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PHOTOCHEMISTRY OF THE NITROGEN-CONTAINING THIOCARBONYL SYSTEM

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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 cojunction 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-alkyl-thiophthalimides, which were, after irradiation, recovered nearly unchanged. However, cycloaddition of 1 to 2 took place giving a thietane 3 accompanyied 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 fisson of 7 followed by addition with 5, in analogy with the reactions of thiones. Photoreaction of thioimide derivative gave two stereoisomers of pyrido-isoindoles 11, which were probably formed via intramolecular thietane intermediate 10.