GX303

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

SUMMER EXAMINATIONS 2000

FINAL EXAMINATION FOR THE DEGREE OF B.Sc. HONOURS

CHEMISTRY

CHEMISTRY AND APPLIED CHEMISTRY (DENOMINATED)

THIRD PAPER CH401/402

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

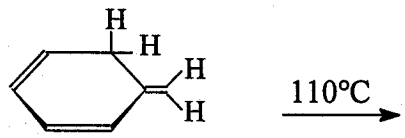
Time Allowed: Three Hours
Answer five questions

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) Briefly explain the principles governing electrocyclic reactions and sigmatropic rearrangements. **[40 Marks]**

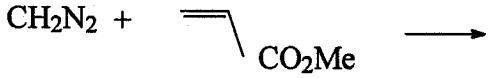
(ii) 5-Methylene-1,3-cyclohexadiene(1) requires heating at 110°C in the gas phase before it aromatises. Identify the product and explain why the molecule is unexpectedly stable.



(1)

[20 Marks]

(iii) Discuss the electronic structure of diazomethane, CH_2N_2, and complete and explain the following cycloaddition reaction with methyl acrylate.



[40 Marks]

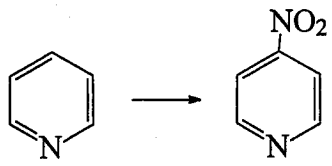
2. Answer <u>each</u> of the following:

(i) Briefly explain the influence of the nitrogen atom in pyridine on
(a) its physical properties and
(b) its chemical behaviour towards electrophiles and nucleophiles

[40 Marks]

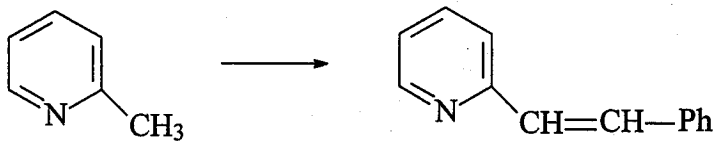
(ii) Suggest synthetic schemes by which the following transformations could be achieved in good yields:

(a)



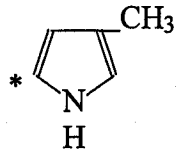
[15 Marks]

(b)



[15 Marks]

(iii) Explain the Hoffman 1,2-elimintion reaction of quaternary ammonium salts. Use it to devise a degradation of 3-methylpyrrole (**A**) so as to isolate the labelled atom.



(A)

[30 Marks]

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

(i) Draw the structure of any nucleotide **[15 Marks]**

(ii) Discuss briefly the basic strategy of nucleic acid sequencing **[15 Marks]**

(iii) Describe the chemical method of Maxam and Gilbert of DNA sequencing **[30 Marks]**

(iv) Describe the chain terminator (primed synthesis) method of Sanger of DNA sequencing **[30 Marks]**

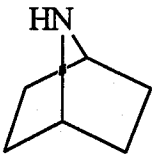
(v) Describe the use of mass spectrometry in DNA sequencing **[10 Marks]**

4. Answer <u>both</u> parts:

(i) Epibatidine is a potent alkaloid isolated from the skin of the Ecuadorian frog, *Epipedobates Tricolor*, however it is only available in small amounts from the natural source. This problem was solved by the synthesis of this molecule in the laboratory. The basic carbon framework, 7-azabicyclo[2.2.1]heptane (shown below), is synthesised in three different ways, discuss each of these in turn with particular reference to any protecting/activating groups or generation of reactive intermediates necessary.

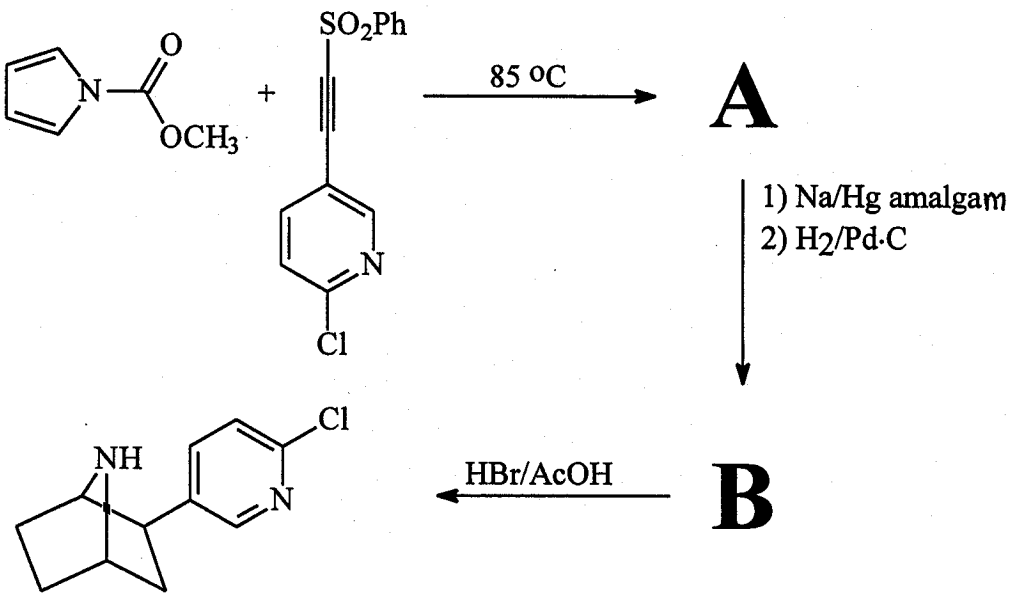
[70 Marks]

7-Azabicyclo[2.2.1]heptane



(ii) Shen *et al.* produced racemic epibatidine from the pyrrole derivative and the alkyne in 4 steps as shown below. Deduce structures for **A** and **B** and explain how they are formed. How might the enantiomers of the racemic epibatidine produced be resolved?

[30 Marks]



Epibatidine

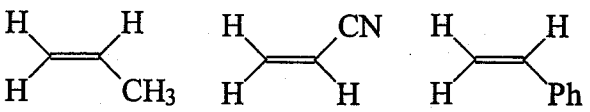
5. Use a Jablonski diagram to discuss the various photophysical processes that can occur after a molecule absorbs a photon of light. Include an indication of the rates of the various processes you mention and explain why most intermolecular photochemical reactions involve the triplet state. **[70 Marks]**

When X ($E(T_1) = 280 kJmol^{-1}$) is irradiated in cyclohexane a product Y is formed. When X is irradiated in the presence of *cis*-1,3-pentadiene ($E(T_1) = 238 kJmol^{-1}$), no product is formed. What can be deduced from these results? **[30 Marks]**

6. Explain what is meant by each of the following and, using simple mechanisms, show how they occur:

anionic polymerisation
polymer chain branching
copolymerization
graft copolymerisation. **[70 Marks]**

Order the following monomers with respect to their expected reactivity in an anionic polymerisation reaction. Draw a simple mechanism for the polymerisation of the most reactive of the three and suggest a suitable initiator.



[30 Marks]

7. Describe the principal methods for determining the correct acidity function and the pK_{XH}^{+} value for the weak base, X. **[30 Marks]**

The following acidity functions have been developed for particular sets of weak bases:

(a) H_A
(b) H_O'''
(c) H_B
(d) H_R (J_O)

Indicate the types of bases involved in each case. **[20 Marks]**

Why do different sets of weak bases need different acidity functions to describe their protonation behaviour? **[25 Marks]**

Write a short note on the basicity function H_-.

8. Discuss the chemistry of the polysaccharide Alginic Acid (Alginate) under the following headings:

(a) Isolation **[20 Marks]**
(b) Structure of repeating unit **[30 Marks]**
(c) Egg box model of solution conformation **[10 Marks]**
(d) Industrially important properties **[20 Marks]**
(e) Industrial uses **[20 Marks]**