EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2022
General Certificate of Education Advanced Level
Higher 3

CANDIDATE NAME	

CIVICS GROUP	2	1	–		

INDEX NUMBER

CHEMISTRY

9813/01

Paper 1

22 September 2022

2 hours 30 minutes

Candidates answer on Question Paper.

Additional Materials: Data Booklet
Insert

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number 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 staplers, 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 **two** questions.

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	
Section A	
1	/ 20
2	/ 10
3	/ 15
4	/ 15
Section B	
5	/ 20
6	/ 20
7	/ 20
Total	/ 100

This document consists of **43** printed pages and **1** blank page.

Section A

Answer all the questions in this section.

1 (a) Most alternative fuels, including bioethanol, are more environmentally-friendly than oil-derived ones and are generally characterised by lower net emissions of CO_2 and other pollutants such as nitrogen oxides (NO_x), CO, particulate matter (PM), unburnt hydrocarbon (HC) and soot.

(i) Write equations for the complete combustion of ethane, and of ethanol. [1]

(ii) Suggest why bioethanol is still considered to provide lower net emissions of CO_2 than fossil fuels, despite producing CO_2 as an end-product in combustion. [1]

(iii) Using your answer to (a)(i), suggest why ethanol burns cleaner than regular petrol and produce lesser CO, PM, HC and soot. [1]

(iv) Using your answer to (a)(i), suggest a disadvantage of using ethanol as a fuel over petrol. [1]

(i) $CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

$CH_3CH_3 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$

(ii) The biomass, used as feedstock for production of bioethanol, will **consume CO₂ during photosynthesis**, hence lowering the net emission of CO_2.

(iii) Ethanol **requires less oxygen per mole** for complete combustion.

(iv) Since ethanol is **oxygenated**, the **enthalpy of combustion** of ethanol is **less exothermic** than that of petrol, per carbon atom, hence a **greater mass** of ethanol is required to supply the same quantity of energy.

(b) **(i)** Suggest the main advantage of second generation bioethanol over first generation bioethanol. [1]

(ii) Suggest two advantages of the thermochemical alternative over the hydrolytic alternative, in relation to the feedstock used in second generation bioethanol production. [2]

At the end of the fermentation process, the ethanol concentration generally does not exceed 15% by volume.

(iii) Suggest a reason why the ethanol concentration generally does not exceed 15%? [1]

(iv) Suggest a method by which the bioethanol (boiling point: 78 °C) produced can be concentrated and purified. [1]

(i) Second generation bioethanol **does not compete against food supplies** as they are based on non-food raw material.

(ii) An advantage of the thermochemical alternative is that it can use a **wider range of different feedstocks** and in the case of lignocellulosic materials the **complete feedstock can be converted into syngas**, unlike the hydrolytic alternative where **lignin cannot be hydrolysed**.

(iii) The accumulation of higher ethanol concentrations in the fermentor may **inhibit yeast or the bacteria**.

(iv) **Fractional distillation**

(c) It is hypothesised that the Wood-Ljungdahl pathway was one of the first biochemical pathways, used by the first autotrophs about 3.8 billion years ago. These organisms used CO and H_2 as energy sources:

$H_2 \rightarrow 2H^+ + 2e^-$

$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$

and CO_2 as an electron acceptor approximately one billion years before significant quantities of O_2 appeared in the Earth's atmosphere.

(i) While elucidating the Wood-Ljungdahl pathway, $^{14}CO_2$-labelling experiments ruled out the other biochemical pathways known at that time.
Using Fig. 1.1, suggest where the ^{14}C will end up in the bioethanol. [1]

(ii) Which stages in the Eastern branch (Fig. 1.1) use H_2 as the energy source directly? [2]

(iii) Write a balanced equation for the production of bioethanol, that uses
- CO as the sole carbon and energy source,
- CO as the carbon source and both CO and H_2 as the energy source,
- CO_2 as carbon source and H_2 as energy source. [2]

(i) $^{14}CH_3{}^{14}CH_2OH$

(ii) Stage **II**, **V** and **VI**

(iii) CO as sole carbon and energy source:

$6CO + 3H_2O \rightarrow CH_3CH_2OH + 4CO_2$

CO as the carbon source and both CO and H_2 as the energy source:

$2CO + 4H_2 \rightarrow CH_3CH_2OH + H_2O$ *or* **$3CO + 3H_2 \rightarrow CH_3CH_2OH + CO_2$**

CO_2 as carbon source and H_2 as energy source:

$2CO_2 + 6H_2 \rightarrow CH_3CH_2OH + 3H_2O$

Question 1 continues on the next page

(d) To reduce the greenhouse gases emissions, biofuels have been used as, in most cases, fuel blending components in nowadays transportations due to their cleaner emissions compared with the conventional fuels. Among all biofuels productions, ethanol is the predominant compound and has been extensively used as a transportation fuel.

Bioethanol is commonly mixed with petrol at the **volume fractions** of 5%, 10% and 85% (fuel names E5, E10 and E85). When blended with petrol, ethanol reduces the emissions of CO and unburnt hydrocarbon in exhaust. Ethanol is also known to have high octane numbers which supress the "knock" in engines and thus improves the engine efficiencies.

Knocking is where the fuel ignites prematurely and this reduces engine efficiency. Branched chain isomers of octane knock much less and a lot of these are found in petrol. One major isomer is 2,2,4-trimethylpentane.

One of the characteristics of an effective fuel is the amount of energy it releases.

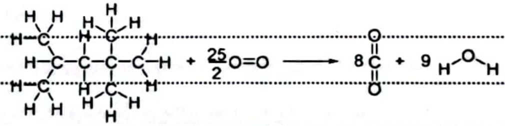
(i) Using data from the *Data Booklet*, calculate the enthalpy change of combustion of 2,2,4-trimethylpentane. **[2]**

(ii) Using for your answer to **(d)(i)** and the information below, calculate the energy, in kJ, released when 1 dm^3 each of both E5 and E10 fuel is burnt. **[2]**

density of pure ethanol	0.789 g cm^{-3}
density of pure octane isomers	0.703 g cm^{-3}
enthalpy change of combustion of ethanol	–1276 kJ mol^{-1}

(iii) The contribution from bioethanol is not counted when the CO_2 footprints of the E fuels are compared. Using your answer to **(d)(ii)** and any other information given, suggest whether E5 or E10 fuel is the preferred fuel. **[2]**

(i)



$$\Delta H_c = \sum \text{B.E.(bonds broken)} - \sum \text{B.E.(bonds formed)}$$

$$= 7\text{B.E.(C–C)} + 18\text{B.E.(C–H)} + \frac{25}{2}\text{B.E.(O=O)}$$

$$-\left[16\text{B.E.(C=O in CO}_2) + 18\text{B.E.(O–H)}\right]$$

$$= \left(7 \times 350 + 18 \times 410 + \frac{25}{2} \times 496\right) - (16 \times 805 + 18 \times 460)$$

$$= 16030 - 21160 = \underline{-5130\ \text{kJ mol}^{-1}}$$

(ii) ethanol: $\dfrac{-1276\ \text{kJ mol}^{-1}}{46.0\ \text{g mol}^{-1}} = -27.74\ \text{kJ g}^{-1}$

$-27.74\ \text{kJ g}^{-1} \times 0.789\ \text{g cm}^{-3} = -21.89\ \text{kJ cm}^{-3}$

octane: $\dfrac{-5130\ \text{kJ mol}^{-1}}{114.0\ \text{g mol}^{-1}} = -45.00\ \text{kJ g}^{-1}$

$-45.00\ \text{kJ g}^{-1} \times 0.703\ \text{g cm}^{-3} = -31.635\ \text{kJ cm}^{-3}$

energy released from 1 dm³ of E5 fuel

$= \left(\dfrac{95}{100} \times 1000\ \text{cm}^3 \times 31.635\ \text{kJ cm}^{-3}\right) + \left(\dfrac{5}{100} \times 1000\ \text{cm}^3 \times 21.89\ \text{kJ cm}^{-3}\right)$

$= 31148 \approx \underline{31100\ \text{kJ}}$

energy released from 1 dm³ of E10 fuel

$= \left(\dfrac{90}{100} \times 1000\ \text{cm}^3 \times 31.635\ \text{kJ cm}^{-3}\right) + \left(\dfrac{10}{100} \times 1000\ \text{cm}^3 \times 21.89\ \text{kJ cm}^{-3}\right)$

$= 30661 \approx \underline{30700\ \text{kJ}}$

(iii) Taking the energy released from burning 1 dm³ of E5 as 100%,

%tage of energy released from burning 1 dm³ of E10 $= \dfrac{30700}{31100} \times 100$

$= 98.7\%$

Taking the CO_2 produced from burning 1 dm³ of E5 as 100%,

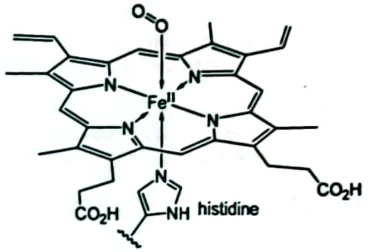
%tage of CO_2 produced from burning 1 dm³ of E10 $= \dfrac{90}{95} \times 100$

$= 94.7\%$

Although E10 fuels produces slightly less energy per dm³ compared t o E5 fuels, however, the **reduction in the percentage of CO_2 produced per dm³ of E10 is larger** and hence **E10 fuel** more environmentally benign and preferred.

[Total: 20]

2 (a) Gaseous molecules, such as CO and O_2, can bind to central Fe^{2+} ion in the porphyrin-iron(II) system of haemoglobin to form carboxyhaemoglobin and oxyhaemoglobin (shown in Fig. 2.1) respectively. In this binding process, water or another histidine molecule is also incorporated into the sixth coordination slot of the central Fe^{2+} ion.



oxyhaemoglobin

Fig. 2.1

The molecular orbitals of carbon monoxide and oxygen have similar shapes, and the difference in their molecular orbital arrangements occurs due to a phenomenon known as "s-p mixing".

(i) Sketch the molecular orbital diagrams for the CO and O_2 molecules. In your diagrams, indicate clearly the symmetry of the molecular orbitals, as well as the HOMO and LUMO of these molecules. [4]

Two types of electronic interactions take can occur in the binding of CO with a metal cation as shown in Fig. 2.2.

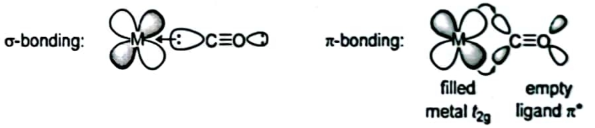


Fig. 2.2

(ii) By considering the two types of electronic interactions illustrated in Fig. 2.2 and your answer in (a)(i), suggest why the binding of carbon monoxide with haemoglobin is significantly stronger than that of oxygen. [2]

(iii) Explain why the Fe–O=O angle is 120° whereas the Fe–C≡O angle is 180°. [1]

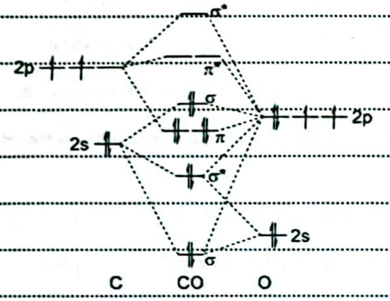
(iv) Draw an energy diagram showing the electrons arrangement in the 3d orbitals for the Fe^{2+} ion in oxyhaemoglobin. Hence, explain why oxyhaemoglobin has no unpaired electrons. [2]

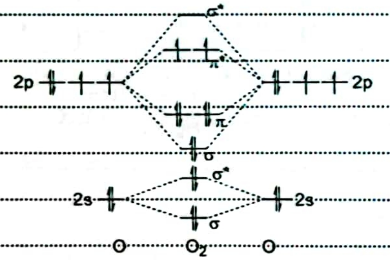
1% of haemoglobin exists in the form of methaemoglobin, in which oxygen oxidises Fe(II) to Fe(III):

$$\mathrm{Fe(II)} + \mathrm{O_2}\ \square\ \mathrm{Fe(III)—O_2^-}$$

(v) Suggest and explain how the bond length of O_2^- will differ from O_2. **[1]**

(i)

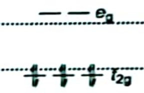




(ii) The π* molecular orbitals of O_2 are **singly occupied molecular orbitals**, while that of CO is unoccupied. Hence, O_2 can only serve as a **weak π-acceptor** as compared to CO and the metal-ligand π-backbonding cannot occur favourably. In terms of end-on bonding, **oxygen is more electronegative than carbon**, and hence the interaction is less favourable. Hence, CO exhibits a higher affinity with haemoglobin than oxygen.

(iii) The O in O_2 is **sp^2 hybridised**, while the C in CO is **sp hybridised**. Hence the Fe–O=O angle is 120° whereas the Fe–C≡O angle is 180°.

(iv) Oxyhaemoglobin is an octahedral complex and its 3d orbitals split into two energy levels. Since (a relatively stronger field ligand is involved) the **energy gap between the 3d orbitals is greater than that of the interelectronic repulsion**, all the electrons present are paired.



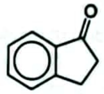
The electronic configuration of Fe^{2+} is given as [Ar] $3d^6$, and a **high-spin configuration is obtained** ($t_{2g}^4e_g^2$).

(v) O_2^- has **an additional electron in the π* anti-bonding orbital**, and hence its bond order is **1.5**, which is less than that in O_2. Since the bond order is lower, the **bond length** (and strength) of O_2^- **is longer than** that of O_2.

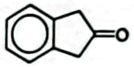
[Total: 10]

Question 3 starts on the next page

3 Indanone is a compound used in organic synthesis and exists as two positional isomers, namely 1-indanone and 2-indanone.



1-indanone



2-indanone

(a) **(i)** Outline the principles of ^1H nuclear magnetic resonance (NMR) spectroscopy. [3]

(ii) State and explain which isomer of indanone will give the ^1H NMR spectrum in Fig. 3.1.

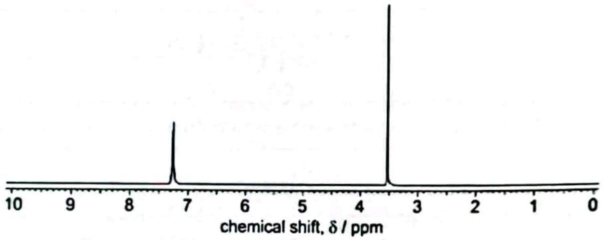


Fig. 3.1

[2]

(i) All nuclei are positively charged and those with odd atomic number possesses **spin**, giving rise to nuclear magnetic moments. When placed in an **external magnetic field**, the magnetic moments adopt specific orientations with respect to the external magnetic field, giving rise to **different energy states**. The nuclei can resonate and be **excited** from the ground state to higher energy states, by absorbing energy in the form of radio frequency, when the wavelength coincides with the energy gap. This **absorption of *radio* wavelength radiation** when nuclei excite is detected, giving rise to a nuclear magnetic resonance (NMR) **signal**.

The electron cloud surrounding the nuclei offers shielding of the nuclei from the external magnetic field. Different **chemical environment** even for the same type of nuclei gives rise to varying electron density and hence **differing extent of shielding**. As a result, the energy gap differs, resulting in distinct NMR signals, for the same type of nuclei in different chemical environment.

Explanation about being **coupled** to adjacent protons and **splitting** pattern.

(ii) The ^{1}H NMR spectrum shows **only one peak corresponding to the alkyl region**, hence there is **only one chemical environment corresponding to the alkyl region**. Thus, it must be **2-indanone since both CH_2 groups are equivalent** and will only give one peak on the ^{1}H NMR spectrum.

OR

The **^{1}H NMR spectrum shows a singlet in the alkyl region, implying that the ^{1}H atoms in the alkyl region have no neighbouring ^{1}H atoms**. This must be the **spectrum for 2-indanone since the CH_2 groups in 2-indanone have no neighbouring ^{1}H atoms**, whereas the **two CH_2 groups in 1-indanone are neighbouring ^{1}H atoms of each other**, which would cause the spectrum to show two triplet signals.

(b) The infrared (IR) spectrum of 2-indanone is given in Fig. 3.2.

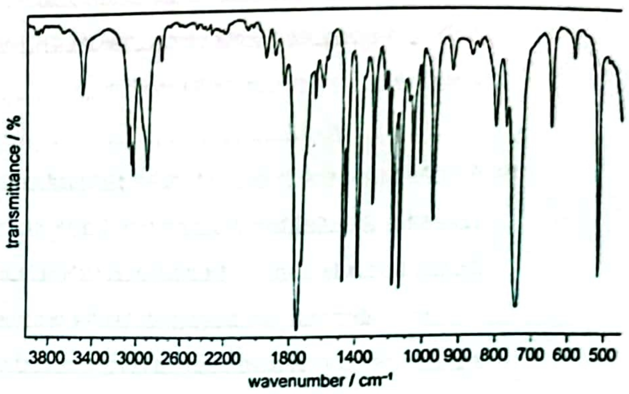
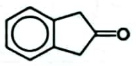
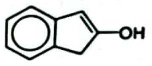


Fig. 3.2

Interestingly, although 2-indanone does not have an OH group in its structure, a small peak at 3500 cm^{-1} characteristic of the O–H stretch can be observed. This is because 2-indanone can exist in two forms, namely its keto form and its enol form.



keto form



enol form

Typical aliphatic ketones, such as propanone, very rarely exist in their enol form because it is highly unstable. As a result, the peak corresponding to the O–H stretch is never observed in the IR spectra of aliphatic ketones. However, the enol form in 2-indanone is sufficiently stabilised by its structure, resulting in the lifetime of the enol form being long enough for the O–H stretch to be detected by IR spectroscopy.

(i) With reference to suitable bond energy values in the *Data Booklet*, explain why the enol form of ketones is more unstable than the keto form. [1]

(ii) Explain why the IR spectrum of 2-indanone shows a small peak corresponding to the O–H stretch, while the IR spectrum of 1-indanone does not show a peak corresponding to the O–H stretch. [2]

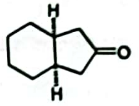
(iii) Suggest another peak on the IR spectrum of 1-indanone that could be used to distinguish it from the IR spectrum of 2-indanone and explain your answer. [2]

(i) The C=O bond is 740 kJ mol^{-1} but the C=C is only 610 kJ mol^{-1}. This implies that the C=O bond is significantly stronger than the C=C bond, imparting greater stability to the keto form than the enol form.

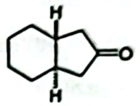
(ii) When 2-indanone exists in the enol form, it is stabilised by the additional conjugation of the C=C bond to the benzene ring. Hence, the lifetime of the enol form is long enough for the O–H stretching to be observed. However, 1-indanone is already conjugated to the benzene ring in the keto form. Hence, the enol form does not experience additional stability, thus making its lifetime shorter. Therefore, no O–H stretch is observed for 1-indanone.

(iii) The C=O stretch can be used to distinguish between 1-indanone and 2-indanone. Since the C=O bond in 1-indanone is conjugated to the benzene ring, it will have an absorption frequency smaller than 1700 cm^{-1}, while the C=O bond in 2-indanone will have an absorption frequency larger than 1700 cm^{-1} since it is not conjugated.

(c) The ring-reduced form of 2-indanone, 2-hydrindanone can exist as two diastereomers.

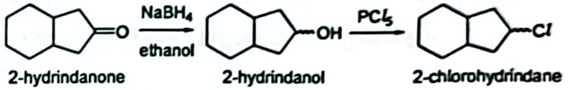


cis-2-hydrindanone



trans-2-hydrindanone

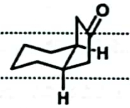
(i) Draw the most stable conformation for both *cis*- and *trans*-2-hydrindanone. [2]



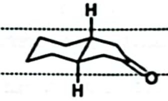
(ii) Using your answer to (c)(i), explain why the NaBH$_4$ reduction of *cis*-2-hydrindanone to the corresponding 2-hydrindanol is stereoselective, while that of *trans*-2-hydrindanone is not. [1]

(iii) Two peaks on the mass spectrum of 2-chlorohydrindane can be observed at *m/z* 103 and 105. State the ratios of the heights of the 103 and 105 peaks and propose the structure of the fragment that could give rise to these peaks. [2]

(i)



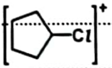
~~*cis*-2-hydrindanone~~



~~*trans*-2-hydrindanone~~

(ii) One face of the C=O in *cis*-2-hydrindanone is blocked by the 6-membered ring, while both faces of the C=O in *trans*-2-hydrindanone are equally exposed to nucleophilic attack by BH$_4^-$.

(iii) The ratio is 3 : 1



[Total: 15]

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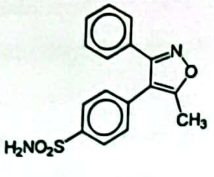
4 Valdecoxib is a non-steroidal anti-inflammatory used in the treatment of osteoarthritis, rheumatoid arthritis, and painful menstruation and menstrual symptoms.



valdecoxib

Valdecoxib is unique in its design as it contains an aromatic isoxazole ring, an analogue of furan, which is also aromatic like benzene.

isoxazole

furan

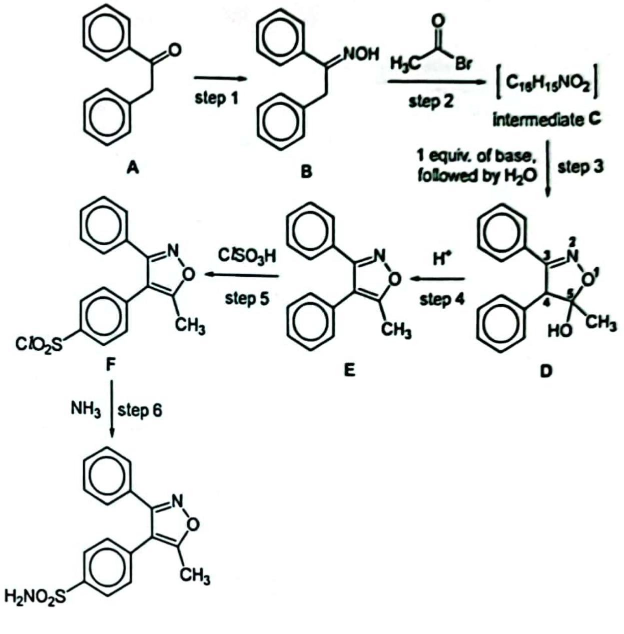
(a) Suggest why isoxazole is less susceptible to electrophilic aromatic substitution when compared to furan. [1]

The presence of **an additional electronegative N atom makes the molecule less nucleophilic** and the delocalized π electrons are less able to attack electrophiles.

OR The nitrogen atom on isoxazole has a tendency to (act as a nucleophile instead) **attack the Lewis acidic electrophiles**. This places a positive charge on the ring, further **deactivating** it from electrophilic substitution.

Question 4 continues on the next page

(b) Valdecoxib can be synthesised in the laboratory through the following scheme shown in Fig 4.1 which assembled the isoxazole ring elegantly.



valdecoxib

Fig. 4.1

(i) Suggest the reagent to be used in step 1. [1]

(ii) Draw the pair of stereoisomers present in **B** and state their configurations. [2]

(iii) Despite C–H bonds being non-polar, explain why the methylene (CH_2) proton in **B** is acidic. [1]

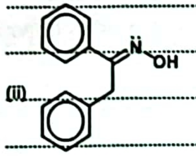
(iv) Suggest the identity of intermediate **C**. [1]

(v) The base initiates the cyclisation in step 3. Name and suggest a mechanism for step 3. You may use B:⁻ to represent the base in the mechanism. [3]

(vi) Using an appropriate Newman projection along the C4–C5 bond (with the C4 being the proximal atom), describe the E2 mechanism for step 4. [2]

(i) NH_2OH

(ii)



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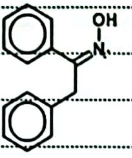

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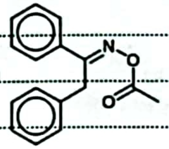
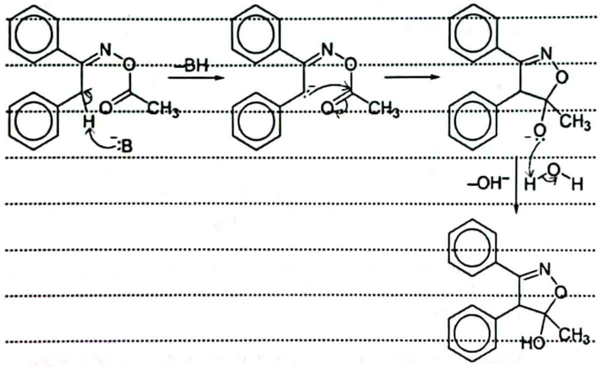
(iii) Removal of one methylene proton results in the formation of a conjugate base that is resonance stabilised.

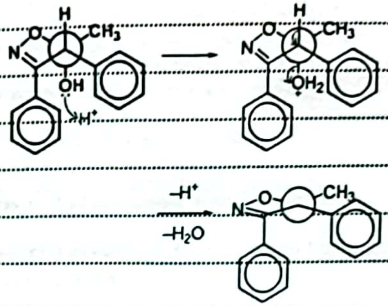
(iv)



(v) Nucleophilic addition

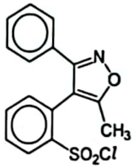


(v)



(c) (i) Draw the structure of the electrophile formed in step 5. Hence, write an equation to illustrate how the electrophile is generated in step 5. [2]

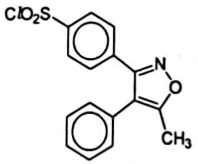
(ii) Explain why **G** is minor product of step 5.



G

[1]

(iii) Suggest why **H** is not formed in step 5.



H

[1]

(i) $3ClSO_3H \rightarrow ClSO_2^+ + 2ClSO_3^- + H_3O^+$

Electrophile:

(ii) There is less steric hindrance experienced by the electrophile (SO_2Cl^+) to approach the 4-position to form **F** as compared to the 2-position to form **G**.

(iii) The benzene involved in the electrophilic substitution for formation of **H** is in conjugation with a highly electronegative N that decreases electron density of the benzene, thus making it less susceptible to electrophilic attack than the other benzene.

[Total: 15]

Section B

Answer two questions from this section.

5 (a) Compound **R** is a flavouring agent. **R** only contains carbon, hydrogen, and oxygen. The IR spectrum and ^1H NMR spectrum of **R** are shown in Fig. 5.1 and Fig. 5.2 respectively.

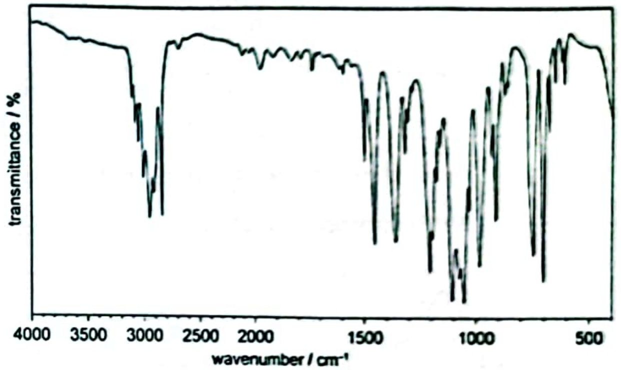


Fig. 5.1

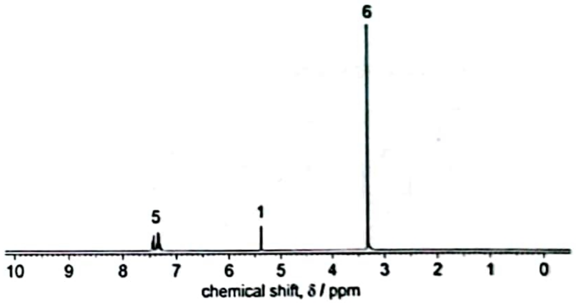


Fig. 5.2

From the mass spectrum of **R**, it is observed that the molecular ion has an *m/z* ratio of 152. The peaks at *m/z* ratios 152 and 153 have relative intensities of 0.244 and 0.0242 respectively.

Deduce the molecular formula and structural formula of compound **R**. Show your reasoning. [7]

(a) Number of C atoms = (100/1.1)(0.0242/0.244) = 9

Total M_r of H and O = 152 – 12×9 = 152 – 108 = 44

Since the integration ratio is 5 : 1 : 6, there should be 12 H atoms.

Not possible to have 24 H atoms, since there are only 9 C atoms.

Total M_r of O = 44 – 12 = 32 = 2(16)

Therefore, there must be 2 O atoms.

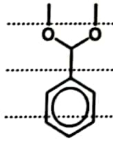
Molecular formula of R is $C_9H_{12}O_2$.

IR spectrum:

Frequency (cm^{-1})	Group present
3050	sp² C–H stretch
2950	sp³ C–H stretch
1050/1100	C–O stretch

NMR spectrum:

Chemical shift	Integration ratio	Spin multiplicity	Group present
7.5–7.3	5	Multiplet	Monosubstituted benzene
5.4	1	Singlet	C<u>H</u> bonded to two O atoms and benzene ring
3.3	6	Singlet	2 OC<u>H</u>$_3$



(b) Compound **S** ($C_8H_{10}O_2$) was synthesised with the intention of making it another analogue of a flavouring agent but was found to be unsuitable, as it was too corrosive to human skin. The NMR spectrum of **S** shows peaks with similar splitting patterns to **R**. However, for **S**, the signal between 7 to 8 ppm shows two doublets. **S** also has an additional singlet peak at 6.0 ppm that disappears upon addition of D_2O.

(i) Explain the purpose of adding D_2O to **S**. [1]

(ii) State the components of **S** that correspond to the two doublets and the singlet that disappears upon addition of D_2O. [2]

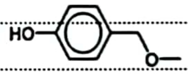
(iii) Hence, draw the skeletal structure of **S** and explain what could be causing the corrosive nature of **S**. [2]

(iv) Propose a chemical test to distinguish between **R** and **S**. [2]

(i) It is to determine the presence of labile protons.

(ii) A 1,4-disubstituted benzene corresponds to the two doublets and an OH group corresponds to the singlet that disappears upon addition of D_2O.

(iii)

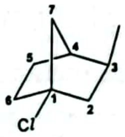


Since it is acidic enough to react with NaOH(aq), it could be corrosive to human skin.

(iv) Add neutral $FeCl_3$(aq) to both compounds. S will give a violet colouration but the solution with R will remain yellowish-brown.

Question 5 continues on the next page

(c) Consider compound **L** containing the bicyclo[2.2.1]heptane core below.



L

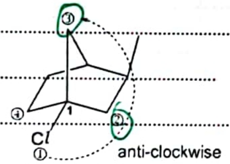
(i) Identify and assign the stereochemistry (*R* or *S*) at each of the chiral centres in **L**, and explain your answer. [3]

(ii) Draw the skeletal structure of a diastereomer of **L**. [1]

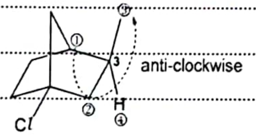
(iii) **L** was heated strongly with NaOH(aq) and after an extended period of heating, **L** was recovered unchanged.

Explain fully the observation made in the above experiment. [2]

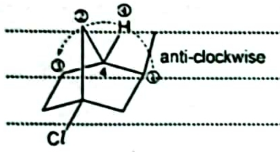
(i) The priority of the four groups around each chiral centre is assigned based on the **Cahn-Ingold-Prelog (CIP) rules**. With the lowest priority group (④) pointing away from the viewer, if the direction from highest priority ① → ② → ③ goes in a **clockwise** manner, the chiral centre is of **(*R*)-configuration**, and if the direction from ① → ② → ③ goes in a **anti-clockwise** manner, the chiral centre is of **(*S*)-configuration**.



C1 : *S*



C3 : *S*



C4 : *S*

(ii)

or

or

or

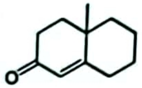
(iii) Nucleophilic substitution cannot occur at all, regardless of S_N1 or S_N2.

The S_N1 mechanism cannot occur because the α-carbon cannot exist as a trigonal planar structure due to the rigid bridged structure if heterolytic fission of the C–Cl bond occurs.

The S_N2 mechanism also cannot occur because the bridged cyclic structure presents too much steric hindrance to allow the OH^- nucleophile to perform a rear-side attack.

[Total: 20]

6 (a) The Woodward's rules for enones can be used to predict the wavelength of the absorption maximum, λ_{max}, which corresponds to a $\pi \rightarrow \pi^*$ transition. As the $\pi \rightarrow \pi^*$ transition is affected in a predictable fashion by structural modifications made, Woodward's rules assign different increments based on the structural modification made to a base molecule, such as a six-membered ring or acyclic parent enone. Compound **L** shown below is an enone and exhibits two uv absorption peaks at 215 nm (molar absorptivity, $\varepsilon = \sim 10^4$) and 305 nm ($\varepsilon = \sim 10^2$).



compound **L**

(i) By considering the allowed and forbidden electronic transitions involved, briefly account for the differences in the two peaks observed for compound **L**. [2]

Fig. 6.1 shows the predicted increment in the λ_{max} with respect to that of compound **L**, according to the Woodward's rule, for structures based on compound **L**.

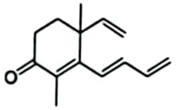
compound **M**
increment = 30 nm

compound **N**
increment = 10 nm

Fig. 6.1

(ii) Account for the increment of 30 nm for the λ_{max} of compound **M** with respect to that of compound **L**. [2]

(iii) Using information from Fig. 6.1, predict the λ_{max} of compound **P**.



compound **P**

[1]

(iv) Suggest the effect on the λ_{max} when the C=O bond in compound **P** is changed to a C=C bond. [1]

(i) The stronger UV absorption occurring at 215 nm is due to **allowed $\pi \rightarrow \pi^*$ transition**, while the weaker UV absorption occurring at 305 nm is due to a **forbidden $n \rightarrow \pi^*$ transition**. The energy gap of the $n \rightarrow \pi^*$ transition is smaller than that of the allowed $\pi \rightarrow \pi^*$ transition.

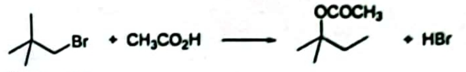
(ii) Relative to Compound L, Compound M has a **more extended conjugated π electron cloud**, and the energy gap between the π and π^* molecular orbitals **will be smaller.** Since $E = h\frac{c}{\lambda}$, the corresponding wavelength absorbed is also **longer** as the energy gap is smaller.

(iii) λ_{max} = 215 + 30 × 2 (2 double-bonds that extend conjugation) + 10 nm

= **285 nm**

(iv) Due to the **higher energy of the carbon 2p orbital** (as compared to the oxygen 2p orbital), the energy gap for the allowed $\pi \rightarrow \pi^*$ transition is smaller and the absorption moves to a **longer wavelength**.

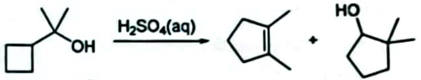
(b) Nucleophilic substitution is a key mechanism in synthesis chemistry.
1-bromo-2,2-dimethylpropane reacts with ethanoic acid to yield a single product. The process involves a rearrangement step.



1-bromo-2,2-dimethylpropane

(i) By considering the structure of the product formed, state and explain whether the S_N1 or S_N2 mechanism is operating for the reaction shown above. [2]

In a similar fashion, compound Q reacts with $H_2SO_4(aq)$ to yield two different products as shown in Fig. 6.2.



compound Q

Fig. 6.2

(ii) Describe the role of the acid used in the reaction. [1]

(iii) Suggest why the rearrangement to form a five-membered ring occurred in the reaction of compound Q with H_2SO_4. [1]

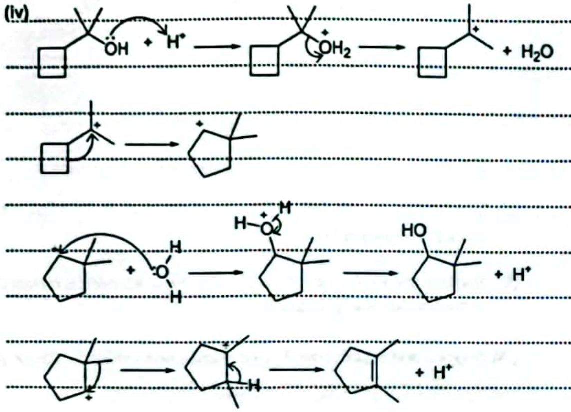
(iv) Describe the mechanism involved in the formation of each of the products shown in Fig. 6.2. [4]

(i) The mechanism for the **reaction is S_N1**. If the mechanism is S_N2, the $CH_3CO_2^-$ group will be attached to the C1 instead of C2 of the product. Hence the mechanism must involve the **formation of a carbocation initial such that the subsequent alkyl rearrangement to form a more stable carbocation is possible**.

(ii) The –OH is a poor leaving group, and the role of the acid is to **protonate the –OH to form $-OH_2^+$, which is a better leaving group**.

(iii) The rearrangement to form the five-membered ring was favoured as it reduced the steric strain present in the four-membered ring, which occurred as the bond angle deviated significantly from the ideal bond angle of 109.5° for sp³ hybridised carbon.

(iv)



(c) The hydrolysis of $Cl(CH_2)_nOH$ by water involves a nucleophilic substitution.

$$Cl(CH_2)_nOH + H_2O \rightarrow HO(CH_2)_nOH + HCl$$

The rate of hydrolysis can be determined based on the measurement of [Cl^-]. A series of $Cl(CH_2)_nOH$ were studied and the relative rate of production of [Cl^-] was measured.

n	2	3	4	5
relative rate	2.37	10.1	2220	90

With $n = 4$ or 5, an additional cyclic compound was also detected as the by-product of the reaction.

(i) Suggest the structure of the cyclic by-product formed when $n = 4$. [1]

(ii) Suggest why the relative rate of Cl^- formation is higher when $n = 4$ or 5. [1]

(iii) Suggest why the relative rate of Cl^- formation is higher when $n = 4$ than when $n = 5$. [1]

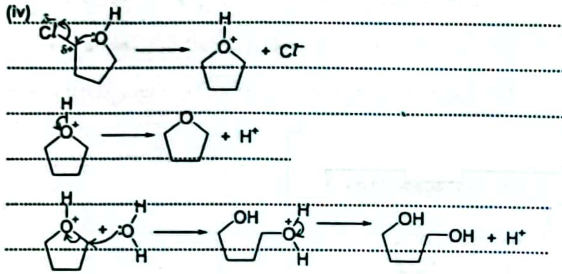
(iv) Draw mechanisms to show the formation of $HO(CH_2)_4OH$ and the cyclic by-product in (c)(iii) when $n = 4$. [3]

(i)

(ii) The higher relative rate of Cl^- formation is due to the neighbouring-group participation that occurs when $n = 4$ or 5, where the leaving group is first expelled by the neighbouring nucleophilic OH group due to the proximity.

(iii) In the formation of transition state for the five-membered ring, the lone pair on the –OH group can approach the reacting C atom in a more linear fashion (opposite to the leaving group) as compared to that for the six-membered ring, which leads to a greater overlap with the σ* molecular orbital of the C–C*l* bond of the reacting C atom. In turn, the activation energy for the reaction is lower, which leads to a higher rate of formation.

(iv)



[Total: 20]

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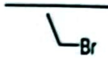
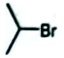
7 (a) When alkyl halides undergo S_N2 reaction mechanism, E2 reactions also occur competitively. In an experiment to study the competition of S_N2 and E2 reactions several alkyl bromides with sodium ethoxide, CH_3CH_2ONa, in ethanol at 55 °C. The experimental rate constants for both reactions and the fraction of alkene obtained are shown in Table 7.1.

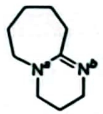
Table 7.1

substrate	k_{S_N2} / 10^{-5} dm^3 mol^{-1} s^{-1}	k_{E2} / 10^{-5} dm^3 mol^{-1} s^{-1}
	118	1.2
	2.1	7.6
	□2.1	79

(i) Explain why k_{E2} increases while k_{S_N2} decreases as the alkyl bromides become more substituted in Table 7.1. [3]

(ii) Suggest and explian how k_{E2} will change when ethoxide is replaced with ammonia in the reaction with $(CH_3)_2CHBr$. [1]

(iii) Suggest and explain how k_{S_N2} will change when ethoxide, $CH_3CH_2O^-$, is replaced with DBU in the reaction with $(CH_3)_2CHBr$.



DBU

[1]

(iv) Despite having two nitrogens atoms, N^a and N^b, DBU only has one measurable pK_b at 1.1 in 1 mol dm^{-3} aqueous solution. With reference to the structure of the conjugate acid of DBU, upon protonation at N^a and N^b, respectively, suggest which nitrogen atom is being assigned with this pK_b value. Hence, explain why there is only one measurable pK_b value. [3]

(v) Using $(CH_3)_2CHBr$ and ethoxide, $CH_3CH_2O^-$, as reactants, illustrate the transition states for the S_N2 and E2 reaction mechanisms, showing the stereochemistry clearly. [2]

(vi) **Using concepts of thermodynamics, explain how the use of a high temperature increases the yield of alkene from $(CH_3)_2CHBr$.** **[2]**

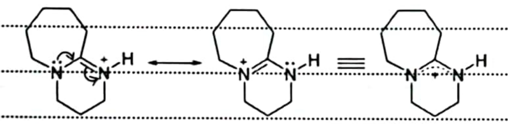
(i) As the alkyl bromides become more substituted from primary to secondary to tertiary, it **becomes increasing more sterically hindered around the electron-deficient α-carbon**, and hence increasingly more difficult for the nucleophile to approach and attack the α-carbon, causing k_{S_N2} to decrease.

On the other hand, it becomes increasing easier for the base to abstract a β-H from the adjacent C to **form more stable elimination products with with an increasing number of alkyl substituents on the resultant C=C double bond**. In addition, there is an **increasing number of H atoms that can be eliminated** as the alkyl bromides become more substituted. Hence k_{E2} increases.

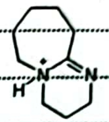
(ii) The k_{E2} **decreases as ammonia is a weaker base than ethoxide.**

(iii) The k_{S_N2} **decreases as DBU is a bulky or sterically hindered non-nucleophilic base.**

(iv) The conjugate acid derived from protonation at N^b is **resonance stabilised** via delocalisation of the lone pair of electrons on N^a:



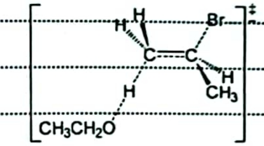
while that derived from protonation at N^a is a **localised** 3° ammonium ion:



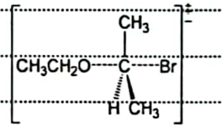
Hence the pK_b value is assigned to N^b.

Since the **lone pair of electrons on N^a is effectively delocalised into the C=N⁺**, the lone pair is **not available for donation** to a H^+, and hence essentially not basic.

(v) The transition states are



E2



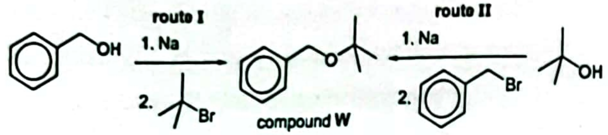
S_N2

(vi) $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$

Elimination reactions has a **more positive entropy change** compared to substitution reaction due to **greater number of products formed**.

The higher the temperature, **the more positive the $T\Delta S^{\ddagger}$, the more negative the $\Delta G^{\ddagger}$**. Hence yield of the eliminated products increases.

(b) The following scheme shows two synthetic routes to the same product, compound W. Explain why both synthetic routes lead to poor yield of W.



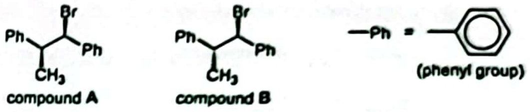
[2]

For route I, elimination reaction is likely to occur leading to formation of side products.

For route II, the $(CH_3)_3CO^-$ poses considerable steric hindrance in the nucleophilic substitution to form Compound W.

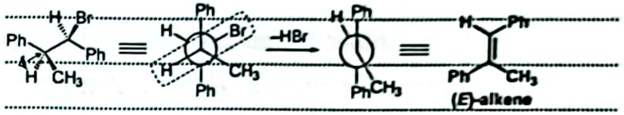
Question 7 continues on the next page

(c) In the presence of a strong base, compounds A and B undergoes E2 elimination to give the respective *(E)*- or *(Z)*-alkenes, stereospecifically.

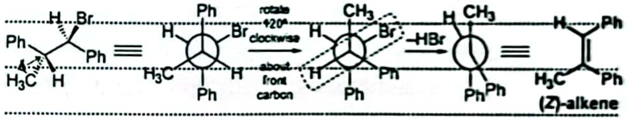


With the aid of appropriate *Newman projections*, determine the major products of elimination of compounds A and B. [2]

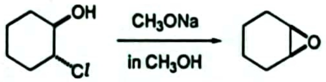
Compound A



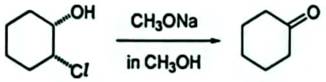
Compound B



(d) Treatment of *trans*-2-chlorocyclohexanol with a strong base such as sodium methoxide, $NaOCH_3$, in methanol yields 1,2-epoxycyclohexane, but reaction of the *cis* isomer under the same conditions yields cyclohexanone. With the aid of appropriate stereochemical structures, propose mechanisms for both reactions.



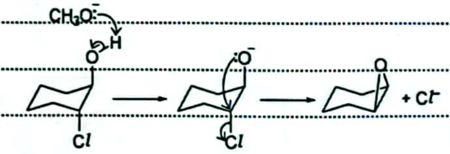
trans-2-chlorocyclohexanol 1,2-epoxycyclohexane



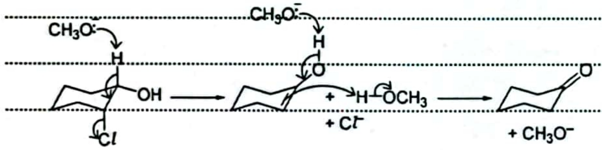
cis-2-chlorocyclohexanol cyclohexanone

[4]

trans-2-chlorocyclohexanol



cis-2-chlorocyclohexanol



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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.