ISSN 1070-4280, Russian Journal of Organic Chemistry, 2009, Vol. 45, No. 4, pp. 629–630. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © E.S. Ostroglyadov, A.A. Nikonorov, O.S. Vasil'eva, M.M. Zobacheva, V.M. Berestovitskaya, 2009, published in Zhurnal Organicheskoi Khimii, 2009, Vol. 45, No. 4, pp. 642–643.

SHORT COMMUNICATIONS

Synthesis and Structure of 1-Methyl-2-(2-nitro-2-phenylethenyl)-1*H*-benzimidazole

E. S. Ostroglyadov, A. A. Nikonorov, O. S. Vasil'eva, M. M. Zobacheva, and V. M. Berestovitskaya

Hertzen Russian State Pedagogical University, nab. r. Moiki 48, St. Petersburg, 191186 Russia
e-mail: kohrgpu@yandex.ru

Received December 5, 2008

DOI: 10.1134/S1070428009040290

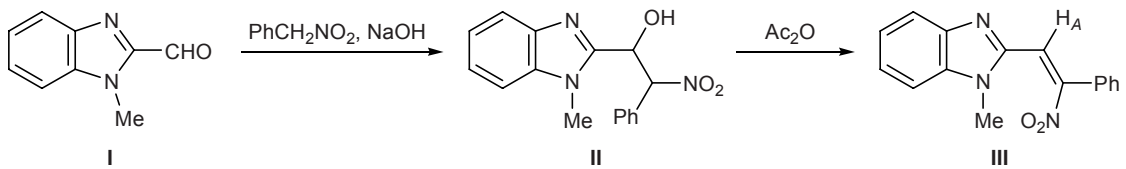
Benzimidazole ring system is a pharmacophoric fragment included into the structure of many natural compounds and drugs, in particular psychostimulators (Bemithyl), antihistaminic agents (Astemizol, Oxatomide), and spasmolytics (Dibazole) [1–3], as well as antihelminthics (Mebendazole, Medamine) widely used in veterinary [4]. Therefore, synthesis of new potential biologically active compounds containing a benzimidazole fragment is a promising line of studies. A convenient starting material for the synthesis of such compounds may be 1-methyl-2-(2-nitro-2-phenylethenyl)-1*H*-benzimidazole (**III**) [5] which is available from 1-methyl-1*H*-benzimidazole-2-carbaldehyde (**I**) [6] and phenylnitromethane.

We have improved the procedure for dehydration of nitro alcohol **II** by changing the order of mixing of the reactants and stirring the reaction mixture both in the course of heating and for 2 h after treatment with water. As a result, compound **III** was isolated in a high yield (83%). The melting point of nitroethenylbenzimidazole **III** thus obtained (mp 210–212°C) considerably differed from that reported in [5] (mp 160–161°C). Presumably, the melting point given in [5] corresponds to another substance, the more so no data in support of its structure were given. We were the first to record the ^{1}H NMR and IR spectra of nitro alcohol **II** (mp 160–161°C) and nitroethene **III** (mp 210–212°C), which unambiguously confirm their structure.

The ^{1}H NMR spectrum of nitroethene **III** in $CDCl_3$ indicated the presence of only one stereoisomer; it contained signals from protons in the benzimidazole (δ 7.30, 7.80 ppm, 4H) and benzene rings (δ 7.50, 7.54 ppm, 5H) and methyl group (δ 3.88 ppm, 3H), and the olefinic proton (H_A) resonated at δ 6.83 ppm. According to [7–10], upfield shift of the H_A signal in the spectrum of **III** as compared to model 1-methyl-2-[(*E*)-2-nitroethenyl]benzimidazole (δ 8.15 ppm) [7] suggests *trans* arrangement of the olefinic proton and the nitro group at the double C=C bond, i.e., its *Z* configuration.

The IR spectrum of nitroethene **III** contained absorption bands typical of stretching vibrations of C=S and C=N bonds (1655, 1595, 1562 cm^{-1}) and conjugated nitro group (1540, 1340 cm^{-1}). Compound **III** displayed in the electronic absorption spectrum [λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 205 (30000), 260 (11000), 335 (25000)] a blue shift of the long-wave absorption maximum ($\Delta\lambda_{max}$ = 33 nm) relative to that in the spectrum of 1-methyl-2-[(*E*)-2-nitroethenyl]benzimidazole [λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 202 (23500), 368 (11500)], which may be attributed to *cis* orientation of the benzimidazole fragment and the nitro group in molecule **III**, unlike *trans* orientation of the same substituents in 1-methyl-2-[(*E*)-2-nitroethenyl]benzimidazole [7].

1-(1-Methyl-1*H*-benzimidazol-2-yl)-2-nitro-2-phenylethanol (II) was synthesized according to the



I II III

procedure described in [5]. mp 160–162°C (from MeOH); published data [5]: mp 160–161°C. IR spectrum, ν, cm^{-1}: 1375, 1555 (NO_2). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 5.83 m (1H, C**H**OH); 6.30 m (2H, C**H**Ph, OH); 7.20 m, 7.25 m, and 7.70 m (4H, 4-H, 5-H, 6-H, 7-H); 7.48 m and 7.60 m (5H, C_6H_5); 3.88 s (3H, NMe).

1-Methyl-2-(2-nitro-2-phenylethenyl)-1*H*-benzimidazole (III). Acetic anhydride, 2.1 ml, was added to 0.9 g (3 mmol) of nitro alcohol **II**, and the mixture was heated for 30 min on a boiling water bath under stirring until it became homogeneous. The mixture was then treated with 16.5 ml of ice water under stirring and was stirred for 2 h more. The precipitate was filtered off and washed on a filter with water, alcohol, and diethyl ether. Yield 0.7 g (83%), mp 210–212°C (from MeOH); published data [5]: mp 160–161°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.83 (1H, H_A), 7.50 and 7.54 (5H, C_6H_5), 7.30 and 7.80 (4H, 4-H, 5-H, 6-H, 7-H), 3.88 (3H, Me). Found, %: C 68.53, 68.78; H 4.27, 4.50; N 15.42, 15.40. $C_{16}H_{13}N_3O_2$. Calculated, %: C 68.82; H 4.66; N 15.05.

The ^1H NMR spectra were recorded on a Jeol JNM ECX400A spectrometer at 400 MHz. The IR spectra were measured on an InfraLYuM FT-02 instrument from samples dispersed in mineral oil. The electronic absorption spectra were obtained on a Shimadzu UV-2401 spectrophotometer from solutions in acetonitrile.

REFERENCES

1. Mashkovskii, M.D., *Lekarstvennye sredstva* (Drugs), Moscow: Novaya Volna, 2007.
2. *Registr lekarstvennykh sredstv Rossii. Entsiklopediya lekarstv* (Russian Registry of Drugs. Encyclopedia of Drugs), OOO RLS-2002, 2002 (9).
3. Kopelevich, V.M., Bulanova, L.N., Marieva, T.D., and Gunar, V.I., *Pikamilon v sovremennoi nevrologicheskoi i psikhiatricheskoi praktike (kliniko-eksperimental'nye issledovaniya)* (Pikamilon in Modern Neurologic and Psychiatric Practice. Clinical and Experimental Studies), Moscow: NPO Vitaminy, 1994, p. 13.
4. Kuz'min, A.A., *Antigel'mintiki v veterinarnoi meditsine* (Antihelminthics in Veterinary), Moscow: Akvarium, 2000.
5. Dolgatov, D.D. and Simonov, A.M., *Zh. Obshch. Khim*., 1964, vol. 34, p. 3052.
6. Le-Bris, M., Wahl, H., and Jambu, T., *Bull. Soc. Chim. Fr*., 1959, p. 343.
7. Berestovitskaya, V.M., Ishmaeva, E.A., Litvinov, I.A., Vasil'eva, O.S., Vereshchagina, Ya.A., Ostroglyadov, E.S., Fattakhova, G.R., Beskrovnyi, D.V., and Aleksandrova, S.M., *Russ. J. Gen. Chem*., 2004, vol. 74, p. 1108.
8. Dore, I.C. and Veil, C., *Recl. Trav. Chim. Pays–Bas*, 1975, vol. 94, p. 225.
9. Descotes, G., Bahurek, Y., Bourillot, M., and Rostraing, R., *Bull. Soc. Chim. Fr*., 1970, p. 282.
10. Trukhin, E.V., Makarenko, S.V., and Berestovitskaya, V.M., *Russ. J. Org. Chem*., 1998, vol. 34, p. 59.