

FINAL PAPER

PART A

1995

## 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.

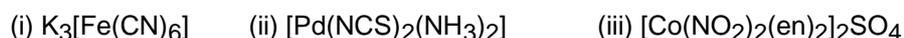
### Question 1

- a) Draw the Lewis structures (including resonance structures where applicable) and predict the electron pair geometries and molecular shapes of the following molecules and ions. What is the hybridisation of the central atom in each of the species? Which ones would be expected to have a dipole moment?



What is the expected bond angle in  $\text{SO}_2$ ? Would the same bond angle be expected in the isoelectronic species  $\text{O}_3$  and  $\text{NO}_2^-$ ? Explain.

- b) Draw and name all the possible stereoisomers for each of the following complexes.





his laboratory on Earth, he had to perform a more detailed set of experiments than is normally required in order to measure thermochemical properties.

He succeeded in making the following measurements.

1. density of solid =  $0.821 \text{ g cm}^{-3}$
2. density of liquid =  $0.793 \text{ g cm}^{-3}$
3. at 290 K, the unknown is a liquid with a vapour pressure of 10.534 kPa
4. at 300 K, the unknown is a liquid with a vapour pressure of 18.000 kPa
5. the normal freezing temperature is 280 K
6. the critical temperature is 412 °C

He also carried out two experiments:

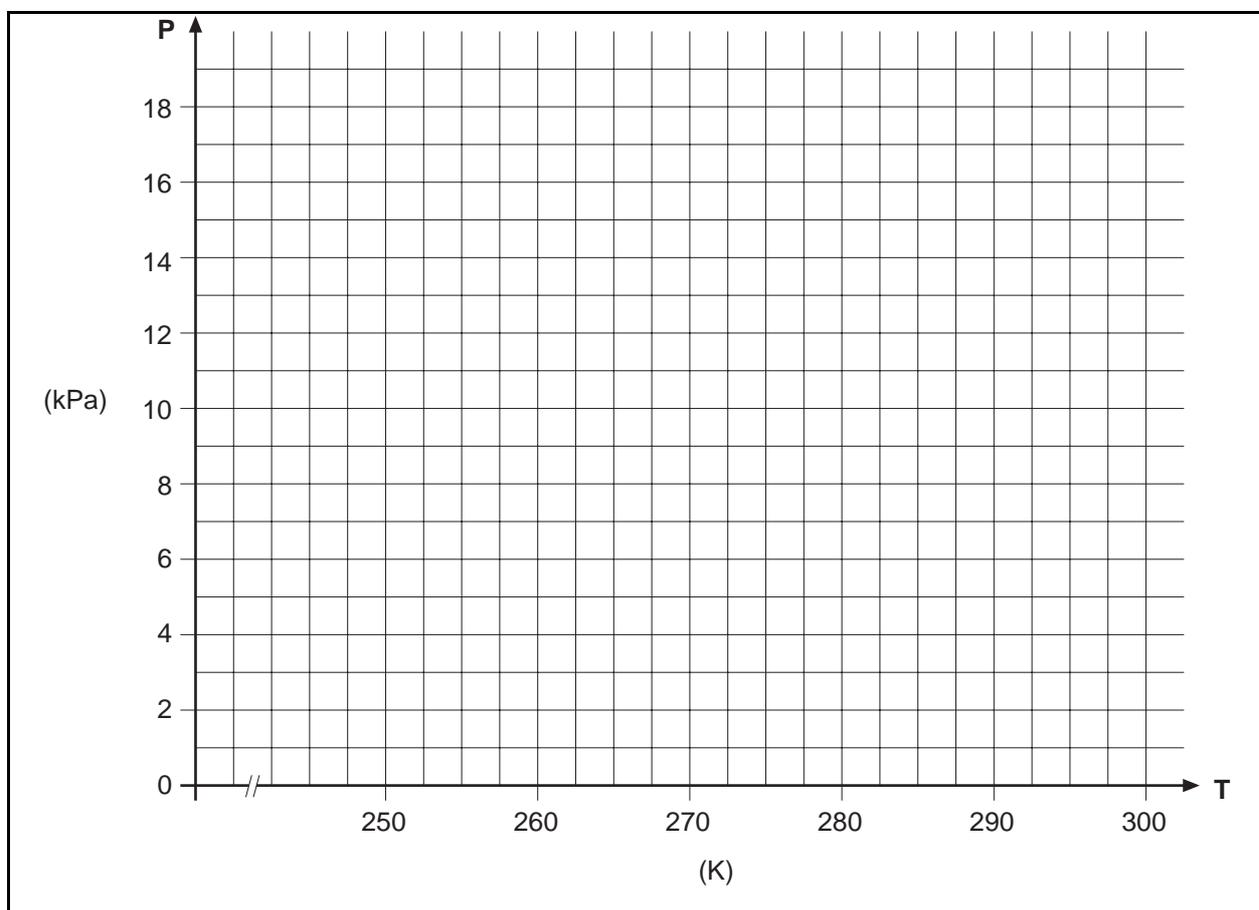
1. When equal masses of benzene ( $\Delta H_{\text{vap}} = 30.8 \text{ kJ mol}^{-1}$ , normal boiling point of 80.1 °C) and the unknown liquid were mixed at 290 K, the total vapour pressure was 10.466 kPa.
2. A small amount of a non-electrolyte was dissolved in the unknown liquid to form a dilute solution. The osmotic pressure of this solution at 290 K was 2.68 kPa. The freezing point of this solution was 5.49 mK lower than the normal freezing point.

Assume that all solutions are ideal.  $R = 8.315 \text{ J/Kmol}$   $0 \text{ °C} = 273.15 \text{ K}$

Calculate the enthalpy of vaporisation of the unknown compound.

Calculate the molar mass of the unknown compound.

By constructing a partial (incomplete) phase diagram, calculate the temperature (to the nearest degree) and the pressure (to the nearest kPa) at the triple point of the unknown compound.



## 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

Ozonolysis is frequently the key to determining the structures of alkenes. The following example illustrates this point.

A hydrocarbon **A** ( $C_7H_{10}$ ) reacts with bromine to afford **B** ( $C_7H_{10}Br_4$ ).

How many double bond equivalents are present in **A** and what form are they likely to take?

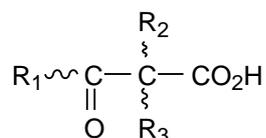
Treatment of **A** with ozone followed by dimethyl sulfide affords two and only two products, one being methanal ( formaldehyde) and the other **B** ( $C_6H_8O_3$ ).

How many double bond equivalents are there in **B** and what general statement can you make concerning the structure of **A** ?

**B** is oxidised with  $K_2Cr_2O_7/H_2SO_4$ (dil) to yield **C**,  $C_6H_8O_5$ , which is soluble in sodium hydrogen carbonate.

Heating **C** causes it to lose  $CO_2$  to afford **D**,  $C_5H_8O_3$ , also soluble in sodium hydrogen carbonate.

Such behaviour is associated with structural fragments



**D** is reduced with sodium borohydride to yield **E** ( $C_5H_{10}O_3$ ) which may be resolved into enantiomers. **E** unlike **D** gives no reaction with 2,4-dinitrophenylhydrazine. Identify **A** to **E**.

### Question 5

- a) Chlorine adds to E-but-2-ene in methylene chloride as solvent to give meso-2,3-dichlorobutane [(2R,3S)-2,3-dichlorobutane]

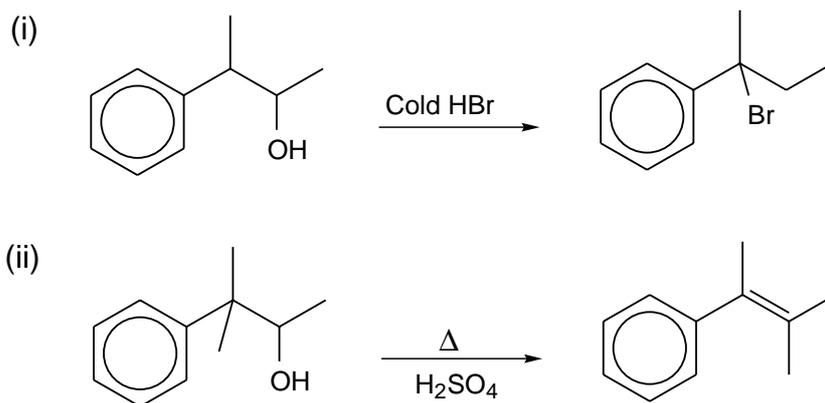
Outline the mechanism for this reaction

If the reaction is conducted in water, a chlorohydrin (a compound bearing OH and Cl on adjacent carbons) is obtained.

Suggest a mechanism for this reaction to predict the stereochemistry of the chlorohydrin and draw a Fisher projection of your final product.

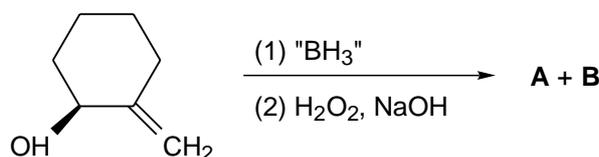
### Either

- b) In the following reactions, a rearranged skeleton is observed in the principal product. Write a mechanism for each reaction that leads to the observed product.



Or

- c) The following reactions were carried out during research into the stereochemistry of the hydroboration reaction



Compounds **A** and **B** are stereoisomers of each other and are formed in roughly equal amounts. Compound **A** is thermodynamically more stable than compound **B**.

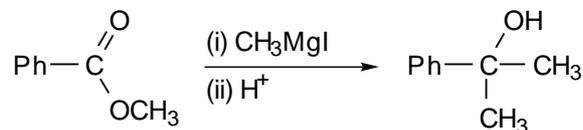
- Draw structural formulas for compounds **A** and **B** which clearly show their stereochemistry.
- Give a mechanism which accounts for the addition of the borane to the alkene.

### Question 6

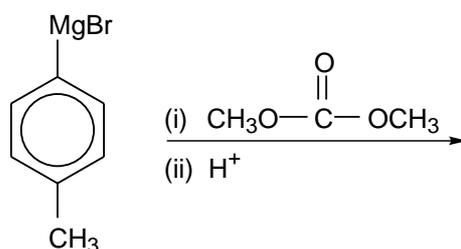
Either

- a) Carbonyl groups are susceptible to attack by nucleophiles such as Grignard reagents (e.g.  $\text{CH}_3\text{MgI}$ ). In the absence of a leaving group the resulting alkoxide anion is subsequently protonated to give an alcohol. However in the presence of a leaving group further reaction can and does occur. Thus esters can be reacted with an appropriate Grignard reagent to yield tertiary alcohols.

Given the above information write a mechanism for the following reaction

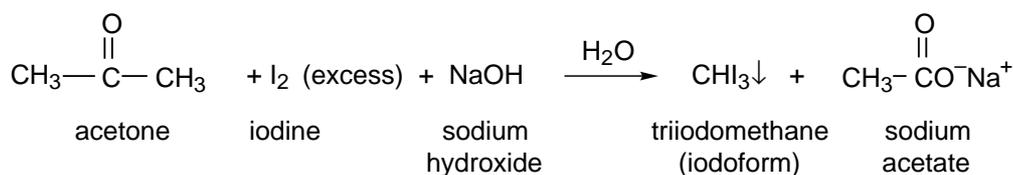


- b) Given your answer to (a) predict the outcome of the following reaction of dimethyl carbonate, in which the Grignard reagent is present in excess.



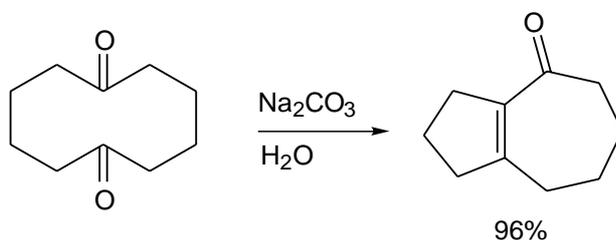
Or

- c) When a methyl ketone is treated with a halogen in the presence of base, the following reaction, using acetone as an example, is observed.



The reaction is known as the haloform reaction because one of the products is a haloform (a trihalomethane) — iodoform in the reaction shown above. Propose a mechanism for the reaction. Some of the points to consider are why all of the halogen atoms substitute on one side of the ketone, and how the carbon—carbon bond is broken to give iodoform and a carboxylate anion.

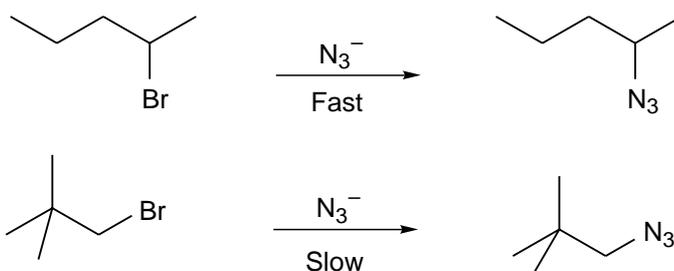
- d) Suggest a mechanism that accounts for the product observed for the following reaction



### Question 7

Either

- a) The azide anion ( $\text{N}_3^-$ ) is known to react by an  $\text{S}_{\text{N}}2$  pathway thousands of times more rapidly with 2-bromopentane than with its isomer neopentyl bromide (1-bromo-2,2-dimethylpropane) despite the fact that the leaving group is at a secondary site in the former compound and at a primary site in the latter.



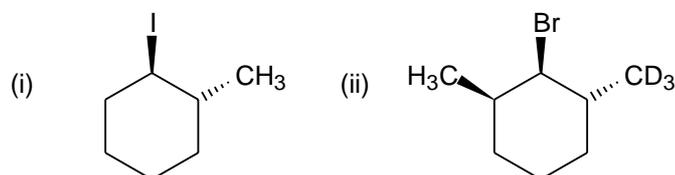
To reach the conclusion that the reaction with 2-bromopentane cited in a) did indeed occur through an  $\text{S}_{\text{N}}2$  reaction, the chemists studying the reaction did several additional experiments in which they:

- used optically active (*R*)-2-bromopentane.
- doubled the concentration of alkyl bromide.
- doubled the concentration of azide ion.

Predict what they would have seen in each experiment if the reaction really took place through an  $\text{S}_{\text{N}}2$  pathway and suggest a reason for the observed differences in reaction rates.

Or

- b) Assume that treatment with base of the following cyclohexyl halides effects an elimination through an E2 mechanism. Using your knowledge of the stable conformations of cyclohexane rings together with the stereochemical requirements of the E2 mechanism, predict the likely products of each reaction and explain your reasoning.

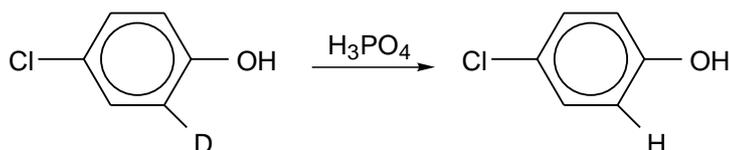


### Question 8

- a) 3,5-Dimethoxyaniline (1-amino-3,5-dimethoxybenzene) reacts with a solution of sodium nitrite in dilute sulfuric acid to afford compound **E**. Reaction of **E** with copper(I) cyanide affords **F**. Boiling **F** with aqueous sodium hydroxide affords after acidification **G**, which has lost no carbons and is soluble in sodium hydrogen carbonate. **G** can also be prepared by vigorous oxidation of 3,5-dimethoxytoluene with potassium permanganate. Identify compounds **E** to **G**

Either

- b) The following reaction has been observed to take place when the deuterated phenol is heated with phosphoric acid



Write a mechanism to explain this observation, based on your knowledge of electrophilic aromatic substitution.

Or

- c) During research into phenol derivatives that have activity against hormones involved in blood clotting, the following synthesis was carried out in two steps. The first is an electrophilic alkylation reaction starting with an alcohol.

Provide structural formulae for the reagents that would be necessary for the transformation of the starting material into the final product, as well as for the structure of the product of the first step.

