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RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Joint Major) Degree in Chemistry & Physics

Fourth Year – Semester II Examination – April/May 2016

CHE 4204 – Photochemistry

Answer all four questions. **Time: Two hours**

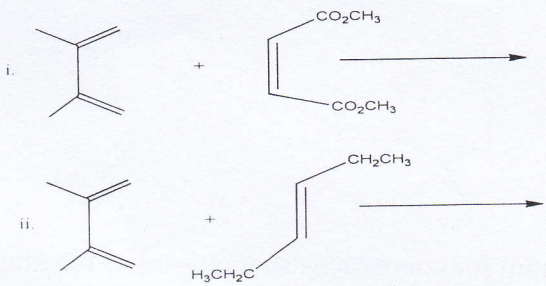
Use of a non programmable calculator is permitted.
Symbols have their usual meaning.

Speed of light = 3.0×10^8 m s^{-1}, Planck's constant = 6.63×10^{-34} J s,

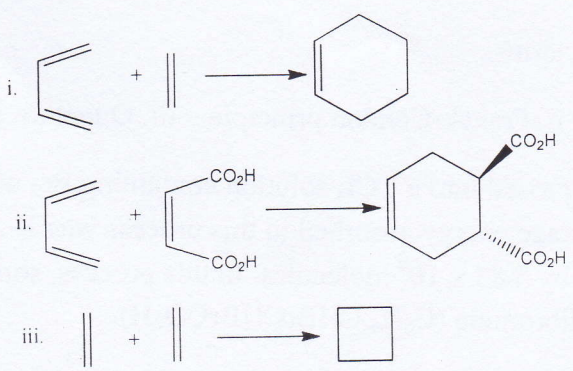
Avogadro constant = 6.02×10^{23} mol^{-1}

1.

(a) Draw the product with correct stereo-specificity of the following pericyclic reactions.



(b) Find whether the following cycloaddition reactions are allowed or forbidden using transition state theory.



(c) What will be the product of reaction (b) ii, if the reaction is thermodynamically allowed? Explain your answer using an interaction diagram and Transition State Theory

(d) i. Define the photopericyclic reactions

ii. If the smallest system ($2\pi_s + 2\pi_s$) is thermodynamically forbidden. State whether the following reactions are thermodynamically or photochemically allowed

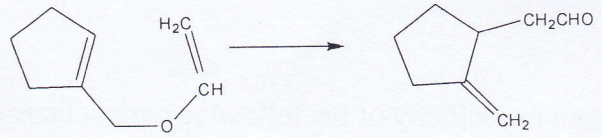
($10\pi_a + 24\pi_s$), ($8\pi_s + 16\pi_s$), ($6\pi_a + 12\pi_a$)

2.

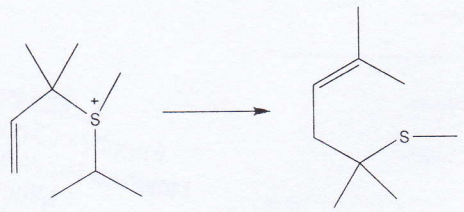
(a) Draw the interaction diagrams for each of the systems ($4\pi_s + 2\pi_s$), ($4\pi_a + 2\pi_a$), ($4\pi_s + 2\pi_a$), and ($4\pi_a + 2\pi_s$). Find whether they are Huckel or Mobius and reaction is allowed or forbidden.

(b) Classify the following sigmatrophic shifts according to their order

i.



ii.



(c) Construct orbital correlation diagram for conrotatory ring closure of butadiene. Find whether the reaction is allowed or forbidden.

3.

(a) Define or explain the following terms:

i. Photochemical reaction ii. Franck-Condon principle iii. Quantum yield

(b) For 900 s, light of 436 nm was passed into a CCl_4 solution containing Br_2 and cinnamic acid (C_6H_5 CH=CHCO_2H). The average energy absorbed in this process was 19.2×10^{-4} J s^{-1} and the total Br_2 content decreased by 3.83×10^9 molecules. In this process, some of the Br_2 reacted to give cinnamic acid dibromide (C_6H_5 CHBrCHBrCO_2H).

i. What was the quantum yield?

ii. State whether or not a chain reaction was involved.

iii. If a chain mechanism was involved, suggest a suitable reaction mechanism which might explain the observed quantum yield

(c) Explain the following observations

i. In some molecules Inter System Crossing (ISC) takes place with 100% efficiency, whereas in others it doesn't happen to any measurable extent.

ii. Observed fluorescence occurs at a longer wavelength than that of absorption and it originates from the lowest vibrational level of the electronic excited state.

(d) List, at least five possible ways of relaxation of an excited species

4.

(a) Explain and draw fully labeled potential energy diagrams for:

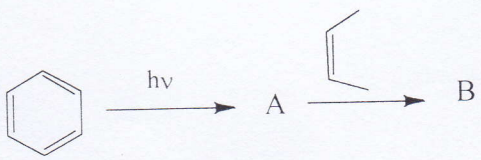
i. electronic transitions with the greatest probability of absorption from $S_0(v=0)$ where the excited state has a larger equilibrium bond distance than the ground state and the emission of fluorescence and phosphorescence.

ii. photodissociation

iii. predissociation

(b) What would be the products for the following photoreactions?

I.



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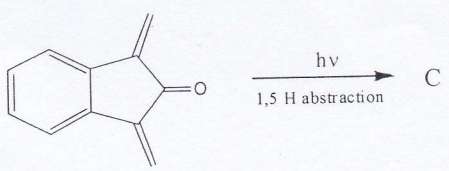
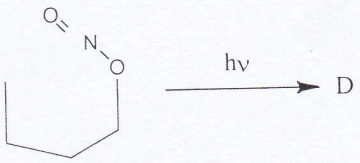


iii.



(c) Describe the (i) formation and (ii) applications of singlet oxygen