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SHORT COMMUNICATIONS

Synthesis of 3(5)-(Nitroamino)-1,2,4-triazol-5(3)-carboxylic Acid and Its Ethyl Ester

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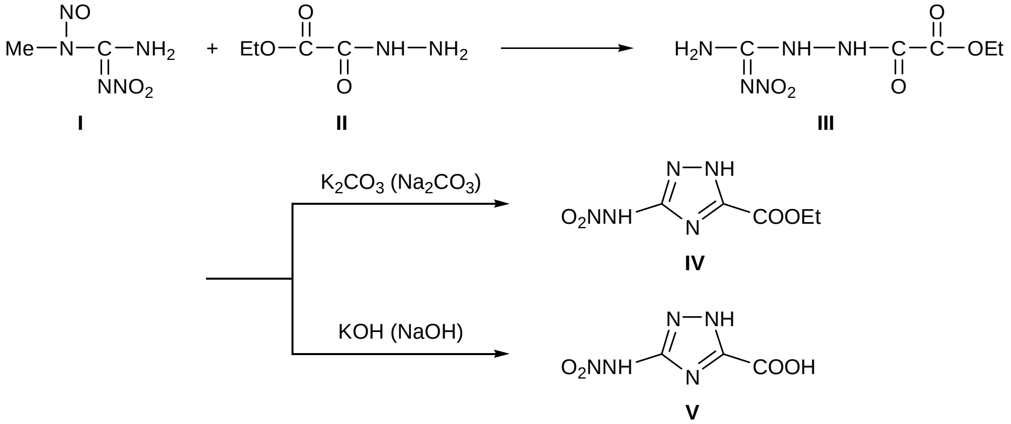
Increased interest in functionalized 1,2,4-triazoles originates from a wide spectrum of practically useful properties of these compounds. For example, 3-amino-1,2,4-triazole is an efficient herbicide [1]. Some amino-1,2,4-triazoles are used in the synthesis of antitumor agents [2], dyes, and explosives [3, 4]. Triazolecarboxylic acids and their esters are intermediate products in the preparation of drugs [5–9]. *N*-Vinyltriazoles are known as valuable monomers for building up polymeric compounds which are promising for technics and medicine [10, 11]. Much attention is also given to search for high-energy compounds in the series of substituted 1,2,4-triazoles [4, 12–14].

We have developed a convenient preparative procedure for the synthesis of new substituted 1,2,4-triazoles, namely 3(5)-(nitroamino)-1,2,4-triazole-5(3)-carboxylic acid and its ethyl ester. The procedure is based on intramolecular cyclization of polynitrogen compound **III** which is obtained by condensation of 1-methyl-2-nitro-1-nitrosoguanidine (**I**) with ethyl (hydrazino)(oxo)acetate (**II**) on heating in water at 80–90°C. Heating of compound **III** in a boiling aqueous solution of alkali metal (potassium or sodium) carbonate leads to formation of ester **IV**, and analogous reaction with potassium or sodium hydroxide yields 3(5)-(nitroamino)-1,2,4-triazole-5(3)-carboxylic acid (**V**). Compounds **IV** and **V** are colorless crystalline substances which are very poorly soluble in organic solvents. Their structure was confirmed by the data of elemental analysis and IR and UV spectra. The UV spectrum of ester **IV** contains an absorption band at λ_{max} 285 nm (logε 4.10), which is typical of 1,2,4-triazoles [3]. In the IR spectrum of **IV** we observed absorption bands corresponding to all functional groups present in the molecule, ν, cm^{-1}: 3450 (NH); 1750 (C=O); 1430, 1310 (NO_2) [15] .

1-Methyl-2-nitro-1-nitrosoguanidine (**I**) was synthesized by the procedure reported in [16], and ethyl hydrazino(oxo)acetate (**II**), as described in [17, 18].

Ethyl {2-[amino(nitroimino)methyl]hydrazino}-(oxo)acetate (III). 1-Methyl-2-nitro-1-nitrosoguanidine, 4.41 g (0.03 mol), was added to a solution of 3.96 g (0.03 mol) of ethyl hydrazino(oxo)acetate (**II**) in water, and the mixture was heated for 1 h at the



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boiling point. During the reaction, the solid dissolved, and vigorous gas evolution was observed. The solution was slowly cooled, and the precipitate was filtered off. Yield 8.7 g (quantitative), mp 170–171°C (from aqueous methanol). IR spectrum, ν, cm^{-1}: 1750, 1720. ^1H NMR spectrum, δ, ppm: 11.04 s (NHC=O), 9.95 s (CNH), 8.74 br.s (NH_2), 4.53 q (OCH_2), 1.52 t (CH_3). Found, %: C 27.44, 27.47; H 4.29, 4.31; N 31.94, 31.92. $C_5H_9N_5O_5$. Calculated, %: C 27.40; H 4.11; N 31.96.

Ethyl 3(5)-(nitroamino)-1,2,4-triazole-5(3)-carboxylate (IV). A mixture of 0.219 g (0.001 mol) of compound **III** and 0.001 mol of alkali metal carbonate in 25 ml of water was heated for 20–30 min at the boiling point (until the originally dark yellow solution turned light yellow). The solution was cooled and acidified with concentrated hydrochloric acid to pH 2–3. After 1 h, the colorless precipitate was filtered off and washed with water. Yield 0.16 g (78%), mp 158–160°C. UV spectrum: λ_{max} 285 nm (logε 4.10). IR spectrum, ν, cm^{-1}: 3450, 1750, 1430, 1310. Found, %: C 29.94, 29.97; H 3.62, 3.65; N 34.97, 34.96. $C_5H_7N_5O_4$. Calculated, %: C 29.85; H 3.48; N 34.83

3(5)-(Nitroamino)-1,2,4-triazole-5(3)-carboxylate (V). A mixture of 0.219 g (0.001 mol) of compound **III** and 0.002 mol of alkali metal hydroxide in 25 ml of water was heated for 15–20 min at the boiling point. During the reaction, the solution became colorless. It was cooled, acidified with concentrated hydrochloric acid to pH 2–3, and was left to stand for 1 h. The colorless precipitate was filtered off and washed with water, ethanol, and diethyl ether. Yield 0.12 g (72%), mp 192–193°C. UV spectrum: λ_{max} 285 nm (logε 4.09). IR spectrum, ν, cm^{-1}: 3600, 3430, 1650, 1440, 1310. Found, %: C 20.98, 20.96; H 2.25, 2.24; N 40.43, 40.45. $C_3H_3N_5O_4$. Calculated, %: C 20.81; H 1.73; N 40.46.

The IR spectra were recorded on an InfraLyum-FT-02 instrument from samples dispersed in mineral oil. The ^1H NMR spectra were obtained on a Bruker AC-200 spectrometer (200 MHz) in DMSO-d_6. The chemical shifts were measured relative to TMS. The UV spectra were recorded from aqueous solutions using an SF-16 spectrophotometer.

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