

SHORT
COMMUNICATIONS

Dedicated to Full Member of the Russian Academy of Sciences
V.A. Tartakovskii on the 70th Anniversary of His Birth

2-Nitroguanidine Derivatives. Synthesis and Structure of 1-(2,2,2-Trinitroethylamino)- and 1-(2,2-Dinitroethylamino)-2-nitroguanidines

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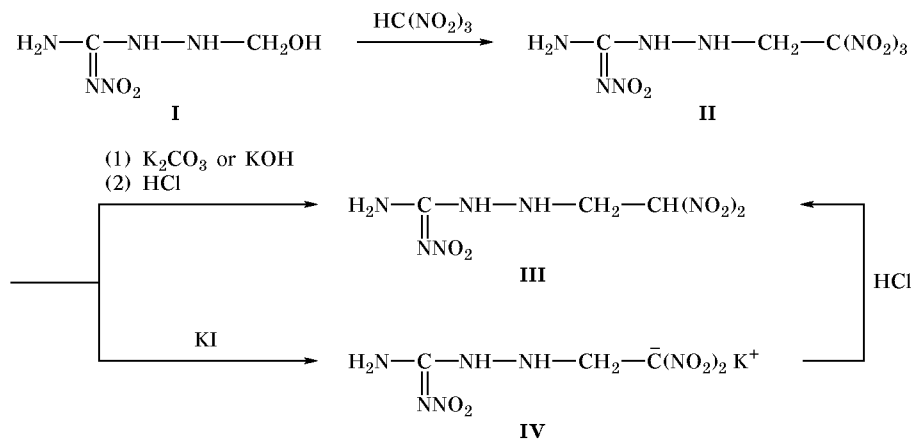
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We previously showed that in polar solvents 1-hydroxymethylamino-2-nitroguanidine (**I**) is converted into a hydrazone, 1-methyleneamino-2-nitroguanidine [1]. Taking into account that trinitromethane is known to readily add at the C=N bond of substituted formaldehyde phenylhydrazones [2], we expected a higher reactivity of compound **I** toward trinitromethane, as compared to 1-hydroxymethyl-2-nitroguanidine [3]. We have found that 1-hydroxymethylamino-2-nitroguanidine (**I**) reacts with trinitromethane at room temperature in methanol, ethanol, and water, yielding 2-nitro-1-(2,2,2-trinitroethylamino)guanidine (**II**) (Scheme 1). Compound **II** was converted into 1-(2,2-dinitroethylamino)-2-nitroguanidine (**III**) by reduction with iodide ion, which is typical of trinitromethyl derivatives [4]. With the use of potassium hydroxide or potassium carbonate as denitrating agents, followed by acidification with

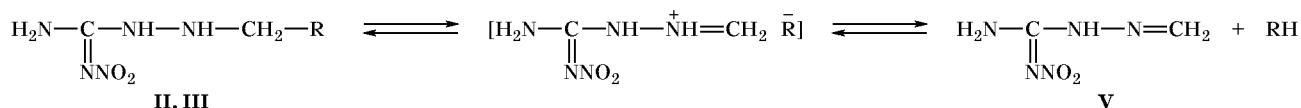
hydrochloric acid, we succeeded in eliminating the stage of isolation of potassium salt **IV** and raising the yield of CH acid **III** from 44 to 78%.

The structure of compounds **II** and **III** was confirmed by elemental analysis and IR and ¹H NMR spectroscopy. The presence of an additional nitro group in molecule **II** only slightly affects the general IR absorption pattern. Moreover, assignment of bands in the IR spectra of **II** and **III** is complicated by overlap of the regions corresponding to stretching vibrations of di- and trinitromethyl groups and asymmetric vibrations of the N–C(=N)–N group and $\nu_s(\text{NO}_2)$ of 1-amino-2-nitroguanidine. Vibrations of the C(NO₂)₃ and CH(NO₂)₂ groups give rise to increased intensity of bands in the regions 1600–1615 cm⁻¹ (**II**) and 1560–1570 cm⁻¹ (**III**) and appearance of a strong absorption band at 800–806 cm⁻¹ [5, 6]. The high-frequency region contains a broad

Scheme 1.



Scheme 2.



II, R = C(NO₂)₃ (II), III, R = CH(NO₂)₂.

band at 2950–3020 cm⁻¹ (CH and CH₂) and also strong bands at 3465 (II, III), 3350 (II, III), 3315 (III), and 3270 cm⁻¹ (II) and a broad band at 3115–3210 cm⁻¹, which are typical of NH and NH₂ groups.

According to the ¹H NMR spectra, Mannich bases II and III in DMSO-*d*₆ exist as equilibrium mixtures with hydrazone V (Scheme 2). The state of the equilibrium depends on the solvent polarity. It shifts toward 1-methyleneamino-2-nitroguanidine (V) as the solvent polarity decreases: in going from DMSO-*d*₆ to acetonitrile-*d*₃, the intensity ratio of signals corresponding to compounds II (III) and V changes from 1:1 to 1:5.

¹H NMR spectrum of II, δ, ppm: DMSO-*d*₆: 4.5–6.3 br.d (6H, II); 6.64 and 7.12 (2H, =CH₂, V); 8.41 and 8.64 (2H, NH₂, V); 11.65 (1H, NH, V); CD₃CN: 4.71 (2H, II); 5.42 (1H, NHCH₂, II); 6.72 and 7.21 (2H, =CH₂, V); 7.21–8.26 br.d (4H, NH₂, II and V); 8.78 (1H, NHC=NNO₂, II); 10.15 (1H, NH, V).

¹H NMR spectrum of III, δ, ppm: DMSO-*d*₆: 5.20–7.00 br.d (7H, III); 6.66 and 7.13 (2H, =CH₂, V); 8.40 and 8.70 (2H, NH₂, V); 11.65 (1H, NH, V); CD₃CN: 4.65 (2H, III); 5.35 (1H, NHCH₂, III); 6.72 and 7.20 (2H, =CH₂, V); 6.00–8.50 br.d [5H, CH(NO₂)₂, NH₂, III and V]; 8.71 (1H, NHC=NNO₂), III], 10.12 (1H, NH, V).

2-Nitro-1-(2,2,2-trinitroethylamino)guanidine (II). Trinitromethane, 0.36 g (2.4 mmol), was added to a suspension of 0.3 g (0.002 mol) of compound I [1] in 10 ml of water, the mixture was stirred for 8 h at room temperature, and the precipitate was filtered off, washed with cold water, and dried in air. Yield 0.54 g (95%). mp 95–96°C (from ethanol). Found, %: C 12.98, 12.96; H 2.47, 2.44; N 39.89, 39.85. C₃H₆N₈O₈. Calculated, %: C 12.77; H 2.13; N 39.72.

1-(2,2-Dinitroethylamino)-2-nitroguanidine (III).
a. A solution of 0.066 g (0.24 mmol) of potassium salt IV in 6 ml of water was adjusted to pH 1–2 by adding concentrated hydrochloric acid at 5–10°C under stirring. After 2 h, the precipitate was filtered off, washed with cold water, and dried in air. Yield 0.038 g (65%). mp 93–94°C. Found, %: C 15.09, 15.12; H 2.99, 2.97; N 41.34, 41.36. C₃H₇N₇O₆. Calculated, %: C 15.19; H 2.95; N 41.35.

b. A solution of 0.16 g (5 mmol) of potassium hydroxide in 4 ml of water was added with stirring at 5–10°C to a suspension of 0.4 g (1.4 mmol) of compound II in 5 ml of water. The mixture was kept for 2 h at 18–20°C and was acidified to pH 1–2 with concentrated hydrochloric acid. After 1 h, the precipitate was filtered off, washed with cold water, and dried in air. Yield 0.3 g (77%). mp 93–94°C.

c. A solution of 0.2 g (1.44 mmol) of potassium carbonate in 4 ml of water was added with stirring at 5–10°C to a suspension of 0.2 g (7 mmol) of compound II in 6 ml of water. The mixture was kept for 3 h at 18–20°C and was acidified to pH 1–2 with concentrated hydrochloric acid. After 2 h, the precipitate was filtered off, washed with water, and dried in air. Yield 0.152 g (78%). mp 94–94.5°C.

1-(2,2-Dinitroethylamino)-2-nitroguanidine potassium salt (IV). Potassium iodide, 0.103 g (0.62 mmol), was added with stirring to a solution of 0.13 g (0.37 mmol) of compound II in 4 ml of methanol. After 3 h, the precipitate was filtered off and washed with alcohol and ether. Yield 0.066 g (65%). mp 131–132°C. Found, %: N 35.81, 35.83. C₇H₆N₇O₆K. Calculated, %: N 35.63.

The IR spectra of samples pelleted with KBr were recorded on a UR-20 spectrometer, and the ¹H NMR spectra were measured on a Bruker spectrometer (200 MHz) using HMDS as external reference.

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