

*Ollscoil na hÉireann, Gaillimh*  
National University of Ireland, Galway

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SUMMER EXAMINATIONS 2000

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FINAL EXAMINATION FOR THE DEGREE OF B.Sc. HONOURS

CHEMISTRY CH401

Fourth Paper

All questions carry 100 marks, distributed as shown where appropriate.

Professor D.J. Cardin  
Professor R.J. Donovan  
Professor R.C.F. Jones  
Professor R.N. Butler  
and Internal Examiners

Time Allowed: Three Hours

Answer four questions – include at least one question from each Section.  
No more than two questions from numbers 3, 6 and 9 to be answered.

Use a separate Answer Book for each Section.

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Gas Constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$	Avogadro constant $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
Planck's Constant, $h = 6.626 \times 10^{-34} \text{ J s}$	Velocity of light, $c = 2.998 \times 10^8 \text{ m s}^{-1}$
Electronic mass, $m_e = 9.109 \times 10^{-31} \text{ kg}$	Boltzmann constant, $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$
Electronic charge, $e = 1.602 \times 10^{-19} \text{ C}$	Bohr magneton, $\mu_B = 9.274 \times 10^{-24} \text{ J T}^{-1}$
Faraday constant, $F = 96485 \text{ C mol}^{-1}$	Atmosphere = $101325 \text{ N m}^{-2}$

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## Section A

1. Answer any *two* of the following parts (a), (b) and (c):

(a) Use the equation  $D = \frac{1}{2} \bar{c} \lambda$  to calculate the self diffusion coefficient of  $N_2$  at  $21^\circ\text{C}$  and one atm pressure; the bond length in nitrogen is 0.370 nm.

[50 marks]

(b) What is the least negative potential which must be applied to a copper cathode immersed in 0.35M  $\text{CuSO}_4$  at 298K in order to deposit copper from solution at a current density of  $51.7 \text{ A m}^{-2}$ ? Assume that concentration polarisation can be neglected. The equilibrium exchange current density ( $i_0$ ) is  $0.20 \text{ A m}^{-2}$  and the transfer coefficient ( $\alpha$ ) is 0.46.  $E^0 \text{ Cu}^{2+}/\text{Cu} = 0.34\text{V}$

[50 marks]

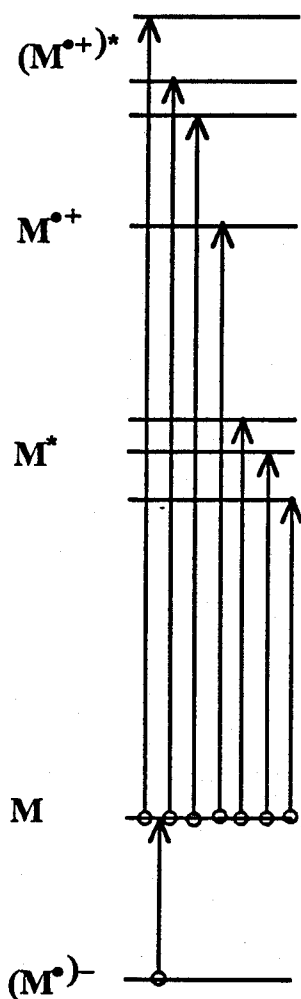
(c) Explain briefly why pulsed voltammetric techniques (normal pulse and differential pulse voltammetry for example) are more sensitive than linear sweep voltammetry.

If a peak current density of  $0.221 \text{ mA cm}^{-2}$  was measured at  $25^\circ\text{C}$  in a linear sweep voltammetric experiment in which the potential was scanned at  $100 \text{ mV s}^{-1}$ , for an electrochemically reversible one-electron redox transition of a species with a diffusion coefficient in the electrolyte of  $6.76 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , what is the concentration, in  $\text{mol dm}^{-3}$ , of the electroactive species in the electrolyte?

[50 marks]

2. The diagram below shows some electronic energy levels for a typical molecule.

Which spectroscopic techniques would be appropriate and what kind of information could you deduce from the transitions indicated?



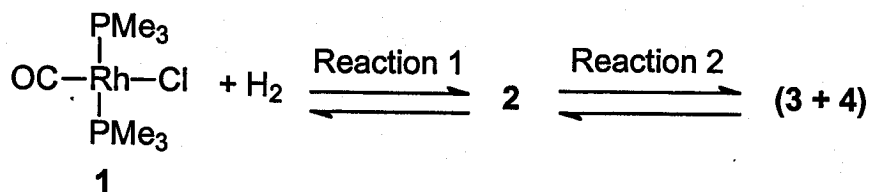
[100 marks]

3. Write an essay entitled: *Fundamentals of Electroplating*

[100 marks]

## Section B

4. Bubbling hydrogen gas through a pentane solution of  $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPr}^i_3)_2$ , **A**, leads to the formation of a white solid **B**. **B** is a mixture of two isomers, **B(1)** and **B(2)**, the ratio of which is solvent dependent, changing from 20:1 in dichloromethane- $\text{d}_2$  to 9:2 in toluene- $\text{d}_8$ . The  $^1\text{H}$  NMR spectrum of **B(1)** shows a 2H doublet at -10.09 ppm. The  $^1\text{H}$  NMR spectrum of **B(2)** has a similar pattern with more complex resonances integrating to 2H in the range -7.5 to -15.04 ppm. Treatment of the **B(1)/B(2)** mixture with  $\text{NaBH}_4$  yields a colourless oil **C** which has a lower P:Os ratio than **B**. When the  $^{31}\text{P}$  decoupled  $^1\text{H}$  NMR spectrum of **C** is observed between -14 and -16 ppm the singlet at -14.6 ppm observed at room temperature collapses as the temperature is reduced and resolves again at the low temperature limit yielding two resonances at -14 and -15 in the ratio of 1:2. Treatment of **A** with  $\text{HBF}_4$  yields an ionic red solid **D**. The  $^1\text{H}$  NMR spectrum of **D** contains a resonance integrating to 1H at -14.36 ppm. **B**, **C** and **D** all show resonances for the  $\text{C}_5\text{H}_5$  and  $\text{PPr}_3$  ligands in addition to those mentioned above. Give reasonable structures for **B(1)**, **B(2)**, **C** and **D** and explain your conclusions. [100 marks]
5. When a solution of  $[\text{Rh}(\text{CO})(\text{Cl})(\text{PMe}_3)_2]$  (**1**) was exposed to 3 atm of  $\text{H}_2$ , a series of reactions occurred to give **2** and (**3+4**) as outlined in the reaction scheme below. Apart from the normal proton resonances arising from the phosphine ligands, compounds **2** and **3** had  $^1\text{H}$  absorption at ca. -17 ppm. When the reaction was monitored by infra-red spectroscopy, it was found that  $\nu(\text{MC-O})$  went from 1905  $\text{cm}^{-1}$  to 1920  $\text{cm}^{-1}$  to 2150  $\text{cm}^{-1}$ .
- Draw a reaction scheme outlining the course of the reactions and identifying **2**, **3** and **4**. Your scheme should show the correct structures for **2** and **3**.
  - Deduce the oxidation states of the Rh in **1**, **2** and **3**.
  - What type of mechanism is involved in the reaction of **1** with  $\text{H}_2$ ? Give the reasoning for your answer.
  - How would you confirm the nature of the mechanism in Reaction 1?
  - Account for the changes in  $\nu(\text{MC-O})$  as the reaction proceeds.
  - What would happen if an excess of  $\text{PMe}_3$  were added to **1**?



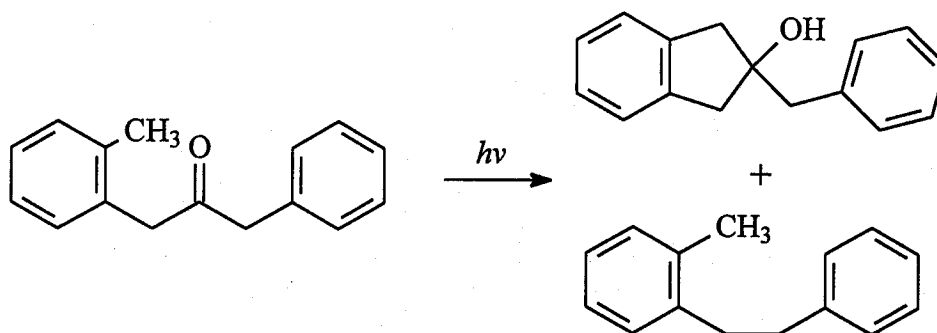
6. Write an essay entitled "Interhalogen Compounds".

[100 marks]

# Section C

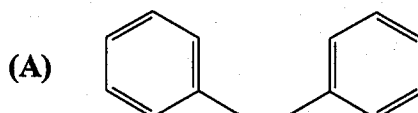
## 7. Answer all parts

- (i) Suggest a mechanism by which the products of the following reaction might be formed:



[25 marks]

- (ii) Bibenzyl (A) is also formed in small amounts. Suggest a mechanism by which it might be formed and, in view of the formation of (A), indicate what other aromatic hydrocarbon might be expected.

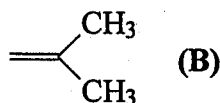


[25 marks]

- (iii) Explain how the reaction could be carried out experimentally, describing in particular a suitable photochemical reactor.

[25 marks]

- (iv) Which type of excited state ( $n \rightarrow \pi^*$  or  $\pi \rightarrow \pi^*$ ) would you expect to be involved in the formation of the cyclopentanol product in Part (i)? Explain why the observed behaviour might be anticipated for this excited state and draw the structure of the products that might be expected were the ketone to be irradiated in the presence of the alkene (B).



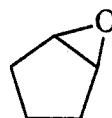
[25 marks]

8. Answer any two of the following:

- (i) Describe how diethylcopper lithium may be prepared in the laboratory and briefly discuss its reactions with both alkyl and aryl iodides and cyclic epoxides, such as cyclopentene-oxide (shown below). Include the stereochemistry of the reactions and products where appropriate.

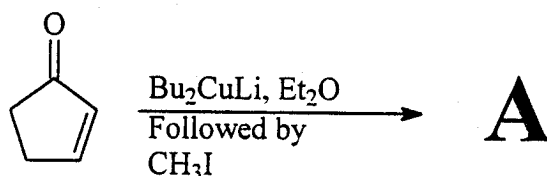
[30 marks]

*Cyclopentene-oxide*



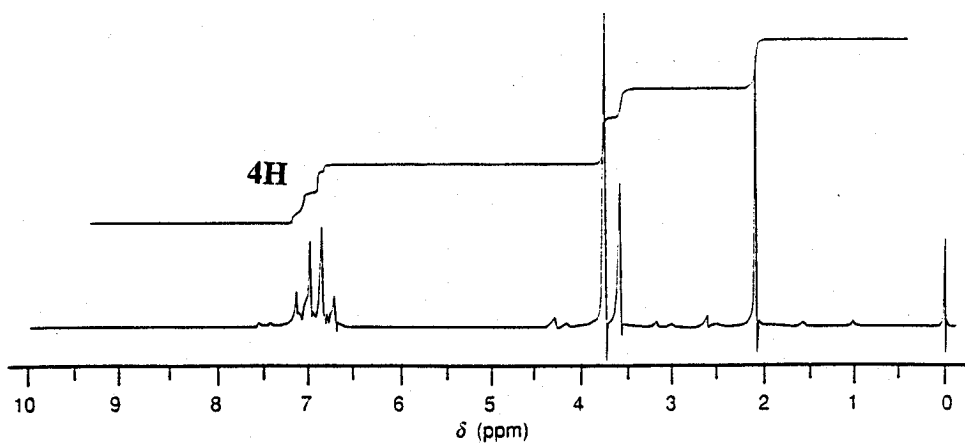
Deduce the structure of A and account for its formation and relative stereochemistry.

[20 marks]

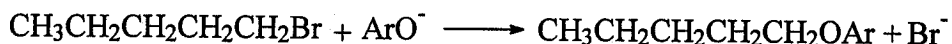


- (ii) A compound of formula  $C_{10}H_{12}O_2$ , was isolated from a chemical reaction. Its i.r. spectrum showed an intense absorption at  $1720\text{cm}^{-1}$ . Its  $^1\text{H}$  NMR spectrum is shown. Identify the compound and explain your reasoning.

[50 Marks]



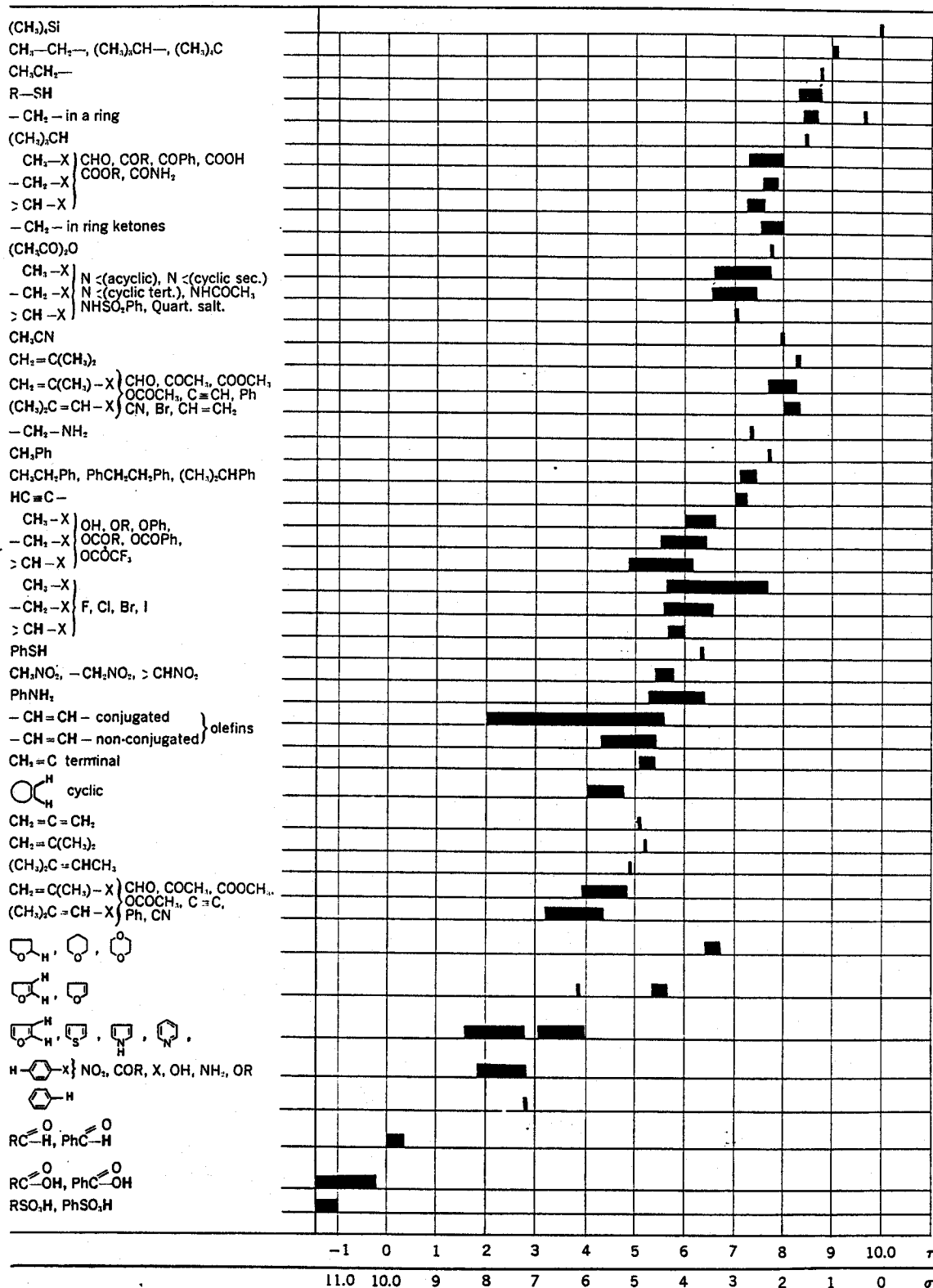
- (iii) The 'quaternary ammonium' catalysed  $S_N2$  reaction shown gave good clean second order kinetics i.e. first order in alkyl bromide and first order in aryloxide ion.



The main channel of the reaction was as shown but some elimination product  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$  was also formed. Describe the experiments that you would design to try to find out whether the reaction is a true phase transfer (PT) catalysed process or simply a micellar/interfacial type of process. **[50 Marks]**

9. Write an essay entitled "Bent Bonds in Organic Chemistry".

## Characteristic NMR Spectral Positions for Hydrogen in Organic Structures



This table is useful for quick qualitative determination of proton spectrum lines by providing a tabulation of line positions obtained using tetramethylsilane as an internal reference. The listing has been kept as simple as possible for this purpose. The proton spectrum lines are arranged according to the chemical shift relative to tetramethylsilane and are given in values of  $\tau$  and  $\sigma$ . The purpose of this table is to supplement tables available in standard references and to summarize information available in the literature.