

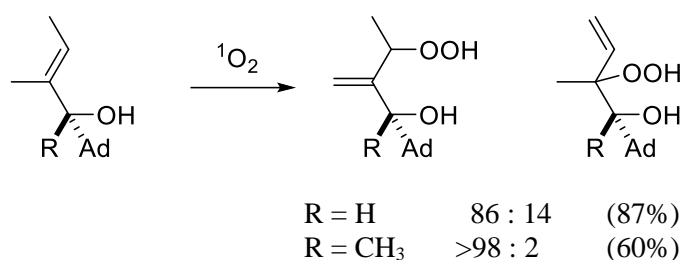
**The Large-Group Effect in the
Singlet Oxygen Ene Reaction with Allylic Alcohols:
Singlet oxygen, hydroperoxides, 1,2-dioxolanes, 1,2,4-trioxepanes**

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The singlet oxygen reaction of sterically crowded allylic alcohols result in the preferentially formation of hydroperoxy alcohols with regioselectivities up to 98:2. These high regioselectivities can be achieved through increasing the steric demands at the α -carbon and directing the singlet oxygen addition towards the γ -carbon. DFT calculations rationalized these results and show the decisive role of the symmetry-breaking bifurcation following the early transition states. The application of the primary oxygenation products is the synthesis of 1,2-dioxolanes and 1,2,4-trioxepanes by rare earth metal complexes as Lewis acids.



References:

[1] A. G. Griesbeck, B. Goldfuss, C. Jäger, E. Brüllingen, T. Lippold, M. Kleczka, *ChemPhotoChem* **2017**, *1*, <http://dx.doi.org/10.1002/cptc.201600041>.