

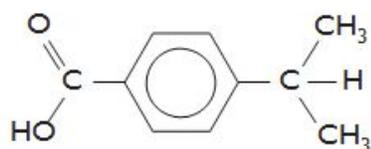
WJEC Chemistry A-level

OA1.2: Aromaticity

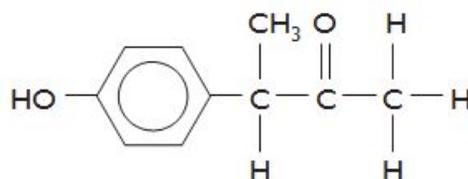
Practice Questions

England Specification

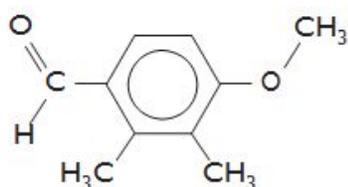
1. This question focuses on the chemistry of some of the many compounds which share the molecular formula $C_{10}H_{12}O_2$. Four compounds with this formula are shown below.



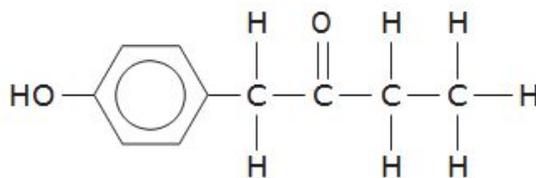
compound W



compound X



compound Y



compound Z

- (a) Draw an **ester** which is an isomer of the compounds above.

[1]

- (b) Only one of the compounds shown can exhibit optical isomerism

- (i) Identify which compound can exhibit optical isomerism.

[1]

- (ii) Indicate the chiral centre in this molecule by labelling it with an asterisk (*).

[1]

(iii) State how the two enantiomers of this compound can be distinguished.

[1]

(c) The four compounds **W**, **x**, **y** and **Z** were tested using a series of reagents. For each of the tests listed below, describe what would be expected to be observed in a positive test. Indicate which compounds would be expected to give a positive result. [6]

All the tests listed will give positive results with at least one compound.

Reagent(s)	Observation if the test is positive	Compounds that would give a positive result
I ₂ /NaOH(aq)
Na ₂ CO ₃ (aq)
FeCl ₃ (aq)

(d) Compound **W** can be oxidised to produce benzene-1,4-dioic acid (*terephthalic acid*). This reaction can be undertaken in the same way as the oxidation of methylbenzene to form benzenecarboxylic acid.



(i) Give the reagent(s) and condition(s) required for this oxidation reaction.

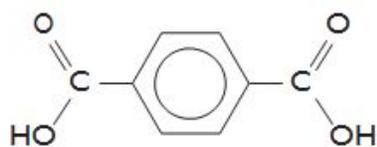
[2]

(ii) Almost all the benzene-1,4-dioic acid produced worldwide is used in the production of condensation polymers

I. Give **two** differences between condensation polymerisation and addition polymerisation.

[2]

II. Draw the repeat unit for the polymer formed between benzene-1,4-dioic acid and ethane-1,2-diol. [1]

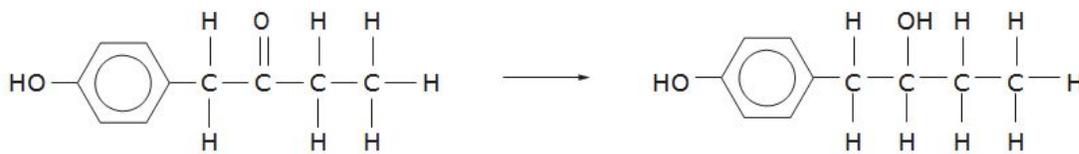


benzene-1,4-dioic acid
(*terephthalic acid*)



ethane-1,2-diol

(e) Compound **Z** may be converted into a secondary alcohol as shown below.



compound **Z**

compound **V**

(i) Give a suitable reagent for this process and classify the reaction that occurs. [2]

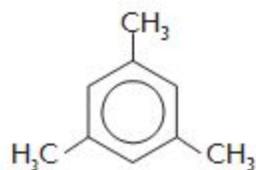
Reagent

Classification of reaction

(b) Methylbenzene can be made by the Friedel-Crafts alkylation of benzene. Give the equation for this reaction and name a catalyst that can be used.

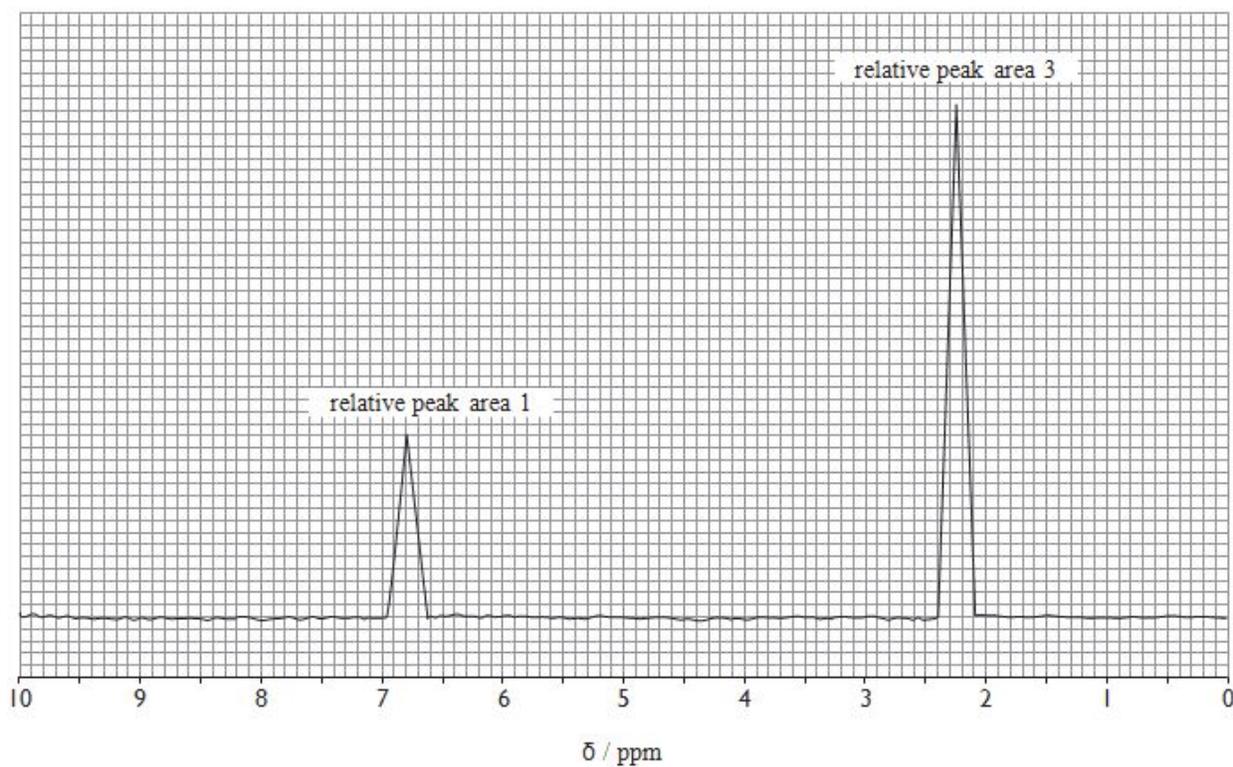
[2]

(c) 1,3,5-Trimethylbenzene (mesitylene) is also an alkylbenzene.

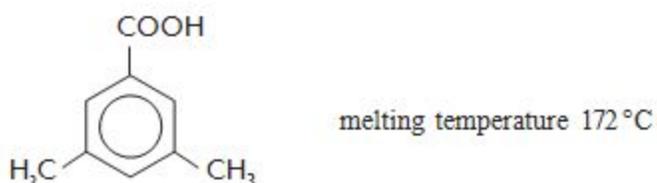


(i) The NMR spectrum of mesitylene is shown opposite. Use the chemical formula to help you explain the peaks in this spectrum, including the relative peak areas and the absence of splitting.

[3]



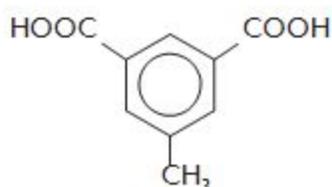
(ii) The presence of three methyl groups makes mesitylene a reactive compound. Mesitylene is oxidised by dilute nitric acid to give 3,5-dimethylbenzenecarboxylic acid.



Describe how you would purify a sample of this acid by recrystallisation. The acid is fairly soluble in hot water but nearly insoluble in cold water.

[4]

(iii) Further oxidation of mesitylene gives 5-methylbenzene-1,3-dicarboxylic acid.

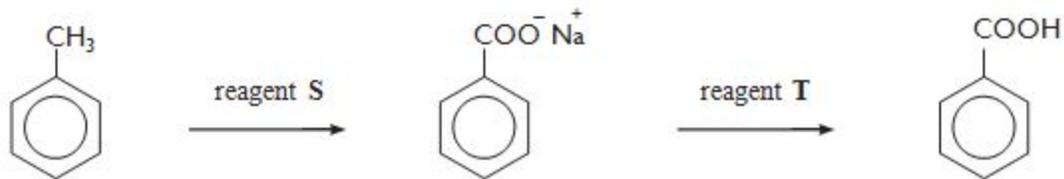


By analogy with the preparation of PET from benzene-1,4-dioic acid and ethane-1,2-diol, give the repeating unit of the polyester formed from 5-methylbenzene-1,3-dicarboxylic acid and ethane-1,2-diol.

[1]

(iv) The oxidation of methylbenzene to benzenecarboxylic acid needs stronger oxidising conditions than are required for the oxidation of mesitylene. State the reagents **S** and **T** necessary for this reaction.

[2]



(Total 20)

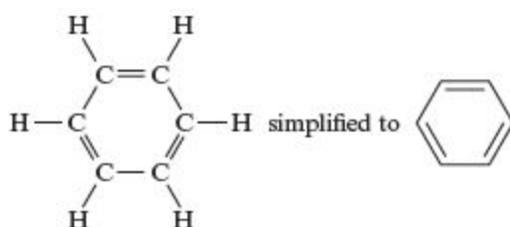
3.

Read the passage below and then answer the questions in the spaces provided.

Benzene

Benzene, C₆H₆, is a colourless, highly flammable liquid with a sweet smell, but it is carcinogenic. The word "benzene" derives historically from "gum benzoin", an aromatic resin known to European pharmacists and perfumers since the 15th century.

5 Discovering the structure of benzene proved to be quite difficult. Benzene was first isolated and identified by Michael Faraday in 1825 from the oily residue derived from the production of illuminating gas. However, it was not until 1865 that Kekulé proposed this structure for benzene.



10 However this structure fails to explain why benzene does not react like an alkene. Ethene reacts readily with bromine as follows:

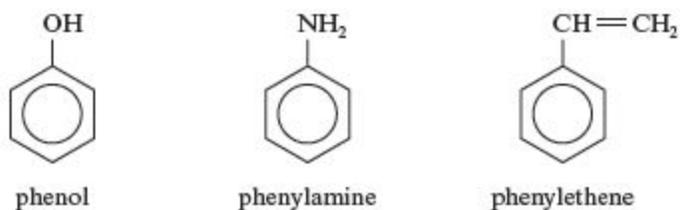


In contrast, benzene needs far more stringent conditions to react with bromine.

15 It was around 1930 that the structure of the benzene ring was finally confirmed using X-ray diffraction. It was shown that all the carbon-carbon bonds were of the same length. To account for this, it was proposed that three pairs of electrons were not localised in particular double bonds, but were shared equally amongst all six carbons. These electrons were said to be delocalised giving benzene great stability (delocalisation energy of benzene). The structure of benzene is therefore usually represented as:

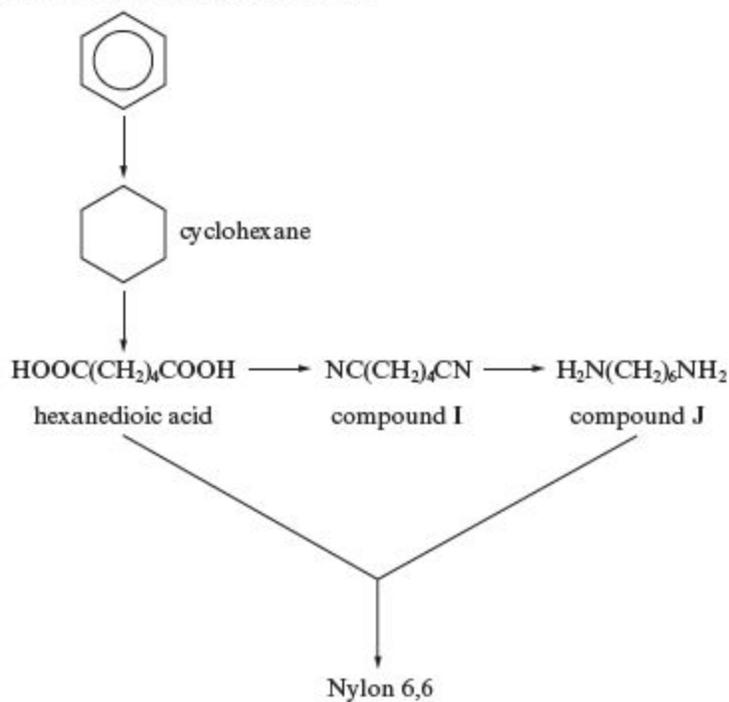


20 An understanding of the structure of benzene was crucial to early chemists since benzene is the parent molecule of all arene or 'aromatic' compounds and a huge variety of compounds are derived from benzene. Simple benzene derivatives include:



25 In the 19th and early 20th centuries, benzene was used as an after-shave lotion because of its pleasant smell, but today benzene is used to make other chemicals.

One of its most widely-produced derivatives is cyclohexane, which is used in the manufacture of Nylon 6,6 as shown in the scheme below:



– End of passage –

(a) Benzene reacts with bromine (*line 12*) in the presence of an iron(III) bromide catalyst to form bromobenzene.

(i) Classify the reaction mechanism.

[1]

(ii) Draw the mechanism for this reaction.

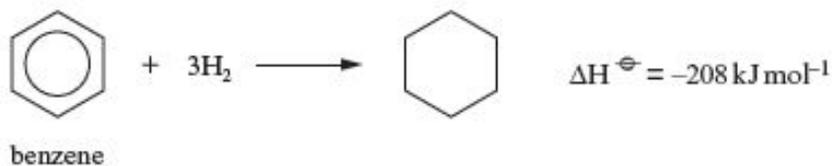
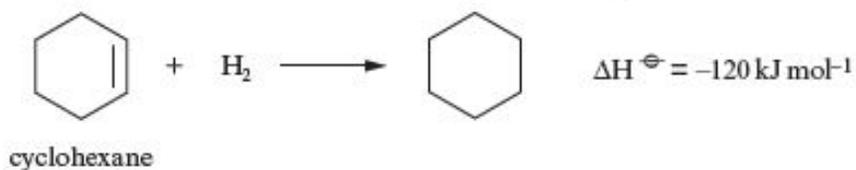
(The mechanism is similar to that for the chlorination of benzene.)

[3]

(b) (i) Explain what is meant by the *delocalisation energy* of benzene (*line 17*)

[1]

(ii) Given that the enthalpy change of hydrogenation of cyclohexene is -120 kJ mol^{-1} and that the enthalpy change of hydrogenation of benzene is -208 kJ mol^{-1} , calculate the delocalisation energy of benzene. [2]



.....
.....
.....

$\Delta H^{\ominus} = \dots\dots\dots \text{ kJ mol}^{-1}$

(c) Use the information in the passage to give a reason why benzene is no longer used in after-shave lotion.

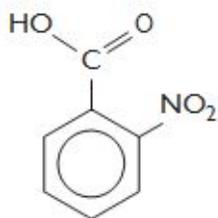
[1]

(Total 6)

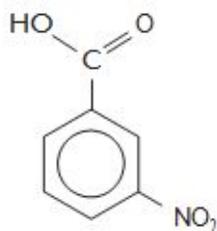
4.

(a) Nitrobenzenecarboxylic acids (*nitrobenzoic acids*) are useful starting materials in the preparation of many dyes and can be prepared by nitration of benzenecarboxylic acid (*benzoic acid*), C_6H_5COOH .

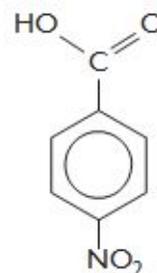
Many nitrobenzoic acids exist including those shown below:



2-nitrobenzoic acid



3-nitrobenzoic acid



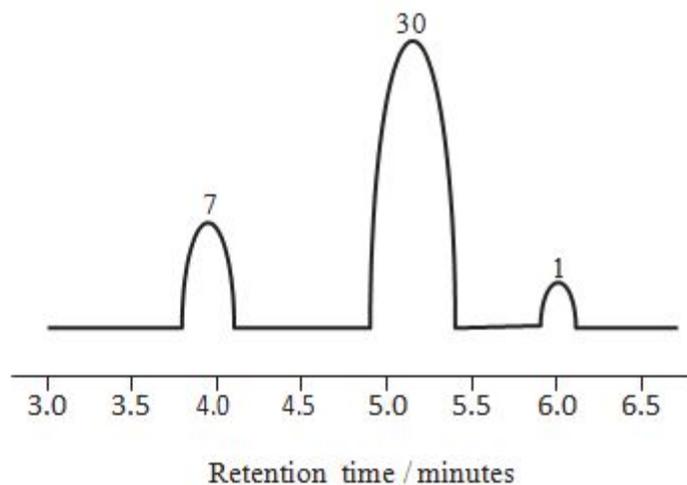
4-nitrobenzoic acid

(i) Benzenecarboxylic acid can be nitrated under similar conditions to the nitration of benzene.

Give the reagent(s) and condition(s) required and classify the mechanism of this reaction.

3

(ii) Nitration of benzenecarboxylic acid gives a mixture of products. These can be identified by gas chromatography followed by mass spectrometry (*GC-MS*). The gas chromatograph for the products of this reaction is shown below, with the relative areas of each peak indicated.



I. The main isomer produced is 3-nitrobenzenecarboxylic acid. Calculate the percentage of this isomer produced.

[2]

II. The mass spectrum of 3-nitrobenzenecarboxylic acid has main peaks at m/z 45, 46, 122 and 167. Suggest which species are responsible for **each** of these peaks.

[2]

(iii) An impure sample of 3-nitrobenzenecarboxylic acid was obtained.

I. State how the melting temperature of the impure sample of 3-nitrobenzenecarboxylic acid would differ from that of pure 3-nitrobenzenecarboxylic acid, if at all.

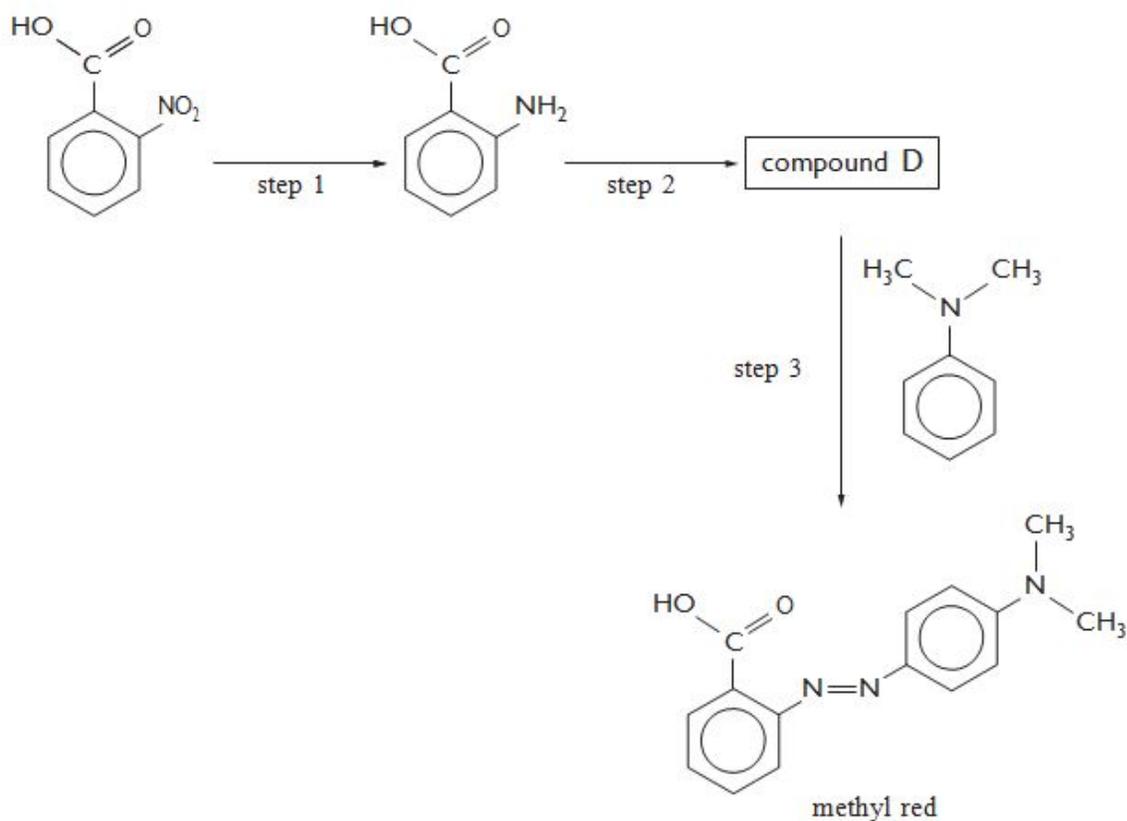
[1]

II. 3-nitrobenzenecarboxylic acid was found to be soluble in boiling water but not in cold water. It has a melting temperature of 142 °C.

Describe how impure 3-nitrobenzenecarboxylic acid could be purified by recrystallisation. Include full experimental details.

[4] QWC [1]

(b) 2-nitrobenzenecarboxylic acid may be used as a starting material for the production of the indicator methyl red. A reaction scheme for this process is given below.



(i) Give the reagent(s) necessary for step 1. [1]

(ii) Step 2 uses a mixture of sodium nitrate(III), NaNO_2 , with dilute hydrochloric acid. Give the conditions required for this reaction and the structure of the product, compound D. [2]

(iii) Methyl red is red below pH 4. Explain the origin of this colour. [2]

(c) Methyl red is used to differentiate between acids and bases. Explain why amines such as ethylamine are bases.

[2]

(Total 20)

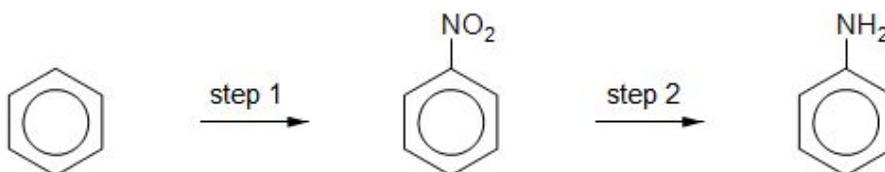
5. This question focuses on molecules that contain the —NH_2 group.

(a) Phenylamine and propylamine are both bases, with phenylamine being a weaker base than propylamine.

(i) Explain why both propylamine and phenylamine can act as bases. [2]

(ii) Give a reason why phenylamine is a weaker base than propylamine. [2]

(iii) Phenylamine can be prepared from benzene in a two-step process.



I. Step 1 uses a mixture of concentrated nitric and sulfuric acids to produce NO_2^+ during the reaction. Draw the mechanism of the reaction between NO_2^+ and benzene. [3]

II. During step 1, some dinitrobenzene is produced. Suggest a method of separating the different compounds in the product mixture. [1]

III. Give the reagent(s) required to produce phenylamine from nitrobenzene in step 2. [2]

(Total 10)

6. (a) Complete the gaps in the following sentences choosing from the words:

[3]

Blue Yellow Higher Lower

Each word can be used once, more than once or not at all.

Benzene is a colourless compound that absorbs energy in the ultraviolet region of the electromagnetic spectrum.

Nitrobenzene is a yellow compound that absorbs energy in the region of the visible spectrum.

The absorption of energy for benzene occurs at a energy and at

a frequency than for nitrobenzene.

(b)Methylbenzene can be produced from benzene using a Friedel-Crafts reaction.

(i) Give an equation for this reaction.

[1]

(ii) State the role of the catalyst used in this reaction, apart from increasing the rate.

[1]

(c) The Friedel-Crafts reaction can also be used to introduce more than one methyl group to the benzene ring giving, for example, 1,4-dimethylbenzene.



The low resolution proton NMR spectrum of this compound shows two peaks with a peak area ratio of 3:2.

Explain how 1,4-dimethylbenzene produces this spectrum.

[2]

- (d) 1,4-Dimethylbenzene reacts with chlorine in a free radical reaction to give the liquid 1,4-di(chloromethyl)benzene.



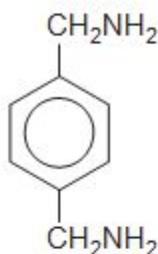
- (i) State the names of **two** methods that could be used to show that a sample of this compound is pure. [2]

Method 1

Method 2

- (ii) Give the displayed formula of the compound produced when 1,4-di(chloromethyl)benzene reacts with an excess of aqueous sodium hydroxide. [1]

- (e) (i) 1,4-Di(chloromethyl)benzene reacts with ammonia to give the diamine below.



Draw the repeating section of the polymer obtained when this diamine reacts with benzene-1,4-dicarboxylic acid. [1]

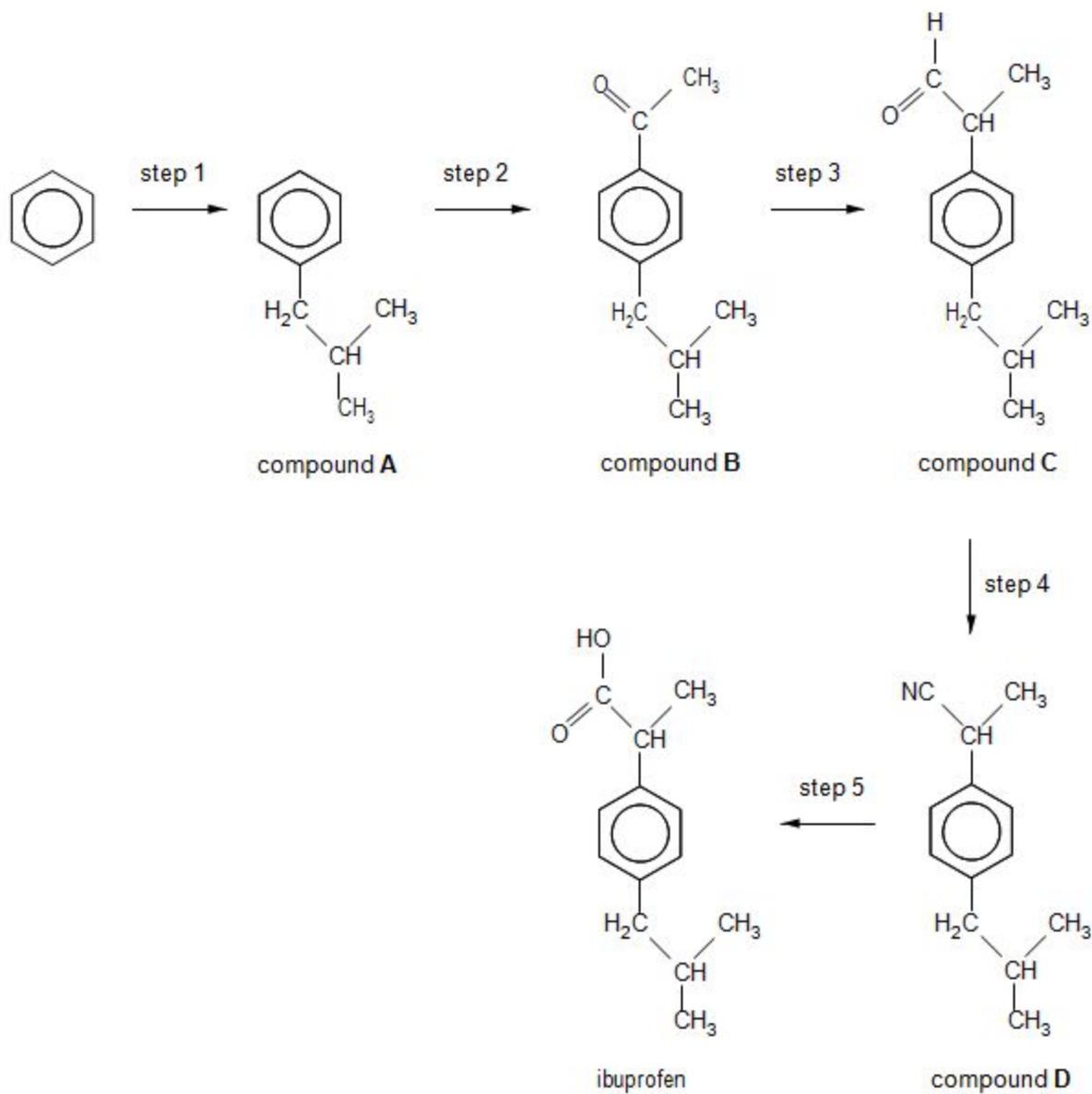
- (ii) The polymer obtained in (e)(i) above contains a peptide linkage.

State the name of a naturally occurring material that also contains a peptide linkage. [1]

7.

Ibuprofen is a common drug taken as an analgesic and anti-inflammatory treatment.

A possible route to the synthesis of ibuprofen is shown below.



(a) Step 1 is a Friedel-Crafts alkylation reaction. Give the reagent(s) and condition(s) required for this step.

[3]

(b) Compounds **B** and **C** can be analysed using chemical tests.

(i) Give a chemical test that would give a positive result for **both** compound **B** and compound **C**. Include reagent(s) and the observation(s) expected for a positive result.

[2]

(ii) Give a chemical test that would give a positive result for compound **C** but **not** for compound **B**. Include reagent(s) and the observation(s) for both compounds.

[2]

(c) Compound **C** shows optical isomerism. Discuss this statement. Your answer should include:

- What is meant by optical isomerism.
- What feature of compound **C** allows it to exhibit optical isomerism.
- Diagrams to show the two optical isomers of compound **C**.
- How the two optical isomers of compound **C** can be distinguished.

[4] QWC [1]

(d) Give the reagent(s) and condition(s) required for step 5 and classify the reaction that occurs.

[3]

(e) A student investigating alternative methods of producing ibuprofen suggests that it would be better to convert compound **C** into ibuprofen in a one-step process. Discuss whether this is correct.

Your answer should include:

- The reagent(s) and condition(s) for a reaction expected to convert compound **C** directly into ibuprofen.
- Why it is generally better to use one step rather than two or more steps when producing a desired compound.
- A suggestion of why a two-step process is chosen for the synthesis of ibuprofen from compound **C** rather than a one-step process.

[4] QWC [1]

(Total 20)