Pericyclic Reactions

1. general Observations/properties
   1. isopolar - neither heterolytic or radical
   2. concerted, no intermediates, one transition state
   3. at least one reactant (or product) has a double bond (or low energy vacant orbital)
   4.  bonds are broken or formed in exchange for bonds (or  bonds migrate across  bonds)
   5. reactions involve transition state with orbitals in a cyclic array
   6. **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
2. electrocyclic reactions -  bonds formed at terminal atoms of  system
   1. thermal reactions: 4n electrons and 4n+2 electrons





* 1. Woodward-Hoffmann rules for thermal electrocyclic reactions
     1. 4n electrons (where n is an integer) are allowed by conrotatory paths
     2. 4n + 2 electrons are allowed if they proceed by disrotatory
  2. the stereochemical course of photochemical reactions is reversed

 

* 1. indicate the mechanism of the following reaction



* 1. which has an activation engery of 27 and which has 45 kcal/mol for ring opening?



1. Frontier Orbital method (acid-base theory): frontier orbitals determine chemistry
   1. HOMO of one system overlaps with LUMO of another
   2. reaction allowed if no new nodes are created in transition state
   3. use HOMO for single  system, rules work on both directions

 

* 1. photolysis reverses stereochemistry since HOMO is next higher orbital

1. Photochemical eletrocyclic reactions
   1. HOMO electron is promoted
   2. New HOMO created and symmetry of HOMO is reversed



1. **Cylcoaddition**
   1. 2 or more reactants form 2 or more  bonds in exchange for  bonds
   2. [2+2+2]



* 1. [4+2]



* 1. [2+2] - radical



* 1. Frontier Orbital theory for **cycloaddition**
     1. 4n [2+2]



* + 1. 4n+2 [4+2]: Diels-Alder reaction



* + 1. Why is this reaction allowed

2 +2 not allowed

* 1. Cycloreversions – can be favorable in certain circumstances [4+2]



* 1. [4+2] **cycloadditions**
     1. Diels Alder readily occurs, even with ring heteroatoms









* + 1. Ionic additions also are known, how many electrons in the electrocycle?



* + 1. Faster if diene is constrained





* + 1. faster if one fragment is electron rich and other electron deficient (a,c above)
    2. simple alkene and dienes react only at high P and T with low yields
    3. electron rich dienophile raises orbitals
    4. electron poor diene lowers orbitals

 

* + 1. kinetic (endo) product is favored for tricyclic products



* + 1. maximum  overlap in transition state
    2. endo only applies to multicylic systems, substitution relative to larger bridge



* 1. photochemical [2+2] supra-supra allowed



* + 1. Low yields because photolysis also isomerizes alkene



* + - 1. What are the products from trans 2-butene?







* 1. Why doesn’t the light reverse the reaction? Consider available electronic transition?
  2. Only applies to singlet state, why? How do triplets react?

1. **Sigmatropic Shift**  bond migration across  system
   1. designated by [i,j]
   2. i = # of atoms in migrating group
   3. j = # of atoms in  system
   4. topology – 4 possible combination of faces
   5. single carbon (i = 1) can have inversion and retention of configuration

i=1, j > 1 

* 1. Examples: first two reactions are hydrogen atom shifts – not a hydride shift.
  2. What is driving force for these shifts? What is the classification? [i,j]





* 1. Frontier Orbital Theory analysis
     1. Treat two groups as radicals: homolytically break bond
     2. Examine the interaction of two singly occupied MOs = SOMO
  2. [1,3] for hydrogen migration yields hydrogen atom and allyl radical
     1. Hydrogen has no node allyl radical has 3 electrons: SOMO is 2.
     2. Migration must be antarafacial, steric constraints? make it unfavorable



* 1. [1,5] for hydrogen
     1. Pentandienyl radical has 5 electrons, SOMO is 3
     2. suprafacial



* 1. apparent [1,3] for hydrogen is two [1,5] sigmatropic shifts



* 1. [1,3] for carbon
     1. Determine SOMO
     2. Allowed suprafacial/antarafacial, inversion at 1 carbon fragment
     3. TS is strained, unlikely even if allowed



* 1. [1,5] carbon only observed for cyclic dienes
     1. Determine SOMO
     2. suprafacial/suprafacial, retention at 1 carbon fragment



* 1. [3,3] Cope and related rearrangements
     1. Determine SOMO
     2. Alkyl substitution effect, pseudo chair confromation



* 1. Cyclic compounds
     1. Ring on one or both ends of migrating groups
     2. Which protons are chemically equivalent protons?



* 1. Claisen rearrangement
     1. oxygen in chain
     2. chair conformation is preferred
     3. What is the driving force?



* 1. 1,2 hydrogen shifts
     1. allowed for carbocation
     2. not carbanion (sterically constrained)



Hints for Analysis of pericyclic reactions:

1. Conrotatory/disrotatory “rules” only apples to electrocyclic ring opening and formation
2. Suprafacial and antarafacial apply to cycloadditions and sigmatropic shifts
3. It is easier to analyze the orbitals for electrocyclic ring formation than ring opening, so if the reaction is a ring opening, determine the stereochemistry for the reverse reaction