

Dietrich Döpp*

Fachgebiet Organische Chemie,
Universität Duisburg -Gesamthochschule-,
Postfach 10 16 29,
D-4100 Duisburg 1, Germany

Czeslawa Orlewska and Franciszek Saczewski*

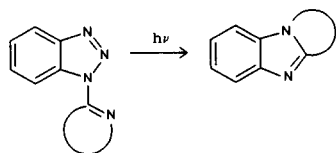
Department of Organic Chemistry,
Medical Academy of Gdańsk,
ul. Gen.Hallera 107,
Pl-80-416 Gdańsk, Poland
Received September 24, 1992

1-(4,5-Dihydro-1*H*-imidazol-2-yl)benzotriazole was photolyzed at 254 nm yielding 1,2-dihydro-4*H*-imidazo[1,2-*a*]benzimidazole.

J. Heterocyclic Chem., **30**, 833 (1993).

The photolyses of some aromatic heterocycles such as pyridine, isoquinoline or thiazole containing a 1-benzotriazolyl substituent have already been studied [1,2]. These reactions occurred with elimination of a nitrogen molecule from the benzotriazolyl moiety followed by ring closure of the nitrogen atom of the heterocyclic substituent (Scheme 1).

Scheme 1



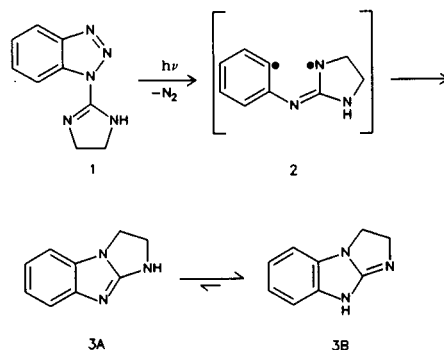
Since the photochemistry of the benzotriazole derivatives of the partially hydrogenated heterocyclic systems has not been reported, we thought it of interest to examine the behaviour of 1-(4,5-dihydro-1*H*-imidazol-2-yl)benzotriazole (**1**).

Photolysis of compound **1** in methanol or benzene after 27 hours irradiation by means of high pressure mercury lamp ($\lambda \geq 280$ nm) gave only an intractable mixture of decomposition products.

However, the photolysis of this compound performed in acetonitrile at 254 nm for 18 hours gave product **3**, which was isolated in 60% yield. The reaction probably proceeds via a diradical intermediate **2**, which couples with the formation of the benzimidazole ring (Scheme 2). The product **3** was claimed to be synthesized earlier by North [3] on an independent way.

This result shows that, for a successful transformation of **1** into **3**, the selective population of a higher excited state of **1** is necessary. Since a genuine AA'BB'-system [5] is observed for the four methylene protons, tautomer **3B** seems to be solely present at least in deuteriochloroform.

Scheme 2



EXPERIMENTAL

Melting points were determined with a Kofler hot stage apparatus and are uncorrected. The ¹H-nmr spectra were obtained on a Bruker WM 300 (300 MHz), the ir spectra on a Perkin Elmer Spectrometer 397, the mass spectra (70 eV, EI mode) on a Varian MAT 311A spectrometer, and the elemental analyses on a Carbo Erba 1106 CHN analyzer. Preparative layer chromatography was obtained on 48 x 20 cm glass plates, 1 mm layer of silica gel Merck PF₂₅₄ applied as an aqueous paste and air-dried. For developing the chromatograms a mixture of chloroform/methanol (12:1) was used.

For irradiation a 200 ml photoreactor with a quartz cooling jacket connected with Hanau TNN15 (15 W) mercury-low pressure lamp was used.

Substrate **1** was prepared according to a described method [4]. 1,2-Dihydro-4*H*-imidazo[1,2-*a*]benzimidazole (**3**).

Two hundred ml of a (0.0021 M) solution of compound **1** [4] (λ_{max} 340, 284, 252, 208 nm) in acetonitrile was irradiated at 254 nm with argon purging for 18 hours at room temperature. The reaction was followed by thin layer chromatography. The solvent was evaporated under reduced pressure and the residue separated by preparative layer chromatography. A crystalline substance was obtained as the major product (31.8 mg, 60%, based on starting material not recovered) and 17.5 mg of unchanged starting

material was isolated. The yield is based upon duplicate runs and is $\pm 5\%$. The crude product was crystallized from 1,4-dioxane, mp 210-213° (lit 204-206°) [3].

A sample for elemental analysis was recrystallized from water, mp 210°; ir (potassium bromide): ν 3080, 1640, 1590, 1500, 1450 cm^{-1} ; ^1H -nmr (deuteriochloroform/TMS): δ 4.15 (symmetric narrow m, 4H, AA'BB', system 16 lines resolved), 5.52 (broad s, 1H, NH), 7.05 (m, 3H, aromat), 7.40 (m, 1H, aromat); ms: m/z (%) 159 (100), 158 (27), 144 (4), 131 (29), 117 (7), 103 (16), 90 (8).

Anal. Calcd. for $\text{C}_9\text{H}_9\text{N}_3$ (159.19): C, 67.90; H, 5.70; N, 26.40.

Found: C, 67.68; H, 5.55; N, 26.30.

REFERENCES AND NOTES

- [1] A. J. Hubert, *J. Chem. Soc. C*, 1334 (1969).
- [2] A. J. Hubert and H. Reimlinger, *Chem. Ber.*, **103**, 2828 (1970).
- [3] R. J. North and A. R. Day, *J. Heterocyclic Chem.*, **6**, 655 (1969).
- [4] A. R. Katritzky and F. Saczewski, *Synthesis*, 561 (1990).
- [5] The general habitus corresponds to a case of $\gamma_0 \delta = 5\text{-}10$ Hz, see H. Günter, *NMR-Spektroskopie*, 3rd, Ed, G. Thieme, Stuttgart, 1992, p 181.