VI. other examples of electrocyclic reactions (identify electrons, compare with cyclobutene)

A.

 

B.



VII. cycloaddition reactions

A. 2 or more reactants form 2 or more  bonds in exchange for  bonds

B. faster if one fragment is electron rich and other electron deficient

C. Diels-Alder reaction, suprafacial-suprafacial, 4s + 2s



maximum  overlap, kinetic (endo) product is favored



D. oxygen addition, photosensitized, stereochemistry



E. concerted addition of 1,3-dipolar compounds, see March, table 15.3 page 837





F. Retro Aza-Diels-Alder: identify six member ring with double bond activated for cycloreversion



G. 2 + 2 cycloaddition (steric and overlap issues)

A. does not occur for unactivated olefins

B. radical and polar mechanisms compete in some cases

C. concerted reaction: 2s + 2a, suprafacial + antarafacial (reverse Cp signs)



4n electrons: thermally allowed Möbius TS

4n electrons: photochemical is Hückel allowed, 2s + 2s, suprafacial + suprafacial





Why doesn’t the light reverse the reaction? Consider available electronic transition?

Sigmatropic Rearrangements (treat formally as radical pair)

A. bond migration from one end of a  system to another

B. designated by [i,j]

1. i = # of atoms in migrating group

2. j = # of atoms in  system

C. [1,3] for hydrogen, antarafacial, steric constraints make it unfavorable



D. [1,5] for hydrogen, suprafacial



E. [1,3] for carbon, supra/antarafacial, inversion at 1 carbon fragment





F. [1,5] for carbon, supra/suprafacial, retention at 1 carbon fragment



G. [3,3]

