Nitropyrazoles
16.* The use of methoxymethyl group as a protecting group for the synthesis of 4-methyl-3-nitro-5-R-pyrazoles

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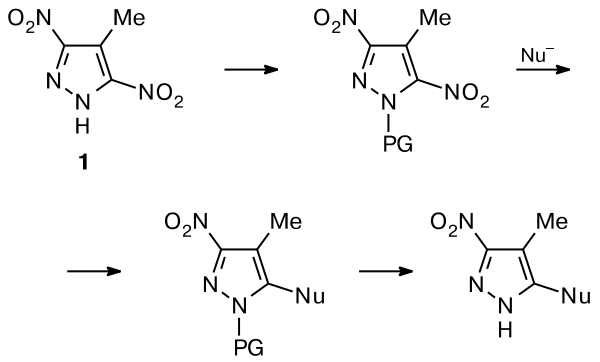
4-Methyl-3,5-dinitropyrazole prepared by nitration of 1,4-dimethylpyrazole readily reacts with methoxymethyl chloride and methyl vinyl ketone in acetonitrile in the presence of a base giving 1-methoxymethyl-4-methyl-3,5-dinitropyrazole and 4-methyl-3,5-dinitro-1-(3-oxobutyl)pyrazole, respectively. The action of the thioglycolanilide anion on 4-methyl-3,5-dinitro-1-(3-oxobutyl)pyrazole results only in the removal of 1-protecting group and the formation of 2-[(3-oxobutyl)thio]acetanilide, while the action of anionic S-nucleophiles on 1-methoxymethyl-4-methyl-3,5-dinitropyrazole leads to the substitution products of the 5-NO_2 group in which the methoxymethyl group can be removed by acid hydrolysis.

Key words: nitropyrazoles, dinitropyrazoles, nitration, nucleophilic substitution, nucleophiles, protecting groups.

In our previous work,[1] we have demonstrated the possibility of the use of 2,4-dinitrophenyl group as a protecting group in the synthesis of some NH-pyrazoles that cannot be obtained by other methods. The role of the 2,4-dinitrophenyl substituent in the position 1 of the pyrazole ring consists, from the one hand, of increasing the mobility of hydrogen atoms of the 4-Me group of 3,5-dinitropyrazoles in comparison with 1-Me-analog, and, from the other hand, of a possibility of easy removal of this substituent by nucleophiles. However, the latter fact does not allow functionalization of the position 5 of the pyrazole ring (which can be carried out using nucleophilic substitution of the 5-NO_2 group in the case of 1-methyl-substituted nitropyrazoles[2]), since it is the dinitropyrazolate anion that is substituted instead of the nitro group. At the same time, nucleophilic substitution is not possible directly in the *N*-unsubstituted 3,5-dinitropyrazoles, as the latter are moderate-strength acids (pK_a 3—4)[3] and form nonreactive anions under basic conditions of substitution.

Synthesis of NH-3-nitropyrazoles that have a functional group in the position 5 can be effected by the introduction of an appropriate protecting group into the 4-methyl-3,5-dinitropyrazole molecule that is resistant to the action of a nucleophile, subsequent nucleophilic substitution, and removal of the protecting group (Scheme 1).

Scheme 1



PG is a protecting group

Earlier unknown 4-methyl-3,5-dinitropyrazole (**1**) was synthesized by nitration of 4-methylpyrazole (**2**) with nitric—sulfuric acid mixture (Scheme 2), which is in contradiction with the previous reports that it is impossible to introduce 4-substituted NH-pyrazoles in nitration reaction with the formation of 3,5-dinitropyrazoles.[4] It is worth mentioning that the amount of water in the reaction medium in the synthesis of 3,5-dinitropyrazole plays the critical role: to obtain the products in acceptable yields one has to use, first, concentrated nitric acid with density d = 1.5 g cm^{-3}, and, second, concentrated sulfuric acid with concentration of at least 96%. With standard com-

* For Part 15, see Ref. 1.

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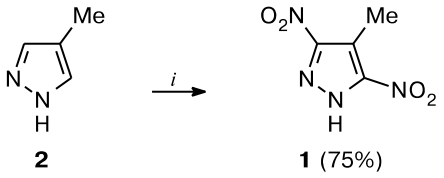
mercially available 92.5% sulfuric acid (SSS 4204-77), the product yields are negligible (see Ref. 5 for details).

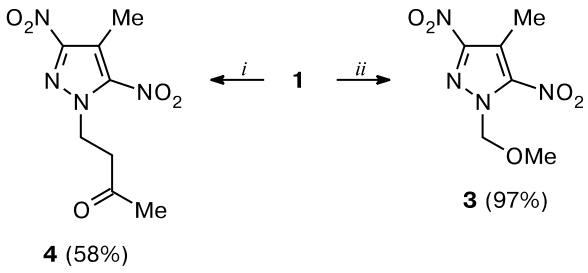
Scheme 2



i. HNO_3 (d = 1.5 g cm^{-3}), H_2SO_4 (~97.5%), 100 °C, 2 h.

Analysis of literature data on nitroazoles[6] allows us to assume that methoxymethyl and 3-oxobutyl groups might be used as protecting groups. The corresponding dinitropyrazoles **3** and **4** were easily prepared by the reaction of dinitropyrazole **1** with methoxymethyl chloride (MOMCl) and methyl vinyl ketone, respectively in acetonitrile in the presence of potassium carbonate (Scheme 3).

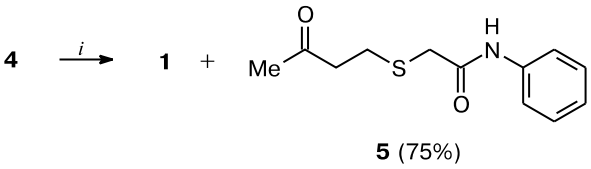
Scheme 3



i. $MeCOCH{=}CH_2$, K_2CO_3, MeCN, 80 °C, 20 h; *ii*. MOMCl, K_2CO_3, MeCN, 25 °C, 1 h.

2-[(3-Oxobutyl)thio]acetanilide (**5**) is formed under the action of the thioglycolanilide anion of on 4-methyl-3,5-dinitro-1-(3-oxobutyl)pyrazole (**4**) instead of the substitution product of the NO_2 group (Scheme 4). Apparently, this is due to the substitution of dinitropyrazolate anion at the C_β atom rather than the result of sequential abstraction of the pyrazolate ion and addition of the $PhNHCOCH_2S^-$ anion. This can be inferred from the fact that direct reaction of the thioglycolanilide anion with methyl vinyl ketone does not result in compound **5**.

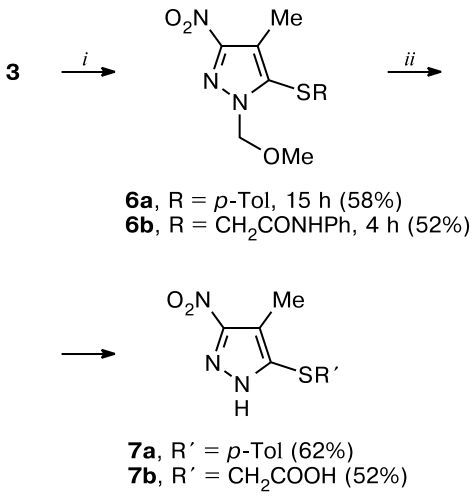
Scheme 4



i. $HSCH_2CONHPh$, K_2CO_3, MeCN, 80 °C, 4 h.

The action of *p*-toluenethiolate and the thioglycolanilide anion on compound **3** affords the corresponding substitution products of the NO_2 group of the pyrazole ring **6a** and **6b** (Scheme 5). It is worth noting that the reactivity of compound **3** in the reaction with the $^-SCH_2CONHPh$ anion exceeds that of 1,4-dimethyl-3,5-dinitropyrazole. In the case with the latter compound, no total conversion could be attained over reasonable time when the reaction was carried out in acetonitrile,[2c] *i.e.*, the methoxymethyl group in the position 1 has the activating influence on the nucleophilic substitution of the 5-NO_2 group in comparison with the Me substituent. However, the attempts to involve compound **3** in reactions with O-nucleophiles (phenolate and glycolic acid anions), as in the case of 1,4-dimethyl-3,5-dinitropyrazole, failed: compound **3** did not react.

Scheme 5



i. RSH, K_2CO_3, MeCN, 80 °C; *ii*. Conc. HCl/EtOH (HOAc), reflux.

By the example of compound **6b**, we demonstrated that it is the nitro group in the position 5 in dinitropyrazole **3** that is substituted. This was established, as in our previous studies,[1,2c] using 2D correlation NMR spectroscopy on the basis of long-range spin-spin coupling constant $^1H—^{13}C$ (HMBC): the spin-spin interaction of protons of both the OCH_2 and SCH_2 groups is observed with the same carbon atom of the pyrazole ring (δ 135.09), which is possible only in the case where the $PhNHCOCH_2S$ group is linked to the C(5) carbon atom.

The methoxymethyl group in compounds **6a** and **6b** can be removed by acid hydrolysis. Thus, refluxing of compound **6a** in ethanol containing concentrated HCl gives NH-pyrazole **7a**. Under these conditions, compound **6b** does not undergo hydrolysis; the use of more drastic conditions, *viz.*, refluxing in acetic acid containing concentrated hydrochloric acid at ~120 °C affords carboxylic acid

7b, *i.e.*, hydrolysis of the $SCH_2CONHPh$ group accompanies removal of the CH_2OMe group.

Thus, one can state that the methoxymethyl group can be successfully used as a protecting group in the synthesis of some N-unsubstituted 5-R-4-methyl-3-nitropyrazoles.

Experimental

^1H and ^{13}C NMR spectra were recorded on Bruker AC-300 (300.13 MHz) and Bruker DRX-500 (125 MHz) spectrometers, respectively, at 295 K (unless other temperature is indicated). Chemical shifts for ^1H and ^{13}C are given relative to Me_4Si. IR spectra were recorded on a Specord M-80 in KBr pellets. Mass spectra were obtained on a Kratos MS-30 spectrometer (direct inlet, electron impact, ionization energy 70 eV). The course of the reactions and purity of compounds were monitored by TLC on Silufol UV-254 plates, $CHCl_3$—Me_2CO (10 : 1). Elemental analysis was carried out on a Perkin—Elmer Series II 2400 apparatus.

4-Methylpyrazole,[7] methoxymethyl chloride,[8] and thioglycolanilide[9] were prepared as described.

4-Methyl-3,5-dinitropyrazole (1). Oleum (41%, d = 1.963 g cm^{-3}, 12.0 mL) was added to 92.5% sulfuric acid (30.0 mL, d = 1.826 g cm^{-3}) at a temperature of 30—40 °C; at this temperature, 4-methylpyrazole (**2**) (2.00 mL, 24.2 mmol) and then fuming nitric acid (d = 1.5 g cm^{-3}) (3.1 mL, 73.8 mmol) were added dropwise. The reaction mixture was heated at 100—105 °C for 2 h, cooled to ~20 °C, poured onto ~300 g of crushed ice; air was passed for 3-4 h through the suspension thus obtained until total removal of nitrogen oxides. The precipitate was filtered off, washed with water and dried in air. White crystalline product **1** (2.22 g) was obtained. The aqueous layer was extracted with ethyl acetate (2×40 mL), the organic layers were combined, washed with water to neutral pH, and dried with Na_2SO_4. The solvent was removed under reduced pressure, the residue was crystallized from ethanol. The target product (0.92 g) was obtained additionally. The total yield of compound **1** is 3.14 g (75%), m.p. 211—213 °C. Found (%): C, 27.84; H, 2.18; N, 32.26. $C_4H_4N_4O_4$. Calculated (%): C, 27.92; H, 2.34; N, 32.56. ^1H NMR ($(CD_3)_2SO$), δ: 2.57 (s, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 149.14 (C(3)); 112.55 (C(4)); 9.13 (Me). IR, ν/cm^{-1}: 3164 (NH); 1548, 1336 (NO_2). MS, m/z: 172 $[M]^+$.

1-Methoxymethyl-4-methyl-3,5-dinitropyrazole (3). Potassium carbonate (4.5 g, 32.6 mmol) and methoxymethyl chloride (2.4 mL, 31.6 mmol) were added to a solution of dinitropyrazole **1** (5.0 g, 29.1 mmol) in acetonitrile (100 mL). The reaction mixture was stirred for 1 h (TLC) and then poured into water (300 mL), extracted with ethyl acetate (2×60 mL), dried with Na_2SO_4, and the solvent was removed under reduced pressure. White crystalline product **3** was obtained (6.1 g, 97%). M.p. 78—80 °C. Found (%): C, 33.38; H, 3.51; N, 25.94. $C_4H_8N_4O_5$. Calculated (%): C, 33.34; H, 3.73; N, 25.92. ^1H NMR ($(CD_3)_2SO$), δ: 5.83 (s, 2 H, CH_2); 3.34 (s, 3 H, OMe); 2.57 (s, 3 H, CMe). ^1H NMR ($CDCl_3$), δ: 5.90 (s, 2 H, CH_2); 3.41 (s, 3 H, OMe); 2.70 (s, 3 H, CMe). ^{13}C NMR ($(CD_3)_2SO$), δ: 151.51 (C(3)); 143.63 (C(5)); 115.34 (C(4)); 84.18 (CH_2); 57.14 (OMe); 9.60 (Me). IR, ν/cm^{-1}: 1528, 1336 (NO_2). MS, m/z: 216 $[M]^+$.

4-(4-Methyl-3,5-dinitropyrazol-1-yl)butan-2-one (4). Methyl vinyl ketone (0.50 mL, 6.2 mmol) and potash (0.16 g, 1.2 mmol) were added to a solution of dinitropyrazole **1** (1.00 g, 5.8 mmol) in acetonitrile (25 mL). The reaction mixture was refluxed for 20 h, cooled to ~20 °C, and then poured into 2% HCl (100 mL) and extracted with ethyl acetate (2×30 mL); the organic layers were combined, washed with water to neutral pH, and dried with Na_2SO_4. The solvent was removed under reduced pressure, the residue was chromatographed on silica gel ($CHCl_3$). White crystalline compound **4** was obtained (0.82 g, 58%). M.p. 66—68 °C. Found (%): C, 39.69; H, 4.03; N, 23.16. $C_8H_{10}N_4O_5$. Calculated (%): C, 39.67; H, 4.16; N, 23.13. ^1H NMR ($(CD_3)_2SO$), δ: 4.76 (t, 2 H, NCH_2, J = 6.6 Hz); 3.15 (t, 2 H, CH_2CO, J = 6.6 Hz); 2.53 (s, 3 H, 4-Me); 2.14 (s, 3 H, COMe). ^{13}C NMR ($(CD_3)_2SO$), δ: 205.64 (CO); 150.66 (C(3)); 144.21 (C(5)); 114.25 (C(4)); 48.88 (NCH_2); 41.04 ($\underline{C}H_2CO$); 29.76 ($\underline{C}H_3CO$); 9.65 (4-Me). IR, ν/cm^{-1}: 1720 (CO); 1520, 1336 (NO_2). MS, m/z: 242 $[M]^+$.

2-[(3-Oxobutyl)thio]acetanilide (5). Potassium carbonate (0.138 g, 1.0 mmol) was added to a solution of thioglycolanilide (0.167 g, 1.0 mmol) in acetonitrile (20 mL), the mixture was stirred for 10 min, then compound **4** (0.242 g, 1.0 mmol) was added. The reaction mixture was refluxed for 4 h (TLC), cooled to ~20 °C, poured into water (80 mL) acidified with HCl pH 2—3, extracted with ethyl acetate (2×20 mL), the organic layers were combined, washed with water to neutral pH, and dried with Na_2SO_4. The solvent was removed under reduced pressure, the residue was chromatographed on silica gel ($CHCl_3$—Me_2CO (20 : 1)). Compound **5** was obtained in the form of light-yellow oil (0.178 g, 75%); the yield of compound **1** was (white crystals) 0.077 g (65%). Compound **5**. Found (%): C, 60.58; H, 6.30; N, 5.59; S, 13.42. $C_{12}H_{15}NO_2S$. Calculated (%): C, 60.73; H, 6.37; N, 5.90; S, 13.51. ^1H NMR ($(CD_3)_2SO$), δ: 10.00 (s, 1 H, NH); 7.57 (d, 2 H, *o*-H, Ph, J = 8.1 Hz); 7.30 (t, 2 H, *m*-H, Ph, J = 8.1 Hz); 7.05 (t, 1 H, *p*-H, Ph, J = 7.3 Hz); 3.30 (s, 2 H, SCH_2CO); 2.78 (br.s, 4 H, $COCH_2CH_2$); 2.09 (s, 3 H, Me). ^1H NMR ($CDCl_3$), δ: 8.97 (s, 1 H, NH); 7.62 (d, 2 H, *o*-H, Ph, J = 8.1 Hz); 7.33 (t, 2 H, *m*-H, Ph, J = 7.7 Hz); 7.12 (t, 1 H, *p*-H, Ph, J = 7.3 Hz); 3.38 (s, 2 H, SCH_2CO); 2.81 (m, 4 H, $COCH_2CH_2$); 2.17 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$), δ: 206.97 ($\underline{C}OMe$); 167.64 (CONH); 137.39 (*ipso*-C, Ph); 129.04 (*m*-C, Ph); 124.85 (*p*-C, Ph); 120.16 (*o*-C, Ph); 42.64 ($CO\underline{C}H_2CH_2$); 37.15 ($S\underline{C}H_2CO$); 30.10 (Me); 26.40 ($CH_2\underline{C}H_2S$). IR, ν/cm^{-1}: 3308 (NH); 1716 ($\underline{CO}Me$); 1668 ($\underline{CO}NH$). MS, m/z: 237 $[M]^+$.

1-Methoxymethyl-4-methyl-5(3)-[(4-methylphenyl)thio]-3(5)-nitropyrazole (6a). Potash (0.75 g, 5.4 mmol) was added to a solution of dinitropyrazole **3** (1.00 g, 5.8 mmol) and *p*-toluenethiol (0.80 g, 6.4 mmol) in acetonitrile (40 mL). The reaction mixture was refluxed for 15 h in a flow of argon (TLC), cooled to ~20 °C, poured into water (150 mL), extracted with ethyl acetate (2×30 mL), the organic layers were combined and dried with Na_2SO_4. The solvent was removed under reduced pressure, the residue was chromatographed on silica gel (CCl_4, then $CHCl_3$). Solid yellow compound **6a** was obtained (0.79 g, 58%). M.p. 45—47 °C. Found (%): C, 53.62; H, 5.15; N, 13.24; S, 10.16. $C_{13}H_{15}N_3O_3S$. Calculated (%): C, 53.23; H, 5.15; N, 14.32; S, 10.93. ^1H NMR ($(CD_3)_2SO$), δ: 7.16 (d, 2 H, *o*-H, C_6H_4Me-*p*, J = 8.1 Hz); 7.12 (d, 2 H, *m*-H, C_6H_4Me-*p*, J = 8.1 Hz); 5.59 (s, 2 H, CH_2); 3.25 (s, 3 H, OMe); 2.27 (s, 3 H, Me), 2.26 (s, 3 H, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 153.41 (C(3)); 136.93 (C(4′)); 134.00 (C(5)); 130.15 (C(2′)); 129.28 (C(1′)); 128.01 (C(3′)); 120.36 (C(4)); 80.45 (CH_2); 56.58 (OMe); 20.33 ($\underline{C}H_3C_6H_4$); 9.79 (4-Me). IR, ν/cm^{-1}: 1560, 1516, 1348 (NO_2). MS, m/z: 293 $[M]^+$.

2-[(1-Methoxymethyl-4-methyl-3(5)-nitropyrazole-5(3)-yl)thio]acetanilide (6b). Potassium carbonate (1.06 g, 7.7 mmol) was added to a solution of dinitropyrazole **3** (1.50 g, 6.9 mmol) and thioglycolanilide (1.16 g, 6.9 mmol) in acetonitrile (50 mL). The reaction mixture was refluxed for 4 h (TLC), cooled to ~20 °C, poured into water (200 mL), extracted with ethyl acetate (2×60 mL), the organic layers were combined and dried with Na_2SO_4. The solvent was removed under reduced pressure, the residue was chromatographed on silica gel ($CHCl_3$). Solid light-yellow compound **6b** was obtained (1.10 g, 52%). M.p. 97—99 °C. Found (%): C, 49.32; H, 4.76; N, 17.74; S, 8.86. $C_{14}H_{16}N_4O_4S$. Calculated (%): C, 49.99; H, 4.79; N, 16.66; S, 9.53. ^{1}H NMR ($(CD_3)_2SO$), δ: 10.10 (s, 1 H, NH); 7.49 (d, 2 H, *o*-H, Ph, J = 7.3 Hz); 7.30 (t, 2 H, *m*-H, Ph, J = 7.3 Hz); 7.06 (t, 1 H, *p*-H, Ph, J = 6.7 Hz); 5.65 (s, 2 H, OCH_2); 3.64 (s, 2 H, SCH_2); 3.30 (s, 3 H, OMe); 2.30 (s, 3 H, CMe). ^{13}C NMR ($(CD_3)_2SO$), δ: 166.04 (CO); 153.11 (C(3)); 138.63 (*ipso*-C, Ph); 135.09 (C(5)); 128.85 (*m*-C, Ph); 123.67 (*p*-C, Ph); 120.90 (C(4)); 119.16 (*o*-C, Ph); 80.51 (OCH_2); 56.71 (OMe); 39.70 (SCH_2); 10.10 ($C\underline{C}H_3$). IR, ν/cm^{-1}: 3296 (NH); 1664 (CO); 1544, 1528, 1336 (NO_2). MS, *m/z*: 336 $[M]^+$.

4-Methyl-5(3)-(4-tolylthio)-3(5)-nitropyrazole (7a). Concentrated HCl (10 mL) was added to a suspension of compound **6a** (0.480 g, 1.6 mmol) in ethanol (30 mL). The reaction mixture was refluxed for 15 h (TLC), cooled to ~20 °C, poured into water (150 mL), extracted with ethyl acetate (2×40 mL), the organic layers were combined, washed with water to neutral pH, and dried with Na_2SO_4. The solvent was removed under reduced pressure, the residue was chromatographed on silica gel ($CHCl_3$). Solid light-yellow compound **7a** was obtained (0.254 g, 62%). M.p. 106—108 °C. Found (%): C, 53.50; H, 4.37; N, 16.55; S, 12.32. $C_{11}H_{11}N_3O_2S$. Calculated (%): C, 53.00; H, 4.45; N, 16.86; S, 12.86. ^{1}H NMR ($(CD_3)_2SO$), δ: 14.56 (br.s, 1 H, NH); 7.16 (d, 2 H, *o*-H, C_6H_4Me-*p*, J = 8.1 Hz); 7.11 (d, 2 H, *m*-H, C_6H_4Me-*p*, J = 8.1 Hz); 2.26 (s, 3 H, Me); 2.25 (s, 3 H, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 154.28 (C(3)); 136.90 (C(4′)); 132.32 (C(5)); 130.27 (C(2′)); 130.16 (C(1′)); 128.19 (C(3′)); 118.25 (C(4)); 20.47 ($\underline{C}H_3C_6H_4$); 9.32 (4-Me). IR, ν/cm^{-1}: 3112, 2928 (NH); 1568, 1548, 1360, 1352, 1344 (NO_2). MS, *m/z*: 249 $[M]^+$.

[(4-Methyl-3(5)-nitropyrazole-5(3)-yl)thio]acetic acid (7b). Concentrated HCl (10 mL) was added to a solution of amide **6b** (0.200 g, 0.59 mmol) in acetic acid (30 mL). The reaction mixture was refluxed for 2 h (TLC), cooled to ~20 °C, and the solvent was removed under reduced pressure. Solid light-yellow compound **7b** was obtained (0.067 g, 52%). M.p. 92 °C. Found (%): C, 33.10; H, 3.00; N, 19.75; S, 14.99. $C_6H_7N_3O_4S$. Calculated (%): C, 33.18; H, 3.25; N, 19.35; S, 14.76. ^{1}H NMR ($(CD_3)_2SO$), δ: 3.62 (s, 2 H, SCH_2); 2.29 (s, 3 H, Me). IR, ν/cm^{-1}: 2920 (NH); 1712 (CO); 1564, 1552, 1360, 1352, 1344 (NO_2).

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