Chapter 15 Lecture Outline **Thermal Pericyclic Reactions**

assigned problems: 3, 4, 7, 10, 13, 15, 17-19, 21, 26-28, 32, 36

**Key Concepts and Learning Goals**

- be able to classify a pericyclic reaction according to its type and by it orbital components
- provide D-Z interaction diagrams for pericyclic reaction ≠'s to predict allowed and forbidden pathways
- be able to predict the stereochemical outcome of pericyclic reactions based on ≠ geometry for the process
- analyze a pericyclic reaction by D-Z analysis, FMO theory, and W-H rule
- write an orbital correlation diagram for a pericyclic reaction and use it to predict the nature of the reaction
- predict the regiochemistry of a Diels-Alder reaction

I. Pericyclic Reaction Types
- A. pericyclic rxn: concerted rxn with cyclic array of interacting orbitals at the transition state
- B. cycloaddition reactions
  - 1. electronic and stereochemical classification of cycloadditions
    - a. electron components - # e's and orbital types involved in reaction
    - b. faciality of overlap at transition state: suprafacial or antarafacial
  - 2. Diels-Alder reaction, a $4\pi_s + 2\pi_s$ cycloaddition
    - a. general features of reaction
    - b. dienophile stereochemistry
    - c. diene stereochemistry
    - d. endo rule
  - 3. 1,3-dipolar cycloadditions - Criegee mechanism of ozonlysis
- C. electrocyclic reactions
- D. sigmatropic reactions
- E. cheletropic reactions

II. Dewar-Zimmerman Analysis: Transition State Aromaticity
- A. orbital interaction diagram of transition state
- B. Hückel 4n+2 aromatic arrays and Möbius 4n aromatic arrays
- C. examples: Diels-Alder rxn, hexatriene cyclization, cyclobutene ring opening, [1,5] H-shift

III. Frontier Molecular Orbital (FMO) Analysis
- A. HOMO and LUMO interactions: cycloaddition transition states for 4+2 and 2+2 rxns
- B. effects of EWGs and ERGs on pi MO energies

IV. Woodward-Hoffmann Rules
- A. orbital correlation diagrams
- B. state correlation diagrams
- C. generalized W-H rule: ≠ allowed for an odd number of $(4q+2)_s + (4r)_a$ components

V. Examples
- A. cycloadditions: [4+2] and [2+2] reactions
  - 1. [4+2] - Diels-Alder rxns and 1,3-dipolar cycloadditions
  - 2. [2+2] - olefin/ketene cycloadditions and carbene/olefin reactions
- B. electrocyclic reactions - 2, 4, 6-electron systems
- C. sigmatropic rearrangements
  - 1. [1,n] and [2,3] rearrangements
  - 2. Cope and Claisen [3,3] reactions
- D. the ene reaction
- E cheletropic reactions