A COLLABORATION BETWEEN
DUNMAN HIGH SCHOOL, RIVER VALLEY HIGH SCHOOL &
TEMASEK JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 3

CANDIDATE NAME

CLASS

H3 CHEMISTRY

9813/01

Paper 1
INSERT

25 September 2020
2 hour 30 minutes

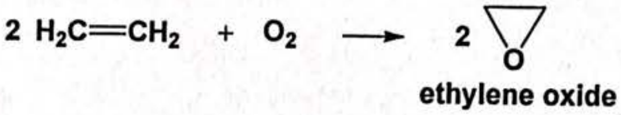
INSTRUCTIONS

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

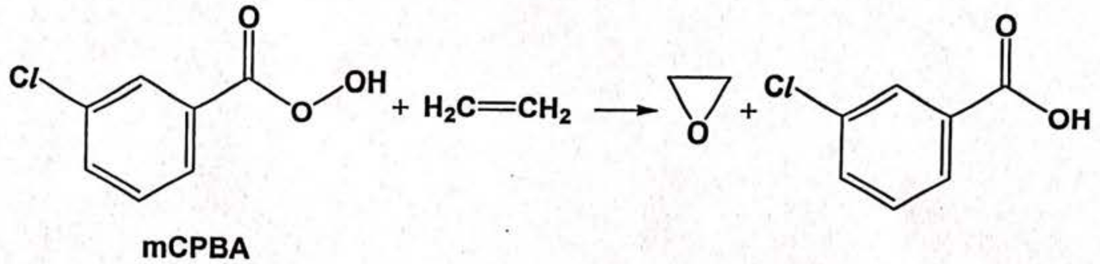
This document consists of **2** printed pages.

Information for Question 1

Epoxides are useful intermediates for the manufacture of a diverse set of chemical products. Traditionally, ethene can be oxidised to ethylene oxide using molecular oxygen at 270 – 290 °C and 1 – 3 MPa with a silver–based catalyst.



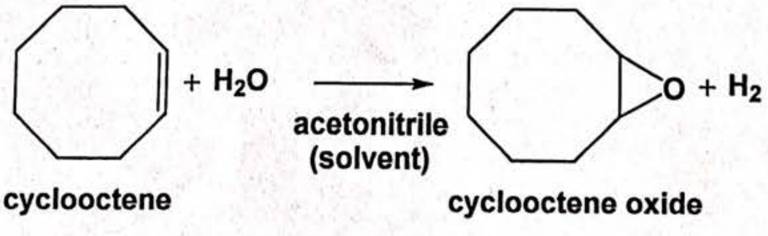
Ethene can also be directly oxidised in the laboratory using peroxide–based oxidants such as *m*–chloroperoxybenzoic acid (mCPBA).



Abstract 1 (*J. Am. Chem. Soc.* 2019, 141, 6413–6418)

Electrochemical epoxidation

Here, we demonstrate a sustainable and safe route to epoxidise alkene substrates using water as the oxygen atom source at room temperature and ambient pressure. Manganese oxide nanoparticles are shown to catalyse cyclooctene epoxidation with Faradaic efficiency of 30%. This means that 30% of the electric current supplied to the cell goes into making the desired product. These Faradaic losses are due to energy loss as heat and formation of the cyclooctanone byproduct. Isotopic studies using $H_2{}^{18}O$–enriched electrolyte and detailed product analysis reveal an overall reaction in which water and cyclooctene are converted to cyclooctene oxide and hydrogen. Electrokinetic studies provide insights into the mechanism of alkene epoxidation.



$M_r = 126.0$

Copyright Acknowledgements:

Questions 1 © Kyoungsuk Jin, Joseph H. Maalouf, Nikifar Lazouski, Nathan Corbin, Dengtao Yang and Karthish Manthiram *J. Am, Chem, Soc.* 2019, 141, 6413–6418

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Candidates answer on Question Paper.
Additional Materials: Data Booklet
Insert

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, highlighters, 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. Do not write anything on it.

The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **36** printed pages.

Section A

Answer **all** questions in this section.

1 The information provided in the insert is taken from a published scientific article. Other published articles may not agree with all of this information.

You should read the whole insert before you start to answer any questions and use the information it contains to answer the questions.

(a) State two advantages of the electrochemical epoxidation method compared to the current methods. [2]

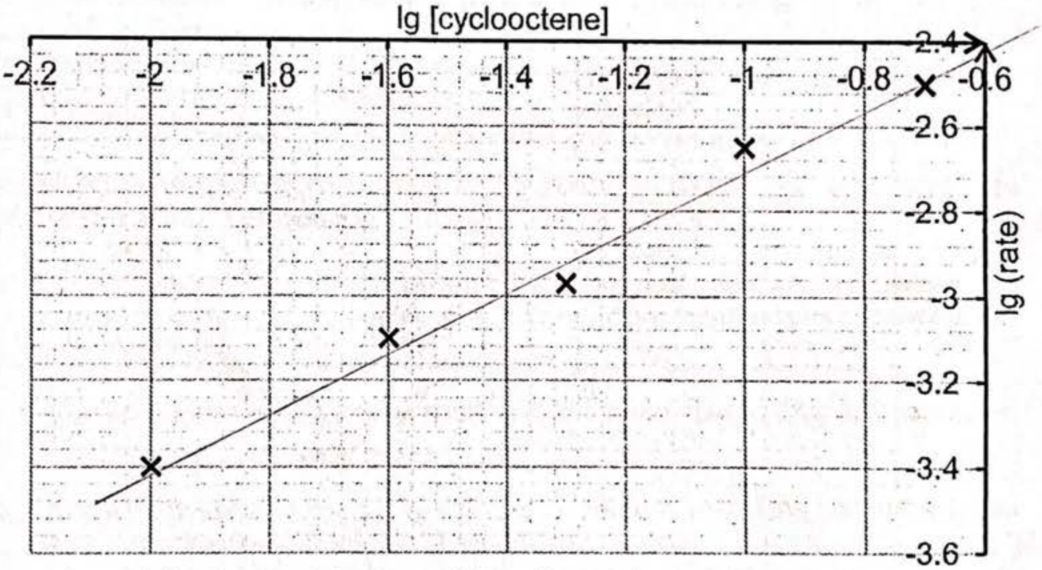
(b) **(i)** Write the balanced half–equation for the reaction at the anode. [1]

(ii) Hence calculate the total charge passed through the cell to produce 50 g of cyclooctene oxide. [2]

(c) **(i)** Outline how the oxygen source is confirmed to be water using isotopic studies. [2]

(ii) Suggest an area of further work to improve the system. [1]

(d) Kinetic studies were carried out in 5 mol dm^{-3} water and varying concentrations of cyclooctene. The results were plotted in the graph below.



Draw a best–fit line for the data above. Using the gradient of the graph, determine the order of reaction with respect to [cyclooctene] to 1 decimal place. Show your reasoning clearly. [3]

(e) The energy required to break the covalent bonds in one mole of epoxide ring is 105 kJ mol^{-1} less than the sum of relevant bond energies from the *Data Booklet*.

(i) Suggest a reason for this discrepancy. [1]

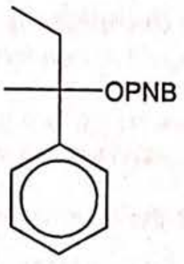
(ii) Using the *Data Booklet* and the information given in **(e)**, estimate the enthalpy change of reaction for the epoxidation of ethene using the method described in **Abstract 1**. [2]

[ΔH_{vap} of water = + 40.8 kJ mol^{-1}; boiling point of ethylene oxide = 10 °C]

(iii) Predict how the spontaneity of the epoxidation of ethene using the method in **Abstract 1** changes as temperature increases to 80°C. Explain your answer. [2]

[Total: 16]

2 Steigman and Hammett published the results of their research into the stereochemistry of the nucleophilic substitution reactions of an enantiomerically pure compound **X**.



compound **X**

OPNB =

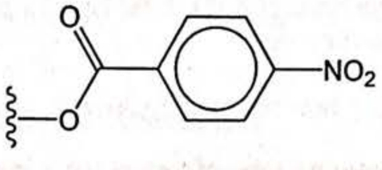
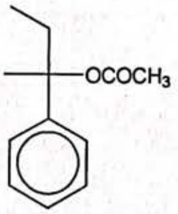
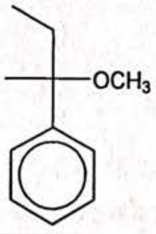
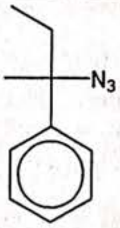
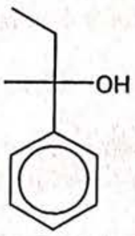


Table 2.1 shows three reacting systems they investigated.

Table 2.1

system	reagents and conditions	product	stereochemical results	
			% retention	% inversion
I	$CH_3CO_2^-K^+$ in CH_3CO_2H at 23 °C	 $OCOCH_3$	47.5	52.5
II	NaN_3 in CH_3OH at 65 °C	 OCH_3	43	57
		 N_3	22	78
III	aqueous CH_3COCH_3	 OH	69	31

(a) **(i)** Explain how the stereochemical results could be obtained experimentally using a physical method. [1]

(ii) Deduce the most probable mechanism for system I. Justify your deduction using the structure of compound **X** and information about system I in Table 2.1. [3]

(iii) Suggest an advantage of dissolving the ionic salt, $CH_3CO_2^-K^+$, in CH_3CO_2H instead of another polar solvent for system I. [1]

(iv) Suggest an explanation for the difference in percentage inversion observed for the two products of system II. [1]

(v) Complete Fig. 2.1 by labelling the interaction between the anionic leaving group and the water molecule. Hence use it to explain the stereochemical result observed in system III. [2]

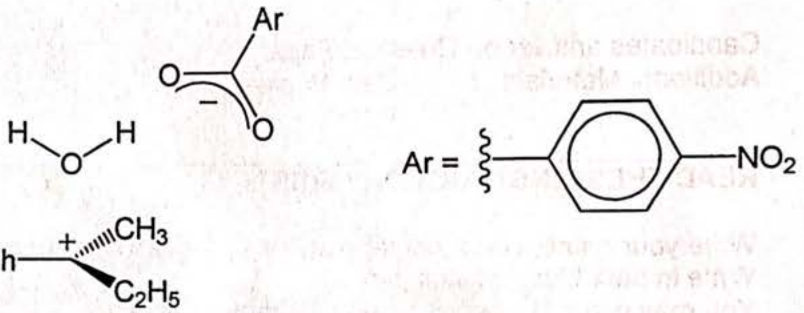
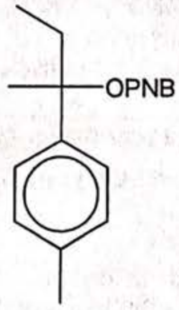


Fig. 2.1

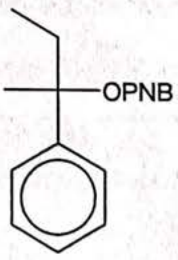
(b) **(i)** Using your answer in **(a)(ii)**, draw a labelled energy profile diagram for the reaction in system I. Assume that the reaction is exothermic. [2]

(ii) Hence explain whether the steady state approximation is applicable to the mechanism. [2]

(iii) Using your answer in **(b)(i)** and Hammond's postulate, predict how the rate of reaction of compound **Y** will differ from that of compound **X** under system I conditions.



compound **Y**



compound **X**

Explain your answer. [2]

[Total: 14]

3 The mechanism of elimination and substitution reactions are commonly based on the knowledge of the order of reaction, the relative reactivities of the reactants and structures of products.

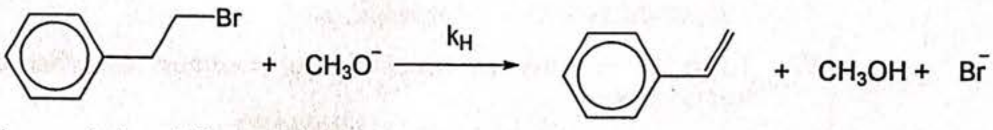
A useful tool for determining the mechanism is the deuterium kinetic isotopic effect (KIE). The deuterium KIE is the ratio of the rate constant for a compound containing hydrogen, k_H, to the rate constant observed for an identical compound with one or more hydrogen atoms substituted with deuterium atoms, k_D.

$$\text{deuterium kinetic isotopic effect} = \frac{k_H}{k_D}$$

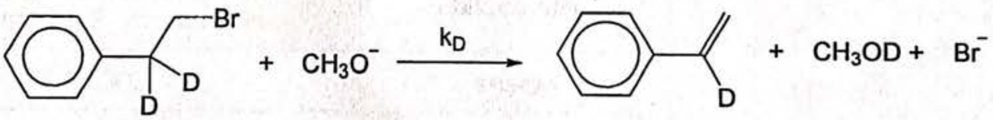
Hydrogen and deuterium behave the same chemically, but the C–H bond is stronger than the C–H bond by 3 kJ mol^{-1}. The rate constant and hence the overall rate of reaction will differ if the C–H bond is broken in the rate determining step.

Deuterium is ${}^{2}_{1}H$.

(a) To determing the mechanism for the elimination reaction between 1–bromo–2–phenylethane and sodium methoxide, the deuterium KIE experiment was conducted using 2–bromo–1,1–dideuterio–1–phenylethane.



1-bromo-2-phenylethane



2-bromo-1,1-dideuterio-
1-phenylethane

At 30 °C, the deuterium KIE for the reaction is 7.

With reference to the equation above and the bonds broken in the rate determining step, suggest the type of elimination reaction that 1–bromo–2–phenylethane has undergone. Explain your answer. [3]

When alkyl halides undergo S_N2 reaction mechanism, E2 reactions also occur competitively, due to similarities in reaction conditions, structure of substrate and solvent effects.

In 2006, Bierbaum and co–workers conducted a deuterium KIE experiment to study the competition of S_N2 and E2 reactions in the *gas phase* of several alkyl chlorides with hypochlorite ion, ClO^-. The experimental rate constants for several alkyl chlorides and their deuterated analogues are shown in Table 3.1.

Table 3.1

alkyl chloride	k / $cm^3\ s^{-1}$	deuterium KIE
CH_3CH_2Cl	2.25	0.99
CD_3CD_2Cl	2.27	
$(CH_3)_2CHCl$	1.74	1.71
$(CD_3)_2CDCl$	1.01	
$(CH_3)_3CCl$	2.33	2.31
$(CD_3)_3CCl$	1.01	

(b) Suggest an advantage of conducting a *gas phase* deuterium KIE experiment, as opposed to a similar experiment in the liquid phase. [1]

(c) **(i)** Using chloroethane and hypochlorite, ClO^-, as reactants, illustrate the transition states for the S_N2 and E2 reaction mechanisms, showing the stereochemistry clearly. [2]

(ii) Hence, suggest why the deuterium KIE is approximately 1 for S_N2 reactions. [1]

(iii) Explain the trend of the deuterium KIE in Table 3.1, making reference to the dominant reaction mechanism that has taken place. [2]

(d) In a separate experiment under similar conditions, $(CH_3)_2CHCl$ is reacted with CH_3COO^- instead of ClO^-.

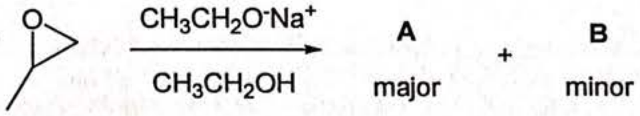
With reference to the acid dissociation constants listed in Table 3.2, suggest how the deuterium KIE will change. Explain your answer.

Table 3.2

acid	K_a / mol dm^{-3}
CH_3COOH	1.8×10^{-5}
$HClO$	2.9×10^{-8}

[2]

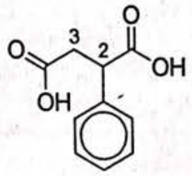
(e) 1,2–epoxypropane undergoes S_N2 reaction when treated with sodium ethoxide in ethanol. Two constitutional isomers **A** and **B** are formed in different proportions.



(i) Draw the mechanism leading to the formation of isomer **A**. [2]

(ii) Suggest the structure of isomer **B**. [1]

(f) Phenylsuccinic acid exists as 2 enantiomers. Its structure is shown below.



phenylsuccinic acid

(i) Draw the Newman projection along the C2–C3 axis of (*S*)-phenylsuccinic acid in its most stable conformation. [2]

(ii) Pure (+)-phenylsuccinic acid has an optical rotation of $[\alpha]_D = +168°$. A sample of phenylsuccinic acid is measured to have an optical rotation of $[\alpha]_D = -25°$.

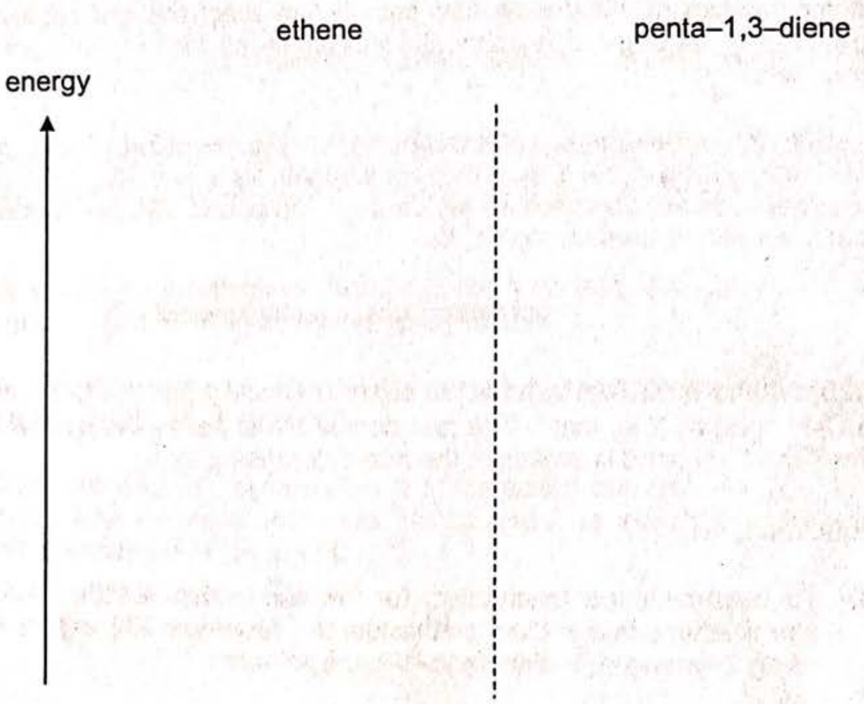
Determine the composition of (+)-phenylsuccinic acid and (–)-phenylsuccinic acid in the mixture. [2]

[Total: 18]

4 (a) Define the term "chromophore". [1]

(b) (i) On the same axis below, draw the π molecular orbital (MO) diagrams of ethene and penta–1,3–diene, showing the electrons. In your diagram, label the HOMO and the LUMO for both compounds. [3]

(ii) On your diagram below, identify the transitions that are most likely responsible for the absorption of UV light by each molecule. [1]



(iii) Table 4.1 lists the UV wavelength of maximum absorbance, λ_{max}, of two hydrocarbons.

Table 4.1

compound	wavelength of maximum absorbance, λ_{max} / nm
ethene	171
hexa–1,3,5–triene	268

Using your answer in **(b)** and the information given in Table 4.1, predict and explain the λ_{max} value of penta–1,3–diene. [3]

(c) When buta–1,3–diene and bromine are dissolved in ethanol, four different unsaturated products **A$_1$**, **A$_2$**, **B$_1$** and **B$_2$** are formed.

B$_1$ and **B$_2$** contains oxygen.
A$_1$ and **A$_2$** are positional isomers of each other.
B$_1$ and **B$_2$** are positional isomers of each other.

(i) Draw all four unsaturated products **A$_1$**, **A$_2$**, **B$_1$** and **B$_2$**. [2]

(ii) A detailed analysis of the reaction reveals that there are more than four unsaturated organic products. State the actual number of organic products and account for their presence. [2]

[Total: 12]

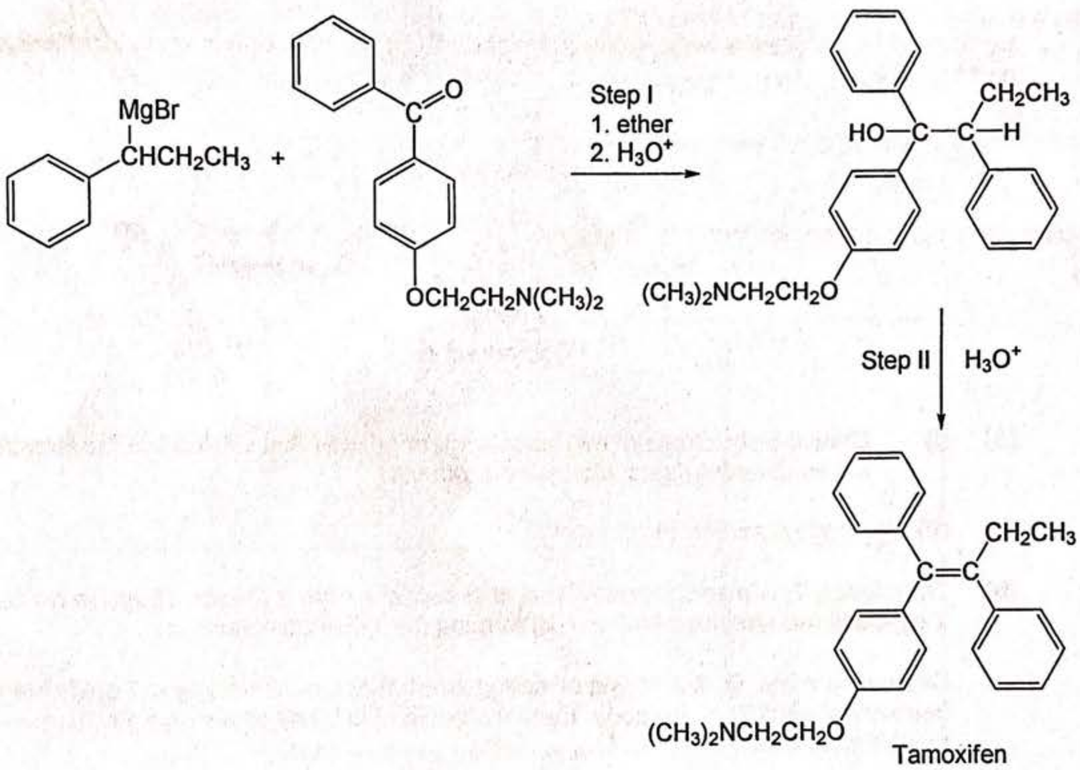
Section B

Answer **two** questions from this section.

5 Carbon-carbon double bonds are commonly present in biologically active entities and serve as versatile precursors for many different chemical transformations.

(a) The stereochemistry of C=C double bonds determines the properties of the molecules, and in the case of drugs, can influence pharmacological activity.

The following scheme outlines the synthesis of *Tamoxifen*, which is used in the chemoprevention of breast cancer.



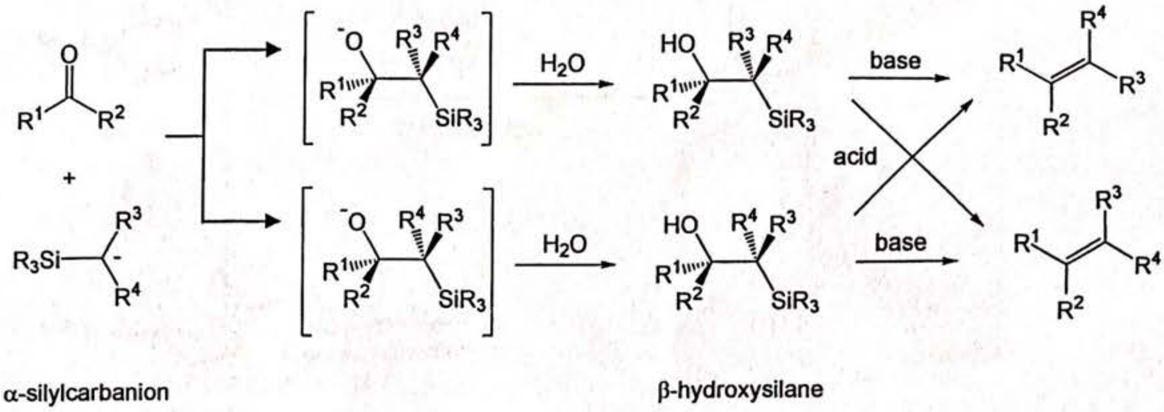
(i) With reference to the Step II in the reaction scheme shown above, name the type of reaction, and suggest a mechanism for the reaction.

You may represent $-OCH_2CH_2N(CH_3)_2$ as –OR. [3]

(ii) Explain why the reaction proceeds via the mechanism proposed in **(a)(i)**. [1]

(b) The stereo-defined synthesis of either the E or the Z isomer is crucial and has been one of the major topics in synthetic organic chemistry for many decades.

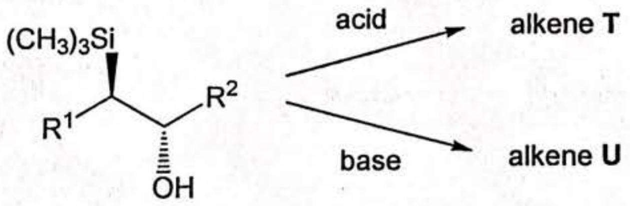
The Peterson olefination allows the preparation of alkenes from α-silylcarbanions.



One attractive feature of the Peterson olefination is that it can be used to prepare either the E or the Z isomer from the same β-hydroxysilane.

(i) Assuming R^1, R^2, R^3 and R^4 are different alkyl substituents, explain why a mixture of two β-hydroxysilane is formed in the reaction. [1]

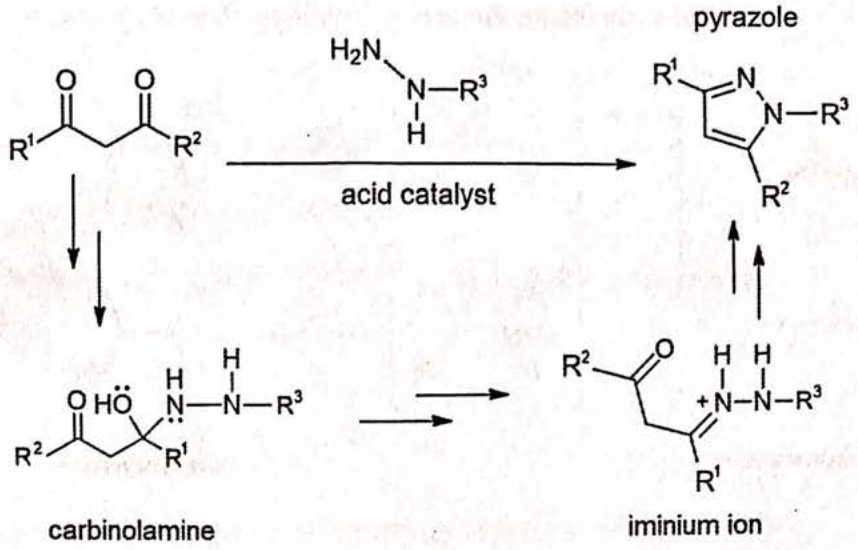
The β-hydroxysilane shown below undergoes Peterson olefination under acidic and basic conditions to form **T** and **U** respectively.



(ii) Draw the structures of alkenes **T** and **U**, identifying each alkene as the E or Z isomer. [2]

(iii) Using Newman projection, show the conformation that the β-hydroxysilane molecule must adopt for reaction under each condition. [2]

(c) The pyrazole ring is an important scaffold for the preparation of several new cyclooxygenase inhibitors, a type of anti-inflammatory drug. It may be synthesised using the following reaction:



(i) Explain why the reaction requires an acid catalyst. [1]

(ii) Suggest a mechanism to obtain the pyrazole ring from the iminium ion, given that it follows an addition–elimination mechanism. [3]

(d) The structures of two isomeric cyclohexyl chlorides derived from menthol are shown below.

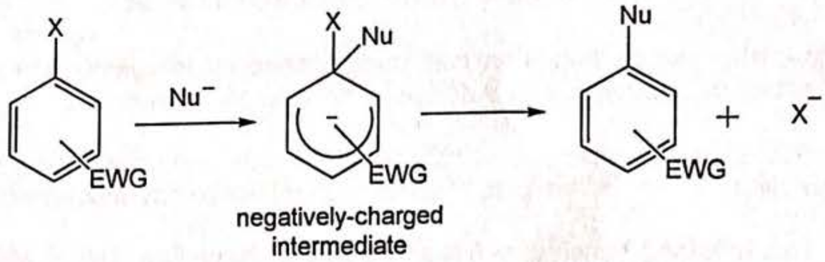
(i) Identify the R/S configuration about each chiral carbon of compound **B**. Hence, state the stereochemical relationship between **A** and **B**. [2]

(ii) Draw two possible chair conformations of **B**, hence comment on their relative stabilities. [3]

(iii) When **A** and **B** are separately treated with sodium ethoxide, one isomer reacts much faster than the other. Using your answer to **(d)(ii)**, account for this observation. [2]

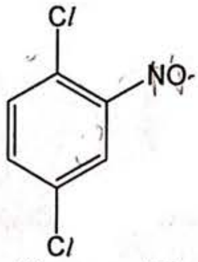
[Total: 20]

6 The reaction scheme of nucleophilic aromatic substitution (S_NAr) is shown below.



EWG: electron-withdrawing group.

Compound **A** undergoes S_NAr in the presence of OH^- to give only one monochlorinated compound **B**.



Compound **A**

(a) **(i)** Draw the structures of two anionic intermediates that will lead to the formation of two different monochlorinated products. [2]

(ii) Hence draw the structure of **B**. [1]

(b) Transferrin, **T**, is a serum protein that is essential for the transport of iron in humans. **T** contains two sites that bind Fe(III) forming the **T**-Fe_2 complex.

Desferrioxamine, **D**, is a strong chelating agent that binds strongly to Fe(III) thereby removing Fe(III) from the body. Each molecule of **D** binds to a single Fe(III) forming the **D**-Fe complex.

The relative amounts of Fe(III) bound to **T** and **D** can be determined by UV–VIS spectrophotometry. The molar absorptivities, ε, of both complexes at wavelengths of 428 nm and 470 nm are summarised in Table 6.1.

Table 6.1

Complex	ε / mol^{-1} dm^3 cm^{-1}	
	λ = 428 nm	λ = 470 nm
T-Fe_2	3540	4170
D-Fe	2730	2290

In the absence of Fe(III), neither **T** nor **D** absorb at these wavelengths.

(i) A sample of **T** that is saturated with Fe(III) has an absorbance of 0.463 at 470 nm when using a 1.00 cm cell.

Given that the molecular weight of **T** is 81 000 g mol^{-1}, calculate the concentration of **T** in the sample in g dm^{-3}. [1]

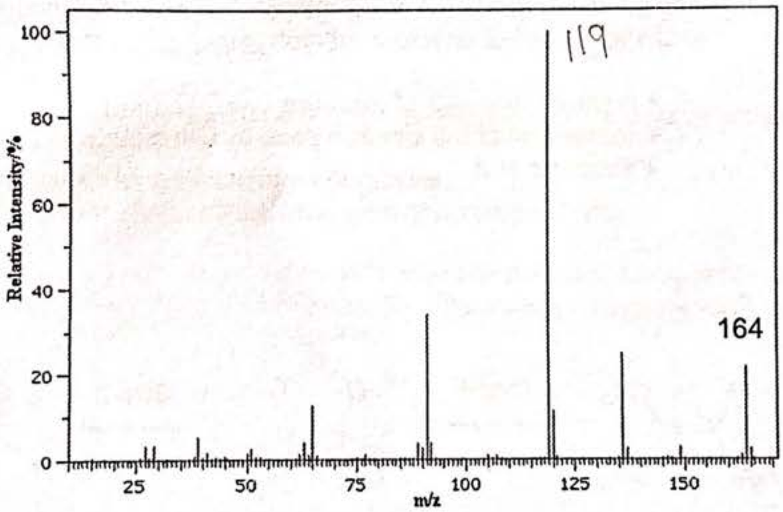
After adding some **D** to the sample, the absorbance is measured at both wavelengths, giving a value of 0.401 at 428 nm and 0.424 at 470 nm.

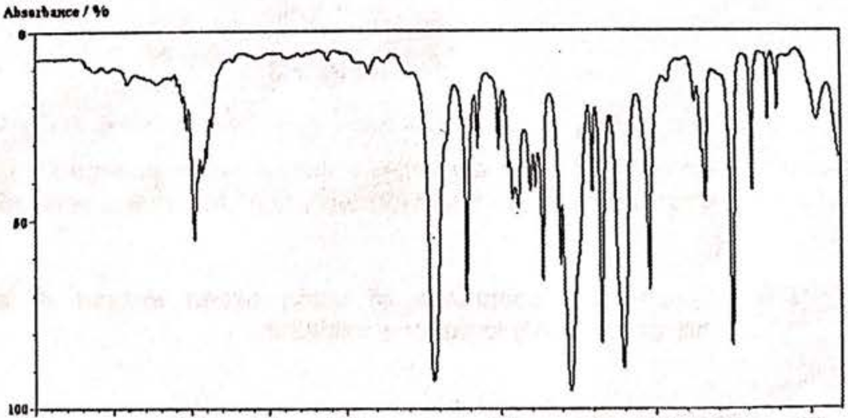
(ii) Calculate the concentration of both complexes in the sample and the percentage of Fe(III) that is bound to **T**. [3]

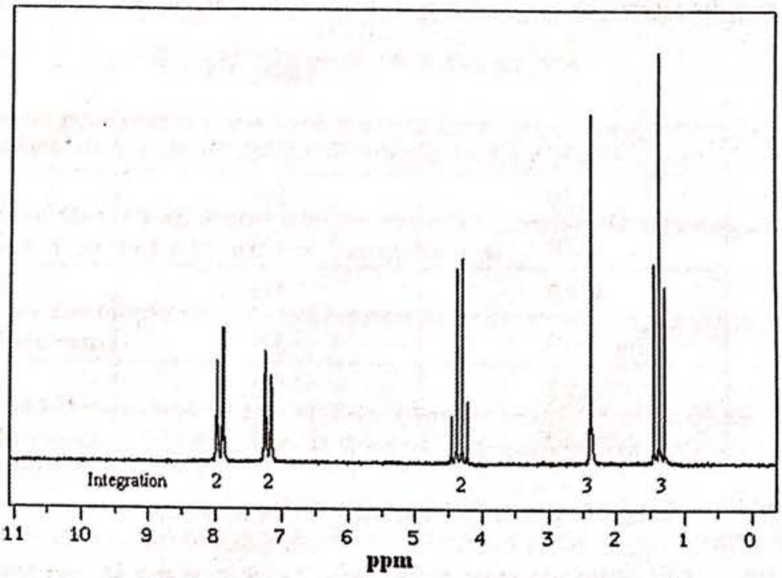
(c) In addition to UV–VIS spectrophotometry, mass spectrometry (MS), infra–red (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy are other techniques that are useful in structure elucidation of organic compounds.

(i) Using benzene ring as an example, explain how the anisotropic effect affects the chemical shift values of aromatic protons. [2]

(ii) The MS, IR and ^1H NMR spectra of an unknown compound **C** are given below. Determine its structure and explain your answer. [8]







(iii) In ^{1}H NMR, TMS is used as a reference compound.
Draw its structure and explain why it is chosen as a reference compound. [3]

[Total: 20]

7 Compound **P**, $C_{10}H_{12}O$, is a small molecule that is used in the synthesis of many pharmaceutical drugs. It is the major product formed when a suitable alkyl bromide is treated with hot alcoholic potassium ethoxide. The product mixture is shown in Fig. 7.1.

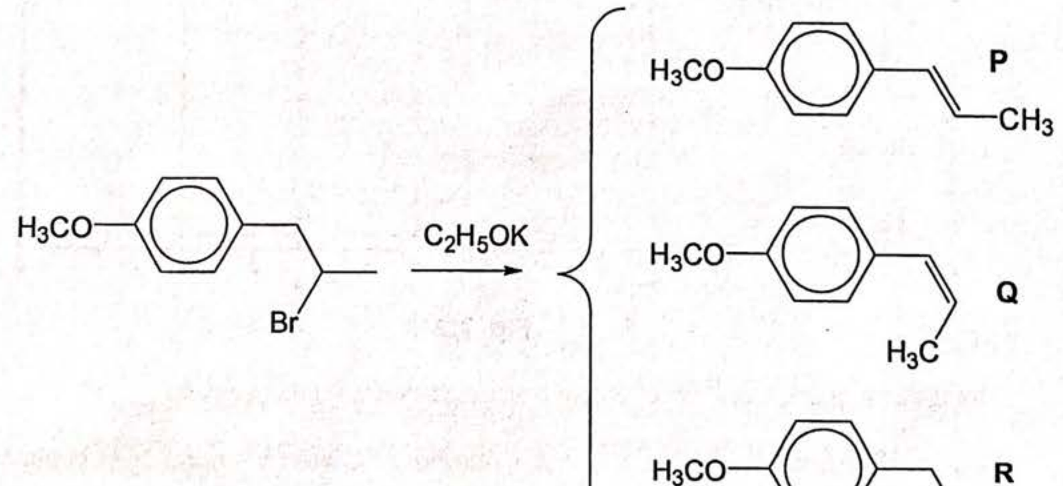


Fig. 7.1

(a) Explain why **P** is the major product. [2]

(b) The ^1H NMR spectrum of **P** is summarised in Table 7.1.

Table 7.1

chemical shift δ/ ppm	integration value	splitting pattern
7.30	2H	doublet
6.70	2H	doublet
6.40	1H	doublet
6.10	1H	multiplet
3.70	3H	singlet
1.80	3H	doublet

(i) Explain how the multiplet at δ 6.1 ppm arose. [2]

(ii) Calculate the ratio of the peak heights of the M and M+1 peaks in the mass spectra of **P**. [1]

(iii) Suggest the structure of the fragment at *m/z* 117 in the mass spectra of **P**. [1]

(c) **P** was reacted with sodium nitrite in ethanoic acid to produce solid **S** as the only organic product. **S** contains two rings, two nitrogen atoms and three oxygen atoms. The ^1H NMR spectrum of **S** is shown in Fig. 7.2.

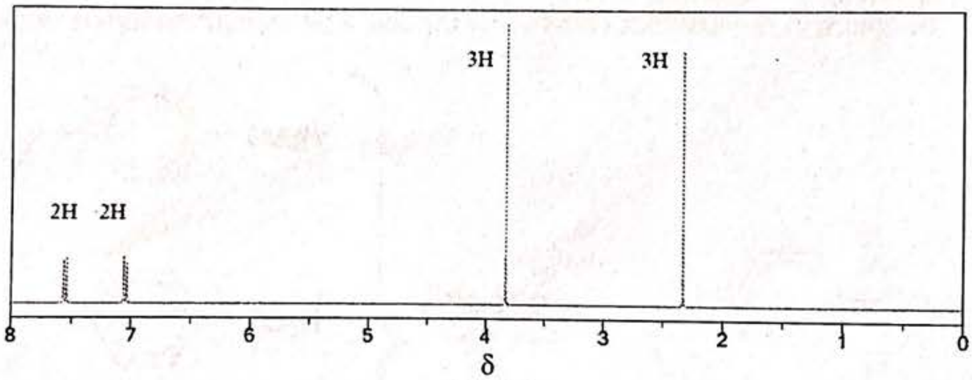


Fig. 7.2

The degree of unsaturation of **S** can be evaluated using the formula

Degree of unsaturation = 0.5 × (2 + 2 × number of C atoms – number of H atoms + number of N atoms)

(i) Calculate the degree of unsaturation of **S**. [1]

(ii) By comparing the ^1H NMR spectrum of **S** and that of **P**, state the difference in structure between the two compounds. [1]

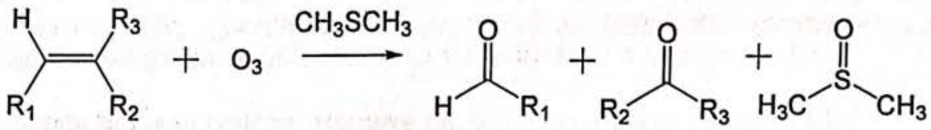
(iii) Suggest a structure of **S** that is consistent with the given information, including any formal charges. [1]

(d) Ozone, O_3, can be found in the strastosphere of Earth and absorbs both ultraviolet and infra-red (IR) rays.

(i) Outline the principles underlying infra–red spectroscopy. [2]

(ii) State the shape of an ozone molecule and predict the number of IR absorptions in the spectrum of ozone. Identify the molecular vibrations that give rise to these absorptions. You may assume that ozone shows similar absorptions as sulfur dioxide. [3]

(e) Ozonolysis allows the cleavage of alkene double bonds by reaction with ozone. An example involving dimethyl sulfide is given below.



(i) Complete Fig. 7.3 to suggest the mechanism for the first two steps of the reaction. 2–methyl but–2–ene and ozone react together to form ethanal and a zwitterionic species, **X**. Dimethyl sulfide is not involved in these two steps.

You should begin step 1 of the mechanism with the concerted addition of ozone to 2–methyl but–2–ene to form molozonide. Your mechanism should include

- relevant lone pair of electrons
- movement of the electron pairs by using curly arrows
- structure of **X**

[3]

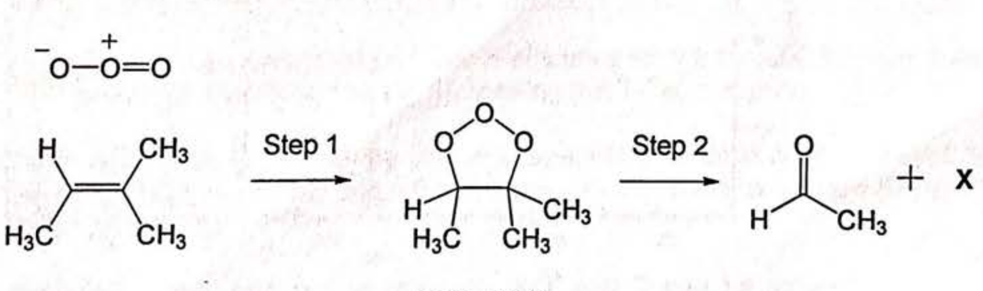


Fig. 7.3

(ii) Limonene is a monoterpene that is used in organic synthesis. Draw the structure of the products formed when limonene is reacted with ozone. [2]

(iii) Suggest an advantage of using ozone instead of acidified potassium manganate (VII) to perform oxidation. [1]

[Total: 20]