Cambridge Assessment
International Education

Cambridge International AS & A Level

CANDIDATE NAME			
CENTRE NUMBER		CANDIDATE NUMBER	

9281939058

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **February/March 2024**

2 hours

You must answer on the question paper.

No additional materials are needed.

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 and use appropriate units.

INFORMATION
- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [ ].
- The Periodic Table is printed in the question paper.
- Important values, constants and standards are printed in the question paper.

This document has **28** pages. Any blank pages are indicated.

DC (JP/SW) 327718/2

1 Potassium iodide, KI, is used as a reagent in both inorganic and organic chemistry.

(a) KI forms an ionic lattice that is soluble in water.

(i) Define enthalpy change of solution, ΔH_{sol}.

....

....

.... [1]

(ii) KI(s) has a high solubility in water although its enthalpy change of solution is endothermic.

Explain how this high solubility is possible.

....

....

.... [2]

(b) Table 1.1 gives some data about the halide ions, Cl^-, Br^- and I^-, and their potassium salts.

Table 1.1

halide ion	enthalpy change of hydration, ΔH_{hyd} / kJ mol^{-1}	lattice energy of potassium halide, ΔH_{latt} / kJ mol^{-1}
Cl^-	–364	–701
Br^-	–335	–670
I^-	–293	–629

(i) Explain the trend in the enthalpy change of hydration of the halide ions.

....

....

....

.... [2]

(ii) The ΔH_{sol} values of these potassium halides are almost constant.

Use the ΔH_{hyd} and ΔH_{latt} data in Table 1.1 to suggest why.

....

....

.... [1]

(iii) The enthalpy change of solution of KI(s) is +21.0 kJ mol^{-1}.

Use this information and the data in Table 1.1 to calculate the enthalpy change of hydration of the potassium ion, K^+(g).

ΔH_{hyd} of K^+(g) = ... kJ mol^{-1} [1]

(iv) Solid PbI_2 forms when KI(aq) is mixed with Pb^{2+}(aq) ions.

The solubility product, K_{sp}, of PbI_2 is 7.1×10^{-9} mol^3 dm^{-9} at 25 °C.

Calculate the solubility, in mol dm^{-3}, of PbI_2(s).

solubility of PbI_2(s) = ... mol dm^{-3} [2]

(v) The ionic radius of Pb^{2+} is 0.120 nm compared to 0.133 nm for K^+.

Suggest how the $\Delta H^{\ominus}_{latt}$ of PbI_2(s) differs from $\Delta H^{\ominus}_{latt}$ of KI(s).

Explain your answer.

....

....

.... [2]

(c) KI slowly oxidises in air, forming I_2.

reaction 1 $4KI(s) + 2CO_2(g) + O_2(g) \rightarrow 2K_2CO_3(s) + 2I_2(s)$ $\Delta H^{\ominus} = -203.4\,kJ\,mol^{-1}$

Table 1.2 shows some data relevant to this question.

Table 1.2

substance	standard entropy, $S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$
$CO_2(g)$	213.6
$I_2(s)$	116.1
$K_2CO_3(s)$	155.5
$KI(s)$	106.3
$O_2(g)$	205.2

(i) Calculate the standard entropy change, $\Delta S^{\ominus}$, of reaction 1.

$\Delta S^{\ominus}$ = ... $J\,K^{-1}\,mol^{-1}$ [2]

(ii) Use your answer to **(c)(i)** to show that reaction 1 is spontaneous at 298 K.

[2]

(iii) The Group 1 carbonates are much more thermally stable than the Group 2 carbonates.

State and explain the trend in the thermal stability of the Group 2 carbonates.

....

....

....

.... [2]

(d) A student electrolyses a solution of KI(aq) for 8 minutes using a direct current.

The half-equation for the reaction that occurs at the anode is given.

$$2I^-(aq) \rightarrow I_2(aq) + 2e^-$$

(i) Write a half-equation for the reaction that occurs at the cathode.

Include state symbols.

.... [1]

(ii) After the electrolysis, the I_2(aq) produced requires 21.35 cm^3 of 0.100 mol dm^{-3} $Na_2S_2O_3$(aq) to react completely.

$$I_2(aq) + 2Na_2S_2O_3(aq) \rightarrow 2NaI(aq) + Na_2S_4O_6(aq)$$

Calculate the average current used in 8 minutes during the electrolysis.

current = ... A [3]

(e) KI is used as a source of I⁻ ions in organic synthesis.

One example of this is shown in the synthetic route in Fig. 1.1.

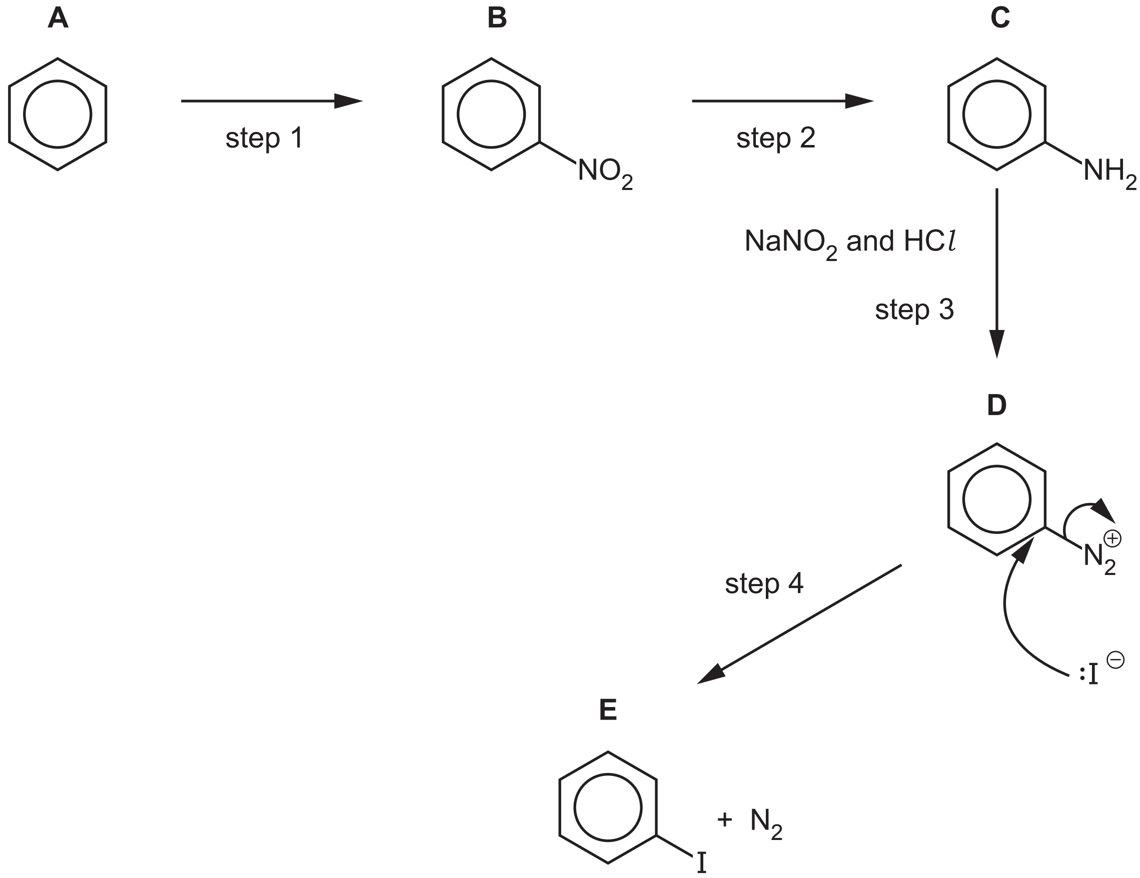


Fig. 1.1

(i) Identify the reagents required for steps 1 and 2.

step 1 ....

step 2 .... [2]

(ii) Step 3 occurs in two stages.

stage I $NaNO_2$ and HCl undergo an acid–base reaction to produce HNO_2.

stage II HNO_2 reacts with **C**, $C_6H_5NH_2$, to produce **D**, $C_6H_5N_2^+$.

Complete the equations for stage I and for stage II.

stage I $NaNO_2 + HCl \rightarrow$ ....

stage II ....

[2]

(iii) The I^- from KI reacts with **D** in step 4. The mechanism is shown in Fig. 1.1.

Suggest the name for this mechanism.

.... [1]

[Total: 26]

2 Water is an amphoteric compound that also acts as a good solvent of polar and ionic compounds.

(a) Equation 1 shows water acting as a Brønsted–Lowry acid.

equation 1 $H_2O + NO_2^- \rightleftharpoons HNO_2 + OH^-$

(i) Identify the **two** conjugate acid–base pairs in equation 1.

acid I	H_2O	conjugate base of acid I	
acid II		conjugate base of acid II	

[1]

(ii) Water also behaves as a Brønsted–Lowry acid when it dissolves CH_3NH_2.

Explain the ability of CH_3NH_2 to act as a base.

.... [1]

(iii) Write an equation to show water acting as a base with CH_3COOH.

.... [1]

(b) The ionic product of water, K_w, measures the extent to which water dissociates.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Fig. 2.1 shows how K_w varies with temperature.

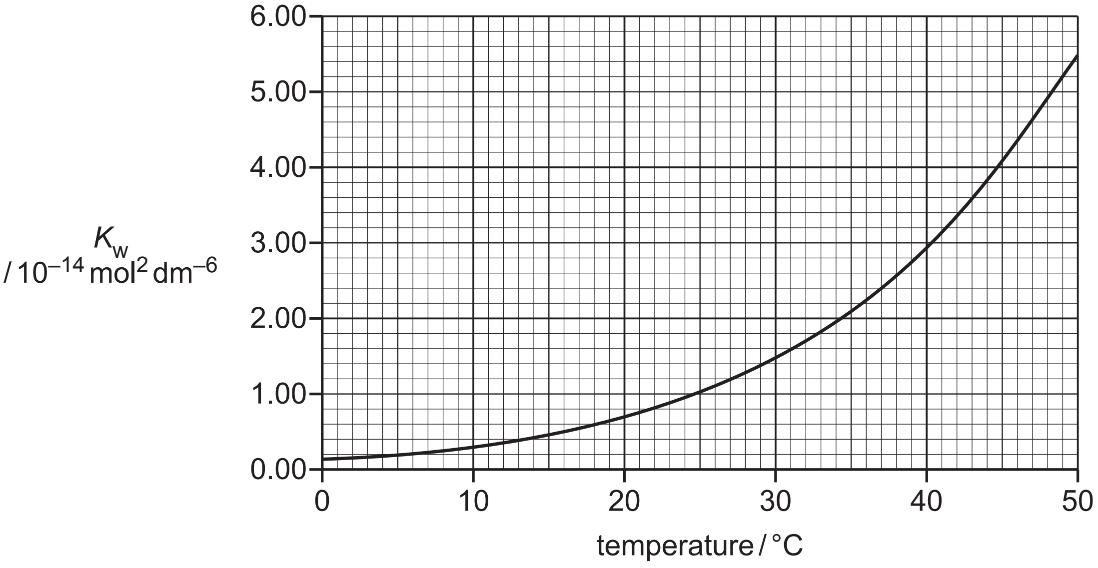


Fig. 2.1

(i) Write an expression for K_w.

.... [1]

(ii) Use information from Fig. 2.1 to deduce whether the dissociation of water is an exothermic or an endothermic process.

Explain your answer.

....

....

.... [1]

(iii) An aqueous solution has pH = 7.00 at 30 °C.

Use information from Fig. 2.1 to explain why this solution can be considered to be alkaline at 30 °C.

....

....

....

.... [2]

(c) The three physical states of H_2O have different standard entropies, $S^{\ominus}$, associated with them. Table 2.1 shows these $S^{\ominus}$ values.

Table 2.1

state of H_2O	standard entropy, $S^{\ominus}$ / J K^{-1} mol^{-1}
solid	+48.0
liquid	+70.1
gas	+188.7

(i) Explain the difference in the $S^{\ominus}$ values of H_2O(s) and H_2O(l).

....

.... [1]

(ii) Explain why the increase in $S^{\ominus}$ is **much** greater when H_2O boils than when it melts.

....

.... [1]

(iii) The energy changes for $H_2O(s) \rightarrow H_2O(l)$ are shown.

$$\Delta G = \ \ 0.00\,\text{kJ mol}^{-1}$$
$$\Delta H = +6.03\,\text{kJ mol}^{-1}$$

Use these data to show that the melting point of H_2O(s) is 0 °C.

[1]

(d) Metal–air batteries are electrochemical cells that generate electrical energy from the reaction of metal anodes with air.

The standard electrode potentials for the zinc–air battery are shown.

$[Zn(OH)_4]^{2-} + 2e^- \rightleftharpoons Zn + 4OH^-$ $\quad E^{\ominus} = -1.22\,V$

$\frac{1}{2}O_2 + H_2O + 2e^- \rightleftharpoons 2OH^-$ $\quad E^{\ominus} = +0.40\,V$

(i) Calculate the standard cell potential, $E^{\ominus}_{cell}$, of the zinc–air battery.

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

(ii) The zinc–air battery usually operates at pH 11 and 298 K. The overall cell potential is dependent on $[OH^-]$.

The Nernst equation shows how the electrode potential at the cathode changes with $[OH^-]$.

$$E = 0.40 - \left(\frac{0.059}{z}\right)\log([OH^-]^2)$$

Calculate the electrode potential, E, at pH 11.

E = ... V [2]

[Total: 13]

3 Iron is a transition metal in Group 8 of the Periodic Table.

(a) **(i)** Explain why iron has variable oxidation states.

....

....

.... [1]

(ii) Complete the shorthand electronic configurations of Fe and Fe^{3+}.

Fe [Ar] ....

Fe^{3+} [Ar] ....

[1]

(b) An aqueous solution of $Fe(NO_3)_3$ contains the complex $[Fe(H_2O)_6]^{3+}$.

When solutions of KSCN(aq) and $[Fe(H_2O)_6]^{3+}$(aq) are mixed, a colour change is observed. The red complex $[Fe(H_2O)_5SCN]^{2+}$ forms.

(i) Define complex.

....

.... [1]

(ii) State the coordination number of Fe in $[Fe(H_2O)_6]^{3+}$.

.... [1]

(iii) The H—O—H bond angle in water is 104.5°.

Suggest the H—O—H bond angle in $[Fe(H_2O)_6]^{3+}$.

Explain your answer.

....

....

.... [1]

(iv) Explain why iron complexes are coloured.

....

....

....

....

....

.... [3]

(v) Aqueous solutions of complexes $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_5SCN]^{2+}$ are different colours.

Explain why these complexes are different colours.

....

....

....

.... [2]

(c) Table 3.1 gives values for the stability constants, K_{stab}, of different complexes of iron.

Table 3.1

complex	stability constant, K_{stab}
$[Fe(H_2O)_5(H_2PO_4)]^{2+}$	5.90×10^1
$[Fe(H_2O)_5SCN]^{2+}$	1.30×10^2

(i) $[Fe(H_2O)_5(H_2PO_4)]^{2+}$ can form when H_3PO_4 reacts with $[Fe(H_2O)_6]^{3+}$.

Write an equation for this reaction.

.... [1]

(ii) Write an expression for K_{stab} of $[Fe(H_2O)_5SCN]^{2+}$ and give its units.

K_{stab} =

units = ... [2]

(iii) Use the stability constant data in Table 3.1 to calculate the value of the equilibrium constant, K_c, for the following equilibrium.

$$[Fe(H_2O)_5(H_2PO_4)]^{2+} + SCN^- \rightleftharpoons [Fe(H_2O)_5SCN]^{2+} + H_2PO_4^-$$

value of K_c = ... [1]

[Total: 14]

4 Ruthenium and osmium are transition metals below iron in Group 8 of the Periodic Table.

(a) Two different complex ions, **X** and **Y**, can form when anhydrous $RuCl_3$ reacts with water under certain conditions.

X and **Y** have octahedral geometry.

Aqueous samples of **X** and **Y** react separately with an excess of $AgNO_3(aq)$. Different amounts of AgC*l* are precipitated:

- 1 mole of complex ion **X** produces 2 moles of AgC*l*
- 1 mole of complex ion **Y** produces 1 mole of AgC*l*.

(i) Complete Table 4.1 to suggest formulae for **X** and **Y**.

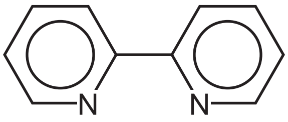
Table 4.1

	X	**Y**
formula of complex		

[2]

(ii) Both complexes react with an excess of bipyridine, bipy, to form a mixture of two stereoisomers of $[Ru(bipy)_3]^{3+}$.

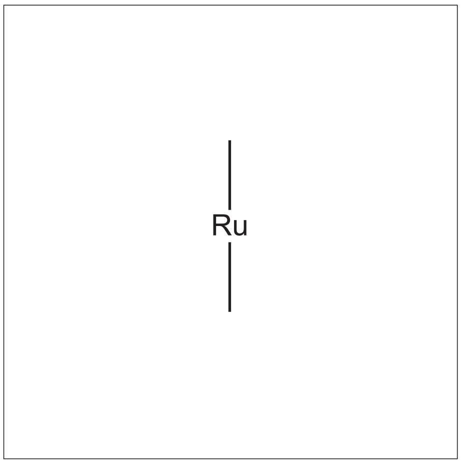
bipy

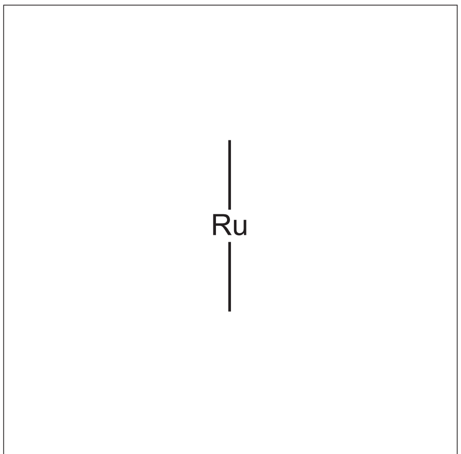


Bipyridine is a bidentate ligand.

Draw three-dimensional diagrams of the two stereoisomers of $[Ru(bipy)_3]^{3+}$.

Use  to represent the bipy ligand in your structures.





[2]

[Turn over

(b) Fig. 4.1 shows another ruthenium complex.

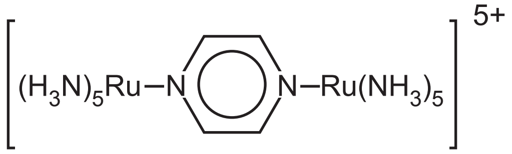


Fig. 4.1

This complex contains the neutral ligand pyrazine.

pyrazine

(i) Suggest how pyrazine is able to bond to two separate ruthenium ions.

....

....

.... [1]

(ii) Pyrazine is an aromatic compound. The bonding and structure of pyrazine is similar to that of benzene.

Describe and explain the shape of pyrazine.

In your answer, include:

- the hybridisation of the nitrogen and carbon atoms
- how orbital overlap forms π bonds between the atoms in the ring.

....

....

....

.... [2]

(iii) Predict the number of peaks seen in the carbon–13 NMR spectrum of pyrazine.

Explain your answer.

....

....

.... [2]

(iv) The overall charge of the ruthenium complex in Fig. 4.1 is 5+.

Deduce the possible oxidation states of the two ruthenium ions in the complex.

.... [1]

(c) Osmium tetroxide, OsO_4, reacts with alkenes in a similar manner to cold dilute acidified MnO_4^-.

Fig. 4.2 shows a proposed synthesis of a condensation polymer **G**.

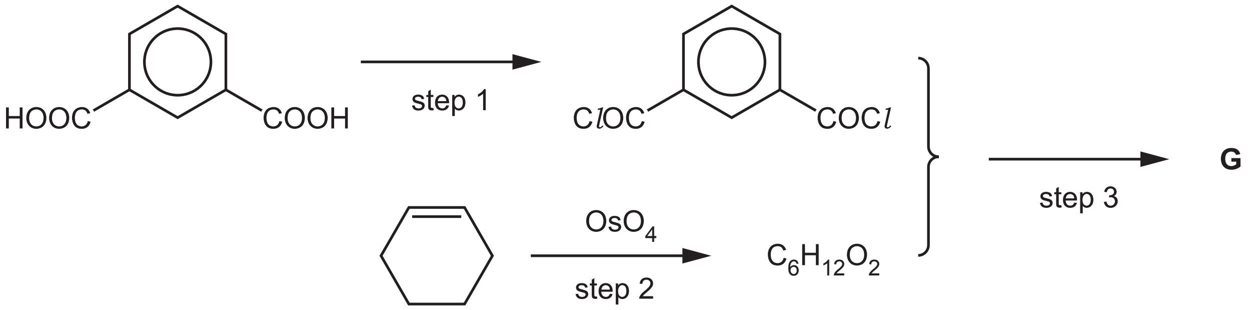


Fig. 4.2

(i) Suggest a reagent for step 1.

.... [1]

(ii) Draw the structure of exactly **one** repeat unit of the condensation polymer **G**.

The ester linkage should be shown fully displayed.

[2]

[Total: 13]

5 Compound **Q** can be synthesised from chlorobenzene in seven steps, using the route shown in Fig. 5.1.

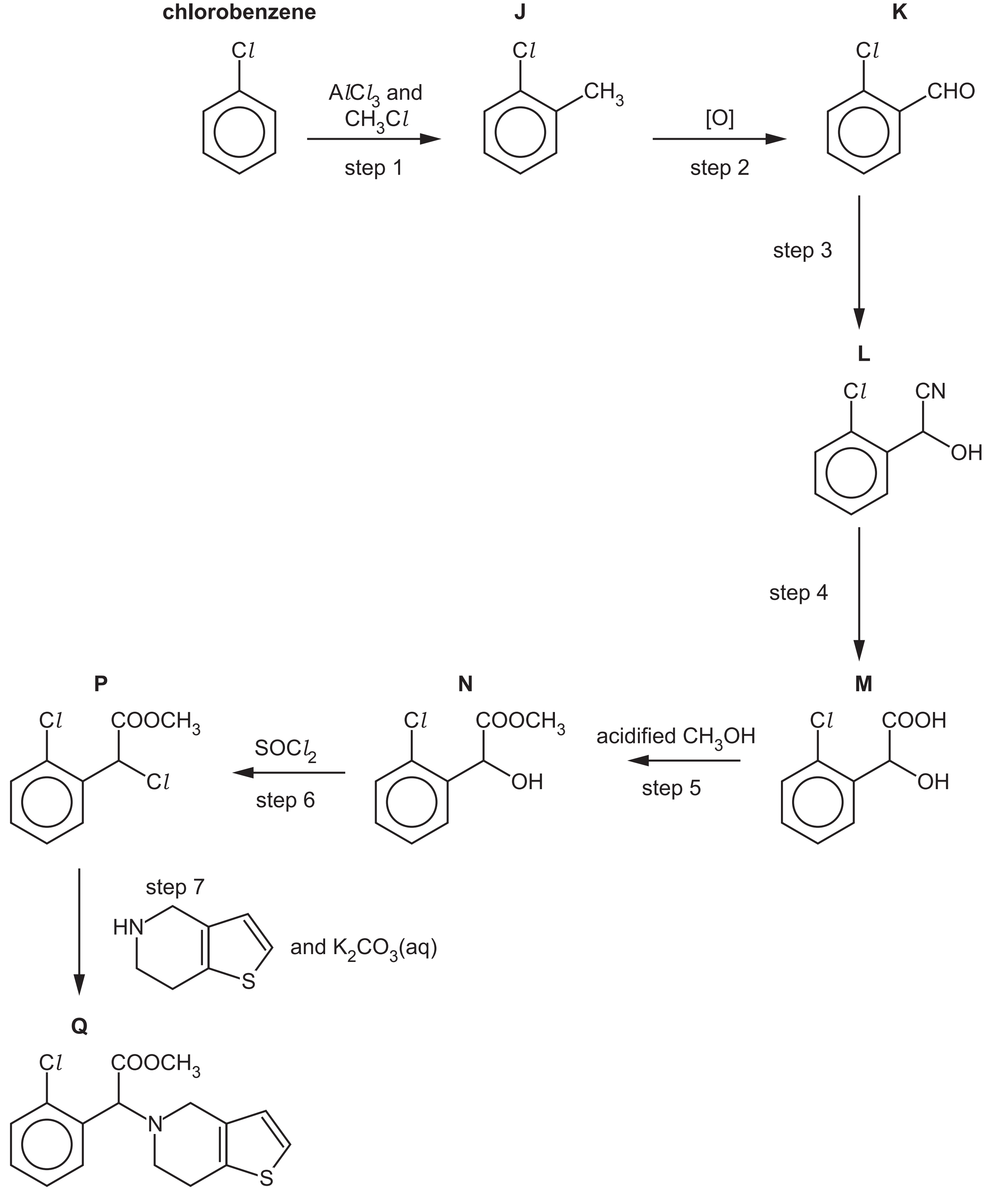


Fig. 5.1

(a) **(i)** Write an equation for the formation of the electrophile for step 1.

.... [1]

(ii) Complete the mechanism in Fig. 5.2 for step 1, the alkylation of chlorobenzene.

Include all relevant curly arrows and charges.

Draw the structure of the intermediate.

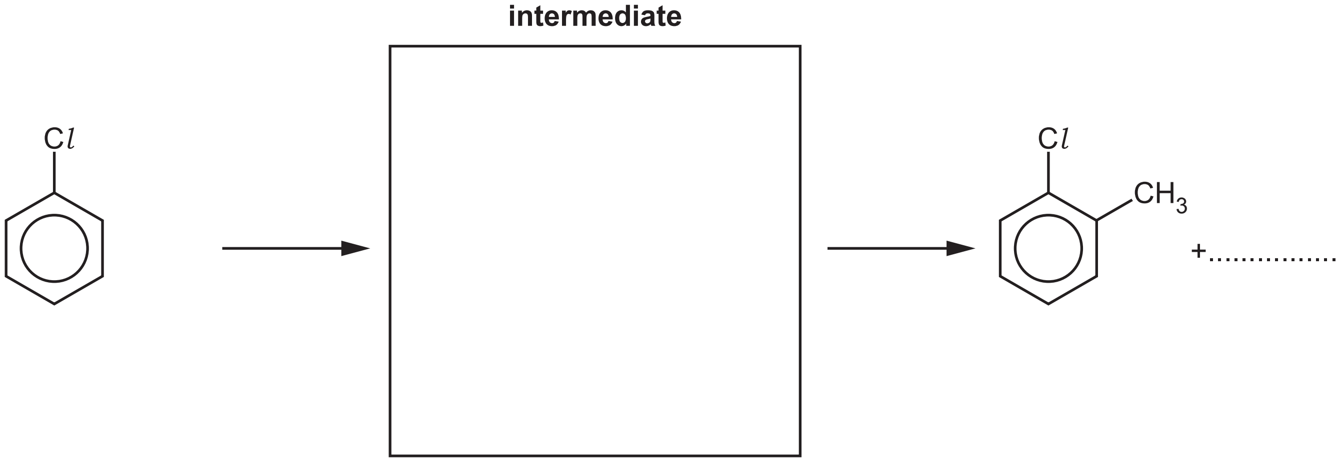


Fig. 5.2

[3]

(iii) Step 2 is an oxidation reaction.

Construct an equation for the reaction in step 2.

Use [O] to represent an atom of oxygen from an oxidising agent.

.... [1]

(iv) Suggest reagents for the conversion of **K** to **M** in steps 3 and 4.

step 3 ....

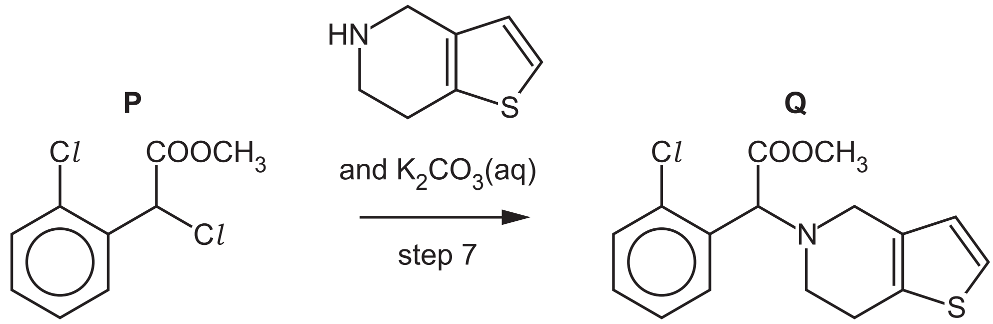
step 4 ....

[2]

(v) Identify the type of reaction that occurs in step 5.

.... [1]

(vi) Step 7 takes place when **P** is heated with a weak base such as $K_2CO_3(aq)$.



Suggest why a strong base such as NaOH(aq) is **not** used for this reaction.

....

.... [1]

(vii) **Q** is optically active.

Explain the meaning of optically active.

....

....

.... [1]

(viii) Give **two** reasons why it might be desirable to synthesise a single optical isomer of **Q** for use as a drug.

1 ....

....

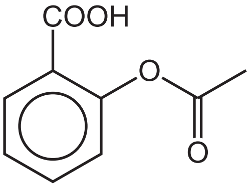
2 ....

....

[2]

(b) **Q** is commonly used in conjunction with aspirin.

aspirin



Aspirin is a weak Brønsted–Lowry acid.

(i) The pK_a of aspirin is 3.49.

75 mg of aspirin dissolves in water to form 100 cm^3 of an aqueous solution.

Calculate the pH of this solution.

[M_r: aspirin, 180.0]

pH = ... [3]

(ii) Aspirin undergoes acid hydrolysis in the stomach.

Give the structures of the organic products of this acid hydrolysis.

[2]

[Total: 17]

6 Amino acids are molecules that contain —NH_2 and —COOH functional groups.

Glycine, H_2NCH_2COOH, is the simplest stable amino acid.

(a) The isoelectric point of glycine is 6.2.

(i) Define isoelectric point.

....

.... [1]

(ii) Draw the structure of glycine at pH 4.

[1]

(b) Fig. 6.1 shows two syntheses starting with glycine.

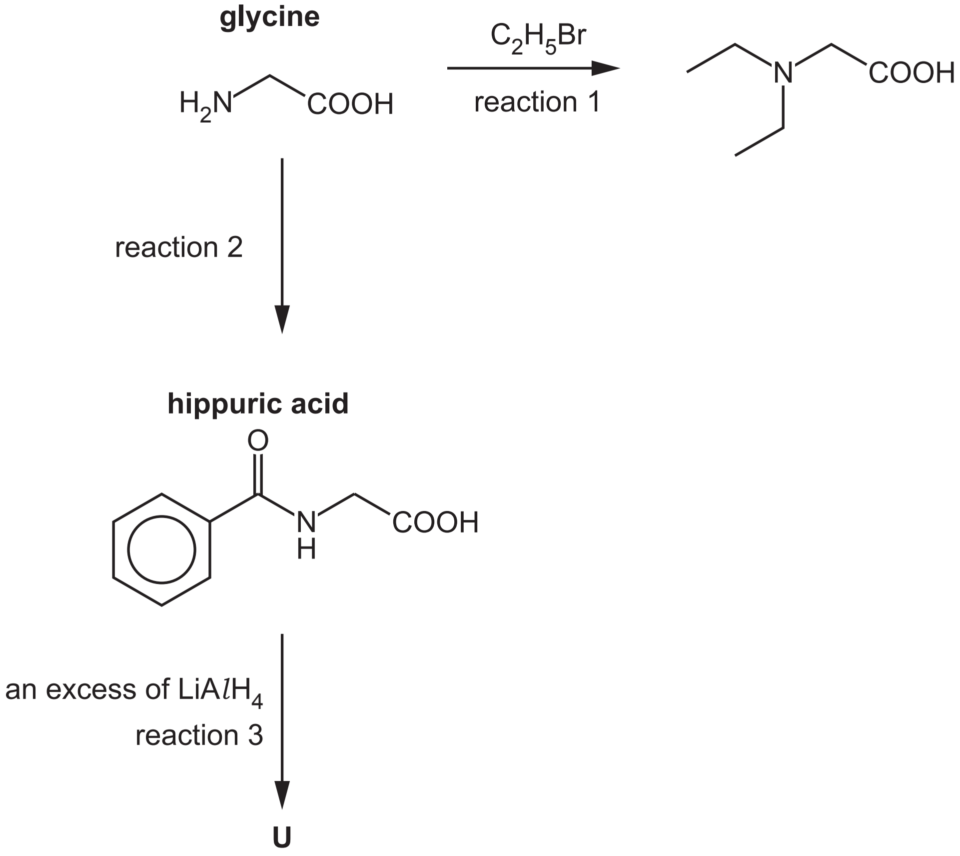


Fig. 6.1

(i) State the essential conditions for reaction 1.

.... [1]

(ii) Identify the reagent used in reaction 2.

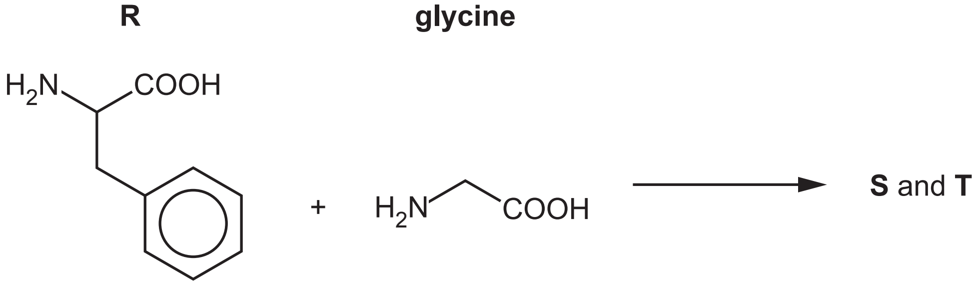
.... [1]

(iii) Draw the structure of the organic product **U** that forms when hippuric acid reacts with an excess of $LiAlH_4$ in reaction 3.

[2]

(iv) A molecule of phenylalanine, **R**, can react with a molecule of glycine to form two dipeptides, **S** and **T**.

S and **T** are structural isomers.



Draw the structures of these dipeptides. The peptide bond formed should be shown fully displayed.

S	**T**

[2]

(c) A student proposes a synthesis of hippuric acid by the reaction of benzamide, $C_6H_5CONH_2$, and chloroethanoic acid, $C\mathit{l}CH_2COOH$.

The reaction does **not** work well because benzamide is a very weak base.

(i) Explain why amides are weaker bases than amines.

....

....

....

.... [2]

(ii) The pK_a of chloroethanoic acid is 2.86 whereas the pK_a of ethanoic acid is 4.76.

Explain the difference between these two pK_a values.

....

....

....

.... [2]

(d) Compound **V** is another amino acid.

The proton (^{1}H) NMR spectrum of **V** shows hydrogen atoms in five different environments, **a**, **b**, **c**, **d** and **e**, as shown in Fig. 6.2.

V

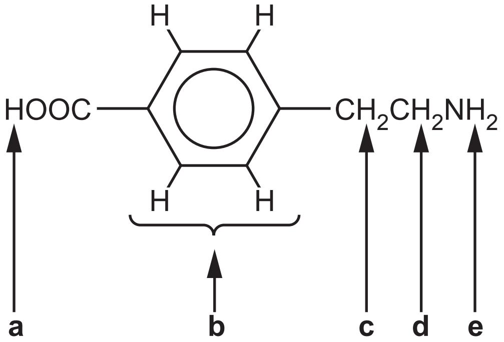


Fig. 6.2

Table 6.1

environment of proton	example	chemical shift range, δ / ppm
alkane	$–C\mathbf{H}_3$, $–C\mathbf{H}_2–$, $>C\mathbf{H}–$	0.9–1.7
alkyl next to C=O	$C\mathbf{H}_3–C=O$, $–C\mathbf{H}_2–C=O$, $>C\mathbf{H}–C=O$	2.2–3.0
alkyl next to aromatic ring	$C\mathbf{H}_3–Ar$, $–C\mathbf{H}_2–Ar$, $>C\mathbf{H}–Ar$	2.3–3.0
alkyl next to electronegative atom	$C\mathbf{H}_3–O$, $–C\mathbf{H}_2–O$, $–C\mathbf{H}_2–Cl$, $–C\mathbf{H}_2–N$	3.2–4.0
attached to alkene	=C**H**R	4.5–6.0
attached to aromatic ring	**H**–Ar	6.0–9.0
aldehyde	**H**COR	9.3–10.5
alcohol	RO**H**	0.5–6.0
phenol	Ar–O**H**	4.5–7.0
carboxylic acid	RCOO**H**	9.0–13.0
alkyl amine	R–N**H**–	1.0–5.0
aryl amine	$Ar–N\mathbf{H}_2$	3.0–6.0
amide	RCON**H**R	5.0–12.0

(i) Complete Table 6.2 for the proton (^1H) NMR spectrum of **V** taken in $CDCl_3$.

Table 6.1 gives some relevant data.

Table 6.2

proton	**a**	**b**	**c**	**d**	**e**
chemical shift range, δ / ppm					
name of splitting pattern		multiplet			

[4]

(ii) Complete Table 6.3 by placing a tick (✓) to indicate any protons whose peaks are still present in the proton (^1H) NMR spectrum of **V** taken in D_2O.

Table 6.3

proton	**a**	**b**	**c**	**d**	**e**
present in D_2O					

[1]

[Total: 17]

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Important values, constants and standards

molar gas constant	$R = 8.31\,\mathrm{J\,K^{-1}\,mol^{-1}}$
Faraday constant	$F = 9.65 \times 10^{4}\,\mathrm{C\,mol^{-1}}$
Avogadro constant	$L = 6.022 \times 10^{23}\,\mathrm{mol^{-1}}$
electronic charge	$e = -1.60 \times 10^{-19}\,\mathrm{C}$
molar volume of gas	$V_m = 22.4\,\mathrm{dm^3\,mol^{-1}}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0\,\mathrm{dm^3\,mol^{-1}}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14}\,\mathrm{mol^2\,dm^{-6}}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18\,\mathrm{kJ\,kg^{-1}\,K^{-1}}$ ($4.18\,\mathrm{J\,g^{-1}\,K^{-1}}$)

The Periodic Table of Elements

Key

atomic number
atomic symbol
name
relative atomic mass

Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
							1 H hydrogen 1.0										2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0											5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3											13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –	113 Nh nihonium –	114 Fl flerovium –	115 Mc moscovium –	116 Lv livermorium –	117 Ts tennessine –	118 Og oganesson –

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –