

PHOTOCHEMICAL REARRANGEMENTS OF ISOTHIAZOLES

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Vycol-filtered low-pressure mercury arc irradiation of 3-, 4-, and 5-phenylisothiazoles in dry ether gave 4-phenylthiazole(12%), β -cyanostyryl disulfide(15%), and 3-phenylisothiazole(2.3%) respectively. Irradiation of those isothiazoles in MeOH produced small amounts of 2- and 4-phenylthiazoles, 4-phenylthiazole(30%), and 3-phenylisothiazole(9.0%) along with 4-(6.1%) and 5-phenylthiazoles(20%), respectively. In irradiation of 3,5-diphenylisothiazole in ether, 2,4-diphenylthiazole was obtained in 48% yield. The photorearranged products obtained in ether solutions are likely to form via the most stable tricyclic sulfonium cation intermediate, while those in MeOH are accounted for in terms of Ullman's ring-contraction-ring-expansion mechanism. The difference in photochemical behavior of isoxazoles from isothiazoles is nicely explained in terms of the change of bond orders (ΔP_{rs}) upon excitation.

Irradiation of benzo[d]isothiazole in ether with a medium pressure mercury arc gave 2-cyanophenyl disulfide in 12% yield, while in MeOH 2-cyanophenyl sulfide in 8% yield. Irradiation of 5-chloro-3-phenylbenzo[c]isothiazole in MeOH produced 2-amino-5-chlorobenzophenone in 31% yield, while in acetonitrile 2,8-dichloro-6,12-diphenyldibenzo[b,f][1,5]diazocine(39%) along with 2-amino-5-chlorobenzophenone(8%). These observations are in sharp contrast to the cases of the oxygen and nitrogen analogues.