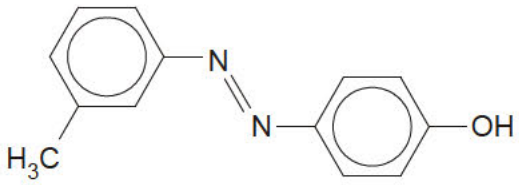
F324: Rings, Polymers and Analysis
4.1.4 Amines

1. Compound **A**, shown below, is being considered as an azo dye by a chemical company. A chemist planned a two-stage synthesis of compound **A** starting from an aromatic amine.



compound A

The aromatic amine is first converted into a diazonium ion.

- Draw the displayed formula of the aromatic amine **and** of the diazonium ion.
- State the reagents and conditions for each stage in the synthesis of compound **A** from an aromatic amine.

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[Total 5 marks]

2. The method below can be used to make phenylamine from nitrobenzene in the laboratory.

3.69 g of nitrobenzene and 8 g of tin (an excess) were placed into a flask. The flask was fitted with a reflux condenser. Concentrated hydrochloric acid was then added dropwise to the flask.

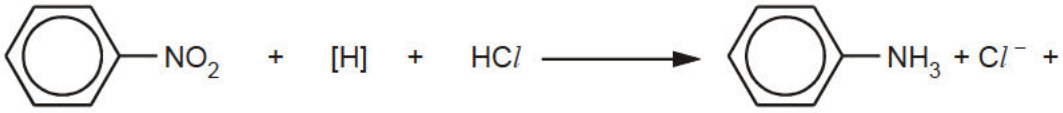
The mixture was heated for 30 minutes to complete the reaction.

Once the mixture had cooled, concentrated sodium hydroxide solution was added until the mixture was alkaline.

Purification gave a 72.1% yield of phenylamine.

(a) Reaction of nitrobenzene with the tin and hydrochloric acid produces phenylammonium chloride as the organic product.

(i) Complete the equation for this reaction.



phenylammonium chloride

[2]

(ii) State what the symbol [H] in the equation represents.

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[1]

(b) When the sodium hydroxide was added, the phenylammonium chloride was converted to phenylamine.

Write an equation for this reaction.

[2]

(c) Calculate the mass of phenylamine that was produced from the 3.69 g of nitrobenzene in this experiment. Give your answer to three significant figures.

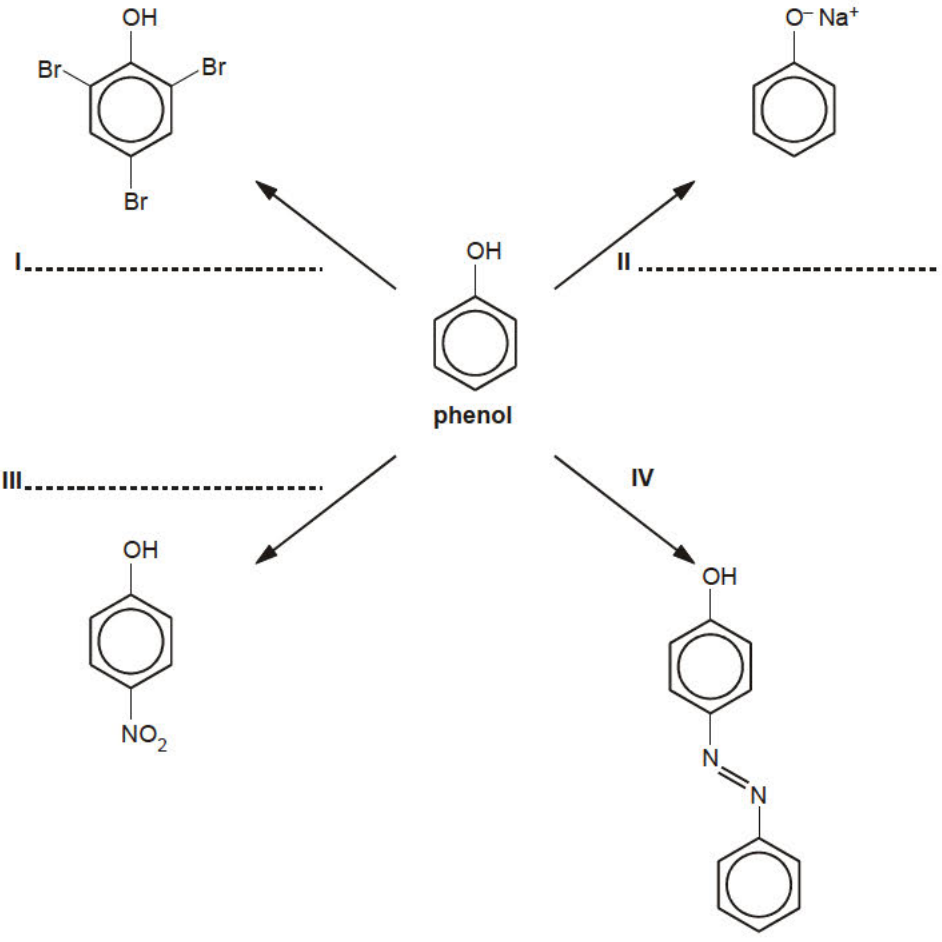
M_r: nitrobenzene,123; phenylamine, 93.1

mass of phenylamine = ... g

[4]

[Total 9 marks]

3. 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]

4. Coloured organic compounds also include azo dyes.

Describe how an azo dye can be made from phenylamine. Show the structure of the azo dye and the organic intermediate in your answer.

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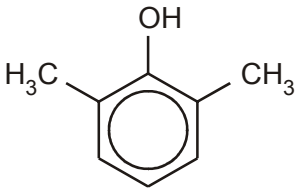
[Total 6 marks]

5. A dye can be made from 4-methylphenylamine and 2,6-dimethylphenol, shown below.

4-methylphenylamine



2,6-dimethylphenol

4-Methylphenylamine is dissolved in ice-cold hydrochloric acid and sodium nitrite is added.
This mixture is then slowly added to an alkaline solution of the phenol to form the dye.

(i) Identify the inorganic nitrogen-containing compound formed by the mixture of hydrochloric acid and sodium nitrite.

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[1]

(ii) Draw the structure of the organic compound formed in the ice-cold acidic mixture, showing a displayed formula of the nitrogen-containing group.

[1]

(iii) State the name of the type of organic compound drawn in (ii).

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[1]

(iv) Suggest why the mixture must be kept at a low temperature.

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[1]

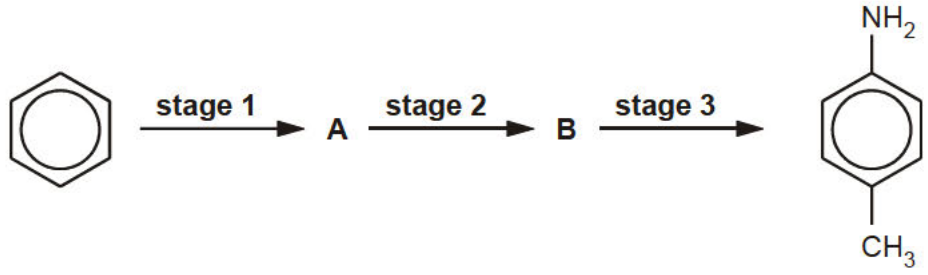
(v) Suggest the structure of the dye.

[2]

[Total 6 marks]

6. 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]

7. E110 is a yellow colouring agent that is commonly added to a variety of foods.

E110 contains an azo dye made from an amine and a phenol.

(a) Describe how you would prepare a sample of an azo dye in the laboratory from an amine, a phenol and any other necessary reagents.

Include in your answer

- essential reagents and conditions for each stage
- names of any functional groups formed during the process.

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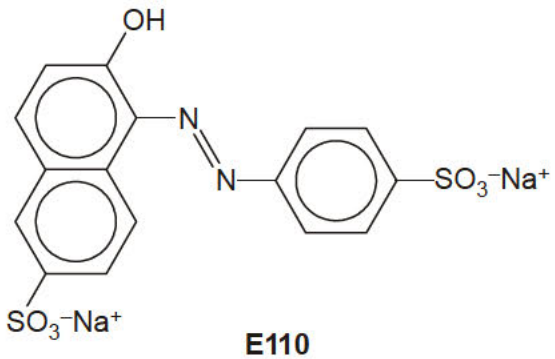
[7]

(b) The structure of E110 is shown below.



E110

(i) On the structure above, draw a circle around the functional group that identifies this molecule as an azo dye.

[1]

(ii) Deduce how many carbon and hydrogen atoms are in a molecule of E110.

..... carbon atoms and ..... hydrogen atoms.

[2]

(c) The solubility of E110 in water can be improved by converting the phenolic −OH group into a charged $-O^-$ group.

Suggest a suitable reagent that will convert the −OH group in E110 into an $-O^-$ group.

.....

[1]

(d) In the boxes below, draw the structures of a phenol and an amine that could be used to make E110 by the method in part (a).

Assume that the $SO_3^-Na^+$ groups do not change during the process.

phenol		amine

[2]

[Total 13 marks]

8. 1,4-Diaminobenzene is used in the manufacture of a variety of materials including dyes and polymers.

1,4-diaminobenzene

(a) Explain what is meant by the term *1,4-diamino* in the name of this compound.

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[2]

(b) 1,4-diaminobenzene can be manufactured from 1,4-dinitrobenzene.

1,4-dinitrobenzene 1,4-diaminobenzene

(i) What type of reaction is this?

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[1]

(ii) State reagents and conditions that could be used to carry out this reaction.

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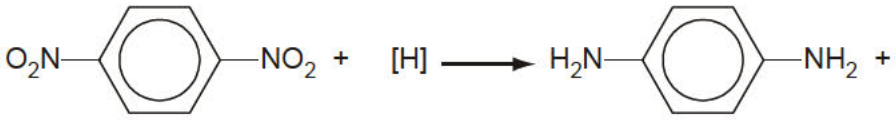
[2]

(iii) Complete and balance the equation below for this reaction.



[2]

(c) 1,4-Diaminobenzene is used to make permanent black dye for hair.

1,4-Diaminobenzene can irritate the skin because it is basic. Therefore, it is sometimes neutralised with **excess** hydrochloric acid to give the salt.

(i) Explain how the amino groups in a primary amine such as 1,4-diaminobenzene allow the molecule to act as a base.

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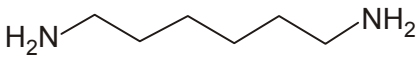
[2]

(ii) Draw the structure of the salt formed in this reaction.

[2]

(iii) State whether you would expect hexane-1,6-diamine to be a stronger or weaker base than 1,4-diaminobenzene. Explain your reasoning.



hexane-1,6-diamine

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[3]

[Total 14 marks]