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Nucleophilic substitution in 1-methyl-3,4,5-trinitro-1*H*-pyrazole

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NMR spectra were recorded in DMSO-d_6 (unless otherwise states) at 298 K on Bruker AC-300 and Bruker DRX-500 spectrometers, chemical shifts are referred to TMS.

*5-Amino-1-methyl-3,4-dinitro-1*H-*pyrazole* **2a**: yield 70 %, mp 122–123 °C. ^{1}H NMR, δ: 3.65 (s, 3H, NMe), 7.87 (br. s, 2H, NH_2). ^{13}C NMR, δ: 35.81 (NMe), 108.25 (C^4), 146.95 (2C, C^3, C^5).

*1-Methyl-5-methylamino-3,4-dinitro-1*H-*pyrazole* **2b**: yield 84 %, mp 165–166 °C. ^{1}H NMR, δ: 3.15 (d, 3H, *J* 5.4 Hz, NHC$\underline{H}_3$), 3.85 (s, 3H, NMe), 7.65 (br. q, 1H, *J* 5.2 Hz, N$\underline{H}$Me). ^{13}C NMR, δ: 31.05 (NHMe), 39.33 (NMe), 110.05 (C^4), 147.50 (2C, C^3, C^5).

*1-Methyl-3,4-dinitro-5-(pyrrolidin-1-yl)-1*H-*pyrazole* **2c**: yield 60 %, mp 64–65 °C. ^{1}H NMR, δ: 1.96 (m, 4H), 3.50 (m, 4H), 3.86 (s, 3H, NMe). ^{13}C NMR, δ: 25.39, 39.49 (NMe), 50.48, 115.07 (C^4), 145.28 (C^5), 146.96 (C^3).

*4-(1-Methyl-3,4-dinitro-1*H-*pyrazol-5-yl)morpholine* **2d**: yield 64 %, mp 92–93 °C. ^{1}H NMR, δ: 3.32 (m, 4H), 3.73 (m, 4H), 3.82 (s, 3H, NMe). ^{13}C NMR, δ: 37.61 (NMe), 49.27, 66.31, 118.18 (C^4), 146.49 (C^5), 146.77 (C^3).

*1-(1-Methyl-3,4-dinitro-1*H-*pyrazol-5-yl)azepane* **2e**: yield 61 %, mp 65–66 °C. ^{1}H NMR, δ: 1.72 (m, 8H), 3.33 (m, 4H), 3.82 (s, 3H, NMe). ^{13}C NMR, δ: 27.18, 29.27, 37.15 (NMe), 52.61, 118.44 (C^4), 146.62 (C^3), 148.72 (C^5).

*Ethyl 4-(1-methyl-3,4-dinitro-1*H-*pyrazol-5-yl)piperazine-1-carboxylate* **2f**: yield 82 %, mp 123–124 °C. ^{1}H NMR, δ: 1.20 (t, 3H, Me), 3.25 (m, 4H), 3.50 (m, 4H), 3.82 (s, 3H, NMe), 4.10 (q, 2H, CH_2). ^{13}C NMR, δ: 14.44, 37.62 (NMe), 43.70, 50.04, 60.93, 118.26 (C^4), 146.64 (C^5), 146.78 (C^3), 154.57 (CO).

*5-(4-Fluorophenylamino)-1-methyl-3,4-dinitro-1*H-*pyrazole* **2g**: yield 71 %, mp 160–162°C. ^{1}H NMR, δ: 3.59 (s, 3H, NMe), 7.15 (m, 4H), 9.50 (br. s, 1H, NH). ^{13}C NMR, δ: 38.07 (NMe), 115.05 (C^4), 115.64 (CH), 121.12 (CH), 136.22, 141.95 (C^5), 147.17 (C^3), 158.35 (d, CF, *J* 240 Hz).

*5-(4-Chlorophenylamino)-1-methyl-3,4-dinitro-1*H-*pyrazole* **2h**: yield 90 %, mp 110–111°C. ^{1}H NMR, δ: 3.67 (s, 3H, NMe), 7.02 (m, 2H), 7.32 (m, 2H), 9.60 (br. s, 1H, NH). ^{13}C NMR, δ: 37.87 (NMe), 119.72 (C^4, CH), 126.40, 128.92 (CH), 139.31, 141.01 (C^5), 147.12 (C^3).

*1-Methyl-3,4-dinitro-5-(3-nitrophenylamino)-1*H-*pyrazole* **2i**: yield 75 %, mp 173–174 °C. ^{1}H NMR, δ: 3.72 (s, 3H, NMe), 7.34 (m, 1H), 7.56 (m, 1H), 7.85 (m, 2H), 10.0 (br. s, 1H, NH). ^{13}C NMR, δ: 37.76 (NMe), 111.60 (CH), 116.58 (CH), 117.12 (C^4), 123.31 (CH), 130.40 (CH), 140.10 (C^5), 142.12, 147.20 (C^3), 148.41.

*3-[(1-Methyl-3,4-dinitro-1*H-*pyrazol-5-yl)amino]-1-propyl-1*H-*pyrazole* **2j**: yield 60 %, mp 120–121 °C. ^{1}H NMR, δ: 0.80 (t, 3H, Me), 1.72 (m, 2H, CH_2), 3.62 (s, 3H, NMe), 3.93 (q, 2H, CH_2), 6.00 (m, 1H), 7.65 (m, 1H), 9.65 (br. s, 1H, NH). ^{13}C NMR, δ: 10.69, 22.23, 38.15 (NMe), 52.84, 95.57 (CH), 113.82 (C^4), 131.65 (CH), 141.98, 146.62 (C^5, C^3).

1-Ethyl-N'-*(1-methyl-3,4-dinitro-1*H-*pyrazol-5-yl)-1*H-*pyrazole-4-carbohydrazide* **2k**: yield 90 %, mp 225–226 °C. ^{1}H NMR, δ: 1.36 (t, 3H, Me), 3.76 (s, 3H, NMe), 4.21 (q, 2H, CH_2), 7.93 (s, 1H), 8.29 (s, 1H), 9.32 (br. s, 1H, NH), 10.64 (br. s, 1H, NH). ^{13}C NMR, δ: 15.22, 39.11 (NMe), 46.75, 111.68 (C^4), 114.34, 131.47 (CH), 138.66 (CH), 146.77 (C^5, C^3), 162.42 (CO).

*1-Methyl-3,4-dinitro-5-(1*H-*pyrazol-1-yl)-1*H-*pyrazole* **3a**: yield 76 %, mp 104–105 °C.
^{1}H NMR, δ: 3.88 (s, 3H, NMe), 6.71 (m, 1H), 8.05 (m, 1H), 8.34 (m, 1H). ^{13}C NMR, δ: 38.61 (NMe), 108.79 (CH), 119.98 (C^4), 134.65 (CH), 136.14 (C^5), 144.24 (CH), 145.91 (C^3).

*5-(Imidazol-1-yl)-1-methyl-3,4-dinitro-1*H-*pyrazole* **3b**: yield 60 %, mp 125–126 °C.
^{1}H NMR, δ: 3.80 (s, 3H, NMe), 7.23 (m, 1H), 7.63 (m, 1H), 8.15 (m, 1H). ^{13}C NMR, δ: 36.99 (NMe), 120.12 (C^4), 120.91 (CH), 129.92 (CH), 134.68 (C^5), 138.68 (CH), 146.36 (C^3).

*1-Methyl-3,4-dinitro-5-(1,2,4-triazol-1-yl)-1*H-*pyrazole* **3c**: yield 63 %, mp 110–111 °C.
^{1}H NMR, δ: 3.91 (s, 3H, NMe), 8.62 (s, 1H), 9.23 (s, 1H). ^{13}C NMR, δ: 38.76 (NMe), 120.51 (C^4),

133.30 (C^5), 146.21 (C^3), 148.44 (CH), 154.13 (CH).

*1-Methyl-3,4-dinitro-5-(3-nitro-1*H*-pyrazol-1-yl)-1*H*-pyrazole* **4a**: yield 92 %, oil. ^{1}H NMR, δ: 3.95 (s, 3H, NMe), 7.50 (m, 1H), 8.15 (m, 1H). ^{13}C NMR, δ: 38.64 (NMe), 104.86 (CH), 120.98 (C^4), 134.40 (C^5), 139.26 (CH), 146.05 (C^3), 158.67 ($C^{3'}NO_2$).

*1-Methyl-3,4-dinitro-5-(4-nitro-1*H*-pyrazol-1-yl)-1*H*-pyrazole* **4b**: yield 71 %, mp 108–109 °C. ^{1}H NMR, δ: 3.97 (s, 3H, NMe), 8.86 (s, 1H), 9.52 (s, 1H). ^{13}C NMR, δ: 38.67 (NMe), 120.09 (C^4), 134.27 (C^5), 135.36 (CH), 137.34 ($C^{4'}NO_2$), 139.35 (CH), 146.04 (C^3).

*5-(4-Bromophenoxy)-1-methyl-3,4-dinitro-1*H*-pyrazole* **5a**: yield 82 %, mp 118–120 °C.
^{1}H NMR, δ: 3.82 (s, 3H, NMe), 7.31 (d, 2H), 7.63 (d, 2H). ^{13}C NMR, δ: 36.35 (NMe), 115.08 (C^4), 117.15 (CBr), 117.89 (CH), 132.58 (CH), 145.15 (C^5), 145.83 (C^3), 154.26 (CO).

*5-(3-Methoxyphenoxy)-1-methyl-3,4-dinitro-1*H*-pyrazole* **5b**: yield 80 %, mp 91–92 °C.
^{1}H NMR, δ: 3.73 (s, 3H, NMe), 3.81 (s, 3H, OMe), 6.84 (m, 3H), 7.37 (m, 1H). ^{13}C NMR, δ: 36.30 (NMe), 54.76 (OMe), 102.32 (CH), 107.66 (CH), 110.84 (CH), 115.19 (C^4), 130.80 (CH), 145.37 (C^5), 145.75 (C^3), 155.89, 160.81.

*1-Methyl-3,4-dinitro-5-(2-nitrophenoxy)-1*H*-pyrazole* **5c**: yield 70 %, mp 151–152 °C.
^{1}H NMR, δ: 3.95 (s, 3H, NMe), 7.51 (m, 1H), 7.62 (m, 1H), 7.76 (m, 1H), 8.21 (m, 1H). ^{13}C NMR, δ: 36.49 (NMe), 114.86 (C^4), 117.88 (CH), 126.12 (2 CH), 135.41 (CH), 139.04, 144.46 (C^5), 145.91 (C^3), 146.98.

*1-Methyl-3,4-dinitro-5-(3,5-dinitrophenoxy)-1*H*-pyrazole* **5d**: yield 85 %, mp 205–206 °C. ^{1}H NMR, δ: 3.90 (s, 3H, NMe), 8.67 (s, 2H), 8.71 (s, 1H). ^{13}C NMR, δ: 36.68 (NMe), 115.25 (C^4), 115.31 (CH), 117.83 (2 CH), 144.05 (C^5), 146.03 (C^3), 148.97, 155.10.

*5,5'-[1,4-Phenylenebis(oxy)]bis(1-methyl-3,4-dinitro-1*H*-pyrazole)* **5e**: yield 84 %, mp 230–232 °C.
^{1}H NMR, δ: 3.83 (s, 6H, NMe), 7.49 (s, 4H). ^{13}C NMR, δ: 36.41 (NMe), 114.95 (C^4), 117.51 (4 CH), 145.53 (C^5), 145.86 (C^3), 151.87 (CO).

Acetone O*-(1-methyl-3,4-dinitro-1*H*-pyrazol-5-yl)oxime* **6a**: yield 82 %, mp 90–92 °C.
^{1}H NMR, δ: 1.96 (s, 3H, CMe), 2.17 (s, 3H, CMe), 3.84 (c, 3H, NMe). ^{13}C NMR ($CDCl_3$), δ: 16.79,

20.95, 36.91 (NMe), 115.63 (C^4), 145.80 (C^5), 148.96 (C^3), 165.57.

*(1*E*)-1-Phenylethanone* O-*(1-methyl-3,4-dinitro-1*H*-pyrazol-5-yl)oxime* **6b**: yield 86 %, mp 135–136 °C (decomp.). ^{1}H NMR ($CDCl_3$), *δ*: 2.61 (s, 3H, CMe), 3.96 (c, 3H, NMe), 7.50 (m, 3H), 7.63 (m, 2H). ^{13}C NMR ($CDCl_3$), *δ*: 14.45, 37.09 (NMe), 113.65 (C^4), 126.94 (CH), 129.06 (CH), 131.49 (CH), 132.97 (CH), 138.65 (C^5), 148.85 (C^3), 164.87.

*5-Ethylthio-1-methyl-3,4-dinitro-1*H*-pyrazole* **7a**: yield 80 %, mp 68–70 °C. ^{1}H NMR, *δ*: 1.22 (t, 3H, Me), 3.08 (q, 2H, CH_2), 4.05 (s, 3H, NMe). ^{13}C NMR ($CDCl_3$), *δ*: 15.19, 30.15, 38.89 (NMe), 129.85 (C^4), 136.96 (C^5), 146.14 (C^3).

*1-Methyl-3,4-dinitro-5-phenylthio-1*H*-pyrazole* **7b**: yield 72 %, mp 100–101 °C. ^{1}H NMR, *δ*: 3.95 (s, 3H, NMe), 7.42 (m, 5H, Ph). ^{13}C NMR, *δ*: 39.19 (NMe), 128.49 (CH, C^4), 129.65 (CH), 130.21, 130.31 (C^5), 146.72 (C^3).

*1-Methyl-5-(4-methylphenylthio)-3,4-dinitro-1*H*-pyrazole* **7c**: yield 95 %, mp 103–104 °C. ^{1}H NMR, *δ*: 2.26 (s, 3H, Me), 3.90 (s, 3H, NMe), 7.21 (m, 2H), 7.36 (m, 2H). ^{13}C NMR, *δ*: 20.72, 38.94 (NMe), 129.98 (2 CH, C^4), 134.24, 135.91, 137.91 (C^5), 146.17 (C^3).

*5-(4-Chlorobenzylthio)-1-methyl-3,4-dinitro-1*H*-pyrazole* **7d**: yield 90 %, mp 80–82 °C.
^{1}H NMR, *δ*: 3.76 (s, 3H, NMe), 4.30 (s, 2H, CH_2), 7.25 (m, 2H), 7.38 (m, 2H). ^{13}C NMR, *δ*: 38.21 (NMe, CH_2), 128.97 (CH, C^4), 130.87 (CH), 131.07, 135.25 (C^5), 136.38, 145.96 (C^3).