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NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

CLASS

TUTOR'S NAME

CHEMISTRY

9729/03

Paper 3 Free Response

15 September 2022

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question. Circle the question you attempted in the box below.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/25
2	/15
3	/20
4 or 5	/20
Total	/80

This document consists of **32** printed pages.

Section A

Answer **all** questions in this section.

1 This question is about alkene and diene. Diene is an unsaturated compound containing two double bonds between carbon atoms.

(a) Table 1.1 shows the structures of hexa-1,2-diene, hexa-1,3-diene and hexa-1,5-diene.

Table 1.1

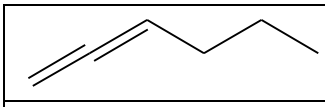	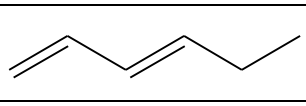	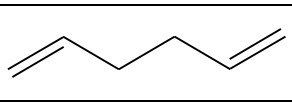
hexa-1,2-diene	hexa-1,3-diene	hexa-1,5-diene

Table 1.2 shows the enthalpy change of combustion of some organic compounds.

Table 1.2

substance	**ΔH_c / kJ mol^{-1}**	**$\Delta H_{hydrogenation}$ / kJ mol^{-1}**
Liquid hexa-1,2-diene	−3867	ΔH_1
Liquid hexa-1,3-diene	−3816	−225
Liquid hexa-1,5-diene	−3843	−252
Liquid hexane	−4163	NA
Hydrogen gas	−286	NA

(i) Use data in Table 1.2 to draw an energy level diagram to calculate the enthalpy change of hydrogenation of hexa-1,2-diene, ΔH_1. [2]

(ii) Suggest which isomer, hexa-1,3-diene or hexa-1,5-diene, is more stable using data in Table 1.2. Explain your answer by considering the type of orbitals present in the carbon atoms of the isomer. [2]

(iii) Choose a suitable isomer of hexadiene from Table 1.1 and devise a three-step synthetic route to synthesise buta-1,3-diene. [5]

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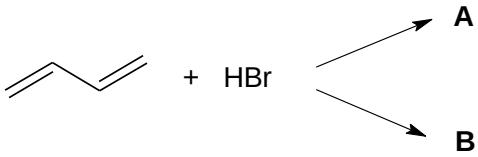
(b) When buta-1,3-diene undergoes electrophilic addition reaction with 1 mol of HBr, a mixture of two products, **A** and **B** is formed. Both **A** and **B** have molecular formula of C_4H_7Br.



A exhibits cis-trans isomerism while **B** contains a chiral centre.

(i) Draw the structures of **A** and **B**. [2]

(ii) By referring to your structure in **(b)(i)**, explain how cis-trans isomerism arises in **A**. [2]

Kinetic and thermodynamic factors decide the type of addition product that is obtained. **A** is known as the kinetic product as it is formed faster while **B** is known as the thermodynamic product as it is formed more slowly and is also more thermodynamically stable than the kinetic product.

(iii) In a **single** set of axis, sketch and label two reaction pathway diagrams for the second step of the mechanism to form **A** and **B** respectively. The carbocation intermediates used to form **A** and **B** occupy the same energy level. Use E_{a1} and E_{a2} to label the activation energies and ΔH_1 and ΔH_2 to label the enthalpy changes to form **A** and **B** respectively. [2]

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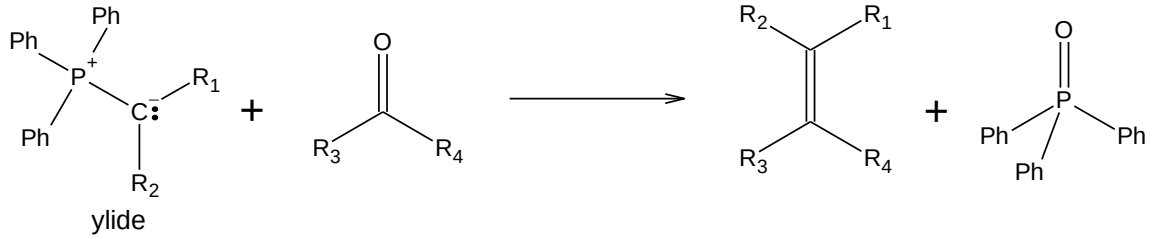
(c) The Wittig reaction is an organic chemistry synthesis technique that involves the conversion of carbonyl compounds into alkenes using an ylide as the reagent and via a nucleophilic addition pathway.



where Ph is phenyl and R_1, R_2, R_3, and R_4 is either H atom or alkyl group

Fig 1.1: The Wittig reaction

Ylides can be synthesised from triphenyl phosphine and an alkyl halide. The first step is to react the triphenyl phosphine and alkyl halide via a nucleophilic substitution reaction. This step is an elementary reaction. The second step is to add a very strong base such as butyl lithium, $CH_3CH_2CH_2CH_2^-Li^+$ to deprotonate the intermediate product formed in step 1.

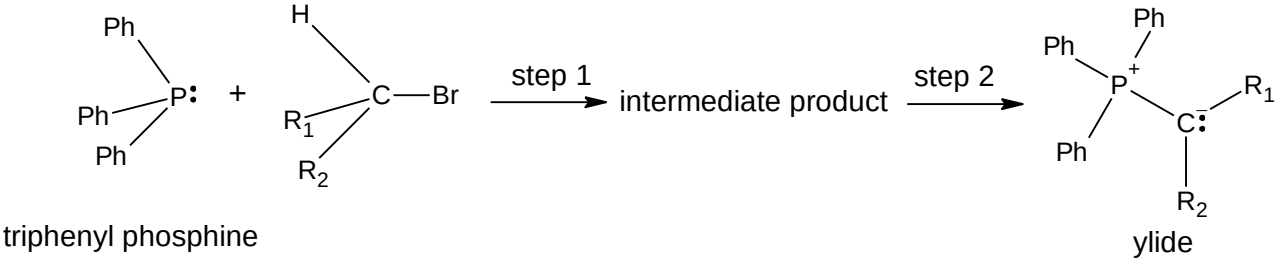


Figure 1.2: Synthesis of ylide

(i) Draw the full structural formula of the intermediate product for the reaction shown in Fig. 1.2 when R_1 is hydrogen atom and R_2 is methyl group. [1]

(ii) Predict the organic products **L** and **M** of the reactions shown in Fig. 1.3. [2]

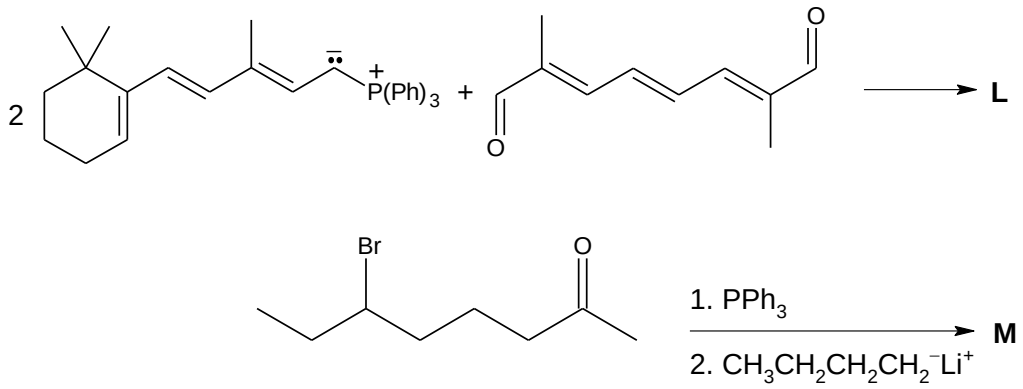


Fig. 1.3

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(d) Coumarin, $C_9H_6O_2$, is a colourless crystalline solid with a sweet odour resembling the scent of vanilla. It is formed when compound **T**, $C_9H_7O_3Br$ is treated with triphenyl phosphine followed by a strong base.

Both coumarin and **T** are neutral.

When heated with aqueous sulfuric acid, **T** gives **U**, $C_7H_6O_2$ and **V**, $C_2H_3O_2Br$.

U reacts with 2 moles of aqueous bromine to give a white ppt and forms a silver mirror with Tollens' reagent.

Both **T** and **U** do not rotate plane-polarised light.
Both **U** and **V** "pop" with a lighted splint when treated with Na metal.

Deduce the structures of compounds **T**, **U**, **V** and coumarin, explaining the observations described. [7]

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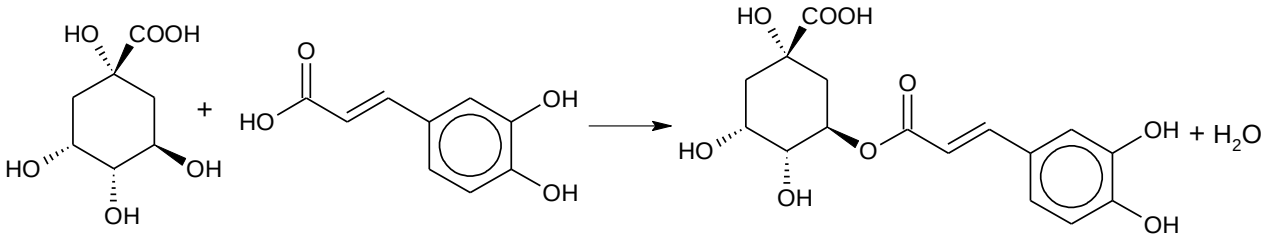
[Total: 25]

2 Green coffee beans contain chlorogenic acid. It is an ester formed from quinic acid and caffeic acid.



quinic acid caffeic acid chlorogenic acid

(a) Describe a simple chemical test to distinguish quinic acid and caffeic acid. State what you would observe for **each** compound. [2]

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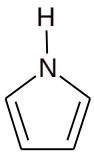
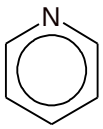
(b) During roasting, chlorogenic acid readily decomposes to quinic acid and caffeic acid. Quinic acid creates bitterness and astringency thus the very dark roasts taste bitter.

After roasting, there are more than 1000 volatile compounds found in coffee. However, there are only 20 – 30 volatile compounds that contributed to the perceived aroma. These include aldehydes, ketones, carboxylic acids, esters, pyrroles, and pyridines.



pyrrole

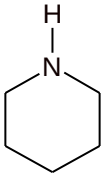


pyridine

(i) Given that both pyrrole and pyridine are aromatic and the nitrogen atoms in pyrrole and pyridine are sp^2 hybridised, explain why pyrrole is a weaker base than pyridine.

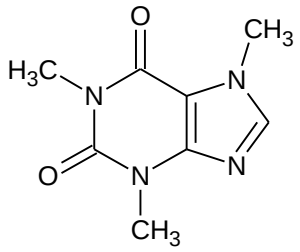
You may draw a labelled diagram to illustrate all the orbitals on nitrogen atom in pyrrole. Identify the orbital which the lone pair of electrons on nitrogen atom resides. [3]

(ii) State the type of hybridisation of nitrogen atom in piperidine. Hence, explain the relative basicity of piperidine and pyridine. [2]



piperidine

(c) Caffeine is a natural stimulant found in coffee and tea. It is soluble in water.



caffeine (M_r = 194.0)

(i) Draw a labelled diagram to show how a water molecule can be attached to a caffeine molecule. [2]

(ii) Draw the structural formula of the organic products when caffeine is heated with aqueous sodium hydroxide. [3]

(iii) Decaffeinated coffee and tea are made by extracting the caffeine from solid coffee or tea using a solvent.

Suggest a reason, which of the following industrial solvents would be most suitable. [1]

- benzene
- cyclohexane
- liquid carbon dioxide

(iv) Caffeine can also be added to cola drinks. A can of cola contains 50 mg of extracted caffeine in a volume of 330 cm^3. Calculate the concentration of caffeine in mol dm^{-3}. [2]

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3 Hydrogen peroxide decomposes according to the equation below.

$$2H_2O_2(aq) \rightarrow O_2(g) + H_2O(l)$$

There are several ways to monitor the decomposition reaction of hydrogen peroxide by a catalyst.

(a) The decomposition of hydrogen peroxide has been shown to have first order kinetics. It was found that 10 % of hydrogen peroxide was left after 9 hours.

(i) Determine the half-life of hydrogen peroxide. [1]

(ii) Hence, determine the rate constant, *k*, of the reaction. [1]

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(b) **(i)** Sketch the graph of rate against $[H_2O_2]$ for the reaction. [1]

(ii) This reaction is significantly faster when a particular enzyme is used. On the same axes, as the graph in **b(i)**, show how the rate of reaction would be affected by the presence of a very small amount of the enzyme. Label this line clearly as "in the presence of enzyme". [2]

(iii) Explain the relationship between $[H_2O_2]$ and the rate of the enzyme catalysed reaction. [2]

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(c) A sample of iron(III) nitrate solution is added to a solution of hydrogen peroxide. It was found that upon mixing of the chemicals, vigorous effervescence was observed. The yellow iron(III) solution turned brown upon mixing and after a while, the colour of the mixture turned yellow again.

(i) The solution of iron(III) was found to give a dark orange colour with universal indicator. Explain this observation with the use of a relevant equation. [2]

(ii) A possible mechanism for the iron(III) catalysed decomposition of hydrogen peroxide, is provided below. In this mechanism, the HO_2^- ligand on one of the complex ions represents the H–O–O^- ion and the O represents an oxygen atom.

Step 1 $[Fe(H_2O)_6]^{3+}(aq) + H_2O_2(aq) \rightleftharpoons [Fe(H_2O)_5(HO_2)]^{2+}(aq) + H_3O^+(aq)$

Step 2 $[Fe(H_2O)_5(HO_2)]^{2+}(aq) \rightarrow OH^-(aq) + [Fe(H_2O)_5O]^{3+}(aq)$

Step 3 $[Fe(H_2O)_5O]^{3+}(aq) + H_2O_2(aq) \rightarrow [Fe(H_2O)_6]^{3+}(aq) + O_2(g)$

Step 4 $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$

Explain fully how you can tell that the $[Fe(H_2O)_6]^{3+}$ ion is acting as a catalyst in this reaction, using evidence from the observations provided in **(c)** and the mechanism. [2]

(iii) The transition metals such as iron tend to have variable oxidation states, whereas s-block elements such as calcium do not. Suggest an explanation for this difference. [2]

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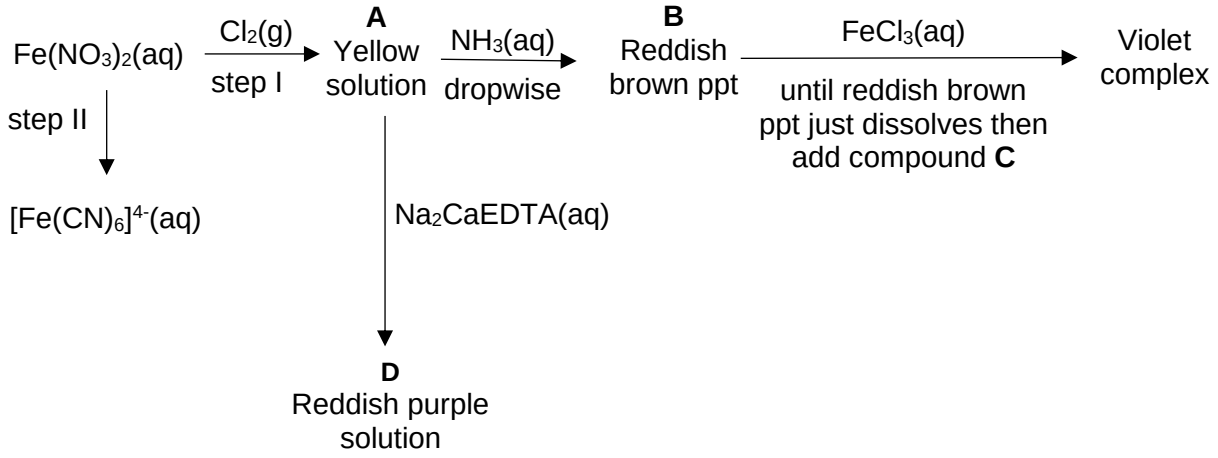
(d) The following scheme shows the reactions of iron and its compounds.



(i) Identify compounds **B** and **C**. [2]

(ii) Explain why **A** and **D** have different colours. [2]

(iii) Write an ionic equation for the formation of **D** from **A**. [1]

(iv) State the types of reactions that occurred in steps I and II. [2]

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Section B

Answer **one** question from this section.

4 Glucose comes from the Greek word for "sweet". It is the simplest carbohydrate with molecular formula $C_6H_{12}O_6$ and is the major free sugar circulating in the blood of mammals, serving as the primary source of energy for cell function.

(a) The oxidative breakdown of glucose by our body to produce energy is called respiration. The reaction for the complete combustion of glucose is

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

$\Delta H\ominus = -2816 \text{ kJ mol}^{-1}$

$\Delta S\ominus = +181 \text{ J mol}^{-1} \text{ K}^{-1}$

(i) Write a half-equation to represent the oxidative breakdown of glucose. [1]

(ii) The energy value of food is measured in Calorie. One Calorie is defined as the amount of heat needed to raise the temperature of 1 kg of water by 1 °C. Use the given information, together with data from the *Data Booklet*, to calculate the number of Calories in 1 g of glucose. [2]

(iii) Comment on the sign of $\Delta S\ominus$ for the combustion of glucose. [1]

(iv) If this combustion reaction could be harnessed as a fuel cell, calculate $\Delta G\ominus$ and hence the theoretical voltage, $E^{\ominus}_{cell}$, that could be produced under standard conditions. [3]

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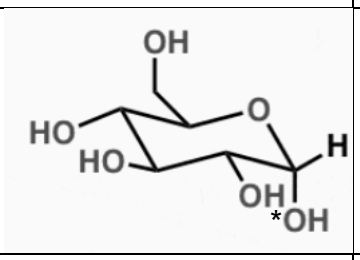
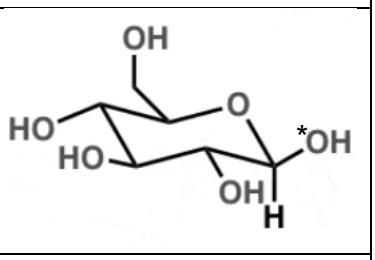
Glucose exists in two forms, α-glucose and β-glucose, with the *OH group occupying different spatial arrangement in each form. Some information about the two forms is given in Table 4.1.

Table 4.1

	α-glucose	**β-glucose**
		
Melting point / ^{o}C	146	150
Angle of rotation of plane-polarised light for a 1 mol dm^{-3} sample / ^{o}	+20.2	+3.4

(b) **(i)** Suggest a reason for the difference in melting points between α-glucose and β-glucose. [1]

If a solution of α-glucose is left for some time, it will come into dynamic equilibrium with β-glucose.

$$\alpha\text{-glucose} \rightleftharpoons \beta\text{-glucose}$$

(ii) Explain what is meant by *dynamic equilibrium*. [1]

(iii) 1 dm^3 of a freshly prepared solution of 1.0 mol dm^{-3} solution of α-glucose is left to stand at 298 K. At equilibrium, the solution was found to rotate plane-polarised light by +9.45 ^{o}. Given angle of rotation of plane-polarised light is directly proportional to concentration of isomer, use information from Table 4.1 to determine [β-glucose] at equilibrium. [1]

(iv) Hence calculate the value of the equilibrium constant, K_c, for the conversion of α-glucose to β-glucose at 298 K. If you were unable to determine [β-glucose] at equilibrium, assume the value is 0.60. Note 0.60 is **not** the correct answer for **(b)(iii)**. [1]

(v) The conversion of α-glucose into β-glucose is catalysed by acids. What will be the effect on the equilibrium position if the conversion is now carried out in the presence of dilute sulfuric acid? Explain your answer. [1]

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(c) Fig. 4.1 shows the mechanism for the conversion of α-glucose into β-glucose.

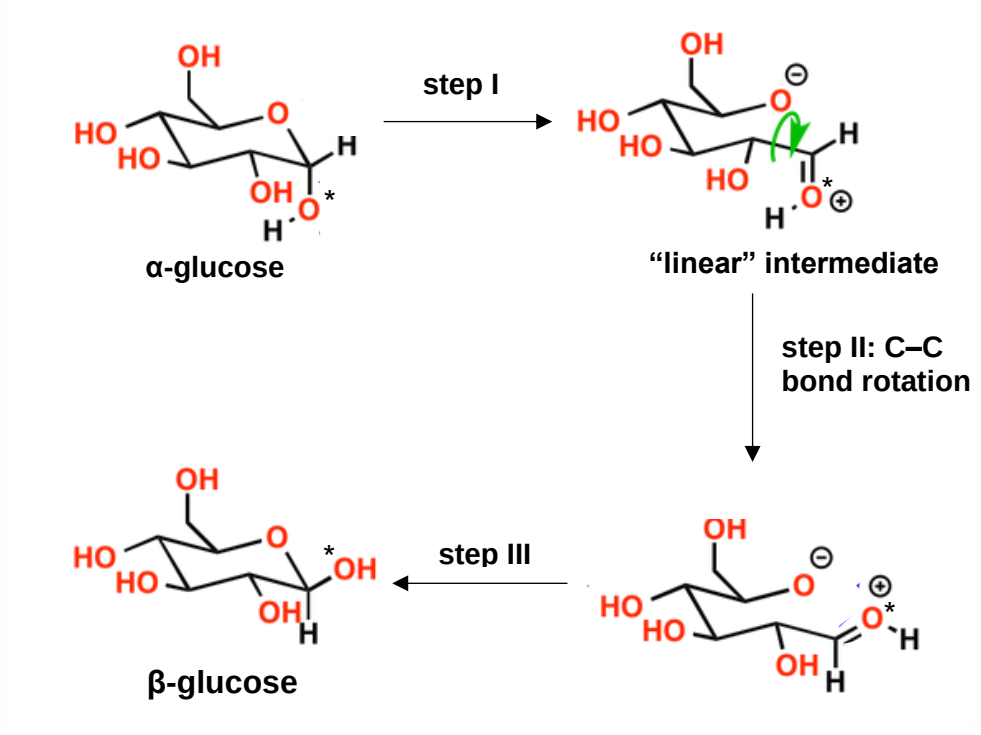

Fig. 4.1

(i) Explain, with reference to the Valence Shell Electron Pair Repulsion theory, why the bond angle around O* increases in step I of the mechanism. [2]

(ii) Complete Fig. 4.1 to suggest the mechanism for steps I and III. Show all relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

(iii) Suggest the types of reaction taking place in steps I and III. [2]

(iv) A proton transfer can occur between the charged groups in the "linear" intermediate to form another stable electrically neutral intermediate. Identify the new functional group present in this other intermediate and hence suggest a suitable chemical test to confirm its presence during the conversion of glucose. [2]

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5(a) Table 5.1 lists the pK_a values for some weak acids.

Table 5.1

Compound	pK_a
H_2S	7.05
H_2O_2	11.7
H_2O	14.0

(i) Using the data provided, and given that NaSH is a weak base, calculate the pH of 0.10 mol dm^{-3} NaSH solution. [2]

(ii) Suggest an explanation for the different pK_a values for H_2S, H_2O_2 and H_2O. [2]

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(b) Hydrogen peroxide acts as an oxidising agent in both acidic and alkaline conditions.

(i) Using suitable data from the *Data Booklet*, calculate the $E^{\ominus}_{cell}$ for the oxidation of Fe(II) ions by hydrogen peroxide under the two conditions. [2]

(ii) Hence, calculate $\Delta G^{\ominus}$ for the two reactions, and deduce whether the oxidation of Fe(II) ions by hydrogen peroxide is more feasible under acidic or basic conditions. Explain your answer. [2]

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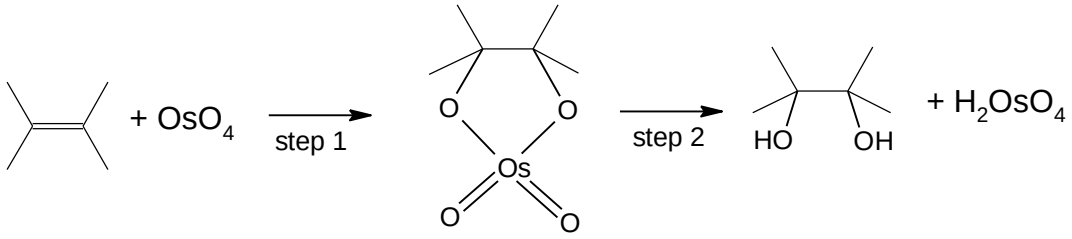
(c) Osmium, Os, is a hard, brittle, bluish-white transition metal that is found as a trace element in alloys. Osmium is among the rarest elements in the Earth's crust, making up only 50 parts per trillion (ppt). Osmium tetroxide, OsO_4, is a mild oxidant and oxidises alkenes to give excellent yields of vicinal diols as shown in Fig. 5.1.

- Osmium tetroxide reacts with alkenes to form an osmate ester,
- which then reacts with water to form the vicinal diols in good yields.
- $NaIO_4$, sodium periodate is added to regenerate osmium tetroxide, thus permitting the use of this expensive and toxic reagent in minimum amounts.



osmate ester

$$H_2OsO_4 + IO_4^- \xrightarrow{\text{step 3}} OsO_4 + IO_3^- + H_2O$$

Fig. 5.1

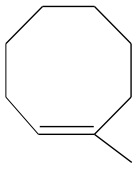
The oxygen atoms add to the same face of the C=C bond. Thus, OsO_4 forms vicinal diols by *syn* addition.

(i) Using VSEPR (valence shell electron pair repulsion) theory, state and explain the bond angles in OsO_4 and IO_3^-. [3]

(ii) Explain why OsO_4 is expected to be very volatile. [1]

(iii) Step 1 in Fig. 5.1 is initiated by an electrophilic attack on OsO_4 by the alkene.

Write out an equation and draw curly arrows to show how the osmate ester intermediate is formed if the alkene is 1-methyl-1-cyclooctene. In your answer, use hash and wedge bonds to show the stereochemistry of the ester intermediate. [3]

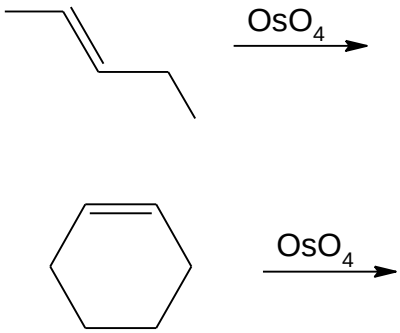


1 –methyl–1–cyclooctene

(iv) By considering the structural formulae and reagents shown above, suggest the type of reaction taking place in step 2 in Fig. 5.1. [1]

When an alkene reacts with osmium tetroxide, stereocenters can form in the diol product. Cis alkenes give meso products and trans alkenes give racemic mixtures. Meso compounds contain 2 or more chiral centres, but they are achiral and have a internal plane of symmetry.

(v) Give the skeletal formulae of the products (including all stereoisomers) of the following reactions. Indicate the presence of any chiral centres in the products with an asterisk *.



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Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

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