

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.

Woodward-Hoffmann Rules for Cycloadditions

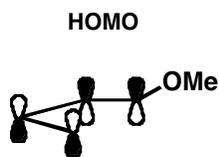
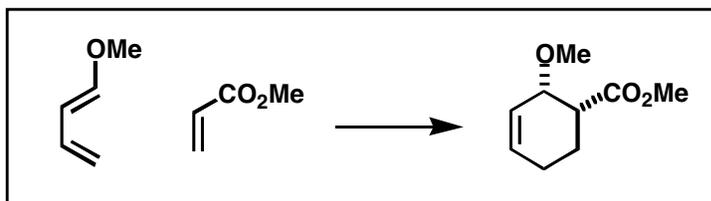
# Electrons	Stereochemical Course	
	Thermal Mode	Photochemical Mode
$4n + 2$	[s + s]	[s + a]
$4n$	[s + a]	[s + s]

Coefficients of Frontier Molecular Orbitals

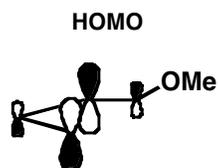
FMO Analysis of the "Ortho-Para Rule" and the "Alder Endo Rule"

For an in-depth discussion, see

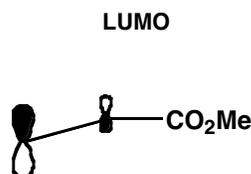
I. Fleming, "Frontier Molecular Orbitals and Organic Chemical Reactions," Wiley, 1976, pp. 121-181.



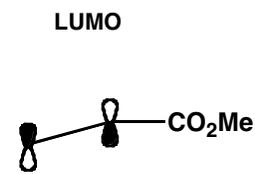
ignoring OMe



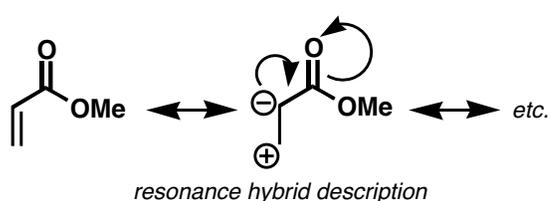
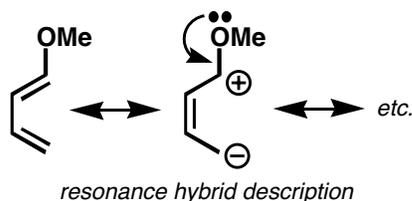
considering OMe



considering CO₂Me

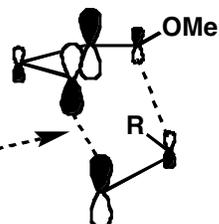


ignoring CO₂Me

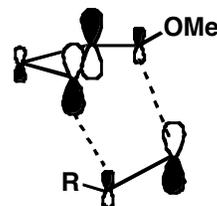


• Regioselectivity?
"ortho-para rule"

overlap maximized



vs.

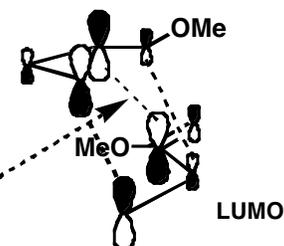


Note: changes to coefficients of anti-bonding orbitals are **opposite** those seen in bonding orbitals.

• Diastereoselectivity?
"Alder endo rule"

consider orbitals of CO₂Me

secondary orbital interaction



vs.

