Understanding Selectivities in Ligand-free Oxidative Cyclizations of 1,5- and 1,6-Dienes with RuO$_4$ from Density Functional Theory

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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