

Poster Presentation

MS59.P14

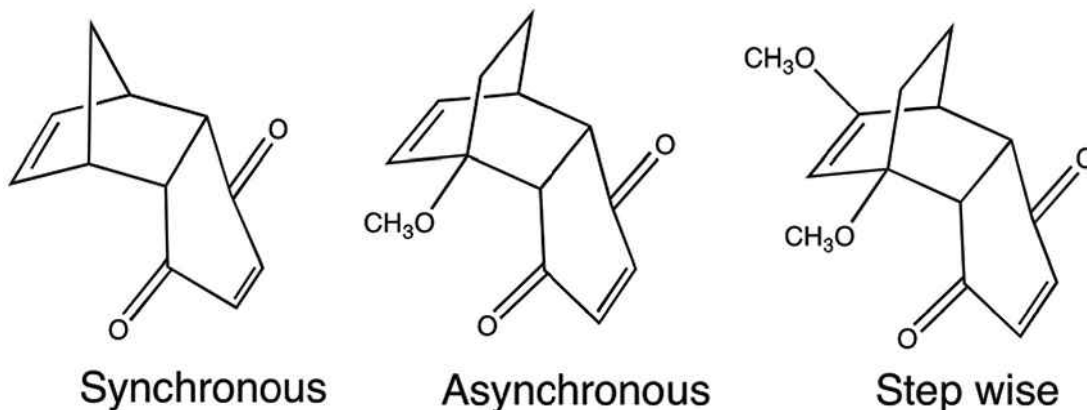
Applying the Structure Correlation Principle to retro Diels Alder Reactions

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The early stages of molecular rearrangements are often apparent in the crystal structures of molecules susceptible to that rearrangement. For example, if a particular bond is broken, or if a particular group migrates during the rearrangement, then deviations of bond distances and angles from their 'standard values' along the reaction coordinate are often observed. This is the structure correlation principle,¹ which holds provided the molecule exists in the ground state, in a geometry, which is similar to the transition state geometry for the reaction. In this geometry the frontier orbitals whose interactions facilitate the reaction, can mix in the ground state. This paper discusses the application of this principle to pericyclic fragmentation reactions related to the retro Diels Alder reaction, using low temperature X-ray structural analysis of a range of model substrates. The substrates can be classified on the basis of this data into three groups: (i) those that undergo a synchronous retro Diels Alder reaction, (2) those that undergo an asynchronous retro Diels Alder reaction, and (3) those that react via a 2-step process. Examples of molecules falling into these three categories are given below.

[1] H. B. Burgi, J. D. Dunitz and E. Shefter, *J. Am. Chem. Soc.*, 1973, 95, 5065, [2] D. Birney, T. K. Lim, J. Peng, et al., *J. Am. Chem. Soc.*, 2002, 124, 5091



Keywords: Structure-Correlation principle, Pericyclic Fragmentations