FINAL PAPER

PART A

1996

AUSTRALIAN CHEMISTRY OLYMPIAD

Please note that this answer book will be photocopied when returned and then split so that answers are sent to the appropriate markers. For this reason it is extremely important that you observe instructions 5 to 7.

Instruction to candidates

(1) You are allowed **10 minutes** to read this paper, and **3½ hours** to complete the questions.

(2) You are **not** permitted to refer to books, notes or periodic tables but you may use a non programmable electronic calculator and molecular models.

(3) You must attempt questions 1, 2 and 3. In the Organic section you must attempt Q4 along with 2 other questions of your choice.

(4) Answers **must** provide **clearly laid out working** and **sufficient explanation** to show how you reached your conclusions.

(5) Answers must be written in the blank space provided immediately below each question in the exam booklet. Rough working must be on the backs of pages. Only material presented in the answer boxes will be assessed.

(6) Your name must be written in the appropriate place on **each page** of your answers.

(7) Use **only black** or **blue ball point pen** for your written and drawn answers, **pencil** or **other coloured pens** are **not** acceptable.

Question 1

In an *in vivo* study of the action of ethanol dehydrogenase (an enzyme that destroys ethanol in the liver), volunteers drank vodka until their blood alcohol level stabilised. They then stopped drinking, and their blood alcohol content was monitored over time. In one particular subject, the following data were recorded.

Time (min)	[EtOH] (% by vol.)
0	0.0507
20	0.0426
40	0.0374
60	0.0305
90	0.0213
120	0.0150
150	0.0104
180	0.0070
210	0.0048
240	0.0034

a) Graph [EtOH] vs time on the paper provided. What is the order in [EtOH] for the first hour of the experiment?

b) By making one or more extra plots (on the same paper), determine the order in [EtOH] during the last hour of the experiment.

c) What are the relevant (pseudo) rate constants for each regime? (Molar mass of ethanol = 46.1 g/mol; density of ethanol = 0.785 g/mL)

Next, some *in vitro* studies were conducted. The enzyme was isolated, and an aqueous solution of 1.0 g/L made up. The pressure required to prevent osmosis against pure water was found to be 43 Pa at 25°C. After buffering to an appropriate pH and the addition of co-factors, the solution was warmed, and ethanol added. The rate of reaction was determined by infrared spectroscopy of the aldehyde formed. The following data were obtained.

Temperature (°C)	Rate (mol.L^{-1}.s^{-1})
35	$6.3\text{x}10^{-4}$
36	$6.8\text{x}10^{-4}$
37	$7.3\text{x}10^{-4}$
38	$8.0\text{x}10^{-4}$
39	$8.5\text{x}10^{-4}$

d) What is the molar mass of ethanol dehydrogenase?

e) What is the activation energy of the rate-determining step of the reaction?

Question 2

(a) With the aid of clearly labelled diagrams illustrate the orbitals and hybrid orbitals used to account for the shapes and bonding in any **three** of the following:

(i) NF_3 (ii) ICl_4^- (iii) C_6H_6 (iv) NO_3^-

(b) Explain by use of the VSEPR model why the bond angle of NF_3 is 102.5° and in NH_3 is 107° while the bond angle in PF_3 is 96.3° and in PH_3 is 93.6°.

(c) Draw and name all the possible stereoisomers of $[CoCl(NCS)(en)_2]Br$. What other types of isomerism could be exhibited by the complex? Give an example of each type and name the isomer.

(d) The oxides TiO, CoO, MnO, NiO and FeO all have the rock salt or sodium chloride structure.

(i) What is the stereochemistry of the metal ion in each of these compounds? Draw a clearly labelled crystal field d-orbital splitting diagram for each of the metal ions in these oxides and determine the crystal field stabilisation energy (CFSE) in terms of Δ_O.

(ii) Which of these oxides would be expected to be the most stable? Explain.

(iii) Would CuO be expected to adopt a similar structure? Explain.

Question 3

(a) Calculate the equilibrium constant for the reaction

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2\,(s) + 4H^+$$

given the following standard reduction potentials

$$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2\,(s) + 2H_2O \qquad E^\circ = +1.695\ V$$

$$MnO_2\,(s) + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O \qquad E^\circ = +1.23\ V$$

(b) The $FeSCN^{2+}$ complex is strongly coloured in solution when its concentration exceeds 10^{-5} M. However, the complex is not very stable, dissociating according to:

$$FeSCN^{2+} \longrightarrow Fe^{3+} + SCN^- \qquad \text{with dissociation constant } K_D = 10^{-2}\ M.$$

(i) 10^{-3} mol of $FeCl_3$ and 10^{-2} mol of KSCN are dissolved in one litre of water. Show that the solution will be coloured.

(ii) Fluoride ions form a colourless complex with ferric ions:

$Fe^{3+} + F^- \longrightarrow FeF^{2+}$ $\quad K = 10^5\ M^{-1}$

What mass of KF must be added to the solution in part (i) to remove the colour?
(Atomic masses: K = 39.10, F = 19.00 g/mol)

(c) A 50.00 mL aliquot of 0.0500 M NaCN is titrated (carefully!) with 0.1000 M HCl. $K_a(HCN) = 6.2 \times 10^{-10}$

Construct the titration curve <u>on the graph paper provided</u> (Y-axis = pH; X-axis = volume of HCl titrant) by calculating the pH after the addition of:

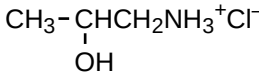
(i) 0.00 mL HCl
(ii) 10.00 mL HCl
(iii) 25.00 mL HCl
(iv) 26.00 mL HCl

Organic Section

Students must attempt Question 4 and any 2 other questions of their choice in this section. Students should spend ~45 minutes on this section.

Question 4

(a) The enantiomers of 1-amino-2-propanol were separated and recovered as their hydrochloride salts:



The samples of (*R*)-(–)-1-amino-2-propanol hydrochloride had $[\alpha]_D^{25}$ –31.5° (c 0.01; methanol)

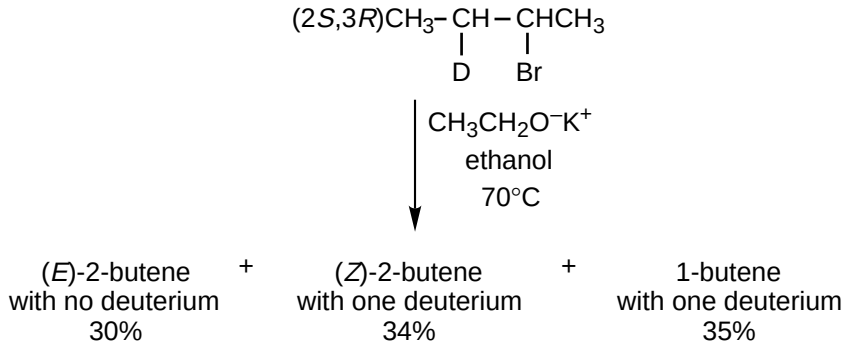
and that of (*S*)-(+)-1-amino-2-propanol hydrochloride had $[\alpha]_D^{25}$ +35° (c 0.01; methanol)

(i) Write correct stereochemical formulas for the levorotatory and dextrorotatory isomers.

(ii) Assuming that the optical rotation observed for the enantiomer of higher purity is the correct optical rotation for the compound, what is the enantiomeric excess in the sample of the other enantiomer?

(b) The stereochemical requirements for the E2 elimination reaction were explored using alkyl halides labelled with deuterium atoms. 2-Bromo-3-deuterobutane was used in two isomeric forms. The products observed in each case are outlined below.

1.



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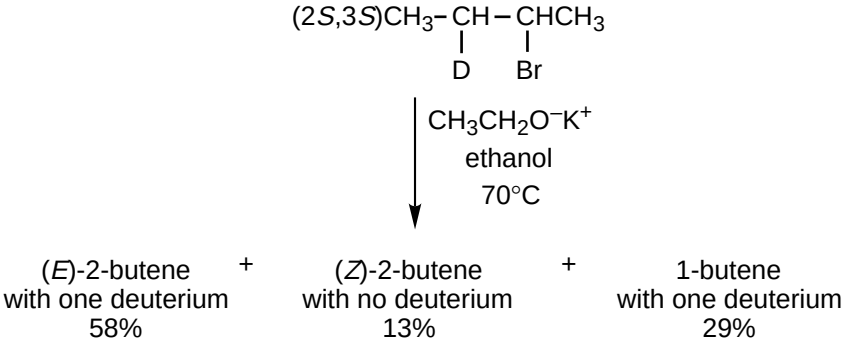
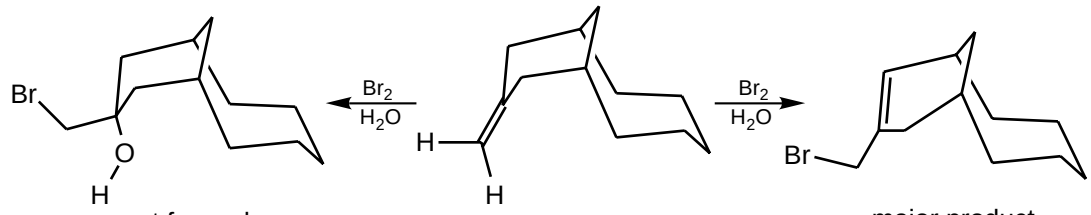


(i) Using Fischer projections with methyl groups arranged on the vertical axis, draw stereochemically accurate representations of (2*S*,3*R*)- and (2*S*,3*S*)-2-bromo-3-deuterobutane.

(ii) Using saw-horse diagrams show the transition states for the reactions leading to (*E*)-2-butene and (*Z*)-2-butene in each case.

Question 5

(a) The following would be expected to produce the bromohydrin shown below on the left. However, the reaction actually gives the allylic bromide on the right.



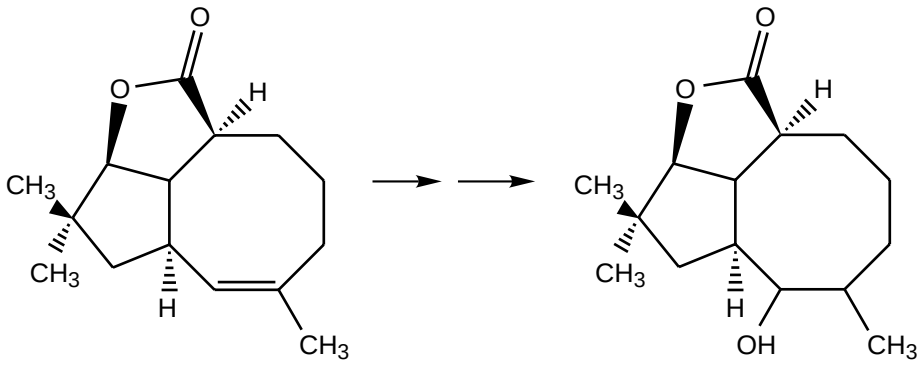
not formed major product

(i) What are the structures for the two different bromonium ion intermediates that could result from the reaction of the alkene with bromine?

(ii) Only one of the bromonium ions is proposed to form in this reaction. Which one is it, and what is wrong with the other one?

(iii) Write a mechanism that rationalises the formation of the allylic bromide from the bromonium ion that you selected as the one that forms in the reaction.

(b) The following reaction was used in the synthesis of (+)-asteriscanolide, a natural product.

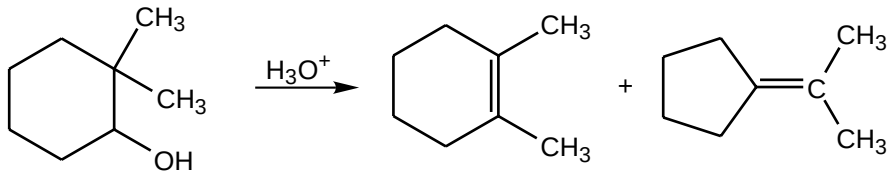


stereochemistry of OH and CH_3 not shown

(i) What reagents would you use for this transformation?

Question 6

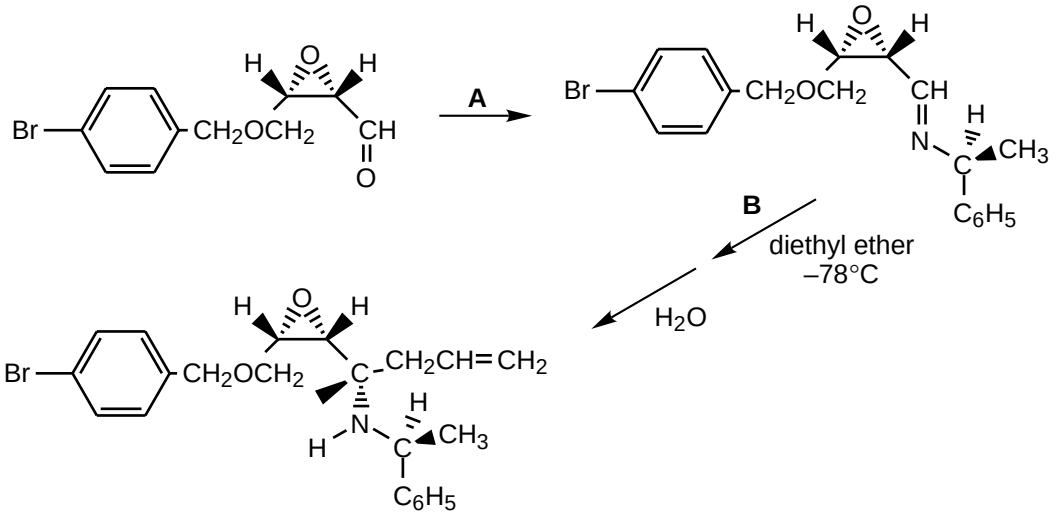
(a) When 2,2-dimethylcyclohexanol is treated with acid, 1,2- dmethylcyclohexene and isopropylidenecyclopentane are the products obtained. Draw a detailed mechanism that explains this result.



2,2-dimethyl-cyclohexanol 1,2-dimethyl-cyclohexene isopropylidene-cyclopentane

(b)

Imines behave toward Grignard reagents in much the same way that carbonyl groups do. The following transformations were carried out.



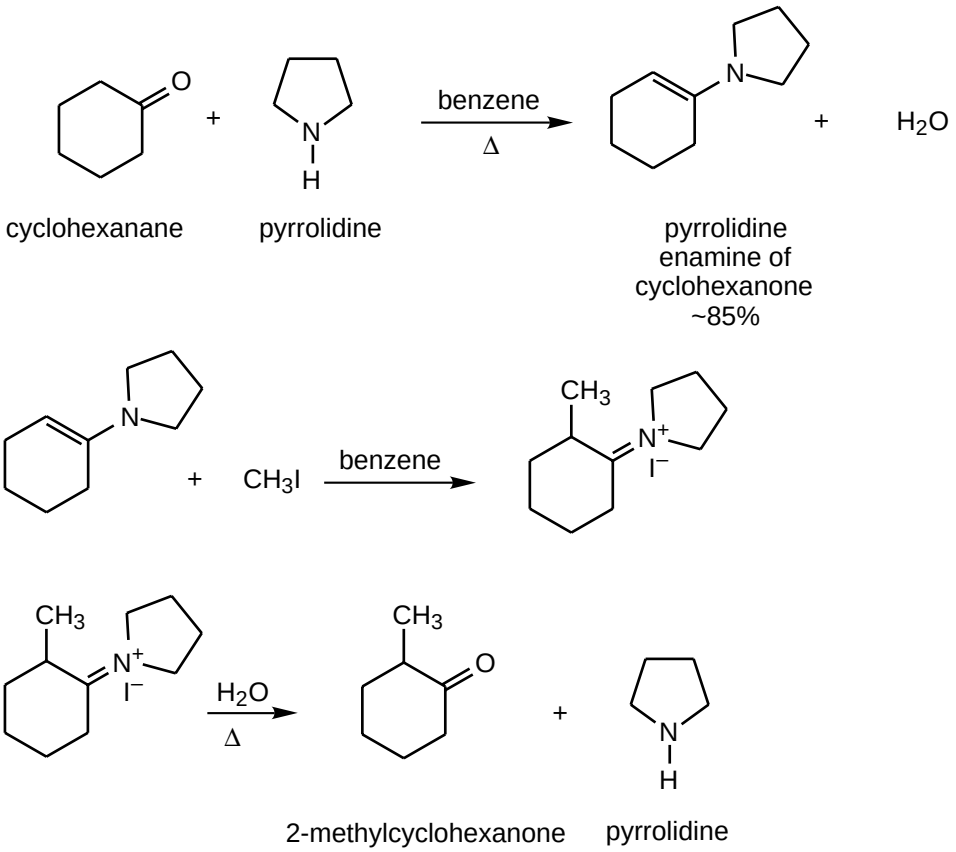
(i) Supply the necessary reagents to complete the transformation.

(ii) Give a reason for why the reaction with **B** is done at –78°.

Question 7

Either

(a) Gilbert Stork of Columbia University discovered that **enamines**, nitrogen-containing compounds that are analogous to enolate anions, can be used as sources of nucleophilic carbon atoms in syntheses. The following equations show the preparation and reactions of an enamine. Provide a mechanism for each step.

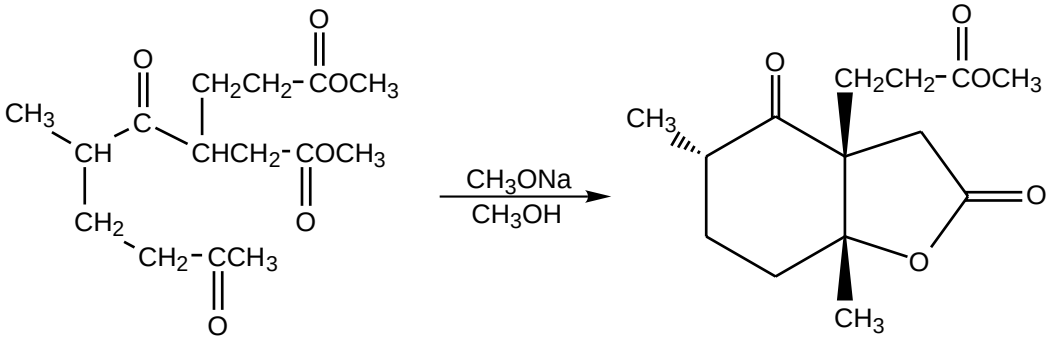


cyclohexanane pyrrolidine pyrrolidine enamine of cyclohexanone ~85%

2-methylcyclohexanone pyrrolidine

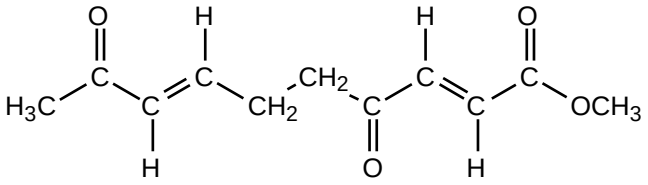
Or

(b) Write a complete mechanism for the following reaction.



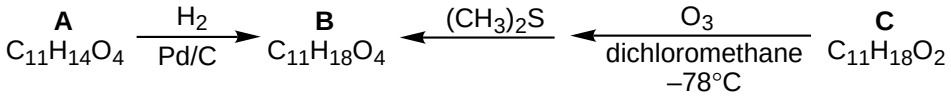
Question 8

(a) Compound **A** , which is a degradation product of the antibiotic vermiculine (see below), has the following structure,

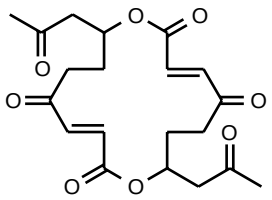


Compound **A**

The structure was confirmed by converting **A** to compound **B**, $C_{11}H_{18}O_4$, which was also prepared by ozonolysis of compound **C**, $C_{11}H_{18}O_2$.



Assign structures to compounds **B** and **C**.

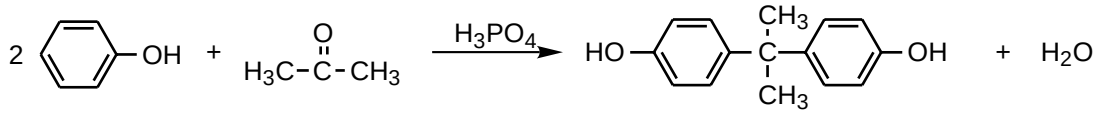


vermiculine

(b) Reactions of *cis*-4,5-dimethylcyclohexene and 3-*tert*-butylcyclohexene with *m*-chloroperoxybenzoic acid give predominately one product in each case. Show the conformation of each starting alkene, and predict, by showing the reaction with the peroxyacid, what the structure of the expected product should be.

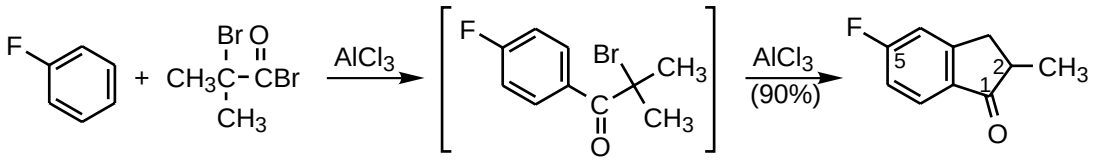
Question 9

(a) Reaction of phenol with acetone in the presence of an acid catalyst gives a compound known as bisphenol A. Bisphenol A is used in the production of epoxy resins and polycarbonate resins. Propose a mechanism for the formation of bisphenol A.



bisphenol A

(b) 5-Fluoro-2-methyl-1-indanone is an intermediate in the synthesis of sulindac (Clinoril), a nonsteroidal anti-inflammatory drug (NSAID) used for the treatment of rheumatoid arthritis, osteoarthritis, and gout. It is formed by treatment of fluorobenzene with 2-bromo-2-methylpropanoyl bromide in the presence of aluminium chloride. Propose a mechanism for this transformation.



flouoro-benzene

2-bromo-2-methyl-propanoyl bromide

(an intermediate not isolated)

5-fluoro-2-methyl-1-indanone