



EASTERN UNIVERSITY, SRI LANKA
THIRD EXAMINATION IN SCIENCE-2010/2011
SPECIAL DEGREE IN CHEMISTRY
CHS 02 Organic Chemistry I

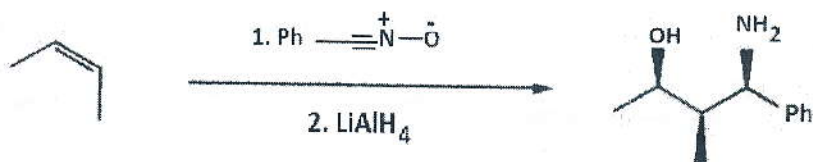
Answer all questions

Time Allowed: Two hour

Answer all the parts (a), (b) and (c).

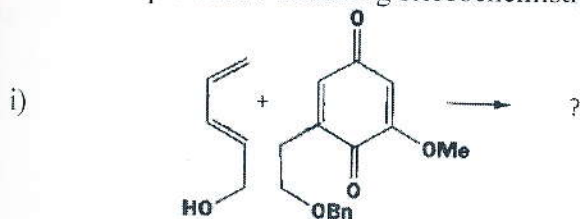
- a) Apply Frontier Molecular Orbital (FMO) theory to determine the preferred mode (conrotatory or disrotatory) of thermal and photochemical cyclisation of 1,3-butadiene. (40 marks)

- b) Explain the following reaction and the stereochemistry of the product formed.

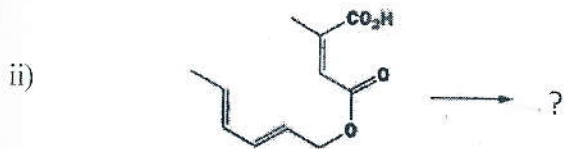


(15 marks)

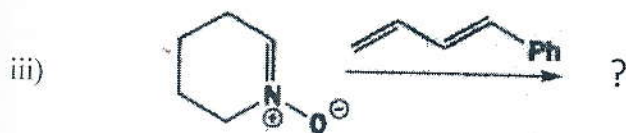
- c) Predict the product/s including stereochemistry of the following cycloaddition reactions.



(15 marks)



(15 marks)



(15 marks)

Contd....

3. Answer **all** the parts (a), (b), (c) and (d).

a) The ρ value for alkaline hydrolysis of substituted methyl benzoate is 2.38. The rate for saponification of methyl benzoate is $2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. Calculate the rate constant for methyl *m*-nitrobenzoate. Substituent constant σ for *m*-NO₂ is 0.70.

(25 marks)

b) Compare the rate of solvolysis of *p*-bromobenzylchloride and *p*-nitrobenzylchloride in water. Reaction constant of the reaction is -1.31 and the substituent constants for *p*-NO₂ and *p*-Br are 0.78 and 0.23 respectively.

(25 marks)

c) i) Define the term 'Kinetic isotopic effect'.

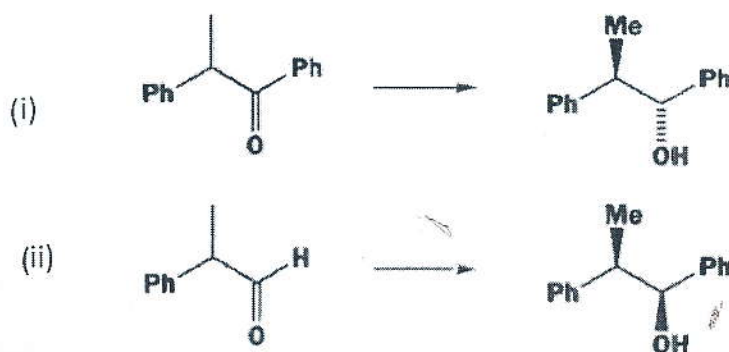
(15 marks)

ii) Iodination of phenol in basic solution is found to have a deuterium isotope effect of $K_H/K_D = 4.1$. Explain how you would determine the rate determining step of the reaction.

(35 marks)

4. Answer **all** the parts (a), (b), (c) and (d).

a) Using Felkin-Ahn model explain how the following two reactions (i) and (ii) give different diastereoisomers of the product.

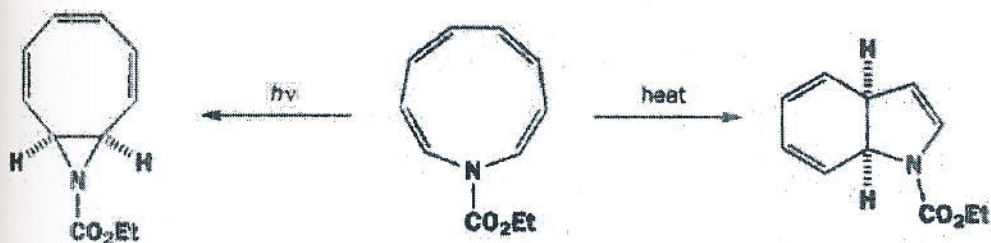


(40 marks)

Contd....

Answer all the parts (a), (b), (c) and (d).

An unsaturated nine-membered ring undergoes reactions as shown below. Explain the behavior of the compound under thermal and photochemical conditions.



(25 marks)

b) Identify the products **A** and **B** in the following reaction sequence. Label each process as conrotatory or disrotatory.



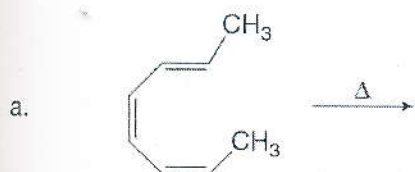
(25 marks)

c) Explain the process of sigmatropic rearrangement using FMO (theory) and give the structure/s, including the stereochemistry, of the product in the following reaction.



(25 marks)

d) Give the structure(s), including configurations, of the product(s) expected from the following reactions.



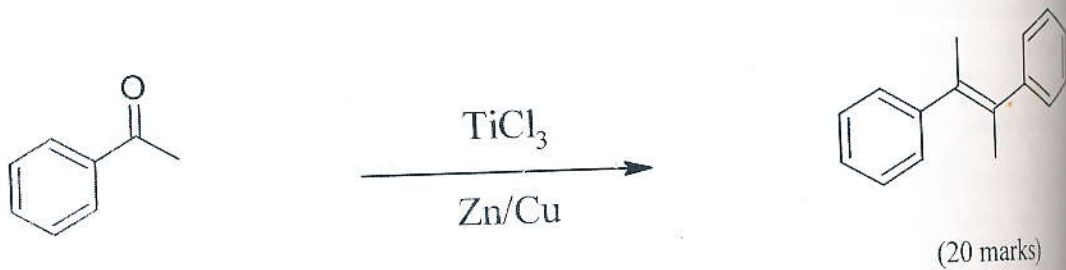
(2E,4Z,6Z)-2,4,6-octatriene



(25 marks)

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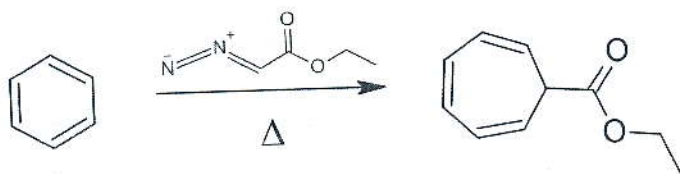
b) Write mechanism for the following radical reaction.



c) i) Explain the two types of carbenes.

(15 marks)

ii) Propose a mechanism for the following reaction.



(25 marks)

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