

## 2-Nitroguanidine Derivatives: VII.\* Reaction of 2-Nitroguanidine with Dicarboxylic Acid Dihydrazides

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**Abstract**—2-Nitroguanidine reacts with dicarboxylic acid dihydrazides to form intermediate condensation product which undergoes intramolecular cyclization, yielding the corresponding bis(3-nitroamino-1,2,4-triazol-5-yl)alkanes and 5,5'-bi(3-nitroamino-1,2,4-triazole) potassium salt. The structure of the products was confirmed by comparing their electron absorption spectra with those of 3,5-bis(nitroamino)-1,2,4-triazole salts.

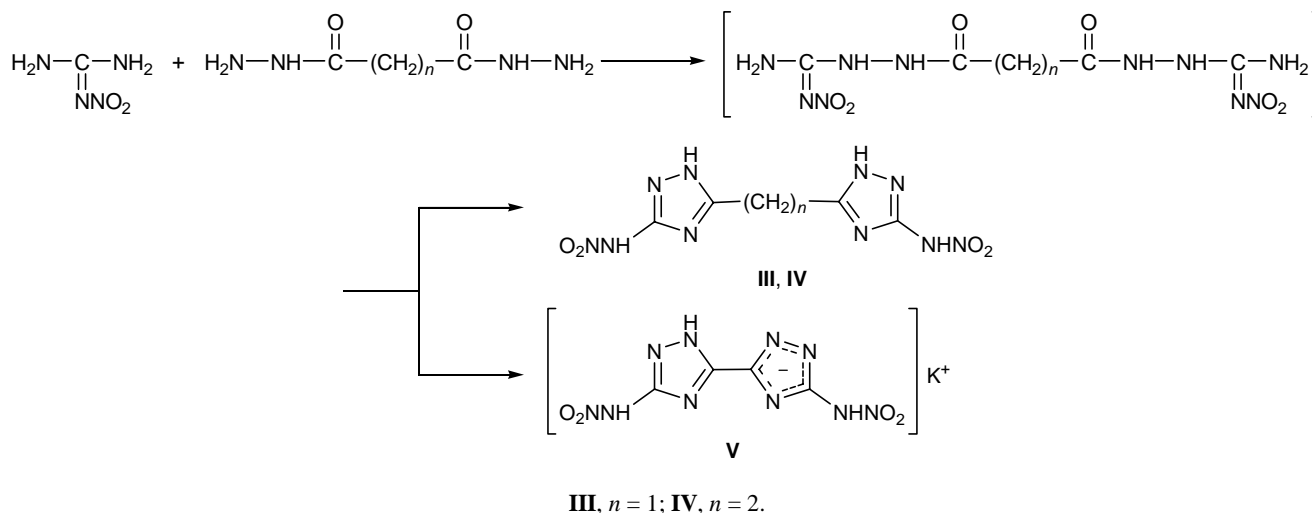
We previously developed an efficient procedure for the synthesis of 5(3)-methyl(phenyl)-3(5)-nitroamino-1,2,4-triazoles **I** and **II** from 2-nitroguanidine and acetic and benzoic acid hydrazides in the presence of bases [2]. It was reasonable to presume that the use of dicarboxylic acid dihydrazides as nucleophiles in reaction with 2-nitroguanidine should give rise to the corresponding nitroamino-substituted bis-triazoles.

In fact, 2-nitroguanidine reacted with dihydrazides derived from malonic and succinic acids in the presence of an equimolar amount of potassium hydroxide at 76–78°C in a way similar to the reaction with monocarboxylic acid hydrazides, but the reaction took 5 h.

Acidification of the reaction mixture afforded colorless crystalline compounds **III** and **IV** in 18–20% yield (Scheme 1). On the basis of the spectral parameters of the products, they were assigned the structure of the corresponding bis(3-nitroamino-1,2,4-triazol-5-yl)-alkanes. Raising the reaction temperature to 85–90°C led to decrease in the yield of compounds **III** and **IV** by a factor of 2.5–3.

Unlike malonic and succinic acid dihydrazides, the reaction of oxalodihydrazide with 2-nitroguanidine in the presence of both equimolar amount and 1.5 equiv of potassium hydroxide occurred under more severe conditions and afforded 5,5'-bi(3-nitroamino-1,2,4-tri-

Scheme 1.



\* For communication VI, see [1].

azole) potassium salt (**V**). The spectral parameters of compound **V** considerably differed from those of bis-triazoles **I–IV**. The main absorption band in the electron spectrum of **V** was displaced to the red region by 13 nm, indicating ionic structure of the product. Analogous spectral patterns were observed for salts derived from 3,5-bis(nitroamino)-1,2,4-triazole [3] and for 5,5'-bi(3-nitroamino-1,2,4-triazole) monopotassium salt (**V**) obtained by cyclization of  $N_\beta, N'_\beta$ -bis( $N^2$ -nitroamidino)oxalodihydrazide which was prepared in turn from 1-methyl-2-nitro-1-nitrosoguanidine and oxalodihydrazide [1]. Presumably, the reaction of 2-nitroguanidine with dicarboxylic acid dihydrazides, as well as with monocarboxylic acid hydrazides [2], involves intermediate formation of linear condensation products which undergo intramolecular cyclization to bis-triazoles **III–V** (Scheme 1).

We examined the electron absorption spectra of compound **V** in 40% sulfuric acid and aqueous buffer solutions in the pH range from 1 to 13 with a view to trace the dynamics of changes in the electronic structure upon ionization (see figure). In the UV spectrum of **V** in 40% sulfuric acid, we observed an absorption band with its maximum at  $\lambda_{\max}$  298 nm ( $\log \epsilon$  4.19). An analogous pattern is typical of 5(3)-phenyl-3(5)-nitroamino-1,2,4-triazole (**II**) ( $\lambda_{\max}$  298 nm,  $\log \epsilon$  4.19). These data suggest, on the one hand, that the spectrum belongs to the neutral form of 5,5'-bi(3-nitroamino-1,2,4-triazole) and, on the other, that the nitroamino-triazole fragments therein are not coplanar, as in substituted biphenyls [4]. Increase in the absorption intensity in going to the corresponding monoanion and insignificant red shift from 298 to 303 nm result from formation of more conjugated structure due to deprotonation of the triazole ring.

Raising the pH value in the range from 8 to 10 only slightly affects the absorption pattern, presumably due to formation of dianion via proton abstraction from the second triazole ring. However, at pH 11.5, the intensity of the main absorption band appreciably decreased, and a new short-wave band appeared as a shoulder on the high-energy flank of the long-wave band ( $\lambda$  240–250 nm). Analogous variations in the short-wave region of the electron absorption spectrum were observed for 3,5-bis(nitroamino)-1,2,4-triazole dianion [3] and 5(3)-methyl(phenyl)-3(5)-nitroamino-1,2,4-triazoles **I** and **II**; therefore, the new band can be attributed to absorption of one ionized nitroamino group. In going to more alkaline solutions (pH 12.5–13.5), the intensity of the main charge-transfer band

UV spectra of mono- and bis-triazoles **I–III**, **V**, and **VI**,  $\lambda_{\max}$ , nm ( $\log \epsilon$ )

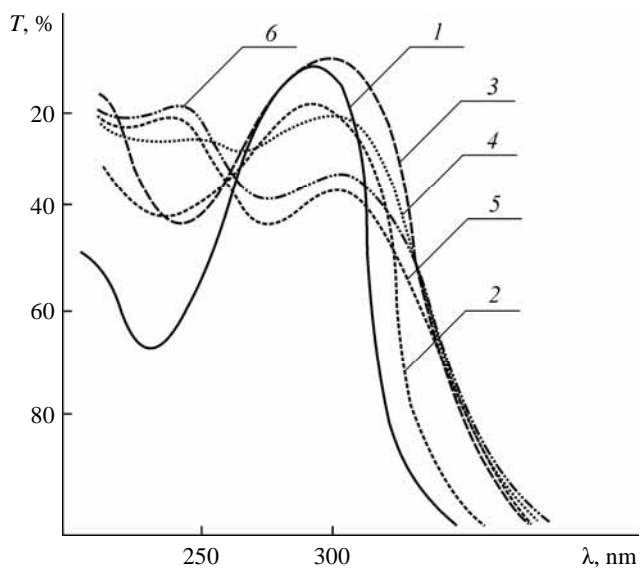
Comp. no.	NM <sup>a</sup> (H <sub>2</sub> O)	A <sup>–</sup> (H <sub>2</sub> O)	pH 13
<b>I</b>	291 (4.11)		230 sh (3.64), 298 (3.69)
<b>II</b>	298 (4.19)		265 (4.14), 307 sh
<b>III</b>	290 (4.34)		235 sh (3.89), 295 (3.94)
<b>V</b>	298 <sup>b</sup> (4.19)	303 (4.32)	243 (4.12), 305 sh
<b>VI</b>	290 <sup>b</sup>	318 (4.21)	235, 305

<sup>a</sup> NM stands for neutral molecule.

<sup>b</sup> In 40% sulfuric acid.

( $\lambda_{\max}$  305 nm) further decreases, while the short-wave shoulder develops into a separate band with its maximum at  $\lambda$  243 nm. These data indicate increase in the number of  $\pi$ – $\pi^*$  transitions in the ionized nitroamino fragments and weakening of conjugation as compared to the mono- and dianion. This conclusion is consistent with the spectral data for compounds **I–III** at the same pH values (see table).

Thus comparison of the electron absorption spectra of compounds **I–III** and **V** shows that the product obtained from 2-nitroguanidine and oxalodihydrazide has a salt-like structure. The low yields of compounds **III–V** may be due to reduced nucleophilicity of dicarboxylic acid dihydrazides and partial decomposition of 2-nitroguanidine on prolonged heating in strongly alkaline medium.



UV spectra of aqueous solutions of 5,5'-bi(3-nitroamino-1,2,4-triazole) monopotassium salt (**V**) with different acidities: (1) 40% H<sub>2</sub>SO<sub>4</sub>, (2) pH 7.0, (3) pH 10.08, (4) pH 11.5, (5) pH 12.5, (6) pH 13.5.

## EXPERIMENTAL

The electron absorption spectra were measured on an SF-9 spectrophotometer equipped with an automatic recorder. The  $^1\text{H}$  NMR spectra were obtained on a Tesla BS-487C spectrometer (80 MHz) using  $\text{DMSO}-d_6$  as solvent and HMDS as external reference.

**Bis(3-nitroamino-1,2,4-triazole)methane (III).** To a solution of 1.32 g (0.01 mol) of malonic acid dihydrazide and 1.12 g (0.02 mol) of potassium hydroxide in 30 ml of water we added at 40°C 2.08 g (0.02 mol) of 2-nitroguanidine and 5 ml of water. The mixture was stirred for 5 h at 76–78°C on a water bath, cooled to 50°C, and acidified with nitric acid to pH 3–2.5. After 24 h, the precipitate was filtered off, washed with cold water, recrystallized from water, and dried at 50–55°C. Yield 0.51 g (20%), decomposes at 198°C. UV spectrum:  $\lambda_{\text{max}}$  290 nm ( $\log \epsilon$  4.32).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 4.25 s ( $\text{CH}_2$ ), 6.18 s (NH). Found, %: N 51.23.  $\text{C}_5\text{H}_6\text{N}_{10}\text{O}_4$ . Calculated, %: N 51.66.

**1,2-Bis(3-nitroamino-1,2,4-triazol-5-yl)ethane (IV)** was synthesized in a similar way using a solution of 0.73 g (0.005 mol) of succinic acid dihydrazide, 0.56 g (0.01 mol) of potassium hydroxide, and 1.04 g (0.01 mol) of 2-nitroguanidine in 20 ml of water. Yield 0.25 g (19%), decomposes at 232°C (from water). UV spectrum:  $\lambda_{\text{max}}$  290 nm ( $\log \epsilon$  4.34).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 4.34 s ( $\text{CH}_2$ ), 6.12 s (NH). Found, %: N 49.32.  $\text{C}_6\text{H}_8\text{N}_{10}\text{O}_4$ . Calculated, %: N 49.12.

**5,5'-Bi(3-nitroamino-1,2,4-triazole) potassium salt (V).** To a solution of 1.2 g (0.01 mol) of oxalic

acid dihydrazide and 1.7 g (0.03 mol) of potassium hydroxide in 30 ml of water we added at 40–45°C 2.08 g (0.02 mol) of 2-nitroguanidine. The mixture was stirred for 5 h at 85°C on a water bath, cooled to 50°C, acidified with nitric or hydrochloric acid to pH 2, and left overnight. The precipitate was filtered off and washed with water, 0.74 g (0.015 mol) of potassium hydroxide in 50 ml of water was added to the solution, and the mixture was heated for 1 h under reflux, cooled to 50°C, and acidified with nitric acid to pH 3–2.5. The precipitate was filtered off, washed with water, and dried at 80–85°C. Yield 0.76 g (25%), decomposes at 234°C (from water). UV spectrum:  $\lambda_{\text{max}}$  298 nm ( $\log \epsilon$  4.13).  $^1\text{H}$  NMR spectrum:  $\delta$  7.46 ppm, s (NH). Found, %: N 47.84.  $\text{C}_4\text{H}_3\text{KN}_{10}\text{O}_4$ . Calculated, %: N 47.62.

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