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 its 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 ozonolysis
      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

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