Synthesis of 3,4,5-trinitropyrazole

I. L. Dalinger, G. P. Popova, I. A. Vatsadze, T. K. Shkineva, and S. A. Shevelev*

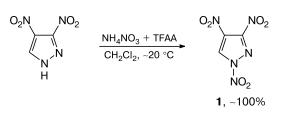
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (499) 135 5328. E-mail: shevelev@ioc.ac.ru

A first representative of exhaustively C-nitrated pyrazoles was obtained by oxidation of 5amino-3,4-dinitropyrazole.

Key words: pyrazole, nitropyrazole, aminonitropyrazole, trinitropyrazole, the nitro group, the amino group, oxidation.

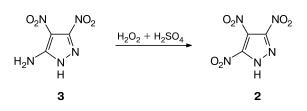
Earlier,¹ we have obtained for the first time 1,3,4-trinitropyrazole 1, a derivative with three nitro groups in the pyrazole ring (Scheme 1).

Scheme 1



In the present work, we report on the synthesis of isomeric N-unsubstituted 3,4,5-trinitropyrazole (2), a first representative of pyrazoles containing nitro groups at all the ring C atoms. Trinitropyrazole 2 was obtained by oxidation of 5-amino-3,4-dinitropyrazole (3)^{1,2} with a mixture of highly concentrated H_2O_2 and conc. H_2SO_4 (Scheme 2).

Scheme 2



A more recent³ alternative route to trinitropyrazole 2 involves oxidation of 4-amino-3,5-dinitropyrazole.⁴

Experimental

(75.47 MHz) and Bruker DRX-500 instruments (36.14 MHz) at

¹³C and ¹⁴N NMR spectra were recorded on Bruker AC-300

295 K. 13 C and 14 N chemical shifts are referenced to SiMe₄ and CH₃NO₂, respectively. IR spectra were recorded on a Specord M-80 instrument (KBr pellets). Mass spectra were measured on a Kratos MS-30 instrument. The course of the reaction was monitored, and the purity of the compound obtained was checked, by TLC on Silufol UV-254 plates with CHCl₃—MeOH (4 : 1) as an eluent. Elemental analysis was carried out on a Perkin Elmer Series II 2400 instrument.

3,4,5-Trinitropyrazole (2). 5-Amino-3,4-dinitropyrazole (1.62 g, 0.009 mol) was dissolved in 92% H_2SO_4 (50 mL). Then 84.5% H_2O_2 (15 mL) was carefully added in small portions with stirring at 0–5 °C. The mixture was allowed to warm to 20 °C, kept at 20–30 °C for 8 h under external cooling, left at ~20 °C for 16 h, and then poured onto ice (a fourfold amount in volume). The product was extracted with ether (2×100 mL). The extract was dried with MgSO₄ and concentrated *in vacuo*. The yield of compound **2** was 0.8 g (42%), m.p. 182–184 °C (decomp. 252 °C). Found (%): C, 18.11; H, 0.13; N, 33.90. C₃HN₅O₆. Calculated (%): C, 17.74; H, 0.50; N, 34.49. ¹³C NMR (DMSO-d₆), δ : 147.1 (C(3), C(5)); 122.4 (C(4)). ¹⁴N NMR ((CD₃)₂CO), δ : –134.7 (N(1)); –71.3 (N(2)); –32.7 (NO₂). IR, v/cm⁻¹: 1552, 1332 (C–NO₂). MS, *m*/z: 203 [M]⁺, 173 [M – NO]⁺, 127 [M – NO – NO₂]⁺.

References

- I. L. Dalinger, T. I. Cherkasova, G. P. Popova, T. K. Shkineva, I. A. Vatsadze, S. A. Shevelev, M. I. Kanishchev, *Izv. Akad. Nauk, Ser. Khim.*, 2009, 404 [*Russ. Chem. Bull.*, *Int. Ed.*, 2009, 58, 410].
- I. L. Dalinger, S. A. Shevelev, *Zh. Org. Khim.*, 1998, 34, 1127 [*Russ. J. Org. Chem. (Engl. Transl.)*, 1998, 34, 1071].
- N. Latypov, G. Jacob, P. Goede, G. Herve, S. Ek, Proc. 12th Seminar on New Trends in Research of Energetic Materials (Pardubice, April 1-3), 2009, 494.
- 4. R. D. Schmidt, G. S. Lee, P. F. Pagoria, A. R. Mitchell, R. Gilardi, J. Heterocycl. Chem., 2001, 38, 1227.

Received July 2, 2009; in revised form September 9, 2009

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 10, p. 2120, October, 2009.

1066-5285/09/5810-2185 © 2009 Springer Science+Business Media, Inc.