Synthesis of 3,4,5-trinitropyrazole

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A first representative of exhaustively C-nitrated pyrazoles was obtained by oxidation of 5-amino-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).

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 H₂O₂ and conc. H₂SO₄ (Scheme 2).

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

Experimental

¹³C and ¹⁴N NMR spectra were recorded on Bruker AC-300 (75.47 MHz) and Bruker DRX-500 instruments (36.14 MHz) at

295 K. ¹³C and ¹⁴N 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% H₂SO₄ (50 mL). Then 84.5% H₂O₂ (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. C₃H₃N₅O₆. 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, ν/cm^{–1}: 1552, 1332 (C–NO₂). MS, *m/z*: 203 [M]⁺, 173 [M – NO]⁺, 127 [M – NO – NO₂]⁺.

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