Nitropyrazoles
1. Synthesis, transformations, and physicochemical properties of nitro derivatives of 1*H*,4*H*-pyrazolo[4,3-*c*]pyrazole

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A method of synthesizing nitro derivatives of 1*H*,4*H*-pyrazolo[4,3-*c*]pyrazole is developed, and some of its transformations are studied. 3-Methyl-6-nitro-, 3-carboxy(methoxycarbonyl, carbamoyl)-6-nitro-, 3-amino-6-nitro-, 3-nitro-, 3,6-dinitro-, 1,4-diacetonyl-3,6-dinitro-, and 1*H*,4*H*-3-aminopyrazolo[4,3-*c*]pyrazoles were obtained from 1*H*,4*H*-3-methylpyrazolo[4,3-*c*]pyrazole. Unsubstituted 1*H*,4*H*-pyrazolo[4,3-*c*]pyrazole, the first member of this series, was obtained for the first time. The compounds prepared were characterized by ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR spectroscopy. NH-Acidity and basicity of the series of pyrazolo[4,3-*c*]pyrazoles synthesized is studied and the effect of the fused pyrazole ring on these properties is examined.

Key words: nitropyrazolo[4,3-*c*]pyrazoles; 1*H*,4*H*-aminopyrazolo[4,3-*c*]pyrazole; 1*H*,4*H*-pyrazolo[4,3-*c*]pyrazole; nitration; NH-acidity; basicity.

The interest in the chemistry of nitropyrazoles is due largely to the use of these compounds as valuable semiproducts for the synthesis of biologically active compounds, including pyrazole-containing antibiotics, as well as dyestuff.[1,2] The presence of a nitro group in the pyrazole ring considerably enlarges the possibility of functionalization of various types of pyrazoles,[1] e.g., by kine-substitution of an N-nitro group.[1]

The basic regularities of the introduction of a nitro group into the pyrazole ring and the properties of nitropyrazoles have been studied mainly for substances with one pyrazole ring.[1,2] Little is known about the methods of preparation and properties of the nitro derivatives of systems with two or more pyrazole rings. The fused systems pyrazolopyrazoles, where the mutual influence of the pyrazole rings must be the greatest, are of particular interest.

The aim of the present work is the preparation and study of the transformations of nitro derivatives of 1*H*,4*H*-pyrazolo[4,3-*c*]pyrazole as well as the synthesis of unsubstituted 1*H*,4*H*-pyrazolo[4,3-*c*]pyrazole, which has not been previously described.

Though several methods for the synthesis of pyrazolo[4,3-*c*]pyrazoles are known,[3—13] the least substituted compound was required for the introduction of nitro groups and for further functionalization, including NH functionalization. Hence, we chose 1*H*,4*H*-3-methylpyrazolo[4,3-*c*]pyrazole (**1**) as the starting material. Its synthesis is based on the intramolecular cyclization of 4-diazo-3,5-dimethylpyrazole (**2**),[8] which was, in turn, prepared by diazotization of 3,5-dimethylpyrazole (Scheme 1).

We found that the nitration of **1** occurred smoothly at room temperature in a mixture of nitric and trifluoroacetic acids, which is unexpected for N-unsubstituted pyrazoles.* The nitro group entered the unsubstituted ring, and 1*H*,4*H*-3-methyl-6-nitropyrazolo[4,3-*c*]pyrazole (**3**) was formed with a 66 % yield (Scheme 1).

The oxidation of pyrazolopyrazole (**3**) with sodium dichromate in sulfuric acid led to the formation of the corresponding carboxylic acid (**4**), which is the key compound for further transformations. It should be noted that attempts to obtain the carboxylic acid devoid of a nitro group by the direct oxidation of compound **1** either with sodium dichromate under acidic conditions or with potassium permanganate under neutral or basic conditions led to the decomposition of the bicyclic system. The presence of a nitro group in the ring apparently prevents the oxidation of the pyrazolo[4,3-*c*]pyrazole system. Carboxylic acid **4** was readily esterified by methanol in the presence of thionyl chloride. On treatment with aqueous ammonia, the methyl ester (**5**) gave amide (**6**), the Hoffmann rearrangement of which led to 1*H*,4*H*-

† Deceased March 18, 1989.

*Pyrazole is nitrated at the more active position 4 under drastic conditions: in a mixture of nitric and sulfuric acids at 110 °C for 48 h. This is related to its nitration in the protonated form.[1]

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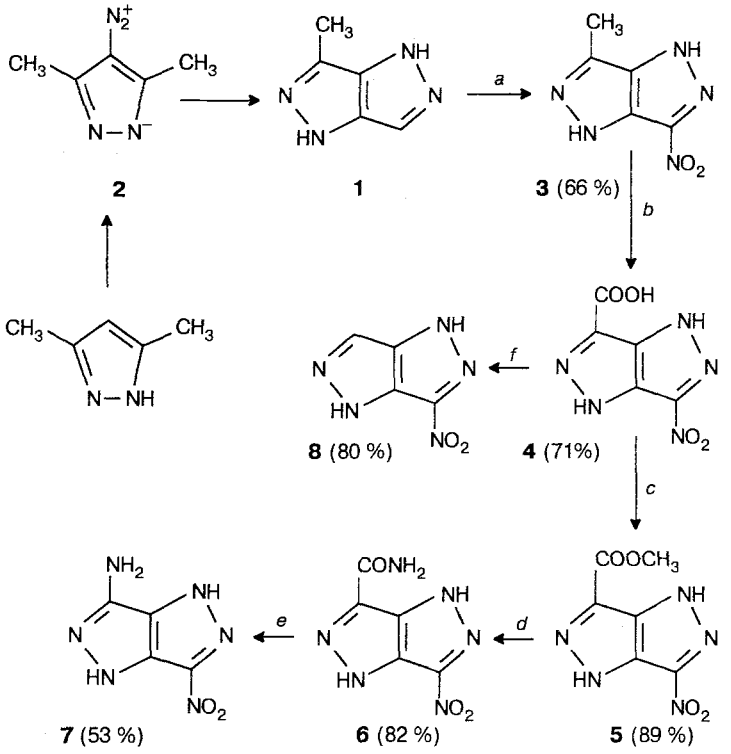
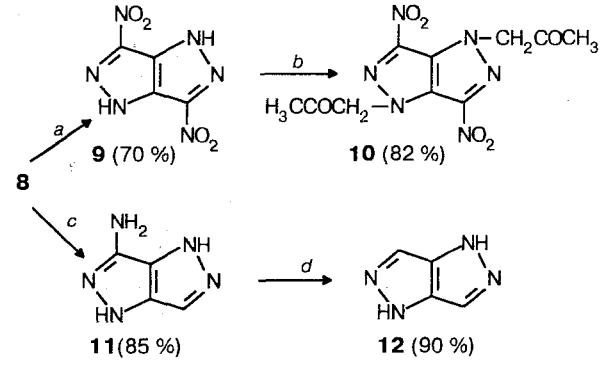
Scheme 1



Reactants and conditions:
a: HNO_3—CF_3COOH, 20 °C, 20 h;
b: $Na_2Cr_2O_7 \cdot 2H_2O$—H_2SO_4, 20—30 °C, 1.5 h;
c: CH_3OH—$SOCl_2$, 60 °C, 4 h;
d: 1. aqueous NH_3, 20 °C, 20 h; 2. 20 % H_2SO_4;
e: 1. NaOH—H_2O—Br_2, 60 °C, 2 h; 2. 20 % H_2SO_4;
f: 1. aqueous NH_3, 190 °C 4 h; 2. 20 % H_2SO_4.

Scheme 2



Reactants and conditions:
a: HNO_3—H_2SO_4, 20 °C, 4 days; *b*: 1. KOH—H_2O;
2. $BrCH_2COCH_3$—dichloroethane, cat. Bu_4NBr, 20°C, 1 h;
c: N_2H_4—Raney-Ni, 70 °C, 11 h;
d: 1. CH_3OH—HCl—BuONO, 0—5 °C, 1 h;
2. CH_3OH, 50 °C, 0.5 h.

3-amino-6-nitropyrazolo[4,3-*c*]pyrazole (**7**), that is to the replacement of the carboxylic group with an amino group.

We have found conditions for smooth decarboxylation of acid **4** (heating at 190 °C in the presence of aqueous ammonia in an autoclave) to form 1*H*,4*H*-3-nitropyrazolo[4,3-*c*]pyrazole (**8**). The obtained mononitro derivative **8** is a convenient starting material for the preparation of several other pyrazolo[4,3-*c*]pyrazole derivatives.

For example, it can be nitrated at an unsubstituted pyrazole ring with the formation of a dinitroderivative, 1*H*,4*H*-3,6-dinitropyrazolo[4,3-*c*]pyrazole (**9**) (Scheme 2).

The presence of nitro groups in both rings of pyrazolopyrazole **9** makes it easy to alkylate under mild conditions at both NH-fragments. This was shown for the reaction with bromoacetone which gives products that are valuable for further functionalization (due to the active methylene group and the carbonyl group). Dinitropyrazolopyrazole **9** was smoothly and regiospecifically alkylated under the PTC conditions in a basic medium (H_2O—$C_2H_4Cl_2$, in the presence of a quaternary ammonium salt) with the formation of only one isomer, in which acetonyl groups are the farthest from the nitro groups, namely, 1,4-diacetonyl-3,6-dinitropyrazolo[4,3-*c*]pyrazole (**10**). The application of reversed phase-transfer catalysis[14] with 2,4,6-collidine-N-oxide as the carrier of bromoacetone from the organic phase into the aqueous phase also led to the formation of compound **10**, but with a somewhat lesser yield (60 % instead of 82 %). It is worth noting that in the absence of the catalyst the alkylation of the dianion of compound **9** by bromoacetone did not take place, and the bromoacetone gradually decomposed. The alkylation of the dipotassium salt of compound **9** under homogeneous conditions in methanol proceeds with much greater difficulty (50—60 °C, 10 h, the yield of product **10** is 50 %).

Nitrocompounds of aromatic and heterocyclic series are convenient precursors of amines. In the pyrazolo[4,3-*c*]pyrazole series this was exemplified by the reduction of nitro compound **8**: the action of hydrazine hydrate in the presence of Raney nickel gave the corresponding amine, 1*H*,4*H*-3-aminopyrazolo[4,3-*c*]pyrazole (**11**). Conventional deamination[15] of amine **11**, diazotization by butyl nitrite with subsequent reduction of the diazo compound by methanol, led to the first member of the series, unsubstituted 1*H*,4*H*-pyrazolo[4,3-*c*]pyrazole (**12**), with an almost quantitative yield.

The synthesized pyrazolo[4,3-*c*]pyrazoles **3**–**12**, including the first member of the series, **12**, were obtained for the first time. Their structure was determined by combined use of ^1H, ^{13}C, ^{14}N, and ^{15}N NMR spectroscopy (Table 1) and was confirmed by IR spectroscopy, mass-spectrometry, and elemental analyses (Table 2). ^1H NMR spectra only point to the presence or the

Table 1. ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR spectral data (δ, *J*/Hz) for pyrazolo [4,3-*c*]pyrazoles (DMSO-d_6)

Compound	^{1}H NMR	^{13}C NMR					^{14}N NMR	^{15}N NMR
		C(3)	C(4)	C(5)	C(6)	Other C atoms		
2	2.34 (s, 3-CH_3) 7.43(s, H(6)) 11.67 (bs, NH)	126.78 (q, J = 7.0)	138.22 (q, d, J = 3.1; 3.4)	139.12 (d, J = 7.7)	117.75 (d, J = 192.2)	12.13 (q, 3-CH_3; J = 127.6)	—	−65.98 (q, N-2; $J_{N-CH_3(3)}$ = 1.4)
3	2.43 (s, 3-CH_3) 12.25 (bs, NH) 12.88 (bs, NH)	128.75 (q, J = 6.8)	139.94 (q, J = 2.7)	136.77 (s)	130.30 (s)	11.51 (q, 3-CH_3; J = 130.5)	—	—
4	13.50 (bs, NH)	125.28 (s)	139.44 (s)	137.67 (s)	131.08 (s)	161.92 (s, 3-CO_2H)	—	—
5	3.90 (s, 3-CO_2CH_3) 14.48 (bs, NH)	124.16 (s)	138.90 (s)	137.23 (s)	130.29 (s)	51.82 (q, 3-CH_3; J = 148.6); 160.41 (q, CO_2H; J = 3.6)	−25.7(s, 6-NO_2)	—
6	7.47 (s, NH_2) 7.77 (s, NH_2) 13.96 (bs, NH) 14.35 (bs, NH)	128.86 (s)	138.94 (s)	137.19 (s)	130.63 (s)	162.12 (s, $CONH_2$)	−22.5 (s, 6-NO_2)	−280.12 (t, NH_2; J = 89.1)
7	—	149.40 (s)	128.88 (t, J = 3.1)	129.67 (s)	147.77 (s)	—	−25.3 (s, 6-NO_2)	−279.82 (t, NH_2; J = 59.5)
8*	7.75 (s, H(6)) 12.05 (bs, NH)	137.12 (s)	129.96 (d, J = 4.5)	140.85 (d, J = 9.3)	120.38 (d, J = 197.6)	—	−22.3 (s, 3-NO_2)	—
9	14.00 (bs, NH)	138.17 (s)	132.38 (s)	132.38 (s)	138.17 (s)	—	−25.3 (s, 3.6-NO_2)	—
10	2.30 (s, CH_3) 5.52 (s, CH_2)	136.43 (t, J = 0.9)	131.60 (t, J = 3.1)	131.60 (t, J = 3.1)	136.43 (t, J = 0.9)	26.57 (q, CH_3; J = 128.2) 61.72 (t, CH_2; J = 144.6) 200.70 (q.t, CO; J = 4.3; 6.0)	−27.1 (s, 3.6-NO_2)	—
11**	4.95 (bs, 3-NH_2) 7.35 (s, H-6) 10.58 (bs, NH) 12.03 (bs, NH)	137.81 (s)	131.61 (d, J = 6.7)	139.64 (d, J = 9.4)	116.12 (d, J = 191.7)	—	—	−81.70(N-5) −99.70 (N-2) −193.00 (N-4) −243.63 (N-1) −338.94 (NH_2)
11***	—	136.70 (s)	128.34 (s)	138.69 (s)	115.99	—	—	−211.70 (N-5) −218.02 (N-2) −229.81 (N-4) −263.70 (N-1) −318.60 (NH_2)
12*	8.07 (s, H-3,6)	119.06 (d, J = 201.7)	137.95 (s)	137.95 (s)	119.06 (d, J = 201.7)	—	—	—

*Spectra of the diamine salt of **8**. **In CD_3OD ***In DMSO-d_6 + CF_3COOH.

absence of protons in a cycle but do not confirm the structure. For the majority of compounds, one or two signals (depending on the symmetry of the molecule) corresponding to NH-protons of the cycle, were detected in the interval 12–14 ppm. Aromatic CH-protons resonate at 7.30–8.10 ppm. In the case of amide **6**, two signals at 7.47 and 7.77 ppm corresponding to the amide group were detected. The exact structure of the obtained compounds was determined on the basis of the analysis of ^{13}C, ^{14}N, and ^{15}N chemical shifts and of the $^{13}C—^{1}H$ and $^{15}N—^{1}H$ spin-coupling constants. The presence of carbon-containing substituents (CH_3, COX) in a cycle followed from the respective signals in the ^{13}C NMR spectra, while the presence of a nitro group in a molecule was indicated both by the broadening of the signals for carbon atoms bearing nitro group due to the quadrupole relaxation of nitro-group ^{14}N nuclei and by the chemical shifts in the ^{14}N NMR spectra (see Table 1).

The ^{13}C NMR data allowed us to unambiguously determine the structure of diketone **10** as a 1,4-diacetyl derivative. Thus, the signal at 131.60 ppm in the proton-decoupled ^{13}C NMR spectrum was assigned to the carbon atoms common to both rings, and the broadened signal at 136.43 ppm, to the carbon atoms bearing a nitro group. Two triplets with δ 131.60 ($^{3}J_{C—CH_2}$ =

Table 2. Characteristics of pyrazolo[4,3-*c*]pyrazoles (**3—12**)

Compound*	*T* initial decomposition /°C** (crystallization solvent)	IR, ν/cm^{-1}	Found / Calculated (%)			Molecular formula
			C	H	N	
3	266 (CH_3OH)	3180—3100 (NH); 1536,1376 (NO_2)	35.68 / 35.94	2.98 / 3.02	41.74 / 41.91	$C_5H_5N_5O_2$
4	260 (H_2O)	3600 (OH); 3200—2760 (NH); 1696 (CO); 1536,1376 (NO_2)	—	1.76 / 1.53	—	$C_5H_3N_5O_4$
5	279 (CH_3OH)	3300—2880 (NH); 1696 (CO); 1520,1372 (NO_2)	33.95 / 34.13	2.30 / 2.39	33.80 / 33.17	$C_6H_5N_5O_4$
6	348 (H_2O)	3400—2800 (NH); 1648 (CO); 1556,1372 (NO_2)	30.26 / 30.62	2.10 / 2.06	43.24 / 42.25	$C_5H_4N_6O_3$
7	141 (dioxane)	3200—2800 (NH); 1550,1357 (NO_2)	28.65 / 28.57	2.49 / 2.40	—	$C_5H_4N_6O_3$
8	306 (CH_3OH)	3200—2700 (NH); 1505,1360 (NO_2)	31.28 / 31.39	2.04 / 1.98	—	$C_4H_3N_5O_2$
9	295 (CH_3OH—H_2O)	3100—2500 (NH) 1516,1384 (NO_2)	24.22 / 24.25	1.01 / 1.02	42.40 / 42.42	$C_4H_2N_6O_4$
10	259 (CH_3CN)	2992 (CH); 1728 (CO) 1540,1392 (NO_2)	38.47 / 38.71	3.20 / 3.25	26.88 / 27.09	$C_{10}H_{10}N_6O_6$
11	187 (CH_3OH)	3400—2900 (NH)	39.10 / 39.02	4.15 / 4.09	—	$C_4H_5N_5$
12	240 (CH_3OH)	3200—2700 (NH)	44.56 / 44.43	3.70 / 3.73	—	$C_4H_4N_4$

*All compounds have a molecular ion in the EI mass spectra.
All synthesized compounds decompose without melting except **5 (melting with decomposition).

3.1 Hz) and 136.43 ($^4J_{C-CH_2}$ = 0.9 Hz) were observed in the ^{13}C NMR spectrum recorded without proton-decoupling but under the conditions of selective decoupling with the ^{14}N nuclei of the nitro group. This testifies to the location of a nitro group at position 3 and not 2 relative to the acetonyl fragment in compound **10**. Using compound **1** as an example we determined the location of the protons at the nitrogen atoms of the pyrazole ring. In the selective polarization transfer from the protons of the CH_3 group to ring nitrogen atoms, spin-coupling of the protons of the CH_3 group (J = 1.4 Hz) was observed with the "pyridine" type nitrogen atom (δ −65.98) in the ^{15}N NMR spectrum. The signal corresponding to the "pyrrole" nitrogen atom resonated at −217.38 ppm. Thus, the CH_3 group is at the carbon atom next to the pyridine nitrogen atom (N(2)), *i.e.*, the atom that carries no proton. Hence, the proton is located at the nitrogen atom N(1) remote from the C—CH_3 fragment. The signals for the nitrogen atoms of the second pyrazole ring at 67.10 ppm and −206.04 ppm are broadened, which testifies to the possible migration of the proton from N(4) to N(5).

Using the spectrometric method we determined NH-acidity and basicity of a representative series of pyrazolo[4,3-*c*]pyrazoles (Table 3*). On the basis of these data one can follow the mutual influence of variously substituted rings in the system. For example, the acidity of 1*H*,4*H*-3-nitropyrazolo[4,3-*c*]pyrazole **8** (pK_{a_1} 7.58) is two orders of magnitude higher than that of monocyclic 3-nitropyrazole (pK_a 9.81), which indicates a substantial electron-acceptor effect of the second, fused pyrazole ring. A similar pattern is observed in the case when the second ring bears an amino or nitro group **7**, **9**. The acidity of dinitroderivative **9** (pK_{a_1} 5.39) is nearly the same as that of 3,4-dinitropyrazole (pK_a 5.48), that is, the influence of the fused nitropyrazole ring is practically the same as that of the 4-NO_2 group. Using compound **9** as an example it is seen that an ionized nitropyrazole ring exhibits electron-acceptor properties, though to a lesser degree than an unsubstituted pyrazole cycle (*cf.* pK_a for compounds **7**, **8**, and nitropyrazole).

On the other hand, the fused pyrazole ring exerts an electron-acceptor effect on the basicity of the other

*For convenience of comparison, Table 3 gives data for several monocyclic pyrazoles.

Table 3. pK_a, pK_{BH^+}, and UV characteristics of pyrazolo[4,3-*c*]pyrazoles (H_2O, 20 °C)

Compound	λ_{max}/nm(log ε)				pK_{a1}	pK_{a2}	pK_{BH^+}
	Neutral molecule	Monoanion	Dianion	Protonated form			
7	333 (3.82)	368 (3.95)		301 (3.65)	8.50		3.02
8	329 (3.85)	373 (4.08)	435 (4.07)		7.58	12.60	−1.09
9	330 (4.11)	379 (4.18)	435 (4.39)		5.39	8.54	
11	279 (3.69)			289 (3.80)			3.60
12	262 (3.74)			274 (3.76)			1.29
Pyrazole	211 (3.61)*			217 (3.67)*	14.21**		2.48**
3-Nitro-pyrazole	261 (3.79)***	316 (3.86)***			9.81***		−4.66**
3,4-Dinitro-pyrazole	267 (3.73)***	312 (3.77)***			5.48***		
3-Amino-pyrazole							4.11**

*See ref. 16. **See ref. 17. ***See ref. 18.

pyrazole ring (pK_{BH^+} 1.29 for unsubstituted pyrazole **12** and 2.48 for pyrazole). A similar effect for the second pyrazole ring is observed in the case of amine **11** (pK_{BH^+} 3.60 for compound **11** and 4.11 for 3-aminopyrazole). The second nitropyrazole moiety affects the basicity of nitropyrazole more strongly. The basicity of nitropyrazole **8** is three orders of magnitude less than that of pyrazole (pK_{BH^+} of compound **8** is −1.09). However, unlike acidity, where the effect of the second ring is comparable to the effect of a NO_2 group (see above), the decrease in the basicity of **8** compared to that of 3-nitropyrazole (pK_{BH^+} −4.66) is not so great. Table 3 shows that the presence of the second pyrazole ring leads to a bathochromic shift of the absorption maximum by ~60 nm compared to monocyclic pyrazoles.

Using ^{15}N NMR spectroscopy we could determine the protonation site of 1*H*,4*H*-3-aminopyrazolo[4,3-*c*]pyrazole **11**. The ^{15}N NMR spectrum of compound **11**, which was recorded in DMSO-d_6, contained five signals with δ −81.70 (N(5)), −99.70 (N(2)), −193.00 (N(4)), −243.63(N(1)), and −338.94 (NH_2). The signals at −81.70 and −193.00 are broadened, which may be attributed to the absence of a rigidly fixed position for the NH-proton in the unsubstituted pyrazole ring (as in compound **1**). On addition of trifluoroacetic acid, the signals for N(5) and N(2) shifted the most (to −211.70 and −218.02 ppm, respectively), which attests to the protonation of the nitrogen atoms of the pyrazole ring rather than those of the amino group, as was observed previously[19] for various 3-aminopyrazoles. The other signals are shifted less, which may be due to purely electronic influence of the protonated N(2) and N(5) (see Table 1).

Experimental

^1H NMR spectra were recorded on a Bruker WM-250 spectrometer (operation frequency, 250 MHz). ^{13}C, ^{14}N, and ^{15}N NMR spectra were obtained with a Bruker AM-300 spectrometer (operation frequency, 300 MHz). Chemical shifts (δ) are given relative to Me_4Si (^1H, ^{13}C) and CH_3NO_2 (^{14}N, ^{15}N). High-field chemical shifts have a negative sign. IR spectra were recorded on a Specord M-80 spectrometer in KBr pellets. UV spectra were recorded on a Specord UV-VIS spectrometer, and mass spectra were obtained with a Varian MAT CH-6 spectrometer. Basicity and acidity constants were determined with an accuracy of ±0.02 pK_a units. The reactions were monitored and the purity of the substances was checked by TLC on Silufol UV-254 plates. The temperature of the initiation of decomposition was determined by differential thermal analysis, the heating rate was 5 deg · min^{-1}.

1*H*,4*H*-3-Methyl-6-nitropyrazolo[4,3-*c*]pyrazole (3). Compound **1**[8] (16 g, 0.13 mol) was dissolved in CF_3COOH (80 mL), HNO_3 (d = 1.5, 25 mL) was added, and the mixture was stirred for 5 h at 20—25 °C and kept overnight. Then it was poured into ice-water (5×), and the precipitate was filtered, washed with cold water, and dried in air. The yield of **3** was 14.5 g (66 %).

1*H*,4*H*-3-Carboxy-6-nitropyrazolo[4,3-*c*]pyrazole (4). Compound **3** (13.5 g, 0.081 mol) was dissolved in conc. H_2SO_4 (150 mL), $Na_2Cr_2O_7$ $2H_2O$ (28.5 g, 0.096 mol) was added over a period of 1 h at a temperature below 30 °C, and the mixture was stirred for 1.5 h at this temperature and worked up as described above. The yield of acid **4** was 11.5 g (71 %).

1*H*,4*H*-3-Methoxycarbonyl-6-nitropyrazolo[4,3-*c*]pyrazole (5). Thionyl chloride (2.6 mL) was added with vigorous stirring to a suspension of acid **4** (2.37 g, 0.012 mol) in CH_3OH (50 mL) at 20 °C. The mixture was refluxed for 4 h, cooled, and concentrated to 10 mL, and the precipitate was filtered. The yield of ester **5** was 2.25 g (89 %).

1*H*,4*H*-3-Carbamoyl-6-nitropyrazolo[4,3-*c*]pyrazole (6). Ester **5** (2 g, 0.009 mol) was dissolved in aqueous ammonia (100 mL) and left overnight. It was concentrated to half its volume and acidified by 20 % H_2SO_4 to pH 1. The precipitate was filtered, washed with water, and dried in air. The yield of amide **6** was 1.52 g (82 %).

1*H*,4*H*-3-Amino-6-nitropyrazolo[4,3-*c*]pyrazole (7). Bromine (1.47 g, 0.009 mol) was added to a solution of NaOH (1.84 g, 0.046 mol) in water (20 mL) at 0—5 °C and stirred for 10 min. Powdered amide **6** (1.32 g, 0.07 mol) was added at 0—5 °C to the obtained solution of hypobromite. The mixture was heated to 60 °C and kept at this temperature for 2 h. Then it was cooled, acidified by 20 % H_2SO_4 to pH 1, and extracted with ethyl acetate (2×20 mL). The extracts were dried with $MgSO_4$ and evaporated. The yield of amine **7** was 0.6 g (53 %).

1*H*,4*H*-3-Nitropyrazolo[4,3-*c*]pyrazole (8). A suspension of acid **4** (9 g, 0.045 mol) in 200 mL of aqueous ammonia was heated in an autoclave for 4 h at 190 °C, cooled, and evaporated to dryness. The diammonium salt of compound **8** (6.83 g, 80 %) was obtained and converted into nitro compound **8** by acidification with 20 % H_2SO_4.

1*H*,4*H*-3-Dinitropyrazolo[4,3-*c*]pyrazole (9). The diammonium salt of compound **8** (6.83 g, 0.037 mol) was dissolved in conc. H_2SO_4 (22 mL), then fuming nitric acid (32 mL) was added. The solution was kept for 4 days at ~20 °C, then it was poured into cold water (5×). The precipitate was filtered, washed with cold water, and dried in air. The yield of dinitro compound **9** was 5 g (70 %).

1*H*,4*H*-3-Diacetonyl-3,6-dinitropyrazolo[4,3-*c*]pyrazole (10). Compound **9** was added to a solution of KOH (1.81 g, 0.032 mol) in 36 mL of H_2O and stirred for 10 min. Bu_4NBr (5.22 g, 0.016 mol) and bromoacetone (3 mL, 0.036 mol) in dichloroethane (21 mL) were added to the obtained suspension of dipotassium salt, and vigorously stirred for 1 h at 20—25 °C. The precipitate was filtered and dried in air. The yield of product **10** was 4.16 g (82 %).

1*H*,4*H*-3-Aminopyrazolo[4,3-*c*]pyrazole (11). Freshly prepared Raney nickel (from 2 g of alloy) and hydrazine hydrate (5.5 g) were added to a suspension of nitro compound **8** (3.06 g, 0.02 mol) in ethanol (200 mL). A bulky precipitate of dihydrazinium salt of compound **8** setted out. The reaction mixture was boiled for 9 h with stirring, then more catalyst (from 1 g of alloy) was added. The reaction mixture was boiled for 2 h, then cooled, and the catalyst was filtered and the filtrate was evaporated to dryness. The yield of **11** was 2.03 g (85 %).

1*H*,4*H*-Pyrazolo[4,3-*c*]pyrazole (12). A solution of amine **11** (0.51 g, 0.004 mol) was saturated with dry HCl at 0—5 °C. Then 2 mL of butyl nitrite was added and the mixter was stirred for 1 h at 0—5 °C. Then it was poured into 200 mL of ether, the precipitate was filtered off, dissolved in methanol (40 mL), and boiled under reflux under nitrogen for 30 min. The solution was taken to dryness to give 0.4 g (90 %) of product **12**.

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