

Eastern University Sri Lanka

Third Examination in Science (Special Degree in Chemistry)-2010/2011

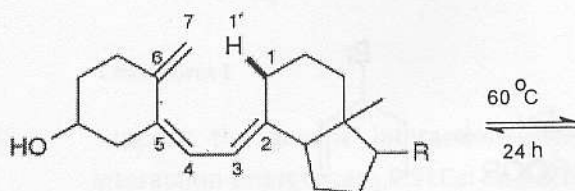
CH 402 Advanced Organic Chemistry

Answer All the questions

Time Allowed: Two hours

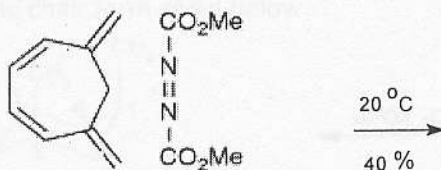
1. (a) Predict the product(s) formed in the pericyclic reactions as indicated below

(i)



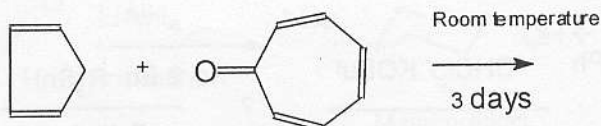
(15 marks)

(ii)



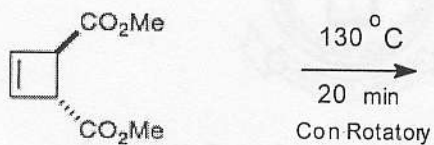
(15 marks)

(iii)



(15 marks)

(iv)



(15 mar)

(b) State the steps involved in the aromatic transition state theory in following the course of therm electrocyclic ring closure using the hexa-1,3,5-triene system. (Consider the con-rotatory process)

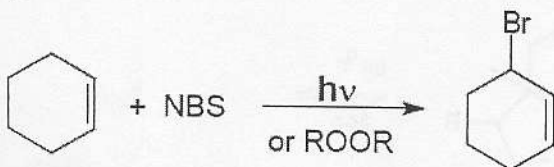
(40 mar)

2. (a) List all kinds of reactive intermediates encounter in organic reactions and give o example for each.

(20 mar)

(b) Explain the following observations

(i)



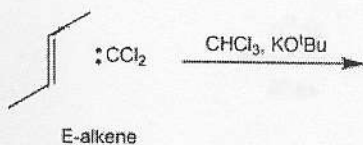
(20 mar)

(ii) Singlet carbene reacts with alkene in a concerted fashion whereas the triplet carbene reacts with alkene in a stepwise fashion.

(20 mar)

(c) Give the structure of the product(s) formed in each of the following reactions

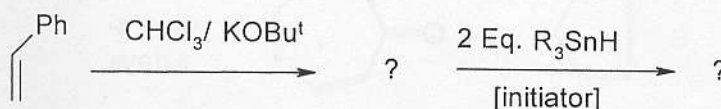
(I)



(Hint: Singlet carbene involvement)

(20 mar)

(II)



(Hint: Radical involvement)

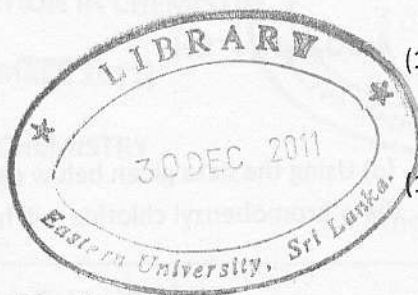
(20 mar)

3. (a) Draw the all possible conformations for the following compounds and indicate the least energy conformation in each. Give reasons for your answer

(i) Neopentane

(ii) 1,2-dichloroethane

(iii) *Trans*-1,2-dimethylcyclohexane (Two Chair forms)

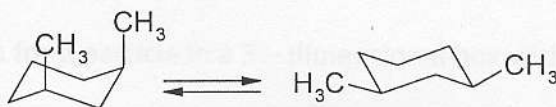


(10 marks)

(10 marks)

(10 marks)

(b) The *Cis*-1,3-dimethylcyclohexane exists in equilibrium between two chair forms as indicated below.



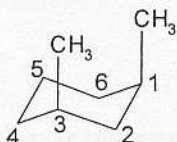
Chair form I

Chair form II

(i) Suppose the gauche interaction energy and the Me - Me 1,3-diaxial interaction energies are 0.9kCal and 3.7kCal respectively and neglecting the diaxial CH₃-H, what will be the conformational free energy of the chair form I.

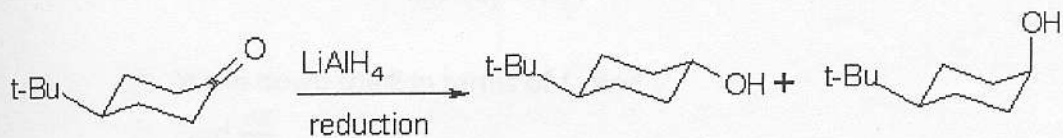
(20 marks)

(ii) By looking along the bonds C3-C4 and C1-C6 draw the Newman projection of the chair form given below.



(20 marks)

(c) Explain the following observation



Major product

Minor product

(30 marks)

4. (a) Write down the Hammett Equation and explain all the terms in it.

(15 marks)

(b) "The Hammett Equation is a Linear Free Energy Relationship". Explain this statement

(20 marks)

(c) Predict the sign and magnitude of the ρ values for the following reaction



(25 mar

(d) Using the data given below calculate how much faster than the p-nitrobenzyl chloride the p-bromobenzyl chloride will hydrolyze in water.



Reaction constant value is -1.31

$$\sigma_{\text{p-NO}_2} = 0.78 \text{ and } \sigma_{\text{p-Br}} = 0.23$$

(40 mar
