F324: Rings, Polymers and Analysis
4.1.1. Arenes

1. A chemist was investigating the reactions of benzene, phenol and cyclohexene with bromine. She found that they all reacted with bromine but under different conditions.

(a) The chemist found that when benzene reacts with bromine, a halogen carrier is required as a catalyst.

Write an equation for this reaction.
You do **not** need to show the halogen carrier in your equation.

[1]

(b) The chemist also found that when phenol or cyclohexene reacts with bromine, a halogen carrier is **not** required.

(i) The chemist observed that bromine decolourises when it reacts with phenol.

What other observation would she have made?

Draw the structure of the organic product formed.

Observation .....

Organic product:

[2]

(ii) Cyclohexene also decolourises bromine.

Name the organic product formed.

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[1]

(iii) Explain the relative resistance to bromination of benzene compared to phenol and compared to cyclohexene.

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

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[5]

[Total 9 marks]

2. Benzene reacts with chlorine in the presence of a halogen carrier, such as AlCl_3.

(a) (i) Write the equation for the reaction of benzene with chlorine.

[1]

(ii) How does the halogen carrier allow the reaction to take place?

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[1]

(iii) Outline a mechanism for this reaction.

Include curly arrows and relevant dipoles.

[4]

(iv) State the name of this mechanism.

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[1]

(b) In contrast to benzene, the reaction of an alkene with bromine does **not** need a halogen carrier.

Compare the different reactivities of benzene and alkenes towards chlorine.

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[3]

[Total 10 marks]

3. In this question, one mark is available for the quality of spelling, punctuation and grammar.

Describe with the aid of suitable diagrams the bonding and structure of a benzene molecule.

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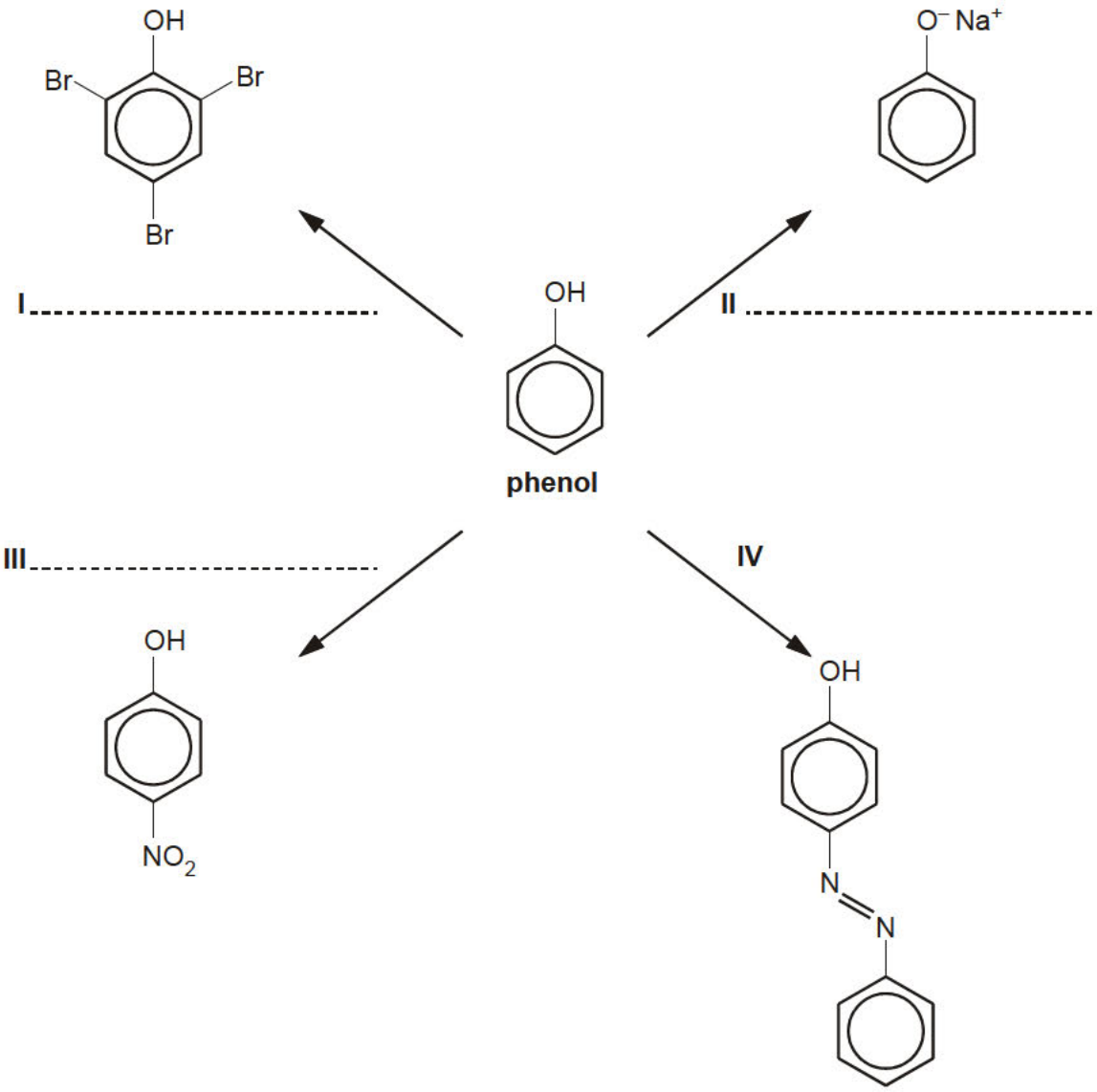
[6]

Quality of Written Communication [1]

[Total 7 marks]

4. The diagram below shows some reactions of phenol.



(i) On the diagram above, identify suitable reagents that could be used to carry out reactions **I**, **II** and **III**.

[3]

(ii) State a use for the compound formed in reaction **IV**.

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[1]

(iii) Outline how you could carry out reaction **IV** in the laboratory starting from phenol and a suitable aromatic amine.

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[5]

[Total 9 marks]

5. In this question, one mark is available for the quality of spelling, punctuation and grammar.

Phenol reacts much more readily with bromine than benzene does.

- Describe, with the aid of a diagram, the bonding in benzene.
- Explain why electrophiles, such as bromine, react much more readily with phenol than with benzene.

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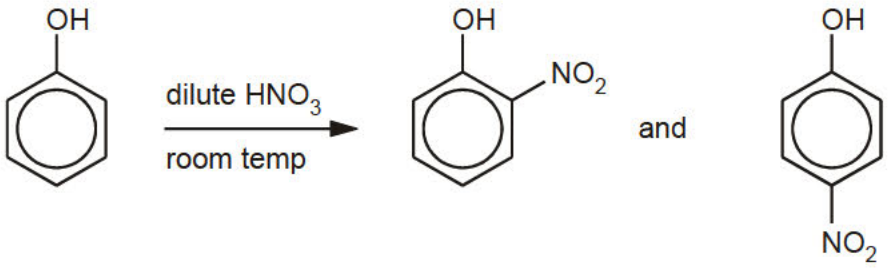
[7]

Quality of Written Communication [1]

[Total 8 marks]

6. Phenol reacts readily with dilute nitric acid at room temperature in a nitration reaction to produce a mixture of products as shown below.



(a) Suggest the structure of another organic product that is likely to be formed in the nitration of phenol.

[1]

(b) Assuming a yield by mass of 27% for 4-nitrophenol, calculate the mass of 4-nitrophenol that would be produced from 100 g of phenol. Show your working.

Give your answer to an appropriate number of significant figures.

mass of 4-nitrophenol = ... g

[4]

(c) In this question, one mark is available for the quality of spelling, punctuation and grammar.

Compare the reagents and conditions for the nitration of phenol with those used for the nitration of **benzene**.

State and explain the effect of the –OH group on the reactivity of the benzene ring in phenol.

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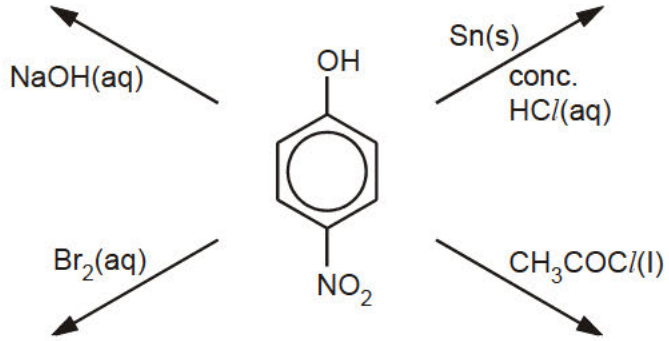
Quality of Written Communication [1]

[Total 13 marks]

7. 4-Nitrophenol can be converted into a range of useful organic chemicals. Draw the structures of the organic products formed in the following reactions.



[Total 4 marks]

8. Diphenylethanedione is a pale yellow colour, which disappears when it is reduced.

The colour results from the arrangement of the delocalised π-bond electrons.

Explain what is meant by the term *delocalised π-bond electrons*.

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[Total 2 marks]

9. (a) In this question, one mark is available for the quality of use and organisation of technical terms.

Bromine is used in organic chemistry to carry out a variety of electrophilic reactions.

(i) Describe and explain how a molecule of bromine acts as an electrophile. Illustrate your answer with a diagram showing relevant dipoles and curly arrows.

(ii) Use your answer to (i) to explain why bromine reacts much more readily with cyclohexene than it does with benzene.

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Quality of Written Communication [1]

(b) The compound iodine monobromide, IBr, also reacts with benzene in an electrophilic reaction.

(i) Which compound would be the main product of this reaction, iodobenzene or bromobenzene? Explain your answer.

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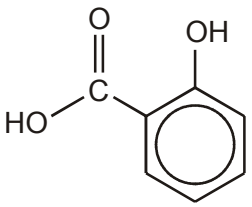
[2]

(ii) Deduce an equation for the reaction of iodine monobromide with benzene.

[1]

[Total 11 marks]

10. Salicylic acid is used in the manufacture of aspirin tablets. In the UK around 3500 tonnes of salicylic acid are manufactured per year.



salicylic acid

Salicylic acid is manufactured from phenol in three stages.

(a) Phenol is first converted to sodium phenoxide, $C_6H_5O^-Na^+$.

(i) State a reagent that could be used for this reaction.

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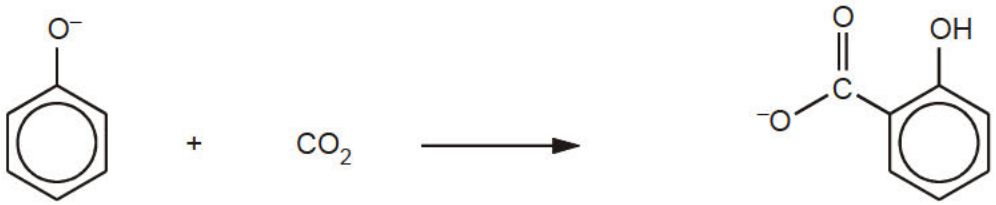
[1]

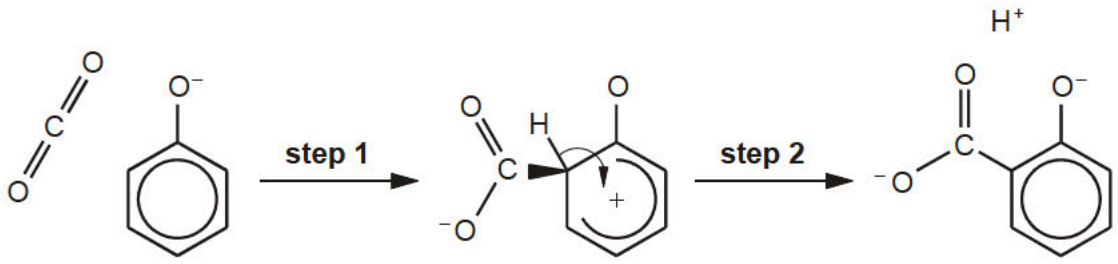
(ii) Write a balanced equation for this reaction.

[1]

(b) The phenoxide ion is then combined with carbon dioxide under high pressure to form the salicylate ion.



This reaction is an electrophilic substitution reaction, which occurs by the incomplete mechanism shown below. Carbon dioxide acts as the electrophile.



intermediate

(i) Add partial charges δ^+ and δ^- to show the polarisation of the C=O bonds in the carbon dioxide molecule above.

[1]

(ii) Complete the mechanism by adding curly arrows to show the movement of electron pairs in **step 1** to give the intermediate shown.

[2]

(iii) Carbon dioxide is normally a very poor electrophile. However, this reaction does occur because the benzene ring in the phenoxide ion is activated.

Explain how the benzene ring in the phenoxide ion is activated.

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[3]

(c) In the final stage of this process, the salicylate ion is acidified to give salicylic acid.

Assuming an overall yield by mass of 45% for this three stage process, calculate the mass of phenol that is needed to produce the annual UK output of 3500 tonnes of salicylic acid.

M_r of phenol = 94.0; 1 tonne = 10^6 g

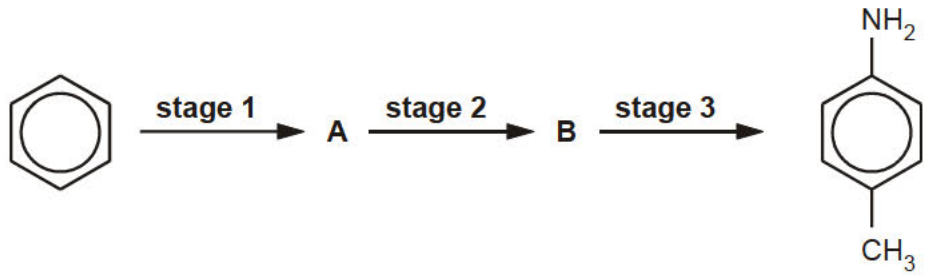
mass of phenol = ... tonnes

[4]

[Total 12 marks]

11. In this question, one mark is available for the quality of use and organisation of scientific terms.

4-Methylphenylamine can be manufactured from benzene in three stages.



benzene **4-methylphenylamine**

Describe how benzene could be converted by these three stages into 4-methylphenylamine.

Include the structures of the intermediate compounds **A** and **B**. State the reagents and conditions. Give a balanced equation for each stage.

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[11]

Quality of Written Communication [1]

[Total 12 marks]

12. The nitration of benzene is a very important industrial reaction.

(a) Name **two** types of commercially important material whose manufacture involves the nitration of benzene.

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[2]

(b) State the conditions required for the nitration of benzene using nitric acid and sulphuric acid.

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[2]

(c) Write a balanced equation for the nitration of benzene.

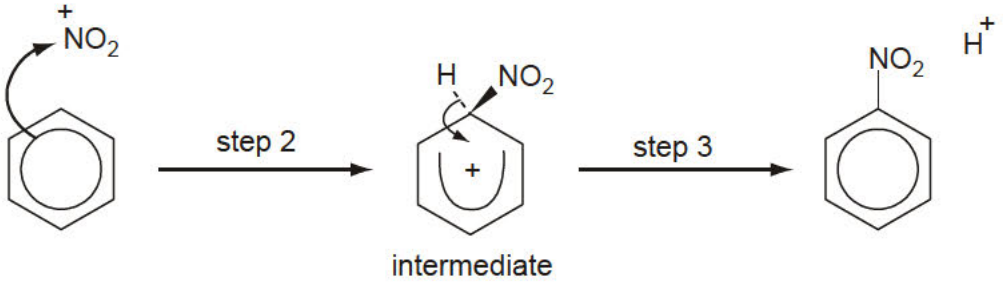
[2]

(d) The mechanism for the reaction is given below.

Step 1: formation of the electrophile, NO_2^+, from HNO_3 and H_2SO_4

$$HNO_3 + H_2SO4 \rightarrow H_2O + NO_2^+ + HSO_4^-$$

Steps 2 and 3: substitution of NO_2^+ into the benzene ring



intermediate

Step 4: protonation of the HSO_4^-

$$H^+ + HSO_4^- \rightarrow H_2SO_4$$

(i) Explain what a curly arrow represents in this type of mechanism.

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[2]

(ii) State why the NO_2^+ is described as an electrophile in this mechanism.

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[1]

(iii) State why this mechanism is described as substitution.

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[1]

(iv) How does the mechanism show that the sulphuric acid is acting as a catalyst?

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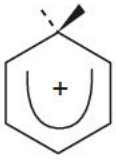
[1]

(e) In this question, one mark is available for the quality of spelling, punctuation and grammar.

The benzene ring and the ring in the intermediate formed after **step 2** have different structures shown below. Both structures have π-bonds.

benzene ring



ring in the intermediate

Deduce how many electrons are involved in the π-bonding in each structure and describe how their arrangements are different.

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Quality of Written Communication [1]

[Total 17 marks]