Nitropyrazoles
10.* *N*-Nitration of 3(5)-substituted pyrazoles

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A number of substituted *N*-nitropyrazoles were prepared by direct nitration of substituted pyrazoles. The dependence of the direction of nitration on the reaction conditions was studied.

Key words: substituted *N*-nitropyrazoles, *N*-nitration.

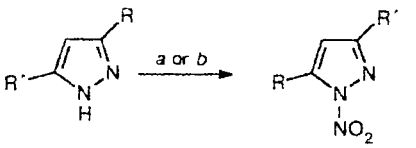
One of the most prominent discoveries in human biology and the biology of animals made in the last decade is the discovery of endogenic nitrogen monoxide, which plays an important role in the regulation of diverse physiological processes;[2,3] this is why nitric oxide was called the molecule of the year in 1992.[4] At present, a new line of research in medicinal chemistry is being vigorously developed; it is associated with the search for compounds able to generate NO as a result of biotransformations and thus exhibiting various biological activities: vasodilatory, antihypertensive, antithrombotic, *etc.*[2,3,5]

Previously, it has been shown in relation to *N*-nitropyrazole and some its *C*-methyl-substituted derivatives that *N*-nitropyrazoles are a new type of stable sources of NO that generate NO under the conditions of reduction including reduction by cysteine, which models the action of endogenic thiols. It follows from the preliminary results obtained[6] that the ease of liberation of NO depends on the structure of the particular *N*-nitropyrazole. An important role is played by steric factors: when the substituent is located close to the N—NO_2 fragment, elimination of NO is facilitated.

Systematic studies of the effect of the structure of *N*-nitropyrazoles on their ability to generate NO and on their biological activities are held up by the fact that the structures of known *N*-nitropyrazoles are not sufficiently diverse (see, for example, Refs. 7 and 8). The examples of *N*-nitropyrazoles in which the *C*-substituent and *N*-nitro group are located close to each other are especially few in number. In addition, *N*-nitration of 3,5-disubstituted asymmetrical pyrazoles has hardly been studied, and therefore it is difficult to evaluate the effects of particular substituents on the direction of *N*-nitration (at the N(1) or N(2) atom of the ring). The nitration of 3(5)-monosubstituted pyrazoles is directed almost in all cases (the exception is mentioned below) at the N atom, most remote from the substituent.[7,8]

The purpose of this work is to study the effects of substituents on the pathway of *N*-nitration of the ring and to synthesize new *N*-nitropyrazoles; attention is concentrated on the preparation of *N*-nitropyrazoles in which the *C*-substituent and *N*-nitro group are located at the neighboring atoms.

Scheme 1

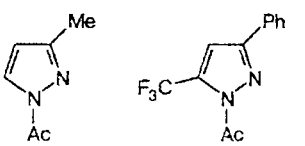


1, 4, 6, 8, 11, 15 **2, 5, 7, 9, 12, 16**

1: R = Me, R′ = H
4: R = CF_3, R′ = Ph
6: R = Me, R′ = Ph
8: R = Me, R′ = *p*-$MeOC_6H_4$
11: R = COOH, R′ = H
15: R = COOH, R′ = NO_2

2a: R = Me, R′ = H
2b: R = H, R′ = Me
5: R = CF_3, R′ = Ph
7: R = Me, R′ = Ph
9: R = Me, R′ = 3-NO_2-4-$MeOC_6H_3$
12: R = H, R′ = COOH
16: R = COOH, R′ = NO_2

Reagents and conditions. *a.* HNO_3+Ac_2O+AcOH, 20—25 °C, 2—3 h; *b.* $Cu(NO_3)_2 \cdot 3\ H_2O$+Ac_2O, 20—25 °C, 1—3 h.



3 **10**

* For Part 9, see Ref. 1.

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A known method for the preparation of *N*-nitropyrazoles involves treatment of *N*-unsubstituted pyrazoles with acetyl nitrate or trifluoroacetyl nitrate.[7,8] Only in these cases does *N*-nitration of the ring occur; the use of HNO_3 or $HNO_3+H_2SO_4$ mixtures leads to the formation of *C*-nitropyrazoles.[9] In the present study, we used two known sources of acetyl nitrate, *viz.*, a mixture of HNO_3 with Ac_2O in AcOH [8] and a mixture of $Cu(NO_2)_3$ with Ac_2O [10] (Scheme 1).

Previously, it has been reported[8,11] that *N*-nitration of 3(5)-methylpyrazole (**1**) with an excess of a mixture of HNO_3 with Ac_2O in AcOH yields 3-methyl-1-nitropyrazole (**2b**); when stoichiometric quantities of **1** and HNO_3 in $AcOH+Ac_2O$ are used, the reaction affords a mixture of 5-methyl-1-nitropyrazole (**2a**), nitropyrazole **2b**, and 1-acetyl-3-methylpyrazole (**3**). We found that the reaction with the $Cu(NO_3)_2 \cdot 3H_2O+Ac_2O$ system gives no nitro derivative **2b** at all; this reaction affords nitropyrazole **2a** and *N*-acetyl derivative **3**, which can be easily separated by column chromatography. These results confirm our data[7] on the effect of the presence (or absence) of a strong acid in the nitrating system on the direction of *N*-nitration in the pyrazole series. The use of an "acidic" mixture (excess $HNO_3+Ac_2O+AcOH$) results in nitration at the N(1) atom, whereas the nitration with a "non-acidic" system ($Cu(NO_3)_2 \cdot 3H_2O+Ac_2O$) occurs at the N(2) atom. Spectral characteristics of the resulting compounds are presented in Table 1. The signal for the H(3) proton in the ^1H NMR spectrum of compound **2a** is exhibited in a higher field, while the signal for the CH_3 protons is in a lower field than the signals for the H(5) and CH_3 protons in the spectrum of isomer **2b**. The ^{13}C NMR signal for the C(5) atom in *N*-substituted pyrazoles is

Table 1. Spectral characteristics of the compounds synthesized

Compound	Yield (%)	M.p. /°C	IR, ν/cm^{-1}	NMR, δ (J/Hz)	
				δ ^1H	δ ^{13}C
2a	32			2.64 (s, 5-Me)[a]; 6.39 (d, H(4), J = 1.1); 7.53 (d, H(3), J = 1.1)	14.05 (q, 5-Me, J = 132.1)[a]; 110.55 (dd, C(4), J = 179.5, 10.0); 139.55 (dq, C(5), J = 190.8, 5.0); 149.90 (dd, C(3), J = 9.3, 3.8)
2b	51	54		2.29 (s, 3-Me)[a]; 6.49 (d, H(4), J = 3.0); 8.47 (d, H(5), J = 3.0)	
3	13			2.58 (s, 3-Me)[a]; 2.26 (s, MeCO); 6.36 (d, H(4), J = 2.6); 8.16 (d, H(5), J = 2.7)	14.27 (q, 3-Me, J = 151.7)[a]; 20.15 (q, MeCO, J = 246.7); 107.73 (dd, C(4), J = 184.5, 19.2); 129.25 (dd, C(5), J = 180.5, 4.0); 154.16 (dd, C(3), J = 8.7, 3.6); 169.49 (s, CO)
5	75	94	1636, 1280 (N—NO_2)	7.49 (m, Ph)[a]; 7.86 (s, H(4)); 7.87 (m, Ph)	112.42 (dq, C(4), J = 185.6, 3.2)[a]; 119.61 (q, CF_3, J = 268.7); 129.86 (dq, C(5), J = 171.8, 4.9); 130.20 (m, Ph); 149.90 (s, C(3))
7	61	108	1612, 1260 (N—NO_2)	2.61 (s, 5-Me)[b]; 6.49 (s, H(4)); 7.39 (m, Ph); 7.80 (m, Ph)	14.28 (q, 5-Me, J = 144.8)[b]; 107.42 (dq, C(4), J = 209.6, 17.0); 128.69 (m, Ph); 140.05 (q, C(5), J = 7.2); 149.72 (d, C(3), J = 3.8)
9	91	—	1620, 1260 (N—NO_2); 1540, 1340 (C—NO_2)	2.72 (s, Me)[a]; 4.06 (s, MeO); 7.10 (s, H(4)); 7.48 (d, H(5'), J = 8.8); 8.20 (dd, H(6'), J = 8.7, 2.2); 8.34 (d, H(2'), J = 2.1)	14.33 (q, 5-Me, J = 144.8)[c]; 57.26 (q, MeO, J = 87.6); 107.85 (dq, C(4), J = 184.6, 17.0); 115.38 (dd, C(6'), J = 168.9, 5.2); 122.88 (d, C(2') J = 46.8); 132.51 (dd, C(5'), J = 205.2, 8.5); 141.39 (q, C(5), J = 6.4); 140.60 (d, C(3'), J = 238.4); 147.26 (d, C(3), J = 4.1); 153.27 (d, C(4'), J = 184.6)

(*to be continued*)

Table 1. (*continued*)

Compound	Yield (%)	M.p. /°C	IR, ν/cm^{-1}	NMR, δ(*J*/Hz) δ ^{1}H	NMR, δ(*J*/Hz) δ ^{13}C
10	75	77	1760 (C=O)	2.83 (s, MeCO)[a]; 7.50 (m, Ph); 7.66 (s, H(4)); 8.03 (m, Ph)	21.37 (q, MeCO, J = 131.3)[b]; 112.42 (dq, C(4), J = 185.6, 3.2); 118.75 (q, CF_3, J = 268.3); 133.24 (q d, C(5), J = 41.8, 6.6); 127.00 (m, Ph); 149.90 (dt, C(3), J = 46.5, 8.6); 169.70 (s, CO)
12	36	178 (decomp.)	1704 (COOH); 1628, 1288 (N—NO_2)	7.01 (d, H(4), J = 7.23)[c]; 8.89 (d, H(5), J = 7.23)	110.28 (dd, C(4), J = 185.9, 7.5);[c] 127.96 (dd, C(5), J = 204.9, 9.9); 143.96 (dd, C(3), J = 9.6, 3.8); 161.67 (s, COOH)
13	88	—	1616 (COO^-); 1629, 1284 (N—NO_2)	6.65 (d, H(4), J = 7.23)[c]; 8.61 (d, H(5), J = 7.23)	
14	92	102		3.95 (s, Me)[c]; 7.09 (H(4)); 8.90 (H(5))	
16	30	188 (decomp.)	1720 (COOH); 1636, 1264 (N—NO_2); 1540, 1332 (C—NO_2)	7.40 (s, H(4))[c]; 12.53 (br.s, COOH)	

Note. For compound 5: ^{14}N NMR, δ($MeNO_2$): −58.72 (NO_2); ^{15}N NMR, δ($MeNO_2$): −54.78 (NO_2); −80.60 (d, N(2), J = 1.1 Hz); −107.56 (N(1), J = 8.0, 3.0 Hz).
[a] In acetone-d_6. [b] In $CDCl_3$. [c] In DMSO-d_6.

known to be shifted upfield with respect to the signal for C(3).[1,12] The signal for the C(5) atom in the ^{13}C NMR spectrum of compound **2a** (dq, δ 139.55) is also manifested in a higher field than that of C(3) (dd, δ 149.90).

According to the data of ^{13}C NMR spectroscopy, of the two isomers that could be formed in the *N*-nitration of 3(5)-trifluoromethyl-5(3)-phenylpyrazole (**4**) with the $Cu(NO_3)_2 \cdot 3H_2O$+Ac_2O system, only 1-nitro-3-phenyl-5-trifluoromethylpyrazole (**5**) was obtained. In fact, the signal for the C(5) atom (δ 129.86), which is manifested in a higher field than the signal for C(3) (δ 149.90), is a doublet of quartets, characterizing the splitting of this signal at H(4) and CF_3. According to published data[7,8] that refer mostly to *C*-nitropyrazoles, it can be assumed that *N*-nitration of the pyrazole ring should involve the N atom that is far removed from the most electron-withdrawing group. In the case of pyrazole **4**, nitration follows a different pathway, which can be explained by steric restrictions, caused by the phenyl substituent, which apparently lies in the plane of the pyrazole ring. This point of view is confirmed by the experiment with 3,5-diphenylpyrazole; it does not react under the conditions of *N*-nitration of pyrazole **4**. The nitration at the N atom ($Cu(NO_3)_2 \cdot 3H_2O$+Ac_2O) of 3(5)-methyl-5(3)-phenylpyrazole (**6**) affords 1-nitro-5-methyl-3-phenylpyrazole (**7**); in the case of 3(5)-methyl-5(3)-(4-methoxyphenyl)pyrazole (**8**), mononitration of the phenyl ring occurs in parallel with *N*-nitration, *i.e.*, 5-methyl-3-(4-methoxy-3-nitrophenyl)pyrazole (**9**) is formed. It can be seen from the above examples that an aryl substituent prevents *N*-nitration of the neighboring N atom. The ^{13}C NMR spectrum of *N*-nitropyrazole **7** exhibits a quartet at δ 140.05 corresponding to the C(5) atom (splitting at the H atoms of the methyl group) and a doublet at δ 149.72 corresponding to C(3) (splitting at H(4)). The fact that in this nitrating system, along with *N*-nitration of pyrazole **8**, *C*-nitration of the phenyl ring occurs, is confirmed by the ^{1}H and ^{13}C NMR spectra and also by the IR spectrum, which contains peaks corresponding to the C—NO_2 and N—NO_2 groups (see Table 1).

It is noteworthy that when compound **4** is treated with another "non-acidic" mixture (NH_4NO_3+Ac_2O+CH_2Cl_2),[13] only 1-acetyl-5-phenyl-3-trifluoromethylpyrazole (**10**) is formed (in a yield of 85%), which is confirmed, most of all, by the presence of a signal corresponding to the *N*-acetyl group in its ^{1}H NMR spectrum as well as by the absence of absorption bands corresponding to the N—NO_2 group and by the presence of an absorption band due to the C=O group in its IR spectrum. The ^{13}C NMR spectrum of compound **10** contains peaks associated with the CO and CH_3 groups (see Table 1).

We also carried out experiments on *N*-nitration of pyrazolecarboxylic acid in acidic and non-acidic mixtures as sources of acetyl nitrates. Irrespective of the nitration conditions, pyrazole-3(5)-carboxylic acid (**11**) is converted into 1-nitropyrazole-3-carboxylic acid (**12**). In this case, the N atom, remote from the *C*-substituent, is attacked. According to the data of ^{13}C NMR spectroscopy for acid **12**, the signal for the C(5) atom (dq, δ 127.96) has a direct splitting constant at the hydrogen atom (^1J = 204.9 Hz), which is not observed for the signal corresponding to the C(3) atom (dd, δ 143.96) attached to the carboxyl group. The ^{15}N NMR spectrum exhibits signals corresponding to the nitrogen atom of the *N*-nitro group (δ −58.72), to N(2) (δ −80.04; d, J = 1.1 Hz), and to N(1) (δ −107.56; dd, J = 8.0 Hz, 3.0 Hz). Acid **12** is readily soluble in water and is stable in weakly acidic, neutral, and weakly alkaline media.

The Na salt of 1-nitropyrazole-3-carboxylic acid **13** can be precipitated from an aqueous solution by adding a 10-fold volume of THF. The signals of the corresponding H atoms in the ^1H NMR spectrum of salt **13** are markedly shifted upfield with respect to those in the spectrum of the initial acid **12** (see Table 1).

Esterification of acid **12** ($MeOH+SOCl_2$) yields methyl ester **14**.

Nitration of 5(3)-nitropyrazole-3(5)-carboxylic acid (**15**) affords *N*-nitro derivative **16**. As noted above, in the case of 3-nitropyrazoles, the attack of the electrophile is directed at the nitrogen atom that is most distant from the nitro group;[7,8] therefore, there are grounds to believe that it is actually 1,3-dinitropyrazole-5-carboxylic acid that was obtained from compound **15**.

Experimental

The ^1H NMR spectra of the reaction products were recorded on a Bruker WM-250 spectrometer (250 MHz); ^{13}C, ^{14}N, and ^{15}N NMR spectra were obtained on a Bruker AM-300 instrument (300 MHz). The chemical shifts are referred to $SiMe_4$ (^1H, ^{13}C) and $MeNO_2$ (^{14}N, ^{15}N). IR spectra were measured on a Specord M-80 spectrophotometer for pellets with KBr. The course of the reactions was monitored and the purity of the isolated products was checked by TLC on Silufol UV-254 plates.

3-Methyl-1-nitropyrazole (2b) was prepared by a procedure reported previously.[8]

5-Methyl-1-nitropyrazole (2a), 1-acetyl-3-methylpyrazole (3). A suspension of $Cu(NO_3)_2 \cdot 3H_2O$ (15 g, 0.062 mol) in 102 mL of Ac_2O was stirred for 1 h, and methylpyrazole **1** (0.061 mol) was added. The mixture was stirred for 3 h, poured into 200 mL water, and stirred for an additional 3 h. The product was extracted with chloroform (3×100 mL), and the organic layer was dried with anhydrous $MgSO_4$. The solvent was removed at a reduced pressure, and the residue was dissolved in 50 mL of CCl_4; then the solvent was removed once again, and the residue was chromatographed on a column (Silpearl, using a hexane—ethyl acetate mixture, 8 : 1, as the eluent) to give 2.5 g (32%) of compound **2a** and 1 g (13%) of compound **3**. Both compounds are oils.[8,10]

1-Nitro-3-phenyl-5-trifluoromethyl-, 5-methyl-1-nitro-3-phenyl-, and 3-(4-methoxy-3-nitrophenyl)-5-methyl-1-nitropyrazoles (5, 7, and 9). A suspension of $Cu(NO_3)_2 \cdot 3H_2O$ (3 g, 125 mmol) in 21 mL of Ac_2O was stirred for 1 h, and pyrazole **4** (5.5 mmol) was added. The mixture was stirred for 1.5 h, poured into 100 mL of water, and stirred for an additional 3 h. The precipitate was filtered off, washed with water, dried for 24 h in a vacuum desiccator over P_2O_5, and recrystallized from CCl_4 to give 1 g (75%) of compound **5**; MS (EI, 70 eV), *m/z*: 257 $[M]^+$, 211 $[M-NO_2]^+$. Found (%): C, 46.65; H, 2.38; $C_{10}H_6F_3N_3O_2$. Calculated (%): C, 46.70; H, 2.35.

Under the same conditions, pyrazole **6** was converted into compound **7** (61%); MS (EI, 70 eV), *m/z*: 203 $[M]^+$, 157 $[M-NO_2]^+$. Found (%): C, 59.25; H, 4.39. $C_{10}H_9N_3O_2$. Calculated (%): C, 59.11; H, 4.46.

N-nitration of pyrazole **8** (5.5 mmol) by $Cu(NO_3)_2 \cdot 3H_2O$ (5.4 g, 0.022 mol) in 50 mL of Ac_2O led to compound **9** (91%); MS (EI, 70 eV), *m/z*: 278 $[M]^+$, 232 $[M-NO_2]^+$. Found (%): C, 47.57; H, 3.56. $C_{11}H_{10}N_4O_5$. Calculated (%): C, 47.49; H, 3.62.

1-Acetyl-3-phenyl-5-trifluoromethylpyrazole (10). A suspension of NH_4NO_3 (1.35 g, 0.017 mol) in a mixture of Ac_2O (15 mL) with CH_2Cl_2 (30 mL) was stirred for 2 h, and pyrazole **4** (1 g, 4.8 mmol) was added. The mixture was stirred for 3 h, poured into 150 mL of water, and stirred for an additional 3 h. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3×80 mL). The combined organic extracts were washed with water (2×50 mL) and dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure, the residue was dissolved in 10 mL CCl_4, and the solvent was again removed. The resulting dry residue was recrystallized from hexane to give 1.03 g (85%) of compound **10**, MS (EI, 70 eV), *m/z*: 254 $[M]^+$. Found (%): C, 56.79; H, 3.52. $C_{12}H_9F_3N_2O$. Calculated (%): C, 56.70; H, 3.57.

1-Nitropyrazole-3-carboxylic acid (12), 1,3-dinitropyrazole-5-carboxylic acid (16). ***A.*** A suspension of $Cu(NO_3)_2 \cdot 3H_2O$ (6 g, 0.025 mol) in 42 mL of Ac_2O was stirred for 1 h, and pyrazolecarboxylic acid (0.011 mol) was added. The mixture was stirred for 3 h, poured into 150 mL of water, and stirred for an additional 3 h. The product was extracted with Et_2O (3×80 mL), and the organic layer was dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was dissolved in 10 mL of CCl_4; the solvent was removed once again, and the dry residue was recrystallized from CCl_4. The reaction of acid **11** gave 0.63 g (36%) of compound **12**, MS (EI, 70 eV), *m/z*: 157 $[M]^+$, 111 $[M-NO_2]^+$. Found (%): C, 30.55; H, 1.93. $C_4H_3N_3O_4$. Calculated (%): C, 30.58; H, 1.92. From acid **15**, 0.67 g (30%) of compound **16** was obtained. Found (%): C, 23.89; H, 0.92. $C_4H_2N_4O_6$. Calculated (%): C, 23.77; H, 1.00.

B. Compound **11** (1 g, 9 mmol) was dissolved in 10 mL of glacial acetic acid. 98% Nitric acid (0.9 mL, 0.02 mol) was added dropwise, the temperature being maintained between 0 and +5 °C. Then the mixture was cooled to −10 °C, and acetic anhydride (2.3 mL) was added dropwise. The mixture was stirred for 3 h at 0 to +5 °C, poured into 50 mL of water, and extracted with Et_2O (3×25 mL). The organic layer was washed with water (2×50 mL) and dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure, the residue was dissolved in 10 mL of CCl_4, the solvent was removed once again, and the residue was recrystallized from CCl_4 to give 0.47 g (33%) of compound **12**.

For the Na salt (**13**), found: Na, 12.85 (%). $C_4H_2N_3NaO_4$. Calculated: Na, 12.80 (%).

Methyl 1-nitropyrazole-3-carboxylate (14). Acid **12** (0.35 g, 0.0022 mol) was dissolved in 5 mL of anhydrous MeOH, and $SOCl_2$ (0.11 mL) was added dropwise. The mixture was stirred for 4 h and poured into 20 mL of water; the precipitate was filtered off, dried in a vacuum desiccator, and recrystallized from heptane to give 0.34 g (92%) of ester **14**. Found (%): C, 35.02; H, 3.02. $C_5H_5N_3O_4$. Calculated (%): C, 35.10; H, 2.95.

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