Notes for Lecture #14

Diels-Alder and Other Cycloaddition Reactions

Molecule of the Day

ferrocene

"(The 1973 Nobel Prize in Chemistry is given to Ernst Otto Fischer and Geoffrey Wilkinson) for their pioneering work on the chemistry of the organometallic, so called sandwich compounds."

From the presentation of the 1973 Nobel Prize in Chemistry
(For more information, see www.noble.se)

Cycloaddition: A pericyclic reaction in which 2 separate conjugated, overlapping arrays of orbitals combine. Cycloadditions proceed by way of a cyclic transition state, and 2 sigma bonds are formed during the course of the reaction.

A suprafacial process ("s" in the table below) is one in which the bonds made or broken lie on the same face of the orbital array undergoing reaction. In an antarafacial process ("a"), the newly formed or broken bonds lie on opposite faces of the reacting orbital array.

<table>
<thead>
<tr>
<th># Electrons</th>
<th>Thermal Mode</th>
<th>Photochemical Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>4n + 2</td>
<td>[s + s]</td>
<td>[s + a]</td>
</tr>
<tr>
<td>4n</td>
<td>[s + a]</td>
<td>[s + s]</td>
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</tbody>
</table>
Coefficients of Frontier Molecular Orbitals
FMO Analysis of the "Ortho-Para Rule" and the "Alder Endo Rule"

For an in-depth discussion, see

Note: changes to coefficients of anti-bonding orbitals are opposite those seen in bonding orbitals.