

Quantitative characterization of group electrophilicity and nucleophilicity for intramolecular Diels-Alder reactions

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In a previous work (L. R. Domingo, M. J. Aurell, P. Perez and R. Contreras, *Tetrahedron* 2002, 58, 4417) we proposed that the difference in global electrophilicity index be taken as a measure of the polarity at the transition state in intermolecular Diels-Alder reactions. We herein extend this model to deal with intramolecular Diels-Alder (IMDA) processes. The transferability of the empirical reactivity rules established for the intermolecular DA reactions to the IMDA reactions is discussed. The analysis based on group electrophilicity and nucleophilicity in general fails because having two different reactivity patterns within the same molecule hampers a clean classification of electrophilicity and nucleophilicity of the interacting fragments. We introduce dual philicity indexes E1 and E2 that solve this problem by separating a series of 30 IMDA reactions into two families, namely the diene to dienophile electron flow (DDpF) and the dienophile to diene electron flow (DpDF) processes. Th