HETEROCYCLES, Vol. 3, No. 1, 1975

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.