WJEC EDUQAS A-LEVEL CHEMISTRY · COMPONENT 2

CHEMISTRY



EXAM QUESTION PACK

OA1.2 AROMATICITY

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/95	%

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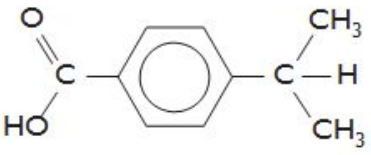
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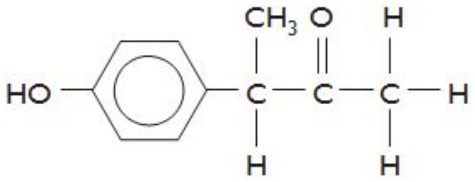
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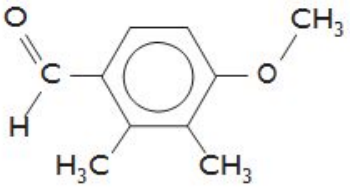
1. This question focuses on the chemistry of some of the many compounds which share the molecular formula $C_{10}H_{12}O_2$. Four compounds with this formula are shown below.



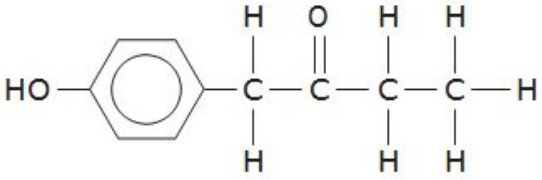
compound **W**



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_2CO_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.



compound **W** benzene-1,4-dioic acid *(terephthalic 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

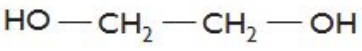
I. Give **two** differences between condensation polymerisation and addition polymerisation.

[2]

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

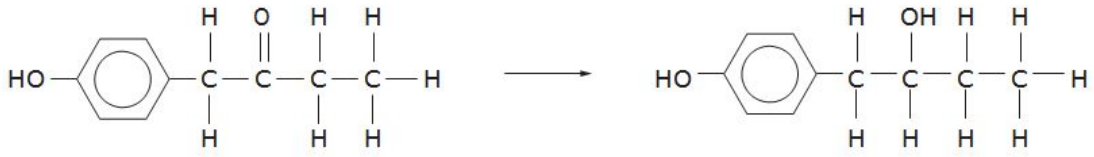


benzene-1,4-dioic acid
(terephthalic acid)



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 .....

(ii) Compound **V** will react with ethanoyl chloride. Give the structure of a carbon-containing product of this reaction.

[1]

(iii) Compound **V** is insoluble in cold water, but reacts with sodium hydroxide solution and then dissolves.Give the structure of the carbon-containing species present in the resulting solution.

[1]

(Total 19)

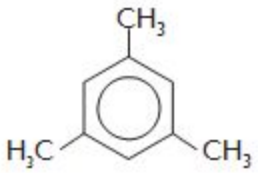
2. (a) Describe the structure and bonding in benzene and explain why it is susceptible to electrophilic substitution reactions.

[6] QWC [2]

(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.

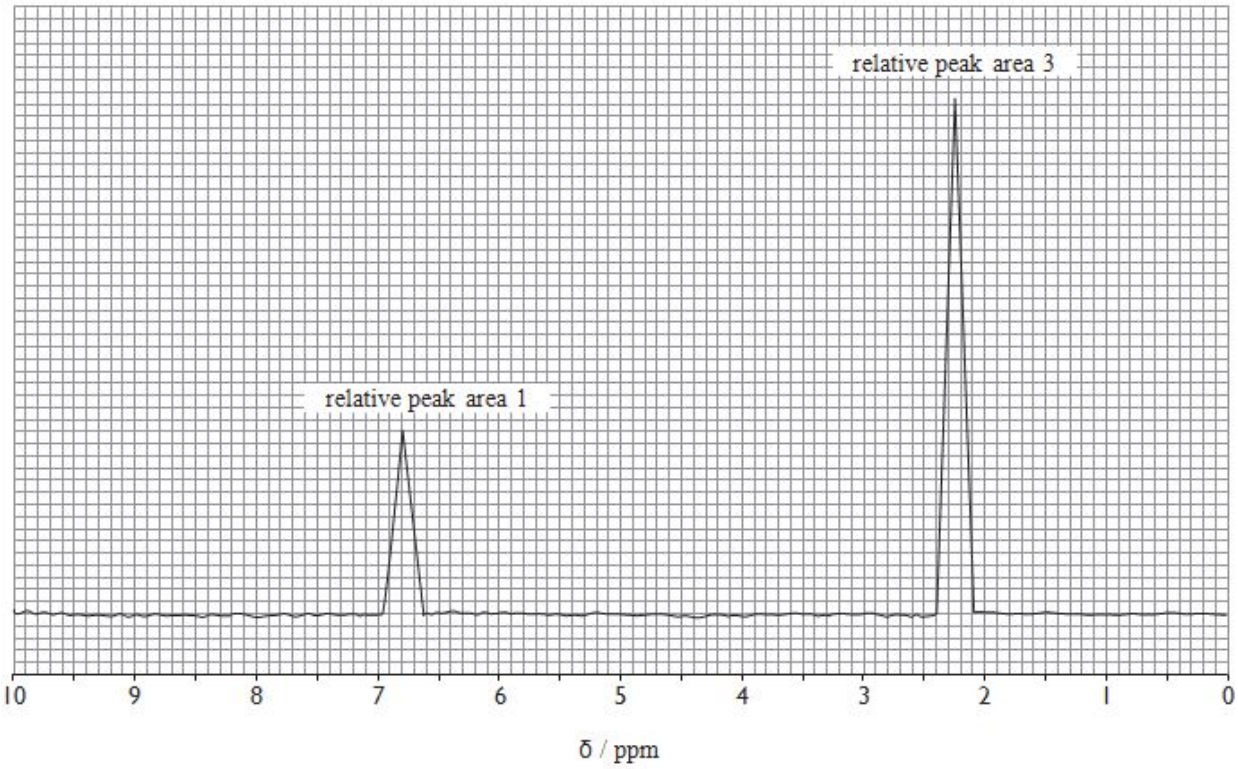
[2]

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

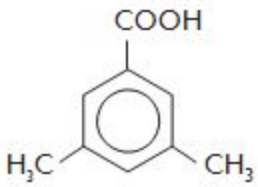


(i) The NMR spectrum of mesitylene is shown opposite.Use the chemical formula to help you explain the peaks in this spectrum, including the relative peak areas and the absence of splitting.

[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.

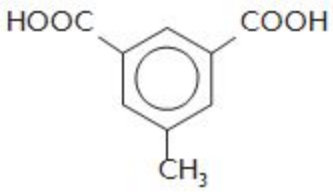


melting temperature 172 °C

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.

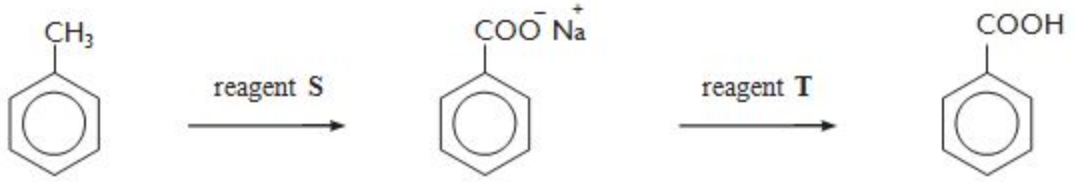


By analogy with the preparation of PET from benzene-1,4-dioic acid and ethane-1,2-diol, give the repeating unit of the polyester formed from 5-methylbenzene-1,3-dicarboxylic acid and ethane-1,2-diol.

[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)

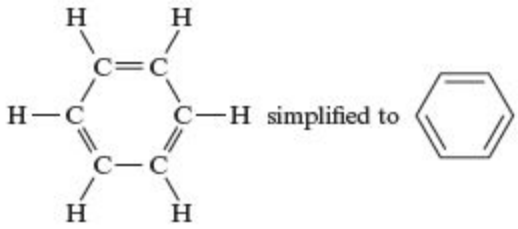
3.

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

Benzene

Benzene, C_6H_6, 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.

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.



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

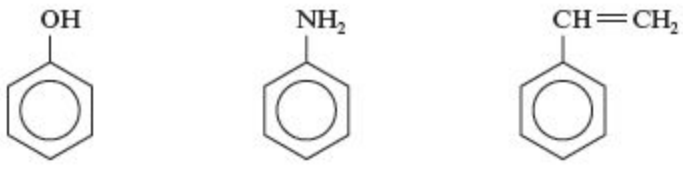
$$CH_2{=}CH_2 + Br_2 \longrightarrow CH_2Br\,CH_2Br$$

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

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:



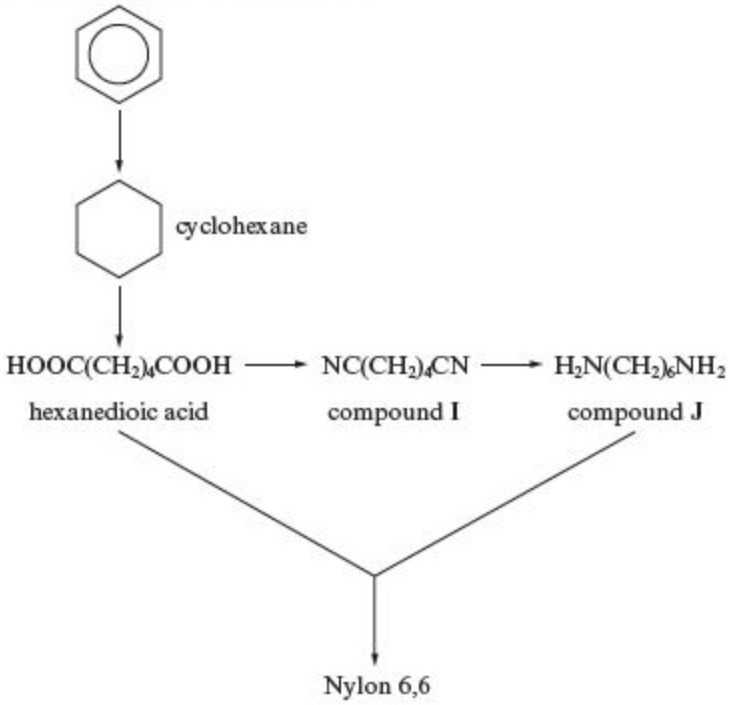
An understanding of the structure of benzene was crucial to early chemists since benzene is the parent molecule of all arene or 'aromatic' compounds and a huge variety of compounds are derived from benzene. Simple benzene derivatives include:



phenol phenylamine phenylethene

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.

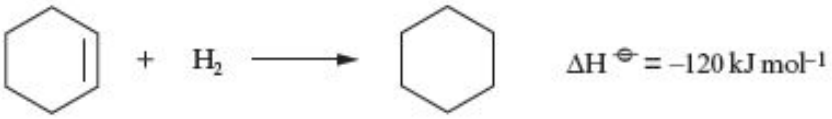
(The mechanism is similar to that for the chlorination of benzene.)

[3]

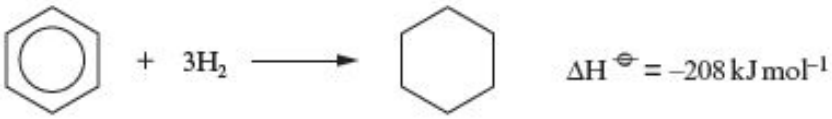
(b) (i) Explain what is meant by the *delocalisation energy* of benzene *(line 17)*

[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]



cyclohexane



benzene

.....

.....

.....

$\Delta H^{\ominus}$ = ... $kJ\,mol^{-1}$

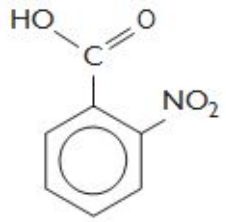
(c) Use the information in the passage to give a reason why benzene is no longer used in after-shave lotion.

[1]

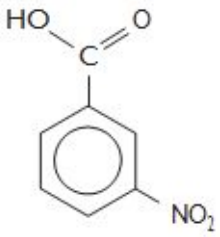
(Total 6)

4.

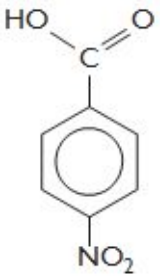
(a) Nitrobenzenecarboxylic acids *(nitrobenzoic acids)* are useful starting materials in the preparation of many dyes and can be prepared by nitration of benzenecarboxylic acid *(benzoic acid)*, C_6H_5COOH.
Many nitrobenzoic acids exist including those shown below:



2-nitrobenzoic acid



3-nitrobenzoic acid



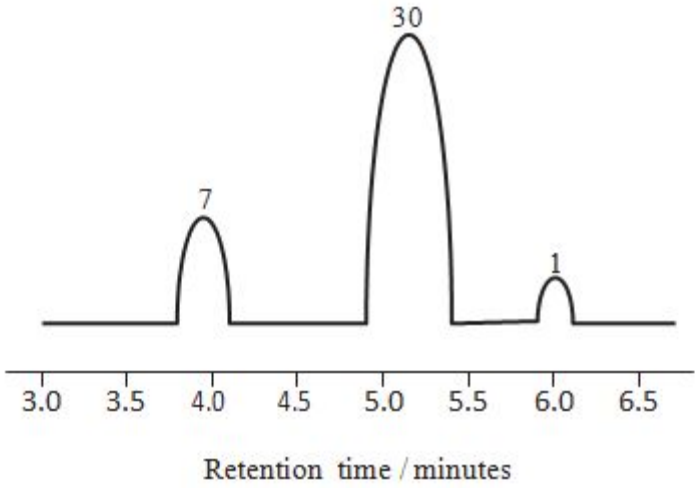
4-nitrobenzoic acid

(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.

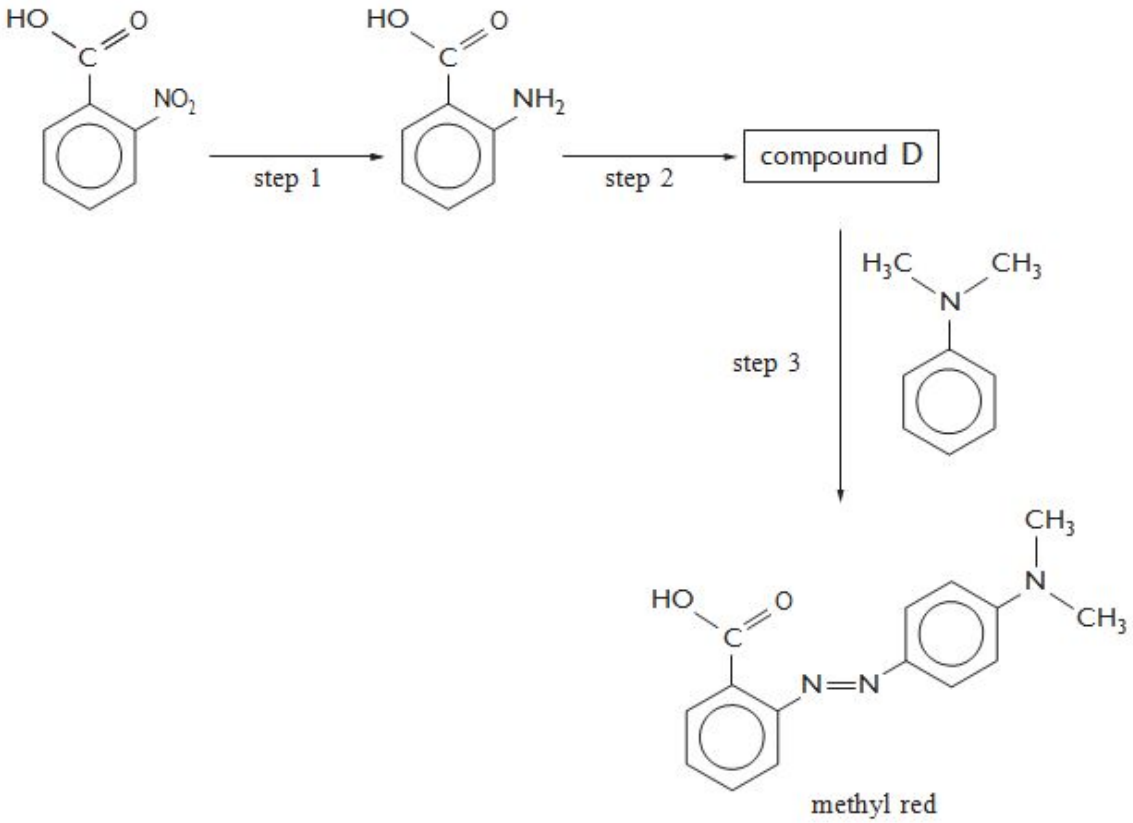
[1]

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.



methyl red

(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)

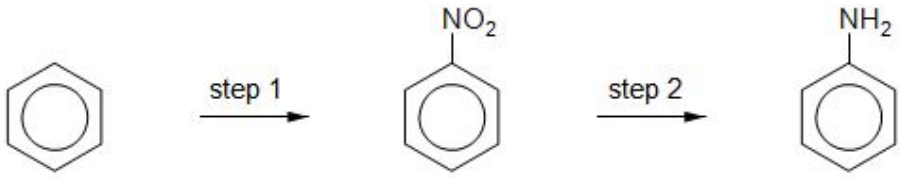
5. This question focuses on molecules that contain the $—NH_2$ group.

(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]

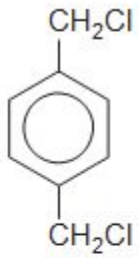
(c) The Friedel-Crafts reaction can also be used to introduce more than one methyl group to the benzene ring giving, for example, 1,4-dimethylbenzene.



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.



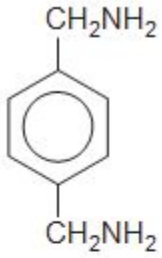
(i) State the names of **two** methods that could be used to show that a sample of this compound is pure. [2]

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]

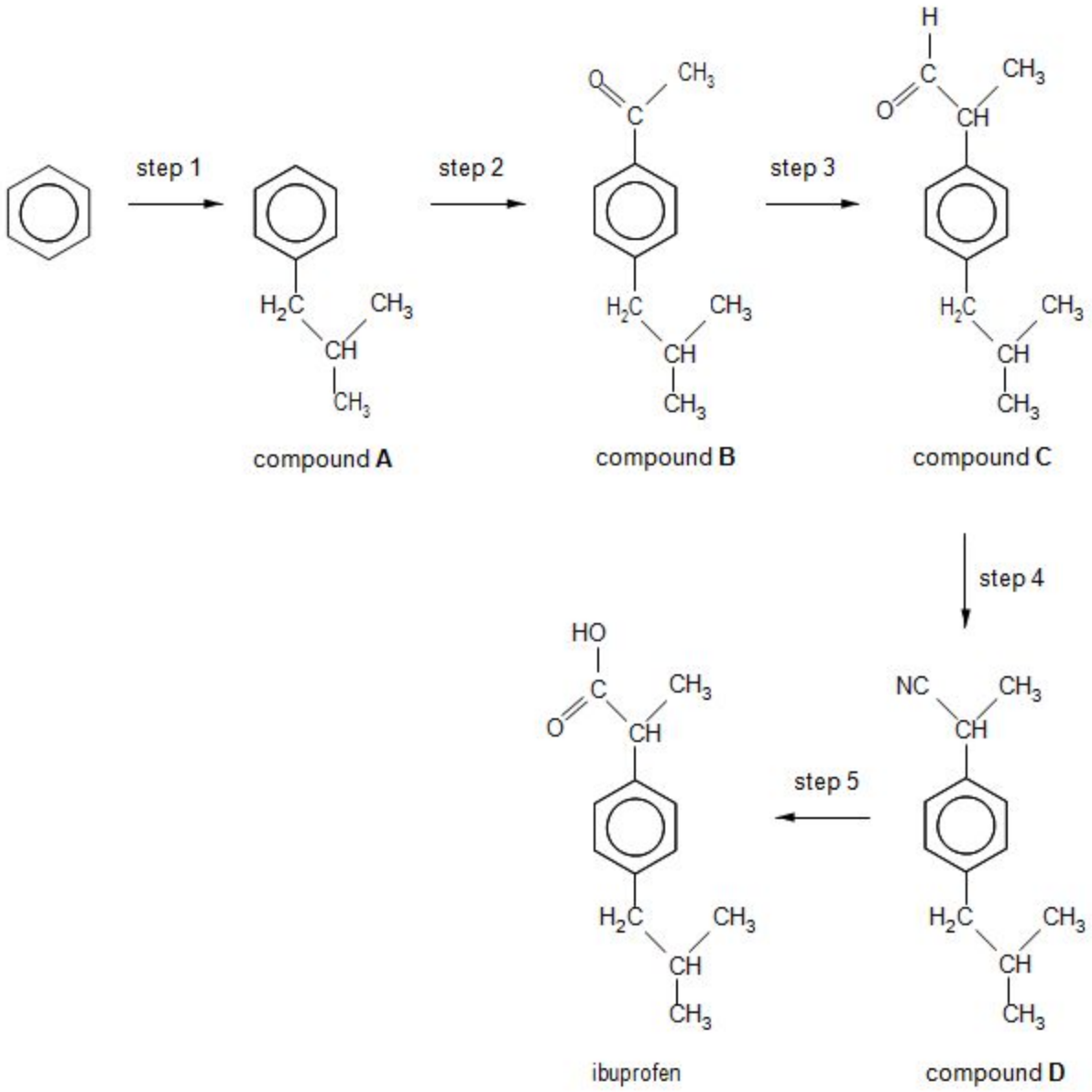
(ii) The polymer obtained in *(e)*(i) above contains a peptide linkage.

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]

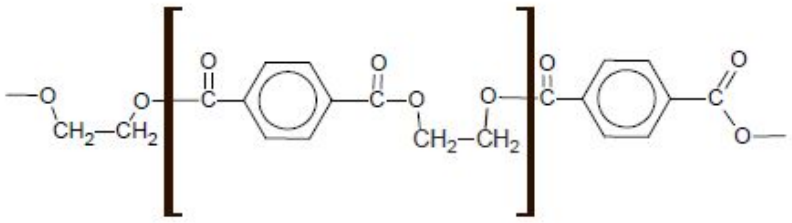
(Total 20)

(d) (i) Heat / Alkaline / Potassium manganate(VII) / then acidify
(1 mark for Potassium manganate + 1 other point; 2 marks for all) [2]

(ii) I. Addition polymer – One large molecule formed only / Condensation polymer – one large molecule with small molecules (e.g. water) lost. (1)

Addition polymer – one starting material / Condensation – two starting materials
OR Addition polymer – one functional group in each molecule/ Condensation polymer – two functional groups in each molecule (1) [2]

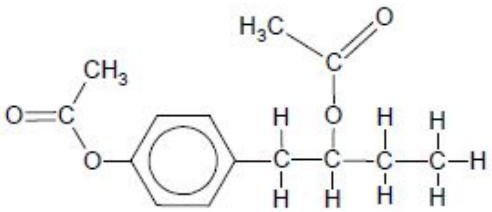
II.



[1]

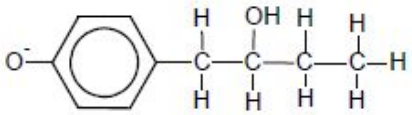
(e) (i) $NaBH_4$ / $LiAlH_4$ or name(1) Reduction (1) [2]
- ignore conditions unless $LiACH_4$ in water
- do not accept 'redox'

(ii)



Accept structures with only one –OH group reacted. [1]

(iii) [1]



[19 marks]

2 (a) Benzene is a compound whose molecules contain six carbon atoms bonded in a (hexagonal) ring (1)
All the carbon to carbon bond lengths are equal / intermediate (1)
Each carbon atom is bonded to two other carbon atoms and a hydrogen atom (1)
by σ-bonds (1)
All the C – $\hat{C}$ – C angles are the same / 120° (1)
The remaining p electron of each carbon atom / overlap of p orbitals forms a delocalised cloud of electrons / π-system (1) above and below the plane (1)
Credit can be gained from labelled diagram
[*Candidates can gain a maximum of (4) for this part*]

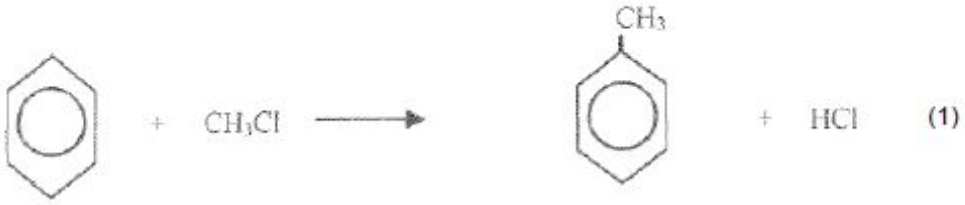
This delocalisation increases the **stability** (1) of the molecule and this stability is maintained by benzene undergoing substitution reactions in preference to addition reactions (that would destroy the delocalised system)
The π-cloud is **electron rich** and will be attracted to electron deficient electrophiles (1)
[*Candidates can gain (2) for this part*]

[6]

QWC *Selection of a form and style of writing appropriate to purpose and to complexity of subject matter* (1)

Legibility of text; accuracy of spelling, punctuation and grammar; clarity of meaning. (1) *QWC* **[2]**

(b)



(1)

catalyst eg $AlCl_3$ (anhydrous) (1) **[2]**

(c) (i) (There are two environments for the protons), the 3 aromatic protons at ~6.8 δ and the 9 methyl / aliphatic protons at ~ 2.3 δ (1)
These give a peak area of 3:9, ie.1:3 (1)
These environments are separate / discrete (1) therefore no splitting pattern

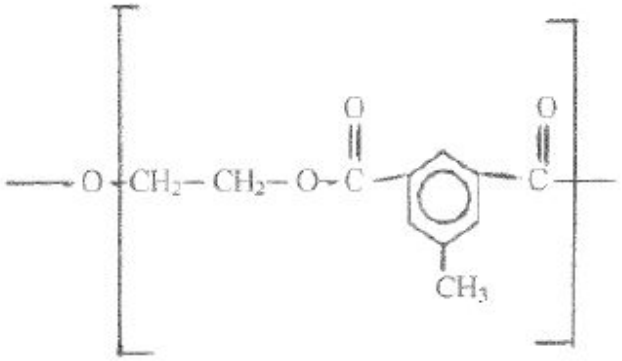
[3]

(ii) Dissolve in the minimum volume (1)
Of hot water (1)
(Filter hot) (1)
Cool (1)
Filter (1)
Dry (1)

(*up to 4 max but candidates must give the first two points in order to gain full credit*)

[4]

(iii)



[1]

(iv) Reagent **S** is alkaline potassium manganate(VII) (1)

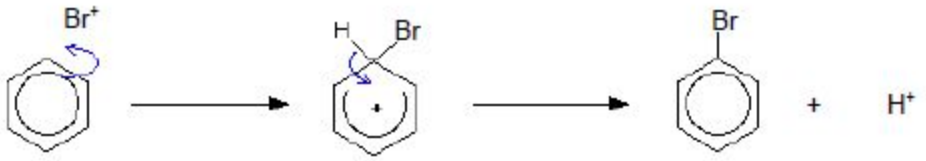
Reagent T is eg hydrochloric acid (1)

[2]

Total [20]

3 (a) (i) Electrophilic substitution [1]

(ii) $Br_2 + FeBr_3 \longrightarrow Br^+ + FeBr_4^-$



Formation of Br^+ (1), curly arrows (1), intermediate (1) [3]

(b) (i) The extra stability in the benzene molecule due to electron delocalisation / the difference in energy between the experimental ΔH^θ reaction for benzene and the ΔH^θ reaction according to the Kekulé structure [1]

(ii) If benzene had 3 double bonds enthalpy change would be $3 \times -120 = -360$ kJ mol^{-1} (1)

Delocalisation energy is difference between -360 and $-208 = 152$ kJ mol^{-1} (1) [2]

(c) Benzene is carcinogenic / toxic [1]

4 (a) (i) (Concentrated) nitric acid / (concentrated) sulfuric acid / Temperature of 40-80°C
(Any 2 = 1 mark; All 3 = 2 marks)
Electrophilic substitution (1) [3]

(ii) I. Peak area is proportional to amount of substance (1)
Percentage = (30 / 38) x 100 = 79% (1)
(Can obtain both marks from correct percentage) [2]

II. 45 = $COOH^+$, 46= NO_2^+, 122 = $C_6H_4NO_2^+$ and 167 = $C_7H_5NO_4^+$.
(Any 2 = 1 mark; All 4 = 2 marks) [2]

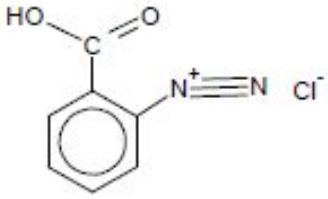
(iii) I. Lower melting point / melts over a range [1]
II. 1 mark for each point.
- Dissolve in the minimum volume
- Of hot water
- Filter hot
- Allow to cool
- Filter
- Dry residue under suction / in oven below 142°C

Max 4 marks [4]

QWC: legibility of text, accuracy of spelling, punctuation and grammar, clarity of meaning.[1]

(b) (i) Tin and concentrated hydrochloric acid [1]

(ii) Below 10°C (1)



(1) [2]

(iii) N=N double bond is chromophore (1)
Compound absorbs blue /green / complementary colours to red / all colours but red (1)
Remaining frequencies are transmitted, giving the red colour seen. (1)
Any 2 out of 3 [2]

(c) Nitrogen has a lone pair (1) which can accept a proton (1) [2]

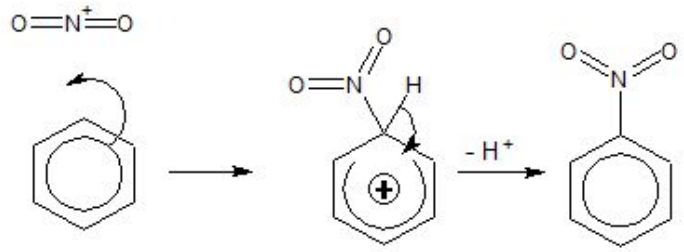
[20 marks]

5 (a) (i) Both molecules have lone pairs on nitrogen (1)

The lone pairs can form (coordinate) bonds with H^+ ions (1) [2]

(ii) Lone pair on N in phenylamine is delocalised over benzene ring (1) therefore less able to accept H^+ (1) [2]

(iii) I Arrow in first step (1)
Cation structure in second step (1)
Arrow in second step (1)



[3]

II (fractional) distillation / steam distillation [1]

III Sn and conc. HCl (1) followed by NaOH (1) [2]

6 (a) ……blue …… (1) ……higher (1) ……higher (1) [3]

(b) (i)



[1]

accept C_6H_5 in place of the ring accept equations that show the catalyst

(ii) It acts as a halogen carrier / it helps produce the electrophile/CH_3^+ / increases polarity of the halogenoalkane [1]

(c) There are 6 methyl protons and 4 aromatic protons, hence a ratio of 3:2 (1)
All the methyl protons are equivalent as are all the aromatic protons (1) [2]

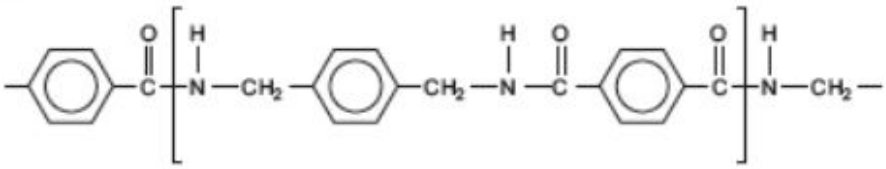
(d) (i) Any 2 from NMR / HPLC / GC / refractive index / mass spectra / boiling temperature [2]

(ii)



[1]

(e) (i)



[1]

(ii) protein / dipeptide / polypeptide [1]

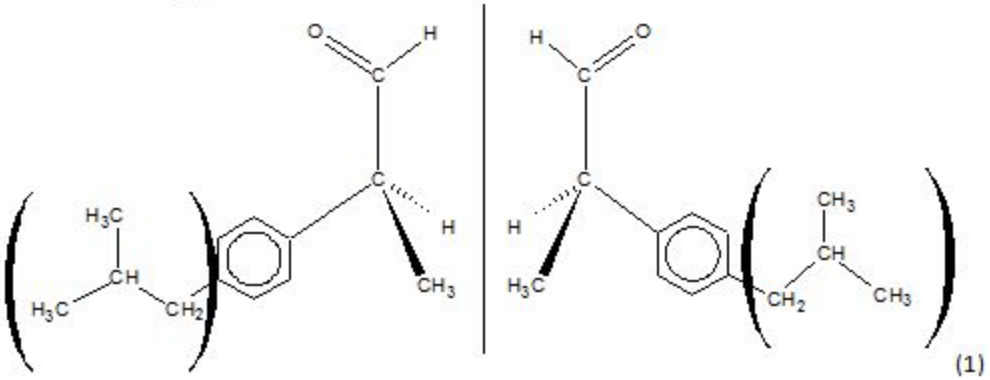
Total [12]

7 (a) $CH_3CH(CH_3)CH_2Cl$ (1) $AlCl_3$ / $FeCl_3$ (1) Room temperature / in the dark (1) [3]

(b) (i) 2,4-DNP (1) Orange precipitate (1) [2]

(ii) Tollen's reagent (1) Silver mirror with **C**, no reaction with **B** (1) [2]

(c) Optical isomerism is where a molecule and its mirror image are different / non-superimposable (1)
Compound **C** has a chiral centre / 4 different groups attached to one carbon atom (1)



(1)

The two isomers rotate the plane of polarised light in opposite directions (1) [4]

QWC: organisation of information clearly and coherently; use of specialist vocabulary where appropriate (1) [1]

(d) Dilute acid (1) heat (1) hydrolysis (1) [3]

(e) Acidified potassium dichromate (VI) (1) / heat (1)

One step reactions are generally better as they have a better yield / there is waste in each stage (1)

Two step process may be cheaper / use more sustainable reagents/ may give a better yield in this case / produce less harmful waste materials / potassium dichromate may react with other parts of the molecule as well / may be easier to separate product (1)

Do not credit same idea twice e.g. if 'better yield' gains first mark, a different point is required to gain second mark [4]

QWC: selection of a form and style of writing appropriate to purpose and to complexity of subject matter [1]

Total [20]