

RING EXPANSION REACTIONS OF THIIRENE 1,1-DIOXIDES

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Thiirenes are one of the 3-heterocyclopropenes which have been of great interest for many chemists not only because of their highly strained structures but also because of their antiaromaticity. While no thiirenes have been isolated, a few thiirene 1,1-dioxides have been prepared and studied from both structural and theoretical points of view. However chemical properties of thiirene 1,1-dioxides are not well clarified. So we studied the nucleophilic addition of metalated nitriles along with cycloadditions of 1,3-dipoles and an amino butadiene derivative, and obtained interesting results.

1) Reactions of thiirene 1,1-dioxides with metalated nitriles

2,3-Diphenylthiirene 1,1-dioxide (1a) was found to act as an ambident electrophile to afford two types of sulfur-containing cyclic products, 5-imino-2-sulfolenes, and a sulfolene-4-one, when the metalated nitriles have no α -hydrogen atom. The former arose from nucleophilic attack of the aryl-substituted carbanions to the ring carbon of 1a and the latter arose from the attack of an alkyl-substituted carbanion to the sulfur atom. When nitriles bear an α -hydrogen atom, an acrylonitrile derivative and vinyl sulfones were obtained. On the other hand, 2,3-diphenylthiirene 1,1-dioxide (1b) suffered only one type of nucleophilic attack to the ring carbon atom, giving the sulfinate salts.

2) Cycloaddition reactions of thiirene 1,1-dioxides with nitrilium betains and an amino butadiene derivative

Thiirene 1,1-dioxides 1a, b underwent 1,3-dipolar cycloaddition with diphenylnitrile imine and p-nitrobenzonitrile benzylide, with a loss of sulfur dioxide, to give pyrazoles and pyrroles, respectively. In the latter reaction, a 4H-1,4-thiazine 1,1-dioxide derivative, corresponding to a 1:1 cycloadduct of diphenylthiirene 1,1-dioxide (1b) and the nitrile ylide, was formed as a major product along with a pyrrole derivative. However in the case of 1a no such a 1:1 adduct but only a pyrrole derivative was obtained. On the other hand, 1b was found to undergo Diels-Alder-type cycloaddition with 1-piperidino-2-methyl-1,3-pentadiene. Such a reaction seems to be the first example of Diels-Alder reaction of thiirene 1,1-dioxide.