M. Sc. Sem. II. (1)

Unit. III.

Topic : PERICYCLIC REACTIONS.

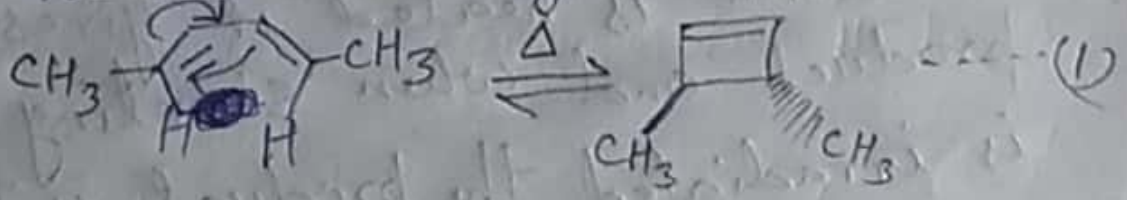
(To be continued ....)

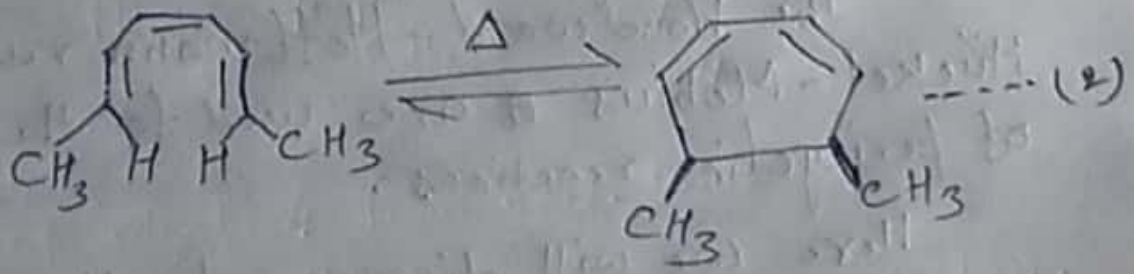
Three features of any pericyclic reaction are intimately interrelated. These are :—

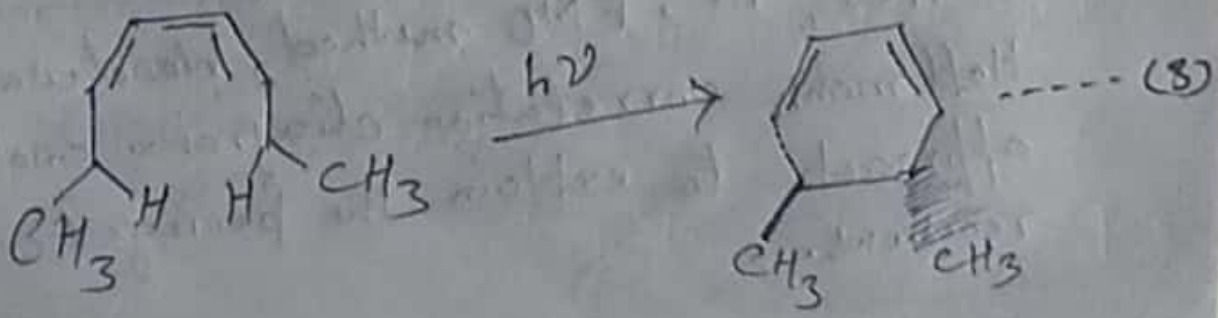
1 Activation ;

2. The Number of π bonds involved in the reaction and

3. The stereochemistry of the reaction.







First two reactions are thermal reactions activated by heat and third reaction is photochemical reaction activated by light. The relationship between the mode of activation and the stereochemistry is examplified by a comparison of reactions (2) and (3). When starting material is heated it gives cis product and when starting material is irradiated the product is trans.

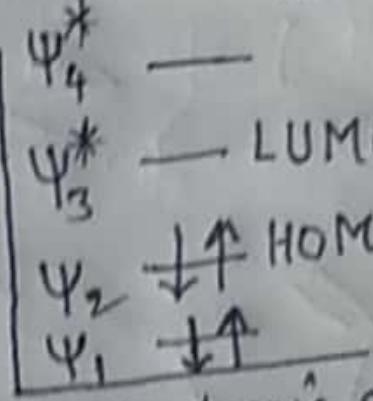
The Woodward - Hoffmann rule and Hückel - Mobius (3) are used for the explanation of pericyclic reactions.

Here we will discuss only three theories, i.e., FMO method, Woodward - Hoffmann correlation diagram and PMO approach to explain the pericyclic reactions.

First understand molecular orbitals of compound containing π - bonds.

Two π - molecular orbitals are of particular importance in understanding pericyclic reactions.

One is occupied molecular orbital of highest energy known as highest occupied molecular orbital (HOMO). The other is the unoccupied molecular orbital of lowest energy known as lowest unoccupied molecular orbital (LUMO).



HOMO and LUMO of any given compound have opposite symmetries. as shown in the fig. → Electronic state of Ground state of 1, 3 - butadiene.

HOMO and LUMO are referred to as frontier molecular orbitals.

(To be continued.....)