(b) The Group 1 iodides all form stable ionic lattices and are soluble in water.

(i) Define enthalpy change of solution.

....

....

.... [1]

(ii) Use the data in Table 1.1 to calculate the enthalpy change of solution of potassium iodide, KI.

Table 1.1

process	enthalpy change, ΔH / kJ mol^{-1}
$K^+(g) + I^-(g) \rightarrow KI(s)$	–629
$K^+(g) \rightarrow K^+(aq)$	–322
$I^-(g) \rightarrow I^-(aq)$	–293

enthalpy change of solution = ... kJ mol^{-1} [1]

(iii) Suggest the trend in the magnitude of the lattice energies of the Group 1 iodides, LiI, NaI, KI.
Explain your answer.

....

....

....

.... [2]

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....

....

.... [1]

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enthalpy change of solution = ... kJ mol^{-1} [1]

(iii) Suggest the trend in the magnitude of the lattice energies of the Group 1 iodides, LiI, NaI, KI.
Explain your answer.

....

....

....

.... [2]

(c) The concentration of $Cu^{2+}(aq)$ in a solution can be determined by the reaction of Cu^{2+} ions with I^- ions.

reaction 1 $\quad 2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$

The I_2 produced in reaction 1 is titrated against a solution containing thiosulfate ions, $S_2O_3^{2-}$, using a suitable indicator.

reaction 2 $\quad 2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

(i) A 25.0 cm^3 portion of a $Cu^{2+}(aq)$ solution reacts with an excess of $I^-(aq)$.
The end-point of the titration occurs when 22.30 cm^3 of 0.150 $mol\,dm^{-3}$ $S_2O_3^{2-}(aq)$ is added.

Calculate the concentration of $Cu^{2+}(aq)$ in the original solution.

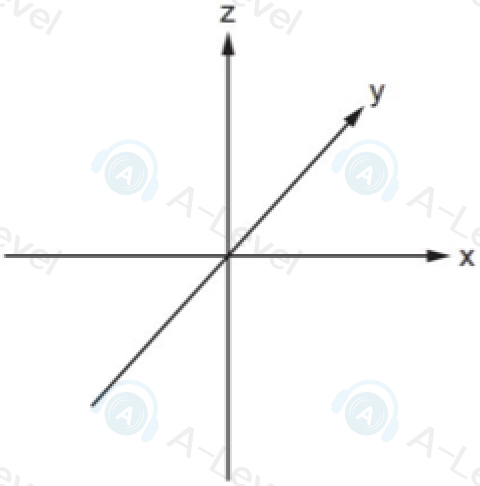
concentration of $Cu^{2+}(aq)$ = ... $mol\,dm^{-3}$ [2]

(ii) Identify a suitable indicator for the titration.

.... [1]

(iii) Copper(I) and copper(II) both contain electrons in all five 3d orbitals.

Sketch the shape of a $3d_{xy}$ orbital on the axes provided.



[1]

(d) The reaction of I^- ions with persulfate ions, $S_2O_8^{2-}$, can be catalysed by Fe^{3+} ions.

$$2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

Write equations to show how Fe^{3+} catalyses this reaction.

....

.... [2]

(e) An orange precipitate of HgI_2 forms when Hg^{2+} ions are added to KI(aq).
The solubility of HgI_2 at 25 °C is $1.00 \times 10^{-7}\,g\,dm^{-3}$.

Calculate the solubility product, K_{sp}, of HgI_2.
Include units in your answer.

[M_r: HgI_2, 454.4]

value of K_{sp} = ...

units = ...
[3]

[Total: 19]

5 **(a)** Describe and explain the relative basicities of phenylamine, ethylamine and 4-nitrophenylamine.

.... > .... > ....

most basic least basic

....

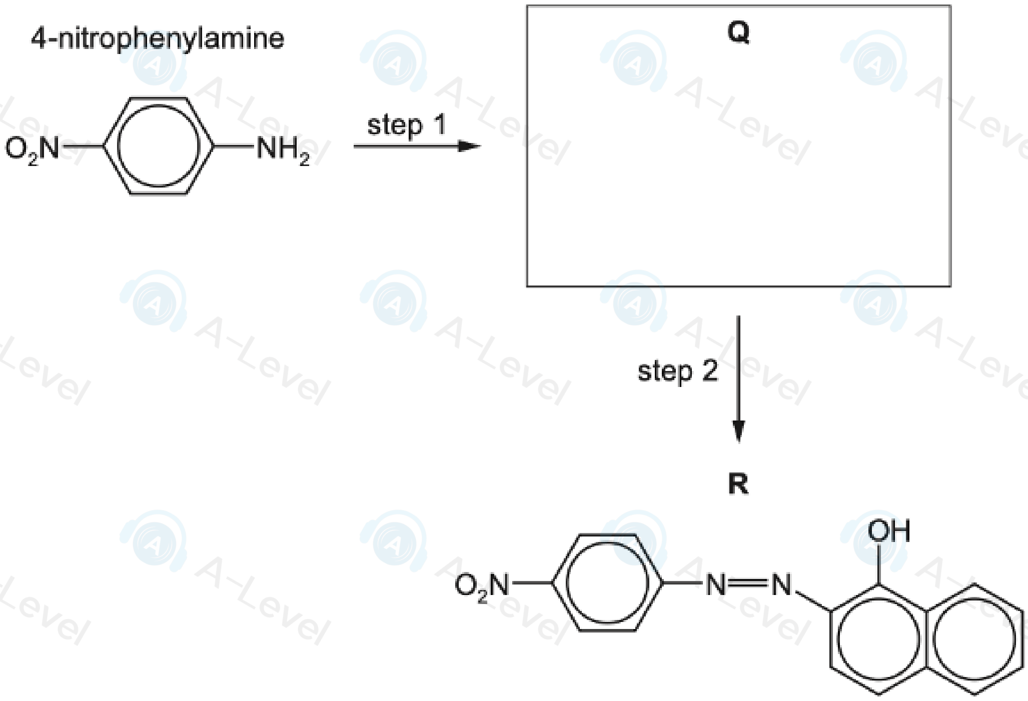
....

....

....

.... [4]

(b) The dye **R** can be synthesised from 4-nitrophenylamine in two steps.



(i) Deduce and draw the structure of the organic salt **Q** in the box. [1]

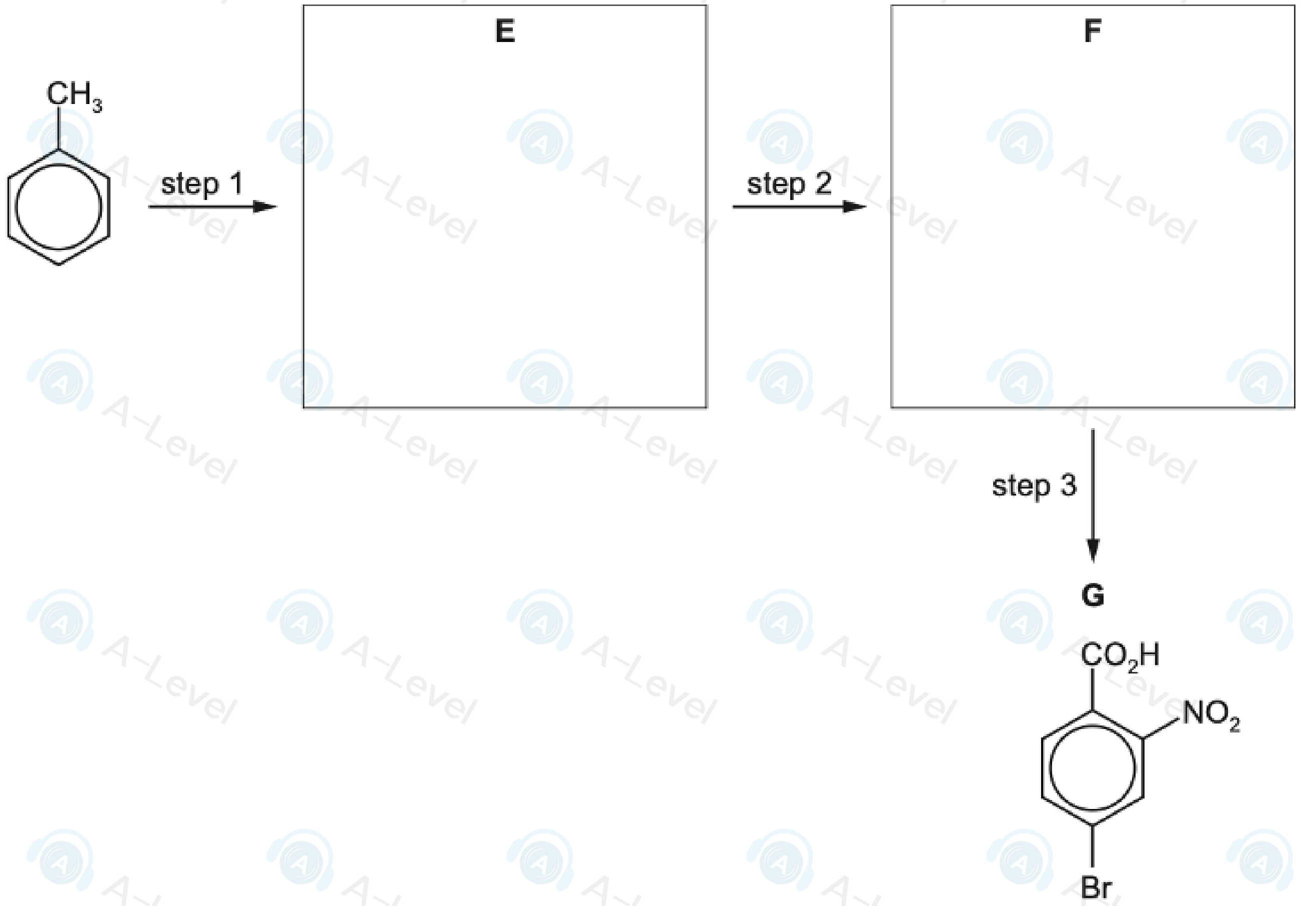
(ii) Suggest reagents and conditions for step 1 and 2 in **(b)**.

step 1 ....

step 2 ....

[2]

(c) Compound **G** can be synthesised from methylbenzene in three steps.



(i) Give the systematic name of compound **G**.

.... [1]

(ii) Deduce the identities of **E** and **F** and draw their structures in the boxes. [2]

(iii) Suggest reagents and conditions for each of steps 1 to 3 in **(c)**.

step 1 ....

step 2 ....

step 3 ....

[3]

[Total: 13]

5 **(a)** Methylbenzene can undergo different reactions, as shown in Fig. 5.1.

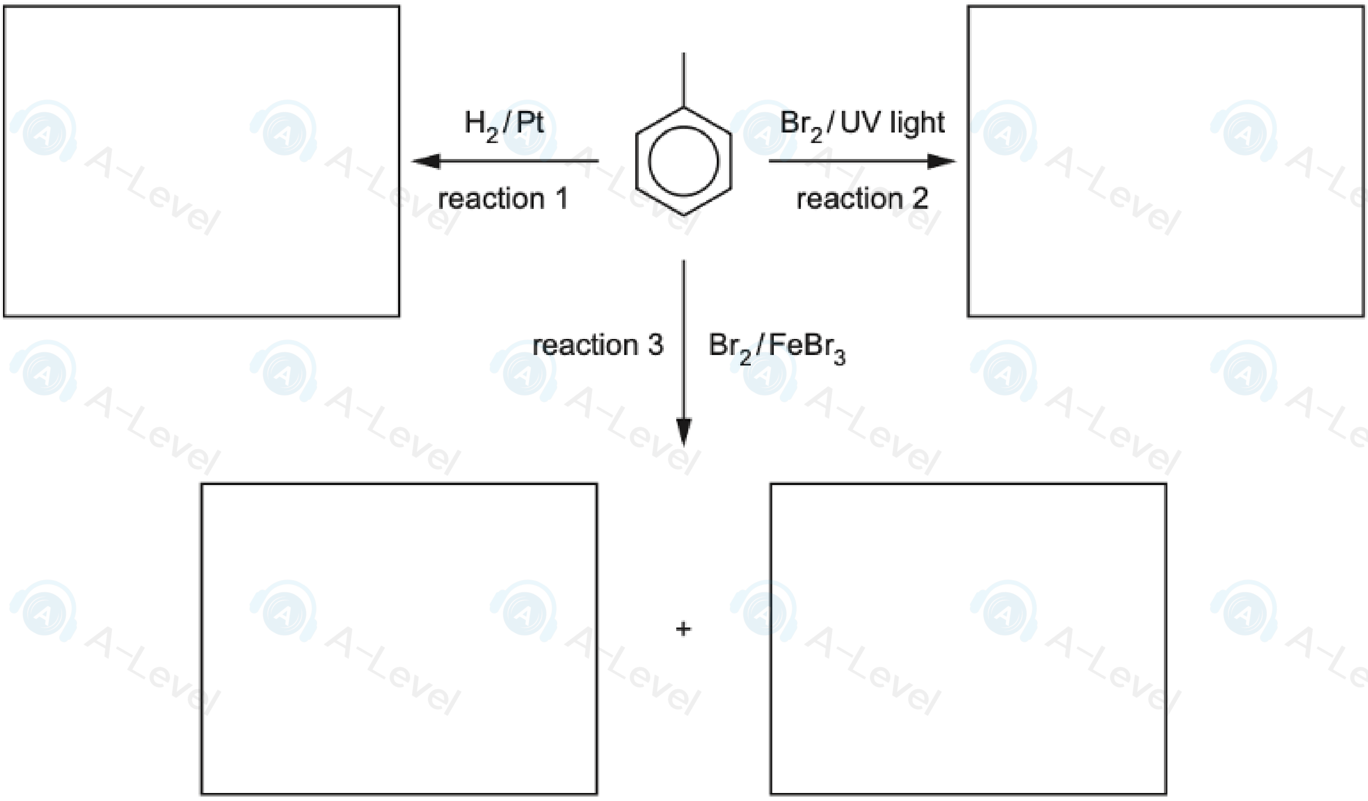


Fig. 5.1

(i) Draw structures in Fig. 5.1 for the possible organic products of the three reactions shown. [3]

(ii) Complete Table 5.1.

Table 5.1

	type of reaction	mechanism
reaction 1		☒
reaction 2	☒	

[2]

(b) When methylbenzene reacts with an electrophile, a substitution reaction occurs. No addition reaction takes place under these conditions.

Explain why no addition reaction takes place.

....

.... [1]

(c) The reaction of methylbenzene with thionyl bromide, $SOBr_2$, in the presence of an iron(III) bromide catalyst, $FeBr_3$, is shown in Fig. 5.2.

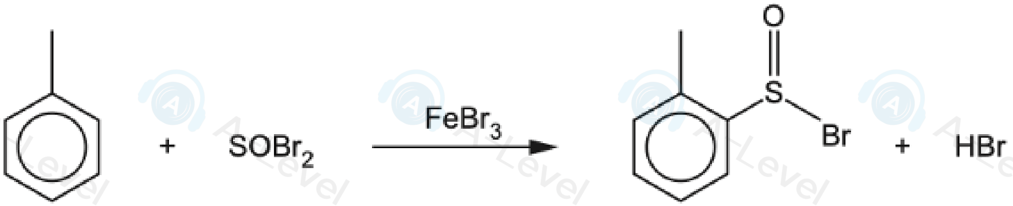


Fig. 5.2

The mechanism of this reaction is similar to that of the bromination of benzene.

The first step of the mechanism generates the $SOBr^+$ electrophile, as shown.

$$SOBr_2 + FeBr_3 \rightarrow SOBr^+ + FeBr_4^-$$

(i) The reaction of methylbenzene with $SOBr^+$ ions is shown in Fig. 5.3. Complete the mechanism in Fig. 5.3.

Include all relevant curly arrows and charges.

Draw the structure of the organic intermediate.

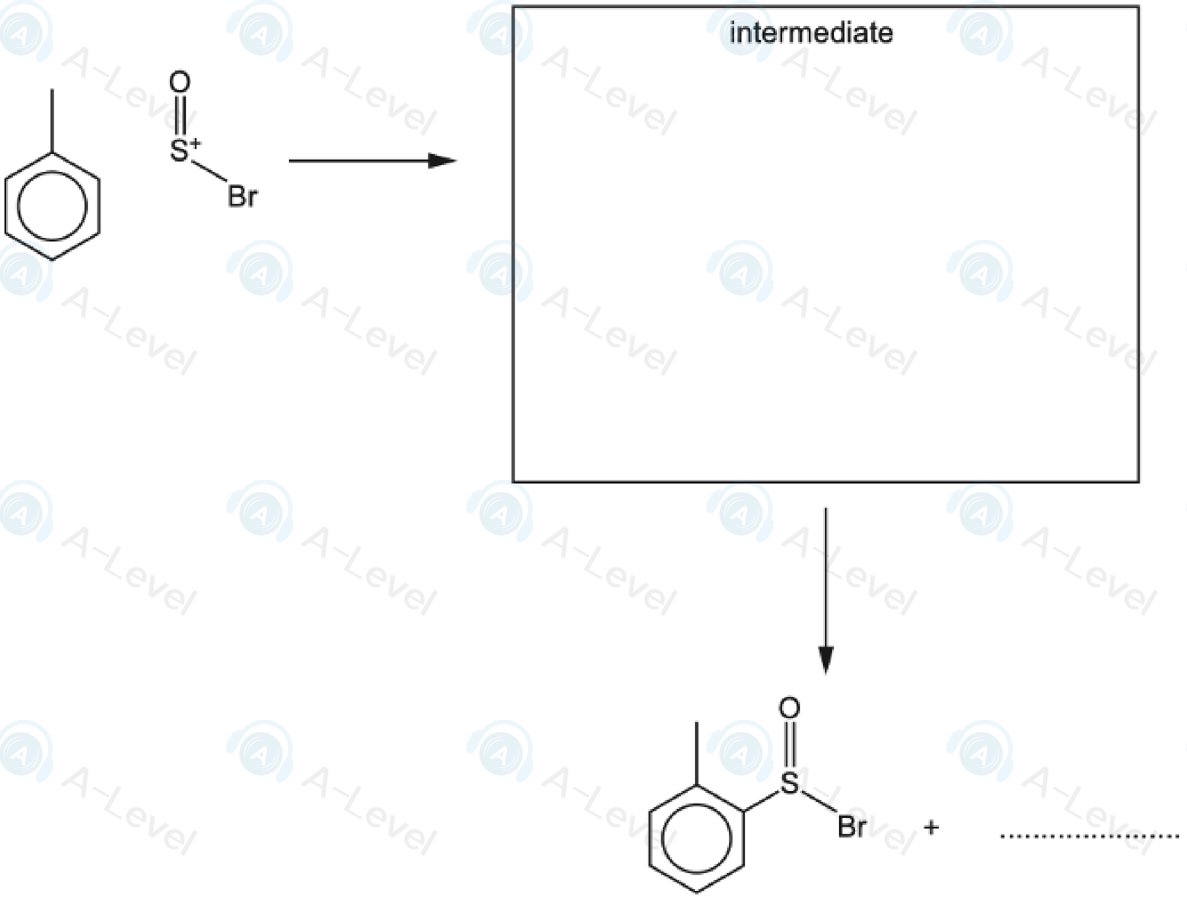


Fig. 5.3

[3]

(ii) The reaction shown in Fig. 5.2 produces a small amount of a by-product, **P**, with the molecular formula $C_{14}H_{14}OS$.

Suggest a structure for by-product **P**.

[1]

(d) Acyl bromides, RCOBr, can be synthesised by the reaction of a carboxylic acid and $SOBr_2$.

This is a similar reaction to the synthesis of acyl chlorides using $SOCl_2$.

(i) Give an equation for the reaction between ethanoic acid and $SOBr_2$.

.... [1]

(ii) Suggest the relative ease of hydrolysis of acyl bromides, RCOBr, acyl chlorides, RCOC*l*, and alkyl chlorides, RC*l*.

Explain your answer.

.... > .... > ....

easiest to hydrolyse　　　　　　　　　　　　　　　　hardest to hydrolyse

....

....

....

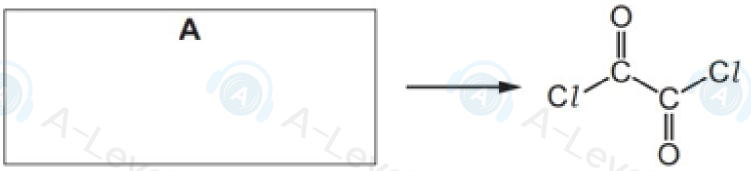
....

....

[3]

[Total: 14]

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

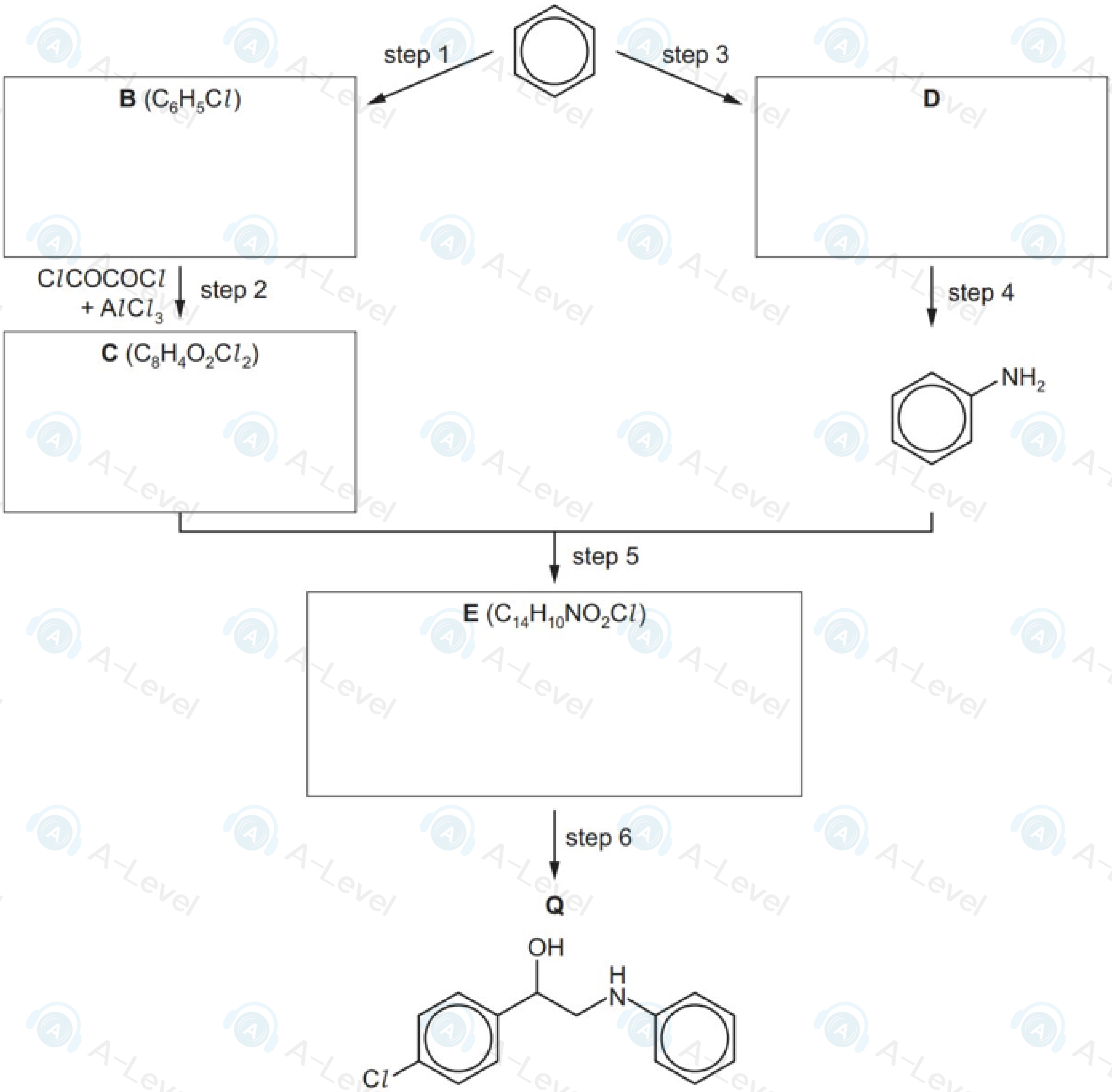


(a) **(i)** Suggest the identity of compound **A** by drawing its structure in the box. [1]

(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.



If the amount of ClCOCOCl 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.

$C_{14}H_8O_2Cl_2$

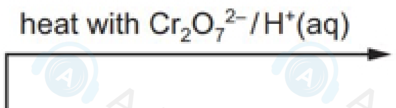
[1]

(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.



6 **(a)** The reagent and conditions required for the nitration of benzene, benzoic acid and phenol are shown in Table 6.1.

Table 6.1

compound	reagents and conditions for nitration
benzene	concentrated HNO_3, 50 °C, concentrated H_2SO_4 catalyst
benzoic acid	concentrated HNO_3, 100 °C, concentrated H_2SO_4 catalyst
phenol	dilute HNO_3(aq), 20 °C

Concentrated HNO_3 reacts with concentrated H_2SO_4 to generate the electrophile NO_2^+.

(i) Complete Fig. 6.1 to show the mechanism of the reaction between benzene and NO_2^+. Include all relevant curly arrows and charges.

Fig. 6.1

[3]

(ii) Write an equation to show how H_2SO_4 is regenerated.

.... [1]

(b) Draw the major products from the mononitration of benzoic acid and of phenol.

major product from benzoic acid	major product from phenol

[2]

(d) The azo compound Congo Red is used as an acid–base indicator and can be made by the route shown in Fig. 6.2.

In step 3 of this synthesis, compound **Y** reacts with compound **Z**. Compound **Z** is made from compound **X**. Assume that the $–SO_3^-Na^+$ groups do not react.

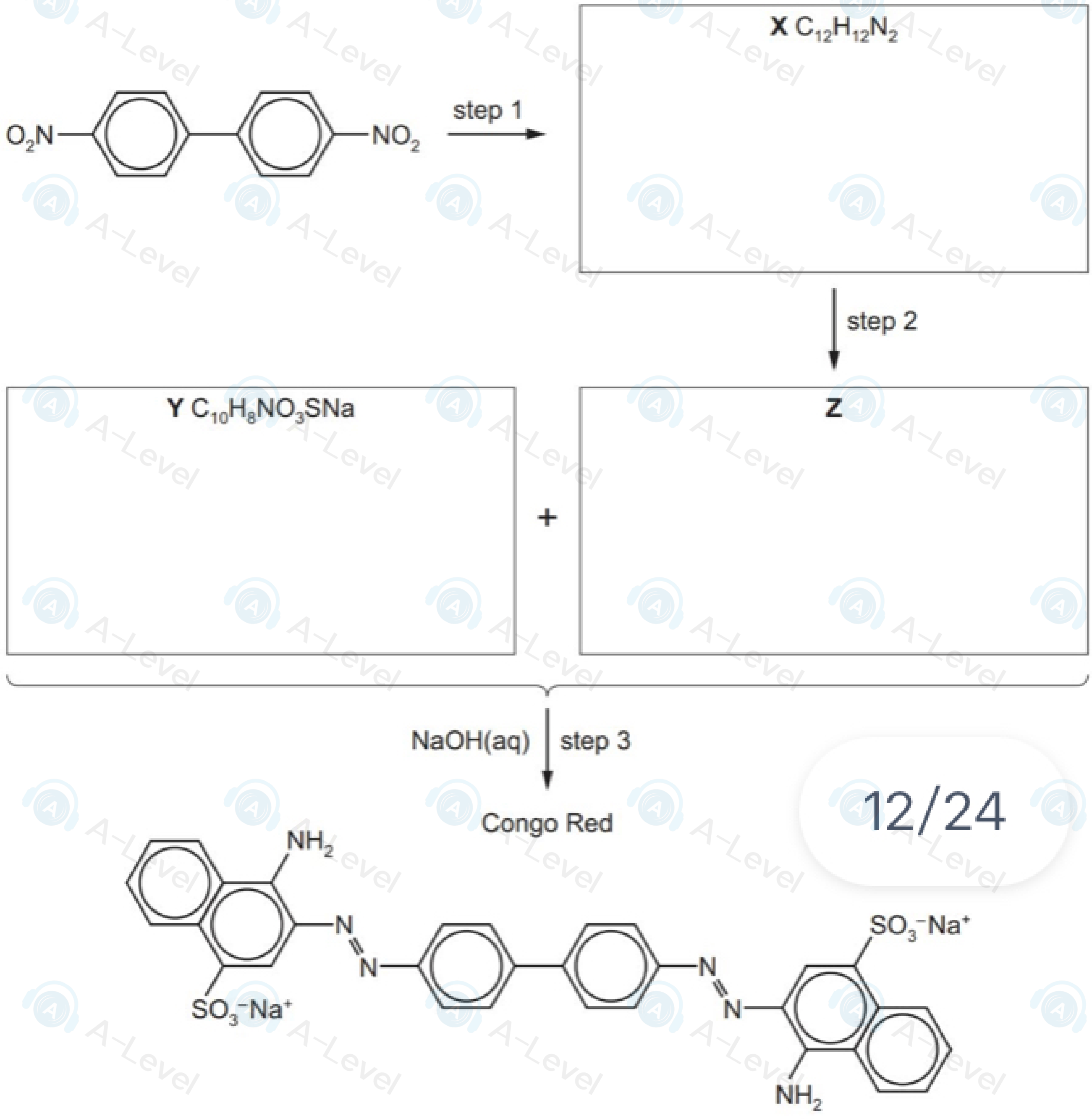


Fig. 6.2

(i) Suggest structures for compounds **X**, **Y** and **Z** and draw them in the boxes in Fig. 6.2. [3]

(ii) Give the reagents and conditions for step 1 and step 2.

step 1 ....

step 2 ....

[3]

[Total: 16]

4 **(a)** Identify the substances liberated at the anode and at the cathode during the electrolysis of saturated $KC\mathit{l}(aq)$.

at the anode ....

at the cathode .... [1]

(b) When dilute sulfuric acid is electrolysed, oxygen is liberated at the anode.

Dilute sulfuric acid is electrolysed for 15.0 minutes using a current of 0.750A.

Calculate the volume of oxygen that is liberated under room conditions.

7/20

volume of oxygen = ... cm^3 [3]

(c) The halogens chlorine, bromine and iodine differ in their strengths as oxidising agents. These strengths are indicated by the $E^\ominus$ values for these halogens.

(i) Give the $E^\ominus$ values for chlorine, bromine and iodine acting as oxidising agents.

.... [1]

(ii) Deduce which of chlorine, bromine and iodine will react with a solution of $Sn^{2+}(aq)$ under standard conditions.

Explain your answer. Include a relevant equation in your explanation.

....

....

.... [3]

(iii) An excess of chlorine is added to a solution of acidified $Mn^{2+}(aq)$ under standard conditions.

Give the formula of the product of this reaction that contains manganese.

.... [1]

(d) An electrochemical cell can be made by connecting an Fe^{3+}/Fe^{2+} half-cell to an $S_2O_8^{2-}/SO_4^{2-}$ half-cell under standard conditions.

(i) Calculate the standard cell potential of this electrochemical cell.

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

(ii) State the material that should be used as the electrode in each half-cell.

in the Fe^{3+}/Fe^{2+} half-cell ....

in the $S_2O_8^{2-}/SO_4^{2-}$ half-cell ....

[1]

(iii) Describe **one** change to each half-cell that would **increase** the value of the cell potential. The temperature should remain at 298 K.

Fe^{3+}/Fe^{2+} half-cell ....

....

$S_2O_8^{2-}/SO_4^{2-}$ half-cell ....

....

[1]

[Total: 12]

8/20

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.

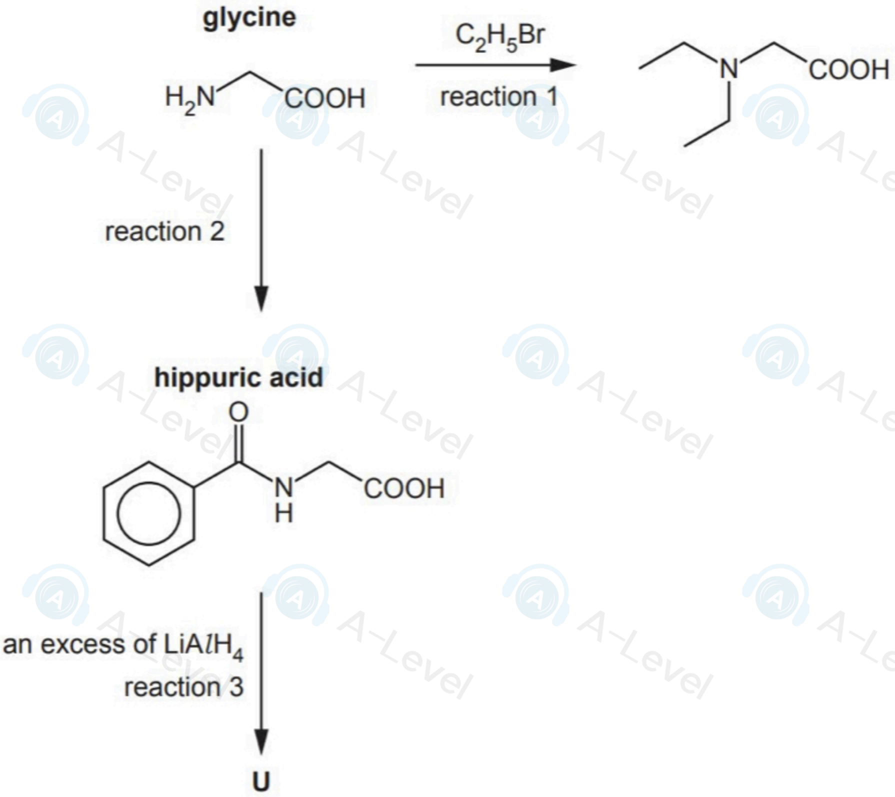
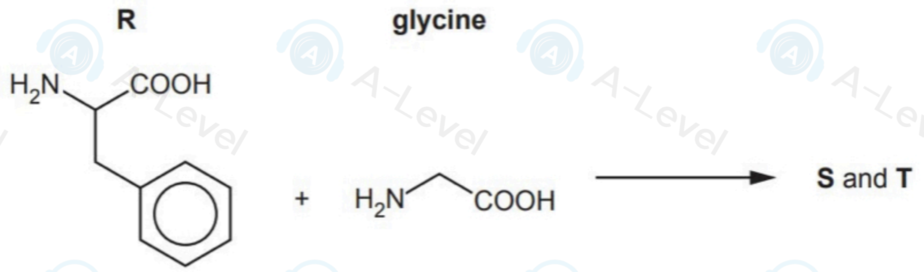


Fig. 6.1

(i) State the essential conditions for reaction 1.

(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, $ClCH_2COOH$.

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.

....

....

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

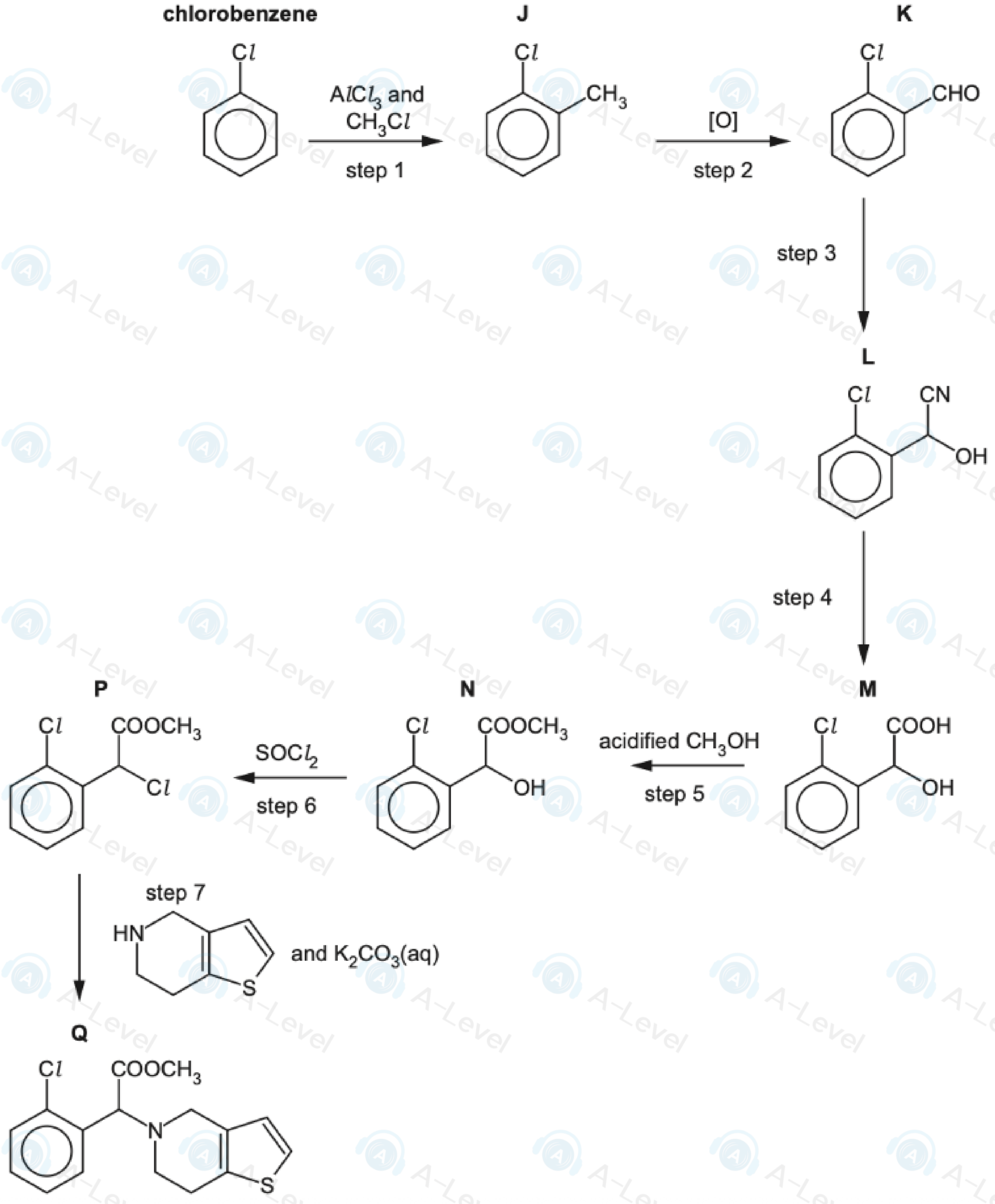


Fig. 5.1

(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.

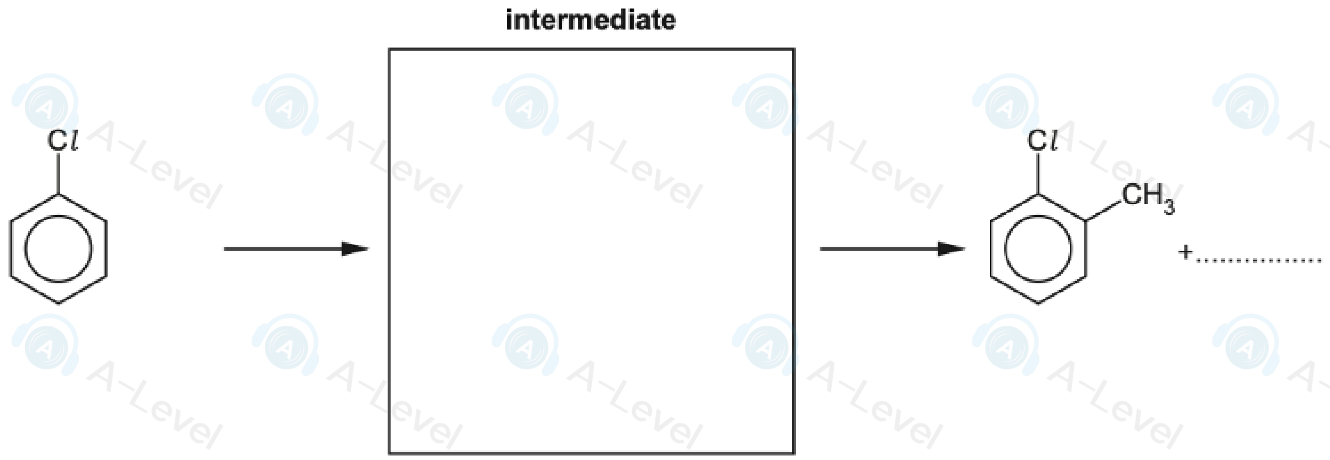


Fig. 5.2

[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 ....

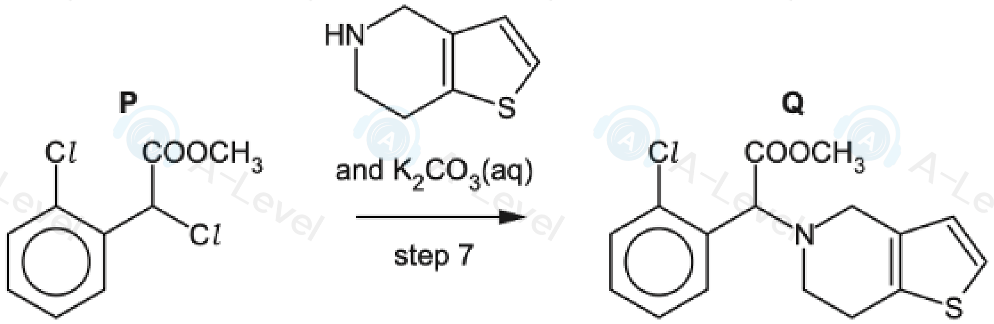
step 4 ....

[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 ....

....

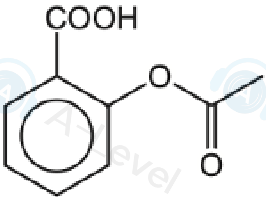
2 ....

....

[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]