Electronic supplementary materials *Mendeleev Commun.*, 2010, **20**, 253–254

The specific reactivity of 3,4,5-trinitro-1*H*-pyrazole

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Experimental

*Preparation of 4-amino-3,5-dinitro-1*H*-pyrazole* **4a** *from carbamate* **9**. The solution of KOH (7.23 g, 0.13 mol) and carbamate **9**[1] (10 g, 0.043 mol) in H_2O (100 ml) was heated at 80–90 °C for 7 h. The resulting mixture was cooled and left overnight. The precipitate of the potassium salt was filtered off, washed with ice-water, suspended in water and acidified with 20% H_2SO_4 to pH 1. The resulting precipitate was filtered off and dried in dessicator over P_2O_5. Yield 5 g (67%), mp 166–168 °C (H_2O) (lit.,[2] mp 169–171 °C).

*4-Hydroxy-3,5-dinitro-1*H*-pyrazole disodium salt* **6**. To the solution of $NaHCO_3$ (0.53 g, 6.3 mmol) in water (5 ml), trinitropyrazole **1** (0.5 g, 2.5 mmol) was added. The mixture was heated at 80–90 °C for 9 h. After cooling, EtOH (5 ml) was added and the resulting mixture was kept at 0–5 °C for 2 h. The precipitate formed was filtered off, washed with EtOH, and dried *in vacuo* over P_2O_5. Yield, 0.153 g (28%). ^{13}C NMR, δ: 145.08 (C^4), 154.15 (C^3, C^5). MS (ESI), *m*/*z*: 172.9956 (calc. for $[M + H]^-$: 172.9952).

*1-Methyl-3,4,5-trinitro-1*H*-pyrazole* **7** *and 1-methyl-4-methylamino-3,5-dinitro-1*H*-pyrazole* **8**. To the solution of $NaHCO_3$ (0.51 g, 6 mmol) in water (10 ml), compound **1** or **4b** (3 mmol), respectively, was added. The mixture was stirred for 10 min followed by addition of Me_2SO_4 (0.34 ml, 3.6 mmol). The stirring was continued for 4 h at room temperature. The precipitate formed was filtered off and dried over P_2O_5.

7: yield 92%, mp 90–91 °C ($CHCl_3$) (lit.,[3] mp 91.3 °C). ^{1}H NMR (acetone-d_6) δ: 4.50 (s, 3H). ^{13}C NMR (acetone-d_6) δ: 43.86, 124.22 (C^4), 139.70 (C^5), 143.20 (C^3). ^{14}N NMR (acetone-d_6) δ: –31.23 (3-NO_2), –32.70 (5-NO_2), –35.51 (4-NO_2), –76.25 (N^2), –182.79 (N^1). MS (ESI), *m*/*z*: 187.0119 (calc. for [M – NO]–: 187.0109).

8: yield 90%, mp 130–131 °C (CH_2Cl_2). ^{1}H NMR, δ: 2.95 (d, 3H, ^3J 5.3 Hz), 4.16 (s, 3H), 7.26 (br. d, 1H, ^3J 4.9 Hz). ^{13}C NMR, δ: 33.10, 43.04, 130.87 (C^4), 133.22 (C^5), 140.80 (C^3).

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