- (b) Explain the following terms: 14
 - (i) Photo-fries reaction of anilides
 - (ii) Singlet molecular oxygen reaction
 - (iii) Dimerization reaction of carbonyl compound
 - (iv) Photodegradation of polymer.
- 4. (a) Discuss the Paterno-Buchi reaction with mechanism and its stereochemical consequences.
 - (b) Give mechanism and synthetic applications of Barton reaction. 8
 - (c) Write the products of bromination of1-butene with NBS and indicate the major product.4

Unit III

5. (a) Under photochemical conditions, will ring closure of (2E, 4Z, 6Z, 8E)-decatetraene be conrotatory or disrotatory? Will the product have the cis or the trans configuration?

6

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M. Sc. EXAMINATION, May 2017

(Fourth Semester)

(Main & Re-appear)

CH-614-B

CHEMISTRY

Organic Chemistry Special-IV

(Photochemistry and Pericyclic Reactions)

Time: 3 Hours [Maximum Marks: 100

Before answering the question-paper candidates should ensure that they have been supplied to correct and complete question-paper. No complaint, in this regard, will be entertained after the examination.

Note: Attempt *Five* questions in all, selecting at least *one* question from each Unit. All questions carry equal marks.

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P.T.O.

Unit I

- 1. Write brief notes on the following: 10
 - (a) Explain electronic excitation and their selection rules. Discuss fate of excited molecule (Jablonskii diagram) and term involved.
 - (b) Discuss the photochemical rearrangement of 1, 4 and 1, 5-dienes with examples. 10
- 2. (a) Explain the following terms: 9
 - (i) Quantum yield and Actinometry
 - (ii) Importance of photosensitiser in photochemistry
 - (iii) Norrish Type-II process with example
 - (b) Suggest mechanism for the following reactions:

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(c) Explain, the photochemical isomerisation (geometrical) of alkenes. 3

Unit II

(a) Irradiation of o-xylene gives a miture of m- and p-xylen, proposed a mechanism for this transformation.6

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3

P.T.O.

Explain, why maleic anhydride reacts rapidly with 1, 3-butadiene but does not react at all with ethene under thermal conditions. With the help of correlation diagram and PMO approach prove that Diels-Alder reaction is thermally allowed. 6 Discuss [1, 3] sigmatropic rearrangement with mechanism. 4 5-methyl-1, 3-cyclopentadience rearranges **6.** (a) to give a mixture of 5-methyl-1, 3-cyclopentadiene, 1-methyl-1, 3-cyclopentadiene, 2-methyl-1, and 3-cyclopentadiene. Show how these products are formed. Write explanatory (b) notes the on following: 6 Claisen rearrangement [1, 5] sigmatropic rearrangement.

- (c) Give the product formed when each of the following compounds undergoes an electrocyclic reaction:6
 - (i) Under thermal conditions
 - (ii) Under photochemical conditions.

$$CH_3$$
 CH_3
 II

(d) With the help of FMO methods show that the [2+2] cycloaddition reaction between alkene and ketene is thermal allowed reaction.

Unit IV

- 7. Write short notes on the following: 20
 - (a) Annomeric effect and double Annomeric effect
 - (b) Ring inversion and pyramidal inversion

- (c) Conformational analysis of medium ring compounds
- (d) 2-alkyle ketone and 3-alkyl ketone effects in cyclohexanone.
- 8. (a) With suitable examples discuss the stereochemistry of nitrogen containing compounds, strain and their consequences in small ring heterocycles.
 - (b) Write an explanatory note on conformation of cyclodecane. 8
 - (c) Explain, trans annular reactions with minimum two examples. 3

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