GX 367

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

AUTUMN EXMAINATIONS 2002

THIRD UNIVERSITY B.Sc. EXAMINATION IN SCIENCE (INCLUDING DENOMINATED DEGREES)

Paper III: Organic Chemistry (CH311)

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Time Allowed: Two Hours

Answer four questions –
Two from Section A and Two from Section B

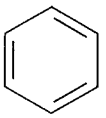
All questions carry equal marks. For a question with a choice between parts, all parts of that question carry equal marks.

Leave the first page of the answer book blank and list on it clearly the numbers of the questions attempted.

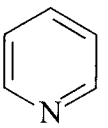
Section A

1. Answer (i) and (ii)

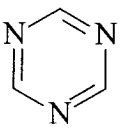
(i) Comment on the chemical and physical criteria of aromaticity and compare the aromaticities of the molecules (A), (B) and (C).



(A)



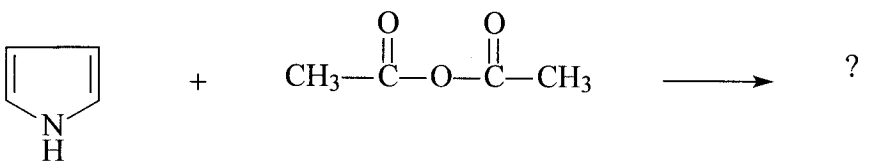
(B)



(C)

[13 marks]

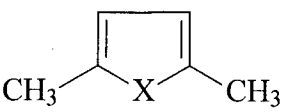
(ii) Complete the following Friedel Crafts reaction. Explain the regiochemistry and why no catalyst is required.



[12 marks]

2. Answer each of the following:

(i) Explain the terms *5-exo-trig* and *5-endo-dig* for the synthesis of ring structures. Give a synthesis of the molecule (A) involving a *5-exo-trig* step and (B) involving a *5-endo-dig* step.



(A) X = NH
(B) X = S

[10 marks]

(ii) Explain the term "chiral recognition" in connection with the biological activity of molecules. **[7 marks]**

(iii) Show how penicillin-G works as an antibiotic. **[8 marks]**

3. Using a number of examples show how mechanistic deductions can be made from experimentally determined rate laws for organic reactions.

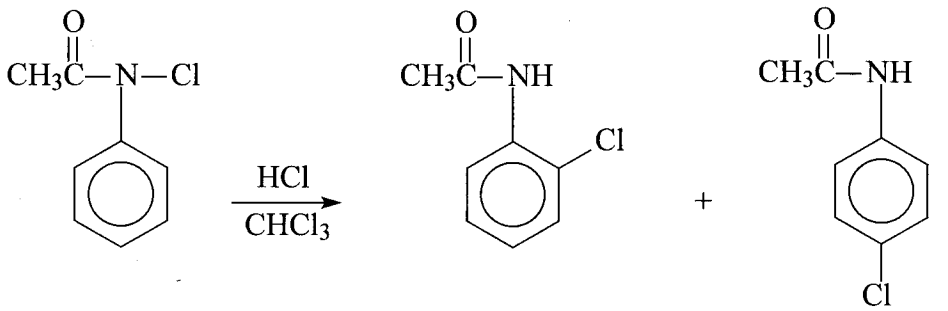
The rate law for the nucleophilic displacement

$$(CH_3)_2CHBr + NaOH \rightarrow HOCH(CH_3)_2 + NaBr$$

in aqueous acetone was $v = k[(CH_3)_2CHBr][NaOH]$. **[18 marks]**

Write a plausible mechanism for the reaction. **[7 marks]**

4. Show how radioisotopes (^{14}C, ^{35}S and ^{3}H (T)) can be employed to probe mechanisms of organic reactions.
One of the earliest uses of a radioisotope to probe an organic reaction was the use of ^{36}Cl ($t_{½}$ = 3.1 x 10^5 yrs) to examine the molecularity, i.e. INTRA or INTER, of the Orton rearrangement shown.



[20 marks]

Devise an experiment using ^{36}Cl to elucidate the mechanism of this rearrangement. Mention any precautions that you might need to take to verify your results. **[5 marks]**

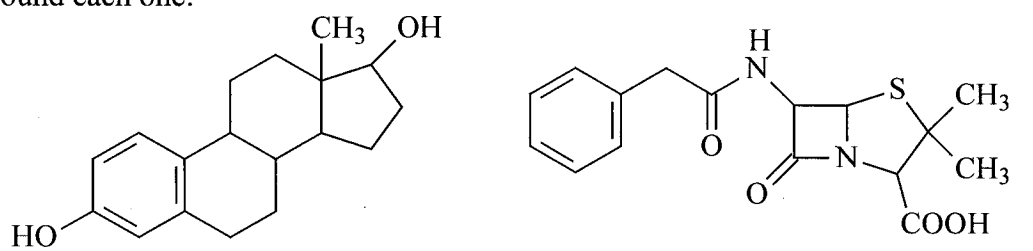
Section B

5. Write brief notes explaining the stereochemical significance of each of the following:

(a) allene enantiomers **[5 marks]**
(b) prochiral carbon **[5 marks]**
(c) resolution **[5 marks]**
(d) enantiomeric excess (and how it might be measured) **[5 marks]**

Appropriate structural diagrams should be used, and examples given, in (a), (b) and (c).

Identify all the asymmetric carbon atoms in the following structures by drawing a circle round each one:



[5 marks]

6. (i) Describe the various categories – for example, total synthesis – into which organic syntheses can be divided. **[8 marks]**

(ii) Explain the difference between a convergent and a linear synthesis and determine the overall yield of a linear synthesis which involves four steps, two of which proceed in 90% yield and two in 50%. **[8 marks]**

(iii) Describe the retrosynthetic analysis of any molecule of your choice, using it to provide examples of a disconnection, a synthon, a synthetic equivalent, and a functional group interconversion. **[9 marks]**

7. **Answer <u>each</u> of the following:**

(i) Give three criteria for a good protecting group in organic synthesis. **[3 marks]**

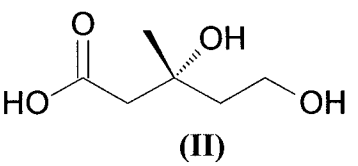
(ii) Draw a Fischer projection of the simplest chiral DNA-encoded amino acid, L-alanine. **[2 marks]**

(iii) Give separate reaction schemes for the **t-Boc** (t-Butyloxycarbonyl) and **Fmoc** (fluorenylmethyloxycarbonyl) protection and de-protection of an amino acid. When is each protecting group useful? **[14 marks]**

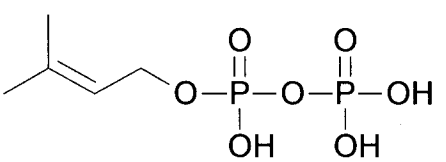
(iv) Give mechanisms for the cleavage of **both** protecting groups. **[6 marks]**

8. **Answer <u>each</u> of the following:**

(i) Treatment of D-glucose with bromine-water gives an aldonic acid **(I)**. An aqueous solution of the sodium salt of **(I)** is heated with a catalytic quantity of iron (III) sulfate in 30% hydrogen peroxide to give D-arabinose. This reaction is commonly known as the Ruff degradation. Using Fischer projections, give reaction schemes for the conversion of D-glucose into D-arabinose. Briefly comment on the reasons for using only a catalytic amount of Iron (III) sulfate in the Ruff degradation.



(II)



(III)

[11 marks]

(ii) Mevalonic acid **(II)** is a key intermediate in the biosynthesis of terpenes, however it is in equilibrium with its lactone. Draw mevalonolactone. **[2 marks]**

(iii) Draw the structure of ATP (adenosine triphosphate). **[3 marks]**

(iv) Use mechanisms to explain the conversion of mevalonic acid (**II**) into dimethylallyl pyrophosphate (**III**). What is the role of ATP and the pyrophosphate group in terpene biosynthesis? **[9 marks]**