GX298

OLLSCOIL NA hÉIREANN, GAILLIMH

THE NATIONAL UNIVERSITY OF IRELAND, GALWAY

SUMMER EXAMINATION 1999

FINAL EXAMINATION FOR THE DEGREE OF B.Sc. HONOURS

CHEMISTRY

CHEMISTRY AND APPLIED CHEMISTRY (DENOMINATED)

THIRD PAPER

Professor R.C.F. Jones
Professor R.N. Butler
and Internal Examiners

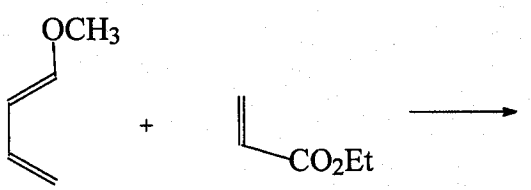
Time Allowed: Three Hours
Answer Five questions

All questions carry 100 marks distributed as shown where appropriate. Leave the first page of the Answer Book blank and list on it clearly the number of the questions attempted.

1. Answer each of the following:

(i) Explain the terms: Pericyclic Reaction; Electrocyclic Reaction; Sigmatropic Rearrangement. **[15 marks]**

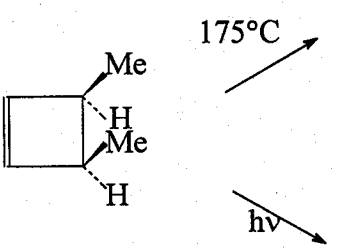
(ii) Discuss and explain the main features of the Diels-Alder reaction. Complete the following reactions and account for the formation of the products. **[45 marks]**



$Me_3C-CH=CH-CMe_3$ → (i) O_3 (ii) Reduction

(iii) Briefly comment on the structure of cyclooctatetraene. **[20 marks]** Explain how the molecule responds to a Diels-Alder reaction with a normal dienophile.

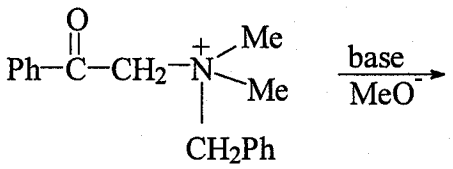
(iv) Complete and briefly explain the following reactions:



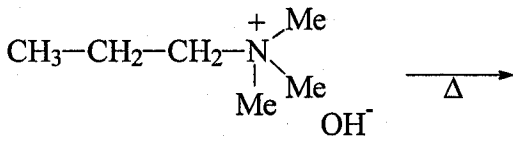
[20 marks]

2. Answer <u>each</u> of the following:

(i) Draw the products and briefly compare and contrast the following reactions of N,N-dimethyl ammonium salts. **[30 marks]**

(a) 

Stevens

(b) 

Hoffmann

(ii) Suggest how <u>electrophilic</u> substitution could be achieved at the 2- and 4- position of pyridine and explain why this is normally difficult to perform. **[30 marks]**

(ii) Comment on the chemical reactivity and industrial importance of the 1,3,5-triazine structure. **[20 marks]**

(iii) Comment on the basicities of the azoles and explain the difference between the basicities of pyrazole and imidazole. **[20 marks]**

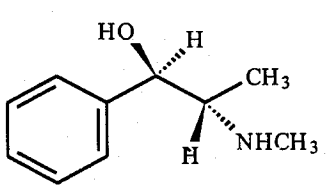
3. Answer <u>all</u> parts

(i) Outline the general approach to alkaloid biosynthesis **[10 marks]**

(ii) Describe the advantages and disadvantages of stable isotopes over radioactive isotopes for biosynthetic studies **[15 marks]**

(iii) Explain how to detect and locate the position of incorporation of
i) a 14-C labelled precursor and
ii) a 13-C labelled precursor into an alkaloid structure
[25 marks]

(iv) Describe how the biosynthetic route to (-) - ephedrine was unveiled **[50 marks]**

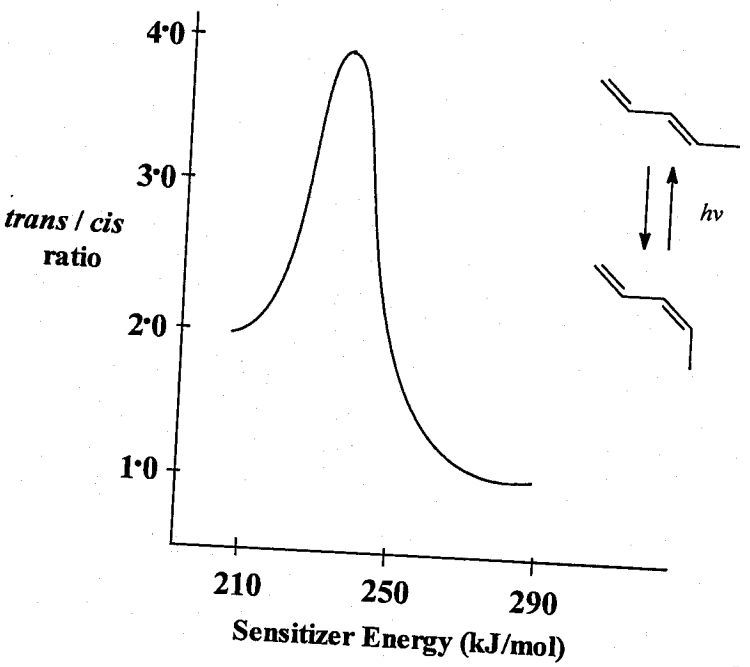


(-) - Ephedrine

4. Discuss both the direct and the photosensitized *cis-trans* isomerization of alkenes.

[60 marks]

A study of the effect of triplet sensitizer energy on the photostationary state composition of penta-1,3-diene produced the data summarized in the figure below. Draw an energy level diagram for this photochemical system and use it to account for the results obtained. [It is the ***trans/cis*** ratio which is plotted on the y-axis].



[40marks]

5. Phase transfer (PT) procedures have found wide application in organic chemistry.
Show how the concept of phase transfer catalysis has been supported with a number of well designed experiments.

[70 marks]

Give **two** examples of the use of PTC in the chemical industry **[30 marks]**

6. **Answer each of the following:**

(a) Draw the structure of any nucleotide. **[20 marks]**

(b) Describe the laboratory synthesis of any nucleotide. **[20 marks]**

(c) Outline the steps involved in the automated synthesis of oligonucleotides using the phosphoramidite coupling method.

[40 marks]

(d) Draw the structure of *either* Acyclovir *or* AZT and briefly discuss its use as a chemotherapeutic agent. **[20 marks]**

7. Answer 7(A) or 7(B)

7(A) Answer all parts

(i) With the aid of a diagram describe ***either*** the electrospray (ESI) ***or*** the matrix assisted laser desorption (MALDI) ionisation technique used in mass spectral analysis.
What is the main advantage of these methods over electron impact (EI) ionisation for analysis of biomolecules? **[25 marks]**

(ii) What is meant by resolution in mass spectrometry? **[5 marks]**

Explain how the two sector double focusing mass analyser [magnetic plus electrostatic] functions to improve resolution over that obtained with a single sector magnetic instrument. **[20 marks]**

What resolving power would be needed for a mass spectrometer to distinguish between the following pairs of compounds?

a. CO and C_2H_4

b. $C_{11}H_{22}O$ and $C_{12}H_{26}$

[monoisotopic masses; C, 12.0000; H, 1.0078; O, 15.9949]
[20 marks]

(iii) Outline the triple quadrupole MS-MS approach to the structural determination of biomolecules, *e.g.* peptide or protein analysis.
[30 marks]

OR

7(B) Discuss each of the following topics:

(i) crosslinking in polymers **[30marks]**

(ii) the stereochemistry of polymers **[30marks]**

In the case of styrene provide a detailed mechanism for its polymerization, explaining how a crosslinked polymer might be produced and how the molecular weight of the polymer can be controlled. **[40marks]**

8. Answer 8(A) or 8(B)

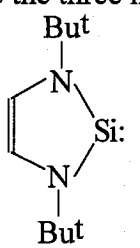
8(A) Write formulae for each of the following species and show how they may be generated.

(i) silylenium ion (silacenium ion)

(ii) silene

(iii) disilene **[50 marks]**

Give a method of preparation of silylenes and show how they can undergo addition and insertion reactions.
Very recently (*J.Am. Chem. Soc.*, **120**, 12714 (1998)), "the truly remarkable" silylene **1** has been prepared. It can be distilled at 85°C (1 Torr) and survives heating in toluene at 150°C; it fails to add to acetylenes or to insert in Si–H bonds. However it does insert into O–H bonds of H_2O and of EtOH and into the C–I bond of CH_3I. Write the three insertion products. **[50 marks]**



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OR

8(B) Discuss the chemistry of industrially important polysaccharides under the following headings:

(a) Source **[10 marks]**

(b) Structure **[40 marks]**

(c) Properties **[25 marks]**

(d) Uses **[25 marks]**