Russian Chemical Bulletin, International Edition, Vol. 50, No. 12, pp. 2481—2482, December, 2001

Synthesis of 3,5-disubstituted 1*H*-1,2,4-triazolium 4-nitroimides

A. I. Glushkov,* O. P. Shitov, and V. A. Tartakovsky

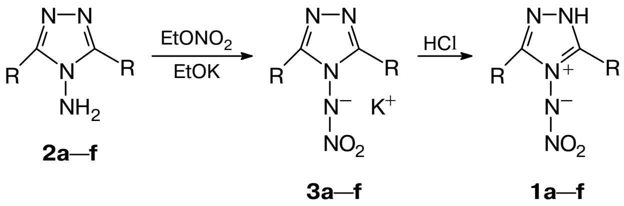
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: gluschkow@mail.ru

In continuation of our studies[1,2] on the preparation of nitrogen- and oxygen-containing organic compounds with a nitroimide fragment at the N atom of N-heterocycles, we developed a method for the synthesis of 3,5-disubstituted 1*H*-1,2,4-triazolium 4-nitroimides.

Compounds of this type have not been described previously.

3,5-Disubstituted 1,2,4-triazolium 4-nitroimides (**1**) were obtained by nitration of 3,5-disubstituted 4-amino-1,2,4-triazoles (**2**) with ethyl nitrate in an alkaline medium and acidification of the resulting potassium salts (**3**) (Scheme 1).

Scheme 1



R = Me (**a**), Et (**b**), Pr^n (**c**), Ph (**d**), CH_2OPh (**e**), CH_2SCH_2Ph (**f**)

The compositions and structures of compounds **1** were confirmed by elemental analysis and IR and NMR data. The IR spectra of these compounds show absorption bands at 1260—1300 and 1380—1415 cm^{-1} characteristic of the stretching vibrations of an aromatic *N*-nitroimido group[3] and contain no bands of the antisymmetrical stretching vibrations of the NO_2 group in nitramines at 1630—1550 cm^{-1}.[4] In the ^{1}H NMR spectra of nitroimides **1**, signals for the protons of the substituents are shifted downfield as compared with those for the starting aminotriazoles **2**, which indicates the presence of a strong electronegative group.

The IR and ^{1}H NMR data for compounds **1** are consistent with the physicochemical parameters of the known nitroimides[3] and with the spectroscopic data for the product obtained by nitration of 4-amino-1,2,4-triazole with alkyl nitrates. Its IR spectrum contains bands of the antisymmetrical stretching vibrations of the nitroimido group at 1276 and 1420 cm^{-1}. The presence of the proton in position 1 of the triazole ring was confirmed by X-ray diffraction analysis.[5]

Melting points were determined on a Boetius microscope stage. ^{1}H NMR spectra were recorded on a Bruker WM-250 instrument (250 MHz) in DMSO-d$_6$. IR spectra were recorded on a UR-20 spectrometer (KBr pellets).

The starting 4-aminotriazoles **2** were prepared according to the known procedure.[6]

3,5-Disubstituted 1*H*-1,2,4-triazolium 4-nitroimides (1) (*general procedure*). Aminotriazole **2** (5 mmol) and ethyl nitrate (6 mmol) were added to a solution of potassium ethoxide (10 mmol) in 30—40 mL of anhydrous EtOH. The reaction mixture was refluxed for 2 h and cooled to 0 °C. The precipitate that formed was filtered off, dissolved in a minimum amount of water, and acidified with dilute HCl to pH 1. The resulting precipitate was filtered off and recrystallized from EtOH.

3,5-Dimethyl-1*H*-1,2,4-triazolium 4-nitroimide (1a), yield 50%, m.p. 185—186 °C (decomp.). Found (%): C, 30.55; H, 4.49; N, 44.73. $C_4H_7N_5O_2$. Calculated (%): C, 30.57; H, 4.46; N, 44.59. IR, ν/cm^{-1}: 1292, 1392 (NO_2 imide). ^{1}H NMR, δ: 2.35 (s, 6 H, Me).

3,5-Diethyl-1*H*-1,2,4-triazolium 4-nitroimide (1b), yield 42.6%, m.p. 149—150 °C (decomp.). Found (%): C, 38.85; H, 6.09; N, 37.49. $C_6H_9N_5O_2$. Calculated (%): C, 38.92; H, 5.95; N, 37.83. IR, ν/cm^{-1}: 1276, 1400 (NO_2 imide). ^{1}H NMR, δ: 1.27 (t, 6 H, Me, J = 7.7 Hz); 2.70 (q, 4 H, CH_2, J = 7.7 Hz).

3,5-Dipropyl-1*H*-1,2,4-triazolium 4-nitroimide (1c), yield 52%, m.p. 128—130 °C (decomp.). Found (%): C, 45.27; H, 6.98; N, 32.93. $C_8H_{15}N_5O_2$. Calculated (%): C, 45.07; H, 7.04; N, 32.80. IR, ν/cm^{-1}: 1288, 1392 (NO_2 imide). ^{1}H NMR, δ: 0.95 (t, 6 H, Me, J = 7.3 Hz); 1.70 (quint, 4 H, $CH_2C\underline{H}_2CH_3$, J = 7.3 Hz); 2.67 (q, 4 H, $C\underline{H}_2CH_2CH_3$, J = 7.3 Hz).

3,5-Diphenyl-1*H*-1,2,4-triazolium 4-nitroimide (1d), yield 67.4%, m.p. 183—185 °C (decomp.). Found (%): C, 60.04; H, 4.22; N, 24.84. $C_{14}H_{11}N_5O_2$. Calculated (%): C, 59.79; H, 3.91; N, 24.91. IR, ν/cm^{-1}: 1292, 1400 (NO_2 imide). ^{1}H NMR, δ: 7.96 (d, 4 H, Ph, J = 7.3 Hz); 7.60—7.67 (m, 6 H, Ph).

3,5-Di(phenoxymethyl)-1*H*-1,2,4-triazolium 4-nitroimide (1e), yield 64.9%, m.p. 177—179 °C (decomp.). Found (%): C, 55.92; H, 4.31; N, 20.12. $C_{16}H_{15}N_5O_4$. Calculated (%): C, 56.31; H, 4.40; N, 20.53. IR, ν/cm^{-1}: 1280, 1412 (NO_2 imide). ^{1}H NMR, δ: 5.22 (s, 4 H, CH_2); 7.00—7.10 (m, 6 H, Ph); 7.32 (t, 4 H, Ph, J = 7.2 Hz).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2367—2368, December, 2001.

3,5-Di(benzylthiomethyl)-1*H*-1,2,4-triazolium 4-nitroimide (1f), yield 50.8%, m.p. 125—128 °C (decomp.). Found (%): C, 53.54; H, 4.54; N, 17.34; S, 16.23. $C_{18}H_{19}N_5O_2S_2$. Calculated (%): C, 53.87; H, 4.74; N, 17.46; S, 15.96. IR, ν/cm^{-1}: 1272, 1404 (NO_2 imide). ^1H NMR, δ: 3.76 (s, 4 H, $CH_2SC\underline{H}_2Ph$); 3.84 (s, 4 H, $C\underline{H}_2SCH_2Ph$); 7.29 (m, 10 H, Ph).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 00-15-97455).

References

1. O. P. Shitov, V. A. Vyazkov, and V. A. Tartakovsky, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, **11**, 2654 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 2440 (Engl. Transl.)].
2. V. A. Myasnikov, V. A. Vyazkov, O. P. Shitov, and V. A. Tartakovsky, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1239 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1116 (Engl. Transl.)].
3. J. Epsztajn, A. R. Katritzky, E. Lunt, J. W. Mitchell, and G. Koch, *J. Chem. Soc.*, *Perkin Trans. 1,* 1973, 2622.
4. A. L. Fridman, V. P. Ivshin, and S. S. Novikov, *Usp. Khim.*, 1969, **38**, 1460 [*Russ. Chem. Rev.*, 1969, **38**, 640 (Engl. Transl.)].
5. A. D. Vasiliev and A. M. Astachov, *Acta Crystallogr., Sect. C, Cryst. Struct. Commun.*, 1999, **55**, 830.
6. A. Katone, M. Hoda, and T. Hori, Ger. Offen. 2,248,257; *Chem. Abstrs.*, 1974, **81**, p25678n.

Received July 18, 2001