Pericyclic Reactions Encyclopedia Article

Pericyclic Reactions

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Pericyclic Reactions

Pericyclic reactions are reactions that involve bond changes in a circle of atoms. In pericyclic reactions, bonds are made or broken in a concerted cyclic transition state. This means that there are no intermediates formed in the course of the reaction (i.e., the reaction is concerted), and the transition state (i.e., the unstable arrangement that the atoms form during the reaction) involves six orbitals and six electrons.

Pericyclic rearrangements are classified based on the migration of a sigma bond, i.e., a **covalent bond** directed along the line joining the centers of two atoms. In this classification scheme, the reactions fall into four major categories: 1) electrocyclic reactions in which there is a concerted formation of a sigma bond between the two ends of certain linear conjugated systems, or the reverse reaction in which the sigma bond is broken (an example is the **ring** opening of cyclobutenes); 2) cycloaddition reactions involving the concerted formation of two or more sigma bonds between the ends of two or more specific conjugated systems (e.g., Diels-Alder reactions used to synthesize 6-membered rings) and the reverse reactions involving the concerted cleavage of two or more sigma bonds; 3) sigmatropic reactions involving the concerted migration of an **atom** or group of atoms from one point of attachment to another point of attachment, during which one sigma bond is broken and another sigma bond is made (e.g., **alkyl group** rearrangements or shifts); and 4) ene reactions involving the formation and cleavage of unequal numbers of sigma bonds in a concerted cyclic transition state.

Pericyclic reactions share a number of characteristics. First, their rates of reaction are scarcely influenced by the solvent. Second, they ordinarily do not require catalysts to proceed. Third, the reactions are ordinarily very stereospecific. Fourth, light or **heat** can frequently promote the reactions. And fifth, very few enzymes capable of catalyzing such reactions are known.