1 Hydrogen cyanide, HCN, reacts with propanal, CH_3CH_2CHO, in the presence of potassium cyanide, KCN.

(a) The mechanism for this reaction is

(1)

☒ **A** nucleophilic addition.

☒ **B** nucleophilic substitution.

☒ **C** electrophilic addition.

☒ **D** electrophilic substitution.

(b) The first stage of the mechanism of this reaction is

(1)

☒ **A** the lone pair of electrons on carbon in CN^- attacking $C^{\delta+}$ of propanal.

☒ **B** the lone pair of electrons on nitrogen in CN^- attacking $C^{\delta+}$ of propanal.

☒ **C** the lone pair of electrons on oxygen in propanal attacking $C^{\delta+}$ of HCN.

☒ **D** the lone pair of electrons on oxygen in propanal attacking $H^{\delta+}$ in HCN.

(c) The product of the reaction is

(1)

☒ **A** 1-hydroxypropanenitrile.

☒ **B** 2-hydroxypropanenitrile.

☒ **C** 1-hydroxybutanenitrile.

☒ **D** 2-hydroxybutanenitrile.

(Total for Question 1 = 3 marks)

---

2 Which of the following does not have hydrogen bonding in a pure sample, but forms hydrogen bonds with water when it dissolves?

☒ **A** Propane

☒ **B** Propanal

☒ **C** Propanol

☒ **D** Propanoic acid

(Total for Question 2 = 1 mark)

3 Which of the following has both optical and E-Z isomers?

☒ **A** $ClCH_2CHClCH{=}CH_2$

☒ **B** $CH_2{=}CClCH_2CH_2Cl$

☒ **C** $ClCH_2CH{=}CHCH_2Cl$

☒ **D** $CHCl{=}CHCHClCH_3$

(Total for Question = 1 mark)

---

4 One optically active isomer of 2-chlorobutane reacts with hydroxide ions to form butan-2-ol.

$$C_2H_5CHClCH_3 + OH^- \rightarrow C_2H_5CH(OH)CH_3 + Cl^-$$

The organic product is a **mixture** of enantiomers because

☒ **A** butan-2-ol contains a chiral carbon atom.

☒ **B** the reaction is a nucleophilic substitution.

☒ **C** 2-chlorobutane forms a carbocation intermediate.

☒ **D** 2-chlorobutane forms a five-bonded transition state.

(Total for Question = 1 mark)

---

5 The organic product of the reaction between ethanoyl chloride and methylamine has the formula

☒ **A** $CH_3NHCH_2C(=O)Cl$

☒ **B** $CH_3CH(NH_2)C(=O)Cl$

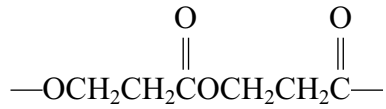
☒ **C** $CH_3C(=O)NH_2$

☒ **D** $CH_3C(=O)NHCH_3$

(Total for Question = 1 mark)

---

6 A section of a polymer is shown below. Which of the following monomers would form this polymer?



☒ **A** $HOCH_2CH_2OH$ and $ClCOCH_2CH_2COCl$

☒ **B** $HOCH_2CH_2OH$ and $HOOCCH_2CH_2COOH$

☒ **C** $ClCH_2CH_2COCl$ alone

☒ **D** $HOCH_2CH_2COOH$ alone

(Total for Question = 1 mark)

7 The compounds below were heated with aqueous sodium hydroxide solution. Which one of them did **not** give sodium ethanoate, CH_3COONa, as one of the products?

☒ **A** CH_3COOCH_3

☒ **B** CH_3COCH_3

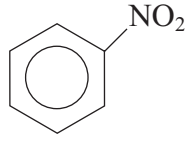
☒ **C** CH_3COOH

☒ **D** CH_3COCl

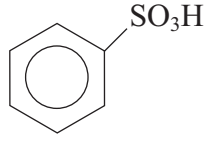
(Total for Question = 1 mark)

8 Which of the following products is formed when phenylamine (aniline) is reacted with **dilute** sulfuric acid?

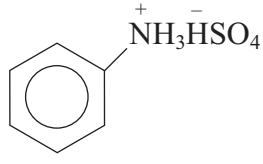
☒ **A**



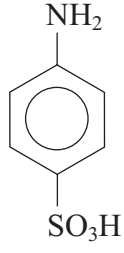
☒ **B**



☒ **C**



☒ **D**



(Total for Question = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

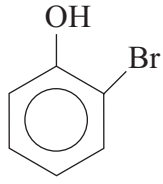
9 For the nitration of phenol, which is the most suitable set of conditions and the reason for its use?

		Conditions	Reactivity of phenol to electrophiles compared with benzene
☒	**A**	dilute nitric acid at room temperature	more reactive
☒	**B**	concentrated nitric and sulfuric acid at room temperature	more reactive
☒	**C**	concentrated nitric and sulfuric acid at 55 °C	the same
☒	**D**	dilute nitric acid and dilute sulfuric acid at room temperature	less reactive

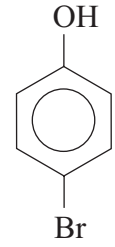
(Total for Question = 1 mark)

10 Phenol reacts with excess bromine water to give as the organic product(s)

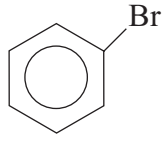
☒ **A**



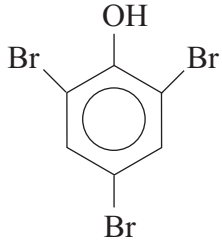
and



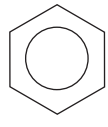
☒ **B**



☒ **C**



☒ **D**



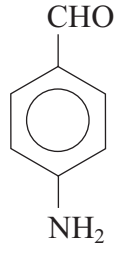
(Total for Question = 1 mark)

11 An organic compound, **X**, shows the following properties:

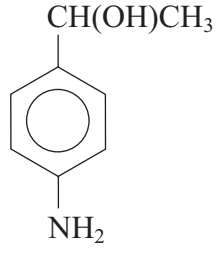
- Oxidation of compound **X** produces a substance that reacts with 2,4-dinitrophenylhydrazine to give a yellow precipitate but does **not** react with Fehling's or Benedict's solution.
- Compound **X** reacts with ice-cold nitrous acid to form a compound that gives a yellow precipitate with an alkaline solution of phenol.

What is the formula of compound **X**?

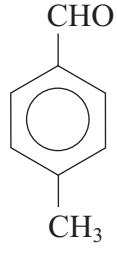
☒ **A**



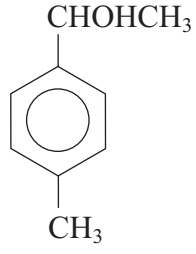
☒ **B**



☒ **C**



☒ **D**



(Total for Question = 1 mark)

12 Which sequence shows the bases in order of decreasing strength?

☒ **A** $C_6H_5NH_2 > CH_3NH_2 > NH_3$

☒ **B** $NH_3 > CH_3NH_2 > C_6H_5NH_2$

☒ **C** $CH_3NH_2 > NH_3 > C_6H_5NH_2$

☒ **D** $NH_3 > C_6H_5NH_2 > CH_3NH_2$

(Total for Question = 1 mark)

---

13 Bromoethane can be made by heating ethanol under reflux with 50% sulfuric acid and sodium bromide. When the mixture is distilled, the products include sulfur dioxide, bromine, hydrogen bromide and water as well as bromoethane.

The product mixture is shaken with sodium carbonate solution and later with anhydrous sodium sulfate before being re-distilled. Which of the following shows the correct list of impurities removed at each step?

		Aqueous sodium carbonate wash	Addition of sodium sulfate
☒	**A**	HBr	SO_2, Br_2, water
☒	**B**	SO_2, Br_2	HBr, water
☒	**C**	SO_2, HBr	Br_2, water
☒	**D**	SO_2, Br_2, HBr	water

(Total for Question = 1 mark)

---

14 A compound is known to have either the structure $H_2NCH_2CH_2NH_2$ or H_2NCH_2COOH. Which of the following tests would best distinguish between the two compounds?

☒ **A** Reaction with concentrated aqueous sodium hydroxide.

☒ **B** Reaction with nitrous acid.

☒ **C** Reaction with aqueous sodium hydrogencarbonate.

☒ **D** Reaction with ethanoyl chloride.

(Total for Question = 1 mark)

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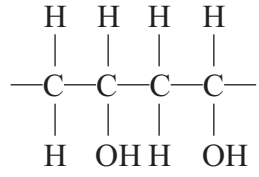
15 Poly(ethenol) is a water-soluble polymer. A section of the chain has the structure shown below.



The polymer is used for making hospital laundry bags so that laundry can be loaded directly into washing machines without it having to be handled.

Poly(ethenol) is water soluble because the polymer

☒ **A** is broken down by the water into monomers.

☒ **B** is broken down by the washing detergent.

☒ **C** breaks into monomers at the temperature of the wash.

☒ **D** forms many strong hydrogen bonds with the water.

(Total for Question = 1 mark)

---

16 Which of the following substances is capable of damaging the ozone layer?

☒ **A** NaCl

☒ **B** CO_2

☒ **C** C_2HF_5

☒ **D** $C_2F_3Cl_3$

(Total for Question = 1 mark)

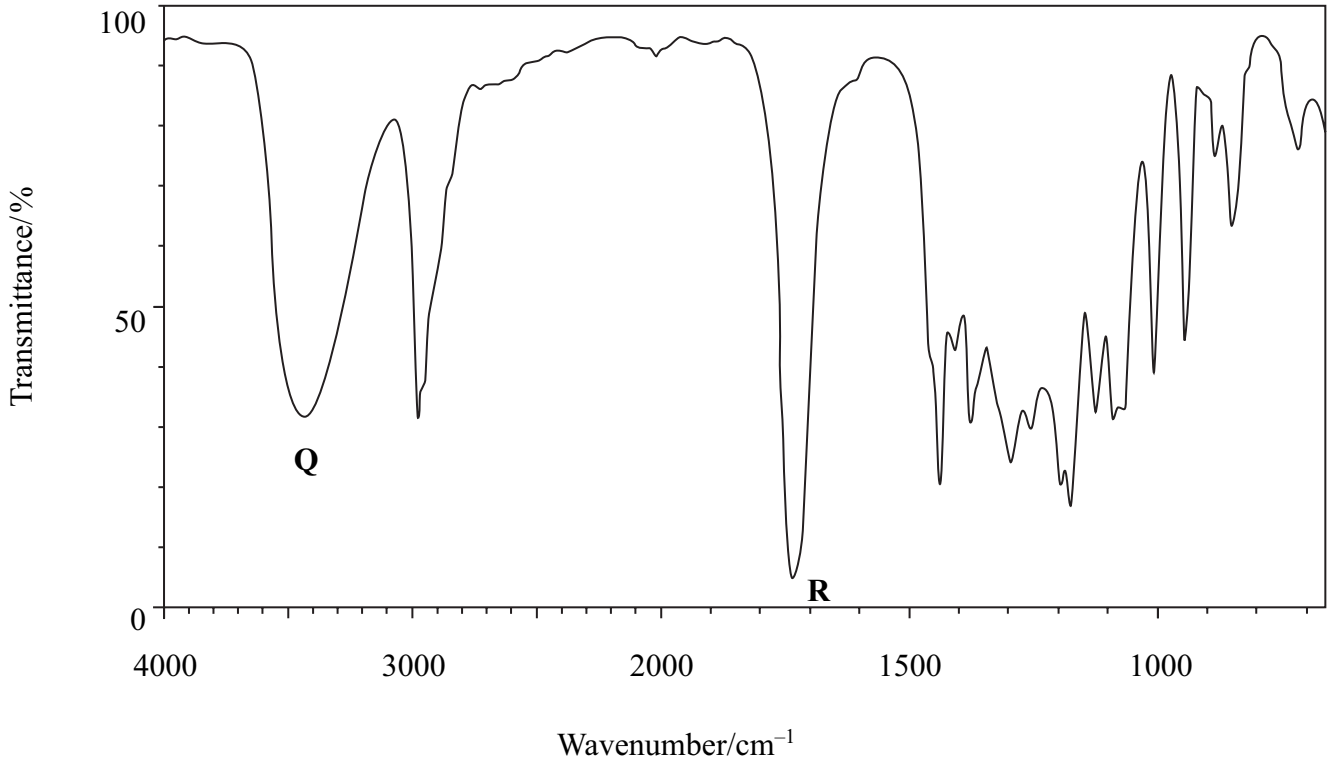
SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

17 An organic compound **X** is an ester found in orange peel and has the molecular formula $C_5H_{10}O_3$.

(a) Identify the bonds responsible for the peaks labelled **Q** and **R** in the infrared spectrum of **X** shown below, referring to your data booklet.

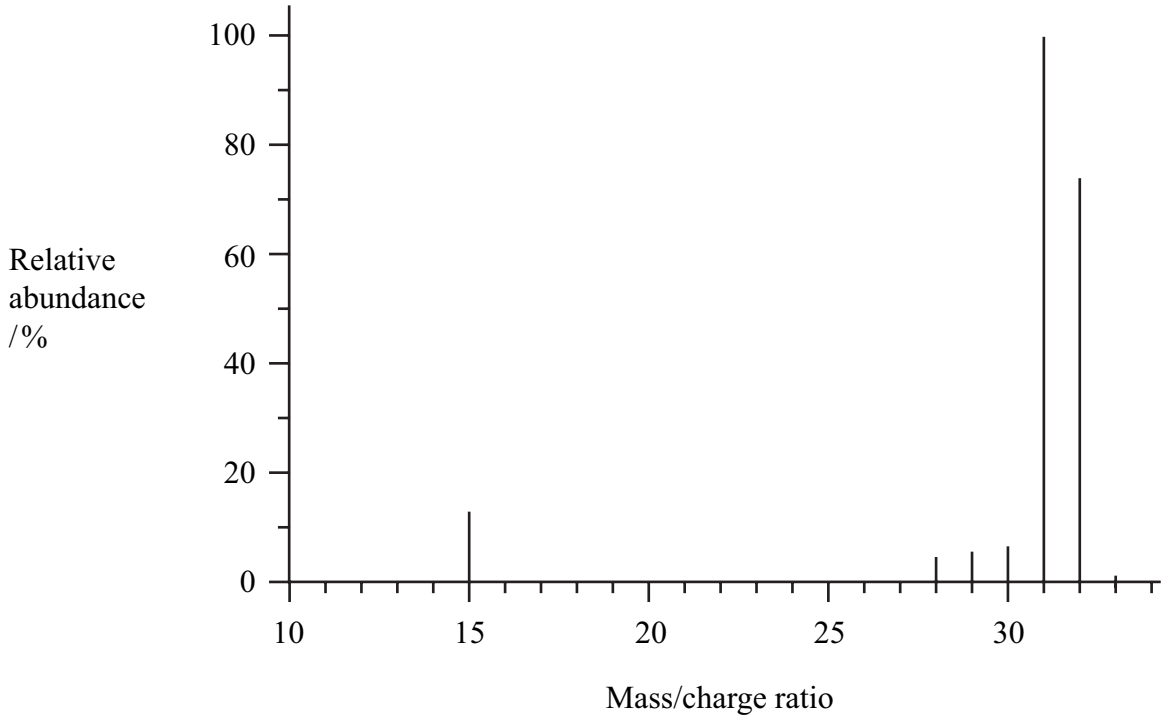
(2)



Q .....

R .....

(b) **X** was heated under reflux with dilute sulfuric acid. The resulting mixture was distilled and a liquid **Y** was collected. The mass spectrum of **Y** is shown below.



(i) Identify **Y**, by name or formula, using the information available. Use **two** pieces of data from the mass spectrum to support your answer.

(2)

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.....

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(ii) The identity of **Y** could be confirmed using nmr spectroscopy. Predict the number of peaks in the low resolution proton nmr spectrum of **Y**. Give the chemical shift range for each peak, referring to your data booklet.

(2)

.....

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.....

(c) A second product from the reaction of **X** with hydrochloric acid is **Z**, which has the molecular formula $C_4H_8O_3$.

What can you deduce about **Z** from the results of the following tests?

(i) One mole of **Z** reacts with two moles of phosphorus(V) chloride, PCl_5.

(1)

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(ii) When sodium carbonate solution is added to **Z**, effervescence is seen.

(1)

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(iii) **Z** is warmed gently with potassium dichromate(VI) and sulfuric acid. The organic product of the reaction gives a yellow precipitate with 2,4-dinitrophenylhydrazine (Brady's reagent) but does not react with Tollens' reagent.

(1)

.....

.....

(iv) **Z** reacts with a solution of iodine in sodium hydroxide to produce a yellow precipitate with an antiseptic smell.

(1)

.....

.....

(d) Use the results of these tests to deduce the structural formula of **Z** and hence the structural formula of **X**.

(2)

(Total for Question 17 = 12 marks)

18 The equation below shows the type of reaction which can be used in the production of biodiesel from vegetable oils.

$$\begin{array}{l} CH_2OOCR_1 \\ | \\ CHOOCR_2 \\ | \\ CH_2OOCR_3 \end{array} + 3C_2H_5OH \rightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + R_1COOC_2H_5 + R_2COOC_2H_5 + R_3COOC_2H_5$$

(a) (i) Name this type of reaction.

(1)

.....

(ii) Suggest why water must not be present when this reaction with ethanol is carried out.

(1)

.....

.....

.....

(b) Give **one** reason why biodiesel is considered a "greener" fuel than diesel produced from crude oil.

(1)

.....

.....

.....

*(c) The products of the type of reaction shown with ethanol can be separated and identified using gas chromatography (GC).

In chromatography, compounds are separated because of the difference in distribution between a mobile phase and a stationary phase.

Explain why this difference in distribution occurs, and contrast the phases used in gas chromatography (GC) and high performance liquid chromatography (HPLC).

(5)

(Total for Question 18 = 8 marks)

19 (a) Tiglic acid is a compound that is used as a defensive agent by some beetles.

(i) Tiglic acid contains, by mass, 60% carbon, 8% hydrogen, with the remainder being oxygen. Show that these data are consistent with the formula $C_5H_8O_2$.

(1)

(ii) Tiglic acid contains a carbon-carbon double bond and a carboxylic acid group.

Suggest **one** test for each of these groups in tiglic acid. State what you would do and what you would see as a positive result for the tests.

(4)

Test for C═C .....

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Test for —COOH .....

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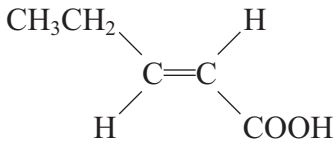
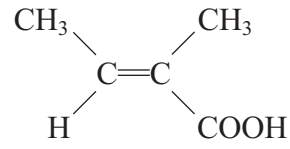
(b) It is suggested that the structure of tiglic acid is either that of **A** or **B**.



A



B

(i) State, with a reason, whether **B** is the *E*- or *Z*- isomer.

(2)

.....

.....

.....

(ii) The mass spectrum of tiglic acid shows two prominent peaks at mass/charge ratios 45 and 55. Write the formulae of the fragments giving rise to each of these peaks.

(2)

45 .....

55 .....

(iii) Does this data from the mass spectrum **alone** enable you to decide which of **A** or **B** is the structure of tiglic acid? Explain your answer.

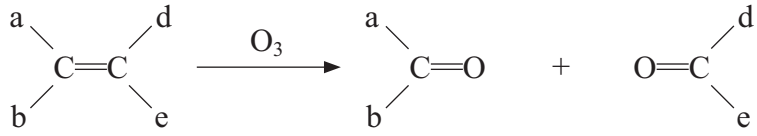
(1)

.....

.....

.....

(c) The position of a C═C double bond in a molecule can be determined by ozonolysis. The compound is reacted with ozone and then dilute acid, two carbonyl compounds being produced as shown below.



Ozonolysis of tiglic acid gives two carbonyl compounds, **C** and **D**.

Compound **C** gives a silver mirror with Tollens' reagent and gives iodoform with iodine in alkali.

Compound **D** does **not** give a silver mirror with Tollens' reagent, but does give iodoform with iodine in alkali.

*(i) From the results of the experiments, deduce the functional groups present in **C** and **D**. By considering the two possible structures for tiglic acid, give the structural formulae of **C** and **D**.

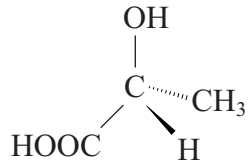
From the structures you have drawn, state which of the structures **A** or **B** could represent tiglic acid.

(6)

(ii) Explain whether or not these tests show definitely that your answer to (c)(i) represents tiglic acid.

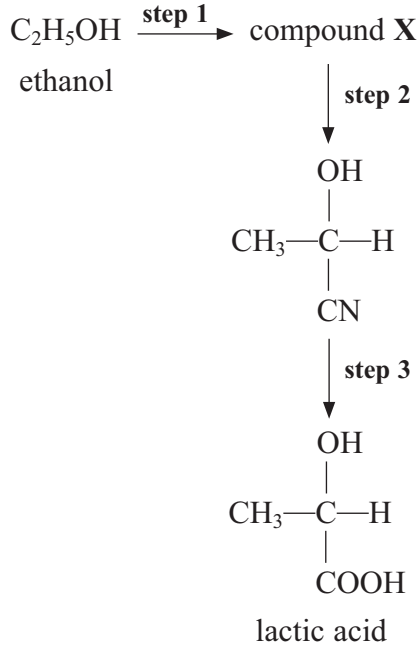
(1)

(d) Lactic acid is a chiral molecule that is found in sweat as the (–) isomer only. Its structural formula is



(–) - lactic acid

(i) Lactic acid can be made from ethanol in three steps.



lactic acid

Give the structural formula of the intermediate **X** and the reagents and conditions required for **steps 1** and **2**.

(4)

Step 1 .....

.....

Step 2 .....

.....

(ii) Classify the type and mechanism of the reaction that occurs in **step 2**.

(1)

.....

*(iii) By considering the stereochemistry of the mechanism in **step 2**, explain why this synthesis would **not** give a single optical isomer of lactic acid.

(2)

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(iv) Suggest why synthetic pathways for the manufacture of pharmaceuticals may require reactions that are highly stereospecific.

(1)

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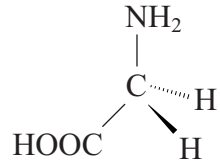
.....

(Total for Question 19 = 25 marks)

20 Proteins are polymers of α-amino acids, the simplest of which is glycine.



(a) (i) Draw the **structural** formula for the zwitterion of glycine in the solid state.

(1)

(ii) Explain, on the basis of your answer to (a)(i), why glycine has a relatively high melting temperature for such a small molecule.

(2)

(iii) Draw the structure of the protein chain that would be formed if glycine alone were to be polymerized. Show part of the chain containing two glycine residues.

(2)

*(b) A solution of hydrolysed protein contains the individual amino acids that make up the protein. Briefly state how you would use chromatography, together with known samples of amino acids, to show which amino acids the protein contained. Do **not** give detailed experimental instructions.

(5)

(Total for Question 20 = 10 marks)

SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

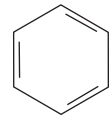
21 Read the passage below carefully and answer the questions which follow.

Molecular structure and colour chemistry

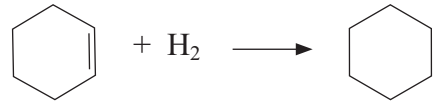
The sight of tubes of paint or of coloured pencils in an artists' supply shop is something that most people enjoy; we love colour.

The ability to synthesise brightly-coloured compounds coincides with the rapid growth of the organic chemicals industry. Synthetic organic dyes started to appear in the mid-19th century when William Perkin synthesised Mauve in 1856 at the age of 18. He was trying to synthesise quinine even though he did not know the structure of the molecule.

In the 19th century many chemists did not believe that molecules existed. The work of Butlerov, Couper, and notably Kekulé showed that molecules not only exist but have specific structures. In 1865 Kekulé suggested a ring structure for the aromatic compound benzene which he represented as



Kekulé knew that benzene does not react with bromine water. Later work showed that the enthalpy change of hydrogenation of the compound is $-205\ kJ\ mol^{-1}$, rather than the value of $-360\ kJ\ mol^{-1}$ that would be expected if the structure was exactly as shown above, given that the enthalpy change of hydrogenation for cyclohexene to cyclohexane



is $-120\ kJ\ mol^{-1}$.

When Greiss in 1856 discovered diazotisation and the azo dyes, he used a reaction characteristic of aromatic amines. Witt, in 1876, found the functional groups in the dye molecule that make it water-soluble and enable it to attach to the cloth fibres. Graebe, Liebermann and Perkin in 1869 patented the synthesis of alizarin, found in madder root grown in Holland and Von Baeyer synthesised indigo in 1880, until then grown in India. Synthetic dyes were made available in large quantities and were cheaper than the sources from plants.

Now the organic chemical industry produces a vast range of pigments and dyestuffs for use in paints and for fabrics, inks and other materials, making our world the most colourful that it has ever been.

(a) (i) Explain why Perkin's attempted synthesis of quinine was almost certain to fail.

(1)

(ii) Suggest the effect that the growth of the organic chemicals industry in the late 19th century had on Holland and India in particular.

(2)

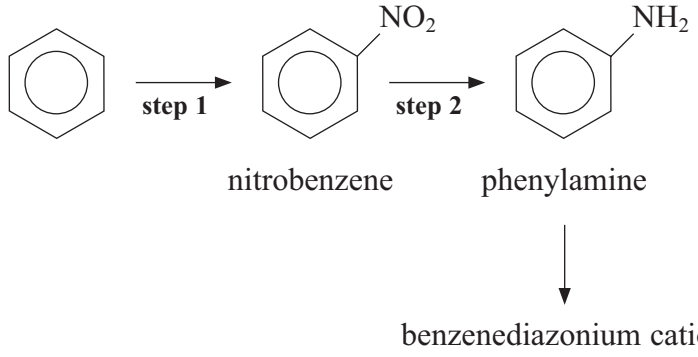
(b) (i) What observation did Kekulé make to show that benzene does **not** react with bromine water? Explain the significance of this with reference to his representation of the molecule.

(2)

(ii) Explain, in terms of the bonding in the benzene ring, why the enthalpy of hydrogenation is less exothermic than would be expected from a molecule with three double bonds.

(3)

(c) The first steps in the preparation of an azo dye from benzene are shown below.



Give the mechanism for the reaction in **step 1**, including the equation for the formation of the electrophile.

(4)

Equation for formation of electrophile

Mechanism

(d) (i) Phenylamine is converted into the benzenediazonium cation using sodium nitrite and hydrochloric acid at a temperature between 0 °C and 10 °C.

Explain why the temperature must **not** be lower or higher than these limits if a good yield is to be obtained.

(2)

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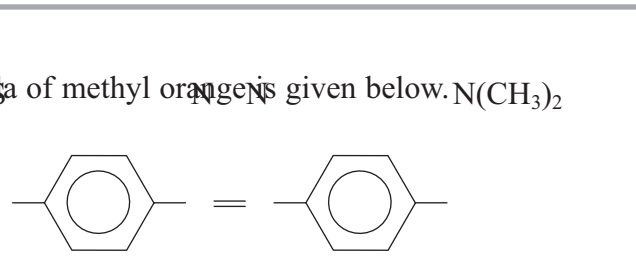
(ii) Draw the structural formula of the benzenediazonium cation showing all the bonds and the charge.

(1)

(iii) Suggest how you could convert a sample of the benzenediazonium cation into an azo dye. Give the name of the other compound you would use and the skeletal formula of the azo dye you would obtain.

(3)

(e) The structural formula of methyl orange is given below.



Suggest the main features of methyl orange which make it water-soluble, giving your reasons.

(2)

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(Total for Question 21 = 20 marks)