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SHORT COMMUNICATIONS

Dimerization of Nitrile Oxides of the 1,2,5-Oxadiazole Series

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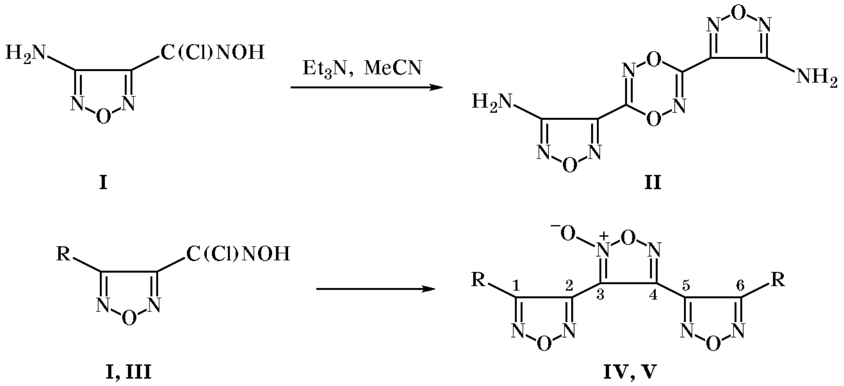
Dimerization of nitrile oxides, either isolated in the pure form or generated *in situ* from appropriate precursors, provides one of the most important methods of synthesis of symmetric 1,2,5-oxadiazole *N*-oxides (furoxans) [1]. Nitrile oxides are often generated from hydroxamoyl chlorides. When the reaction is carried out under heterogeneous conditions, aqueous alkalies are used to promote elimination of hydrogen chloride, and triethylamine is used as hydrogen chloride acceptor in homogeneous media. Dimerization of nitrile oxides is sometimes accompanied by formation of 1,4,2,5-dioxadiazine and 1,2,4-oxadiazole *N*-oxide derivatives. For example, Andrianov *et al.* [2] reported on the formation of 3,6-bis(4-amino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (**II**) in the dimerization of aminofurazancarbonitrile oxide obtained by treatment of 4-amino-1,2,5-oxadiazole-3-carbohydroximoyl chloride (**I**) with triethylamine in acetonitrile [2] (Scheme 1). On the other hand, treatment of 2-hydroxyiminopropionohydroximoyl chloride in ether with an aqueous solution of Na_2CO_3 yields (*E*,*E*)-3,4-diacetylfuroxan dioxime [3].

We have found that dimerization of nitrile oxides derived from 4-amino- and 4-azido-1,2,5-oxadiazole-3-carbohydroximoyl chlorides **I** and **III** also leads to formation of furoxans **IV** and **V** (Scheme 1).

The ^{13}C NMR spectra of compounds **IV** and **V** contain six carbon signals; by contrast, in the ^{13}C NMR spectrum of **II** only three carbon signals are observed due to its symmetric structure. Our attempts to synthesize azido-substituted analog of compound **II** by dehydrohalogenation of 4-azido-1,2,5-oxadiazole-3-carbohydroximoyl chloride (**III**) with triethylamine in organic solvents were unsuccessful.

3,4-Bis(1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole *N*-oxides IV and V. To a suspension of 0.01 mol of compound **I** or **II** in 20 ml of diethyl ether, cooled to 0–3°C, we slowly added under vigorous stirring (maintaining the temperature within 0–3°C) a 3% aqueous solution of Na_2CO_3. The mixture was kept

Scheme 1.



I, **IV**, R = NH_2; **III**, **V**, R = N_3.

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for 2 h below 10°C, the solvent was removed, and the solid residue was washed with a small amount of cold water and dried in air.

3,4-Bis(4-amino-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole *N*-oxide (IV). Yield 70%. mp 167–168°C. IR spectrum, ν, cm^{-1}: 3450, 3330, 1650, 1620, 1470, 1160, 1110, 1050, 970, 890, 850. UV spectrum, λ_{max}, nm (ε): 280 (5300) (pH 1); 289 (6000) (pH 11). ^{1}H NMR spectrum, δ, ppm: 6.6 s. ^{13}C NMR spectrum, δ_C, ppm: 104.33 (C^4), 133.41 (C^5), 136.29 (C^2), 146.66 (C^3), 155.20 (C^6), 156.12 (C^1). Found, %: C 28.41; H 1.75; N 44.56. $M^{+\cdot}$ 252. $C_6H_4N_8O_4$. Calculated, %: C 28.57; H 1.58; N 44.44. *M* 252.

3,4-Bis(4-azido-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole *N*-oxide (V). Yield 70%. mp 51–52°C (from alcohol). IR spectrum, ν, cm^{-1}: 2144, 1632, 1456, 1328, 1232, 992, 960. ^{13}C NMR spectrum, δ_C, ppm: 103.35 (C^4), 135.49 (C^5), 138.19 (C^2), 143.84 (C^3), 152.96 (C^1), 153.65 (C^6). Found, %: C 23.80; N 55.37. $M^{+\cdot}$ 300. $C_6N_{12}O_4$. Calculated, %: C 23.68; N 55.26. *M* 304.

The IR spectra were recorded on a UR-20 instrument from samples prepared as thin films on NaCl support. The UV spectra of aqueous solutions were measured on a Perkin–Elmer 402 spectrophotometer. The ^{1}H NMR spectra of solutions in DMSO-d_6 were obtained on a Perkin–Elmer R12 instrument at 60 MHz using HMDS as internal reference, and the ^{13}C NMR spectra were taken on a Bruker AC-300 spectrometer (75.5 MHz) using the solvent signal as reference. The mass spectra (70 eV) were run on a Varian CH-6 mass spectrometer.

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