Understanding Selectivities in Ligand-free Oxidative Cyclizations of 1,5- and 1,6-Dienes with RuO_4 from Density Functional Theory

Philipp J. di Dio[a], Stefan Zahn[a], Christian B. W. Stark[b], and Barbara Kirchner[a]

[a] Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstraße 2, 04103 Leipzig, Germany
[b] Institut für Organische Chemie, Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany

Reprint requests to B. Kirchner. E-mail: bkirchner@uni-leipzig.de

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Dedicated to Professor Rolf W. Saalfrank on the occasion of his 70th birthday

Quantum-chemical calculations using density functional theory were carried out to investigate the mechanism of the oxidative cyclization of 1,5- and 1,6-dienes with ruthenium tetroxide. Current experimental results show different selectivities for the formation of tetrahydrofuran and tetrahydropyran derivatives. Our theoretical data correctly reproduce the experimental selectivities. Transition structures for the first [3+2]-cycloaddition of RuO_4 with ethene and for the second [3+2]-cycloaddition with two ethene molecules, 1,5-hexadiene, and 1,6-heptadiene were calculated. For the formation of tetrahydrofuran and tetrahydropyran derivatives we observed two reaction pathways. The transition structure for the formation of *cis*-tetrahydrofuran derivatives was found to be more stable than the *trans*-tetrahydrofuran-forming transition structure by about 40 kJ mol^{-1}. By comparison to the reaction with two ethene molecules it was shown that the linking alkyl chain causes the energy gap between stereoisomers by a directing influence. In the tetrahydropyran reaction the *trans*-tetrahydropyran-forming transition structure was less than 4 kJ mol^{-1} more stable than the transition structure leading to the *cis*-tetrahydropyran. The obtained geometries showed that for tetrahydropyrans the energy gap between stereoisomers is not caused by the linking alkyl chain.

Key words: Oxidative Cyclization, DFT, Cycloaddition