I. **Pericyclic Reactions**: General Observations/Characteristics

A. isopolar - neither heterolytic or radical

B. concerted, no intermediates, one transition state

C. at least one reactant (or product) has a double bond

D.  bonds are broken or formed in exchange for double bonds

E. reactions involve orbitals in a cyclic array

F. **controlled by symmetry of MO's participating in reaction**: if a symmetry element is retained during a reaction it must also be retained by MO's involved

II. electrocyclic reactions -  bonds formed at terminal atoms of  system

A. thermal reactions: 4n electrons and 4n+2 electrons





B. the stereochemical course of photochemical reactions is reversed

 

III. Frontier Orbital method (acid-base theory)

A. HOMO of one system overlaps with LUMO of another

B. allowed reaction if no new nodes are created in transition state

C. use HOMO for single  system

 

D. photolysis reverses stereochemistry since HOMO is next higher orbital

IV. Aromatic Transition State or Möbius-Hückel Method

A. construct basis set, connect forming odd or even nodes, calculate MO energies

B. Hückel transition state has even number of nodes

C. Möbius transition state has odd number of nodes





Hückel

disrotatory

Möbius

conrotatory

D. Möbius transition state allowed for 4n electrons

E. Hückel transition state allowed for 4n+2 electrons

 

V. Correlation Diagram Method

A. choose symmetry elements that are preserved during rearrangement and distinguish the two pathways

B. label MO's antisymmetric or symmetric according to symmetry elements

C. connect orbitals of like symmetry, indicates where electrons end up in product

D. reaction is not symmetry allowed if reaction creates exicted state (and vice versa)

