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**ST. JOSEPH’S COLLEGE (AUTONOMOUS), BANGALORE-27**

M.Sc. CHEMISTRY - II SEMESTER

SEMESTER EXAMINATION – APRIL 2017

**CH 8212: Organic Chemistry – II**

**Time: 3 hours Maximum marks: 100**

*This question paper has five printed pages and three parts.*

**Part A**

Answer any TEN questions: **(10x2=20)**

1. Give an example each for (i) inverse electron demand Diels-Alder reaction and (ii) oxy-Cope rearrangement.
2. What is photosensitization? Give an example.
3. Give any two characteristics of pericyclic reactions.
4. Photochemical reactions of a given compound are different from the same reactions carried out in dark. Why?
5. At 100 ºC the relative rates of 1º and 3º H abstraction by Cl are 1 and 6.8 respectively. Assuming only monosubstitution takes place during chlorination of the following compound, calculate the percentage yield of tertiary substituted product.



1. Give the thermolysis reactions of the following compounds: (CH3)3COOC(CH3)3 and PhN=NC(Ph)3
2. Nucleophilic 1,2-shifts are much more common than electrophilicor free-radical 1,2-shifts. Why?
3. Give two examples of carbonyl compounds that would form stable hydrates.
4. Write the reactant(s) required to synthesize the following compound by Wittig reaction.

C6H5CH=CHC6H5

1. Write the mechanism of the reaction between C6H5COCMe3  and NaNH2.
2. What is Japp–Klingemann reaction?
3. Give an evidence to support that carbene insertion can take place in a simple one step process and not via the formation of free radicals or ions.

**CH-8212-A-17**

**Part B**

Answer any **FIVE** questions. **(5x12=60)**

1. a) Using FMO method, arrive at the stereochemical mode of ring opening of (i) cyclobutene under thermal condition and (ii) cyclohexadiene under photochemical condition. b) Identify the product with stereochemistry, wherever applicable, in the following reactions.

 (6+6)

1. a) Using Woodward-Hoffmann orbital correlation method show that thermal supra-supra [4+2] addition is allowed.

b) Employing transition state aromaticity analysis explain why 1, 3 H shifts are not allowed while 1,5 and 1,7 H shifts are allowed. (6+6)

1. a) Write the mechanism of the following reactions.



b) Discuss the photochemical (i) valence isomerization and (ii) cycloaddition reactions of arenes with suitable examples. (6+6)

1. a) Write the mechanism of Sommelet Hauser rearrangement. Which is competing reaction? Under what conditions Sommelet Hauser reaction predominates?

b) Write the acid catalysed reaction mechanism of the α-halogenation reaction of a ketone. Mention any two evidences in favour of the mechanism. Explain what happens if a methyl ketone is subjected to the same reaction under basic conditions?

1. a) Using labeling experiment, how would you establish that the Favorskii rearrangement with the following susbstrate proceeds through a cyclopropane ring intermediate? How does such an intermediate open when the cyclopropane ring is unsymmetrically substituted?



b) Give the mechanism of benzidine rearrangement. Explain the role of kinetic isotope effect data in deducing the mechanism of the reaction.

(6+6)

1. Give the major product and the mechanism of the following reactions:



1. a) How could the following compounds be synthesized, starting with an unsaturated hydrocarbon that has the same number of carbon atoms as the desired product?



b) With a suitable example discuss the mechanisms of the following reactions.

(i) formation of hydrazone from an aldehyde

(ii) addition of Grignard reagent to a ketone

(iii) addition of bromine to an alkene (6+6)

**Part C**

Answer any four questions. **(4x5=20)**

1. *ZZZZ* 1,3,5,7-cyclononatetraene undergoes a spontaneous electrocyclic ring closure at 25ºC. Predict the most likely structure of the product. Describe any other symmetry allowed cyclization product(s) possible. Explain why these products are not formed.
2. Give the the structures of **A**,**B** and **C** and complete the following sequence of reactions. Explain each step briefly stressing on the stereochemistry of the structures wherever applicable.



1. Propose mechanism for the following reactions



1. Write the reactant(s) and reagent(s) required to prepare the following compounds by the rearrangement reaction indicated in each case.



1. Which of the following will give product(s) by the acid catalyzed addition of water which is(are) different from those obtained by the oxymercuration-demercuration reaction? Explain your answer by showing the different product(s) formed. If the products can exist as stereoisomers, show which stereoisomers are obtained. *Note: the product(s) here refer to the major product(s) possible in the reaction.*

