

PHOTOCHEMICAL REACTION OF HALOARENE TETHERED TO ARENE WITH AMIDE BOND

Yong-Tae Park, Chang-Hee Jung, Kwang-Wook Kim, and Ahmed Mayouf
Department of Chemistry, Kyungpook National University, Taegu, 702-701, Korea

The photochemical behavior of 2-halo-*N*-pyridinylbenzamide and *N*-pyridinyl-2-Halobenzamide is studied. The photoreaction of 2-chloro-*N*-pyridinylbenzamide afforded photocyclized products, benzo[*c*]naphthyridinones in high yield, whereas the bromo analogs produced extensively photoreduced products, *N*-pyridinylbenzamides with minor photocyclized product. Since the photocyclization reaction of 2-chloro-*N*-pyridinylbenzamide is retarded by the presence of oxygen and sensitized by the presence of a triplet sensitizer, acetone or acetophenone, a triplet state of the chloro analog is involved in the reaction. Since several radical intermediates are identified in the laser flash photolysis of 2-chloro-*N*-pyridinylbenzamide, a radical-mediated mechanism for the reaction is proposed: the triplet state (78 kcal/mol) of the chloro analog which is populated by the excitation of a distorted conformer having an intramolecular hydrogen bond interaction between a chlorine negative end and a hydrogen of the secondary amide bond and then by its intersystem crossing, undergoes a homolytic cleavage of the C-Cl bond to give phenyl and chlorine radicals. The intramolecular cyclization reaction of the phenyl radical with its close pyridinyl group proceeds to produce a conjugated 2,3-dihydropyridinyl radical and then the conjugated radical aromatizes to afford a cyclized product, benzo[*c*]naphthyridinone by ejecting a hydrogen radical. The photoreduction product can be formed by abstracting of hydrogen atom of the phenyl σ radical from the environment.

We recently and unexpectedly observed that a photoreaction of *N*-(2-chlorophenyl)-4-pyridinylcarboamide in the presence of base gave a 2-pyridinylbenzoxazole (25%), a product of an intramolecular photosubstitution of halogen of the aryl halide with the carbonyl oxygen of the amide bond (Scheme). Bromo analog afforded a 2-pyridinylbenzoxazole in 34% yield. The novelty of the reactions deserve special attention. In order to elucidate the reaction mechanism, kinetic and laser flash photolysis studies have been performed. The yield of 2-pyridinylbenzoxazole under dilute base was lower than that under concentrated base, even though the starting material underwent certain reaction further under dilute base.