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LETTERS
TO THE EDITOR

2,6-Dinitrobenzofuroxanes Containing Aminoacetal Fragments

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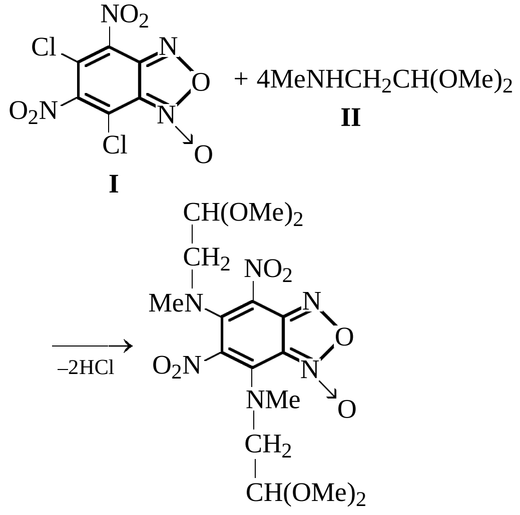
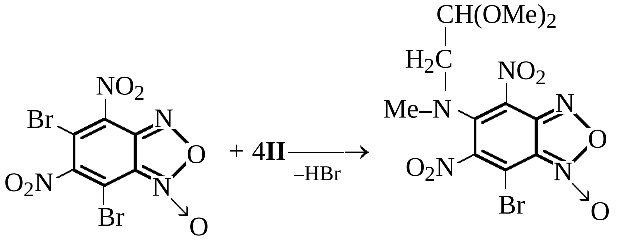
Substituted benzofuroxanes present undoubted interest as biologically active compounds [1]. Therefore, introduction of functional groups providing possibilities for further structural modification of benzofuroxanes is an important problem. In thise connection of great interest are halogen-containing dinitrobenzofuroxanes. They can be used as starting biulding blocks. Recent studies of the reaction of 5,7-dichloro-4,6-dinitrobenzofuroxanes with aromatic amines showed that substitution of chlorine at the C^5 carbon atom proceeds in the first turn, and the resulting mixture contains mono- and disubstituted products [2, 3]. With the purpose to prepare benzofuroxanes containing reactive acetal fragments, we have studied the reactions of 5,7-dichloro-4,6-dinitrobenzofuroxane (**I**) and 5,7-dibromo-4,6-dinitrobenzofuroxane (**IV**) with (2,2-dimethoxyethyl)(methyl)amine **II**.



I, **II**, **III**

It was found that the reaction at room temperature and 1 : 1 or 1 : 2 molar ratios gives a mixture of mono- and disubstituted products. With a double excess of acetal **II**, compound **III** containing two acetal residues preferentially formed and was isolated pure. At the same time, the reaction of dibromobenzofuroxane **IV** with acetal **II** involved substitution of one bromine atom, irrespective of the reagent ratio.



IV **V**

The structure of compounds **III** and **V** was confirmed by IR and ^{1}H NMR spectroscopy, and their composition was established by elemental analysis and MALDI–TOF mass spectrometry.

5,7-Bis[(2,2-dimethoxyethyl)(methyl)amino]-4,6-dinitrobenzofuroxane (III). To a solution of 0.29 g of benzofuroxane **I** in 8 ml of propan-2-ol, 0.48 g of acetal **II** was added. The reaction mixture was kept for 1 h at 20°C. The precipitate that formed was filtered off, washed with diethyl ether, and dried in a vacuum (40°C, 0.06 mm) to constant weight to give 0.28 g (61%) of compound **III**, mp 158°C. IR spectrum, ν, cm^{-1}: 1652, 1508, 1284 (furoxane ring), 1554 (NO_2 asymm), 1349 (NO_2 symm). ^{1}H NMR spectrum ($CDCl_2$), δ, ppm (*J*, Hz): 3.28 s (3H, CH_3N), 3.36 s (6H, CH_3O), 3.44 d (2H, CH_2, $^3J_{HH}$ 4.76), 3.52 s (6H,

CH_2O), 3.61 s (3H, CH_3N), 4.39 d (2H, CH_2, $^3J_{HH}$ 4.97), 4.52 t (1H, CH, $^3J_{HH}$ 5.00), 4.71 t (1H, CH, $^3J_{HH}$ 5.30). Mass spectrum, *m/z*: 460.4 (M^+). Found, %: C 41.69; H 5.35; N 18.13. $C_{16}H_{24}N_6O_{10}$. Calculated, %: C 41.74; H 5.27; N 18.25.

7-Bromo-5-[(2,2-dimethoxyethyl)(methyl)amino]-4,6-dinitrobenzofuroxane (V). A mixture of 0.38 g of benzofuroxane **IV** and 0.48 g of aminoacetal **II** in 10 ml of chloroform was kept for 24 h at 20°C. The solvent was removed, and the precipitate the formed was washed with diethyl ether and dried in a vacuum (2 h, 40°C, 0.06 mm) to give 0.18 g (56%) of compound **V**, mp 108°C. The IR spectrum, ν, cm^{-1}: 1593, 1291 (furoxane ring), 1555 (NO_2 asymm), 1377 (NO_2 symm). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.75 s (3H, CH_3N), 3.18 d (2H, CH_2, $^3J_{HH}$ 5.49), 3.45 s (6H, CH_3O), 5.07 t (1H, CH, $^3J_{HH}$ 5.49). Mass spectrum, *m/z*: 421 (M^+). Found, %: C 30.97; H 2.62; Br 18.09; N 16.18. $C_{11}H_{12}BrN_5O_8$. Calculated, %: C 31.30; H 2.87; Br 18.93, N 16.59.

The ^1H NMR spectra were taken on an AVANCE-600 NMR spectrometer (600 MHz) against residual proton signals of deuterated solvents ($CDCl_3$, DMSO-d_6). The IR spectra were recorded on a Bruker Vector-22 Fourier spectrometer in the range 400–4000 cm^{-1}. Crystalline samples were studied as emulsions in Vaseline oil. The mass spectra were obtained on a MALDI-2 V 5.2.0 device in the 1,8,9-trihydroxyanthracene matrix.

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