STEREOCHEMICAL ASPECTS OF 1,3-DIPOLAR CYCLOADDITION REACTIONS OF HETEROCYCLIC N-YLIDES TO OLEFINIC DIPOLAROPHILES

Otohiko Tsuge, Shuji Kanemasa and Shigeori Takenaka
Research Institute of Industrial Science, and Department of Molecular
Science and Technology, Interdisciplinary Graduate School of Engineering
Sciences, Kyushu University, Kasugakoen, Kasuga 816

The characteristic stereochemical course of 1,3-dipolar cycloadditions of heterocyclic N-ylides to olefinic dipolarophiles has been figured out. When the ylide carries an anion-stabilizing substituent of carbonyl type, the anti form of ylide predominantly participates in the cycloadditions in which the electron-withdrawing substituents of olefins interact with the heterocyclic plane of ylide in an attractive fashion, the formation of endo cycloadducts being favored.

In the reactions with cis olefins, endo adducts to the anti ylide are exclusively obtained. However with trans olefins, the stereochemistry of adducts depends upon the energy balance among the stabilization of anti ylide, the attractive endo interaction, and the steric repulsion between the ylide and olefin substituents. Often the kinetical cycloadducts are not identical with the thermodynamic cycloadducts so that the formers change into the latters through a retro cycloaddition reaction.

When the ylide substituent is not carbonyl type and hence no stabilization of the anti form of ylide is expected, the syn form participates in the cycloadditions to trans olefins since the most favored endo approach causes no sterical repulsion to the ylide-stabilizing substituent.