

Thermal Equilibration of Endiandric Acids and the [1,5] Sigmatropic Shift in Bicyclo[4.2.0]octa-2,4-dienes

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Abstract

The thermal equilibration of the methyl esters of endiandric acids D and E was subject to a computational study employing DFT, DMRG (Density Matrix Renormalization Group)^a and CAS calculations. An electrocyclic pathway *via* an electrocyclic ring opening followed by a ring flip and a subsequent electrocyclization, which was proposed by Nicolaou,^b was explored computationally. The free energy barrier for this electrocyclic route is shown to be very close to the bicyclo[4.2.0]octa-2,4-diene reported by Huisgen. Furthermore, the possibility of a [1,5] sigmatropic alkyl group shift of bicyclo[4.2.0]octa-2,4-diene systems at high temperatures was explored in a combined computational and experimental study. Calculated reaction barriers for a biradical-mediated stepwise [1,5] sigmatropic alkyl group shift were shown to be comparable with the reaction barriers for the bicyclo[4.1.0]hepta-2,4-diene (norcaradiene) walk rearrangement, whereas calculated reaction barriers for a concerted [1,5] sigmatropic alkyl group shift were found to be higher in energy. Experiments conducted on a deuterated analogous diol derivative verify the absence of a sigmatropic rearrangement in the bicyclo[4.2.0]octa-2,4-diene system, confirming computational results.

[a] Chan, G. K.-L.; Head-Gordon, M. *J. Chem. Phys.* **2002**, *116*, 4462.

[b] Nicolaou, K. C.; Chen, J. S. *Chemical Society Reviews* **2009**, *38*, 2993.
