

SHORT  
COMMUNICATIONS

Reaction of 5-Nitrobenzofuroxane with Acetylacetone\*

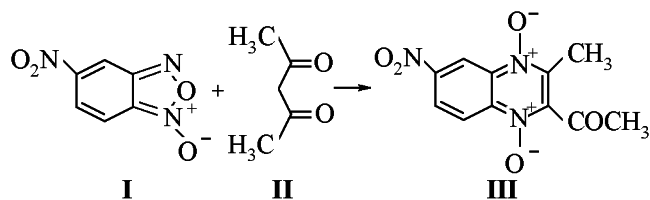
P.M. Panasyuk, S.F. Mel'nikova, and I.V. Tselinskii

St. Petersburg State Technological Institute, St. Petersburg, 198013 Russia

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Reactions of 5(6)-substituted benzofuroxanes with C-nucleophiles (enolate-anions, enamines) resulting in quinoxaline-*N,N'*-dioxides frequently provide better yields than those with unsubstituted benzofuroxane [1, 2]. However the substituents in 4(7) position sharply decrease the reactivity although at long time and elevated temperature the condensation product can be obtained in low yield [2]. At the same time both 4- and 6-nitrobenzofuroxanes vigorously react with enamines [2] to afford a complicated mixture of products that does not contain quinoxaline-*N,N'*-dioxides. Similar results were also obtained at low temperature [2].

Here we report on successful condensation of 5-nitrobenzofuroxane (I) with acetylacetone (II) in the presence of calcium hydroxide or alcoholate.



The structure of obtained 2-acetyl-3-methyl-6-nitroquinoxaline-*N,N'*-dioxide was confirmed by <sup>1</sup>H NMR and IR spectra. The position of the substituents was determined basing on published data [3, 4] indicating that at an electron-withdrawing substituent in 5(6) position formed prevailing type III product.

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The reaction time depends on benzofuroxane to catalyst ratio; at equimolar amounts it is ~2 h, yield 65–67% (catalyst calcium isopropylate), and 50–55% [catalyst Ca(OH)<sub>2</sub>].

**2-Acetyl-3-methyl-6-nitroquinoxaline-*N,N'*-dioxide.** A solution of 1.81 g (10 mmol) of 5-nitrobenzofuroxane, 1.1 g (11 mmol) of acetylacetone in 50 ml of 2-propanol was mixed with a solution of 0.25 g (2.4 mmol) of calcium isopropylate in 10 ml of 2-propanol. The mixture was kept for 5 h at 18–20°C. The separated precipitate was filtered off and recrystallized from acetone. We obtained 1.75 g (67%) of orange needle-like crystals, mp 162°C (decomp.). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1720, 1620, 1537, 1420, 1335, 1250, 1180, 1050, 920. <sup>1</sup>H NMR spectrum (CF<sub>3</sub>COOH),  $\delta$ , ppm: 2.35 s (3H, COCH<sub>3</sub>), 2.4 s (3H, CH<sub>3</sub>), 8.4 q (2H, H<sup>7,8</sup>), 9.15 s (1H, H<sup>5</sup>). Found, % : C 50.16; H 3.51; N 15.89. C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>O<sub>5</sub>. Calculated, %: C 50.20; H 3.45; N 15.96.

<sup>1</sup>H NMR spectra were registered on spectrometer Perkin-Elmer R-12, internal reference HMDS. TLC was performed on Silufol UV-254 plates, eluent chloroform.

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