Semester II Examinations 2013-2014

Exam Code(s)  4BS
Exam(s)        4th year Chemistry

Module Code(s)  CH439
Module(s)       

Paper No.  1 of 1

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Instructions: Answer three 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 numbers of the questions attempted.

Duration          2 hours
No. of Pages      4 (incl. this one)
Discipline(s)     Chemistry

Requirements      None
1. Answer all parts

(a) Draw the π molecular orbitals of 1,3,5-hexatriene (A) in order of increasing energy. Identify (i) the bonding and anti-bonding orbitals, and (ii) the HOMO and LUMO, and indicate whether the HOMO and LUMO are anti-symmetric or symmetric.

![Molecular orbitals of 1,3,5-hexatriene](image)

[30 marks]

(b) (i) Give an example of a [3,3] and a [1,5] sigmatropic shift, and provide simple arrow pushing mechanisms for both reactions.

(ii) Using appropriate diagrams, explain what is meant by a suprafacial and an antarafacial sigmatropic shift. How can the shift of carbon based groups occur suprafacially for both symmetric and anti-symmetric systems?

[20 marks]

(c) The following reaction scheme involves two pericyclic reactions. Provide a structure for the intermediate B, and simple arrow pushing mechanisms for the two stages of the process. What type of pericyclic reaction is involved in each step?

![Reaction scheme](image)

[30 marks]

2. Answer all parts

(a) The carbonyl group in ketones is one of the most photochemically active of all functional groups. Discuss the photochemistry of ketones under the following headings:

(i) basic photochemistry of the carbonyl group [10 marks]
(ii) α-cleavage reactions [20 marks]
(iii) hydrogen abstraction reactions [20 marks]
(iv) addition to alkenes [20 marks]

Examples and simple mechanisms must be provided
(b) Irradiation of the cyclobutanone C in methanol leads to the formation of a number of products; the formation of D also involves the production of carbon monoxide (CO). Provide simple arrow pushing mechanisms by which these products could be formed.

\[
\begin{align*}
\text{C} & \xrightarrow{hv} \text{CH}_3 \text{CH}_3 \\
\text{CH}_3 \text{CH}_3 & + \text{CH}_3 \text{O} \text{CH}_3 \\
\text{OCH}_3 & + \text{CH}_3 \text{CH}_3 \\
\text{H} & + \text{HCH}_2 \text{CH}_3 \\
\text{H}_3 \text{C} & + \text{H}_3 \text{C} \text{CO} \\
\text{D} & \text{11%} \\
\text{13%} & \\
\text{13%} & \\
\end{align*}
\]

[30 marks]

3. **Answer all parts**

(a) Give reaction conditions and curly arrow mechanism for the synthesis of caprolactam from the oxime of cyclohexanone.

[b]caprolactam

[25 marks]

(b) Give reaction conditions and a curly arrow mechanism for the polymerization of caprolactam to give nylon 6.

[25 marks]

(c) Define the term degree of polymerization.

[2 marks]

(d) Sketch average degree of polymerization versus conversion plots for a conventional radical polymerization, living addition polymerization and step growth polymerization. Briefly comment on the reasons for the trend observed in each case.

[18 marks]

(e) Give reaction conditions and a curly arrow mechanism for the preparation of the following block copolymer:

[30 marks]
4. **Answer all parts**

(a) Write notes on the stability of radicals (E-H). Where appropriate draw resonance structures. Predict and compare the half-lives and hybridization of radicals.

![Resonance structures](image)

(b) Sulfonl pyrrolidine (J) was prepared in 87% yield via slow syringe pump addition of n-Bu3SnH and azoisobutyronitrile (AIBN) to a refluxing solution of (I) in benzene. Give a full radical chain mechanism for the formation of (J). Give reasons for relative amounts of n-Bu3SnH and AIBN required. Why is the slow syringe pump addition of these reagents necessary? Name the cyclization and sketch the Beckwith transition state. Why does the kinetic product form?

![Radical mechanism](image)