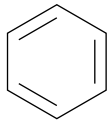
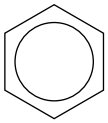
1 Chemists often use two different structures to represent a molecule of benzene, as shown below.



structure A



structure B

(a) (i) Describe, with the aid of suitable diagrams showing orbital overlap, the difference in bonding between structure **A** and structure **B**.

In your answer, you should use appropriate technical terms, spelled correctly.

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

..... **[4]**

(ii) The table below shows the enthalpy changes for the reactions of cyclohexene, C_6H_{10}, and benzene, C_6H_6, with hydrogen.

reaction	enthalpy change / kJ mol^{-1}
$C_6H_{10} + H_2 \rightarrow C_6H_{12}$	−119
$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$	−208

Using this information, suggest and explain whether structure **A** or structure **B** is a better representation of benzene.

.....

.....

.....

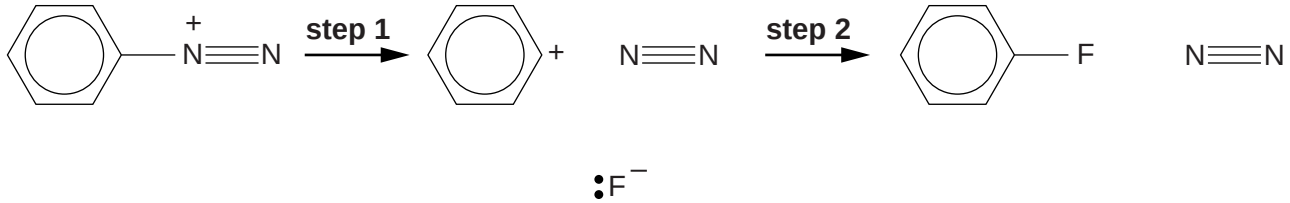
.....

.....

..... **[2]**

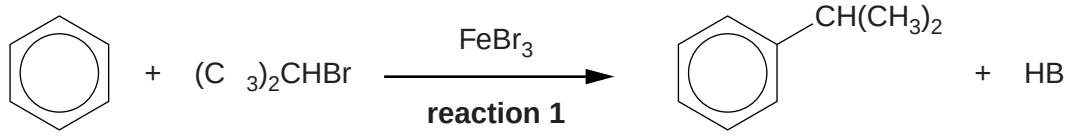
(b) Benzene compounds can undergo nucleophilic substitution reactions.

Add curly arrows to the diagram below to show the two-step mechanism of $C_6H_5N_2^+$ with F^-.



[2]

(c) Benzene can react with halogenoalkanes in the same way as with bromine, as shown in **reaction 1** below.

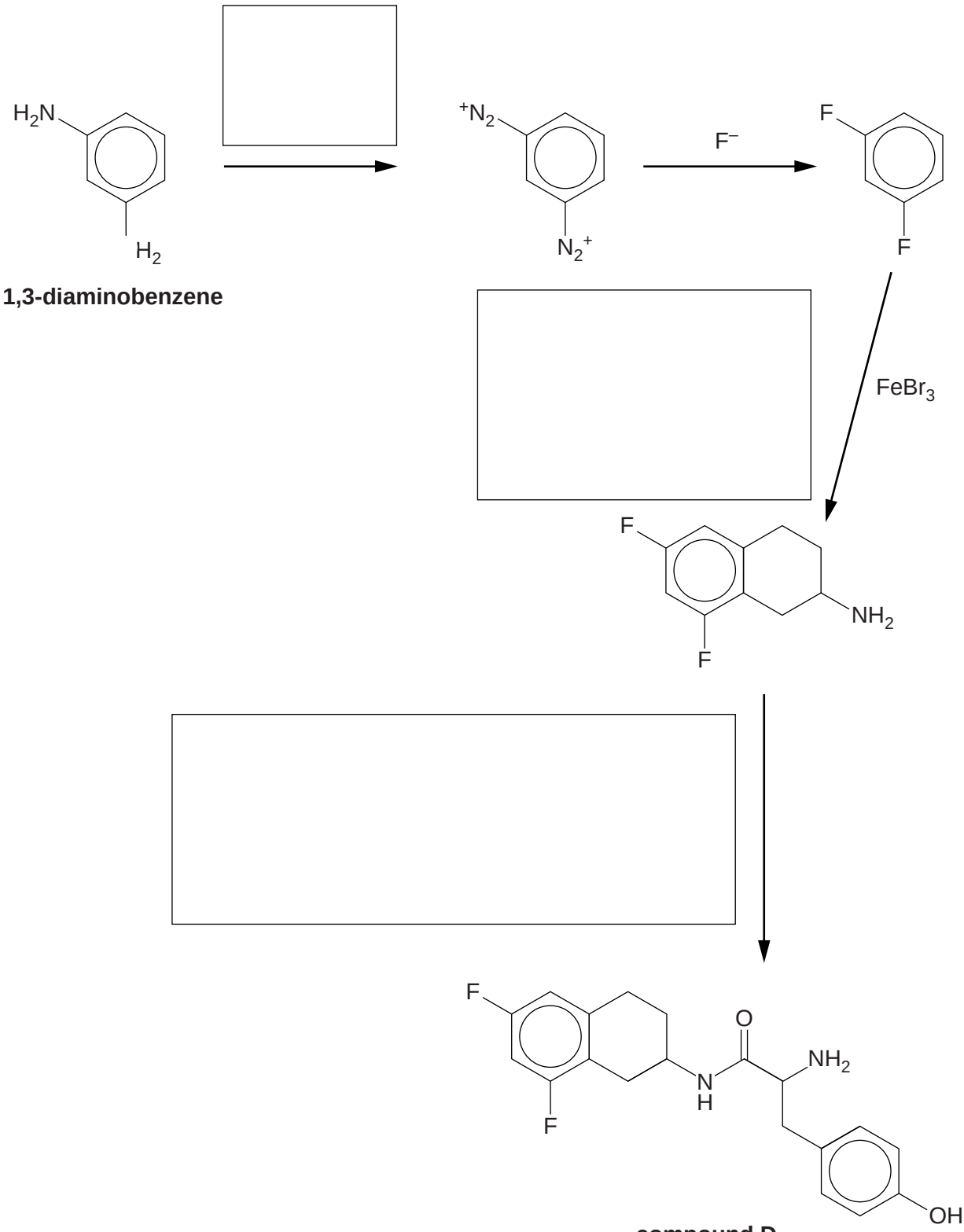


Write an equation to show the formation of the electrophile that reacts with benzene in **reaction 1**.

[1]

(d) The types of reaction in **(b)** and **(c)** can be used to synthesise compound **D**, as shown in the flowchart below.

(i) Complete the boxes below to suggest formulae for the reactants involved in the synthesis of compound **D**.
Give structures for organic compounds.

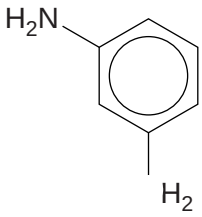


1,3-diaminobenzene

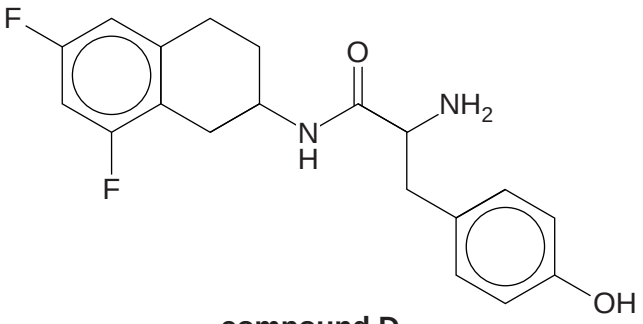
compound D

[3]

(ii) In a synthesis of compound **D** from 1,3-diaminobenzene shown in the flowchart, 1.73 g of compound **D** was prepared. These structures have been repeated below:



1,3-diaminobenzene



compound D

The overall percentage yield of compound **D** was 40.0%.

M_r of compound **D** = 346.0

Calculate the mass of 1,3-diaminobenzene needed for this synthesis.

mass = ... g **[3]**

(iii) Compound **D** has been developed for possible use as a drug to treat heart conditions. When compound **D**, prepared in this synthesis, was given to patients, only 25% of the dose was effective in treating their heart conditions.

Explain why only 25% of the dose was effective. Suggest how the synthesis of compound **D** might be changed to make the dose more effective.

.....

.....

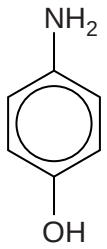
.....

.....

..... **[3]**

[Total: 18]

2 4-Aminophenol is an organic compound that can behave as an acid and a base.



4-aminophenol

(a) State how 4-aminophenol can behave as a base.

.....

..... **[1]**

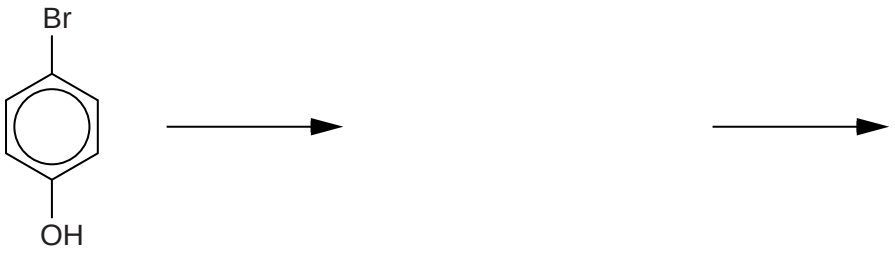
(b) 4-Aminophenol is produced by the reduction of 4-nitrophenol.

Write an equation to show the production of 4-aminophenol from 4-nitrophenol.
Use **[H]** to represent the reducing agent.

[1]

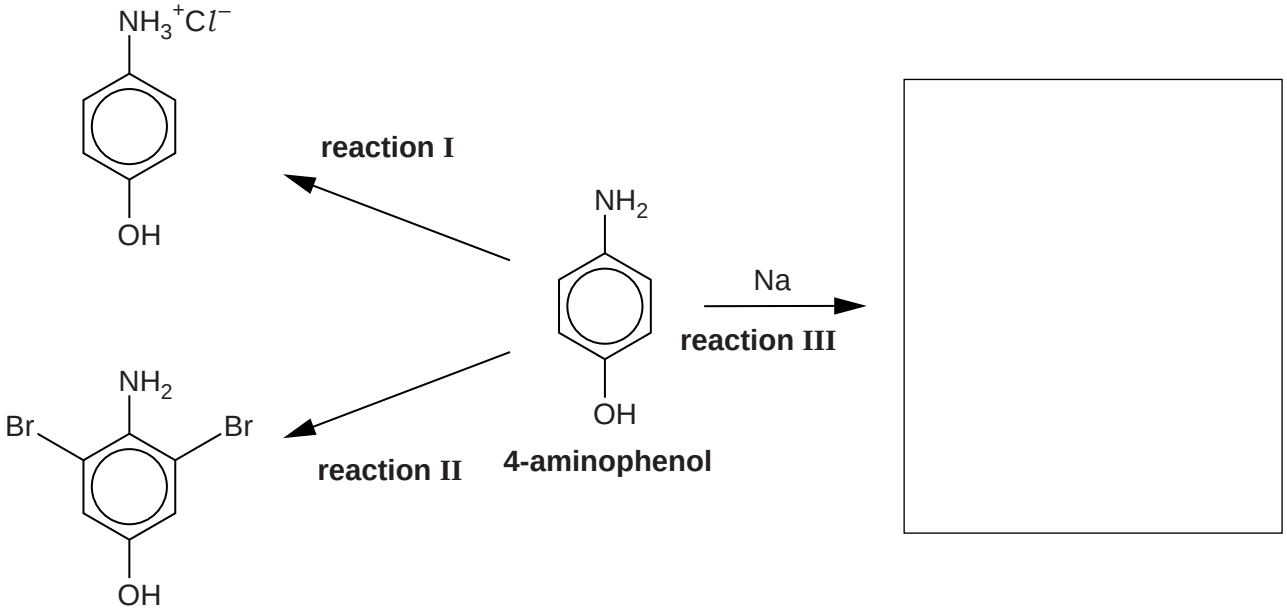
(c) 4-Nitrophenol can be produced from 4-bromophenol.

- Complete the mechanism for this reaction.
- Use $^{+}NO_2$ as the electrophile. Include any intermediate and the products.
- In the mechanism for this reaction, NO_2 substitutes for Br on the ring.



[4]

(d) The flowchart below shows some reactions of 4-aminophenol.



(i) Identity the reagent in **reaction I**.

..... **[1]**

(ii) Name the organic product of **reaction II**.

..... **[1]**

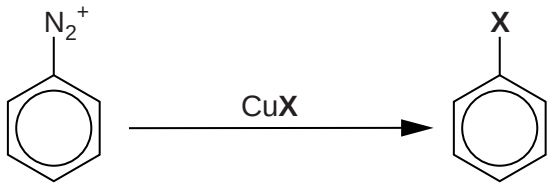
(iii) Write the equation for **reaction II**.

[1]

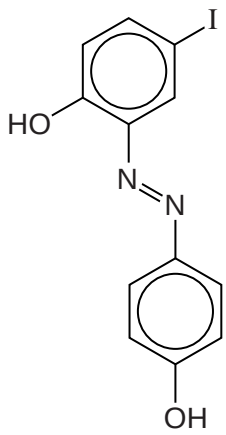
(iv) In the box on the flowchart, draw the structure of the organic compound formed by **reaction III**. **[1]**

(e) The Sandmeyer reaction can be used to replace a diazonium group, N_2^+, with a halogen atom, **X**, on an aromatic ring.

The reagent used for the reaction is a copper(I) halide, Cu**X**.



Compound **C**, shown below, can be synthesised using **only** 4-aminophenol and other standard laboratory reagents. The flowchart on the next page shows this synthesis.



compound C

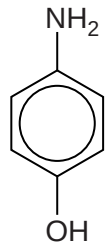
(i) State a possible use for compound **C**.

..... **[1]**

(ii) On the flowchart on the next page:

- state the reagents and conditions used for **reaction 1**
- suggest the structure of compound **B**
- suggest the reagent used for **reaction 2**
- state the conditions used for **reaction 3**.

[5]

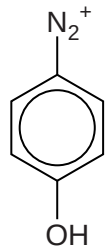


4-aminophenol

reaction 1

reagents .....

conditions .....



compound A

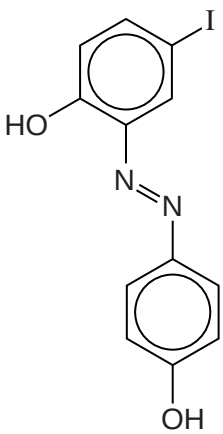
reaction 2

reagent .....

compound B

reaction 3

conditions .....



compound C

[Total: 16]

3 A student was investigating the reactions and uses of organic amines.

(a) The student found that amines such as ethylamine, $C_2H_5NH_2$, and phenylamine, $C_6H_5NH_2$, both behave as bases.

(i) Explain why amines can behave as bases.

.....

..... **[1]**

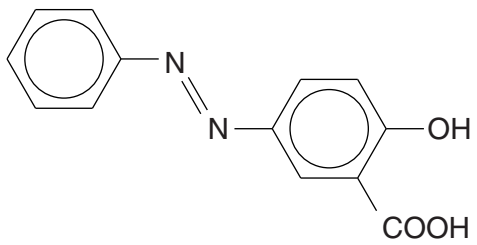
(ii) The student reacted an excess of $C_2H_5NH_2$ with two different acids.

Write the formulae of the salts that would be formed when an **excess** of $C_2H_5NH_2$ reacts with:

sulfuric acid, ...

ethanoic acid. ..... **[2]**

(b) The student reacted phenylamine with a mixture of $NaNO_2$(aq) and HC*l*(aq) whilst keeping the temperature below 10 °C. A diazonium ion was formed. The student then reacted the diazonium ion with compound **B**. After neutralisation, compound **A** was formed.



compound **A**

(i) Draw the structures of the diazonium **ion** and compound **B**.

Display the functional group in the diazonium ion.

diazonium **ion**	compound **B**

[2]

(ii) State the conditions required for the reaction of the diazonium ion with compound **B** and state a possible use for compound **A**.

conditions .....

possible use for compound **A**. ..... **[1]**

(iii) The student added Na_2CO_3 to a solution of compound **A**.

Draw the structure of the organic product and state the formulae of any other products from this reaction.

[2]

(c) The student repeated the experiment in part **(b)** but allowed the temperature to rise above 10 °C.

Under these conditions, the diazonium **ion** in **(b)(i)** reacts with water to produce phenol. A gas with molar mass of 28.0 g mol^{-1} and one other product are also formed.

Construct an equation for this reaction.

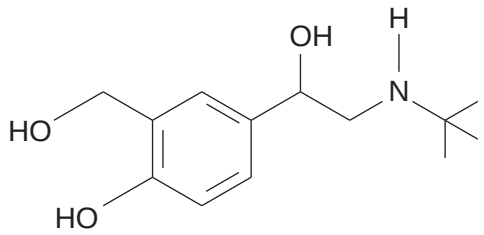
[1]

[Total: 9]

4 Hydroxyamines are organic compounds containing hydroxyl and amino functional groups.

(a) Salbutamol is a hydoxyamine used in the treatment of asthma and bronchitis. Salbutamol is an example of a chiral drug.

(i) Draw a circle around the chiral carbon in the structure of salbutamol shown below.



salbutamol

[1]

(ii) Suggest possible problems of making a chiral drug such as salbutamol and describe **two** ways that the pharmaceutical industry might overcome these problems.

.....

.....

.....

.....

.....

.....

.....

.....

.....

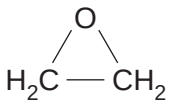
.....

.....

..... **[4]**

(b) Monoethanolamine, MEA, $H_2NCH_2CH_2OH$, is a hydroxyamine that is used in aqueous solution as a gas scrubber to remove acidic gases from emissions in incinerators.

MEA is prepared industrially by reacting ammonia with epoxyethane.



epoxyethane

(i) Write an equation for the industrial preparation of MEA.

[1]

(ii) During the manufacture of MEA, a compound with molecular formula $C_4H_{11}NO_2$ is also formed.

Draw the structure of the compound with molecular formula $C_4H_{11}NO_2$.

[1]

(c) The combustion of some polymers produces emissions containing toxic acidic gases such as HC*l* and H_2S. MEA can remove HC*l* and H_2S from the emissions.

Give the formula of the organic salts formed when MEA removes:

(i) HC*l*,

[1]

(ii) H_2S.

[1]

(d) MEA, $H_2NCH_2CH_2OH$, can be oxidised to form an α-amino acid.

(i) Explain what is meant by an α-amino acid.

.....

.....

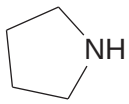
..... **[1]**

(ii) Write an equation for the oxidation of MEA to form an α-amino acid.

Use [O] to represent the oxidising agent.

..... **[1]**

(e) Isomers **F** and **G** are hydroxyamines each with the molecular formula $C_4H_{11}NO$.

- Isomer **F** can be dehydrated to form the cyclic compound 

- Isomer **G** has two chiral centres.

Identify and draw the structural isomers **F** and **G**.

isomer F	**isomer G**

[2]

[Total: 13]