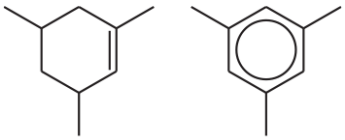
Aromatic Compounds

1. Compounds **B** and **C**, shown below, are unsaturated hydrocarbons containing nine carbon atoms.



B C

Compound **B** reacts with chlorine at room temperature, but compound C requires the presence of a halogen carrier.

In both reactions, the organic compound reacts with chlorine in a 1:1 molar ratio.

i. Draw the structures of the organic product of each reaction.

Organic product with **B**	Organic product with **C**

[2]

ii. Explain the relative resistance to chlorination of compound **C** compared with compound **B**.

---

[3]

iii. Outline the mechanism for the reaction of compound **C** with chlorine.

Show the role of the halogen carrier.

[5]

2. This question is about benzene.

Over time, the Kekulé and delocalised models have been used to describe the bonding and structure of a benzene molecule.

i. Describe, in terms of orbital overlap, the similarities and differences between the bonding in the Kekulé model and the delocalised model of benzene.

[3]

ii. Experimental evidence led to the general acceptance of the delocalised model over the Kekulé model.

Describe **two** pieces of evidence to support the delocalised model of benzene.

---

[2]

3. * Many organic reactions use electrophiles as reagents.

Explain the role of electrophiles in organic chemistry.

Your answer should include **one** reaction of an aliphatic compound and **one** reaction of an aromatic compound, including relevant mechanisms.

[6]

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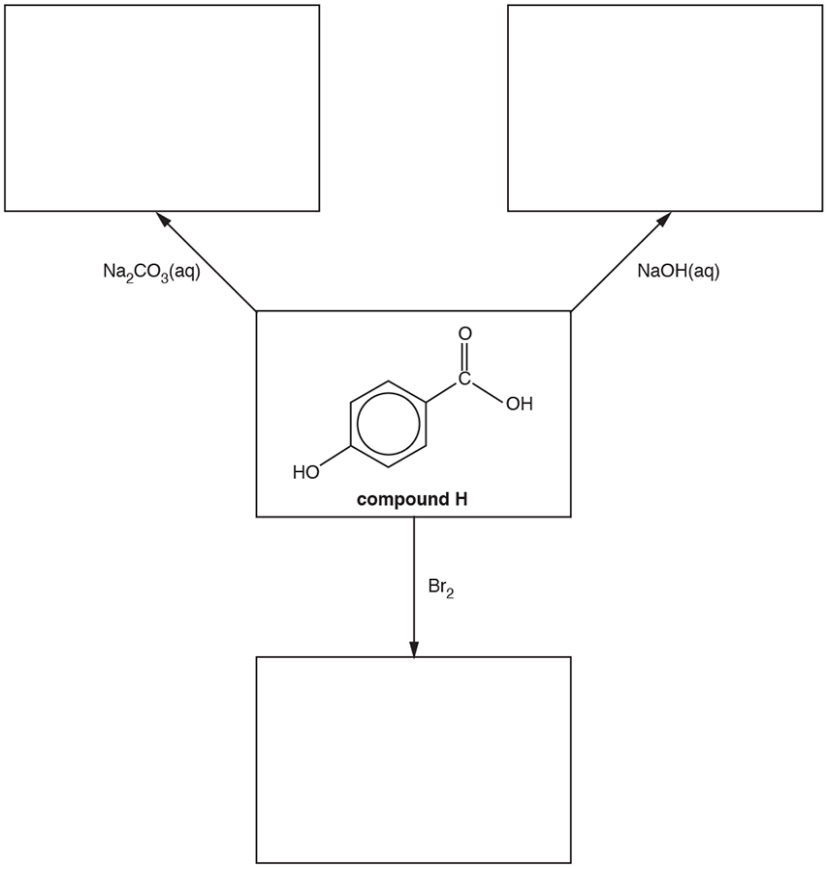
4. This question is about aromatic carboxylic acids and their derivatives.

The flowchart below shows some reactions of compound **H**. In the boxes, draw the organic products of these reactions.



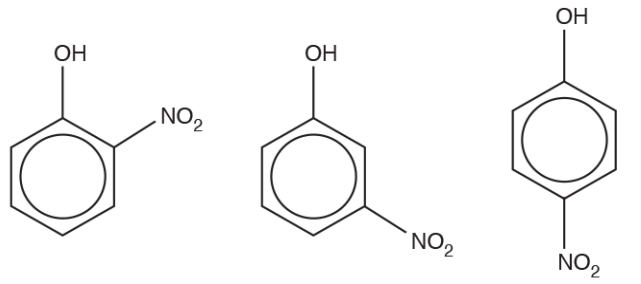
[3]

5(a). This question is about aromatic compounds.

Phenol undergoes nitration more readily than benzene.

i. A student carries out the nitration of phenol with dilute nitric acid to produce 2-nitrophenol and 4-nitrophenol.

A small amount of 3-nitrophenol is also produced.



2-nitrophenol **3-nitrophenol** **4-nitrophenol**

The student thought that ^{13}C NMR spectroscopy could be used to distinguish between these three nitrophenols.

Explain whether the student is correct.

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[3]

ii. Explain why phenol is nitrated more readily than benzene.

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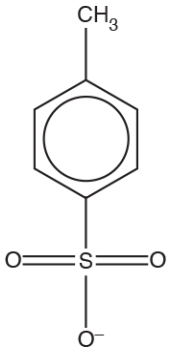
[3]

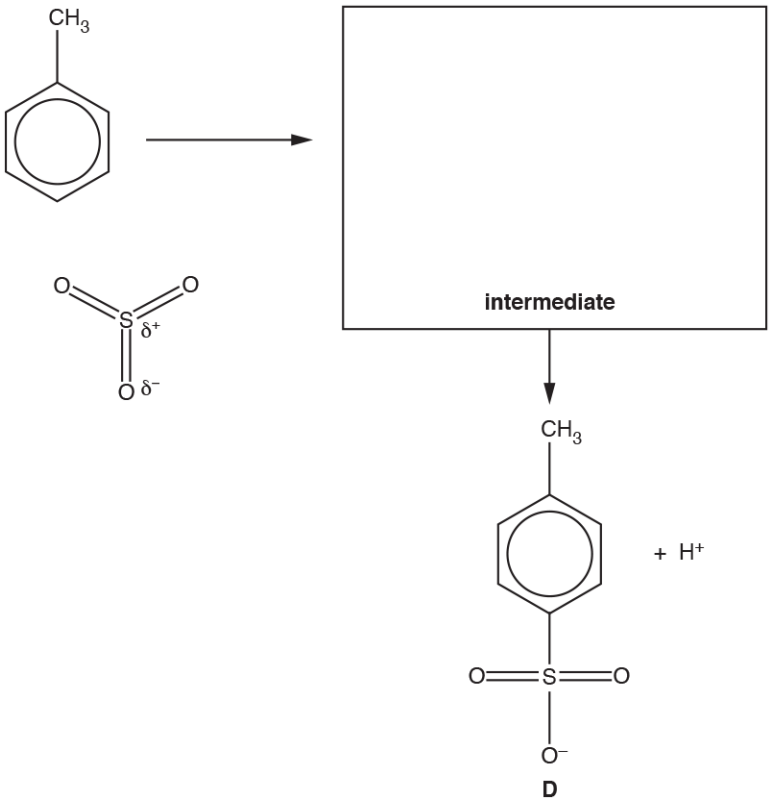
(b). Methylbenzene reacts with sulfur trioxide, SO_3, to form **D**, shown below.



D

The electrophile in this reaction is SO_3.

Complete the mechanism for the formation of **D**.
Show curly arrows and the structure of the intermediate.

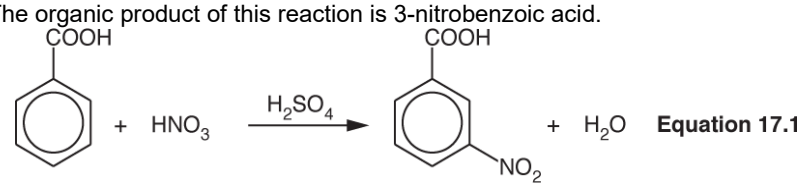


[3]

6(a). This question is about the chemistry of aromatic compounds.

Benzoic acid can be nitrated by concentrated nitric acid in the presence of concentrated sulfuric acid as a catalyst, as shown in **Equation 17.1**.

The organic product of this reaction is 3-nitrobenzoic acid.



Equation 17.1

benzoic acid **3-nitrobenzoic acid**

i. Outline the mechanism for this nitration of benzoic acid.

Show how H_2SO_4 behaves as a catalyst.

ii. A chemist carries out the reaction in **Equation 17.1** using 4.97 g of benzoic acid.

The chemist obtains 3-nitrobenzoic acid as an impure solid.

The chemist purifies the solid to obtain 4.85 g of 3-nitrobenzoic acid.

Describe a method to obtain a pure sample of 3-nitrobenzoic acid from the impure solid, determine the percentage yield and check its purity.

_____

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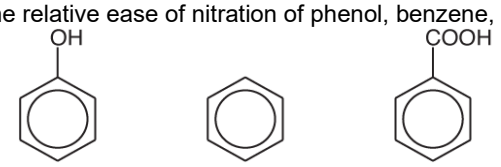
_____ **[6]**

(b). A student investigates the relative ease of nitration of phenol, benzene, and benzoic acid.



phenol **benzene** **benzoic acid**

The student finds that the conditions required for the nitration of each compound are different, as shown in **Table 17.1**.

Compound	**phenol**	**benzene**	**benzoic acid**
Conditions required for nitration	Dilute HNO_3 20 °C No catalyst	Concentrated HNO_3 55 °C H_2SO_4 catalyst	Concentrated HNO_3 100 °C H_2SO_4 catalyst

Table 17.1

i. State the trend in the relative ease of nitration of phenol, benzene, and benzoic acid.

_____

_____

_____ **[1]**

ii. Apply your knowledge of the bonding in arenes to explain the trend in part **(b)(i)**.

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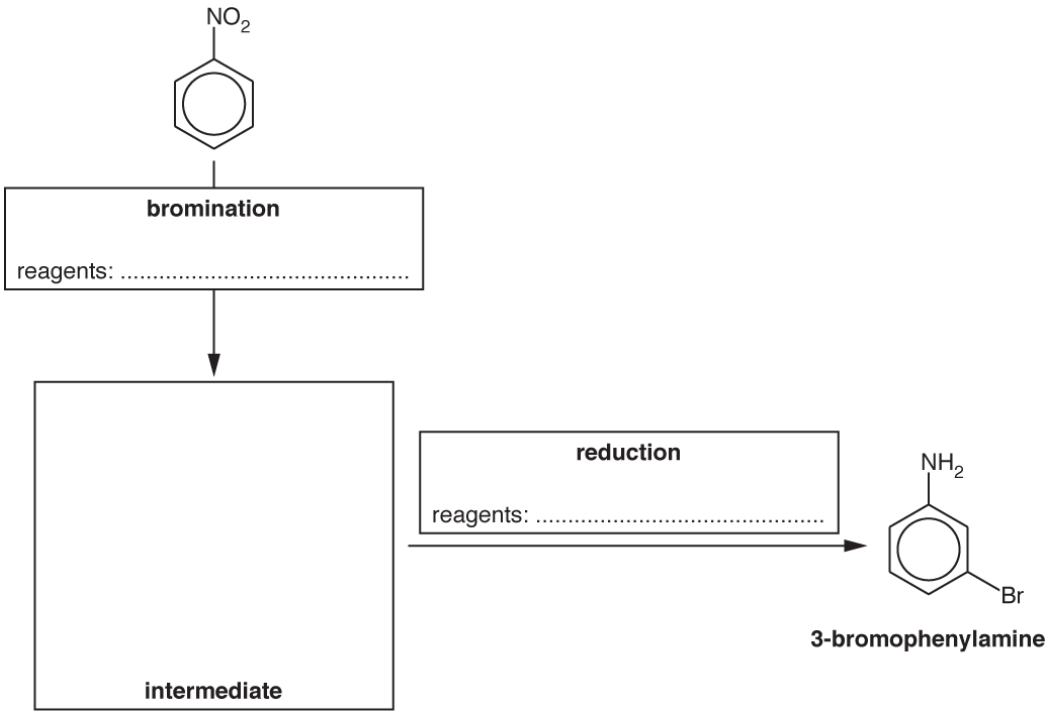
[3]

(c). A student synthesises 3-bromophenylamine, shown below, starting from nitrobenzene.

i. Complete the flowchart showing the structure of the intermediate and the **formulae** of the reagents for each stage.



ii. Another student attempts the same synthesis but carries out reduction **before** bromination. The student was surprised to find that two structural isomers of 3-bromophenylamine had been formed instead of the desired organic product.

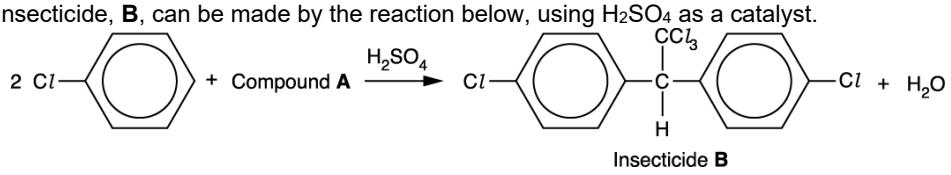
Explain this result and suggest the structures of the two isomers that formed.

Explanation

Structures

7. Concentrated sulfuric acid is often used to catalyse organic reactions.

An insecticide, **B**, can be made by the reaction below, using H_2SO_4 as a catalyst.



Insecticide **B**

i. Draw the structure for compound **A**.

[1]

ii. Sulfuric acid is a catalyst in many reactions.

State **one** other example of an organic reaction in which sulfuric acid is a catalyst.

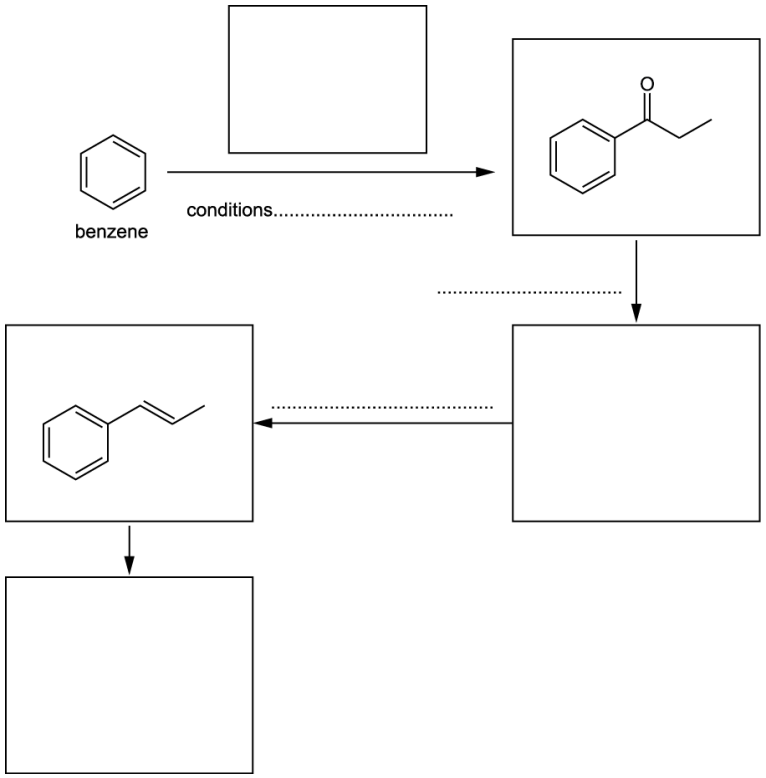
---

[1]

8(a). This question is about the synthesis of a polymer.

The flowchart below shows the synthesis of polymer **I** starting from benzene.

Draw the structures of the missing compounds in the boxes and add the missing reagents on the dotted lines.



repeat unit of polymer **I**

[6]

(b). Polymer **I** cannot be disposed of in landfill sites as it is not biodegradable.

Suggest **one** way of processing waste polymer **I** other than landfill and recycling.

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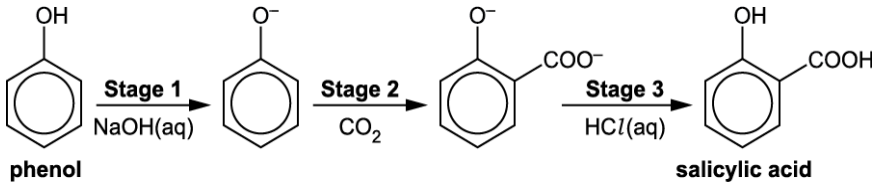
[1]

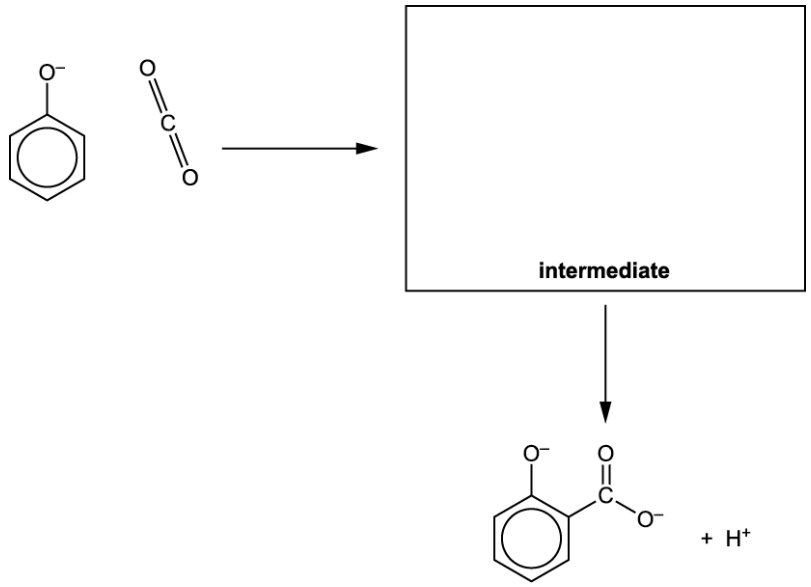
9(a). This question is about medical compounds made from salicylic acid.

Salicylic acid can be made from the reaction of phenol with carbon dioxide as shown below.



i. **Stage 2** takes place by electrophilic substitution and part of the mechanism is shown below.

Complete the mechanism by showing relevant dipoles, curly arrows and the structure of the intermediate.



[3]

ii. What type of reaction takes place during **Stage 1** and **Stage 3**?

Explain your answer.

Type of reaction

.....

Explanation

.....

---

[2]

iii. A chemist prepares 4.83 g of salicylic acid from phenol. The percentage yield of this reaction is 45.0%.

Calculate the mass of phenol that the chemist uses.

Give your answer to **three** significant figures.

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

(b). Aspirin is an ester of salicylic acid.

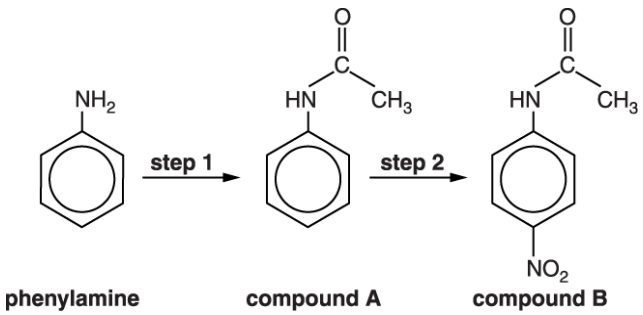
Aspirin can be prepared by reacting salicylic acid with ethanoic anhydride, $(CH_3CO)_2O$. One other organic compound also forms.

Draw **skeletal** formulae for the products of this reaction.

[2]

10. A student plans a two-step synthesis starting with phenylamine.

The steps of the synthesis are shown below.



i. In **step 1**, phenylamine reacts with ethanoic anhydride to make compound **A** and one other organic product.

Draw the structure of ethanoic anhydride, with the functional group displayed, and suggest the structure of the other organic product formed in **step 1**.

ethanoic anhydride	other organic product

[2]

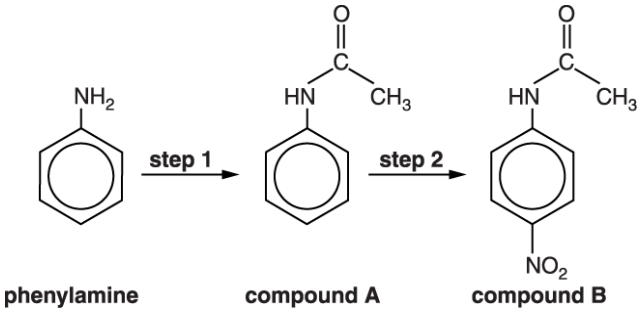
ii. Calculate the mass of compound **A** that can be synthesised from 3.00 g of phenylamine in **step 1**. The percentage yield of this reaction is 61.0%.

M_r (phenylamine) = 93.0

Give your answer to **three** significant figures.

mass of compound **A** = ... g **[3]**

The steps of the synthesis are shown again below.



iii. In **step 2**, compound **A** is converted into compound **B** using a mixture of concentrated nitric acid and concentrated sulfuric acid.

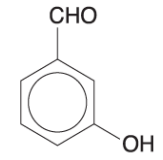
Outline, with the aid of curly arrows, the mechanism for the conversion of compound **A** into compound **B**.

Use equations to explain how sulfuric acid acts as a catalyst in this reaction.

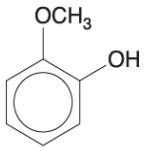
[5]

11. A student analysed a mixture of compounds found in red wine using gas chromatography followed by mass spectrometry (GC-

Two of the compounds found to be present in the mixture are shown below.

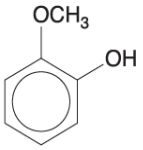


compound A



compound B

1 mol of compound **B** reacts with 2 mol of bromine, Br_2 by electrophilic substitution.

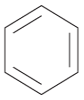


compound B

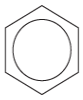
Write a balanced equation for this reaction, showing clearly the structure of the organic compound.

[1]

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



structure A



structure B

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.

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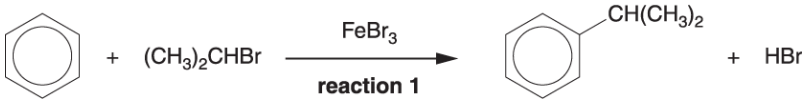
[2]

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

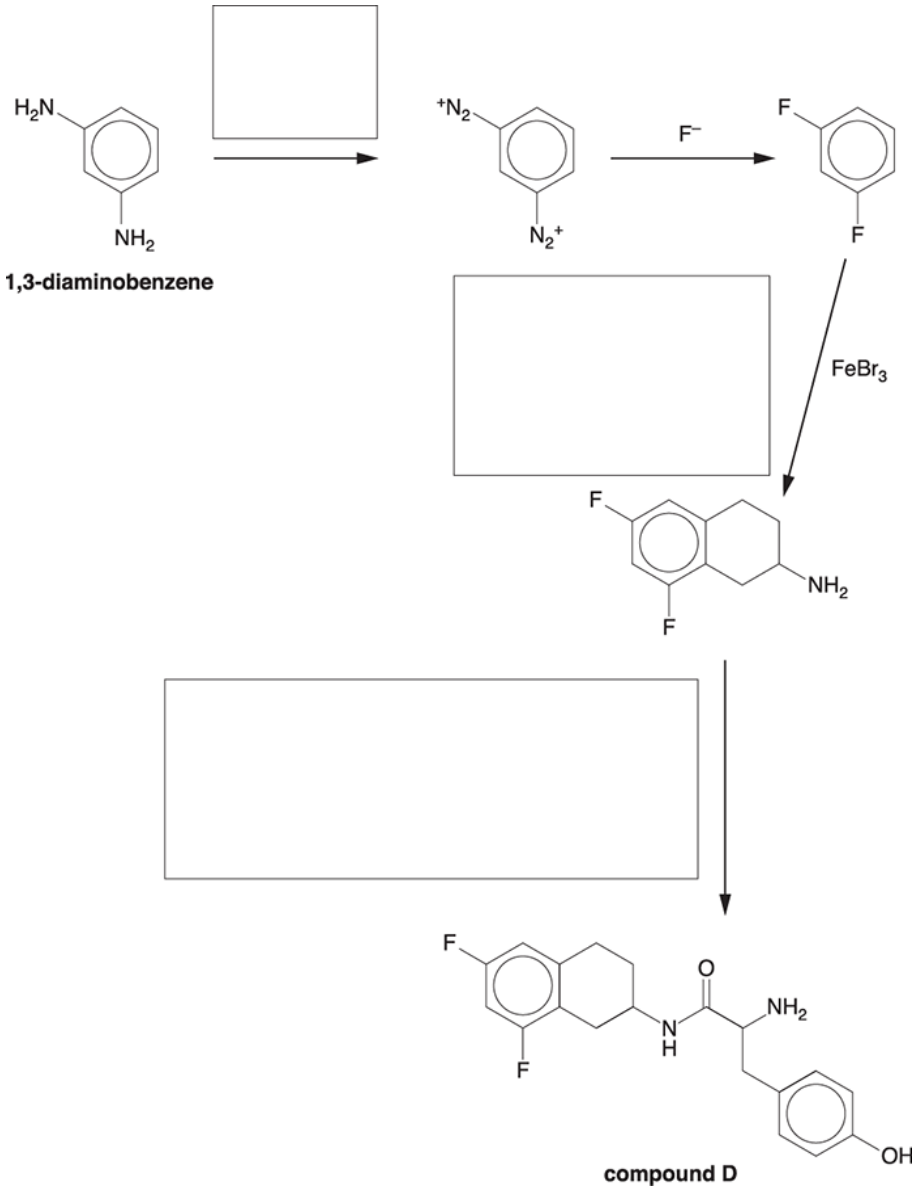


Write an equation to show the formation of the electrophile that reacts with benzene in **reaction 1**.

[1]

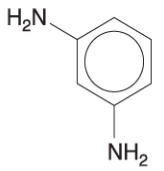
(c). The types of reaction shown in the previous questions can be used to synthesise compound **D**, as shown in the flowchart below.

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

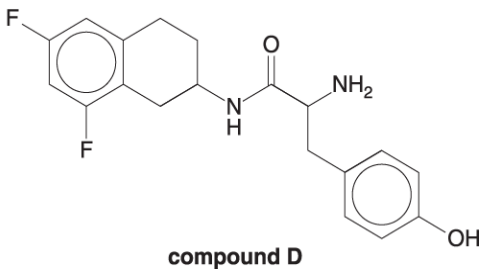


[3]

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.

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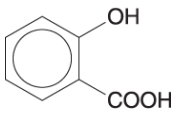
[3]

13(a). Salicylic acid is a naturally occurring carboxylic acid, widely used in organic synthesis.

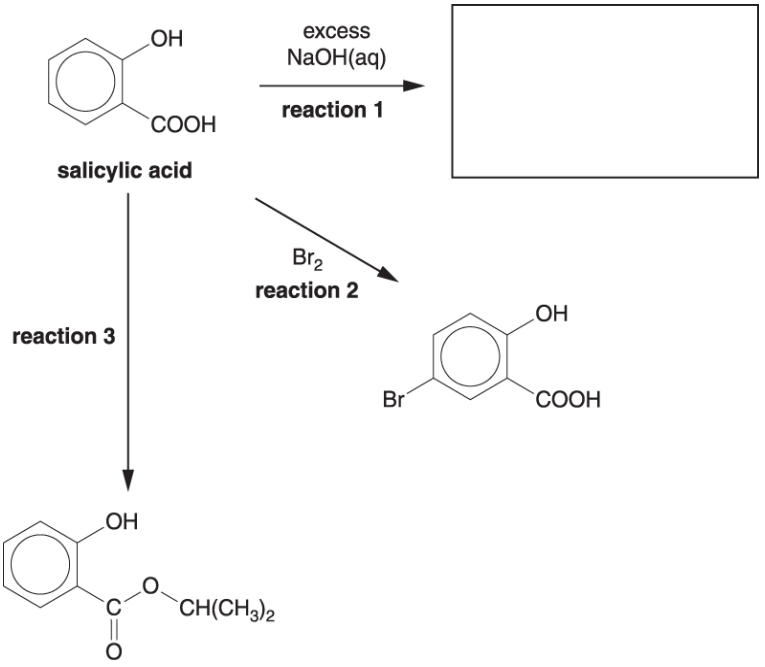


salicylic acid

The flowchart below shows some reactions of salicylic acid.

i. In the box below, draw the structure of the organic compound formed by **reaction 1**.

[1]



ii. Describe what would be **observed** during **reaction 2**.

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[1]

iii. Write a chemical equation to represent **reaction 2**.

[1]

iv. State the reagents and conditions in **reaction 3**.

---

[1]

(b). Bromine reacts more readily with salicylic acid than with benzene.

i. Outline the mechanism for the bromination of salicylic acid shown in **reaction 2** in the flowchart.

A halogen carrier is not required for this reaction.

The electrophile is Br_2.

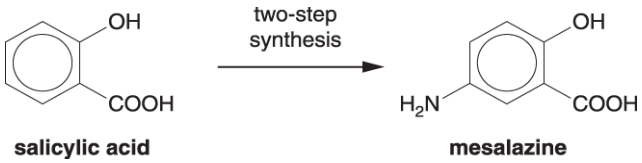
[4]

ii. Explain why bromine reacts more readily with salicylic acid than with benzene.

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

---**[3]**

(c). Mesalazine is a drug that can be synthesised from salicylic acid in two steps.



salicylic acid **mesalazine**

i. Suggest a **two-step** synthesis to prepare mesalazine from salicylic acid.

For **each** step
- state the reagents used,
- write a chemical equation.

[4]

ii. Mesalazine reacts with acids to form salts.

Explain how mesalazine is able to react with acids.

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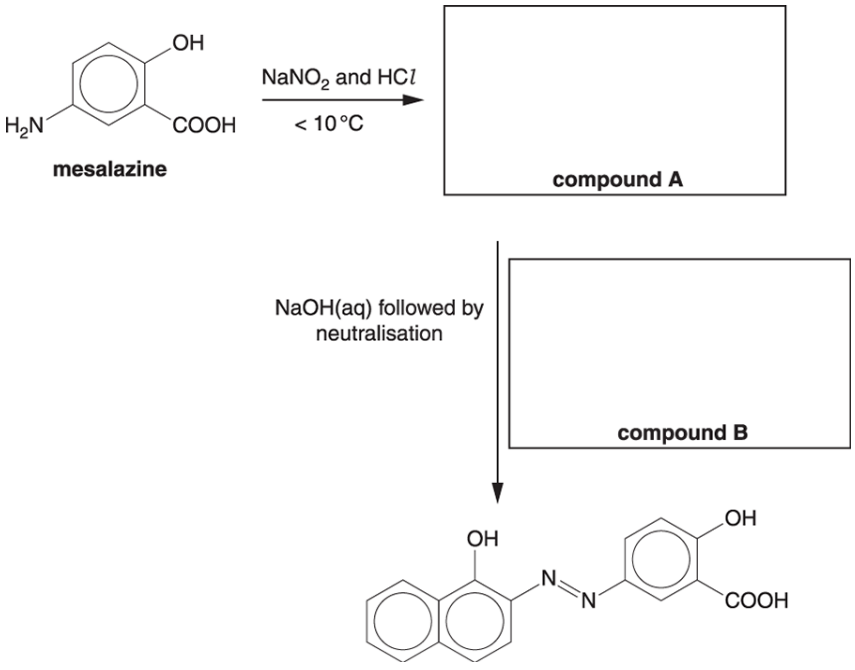
[1]

iii. Mesalazine reacts in another two-stage process as shown below.

In the boxes, draw the structures of organic compounds **A** and **B**.

[2]



14. Give chemical explanations for the following statements.

The carbon–carbon bonds in benzene are all the same length.

---

[1]

15. Information about a monobasic organic acid **D** is shown below.

- **D** reacts by both electrophilic substitution and electrophilic addition.
- The molecular formula of **D** is $C_xH_yO_2$.
- The mass spectrum of **D** has a molecular ion peak at *m/z* = 148.
- The ^{13}C NMR spectrum of **D** contains seven peaks.

Determine and draw a possible structure for **D**.

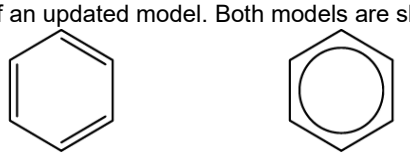
Explain your reasoning from the evidence provided.

---

[5]

16(a). This question is about the chemistry of benzene and substituted benzene compounds.

In 1865, the Kekulé model was suggested for the structure of benzene. Experimental evidence has led to the development of an updated model. Both models are shown below.

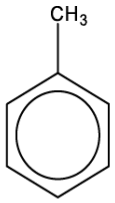


Kekulé model **Updated model**

- Explain the experimental evidence that led to the development of the updated model from the Kekulé model of benzene.
- Describe the bonding in the updated model of benzene.

---**[4]**

(b). A chemist investigates the chlorination of methylbenzene and finds that the methyl group has a 2– and 4– directing effect.



methylbenzene

4-Chloromethylbenzene is one of the products of the chlorination of methylbenzene.

Outline the mechanism for the formation of 4-chloromethylbenzene from methylbenzene and chlorine in the presence of the catalyst, $AlCl_3$.

Show how $AlCl_3$ behaves as a catalyst.

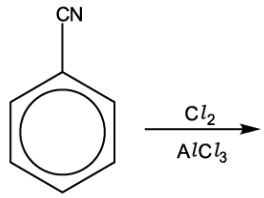
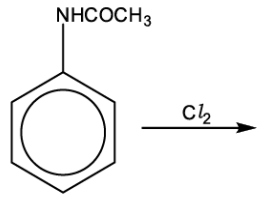
[5]

(c). The chemist carries out further investigations into the reactions of substituted benzene compounds.

The table below shows the directing effects of different groups attached to a benzene ring.

Group	Position to which new substituent is directed
$-NO_2$	3
$-OH$	2, 4
$-COCH_3$	3
$-N(CH_3)_2$	2, 4
$-NHCOCH_3$	2, 4
$-CN$	3

i. Draw all of the organic products from monosubstitution reactions of the substituted benzene compounds shown below.

Reaction	Monosubstituted Product(s)
	
	

[3]

ii. The reactions of $C_6H_5N(CH_3)_2$ are similar to the reactions of phenol.

Draw the organic product that is formed from the tri-substitution of $C_6H_5N(CH_3)_2$ with chlorine.

[1]

iii. Explain why chlorine reacts much more readily with $C_6H_5N(CH_3)_2$ than with benzene.

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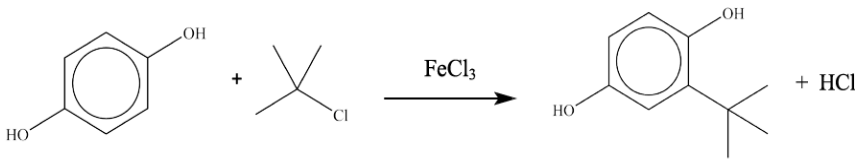
[3]

17. A student investigates reactions of aromatic compounds.

The student first carries out the reaction shown below.



quinol **Compound E**

i. The student obtains a very low yield of compound **E**.
The student obtains a much higher yield of a different organic product with molecular formula $C_{14}H_{22}O_2$.

Suggest an identity for the organic product $C_{14}H_{22}O_2$ and draw its structure below.

[1]

ii. The student is told by a friend that the $FeCl_3$ catalyst is not needed because quinol is more reactive than benzene.

Explain why the student's friend is correct.

You may draw a diagram to support your answer.

---**[3]**

END OF QUESTION PAPER