

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

SUMMER EXAMINATIONS 2002

FINAL EXAMINATION FOR THE DEGREE OF B.Sc. HONOURS

CHEMISTRY (CH401)

Fourth Paper

All questions carry 100 marks, distributed as shown.

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Professor I. Fleming
Professor K.C. Waugh

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.

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 N m^{-2}

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Section A

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

- (a) Using water (vapour pressure, 3 cm Hg approx at 298 K) as an example, estimate the average lifetime of a molecule in the surface of a liquid.

[50 marks]

- (b) The data in the following table refer to the anodic current through a platinum electrode of area 2.0 cm^2 in contact with an Fe^{3+} , Fe^{2+} aqueous solution at 298K

η/mV	50	100	150	200	250	350
I/mA	8.8	25.0	58.0	131	298	300

Estimate the exchange current density (i_0), the transfer coefficient (α) and the limiting current (i_L) for the electrode process.

[50 marks]

- (c) In low energy electron diffraction (LEED), electrons are accelerated towards a surface and the diffraction pattern of the elastically scattered electrons is detected. This technique thus requires electrons that have wavelengths on the order of inter-atomic distances to give information about the atomic surface structure. If an electron beam is accelerated to 0.5kV what is its resultant wavelength? Is this an appropriate source for the LEED experiment? ($1\text{eV} = 1.6022 \times 10^{-19}\text{J}$)

[50 marks]

2. The schematic diagrams shown below refer to what technique?

[10 marks]

Briefly discuss the mode of action with reference to each diagram.

[40 marks]

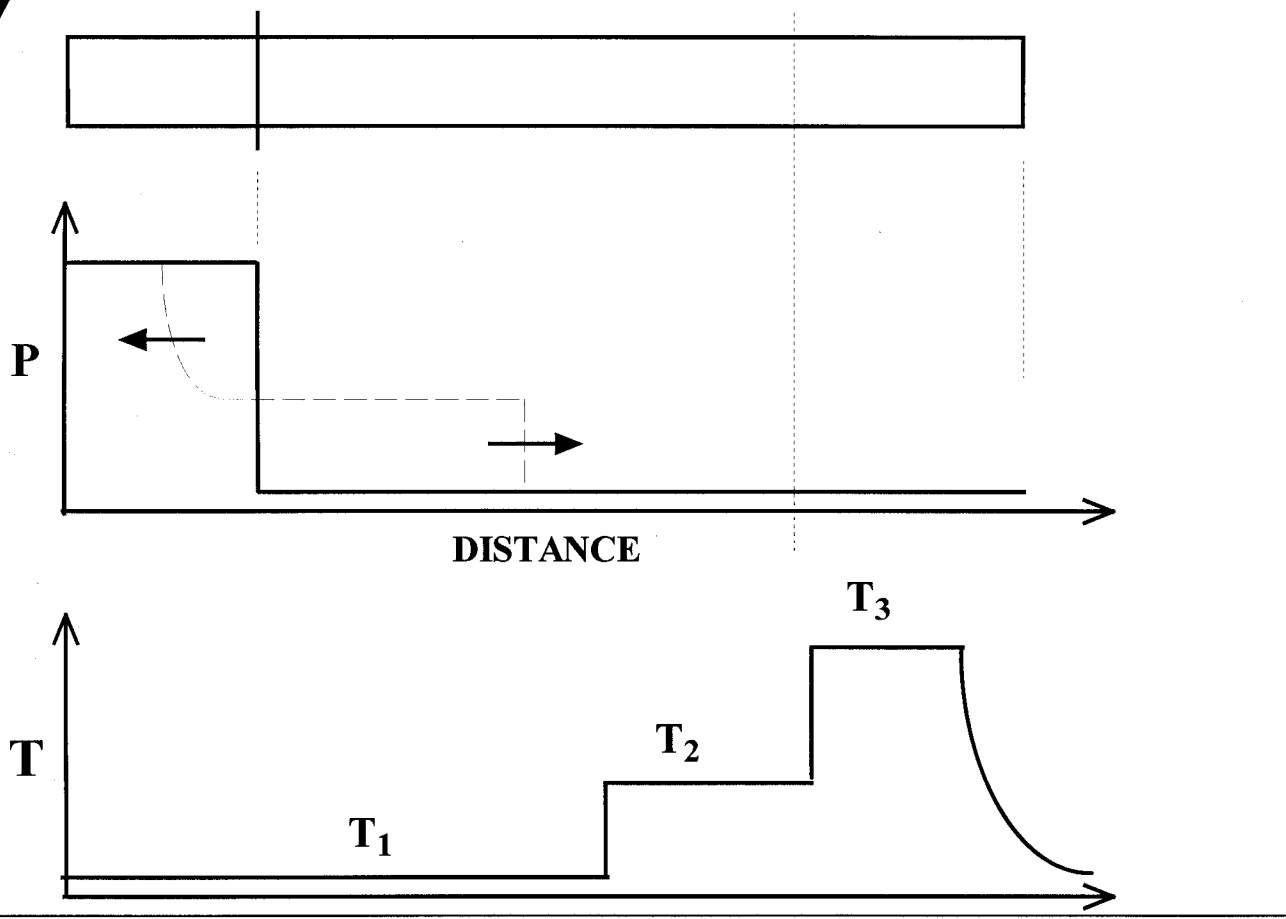
Indicate what kinds of information you could deduce from measurements carried out with the apparatus.

[30 marks]

What additional instrumentation would you think desirable?

[20 marks]

Question continued on next page.....



3. Write an essay entitled: *Voltammetry*

[100 marks]

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Section B

4. When equimolar quantities of green nickelocene, $(\eta^5\text{C}_5\text{H}_5)_2\text{Ni}$, and green $(\text{PPh}_3)_2\text{NiCl}_2$ are heated in tetrahydrofuran (THF) solution the sole product, isolated in near quantitative yield, is red **A**. Treatment of **A** in THF solution with one molar equivalents of PPh_3 and AgBF_4 led to the isolation of yellow **B**. **B** is a 1:1 electrolyte in PhNO_2 solution. Treatment of **A** with one molar equivalent of PPh_3 and excess SnCl_2 in THF led to the isolation of yellow **C**. While there are some differences in the IR spectra of **B** and **C** the spectra are for the most part identical. In solution **C** is unstable in some solvents. It is transformed back to **A** if SnCl_2 is soluble in the solvent.
- Suggest reasonable structures for **A**, **B** and **C**, explain the transformations involved and give valence electron counts for the Ni in each complex. [100 marks]

5. SbPh_3 and SbCl_3 were reacted to give a product **A** in quantitative yield. However, confusion arose as to whether a 1/2 or 2/1 molar ratio respectively of the reactants had been employed. **A** was oxidised with bromine to give a new product **B**. **B** was further reacted with KCl to give exclusively the product **C** which crystallized in the space group $P\bar{1}$. By applying the heavy atom technique, one antimony was located per unit cell. When **C** was reacted with NMe_4Cl rather than KCl the new product **D** was obtained.

Answer **each** of the following;

- (a) Based on the data presented, provide balanced equations leading to the formation of **A**, **B** and **C**. Clearly explain why you decide on these equations, specifically clarifying why you choose 1/2 or the alternative 2/1 molar ratio of reactants in the formation of product **A**. [50 marks]
- (b) List the possible coordinates for Sb in the crystal structure of **C**. [10 marks]
- (c) Why is it not possible for **D** to crystallize in the same space group as **C** with one molecule per unit cell? [10 marks]
- (d) Explain how it would be possible for **B** to crystallise in the space group $P\bar{1}$ with four molecules per unit cell. [10 marks]
- (e) Clearly show how the heavy atom technique is applied to determine the position of atoms? [20 marks]
6. Write an essay entitled "Inter-halogen Compounds". [100 marks]

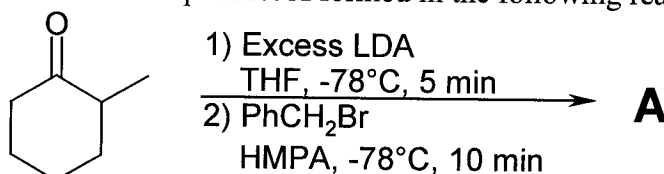
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Section C

7. Answer any two of the following (i), (ii), (iii):

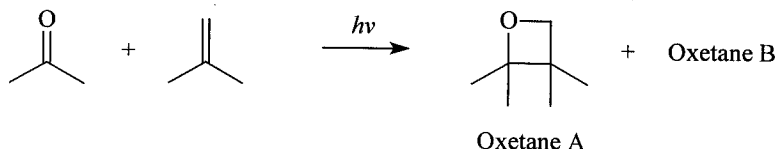
(i) The most widely used non-nucleophilic organolithium base utilised in organic synthesis is lithium di-isopropylamide (LDA).

- (a) Show how LDA may be prepared in the laboratory from 1-bromobutane, di-isopropylamine and any inorganic reagents necessary [10 Marks]
- (b) Draw the two canonical forms of the product of reaction of acetone (CH_3COCH_3) with LDA [10 Marks]
- (c) Predict the structure of product A formed in the following reaction [10 Marks]



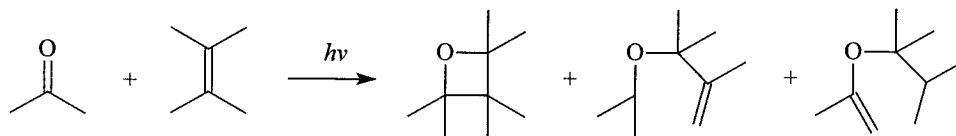
- (d) Also isolated from the above reaction was 1.0% of an isomer of product A. Draw this isomer and explain why A is the major isolated product [20 Marks]

(ii) The photochemical cycloaddition of alkenes to ketones can be used to prepare oxetanes. The reaction of 2-methylpropene with acetone gives a mixture of two oxetanes:



- (a) Provide a structure for oxetane B [5 marks]
- (b) Outline a simple mechanism for the reaction [10 marks]
- (c) Account for the fact that A is the major product formed. [10 marks]

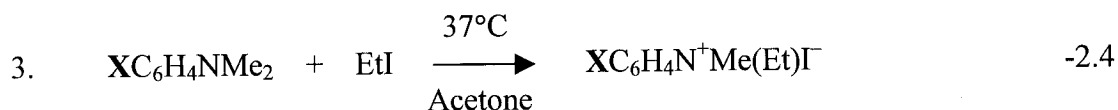
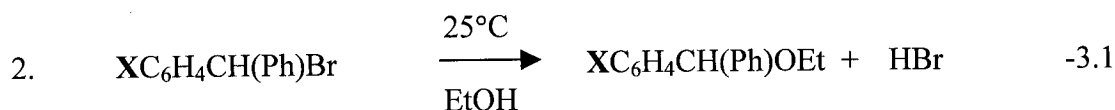
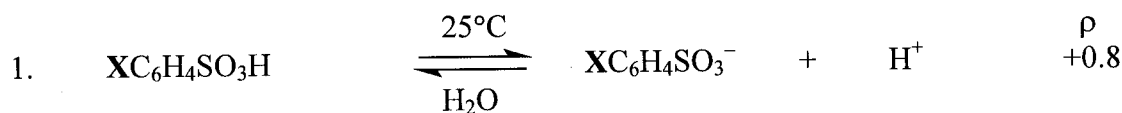
The reaction between acetone and tetramethylethene gives not only an oxetane but also two acyclic products:



- (a) Draw down structures of the corresponding acyclic compounds that could be formed with 2-methylpropene. [5 marks]
- (b) Outline simple mechanisms by which they might be formed. [10 marks]
- (c) How would you show that all these reactions involve the triplet state of the ketone. [10 marks]

(iii)

A Hammett study was carried out on the following equilibrium/reactions by varying the substituent **X** in each substrate and the ρ (rho) values shown were obtained.

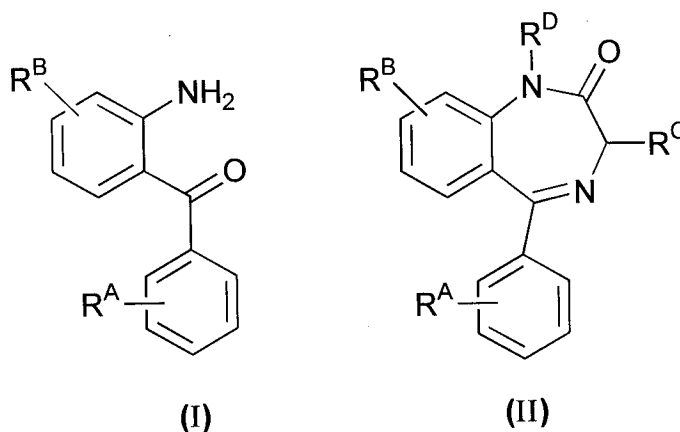


- (a) In the case of 1–3 above make an approximate sketch of the Hammett plots used to obtain the ρ values. **[30 marks]**
- (b) In the case of 1 comment on the value of +0.8 and for 2 and 3 indicate possible mechanisms for the reactions occurring. **[20 marks]**

8. Answer any two of the following (i), (ii), (iii):

- (i) (a) Draw the chemical structure of any base found in nucleic acids. **[15 marks]**
- (b) Draw the chemical structure of any nucleotide found in nucleic acids. **[15 marks]**
- (c) Indicate the hydrogen-bonding found between any base pair in DNA. **[20 marks]**

(ii)

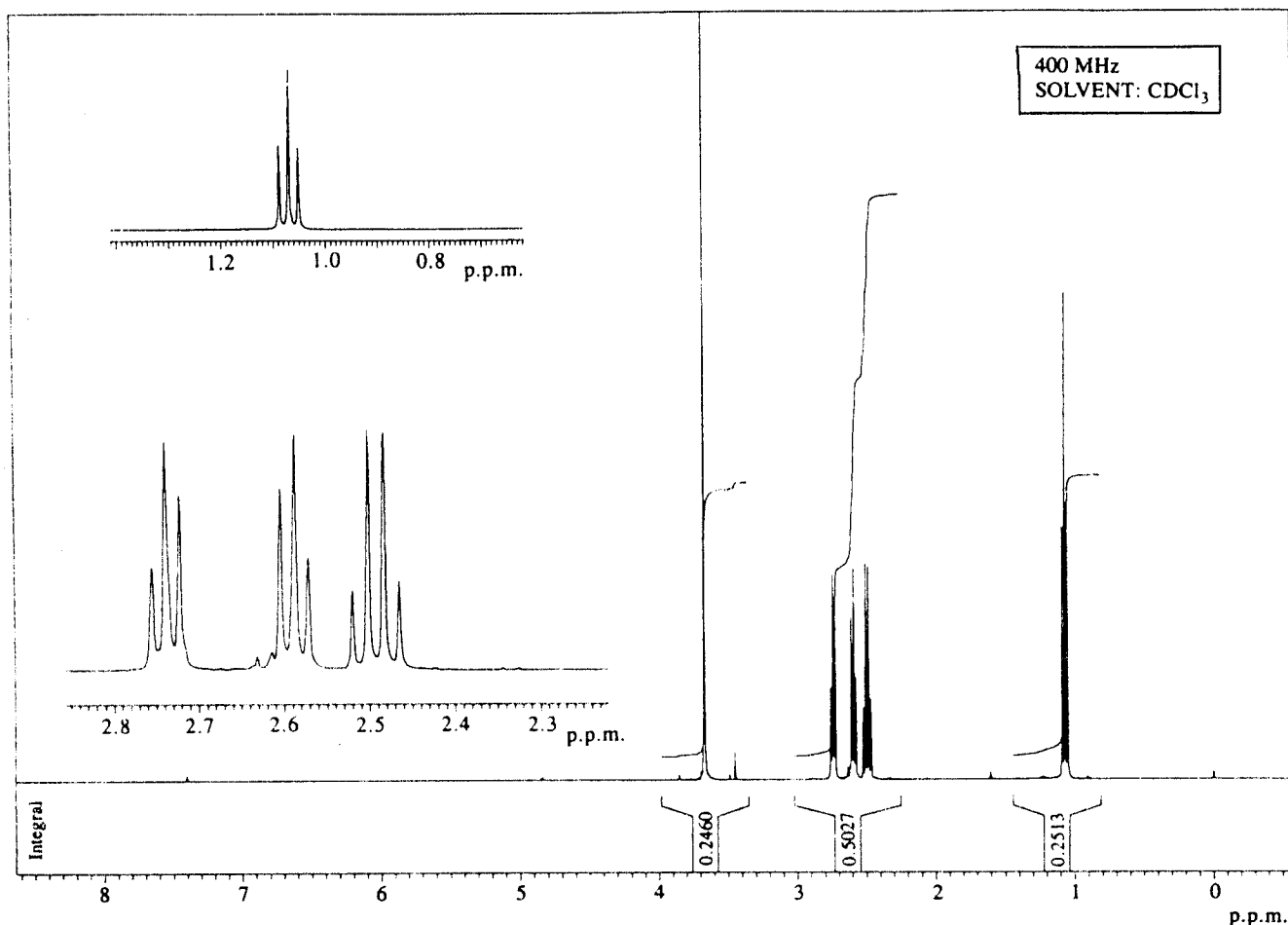


Outline the “Ellman” combinatorial solid-phase synthesis of 1,4-benzodiazepine derivatives (II) from 2-aminobenzophenones (I). Explain the term “Traceless Linker”.

[50 Marks]

- (iii) A compound of formula $C_7H_{12}O_3$ was isolated from a reaction. Its proton NMR spectrum is shown. The region between 1–3 ppm is expanded in the inset to show the splitting patterns more clearly. The i.r. spectrum of the compound showed strong absorption bands at 1720 and 1740cm^{-1} . Identify the compound and explain your reasoning.

[50 Marks]



9. Write an essay entitled "The Sharpless Asymmetric Epoxidation and Dihydroxylation of Alkenes"

[100 Marks]