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SHORT COMMUNICATIONS

2-Methyl-1,2,3-triazol-4-yl(3-phenyl-1,2,4-oxadiazol-5-yl)-dinitromethane in the Reaction with Unsymmetrical Hydrazines

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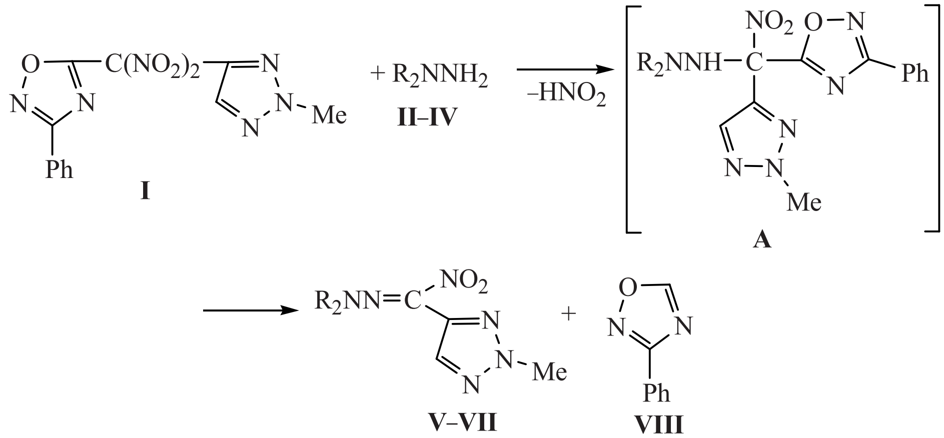
A reaction of unsymmetrical hydrazines with 5-nitromethyl-3-phenyl-1,2,4-oxadiazole gave in a good yield nitro-1,2,4-oxadiazole-5-carbaldehyde hydrazones [1]. In extension of these investigations and aiming at the study of the competing influence of azaheterocycles in the analog of 5-dinitromethyl-1,2,4-oxadiazole, 2-methyl-1,2,3-triazol-4-yl(3-phenyl-1,2,4-oxadiazol-5-yl)-dinitromethane (**I**) we examined its reactions with 1,1-diphenyl- (**II**), 1,1-dibenzyl- (**III**), and 1,1-dimethylhydrazines (**IV**) (see Scheme).

The reactions occurred under mild conditions and resulted in expected nitro-1,2,3-triazol-4-ylcarbaldehyde hydrazones **V–VII** and 3-phenyl-1,2,4-oxadiazole (**VIII**). The reaction presumably proceeded similarly to that of polynitromethanes with unsymmetrical hydrazines [2]. Apparently the nucleophilic attack of the hydrazine component on the carbon atom of the dinitromethyl group of compound **I** led to the formation of intermediate **A**. The latter evidently stabilized into less sterically loaded nitrohydrazones by the elimination of the oxadiazole ring. The retention in the nitrohydrazones of the triazole ring is probably due to its stronger bond with the dinitromethyl group (bond length 1.44 Å) [3] compared to that of the oxadiazole ring with the dinitromethyl group (bond length 1.50 Å) [4]. The mixed probes of the obtained compounds **V** and **VIII** with authentic samples melted without a depression of the melting point. The structure of compounds **VI** and **VII** was established with the use of IR, ^{1}H NMR, and electronic spectra. Their IR spectra contain strong absorption bands of the conjugated nitro group at 1550–1555 and 1290 cm^{-1}, and also of the C=N bond at 1645–1650 cm^{-1}. In the ^{1}H NMR spectra singlets from

Scheme.



R = Ph (**II, V**), PhCH$_2$ (**III, VI**), Me (**IV, VII**).

the groups CH_2 (4.17) and CH_3 (2.90 ppm) were observed. Electron absorption spectra were distinguished by the presence of two definite absorption bands with the maxima at 235 nm (local excitation of π-electrons) and 372–375 nm (intramolecular charge transfer to the nitro group) characteristic of conjugated nitroalkenes. The triazole-containing nitrohydrazones, stable substances, may be interesting as synthons for the study of cycloaddition with various 1,3-dipoles, and also serve as initial compounds in the synthesis of amidrazones.

Compound **I** was obtained by procedure [5], compounds **II–IV**, by treatment of the hydrazines hydrochlorides with alkali solution followed by extraction into ethyl ether.

To a solution of 5 mmol of compound **I** in 15 ml of anhydrous ethyl ether at 0 ± 5°C was added 5 mmol of compound **II–IV** in 50 ml of ether. The reaction mixture was kept for 2 h at 25°C, evaporated, the residue was subjected to descending chromatography on a glass column (250×10 mm) packed with activated Silicagel 100/400μ using Trappe set of eluents. Eluent for compounds **V–VII** was benzene, for compound **VIII**, ethyl ether.

1-(2-Methyl-1,2,3-triazol-4-yl)-1-nitro-3,3-diphenyl-2,3-diazaprop-1-ene (V). Yield 38%, mp 122–123°C (from ethanol) [3].

3,3-Dibenzyl-1-(2-methyl-1,2,3-triazol-4-yl)-1-nitro-2,3-diazaprop-1-ene (VI). Yield 42%, mp 110–112°C (from ethanol). IR spectrum, ν, cm^{-1}: 1555, 1290 (NO_2), 1650 (C=N). UV spectrum, λ_{max}, nm (log ε): 235 (l4.12), 372 (4.01). ^{1}H NMR spectrum, δ, ppm: 7.28 s (CH), 7.10–7.15 m (Ph), 4.17 s (CH_2), 3.77 s (CH_3). Found, %: C 61.58; H 5.03; N 23.78. $C_{18}H_{18}N_6O_2$. Calculated, %: C 61.71; H 5.14; N 24.00.

3-Methyl-1-(2-methyl-1,2,3-triazol-4-yl)-1-nitro-2,3-diazabut-1-ene (VII). Yield 43%, mp 78–80°C (from ethanol). IR spectrum, ν, cm^{-1}: 1550, 1290 (NO_2), 1645 (C=N). UV spectrum, λ_{max}, nm (log ε): 235 (4.06), 375 (4.07). ^{1}H NMR spectrum, δ, ppm: 7.26 s (CH), 3.73 s (CH_3), 2.90 s (CH_3). Found, %: C 36.21; H 4.92; N 42.27. $C_6H_{10}N_6O_2$. Calculated, %: C 36.36; H 5.05; N 42.42.

3-Phenyl-1,2,4-oxadiazole (VIII). Yield 21%, mp 15°C [6].

IR spectra were recorded on a spectrophotometer IKS -29 from solutions in chloroform of concentration 40 mg/ml. ^{1}H NMR spectra were registered on a spectrometer Tesla BS-487C (80 MHz) in acetone-d_6, internal reference HMDS. Electron absorption spectra were taken on a spectrophotometer SF-8 from solutions in ethanol of concentration 0.4 mg/ml. The homogeneity of compounds obtained was checked and the the reaction progress was monitored by ascending TLC on Silufol UV-254 plates in the system acetone–hexane, 2:3, development in iodine vapor.

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