

PHOTOCHEMISTRY OF THE NITROGEN-CONTAINING THIOCARBONYL SYSTEM

Kazuaki Oda, Eiichi Yoshida, and Minoru Machida

Faculty of Pharmaceutical Sciences, Higashi-Nippon-Gakuen University

Ishikari-Tobetsu, Hokkaido 061-02

Yuichi Kanaoka

Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060

The well-known carbonyl photochemistry has been extended to a nitrogen-carbonyl photochemistry by exploring excited reactivities of the imide system, in which a carbonyl chromophore is in conjunction with an amide group. On the other hand, changing a key element in the ketone chromophores from oxygen to sulfur introduced the unique thione photochemistry. To develop a frontier of organic photochemistry, we have explored a new amalgamation of such a key chromophore and a key atom, *i.e.*, imide and sulfur.

First, intramolecular hydrogen abstraction was tested with a series of N-alkylthiophthalimides, which were, after irradiation, recovered nearly unchanged. However, cycloaddition of 1 to 2 took place giving a thietane 3 accompanied by an unsaturated product 4, probably formed by photolysis of the initially formed 3, indicative of promoted photoreactivity of the aromatic imide-thietanes. When stilbene 6 was used, N-methylmonothiophthalimide 5 afforded two stereoisomers of thietanes. In addition to 7, a mixture of products were obtained which turned out to be consisting of 1,2-dithiane 8 and other dithianes, probably formed by subsequent fission of 7 followed by addition with 5, in analogy with the reactions of thiones. Photoreaction of thioimide derivative gave two stereoisomers of pyridoisoindoles 11, which were probably formed via intramolecular thietane intermediate 10.

