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

CANDIDATE NAME

CIVICS GROUP | 2 | 1 | – | | |

INDEX NUMBER | | |

CHEMISTRY

Paper 1

9813/01

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.

[Turn Over

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]

(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]

(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]

(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]

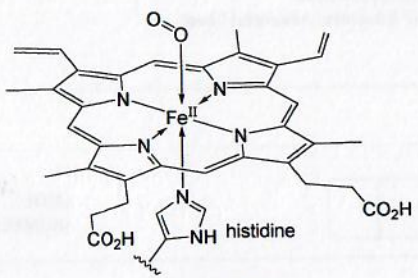
(ii) Using for your answer to **(d)(i)** and the information below, calculate the energy, in kJ, released when 1 dm^3 each of both E5 and E10 fuel is burnt. [2]

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]

[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.

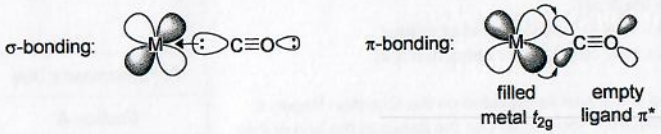


Fig. 2.2

(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]

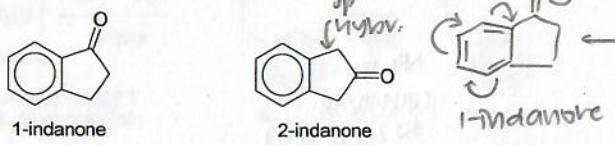
1% of haemoglobin exists in the form of methaemoglobin, in which oxygen oxidises Fe(II) to Fe(III):

$$Fe(II) + O_2 \rightleftharpoons Fe(III)—O_2^-$$

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

[Total: 10]

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



*already resonance stabilised so no incentive to go to enol form as no additional stabilisation can occur

(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.

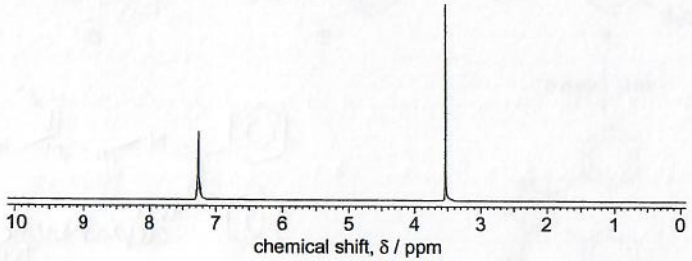


Fig. 3.1

[2]

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

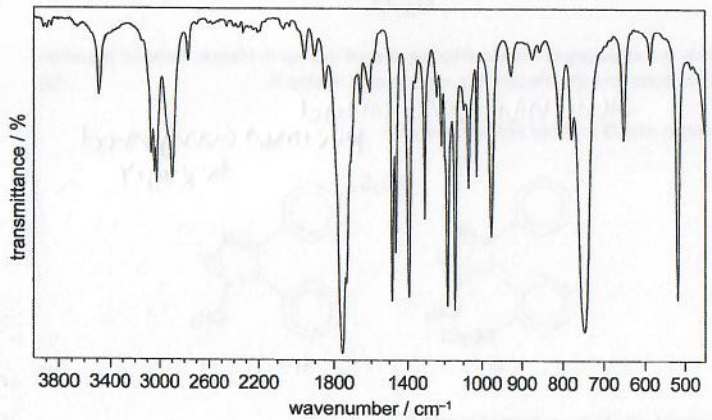
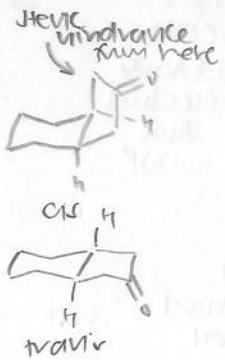


Fig. 3.2



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.

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]

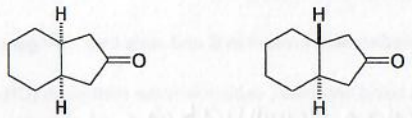
B.E of C=O > B.E of C=C ∴ keto more thermod. stable

(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]

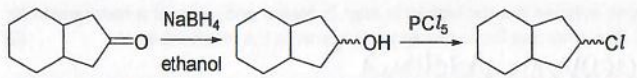
(iii) Suggest another peak on the IR spectrum of 1-indanone that could be used to distinguish it from the IR spectrum of 2-indanone and explain your answer. [2]

* wavenumber of C=O peak or that in 1-indanone is conjugated and in 2-indanone is not.

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



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

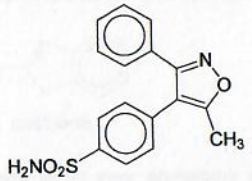


(ii) Using your answer to **(c)(i)**, explain why the $NaBH_4$ reduction of *cis*-2-hydrindanone to the corresponding 2-hydrindanol is stereoselective, while that of *trans*-2-hydrindanone is not. [1]

(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]

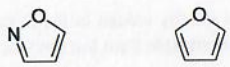
[Total: 15]

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]

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

(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]

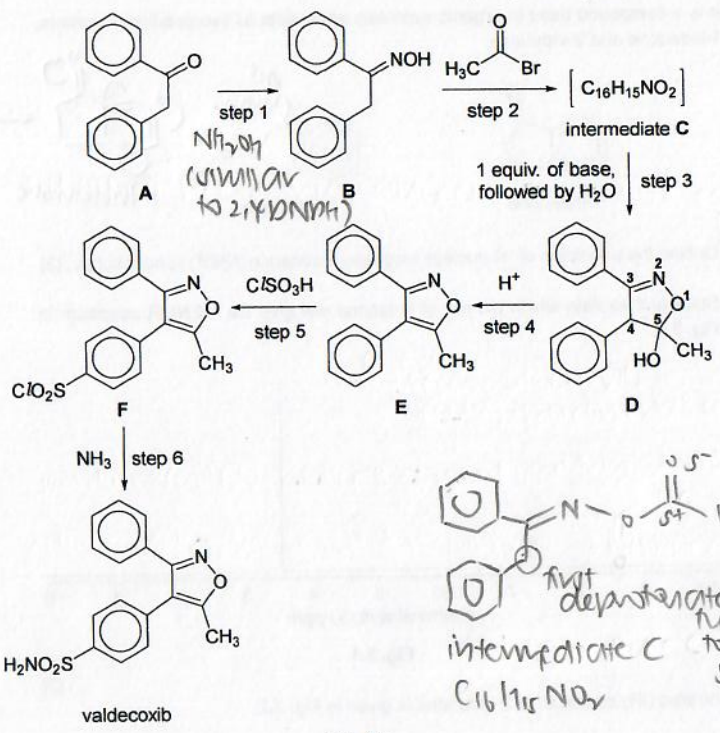
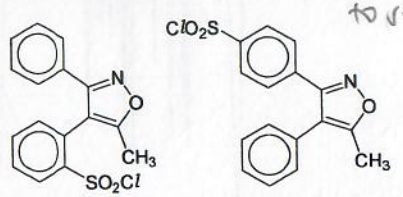


Fig. 4.1

(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 H [1]

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

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 ^{1}H NMR spectrum of **R** are shown in Fig. 5.1 and Fig. 5.2 respectively.

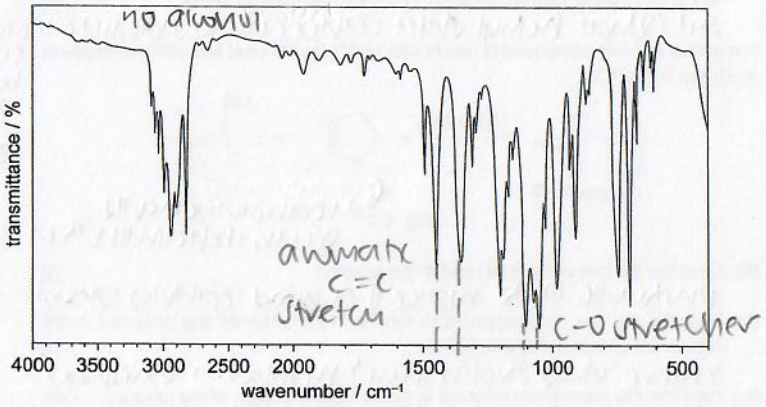


Fig. 5.1

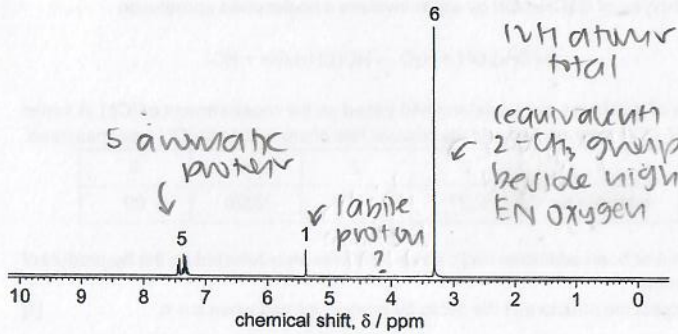


Fig. 5.2

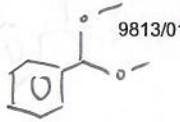
From the mass spectrum of **R**, it is observed that the molecular ion has an *m/z* ratio of 152. The peaks at *m/z* ratios 152 and 153 have relative intensities of 0.244 and 0.0242 respectively.

estimated 20 atoms

$n(C)\text{ atoms} = \frac{1w}{1.1} \times \frac{0.0242}{0.244} = 9C\text{ atoms}$

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

molecular f: $C_9H_{10}O_2$ DoU = 4 (benzene ring)



(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]

determine presence of labile proton

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

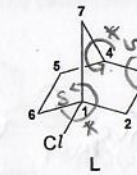
1,4-disub. benzene ring & OH group disappears

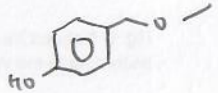
(iii) Hence, draw the skeletal structure of **S** and explain what could be causing the corrosive nature of **S**. [2]

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

Na(s), Effervescence of CO_2

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





= corrosive component

(C) decreasing priority:

C1: Cl > C > C > C6 (S)

C2: C4 > C > Me > H (S)

C4: C3 > C > C5 > H (S)

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

name using CIP rules

(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.

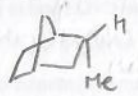
Explain fully the observation made in the above experiment. [2]

[Total: 20]

X S_N1 (a-carbon cannot exist as a trigonal planar)

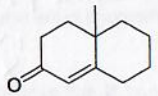
X S_N2 (too much steric hindrance & cannot attack from the rear due to spatial considerations)

(ii) Diastereomer of L:



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 ($\varepsilon = \sim 10^2$).

allowed transition



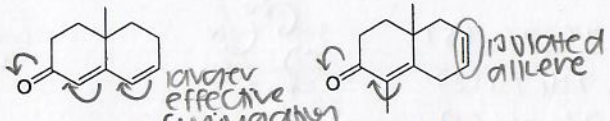
compound **L**

① weak absorption due to forbidden transition ca $n \rightarrow \pi^*$

② λ_{max} of $n \rightarrow \pi^*$ longer as the $n \rightarrow \pi^*$ gap smaller than the $\pi \rightarrow \pi^*$ gap.

(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

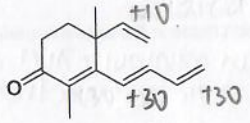
compound **N**
increment = 10 nm

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]

(Cl) O

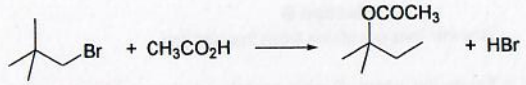
(iii) Using information from Fig. 6.1, predict the λ_{max} of compound **P**.



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. more effective conjugation as LEN ↓ [1]

(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.

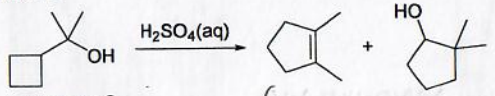


1-bromo-2,2-dimethylpropane

(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]

S_N1 so that methyl shift can occur to stabilise carbocation formed by losing it into a 3° carbocation

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**

↳ 2 rearrangement occur, then elimination

Fig. 6.2

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

protonate OH to make it a good leaving group

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

relieve ring strain from 4 member → 5 member

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

(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]

Neighbouring-group participation due to proximity

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

n=4 can provide a more linear approach in the transition state than the n=5 six-membered ring ↳ greater overlap with the σ* molecular orbital of the C–Cl bond at reacting atom

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

[Total: 20]

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

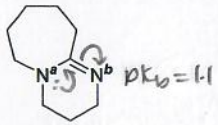
- S_N2 disfavoured increasing steric load around α-carbon.
- E2 favoured increasing no. of H atom that can be abstracted ② more stable elimination product due to hyperconjugation

(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]

k_{E2} decreases as NH_3 is a weaker base.

(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]

① resonance stabilisation ② positive charge when N_b is protonated ③ lone pair on N_a is delocalised ∴ reduced availability

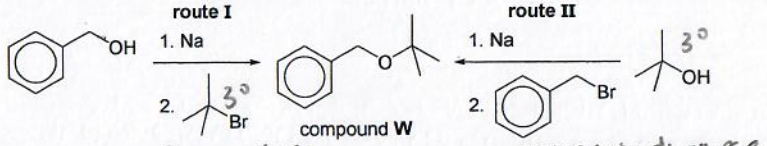
(v) Using $(CH_3)_2CHBr$ and ethoxide, $CH_3CH_2O^-$, as reactants, illustrate the transition states for the S_N2 and E2 reaction mechanisms, showing the stereochemistry clearly. [2]

$\Delta G = \Delta H - T\Delta S$

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

Elimination reactions have higher ΔS than substitution reactions as more products

(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**.

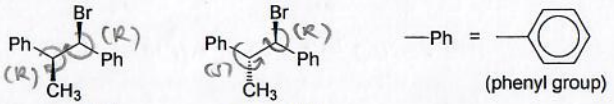


Elimination likely

Benzyl bromide unreactive

[2]

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

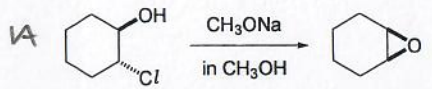


E-isomer

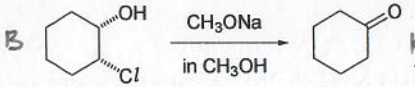
Z-isomer

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

(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

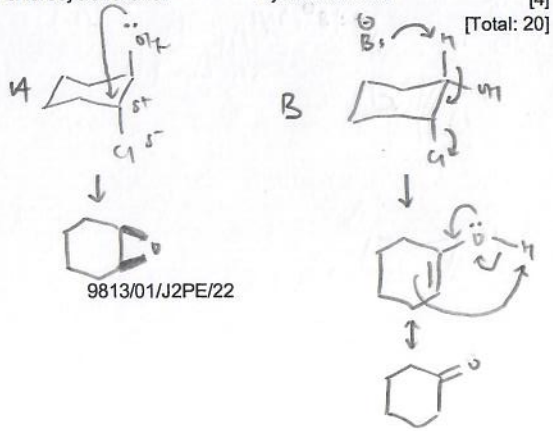


cis-2-chlorocyclohexanol cyclohexanone

keto-enol tautomerisation

[4]

[Total: 20]



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

CHEMISTRY

Paper 1
INSERT

9813/01
22 September 2022

2 hours 30 minutes

INSTRUCTIONS

This insert contains information for Question 1. **Do not write your answers on the insert.**

This document consists of 4 printed pages.

Information for Question 1

Environmental problems associated with the use of fossil fuels as well as their expected scarcity in the near future requires a search for new alternative fuels produced from renewable sources, notably biomass, the material produced by the growth of microorganisms, plants or animals. Bioethanol is such an alternative fuel.

Bioethanol can be produced from renewable feedstocks, mainly lignocellulosic biomass, and waste; the possibility to use autochthonous feedstocks reduces our dependency on imported fossil fuels, which ensures increased political and economic stability.

Extract 1 (adapted from D Kennes et al., *J. Chem. Technol. Biotechnol.*, 2015, 91, 304)

Bioethanol is a biofuel that can be obtained from biomass and waste as feedstocks through fermentation.

First Generation Bioethanol

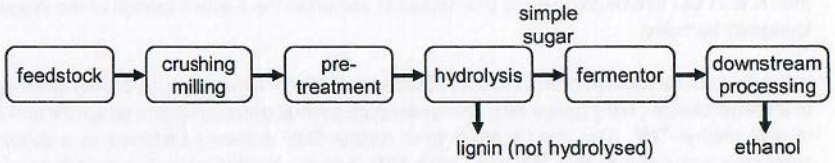
First generation bioethanol production is a mature technology used at commercial scale. The biofuel is obtained through the fermentation of carbohydrates available in feedstocks containing sugars or starch, such as sugarcane, sugar beet, corn, or wheat, among others.

Second Generation Bioethanol

Second generation bioethanol is obtained mainly from lignocellulosic materials (wood), the stems and roots of trees and woody plants consisting of brittle and fibrous tissues. The dominant components found in lignocellulosic feedstocks are lignin (~30%), cellulose (~40%), and hemicellulose (~30%). Lignocellulose is considered to be the most abundant type of renewable biomass on Earth.

Two major routes allow conversion of the feedstocks to fermentable substrates, *i.e.* the hydrolytic route and the thermochemical route.

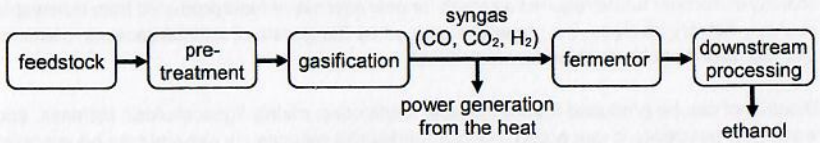
In the hydrolytic route, the feedstock undergoes a pre-treatment stage first, aimed at facilitating the subsequent hydrolytic treatment. Chemical, physical or biological pre-treatments can be applied.



The pre-treatment attacks the lignin and hemicellulose polymers and makes cellulose more accessible in the next hydrolytic stage. The hydrolytic treatment uses enzymes to convert the cellulose polymer to simple, fermentable sugars, mainly glucose. Simple sugars obtained from hemicellulose and cellulose are then fermented by yeasts to bioethanol.

$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$$

In the thermochemical alternative, the feedstock is gasified, yielding syngas – a mixture largely composed of CO, CO_2 and H_2 – which can be fermented anaerobically, usually by *clostridia* (a family of bacteria), to ethanol or other products.



In both cases, downstream processes are then applied to recover and purify the biofuel.

Extract 2 (adapted from L J R Nunes, *Results in Engineering*, 2022, 12, 100408)

Gasification is a thermochemical process caused by changes in the structure of biomass at high temperatures (above 750 °C), in the presence of a gasification agent, which results in a greater production of gaseous products (85%), and small amount of tar (5%), char, and ash (10%), being classified according to the gassing agent used: air, steam, steam and oxygen, air and steam, or oxygen-enriched air.

This gaseous product derived from the gasification of biomass, or other solid fuels, is known as synthesis gas (syngas). Syngas is a mixture of H_2, CO and CO_2. It can be used for the generation of electricity by direct combustion, for the operation of fuel cells if properly purified, or to produce biofuels and chemicals.

Extract 3 (adapted from J Daniell et al., *Energies.*, 2012, 5, 5372)

Acetogens are a group of bacteria capable of fermenting CO and/or CO_2 and H_2 into acetyl coenzyme A (acetyl–CoA) and from there into ethanoic acid, ethanol and other metabolic end-products, *via* the reductive acetyl-CoA pathway, also known as the Wood-Ljungdahl pathway.

The Wood-Ljungdahl pathway is illustrated in Fig. 1.1 and is made up of carbonyl (sometimes referred to as "Eastern") and methyl (or "Western") branches. CO enters the pathway through two routes. One molecule can directly enter the Western branch as CO, while another molecule of CO can be oxidised to CO_2 (stage **I**) and enter the Eastern branch of the Wood-Ljungdahl pathway.

In the Eastern (or methyl) branch, CO_2 is reduced to HCO_2^- (formate), which is then attached to tetrahydrofolate (THF) (stage **III**). This undergoes several transformations (stage **IV** to **VI**) to give methyl–THF. The methyl group from methyl–THF is then transferred to a cobalt-containing iron-sulfur protein (FeS-P) (stage **VII**), and this methyl group is provided as the methyl group of acetyl–CoA (stage **IX**). Used by all organisms in one-carbon metabolism, the genes encoding the enzymes that operate in the Eastern branch are ubiquitous.

The Western (or carbonyl) branch is unique to anaerobic microorganisms. CO can either be used directly, or generated from CO_2 (stage **VIII**), and serves as the carbonyl group for acetyl-CoA synthesis.

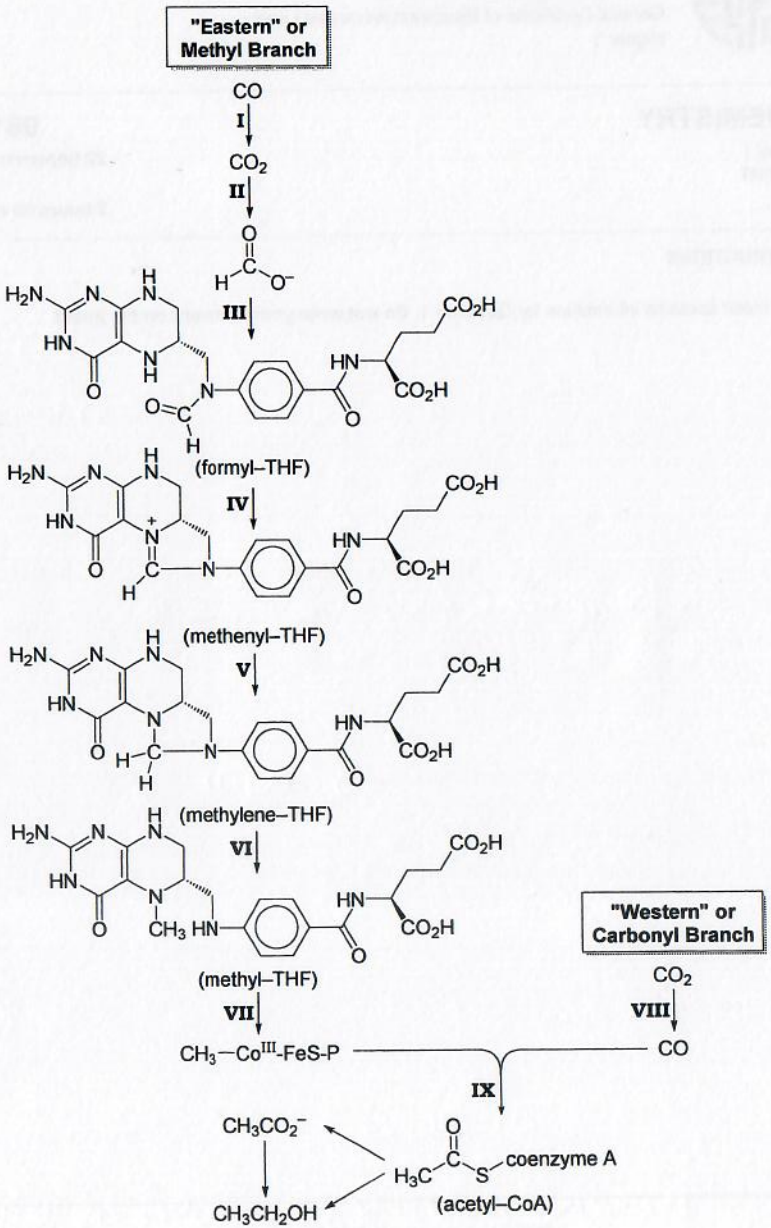


Fig. 1.1