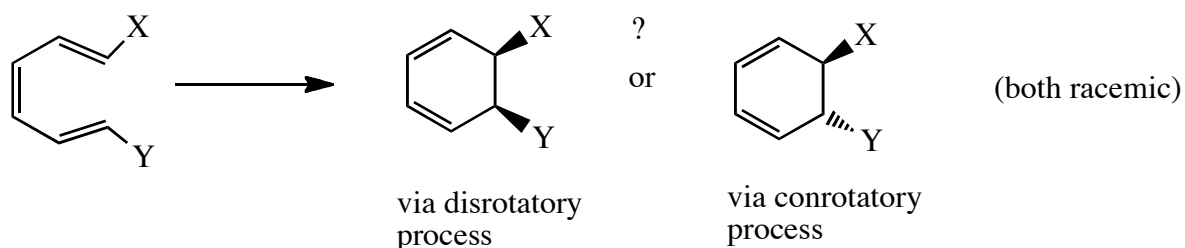


Lecture outline

Aromatic transition state theory (cont'd)

Electrocyclic reactions. These involve a net exchange of one π -bond for one σ -bond. (Two examples were shown on the previous page.)

Formation of a new σ -bond between the ends of a conjugated π -system to form a ring requires the end p-orbitals to rotate — either in the same direction (*conrotation*) or in opposite directions (*disrotation*). Similarly, in the reverse reaction, ring opening, might occur by conrotation or by disrotation.

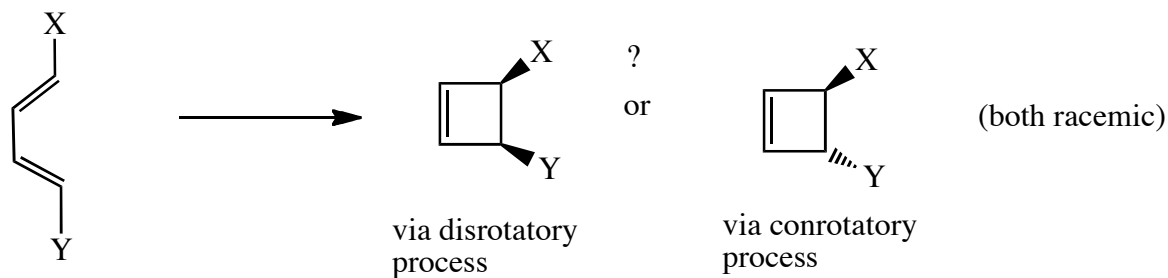


The triene above is *E,E*. What would be the results of dis- and of conrotatory ring closure starting with the *E,Z*-triene? What about the *Z,Z*-triene?

It turns out that for a $6-e^-$ electrocyclic process *disrotation* is favored. To understand why we need to look at the arrays of interacting orbitals in the transition states for the two processes.



The 4- e^- process generally goes in the ring opening direction, but we'll analyze the ring closure for consistency with the example above. Which is favored in this case?

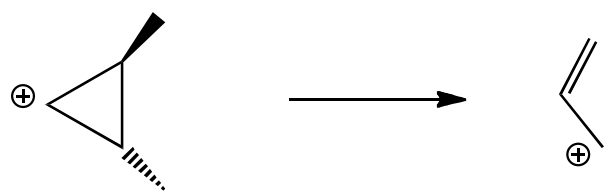
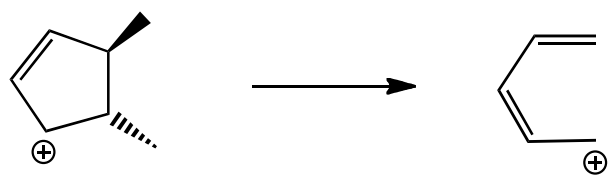


For the 4- e^- electrocyclic process *conrotation* is favored. Here are the corresponding orbital arrays.

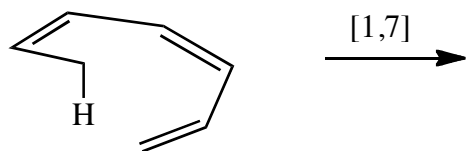
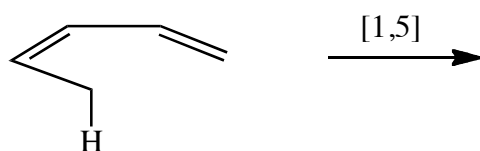
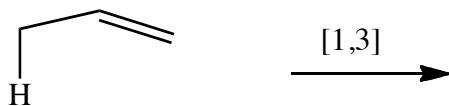


Orbital arrays that have one phase change have the same topology as a Möbius strip. $4n-1$ Möbius arrays are aromatic; $4n+2$ $-e^-$ Möbius arrays are antiaromatic.

Predict the mode of ring-opening (con- or disrotatory) for the following cations, and add the methyl groups to the products.



Aromatic transition state theory also applies nicely to sigmatropic shifts. Experimentally, it is found that [1,3] shifts of H do not occur, but [1,5] shifts do. [1,7] shifts do not occur — unless the H can be transferred to the opposite face of the π -system!



Sigmatropic shifts of C are even more interesting because the C can migrate with retention or inversion of configuration. [1,3] shifts of C occur with inversion of the configuration of the migrating C; [1,5] shifts occur with retention.