

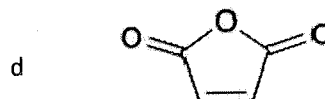
M. Sc. Chemistry
Semester IV First Sessional Examination -2020
Paper Title: Photochemistry and Pericyclic reactions
Paper Code: MCCHO-303

Maximum marks: 75
1½x05

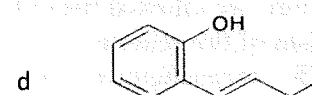
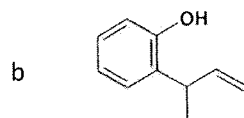
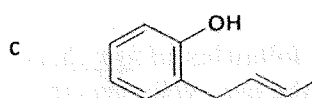
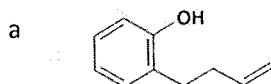
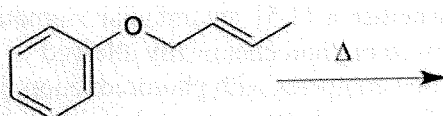
Time Allowed: 3hrs

Q1. A Choose the most appropriate answer

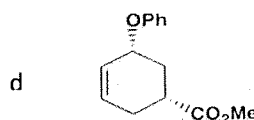
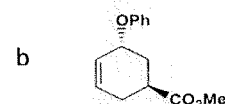
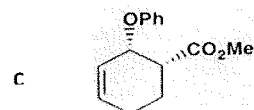
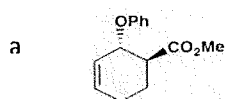
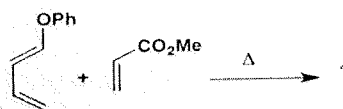
1. Which of the following dienophiles is the most reactive with buta-1,3-diene?



2. Which of the phenols is the main product of the following thermal rearrangement?



3. Which of the following adducts is the main kinetic product of the following Diels-Alder reaction?



4. Because of the difference in -----between the excited and ground states, conformational changes that occur freely in the ground state are often slow in singlet and triplet excited states.

- a. bond orders
- b. bond angles
- c. bond lengths
- d. None of these

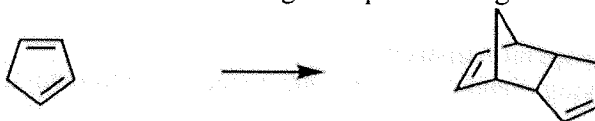
5. Among the cyclic alkenes, -----is the first member to give a stable trans isomer on photo excitation

- a. Cyclopentene
- b. Cyclohexene
- c. Cyclooctene
- d. Cyclopentadiene

Q1 B Answer briefly

1½x05

- a) How many π electrons are involved in the following transformation? Is this reaction an example of an electrocyclic process, a cycloaddition reaction or a sigmatropic rearrangement?



- b) Which unsaturated aldehyde is the sigmatropic rearrangement product obtained by heating the following ether?

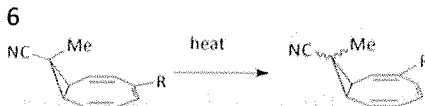
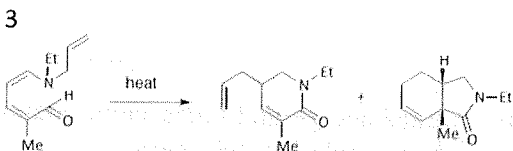
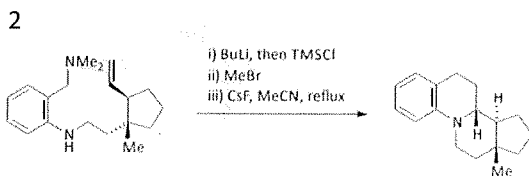
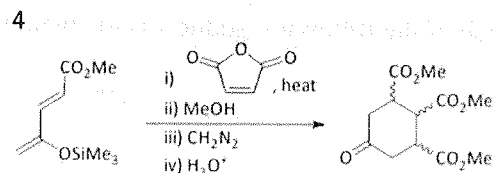
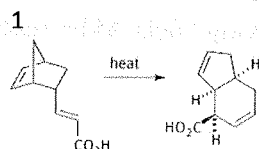


- c) Using FMO approach predict whether a [1,5] antarafacial sigmatropic carbon shift with retention at the migrating centre is thermally allowed or photochemically allowed
 d) For benzophenone, photoenolization competes with photoreduction, justify.
 e) How can ketenes be synthesized from cyclic ketones by photoirradiation? Give mechanism

Q2. Provide the following of any three of the following

3x5=15 marks

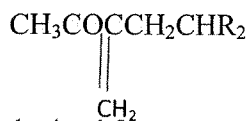
- a) identify the pericyclic process
 b) show if they are allowed using FMO analysis
 c) mechanism of the reaction
 d) predict the stereochemical outcome



Q3. Attempt any three of the following

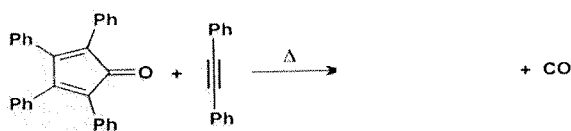
3x5=15 marks

- a. What are the different products that can be obtained on photo-irradiation of the following β -unsaturated ketone?

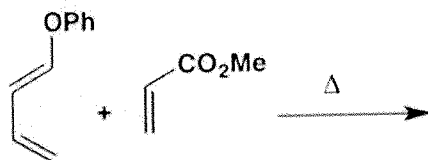


- b. How can 2,3- -diphenyloxetane be obtained from styrene by cycloaddition, what could be the side products obtained?

c. Give the products and mechanism of the following



d. Give the products and mechanism of the following



Q4. Attempt any three of the following

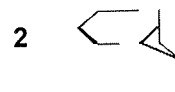
3x5=15 marks

- Discuss in detail various radiative and non-radiative processes by which a molecule in the excited state can return to ground state with special emphasis on kinetics and lifetime of the process. Also discuss concept of intermolecular energy transfer.
- What are Chelotropic reactions? Give suitable examples
- Explain possible pathways available for photoexcited carbonyl compounds to convert into different products by taking suitable example(s)
- What is Ene reaction? Discuss the synthetic utility of the reaction

Q5. Attempt any three of the following

3x5=15 marks

- The two diastereoisomeric trienes 1 and 2 undergo thermal electrocyclic cyclisation reactions each affording a pair of disubstituted conjugated cyclic dienes. Identify all four products by constructing the transition state geometries, and state the stereochemical relationships that exist between the pairs of stereoisomers formed from each reaction and the stereochemical relationship of the products between the pair of reactions



- Discuss photoisomerization of benzene
- Predict the product for the given transformations with detailed mechanism



- Propose the mechanism for the following photo reduction reaction

