

SHORT
COMMUNICATIONS

3(5)-Nitroamino-1,2,4-triazole-5(3)-carbohydrazide: Synthesis and Reactions with Aromatic Aldehydes

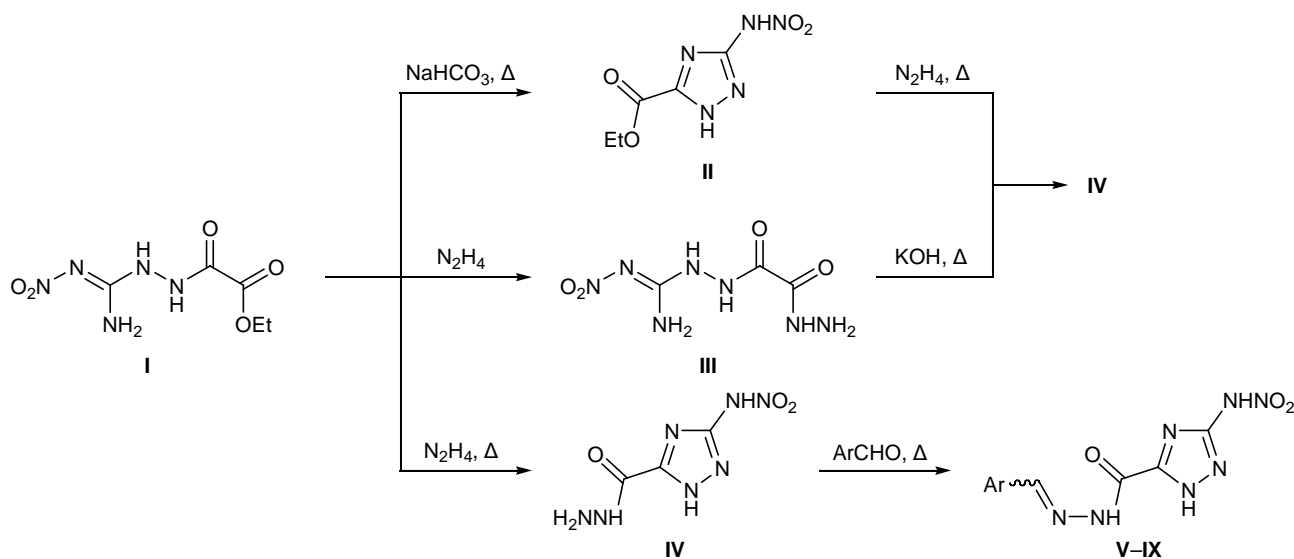
T. A. Novikova, E. L. Metelkina, T. P. Efimova, D. V. Zaskokina, and V. M. Berestovitskaya

Hertzen Russian State Pedagogical University, nab. r. Moiki 48, St. Petersburg, 191186 Russia
e-mail: kohrgpu@yandex.ru

Received March 24, 2005

Triazolecarboxylic acids and their derivatives attract interest as promising starting compounds for the synthesis of energy-rich substances [1–5] and medical agents [6]. We have synthesized a new representative of this series, 3(5)-nitroamino-1,2,4-triazole-5(3)-carbohydrazide. The synthesis was performed in three ways: (1) reaction of previously described [7] hydrazide **I** with excess hydrazine hydrate on heating; (2) hydrazinolysis of known [7] nitroaminotriazolecarboxylate **II**, and (3) intramolecular heterocyclization of hydrazide **III** in alkaline medium. Here, compounds **II** and **III** are readily obtained from **I**. Hydrazide **IV** is a colorless high-melting crystalline substance. It reacted with aromatic aldehydes in the presence of a catalytic amount of acetic acid to give the corresponding hydrazones **V–IX**. The structure of compounds **IV–IX** was confirmed by the spectral data. The ¹H NMR spectrum of hydrazide **IV** contained broadened signals

from protons of the N₂N–NH group at δ 5.00 and 9.80 ppm, which are typical of many hydrazine derivatives [8]; signals from the HNNO₂ proton and NH proton in the heteroring appear as a rule in a very weak field [9, 10]. In the ¹H NMR spectra of hydrazones **V–IX**, protons of the =CH and HNCO groups resonated at δ 8.45–8.80 and 12.30–12.78 ppm, respectively. Hydrazones **V–IX** characteristically showed in the IR spectra absorption bands due to vibrations of the NH (3455–3360 and 3290–3200 cm⁻¹) and C=O groups (1690–1670 cm⁻¹); in addition, a number of strong bands belonging to stretching vibrations of the C=N and N–NO₂ groups and bending vibrations of the N–H group were present in the region 1610–1550 cm⁻¹ [10, 11]. In the electron spectra of hydrazones **V–IX** we observed long-wave absorption bands at λ_{max} 296–356 nm (log ε 4.17–4.46); the red shift relative to the corresponding band in the spectrum of initial com-



V, Ar = Ph; **VI**, Ar = 4-O₂NC₆H₄; **VII**, Ar = 4-Me₂NC₆H₄; **VIII**, Ar = 2-HOC₆H₄; **IX**, Ar = 3-MeO-4-HOC₆H₃.

pound **IV** (λ_{\max} 288 nm, $\log \epsilon$ 4.10) results from considerable extension of the conjugation chain.

Ethyl 2-{2-[amino(nitroimino)methyl]hydrazino}-2-oxoacetate (I), and ethyl 3(5)-nitroamino-1,2,4-triazole-5(3)carboxylate (II) were synthesized by the procedures reported in [7].

2-{2-[Amino(nitroimino)methyl]hydrazino}-2-oxoacetohydrazide (III). Hydrazine hydrate, 5 ml (0.1 mol), was added to a solution of 2.19 g (0.01 mol) of compound **I** in 30 ml of methanol. The mixture was kept for 4–4.5 h at room temperature, the precipitate was filtered off and dispersed in water, the aqueous suspension was acidified with concentrated hydrochloric acid, and the precipitate was filtered off. Yield 1.85 g (90%), decomposition point 193–194°C (from methanol). IR spectrum, ν , cm^{-1} : 3390, 3370 (N–H); 1710, 1670 (C=O); 1410, 1330 (NO_2). Found, %: C 17.89, 17.91; H 3.67, 3.69; N 47.98, 47.95. $\text{C}_3\text{H}_7\text{N}_7\text{O}_4$. Calculated, %: C 17.56; H 3.41; N 47.80.

3(5)-Nitroamino-1,2,4-triazole-5(3)-carbohydrazide (IV). *a.* A solution of 0.9 g (0.004 mol) of compound **II** and 0.9 ml (0.016 mol) of hydrazine hydrate in 10 ml of ethanol was heated for 1 h under reflux. The precipitate was filtered off and dispersed in water, and the aqueous suspension was acidified with concentrated hydrochloric acid to pH ~3. Yield 0.70 g (85%), colorless crystalline substance, mp >300°C. ^1H NMR spectrum, δ , ppm: 5.00 br.s (NH_2), 9.80 br.s (NHC=O). Found, %: C 19.52, 19.54; H 2.91, 2.94; N 52.54, 52.53. $\text{C}_3\text{H}_5\text{N}_7\text{O}_3$. Calculated, %: C 19.25; H 2.67; N 52.41.

b. A mixture of 2.19 g (0.01 mol) of compound **I** and 5 equiv of hydrazine hydrate was heated for 3–4 h at the boiling point. The mixture was cooled, acidified to pH 6–7, and the precipitate was filtered off. Yield 1.51 g (81%).

c. A mixture of 2.05 g (0.01 mol) of compound **III** and 0.1 N aqueous potassium hydroxide was heated at the boiling point until the original dark yellow color disappeared. The solution was cooled and acidified to pH 6–7, and the precipitate was filtered off. Yield 1.58 g (85%).

***N'*-Arylmethylidene-3(5)-nitroamino-1,2,4-triazole-5(3)-carbohydrazides V–IX (general procedure)**. A mixture of 0.11 g (0.0006 mol) of 3(5)-nitroamino-1,2,4-triazole-5(3)-carbohydrazide (**IV**), 10 ml of water, a catalytic amount of acetic acid, and 0.0006 mol of the corresponding aromatic aldehyde was heated for 5 min at 80–90°C. The mixture was cooled, and the precipitate was filtered off. Com-

pounds **V–IX** were yellow high-melting crystalline substances.

***N'*-Benzylidene-3(5)-nitroamino-1,2,4-triazole-5(3)-carbohydrazide (V)**. Yield 81%, mp >300°C (from water). ^1H NMR spectrum, δ , ppm: 7.50 and 7.75 (H_{arom}), 8.60 s (=CH), 12.47 s (NHC=O). Found, %: C 43.78, 43.80; H 3.51, 3.49; N 35.82, 35.78. $\text{C}_{10}\text{H}_9\text{N}_7\text{O}_3$. Calculated, %: C 43.63; H 3.27; N 35.63.

***N'*-(4-Nitrophenyl)methylidene-3(5)-nitroamino-1,2,4-triazole-5(3)-carbohydrazide (VI)**. Yield 83%, mp 220–222°C. ^1H NMR spectrum, δ , ppm: 8.00 d and 8.30 d (C_6H_4), 8.70 s (=CH), 12.75 s (NHC=O). Found, %: C 37.40, 37.42; H 2.83, 2.80; N 34.99, 34.91. $\text{C}_{10}\text{H}_8\text{N}_8\text{O}_5$. Calculated, %: C 37.50; H 2.50; N 35.00.

***N'*-(4-Dimethylaminophenyl)methylidene-3(5)-nitroamino-1,2,4-triazole-5(3)-carbohydrazide (VII)**. Yield 72%, mp >300°C. ^1H NMR spectrum, δ , ppm: 3.00 s (CH_3), 6.75 d and 7.55 d (C_6H_4), 8.40 s (=CH), 12.20 s (NHC=O). Found, %: C 44.98, 45.03; H 4.46, 4.49; N 35.28, 35.27. $\text{C}_{12}\text{H}_{14}\text{N}_8\text{O}_3$. Calculated, %: C 45.28; H 4.40; N 35.22.

***N'*-(2-Hydroxyphenyl)methylidene-3(5)-nitroamino-1,2,4-triazole-5(3)-carbohydrazide (VIII)**. Yield 82%, mp >300°C. ^1H NMR spectrum, δ , ppm: 6.94, 7.33, and 7.55 (C_6H_4); 8.80 s (=CH); 11.00 s (OH); 12.78 s (NHC=O). Found, %: C 41.09, 41.11; H 3.43, 3.41; N 33.84, 33.80. $\text{C}_{10}\text{H}_9\text{N}_7\text{O}_4$. Calculated, %: C 41.24; H 3.09; N 33.67.

***N'*-(4-Hydroxy-3-methoxyphenyl)methylidene-3(5)-nitroamino-1,2,4-triazole-5(3)-carbohydrazide (IX)**. Yield 98%, mp >300°C. ^1H NMR spectrum, δ , ppm: 3.80 s (OCH_3); 6.85, 7.10, and 7.30 (C_6H_3); 8.45 s (=CH); 9.70 s (OH); 12.30 s (NHC=O). Found, %: C 41.22, 41.30; H 3.70, 3.68; N 30.65, 30.60. $\text{C}_{11}\text{H}_{11}\text{N}_7\text{O}_5$. Calculated, %: C 41.12; H 3.43; N 30.53.

The IR spectra were recorded in mineral oil on an InfraLyum-FT-02 spectrometer. The ^1H NMR spectra were obtained on a Bruker AC-300 spectrometer at 300 MHz using $\text{DMSO}-d_6$ as solvent and TMS as reference. The UV spectra were measured from solutions in water on an SF-46 spectrophotometer.

This study was performed under financial support by the International Scientific–Technical Center (project no. 2468r).

REFERENCES

1. Dobosz, *Acta Polon. Pharm.*, 1987, vol. 44, p. 420; *Chem. Abstr.*, 1988, no. 230897.

2. US Patent no. 4109001, 1978; *Chem. Abstr.*, 1979, no. 87472.
3. DDR Patent no. 272844, 1989; *Chem. Abstr.*, 1990, no. 2235321.
4. Nagao, V., Sano, S., Ochiai, M., and Fujita, E., *Tetrahedron*, 1990, vol. 46, p. 3211.
5. Barmin, M.I., Gromova, S.A., Lebedintseva, O.V., Tyuterev, S.L, and Men'shikov, V.V., *Zh. Prikl. Khim.*, 1995, vol. 68, p. 1333.
6. Mashkovskii, M.D., *Lekarstvennye sredstva* (Drugs), Moscow: Novaya Volna, 2002, vols. 1, 2.
7. Novikova, T.A., Metelkina, E.L., Efimova, T.P., and Berestovitskaya, V.M., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 1210.
8. Stopskii, V.S., Lebedev, V.B., Ioffe, B.I., and Petrov, A.A., *Dokl. Akad. Nauk SSSR*, 1966, p. 339.
9. Kofman, T.P., Sushchenko, L.F., and Pevzner, M.S., *Khim. Geterotsikl. Soedin.*, 1980, no. 11, p. 1553.
10. Pevzner, M.S., Gladkova, N.V., and Kravchenko, T.A., *Russ. J. Org. Chem.*, 1996, vol. 32, p. 1186.
11. Kofman, T.P., Kartseva, G.Yu., and Shcherbinin, M.B., *Russ. J. Org. Chem.*, 2002, vol. 38, 1343.