29.9: A SUMMARY OF RULES FOR PERICYCLIC REACTIONS

Before pericyclic reactions can be put to use in a predictable and controlled manner, a broad mechanistic understanding of the factors that influence these concerted transformations must be formulated. The simplest, albeit least rigorous, method for predicting the configurational path favored by a proposed pericyclic reaction is based upon a transition state electron count. In most of the earlier examples, pericyclic reactions were described by a cycle of curved arrows, each representing a pair of bonding electrons. The total number of electrons undergoing reorganization is always even, and is either a **4n+2** or **4n** number (where n is an integer). Once this electron count is made, the following table may be used for predictions. It is important to remember that going from thermal to photochemical conditions or going from 4n to 4n+2 reaction electrons changes the outcome of the reaction.

	Electron Count	**Stereochemistry**
Thermal Reactions (Ground State)	**4n + 2**	Suprafacial or Disrotatory
	4n	Antarafacial or Conrotatory
	Electron Count	**Stereochemistry**
Photochemical Reactions (Excited State)	**4n + 2**	Antarafacial or Conrotatory
	4n	Suprafacial or Disrotatory

? EXERCISE 29.9.1

Predict the stereochemistry of the following reactions:

a. The photochemical cyclization of a conjugated tetraene.
b. The thermal cyclization of a conjugated tetraene
c. A thermal [4+4] cycloaddition
d. A photochemical [2+5] cycloaddition
e. A thermal [3,5] sigmatropic rearrangement

Answer

1)a) Disrotatory

b) Conrotatory

c) Antarafacial

d) Suprafacial

e) Antarafacial