

AUSTRALIAN CHEMISTRY OLYMPIAD

FINAL PAPER

PART A

1992

Instruction to candidates

- (1) You are allowed **10 minutes** to read this paper, and **3 hours** to complete the questions.
- (2) You are **not** permitted to refer to books, notes or periodic tables but you may use a non-programable electronic calculator and molecular models.
- (3) You must attempt **all** questions.
- (4) 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.
- (5) Answers **must** provide **clearly laid out working** and **sufficient explanation** to show how you reached your conclusions.
- (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 answers, pencil or other coloured pens are **not** acceptable.

Question 1

Cyclopentadiene (**A**) dimerises in the gas phase. 0.5 cm^3 of the liquid ($\rho = 0.802 \text{ g cm}^{-3}$) were placed in a stoppered flask ($V = 1000 \text{ cm}^3$) which was heated to 130°C very quickly.



boiling point = 40°C

A

- (a) Calculate the initial pressure, measured by the pressure transducer, in the flask immediately once the temperature reached 130°C .
- (b) This pressure transducer measured total pressure as a function of time at this temperature.

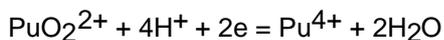
Time (minutes)	10	20	30	40	50	60
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Total pressure (kPa)	18.07	16.62	15.63	14.87	14.33	13.88
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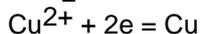
Determine the order of the reaction and the rate constant.

Question 2

Consider the following galvanic cell:



$$E^\circ = +1.067\text{V}$$



$$E^\circ = +0.337\text{V}$$

- Calculate ΔG^0 for the overall cell reaction.
- Calculate the equilibrium constant for the overall cell reaction.
- Calculate the potential of the above cell.
- Which electrode is the negative electrode?
- A bar of pure copper metal weighing 127g was placed into 1L of 0.0500M $\text{PuO}_2(\text{ClO}_4)_2$ solution. The pH of this solution was maintained constant at exactly 3.00. What was the concentration of PuO_2^{2+} at equilibrium?

Question 3

Given the information that



and



where the symbol (aq) indicates unit activity of iodine in the aqueous phase and (s) denotes pure solid iodine at unit activity, calculate the solubility (moles/litre) of solid iodine in water.

Question 4

Consider the titration of 25.00mL of 0.1000M iron(II) with 0.1000M cerium(IV) in a 1M H_2SO_4 medium.

In this medium, the following standard reduction potentials apply:



An inert platinum wire electrode which is immersed in the titration solution will develop a potential which is governed by the iron(II)-iron(III) concentration ratio (or identically, by the cerium(III)-cerium(IV) concentration ratio). This Pt electrode is called the "indicating" electrode.

The potential of the single Pt electrode cannot of course be measured alone, so a second, "reference" electrode is also immersed in the solution and the cell potential $E_{\text{cell}} = E_{\text{Pt}} - E_{\text{ref}}$ is actually measured by a voltmeter. The reference electrode is designed to have a constant potential and does not take part in the titration chemical reaction. In this titration we will use a "saturated calomel electrode" (SCE) as a reference electrode. The SCE has a potential of +0.2415V when measured relative to a standard hydrogen electrode.

- Calculate the equilibrium constant for this reaction.
- Calculate the cell potential versus titre of Ce(IV), by completing the table on the following page. You must clearly show your calculation method, and you may want to insert some extra columns to tabulate any intermediate calculations.

	Volume of Ce(IV) /mL	E _{cell} /V
1	0	
2	1.00	
3	2.00	
4	5.00	
5	10.00	
6	15.00	
7	20.00	
8	24.00	
9	24.50	
10	24.90	
11	24.99	
12	25.00	
13	26.00	
14	30.00	
15	40.00	
16	50.00	

- (c) The barium salt of diphenylamine sulphonate is an indicator molecule which has a colorless reduced form and a red-violet oxidised form. The potential at which equal amounts of these forms exist in 1M H₂SO₄ is 0.84V (relative to the SHE). Is this indicator appropriate for a visual determination of the equivalence point of the above titration? Explain your answer.

Question 5

- (a) For each of the following species draw the Lewis structure and predict the electron pair geometry and molecular structure.

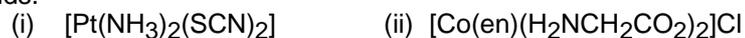


What is the hybridisation of the central atom in each of the species? Which of these species would be expected to have a dipole moment?

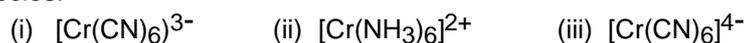
- (b) Explain by use of the VESPR model why the bond angle in NH₃ is 107° and in NF₃ is 102.5° while the bond angle in PH₃ is 93.6° and in PF₃ is 96.3°.

Question 6

- (a) Sketch and name all the possible linkage and stereoisomers of the following coordination compounds.

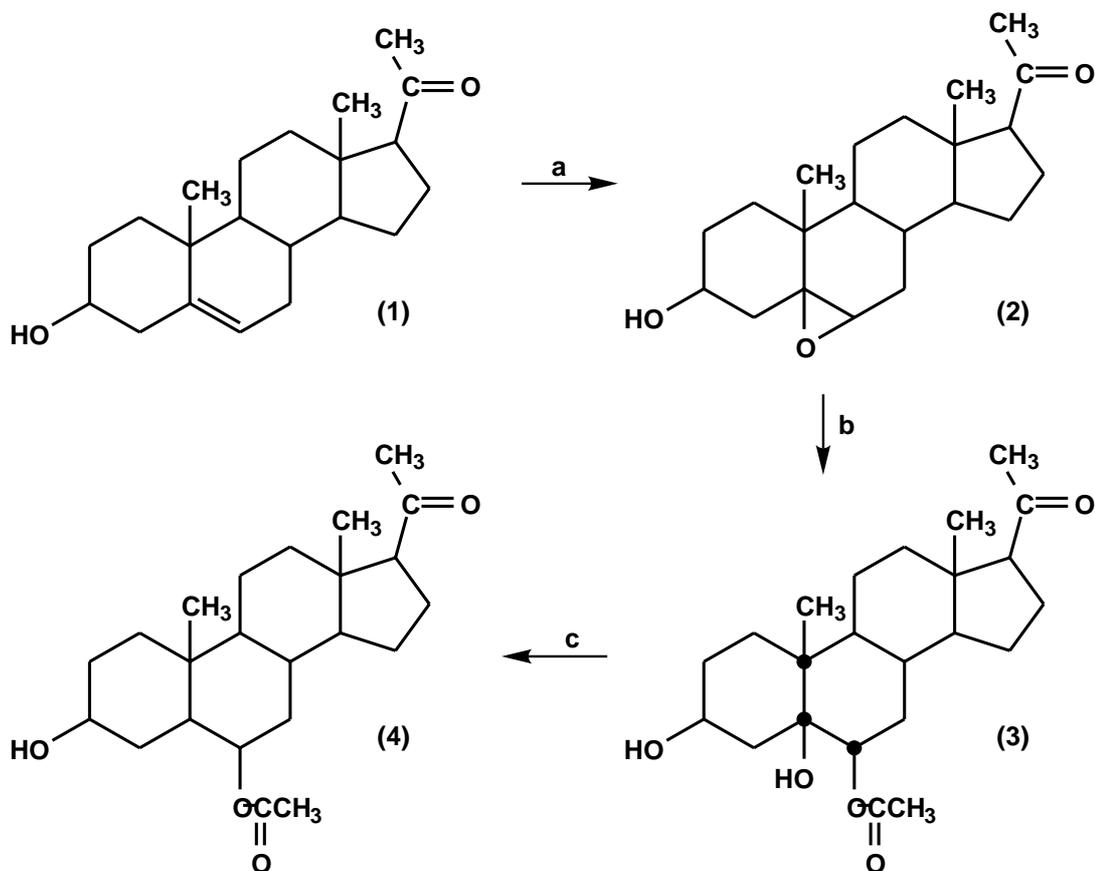


- (b) How many unpaired electrons do each of the following complex ions have in their ground state configuration? Your answer should include a clearly labelled *d*-orbital splitting diagram for each species.

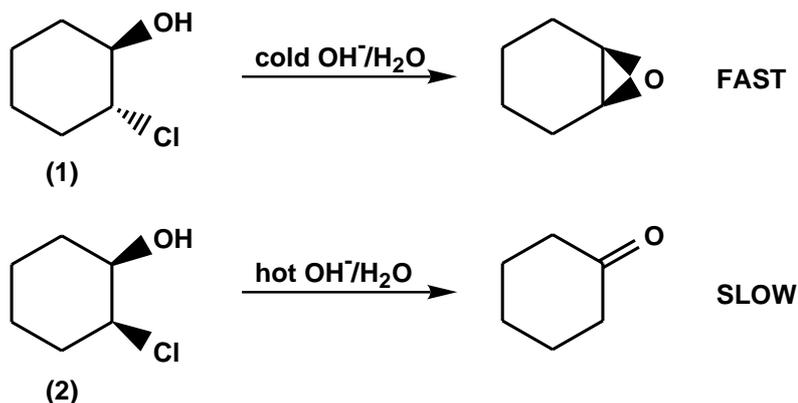


Question 7

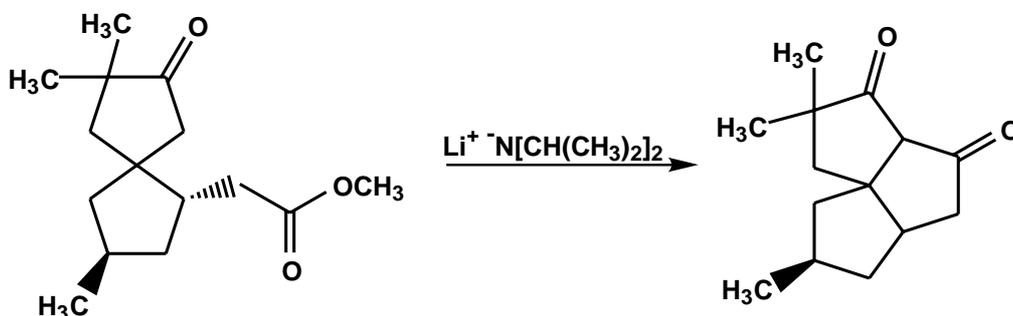
(a) The following transformations have been used in steroid chemistry.



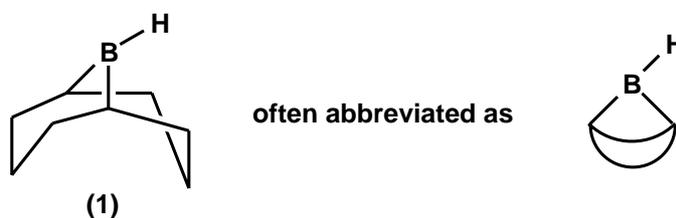
- (i) Suggest suitable reagents **a**, **b**, **c** to bring about the transformations. ((Note: More than one reagent may be required for a single step).)
- (ii) What would be the relative stereochemistry of the three sp^3 centres (•) in compound (3).
- (b) 1,3,5-Trimethylbenzene undergoes electrophilic aromatic substitution with iodine monochloride (ICl).
- (i) Predict the product of monosubstitution and give your reasoning.
- (ii) Write a clear reaction mechanism to account for the formation of this product.
- (iii) Would you expect a similar reaction to take place between 1,3,5-trinitrobenzene and ICl? Justify your answer.
- (c) Account for the difference in the reactivity between the two chlorhydrins (1) and (2) shown below.



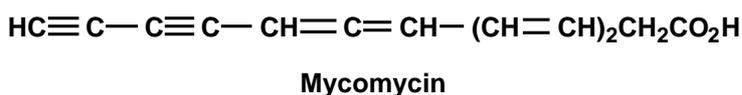
- (d) The anion of diisopropylamine is a strong base which has proved extremely useful in generating enolate anions from ketones. Since enolate anions are good carbon nucleophiles it is not surprising that LDA or lithium diisopropylamide is found commonly in synthetic schemes. Give this information and draw a clear mechanism to account for the following transformation which occurred as one step in a complex synthesis.



- (e) 9-Borabicyclo[3,3,1]nonane (**1**) better known as 9-BBN is frequently used as a replacement for diborane, in hydroboration reactions. (*Its great advantage is that it is an air stable solid unlike diborane which is a gas known to react violently with air.*)

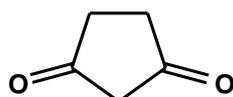


- (i) Predict the products which might result from the addition of 9-BBN to (Z)-4-methyl-2-pentene.
(ii) In practice 9-BBN is a very bulky reagent and the reaction gives 99.8% yield of a single product. Can you suggest its structure?
- (f) A naturally occurring antibiotic called mycomycin has the structure shown below. Mycomycin is optically active. Explain this by drawing clear structures for the enantiomeric forms of mycomycin.



- (g) An optically active compound **A** (assume that it is dextrorotatory) has the molecular formula $\text{C}_7\text{H}_{11}\text{Br}$. **A** reacts with hydrogen bromide, in the absence of peroxides, to yield isomeric products, **B** and **C**, with molecular formula $\text{C}_7\text{H}_{12}\text{Br}_2$. **B** is optically active; **C** is not. Treating **B** with 1 mole of potassium *tert*-butoxide yields (+)**A**. Treating **A** with potassium *tert*-butoxide yields **D** (C_7H_{10}). Subjecting 1 mole of **D** to ozonolysis followed by treatment with dimethyl sulfide yields 2 moles of formaldehyde and 1 mole of 1,3-cyclopentanedione.

Propose stereochemical formulas for **A**, **B**, **C** and **D** and outline the reactions involved in these transformations.



1,3-cyclopentanedione