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SHORT COMMUNICATIONS

Reaction of 2,2-Dinitro-2-(3-phenyl-1,2,4-oxadiazol-5-yl)-acetonitrile with Diazomethane and Diazoethane

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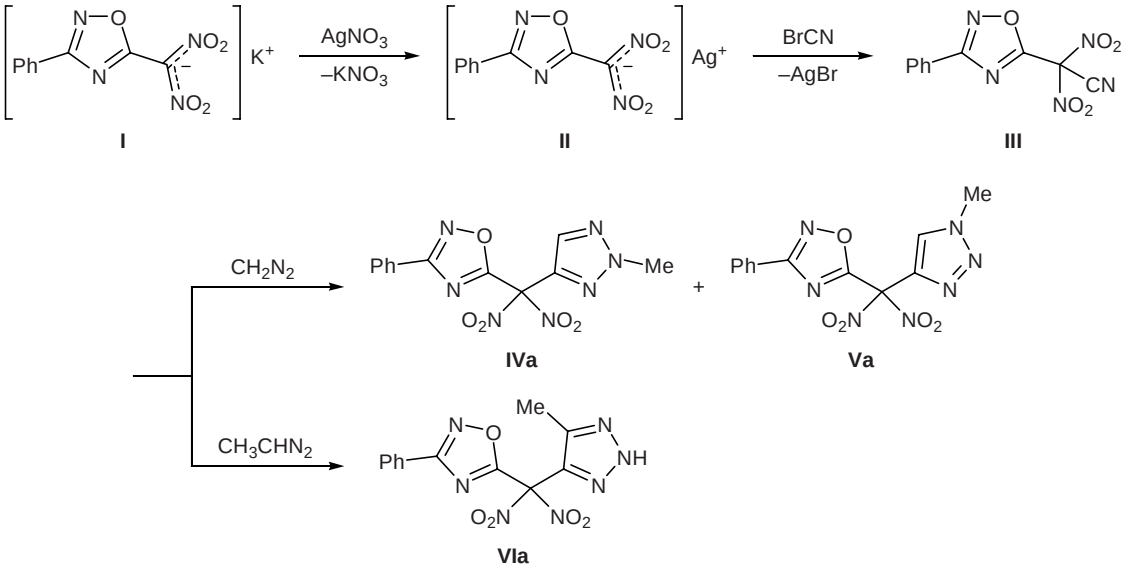
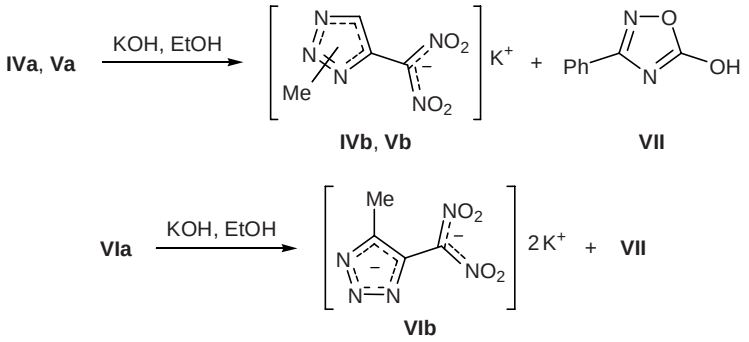
It is known that chloro(dinitro)acetonitrile and trinitroacetonitrile react with diazomethane to give 3-cyanodihydroisoxazole *N*-oxide [1] or *N*-methyl-4-trinitromethyl-1,2,3-triazoles [2]. With the goal of studying how the structure of substituted dinitroacetonitrile affects the direction of their transformations in reactions with diazoalkanes, we examined reactions of 2,2-dinitro-2-(3-phenyl-1,2,4-oxadiazol-5-yl)acetonitrile (**III**) with diazomethane and diazoethane. We found that, like trinitroacetonitrile, the behavior of compound **III** is determined by dipolarophilic activity of the cyano group. The reaction of nitrile **III** with diazomethane followed the 1,3-dipolar cycloaddition pattern to give a mixture of isomeric *N*-methyl-1,2,3-triazol-4-yl(3-phenyl-1,2,4-oxadiazol-5-yl)dinitromethanes **IVa** and **Va** which were separated by column chromatography. In the reaction of **III** with diazoethane, the process stopped at the 1,3-dipolar cycloaddition stage, and the product was dinitromethane **VIa** (Scheme 1).

The structure of compounds **III** and **IVa**–**VIa** was unambiguously confirmed by their IR and ^{1}H NMR spectra, as well as by the transformations of **IVa**–**VIa** under the action of alcoholic potassium hydroxide (Scheme 2). These reactions were accompanied by elimination of the 1,2,4-oxadiazole heteroring, leading to the formation of isomeric *N*-methyl-4-dinitromethyl-1,2,3-triazole potassium salts **IVb** and **Vb** (from **IVa** and **Va**) and 4-dinitromethyl-5-methyl-1,2,3-triazole dipotassium salt (**VIb**; from **VIa**). In addition, 3-phenyl-1,2,4-oxadiazol-5-ol (**VII**) was isolated. Compounds **IVb**–**VIb** and **VII** were reported previously.

Scheme 1.



Scheme 2.



Dinitroacetonitrile **III** was synthesized from 5-dinitromethyl-3-phenyl-1,2,4-oxadiazole potassium salt (**I**) [3] as shown in Scheme 1, and diazomethane and diazoethane were prepared as described in [4, 5].

5-Dinitromethyl-3-phenyl-1,2,4-oxadiazole silver salt (II). A solution of 15 mmol of $AgNO_3$ in a minimal volume of water was added to 10 mmol of potassium salt **I** in 10 ml of water, heated to 40°C. The mixture was cooled to 0°C, and the precipitate was filtered off, washed with water, and dried in air. Yield 80%, decomposition point 156°C. Found, %: N 15.56. $C_9H_5AgN_4O_5$. Calculated, %: N 15.69.

2,2-Dinitro-2-(3-phenyl-1,2,4-oxadiazol-5-yl)-acetonitrile (III). A thick-walled glass ampule was charged with a mixture of 5 mmol of salt **II** and 6 mmol of cyanogen bromide. The ampule was sealed, placed into an explosion-safe box, and heated for 20 h at 80°C. After cooling, the ampule was opened, the mixture was extracted with acetone (2×10 ml), the extract was evaporated, and the residue was subjected to chromatography in a 500×10-mm column filled with activated silica gel (Silicagel, 100–400 μm) using benzene as eluent. Yield 68%, mp 52°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 2250 (CN); 1600, 1290 (NO_2). ^1H NMR spectrum, δ, ppm: 7.76 m (5H, H_{arom}). Found, %: C 43.52; H 1.68; N 25.30. $C_{10}H_5N_5O_5$. Calculated, %: C 43.64; H 1.82; N 25.45.

Dinitro(3-phenyl-1,2,4-oxadiazol-5-yl)(1,2,3-triazol-4-yl)methanes IVa–VIa. A solution of excess diazomethane or diazoethane in diethyl ether was added in portions to a mixture of 7 mmol of compound **III** and 20 ml of anhydrous diethyl ether, cooled to 0°C, until nitrogen no longer evolved. The mixture was kept for 24 h at 25°C and evaporated, and the residue was subjected to column chromatography on silica gel using benzene (**IVa**, **VIa**) or diethyl ether (**V**) as eluent.

2-Methyl-2*H*-1,2,3-triazol-4-yl(dinitro)(3-phenyl-1,2,4-oxadiazol-5-yl)methane (IVa). Yield 46%, n_D^{20} = 1.4815. IR spectrum $CHCl_3$), ν, cm^{-1}: 1580, 1300 (NO_2). ^1H NMR spectrum, δ, ppm: 8.13 s (1H, CH), 7.75 m (5H, H_{arom}), 4.22 s (3H, CH_3). Found, %: C 43.42; H 2.67; N 29.48. $C_{12}H_9N_7O_5$. Calculated, %: C 43.50; H 2.72; N 29.61.

1-Methyl-1*H*-1,2,3-triazol-4-yl(dinitro)(3-phenyl-1,2,4-oxadiazol-5-yl)methane (Va). Yield 24%, mp 96°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1580, 1300 (NO_2). ^1H NMR spectrum, δ, ppm: 8.20 s (1H, CH), 7.73 m (5H, H_{arom}), 4.11 s (3H, CH_3). Found, %: C 43.44; H 2.63; N 29.52. $C_{12}H_9N_7O_5$. Calculated, %: C 43.50; H 2.72; N 29.61.

5-Methyl-2*H*-1,2,3-triazol-4-yl(dinitro)(3-phenyl-1,2,4-oxadiazol-5-yl)methane (VIa). Yield 63%, n_D^{20} = 1.4795. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1580, 1300 (NO_2). ^1H NMR spectrum, δ, ppm: 9.41 br.s (1H, NH), 7.76 m (5H, H_{arom}), 2.34 s (3H, CH_3). Found, %: C 43.40; H 2.69; N 29.50. $C_{12}H_9N_7O_5$. Calculated, %: C 43.50; H 2.72; N 29.61.

4-Dinitromethyl-*N*-methyl-1,2,3-triazole potassium salts IVb and Vb and 3-phenyl-1,2,4-oxadiazol-5-ol (VII). A saturated solution of potassium hydroxide in ethanol was added dropwise under stirring at 0°C to a solution of 5 mmol of isomer mixture **IVa**/**Va** in 10 ml of ethanol until the corresponding potassium salts no longer separated. The precipitate was filtered off and recrystallized from ethanol. The filtrate was evaporated, and the residue was subjected to column chromatography on silica gel using diethyl ether as eluent to isolate 23% of compound **VII**, mp 202°C [6].

4-Dinitromethyl-2-methyl-1,2,3-triazole potassium salt (IVb). Yield 72%, decomp. point 198°C [2].

4-Dinitromethyl-1-methyl-1,2,3-triazole potassium salt (Vb). Yield 78%, decomp. point 182°C [2].

4-Dinitromethyl-5-methyl-1,2,3-triazole dipotassium salt (VIb) and 3-phenyl-1,2,4-oxadiazol-5-ol

(VII). A solution of 5 mmol of compound **VIa** in 10 ml of ethanol was cooled to 0°C, a solution of potassium hydroxide in ethanol was added to pH 9, and the mixture was kept for 1 h at 0°C. The solvent was removed, and the residue was subjected to column chromatography on silica gel. Elution with diethyl ether gave compound **VII**, yield 20%, mp 202°C [6], and the subsequent elution with ethanol gave dipotassium salt **VIb**, yield 52%, decomp. point 205°C (from water) [7].

The IR spectra were recorded on an IKS-29 spectrometer from solutions in chloroform with a concentration of 40 mg/ml (cell path length 0.1 mm). The ^{1}H NMR spectra were measured on a Tesla BS-487C instrument at 80 MHz using acetone-d_6 as solvent and HMDS as internal reference. The purity of the isolated compounds was checked by TLC on Silufol UV-254 plates using acetone–hexane (2:3) as eluent; development with iodine vapor.

REFERENCES

1. Mel'nikov, V.V., Tselinskii, I.V., Mel'nikov, A.A., Terpigorev, A.N., and Trubitsin, A.E., *Zh. Org. Khim.*, 1984, vol. 20, p. 658.
2. Ladyzhnikova, T.D., Mel'nikov, A.N., Solov'ev, N.A., Tselinskii, I.V., and Altukhov, K.V., *Zh. Org. Khim.*, 1987, vol. 23, p. 2624.
3. Tyrkov, A.G., Pashchenko, K.P., Ladyzhnikova, T.D., and Altukhov, K.V., *Izv. Vyssh. Ucheb. Zaved., Ser. Khim. Khim. Tekhnol.*, 2004, vol. 47, p. 148.
4. *Obshchii praktikum po organicheskoi khimii* (General Practicum on Organic Chemistry), Kost, A.N., Ed., Moscow: Mir, 1965, p. 532.
5. James, A., Marshall, J., and Partridgel, J., *J. Org. Chem.*, 1968, vol. 33, p. 4090.
6. Adams, P., Kaiser, D.W., and Peters, G.A., *J. Org. Chem.*, 1953, vol. 18, p. 934.
7. Ladyzhnikova, T.D., Solov'ev, N.A., Altukhov, K.V., Perekalin, V.V., and Berkova, G.A., *Zh. Org. Khim.*, 1988, vol. 24, p. 644.