Cambridge International AS & A Level

Cambridge Assessment International Education
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME			
CENTRE NUMBER		CANDIDATE NUMBER	

9381752094

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **February/March 2019**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, candidate number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.
You may lose marks if you do not show your working or if you do not use appropriate units.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **20** printed pages.

Cambridge Assessment International Education

[Turn over

Answer **all** the questions in the spaces provided.

1 **(a)** State **one** natural and **one** man-made occurrence of oxides of nitrogen.

....

.... [1]

(b) Under conditions of high pressure and a catalyst, nitrogen monoxide, NO, forms two other oxides of nitrogen, dinitrogen monoxide, N_2O, and dinitrogen trioxide, N_2O_3.

...... NO(g) → ...... N_2O(g) + ... N_2O_3(g) $\Delta H^\ominus = -195.2\,kJ\,mol^{-1}$
$\Delta G^\ominus = -102.8\,kJ\,mol^{-1}$

(i) Balance the equation above for the formation of N_2O and N_2O_3 from NO. [1]

(ii) State how the oxidation number of nitrogen changes during this reaction.

NO → N_2O from .... to ....

NO → N_2O_3 from .... to ....

[1]

(iii) Calculate the entropy change for the reaction at 298 K. Include the units in your answer.

$\Delta S^\ominus$ = ...

units = ...

[2]

(iv) State whether the sign of $\Delta S^\ominus$ calculated in **(iii)** agrees with that predicted from your balanced equation in **(i)**. Explain your answer.

....

.... [1]

(c) At room temperature N_2O_3 dissociates.

$$N_2O_3(g) \rightleftharpoons NO(g) + NO_2(g)$$

(i) Write the expression for K_p for this equilibrium. Include the units in your answer.

K_p =

units = ...

[1]

A 1.00 dm^3 flask at 25 °C is filled with pure $N_2O_3(g)$ at an initial pressure of 0.60 atm.
At equilibrium, the partial pressure of $NO_2(g)$ is 0.48 atm.

(ii) Calculate the partial pressures of NO(g) and $N_2O_3(g)$ at equilibrium. Hence calculate the value of K_p at 25 °C.

p(NO(g)) = ...

$p(N_2O_3(g))$ = ...

K_p = ...

[2]

(d) NO reacts readily with oxygen.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The table shows how the initial rate of this reaction at 25 °C depends on the initial concentrations of the reactants.

initial concentration / mol dm^{-3}		initial rate / mol dm^{-3} s^{-1}
[NO(g)]	[O_2(g)]	
0.100	0.0500	3.50
0.0500	0.100	1.75
0.0500	0.0500	0.875

(i) Deduce the order of reaction with respect to each reactant. Explain your reasoning.

order with respect to [NO(g)] ....

....

order with respect to [O_2(g)] ....

....

[2]

(ii) State the rate equation for this reaction. Use the rate equation to calculate the rate constant. Include the units for the rate constant in your answer.

rate =

rate constant, *k* = ...

units of *k* = ...

[3]

(e) NO reacts with iron pentacarbonyl, $Fe(CO)_5$, as shown. NO and CO are both monodentate ligands.

$$Fe(CO)_5 + 2NO \rightarrow Fe(CO)_2(NO)_2 + 3CO$$

During this reaction the co-ordination number of the iron changes.

(i) State what is meant by the term *co-ordination number*.

....

.... [1]

(ii) Describe how the co-ordination number of the iron changes during this reaction.

from .... to .... [1]

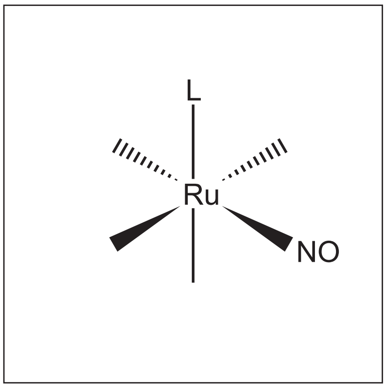
(iii) Only one stereoisomer of $Fe(CO)_2(NO)_2$ exists.

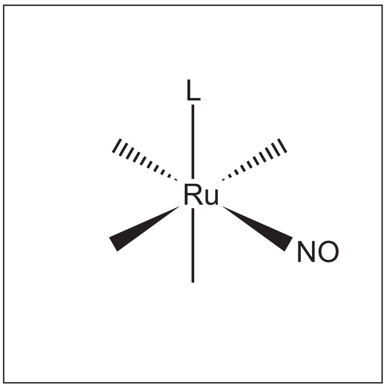
Use this information to suggest the geometry of the complex.

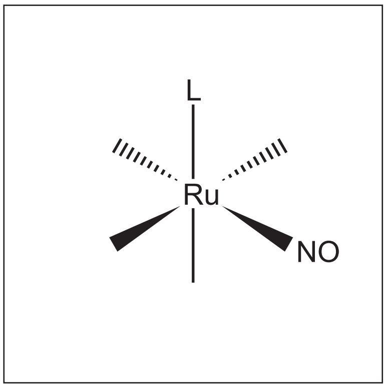
.... [1]

(f) The complex $Ru(NO)L_2Cl_3$ exists in three isomeric forms. L represents the monodentate ligand $C_6H_5P(CH_3)_2$.

(i) Complete the three-dimensional diagrams to show the **three** isomers of $Ru(NO)L_2Cl_3$.







[2]

(ii) Suggest the type of isomerism shown.

.... [1]

[Total: 20]

2 **(a)** The following table lists the solubilities of the hydroxides and carbonates of some of the Group 2 elements, **M**, at 25 °C.

element **M**	solubility / mol dm^{-3}	
	$M(OH)_2$	MCO_3
Mg	2.0×10^{-4}	1.5×10^{-3}
Ca	1.5×10^{-2}	1.3×10^{-4}
Sr	3.4×10^{-2}	7.4×10^{-5}
Ba	1.5×10^{-1}	9.1×10^{-5}

(i) Explain why the solubility of the Group 2 hydroxides, $M(OH)_2$, increases down the group.

....

....

....

....

.... [3]

(ii) Suggest a reason for the general decrease in the solubility of the Group 2 carbonates, MCO_3, down the group.

....

.... [1]

(iii) When carbon dioxide is passed through a saturated solution of calcium hydroxide (limewater), a white precipitate of calcium carbonate is formed.

Use the data in the table to deduce, for **each** of Mg, Sr and Ba, whether or not a saturated solution of its hydroxide could also be used to test for carbon dioxide.
Explain your answer. No calculations are required.

....

....

....

....

.... [2]

(b) **(i)** Calculate the value of the solubility product, K_{sp}, of magnesium hydroxide at 25 °C.

K_{sp} = ...
[2]

(ii) State what would be observed if a few drops of a saturated solution of barium hydroxide are added to a saturated solution of barium carbonate. Explain your answer.

observation ....

explanation ....

....
[2]

(c) The equation for the formation of the gaseous hydroxide ion is shown.

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}O_2(g) + e^- \rightarrow OH^-(g) \qquad \Delta H = \Delta H_f^\ominus(OH^-(g))$$

Use data in the table and from the *Data Booklet* to calculate $\Delta H_f^\ominus(OH^-(g))$. You might find it useful to construct a Born-Haber cycle.

enthalpy change	$\Delta H^\ominus$ / kJ mol^{-1}
atomisation of Mg(s)	+148
formation of $Mg(OH)_2(s)$	–925
lattice energy of $Mg(OH)_2(s)$	–2993

$\Delta H_f^\ominus(OH^-(g))$ = ... kJ mol^{-1}
[3]

[Total: 13]

3 **(a)** **(i)** Use mathematical expressions to define the following terms.

- pH = ...

  ....

- K_a for a weak acid, HA = ...

  ....

[2]

(ii) Write equations to show how a buffer solution consisting of a mixture of HA(aq) and NaA(aq) controls pH when an acid or an alkali is added.

....

....

.... [2]

(b) When chlorine dissolves in water the following reaction occurs.

$$Cl_2(g) + H_2O(l) \rightarrow HClO(aq) + H^+(aq) + Cl^-(aq)$$

When solutions of chlorine are used for water purification, the pH of the solution of chlorine is kept near to pH 7 by the addition of a base.

Chlorine is dissolved in water to produce 1000 cm^3 of a solution containing 0.170 mol of HClO and 0.170 mol of HCl.

A buffer solution is then prepared by adding 0.200 mol of NaOH(s) to this solution. The NaOH reacts initially with the HCl.

Calculate the pH of the buffer solution.

[HClO is a weak acid with $K_a = 2.9 \times 10^{-8}$ mol dm^{-3}.]

pH = ... [3]

[Total: 7]

4 (a) (i) Complete the electronic configuration of a copper atom.

$1s^2 2s^2 2p^6$ .... [1]

(ii) ● Explain why most copper(II) salts are coloured.

....

....

....

....

● Suggest why copper(I) salts are usually white.

....

....

[4]

(b) Brass is an alloy of copper and zinc. The following reaction can be used to determine the amount of copper in a sample of brass.

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$$

The procedure was carried out using the following steps.

- A solution of Cu^{2+}(aq) was obtained by dissolving a 1.50 g sample of brass in concentrated sulfuric acid and diluting with water.
- An excess of I^{-}(aq) was added.
- The iodine produced was titrated against a 0.500 mol dm^{-3} solution of thiosulfate ions, $S_2O_3^{2-}$(aq).

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$$

- The volume of $S_2O_3^{2-}$ solution needed to reach the end-point was 28.35 cm^3.

Calculate the percentage by mass of copper in the sample of brass.

percentage by mass of copper = ...
[3]

(c) (i) Use standard electrode potential data from the *Data Booklet* to calculate $E^{\ominus}_{cell}$ for the reaction.

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$$

$E^{\ominus}_{cell}$ = ... V [1]

(ii) Explain how the value of $E^{\ominus}_{cell}$ calculated in **(i)** predicts that the reaction is **not** likely to occur.

....

.... [1]

In an experiment, a solution of I^{-}(aq) is added to a solution of Cu^{2+}(aq). A reaction **does** occur and a precipitate of sparingly soluble CuI(s) is formed.

The concentration of Cu^{2+}(aq) remaining in the solution is 1.00 mol dm^{-3}.
The concentration of Cu^{+}(aq) in a saturated solution of CuI is 1.3×10^{-6} mol dm^{-3}.

(iii) Use the Nernst equation to calculate the electrode potential, *E*, for the Cu^{2+}/Cu^{+} half cell in this experiment.

$E(Cu^{2+}/Cu^{+})$ = ... V [2]

(iv) Copper(I) chloride is also sparingly soluble in water.

Suggest why the following reaction does **not** occur.

$$2Cu^{2+}(aq) + 4Cl^{-}(aq) \not\longrightarrow 2CuCl(s) + Cl_2(aq)$$

....

.... [1]

(d) When chloride ions are added to a solution containing Cu^{2+}(aq), the complex ion $[CuCl_4]^{2-}$(aq) is formed.

(i) State the colours of Cu^{2+}(aq) and $[CuCl_4]^{2-}$(aq).

Cu^{2+}(aq) ....

$[CuCl_4]^{2-}$(aq) ....
[1]

(ii) Name the type of reaction that occurs when $[CuCl_4]^{2-}$(aq) is formed from Cu^{2+}(aq).

.... [1]

(iii) Write an expression for the stability constant, K_{stab}, for $[CuCl_4]^{2-}$(aq). Include the units in your answer.

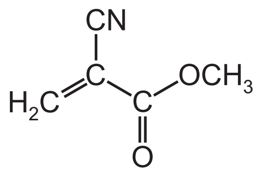
K_{stab} =

units = ...
[2]

[Total: 17]

5 **(a)** Methyl 2-cyanoprop-2-enoate, **W**, is the major component of *Super Glue*, a rapid-setting adhesive.
As the adhesive sets, the monomer **W** polymerises.

W



(i) Draw a section of the polymer showing **two** repeat units.

[2]

(ii) Name the type of polymerisation occurring.

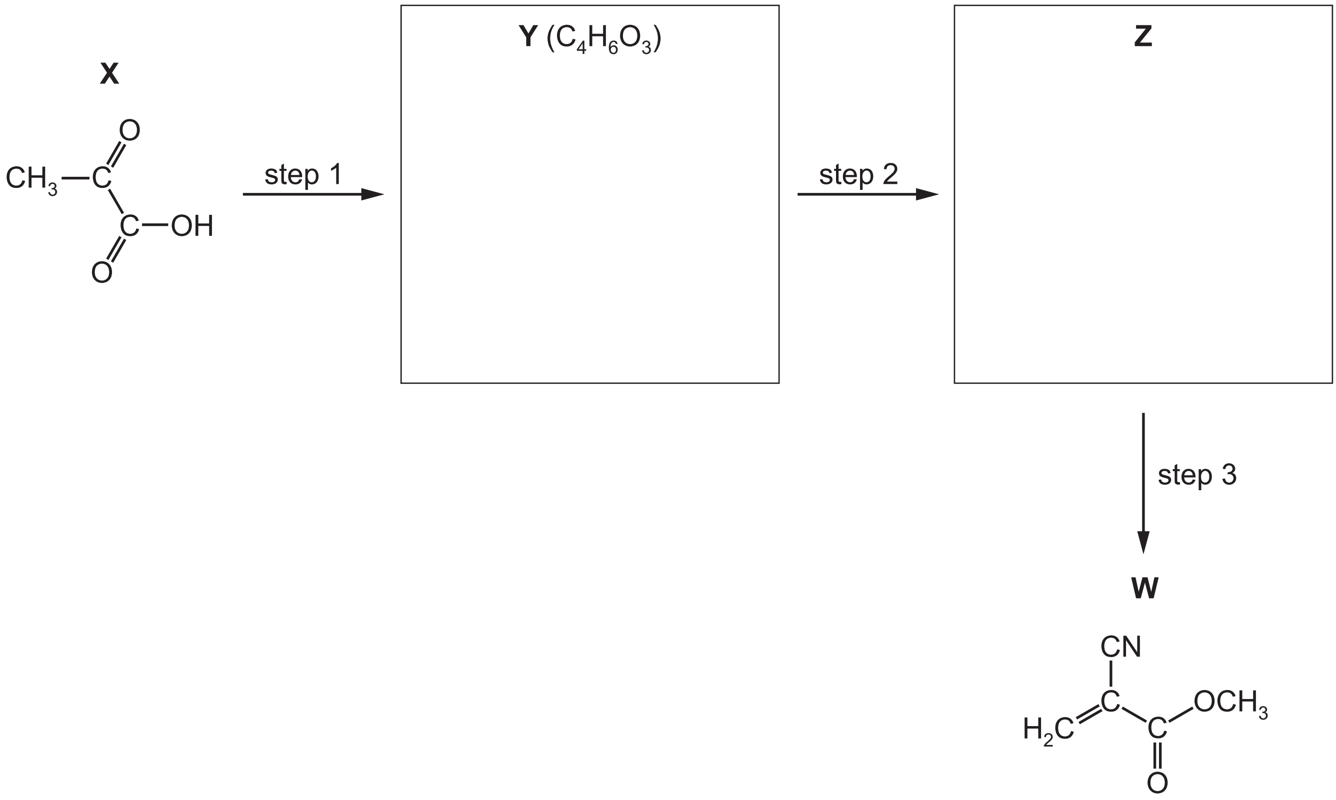
.... [1]

(iii) Suggest **two** types of intermolecular force that could occur between the *Super Glue* polymer and the objects glued together. For each type of intermolecular force, refer to the atoms/groups in the *Super Glue* polymer involved in the attraction.

type of intermolecular force	atoms/groups in the *Super Glue* polymer

[2]

(b) **W** can be synthesised in three steps, starting from 2-oxopropanoic acid, **X**.



(i) Suggest the identities of compounds **Y** and **Z** by drawing their structures in the boxes. [2]

(ii) Suggest suitable reagents and conditions for each of the steps 1–3.

step 1 ....

step 2 ....

step 3 ....
[4]

[Total: 11]

6 The names of many drugs used in medicine often include parts of the names of the functional groups their molecules contain.

(a) Suggest **two** functional groups present in a molecule of the drug named chloramphenicol.

1 ....

2 .... [1]

(b) The drug named ketamine readily reacts with protons as shown.

$$\text{ketamine} + H^+ \rightarrow [\text{ketamine-H}]^+$$

(i) State the role of ketamine in this reaction.

.... [1]

Ketamine gives an orange precipitate with 2,4-dinitrophenylhydrazine (2,4-DNPH).

(ii) Suggest the functional group in the ketamine molecule responsible for this observation.

.... [1]

The mass spectrum of ketamine is determined. Two peaks close to the molecular ion peak, M, are observed with the relative abundances shown in the table.

peak	m / e	relative abundance
M	237	100.0
M+1	238	14.3
M+2	239	33.3

(iii) Use the numbers in the table to show that there are 13 carbon atoms in a ketamine molecule.

[1]

In addition to carbon and hydrogen atoms, each molecule of ketamine contains **one** atom of each of **three** different elements. These are called heteroatoms. One of these heteroatoms is a halogen.

(iv) Use the figures in the table to suggest the identity of this halogen. Explain your answer.

....

.... [1]

(v) Another peak in the mass spectrum of ketamine has an m / e value of 240.

Predict the relative abundance of this peak.

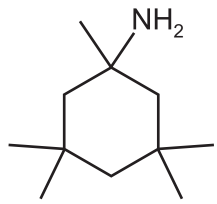
relative abundance = ... [1]

(vi) Use the information in **(b)** to complete the molecular formula of ketamine by working out the identities of the **three** different heteroatoms and the number of hydrogen atoms present.

$$C_{13}H$$

[1]

(c) Neramexane is another drug.



neramexane

(i) Suggest the number of peaks in the carbon-13 NMR spectrum of neramexane.

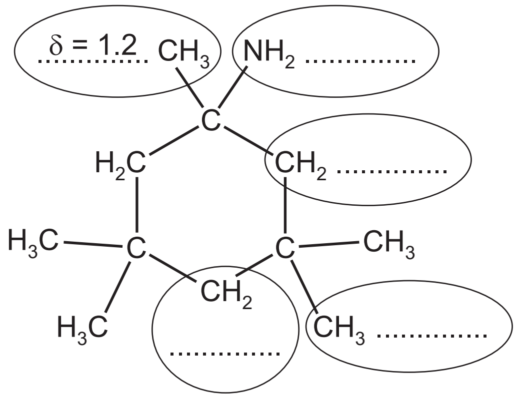
.... [1]

The proton (^{1}H) NMR spectrum of neramexane in $CDCl_3$ shows five peaks with the following chemical shifts (δ).

δ / ppm	number of protons responsible	splitting pattern (singlet, doublet, triplet, quartet or multiplet)
0.9		singlet
1.2	3	
1.4	2	
1.7	4	
2.2		broad singlet

(ii) Complete the table. [4]

(iii) Use the *Data Booklet* and the table in **(c)(ii)** to complete the assignment of the correct δ values to each of the circled hydrogen atoms on the structure of neramexane.



[2]

(iv) One of the peaks in the proton (^{1}H) NMR spectrum disappears when the sample is shaken with D_2O.

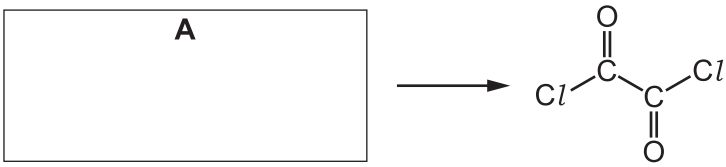
Identify the peak and explain why it disappears.

....

.... [1]

[Total: 15]

7 Ethanedioyl dichloride, C*l*COCOC*l*, is a useful reagent in organic synthesis. It can be made from compound **A** in one step.

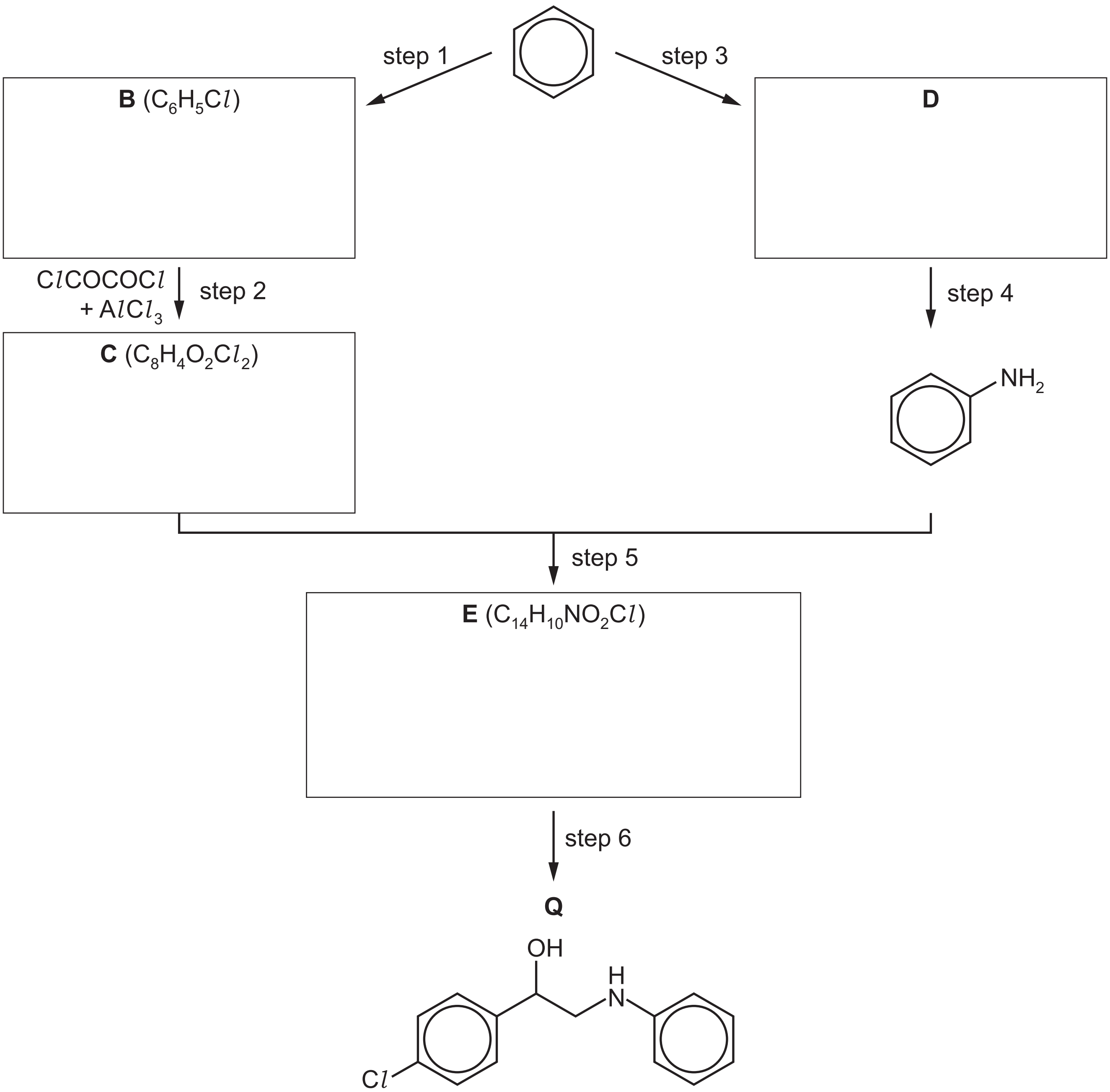


(a) (i) Suggest the identity of compound **A** by drawing its structure in the box. [1]

(ii) State the reagents and conditions needed to convert **A** into C*l*COCOC*l*.

.... [1]

Ethanedioyl dichloride is used in the following synthesis of compound **Q**. It is used in a 1:1 stoichiometric ratio with **B** in step 2.



(b) **(i)** Suggest the identities of the compounds **B**–**E** by drawing their structures in the boxes. [4]

(ii) State the reagents and conditions for the following steps.

step 1 ....

step 3 ....

step 4 ....

step 6 ....
[5]

If the amount of C*l*COCOC*l* used in step 2 is decreased, another compound is formed in step 2 with the molecular formula $C_{14}H_8O_2Cl_2$.

(iii) Suggest the structure of this compound.

$C_{14}H_8O_2Cl_2$

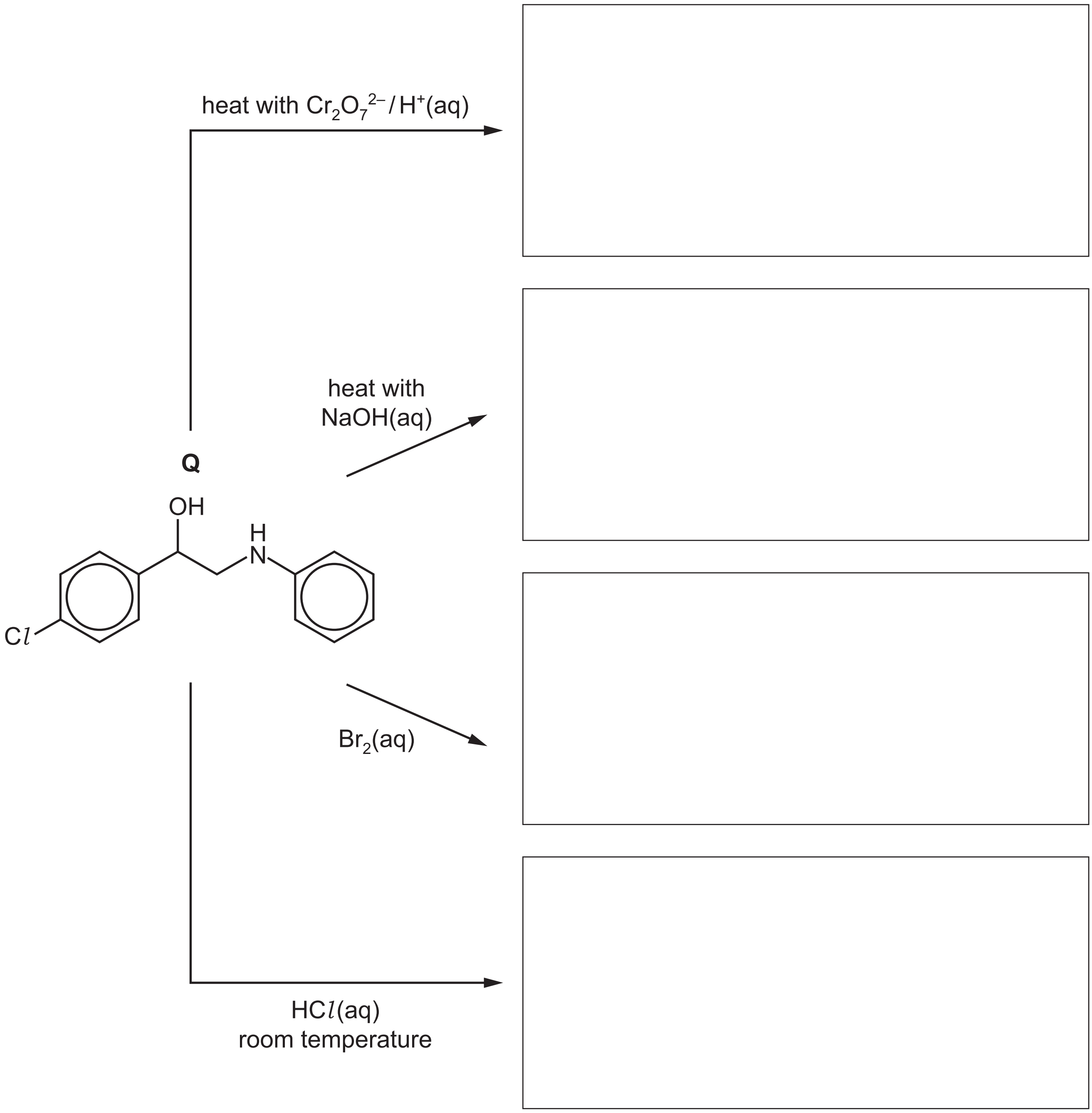
[1]

(iv) Identify **all** the steps in the synthesis of **Q** from benzene that are electrophilic substitution reactions.

.... [1]

Question 7 continues on page 20.

(c) Draw structures of the compounds formed when **Q** is treated with the following reagents. If there is no reaction, write 'no reaction' in the box.



[4]

[Total: 17]