

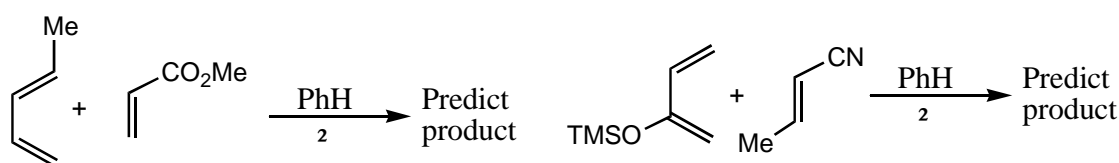
Organic Synthesis
Chem 144
M. E. Jung

Regiochemistry (Orientation) of Diels-Alder Reaction

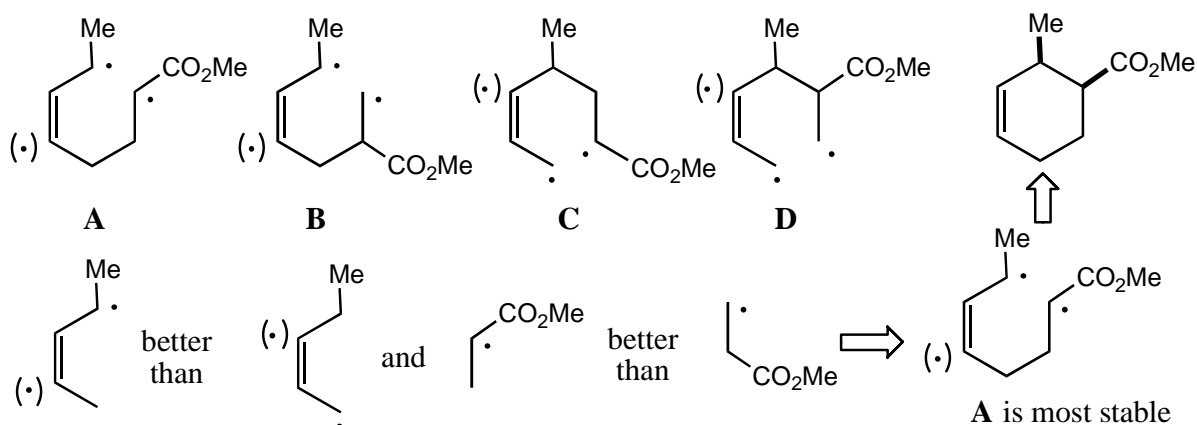
Woodward-Katz Rules (superceded by Houk's Theory)

"If one assumes that the mechanism of the Diels-Alder Reaction involves the concerted but non-synchronous formation of the two new sigma bonds, then close examination of the possible intermediate diradicals (or cation-anion pairs) allows one to predict the major orientation as that arising from the most stable diradical."

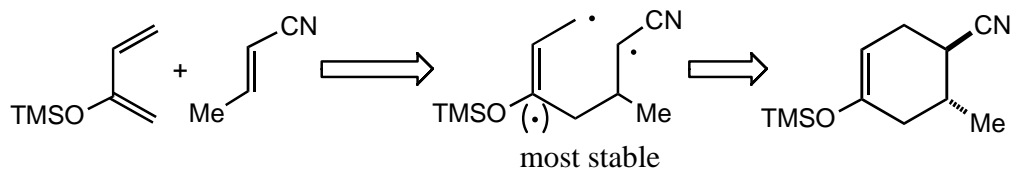
How to apply these rules:



Draw out all four possible diradical pairs (made by making one sigma bond) and show the resonance structures too). Pick the more stable radical from each half (eliminate the less stable ones). The resulting most stable diradical will correctly predict the major product.



For a 2-substituted diene



In general, the 1,2 ('ortho') and 1,4 ('para') products are favored while the 1,3 ('meta') are not! The effects are additive and can be supporting or opposing. When opposed, a 1-substituent is more directing than a 2-substituent.