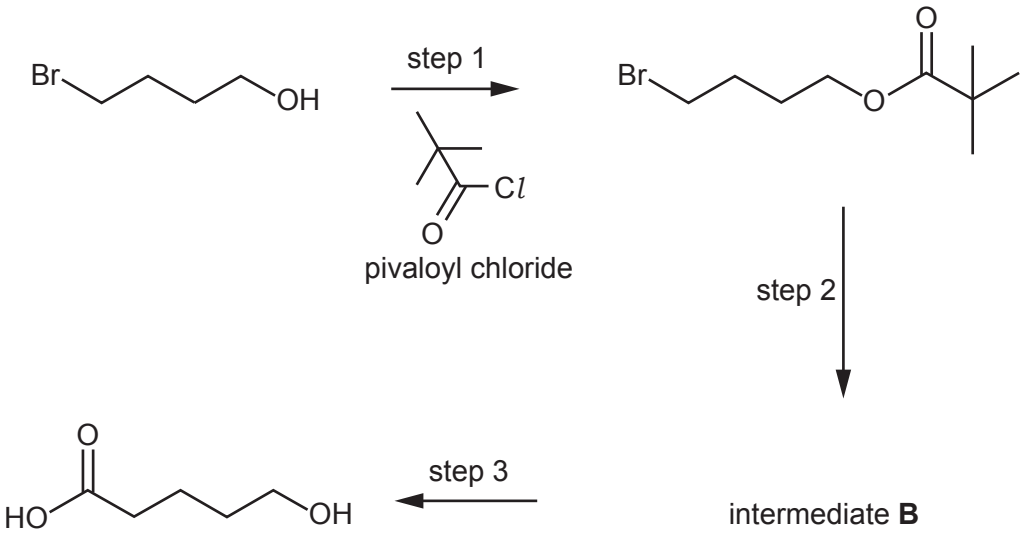
.....

.....

.....

..... [3]

(d) Pivaloyl chloride, $CH_3C(CH_3)_2COCl$, is a derivative of pivalic acid. It can be used to provide a protecting group in organic syntheses, preventing unwanted reactions.
In the following synthesis, 4-bromobutan-1-ol is converted into 5-hydroxypentanoic acid. Unwanted reactions of the OH group are prevented.



The protecting group is added to the alcohol in step 1 and removed in step 3.

(i) Name a reagent used to convert pivalic acid to pivaloyl chloride.

..... [1]

(ii) State the type of reaction occurring in step 1.

..... [1]

(iii) Draw the structure of intermediate **B**.

[1]

(iv) State the reagent used in step 2.

..... [1]

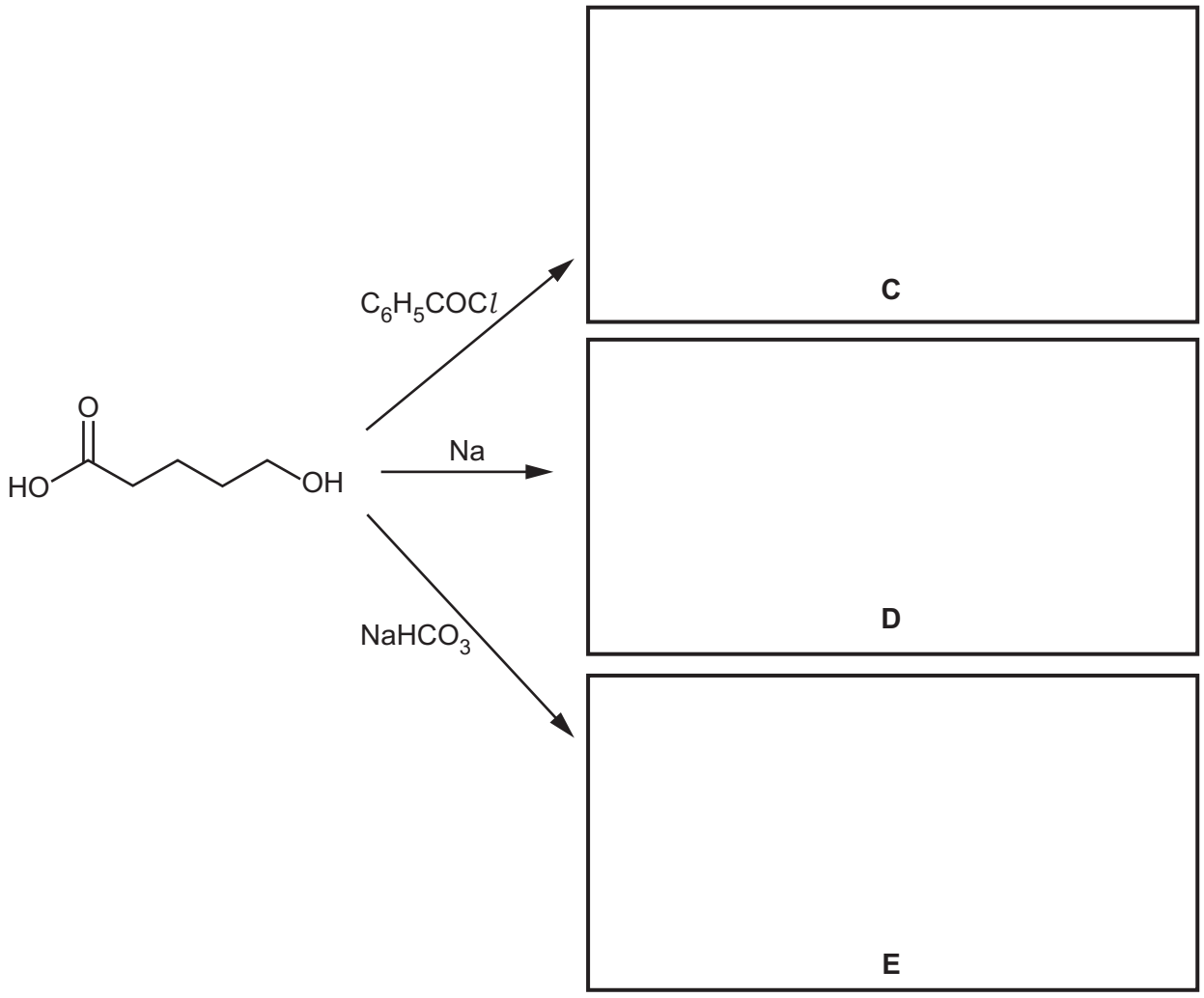
(v) State the reagents and reaction type for step 3.

reagents .....

reaction type .....

[2]

(e) The reaction scheme shows three reactions of 5-hydroxypentanoic acid.
Complete the reaction scheme by drawing the structures of the organic products **C**, **D** and **E** in the boxes provided.

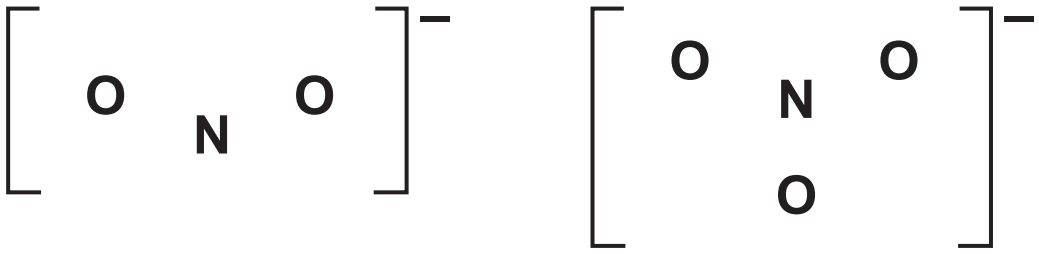


[3]

[Total: 19]

3 This question is about compounds containing the nitrite ion, NO_2^-, and the nitrate ion, NO_3^-.

(a) Complete the dot-cross diagrams for NO_2^- and NO_3^-.
- Use dots (●) for electrons from oxygen.
- Use crosses (×) for electrons from nitrogen.
- Use triangles (▲) for electrons from elsewhere.
- Show outer electrons only.



[2]

(b) State why NO_2^- can act as a Lewis base.

.....

..... [1]

(c) NO_2^- ions can act as ligands in complex ions.

(i) State the meaning of the term *complex ion*.

.....

..... [1]

(ii) A complex ion consists of five NH_3 molecules, one Co^{3+} ion and one NO_2^- ion.
- Draw the three-dimensional structure of the complex, including the overall charge. Assume the NO_2^- ion bonds through the nitrogen atom.
- State the shape of the complex.
- Give the formula for the complex.

complex shape .....

complex formula .....
[4]

(d) Sodium nitrite decomposes when heated strongly.

$$2NaNO_2 \rightarrow Na_2O + NO + NO_2 \qquad \Delta H^{\ominus} = +426.6\,kJ\,mol^{-1}$$
$$\Delta S^{\ominus} = +318.2\,J\,K^{-1}\,mol^{-1}$$

Some thermodynamic data is shown in the table.

	$\Delta_f H^{\ominus}$ / kJ mol^{-1}	$S^{\ominus}$ / J K^{-1} mol^{-1}
$NaNO_2$	–358.7	
Na_2O	–414.2	75.1
NO		210.7
NO_2	+33.2	240.0

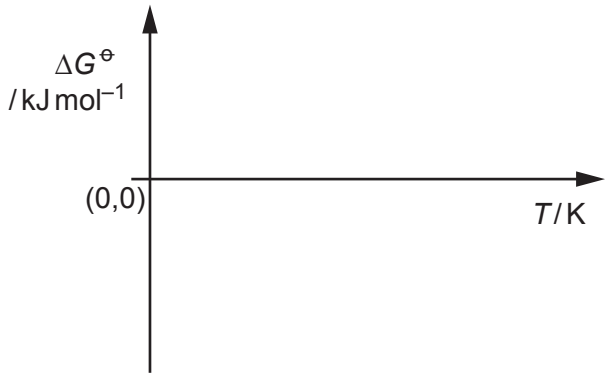
(i) Calculate $\Delta_f H^{\ominus}$ for nitrous oxide, NO.
Show your working.

$\Delta_f H^{\ominus}$(NO) = ... kJ mol^{-1} [2]

(ii) Calculate $S^{\ominus}$ for $NaNO_2$.

$S^{\ominus}(NaNO_2)$ = ... J K^{-1} mol^{-1} [1]

(iii) Use the relevant equation in the *Data Booklet* to sketch a graph to show how $\Delta G^{\ominus}$ changes with temperature, T, for this reaction.



[2]

(iv) Calculate the temperature, in K, at which the reaction becomes spontaneous. Use the relevant equation in the *Data Booklet*.
Show your working.

temperature = ... K [3]

(e) Nitrous acid, HNO_2, reacts with aqueous iron(II) ions, $Fe^{2+}(aq)$, as shown.

$$Fe^{2+} + HNO_2 + H^+ \longrightarrow Fe^{3+} + NO + H_2O \quad E^{\ominus} = +0.17\,V$$

(i) The half-cell data for the reduction of Fe^{3+} is shown.

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^{\ominus} = +0.77\,V$$

Deduce the half-equation for the reduction of HNO_2 and calculate its half-cell potential.

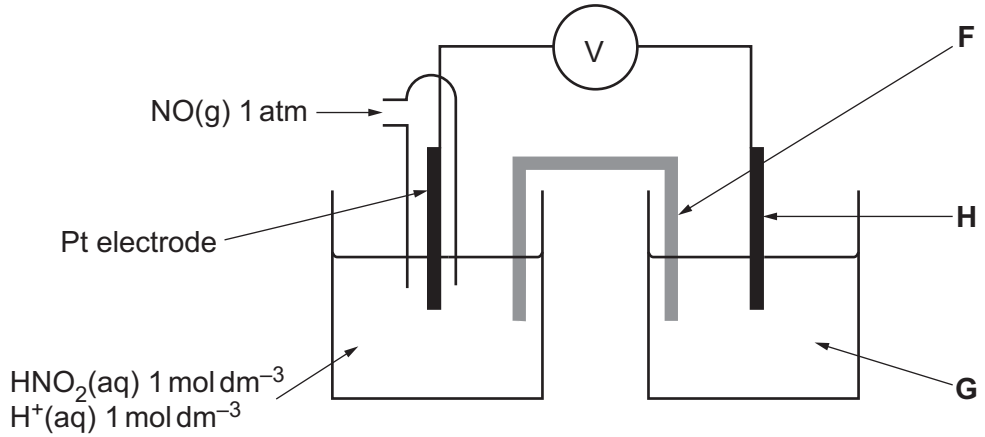
.....

.....

half-cell potential = ... V

[2]

(ii) The diagram of apparatus to measure $E^{\ominus}_{cell}$ for this system is incomplete.



Indicate on the diagram the direction of electron flow through the apparatus.

State the labels for **F** and **G**. State a suitable material for **H**.

F .....

G .....

H .....

[4]

(iii) Predict the effect on E_{cell}, if any, of lowering the concentration of $Fe^{2+}(aq)$ in the right-hand beaker.
Explain your answer, including any effects on the half-cell potentials involved.

.....

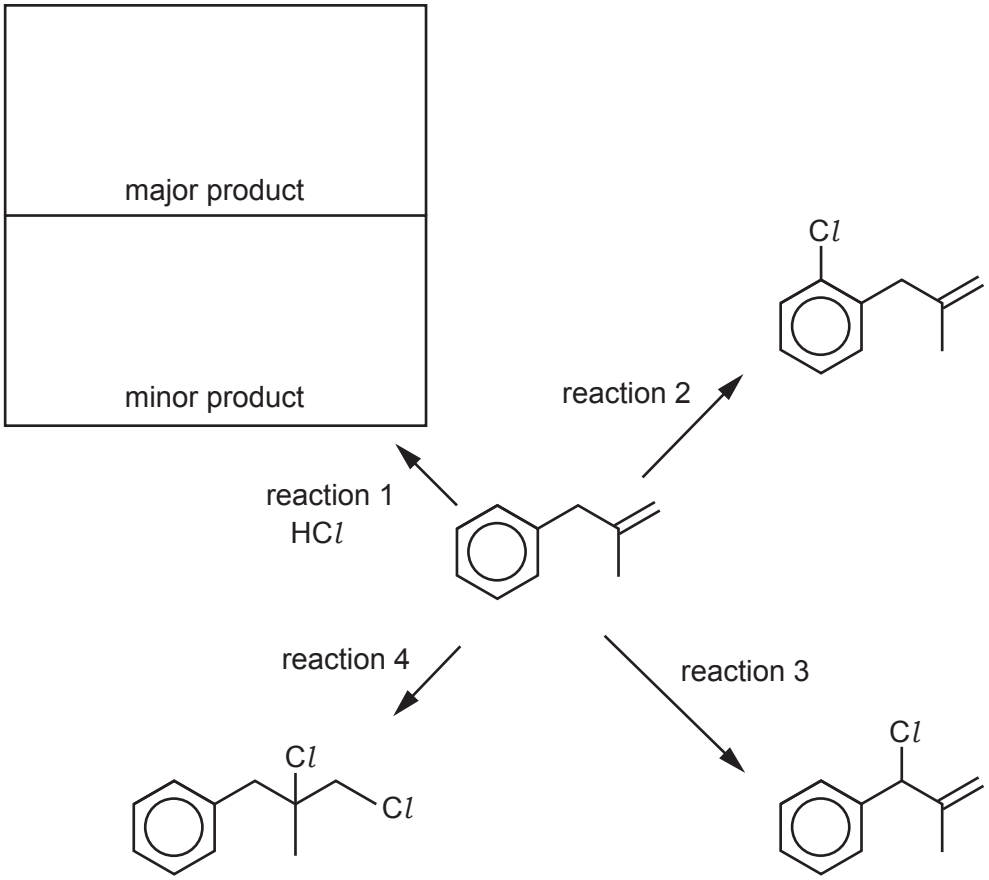
.....

.....

..... [2]

[Total: 24]

4 2-methyl-3-phenylprop-1-ene is a useful precursor in organic synthesis. Some reactions of 2-methyl-3-phenylprop-1-ene are shown.



(a) (i) Draw the structures of the major and minor products of reaction 1 in the boxes provided. [2]

(ii) Reaction 3 takes place at room temperature.
State the reagent and conditions for reaction 3.

reagent .....

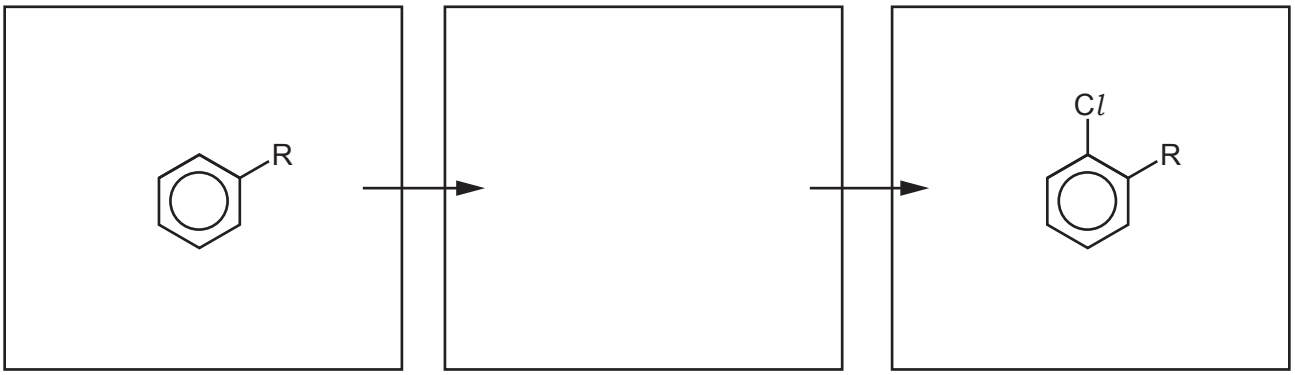
conditions .....
[1]

(iii) Circle **all** the chiral centres in the products of reactions 2, 3 and 4. [1]

(b) The chlorination of a benzene ring follows a similar mechanism as for bromination, but uses Cl_2 as the reagent and an $AlCl_3$ catalyst.

(i) Draw the mechanism for reaction 2, including the steps involving the catalyst.
R is used to represent the rest of the molecule.
Use curly arrows and show all relevant lone pairs and dipoles.

initial reaction involving catalyst .....

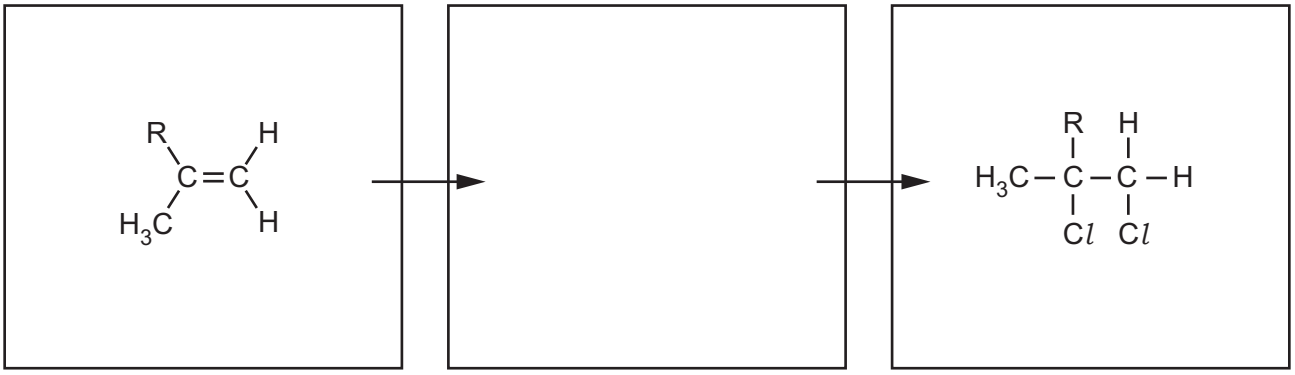


final reaction involving catalyst .....
[4]

(ii) State the name of the reaction mechanism for reaction 2 in **(b)(i)**.

..... [1]

(c) **(i)** Draw the reaction mechanism for reaction 4. R is used to represent the rest of the molecule.
Use curly arrows and show all relevant lone pairs and dipoles.

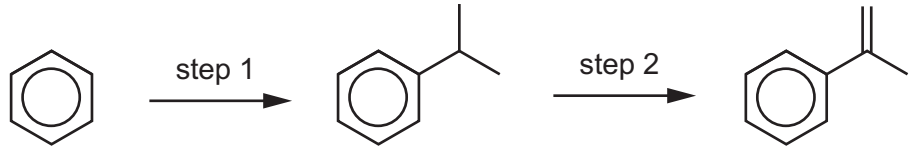


[4]

(ii) State the name of the reaction mechanism for reaction 4 in **(c)(i)**.

..... [1]

(d) 2-phenylpropene is another precursor in organic synthesis. It can be synthesised from benzene using the following route.



(i) Name the organic reagent in step 1.

..... [1]

(ii) State the type of reaction occurring in step 2.

..... [1]

[Total: 16]

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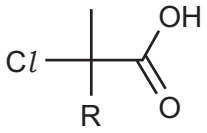
5 Compound **X** is an organic acid. R represents an alkyl group.



X

(a) The mass spectrum of **X** has an M+2 peak at m/z = 152.

(i) State the relative heights of the molecular ion and M+2 peaks.

..... [1]

(ii) Show that the formula of the R group is C_3H_7.

[1]

(iii) Write an equation to show the formation of the particle that causes the M+2 peak at m/z = 152.

..... [1]

(b) **X** has the following proton NMR peaks.

peak	δ/ppm	splitting pattern	integral
S	0.8	doublet	6
T	1.2	multiplet	
U	4.2	singlet	3
V	11.2	singlet	1

The δ value is given relative to tetramethylsilane, TMS.

(i) Suggest **three** reasons why TMS is used as a reference compound in proton NMR spectroscopy.

.....

.....

.....

..... [3]

(ii) State the value of the integral for peak **T**.

..... [1]

(iii) Draw the structure of **X**.
Indicate the hydrogen atoms that give rise to peaks **S**, **T**, **U** and **V**.

[3]

(iv) Explain why peak **U** has a larger δ value than peak **S**.

.....

.....

.....

.....

..... [4]

(v) On addition of D_2O, one peak disappears.
State which peak disappears. Give an equation to explain why the peak disappears.

peak that disappears .....

equation

[2]

[Total: 16]

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