Reactivity, Regiochemistry, and Stereochemistry of a Cyclic Nitrone and its α-Keto Derivative in 1,3-Dipolar Cycloaddition Reactions

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ABSTRACT

Rate consts. for the cycloaddns. of nitrones I and II to several mono- and disubstituted alkenes have been detd. by 1H NMR. The small solvent effect on the rate const. indicates the concerted nature of the reaction. II reacts more slowly than I because of bond opposition strain in the transition state for II. The addn. rates are influenced by the dipole moments of the nitrones. The addn. reactivity usually follows the prediction of the frontier-orbital approxn. Both nitrones exhibit very similar regiochem. and stereochem. properties. Significant secondary orbital interaction is obsd. with several electron deficient alkenes. However, maleic anhydride undergoes addn. predominantly via the exo mode of attack.