

Regiochemistry and stereochemistry of 1,3-dipolar cycloaddition of a cyclic nitron. Ali, S. Asrof; Wazeer, Mohammed I. M.. Chem. Dep., Univ. Pet. Miner., Dhahran, Saudi Arabia. Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999) (1988), (3), 597-605.

Abstract

A study of the regio- and stereochem. of the 1,3-dipolar cycloaddn. reaction of alkenes with tetrahydropyridine N-oxide I is reported. The high degree of both regio- and stereochem. control obsd. in these reactions is explained in terms of max. overlap of frontier orbitals, repulsive steric encumbrance, and attractive secondary orbital interaction in the transition state. Most mono- and 1,1-disubstituted alkenes (e.g., EtOCH:CH₂ and MeO₂CCMe:CH₂, resp.) give 2-substituted cycloadducts (e.g., II; R = OEt; R¹ = H; R = Me, R¹ = CO₂Me, resp.). As the electron affinity of the monosubstituted alkene increases, an increasing tendency towards formation of the regioisomeric 3-substituted cycloadduct is encountered. 1,2-Disubstituted alkenes (e.g., MeCH:CHCHO) react to afford cycloadducts (e.g., III) with electron-withdrawing substituents always in the 3-position.

