Nitropyrazoles
18.* Synthesis and transformations of 5-amino-3,4-dinitropyrazole

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A method of preparation of 5-amino-3,4-dinitropyrazole (**1**) from 3(5)-methyl-5(3)-nitro- and 3(5)-methyl-4,5(3)-dinitropyrazoles was developed, the key step of which was the Hofmann rearrengement of nitro- and dinitropyrazolecarboxamides. The protonation of 5-amino-3,4-dinitropyrazole was studied by spectral methods (UV spectroscopy, NMR spectroscopy). In spite of low basicity of the amino group, compound **1** undergoes N-arylation, N-nitration, and annulation reactions with formation of dinitropyrazolo[5,1-*a*]pyrimidine derivatives and hitherto unknown dinitroimidazo[1,2-*b*]pyrazole derivatives. Diazotization of **1** leads to 5-diazo-3,4-dinitropyrazole (**19**), which exists in the form of the internal salt. Some reactions of this compound were studied and the formation of the corresponding 5-halogeno(azido)-3,4-dinitropyrazoles under the action of the halide and azide ion was shown. Dinitropyrazolo-[5,1-*c*][1,2,4]triazine and 7-hydroxydinitro-4,7-dihydropyrazolo[5,1-*c*][1,2,4]triazine derivatives were obtained by the action of active methylene compounds on the betaine **19**.

Key words: pyrazole, dinitropyrazole, 5-amino-3,4-dinitropyrazole, 5-diazo-3,4-dinitropyrazole, the Hofmann rearrangement, N-arylation, N-nitration, annulation, imidazo[1,2-*b*]-pyrazole, pyrazolo[5,1-*a*]pyrimidine, diazotization, active methylene compounds, pyrazolo-[5,1-*c*][1,2,4]triazine, dihydropyrazolo[5,1-*c*][1,2,4]triazine.

Earlier,[2] we have reported on the preparation and some properties of 5-amino-3,4-dinitropyrazole (**1**), which is an important intermediate in the synthesis of pyrazole nitro derivatives, however, experimental details have not been given. Recently,[3] we have published the synthesis of pyrazole **1** based on the transformation of the product of *cine*-substitution of an N-nitro group in 1,3,4-trinitropyrazole by the azide ion, *viz.*, 5-azido-3,4-dinitropyrazole. An alternative method for the synthesis of pyrazole **1** and results of detailed study on its properties and reactions are reported in the present study.

In our opinion, aminodinitropyrazole **1** can be obtained using the developed earlier method for the synthesis of aminodinitropyrazoles[4,5] the key step of which is the Hofmann rearrangement of the corresponding nitropyrazolecarboxamides. Let us consider in detail the method of synthesis based on the use of commercially available 3-methyl-5-nitropyrazole **2a** (Scheme 1). Oxidation of the methyl group in pyrazole **2a** smoothly proceeds under the action of sodium dichromate in concentrated sulfuric acid at elevated temperature to afford 3-nitropyrazole-5-carboxylic acid **3a** in high yield. This method of oxidation of the methyl group is general and makes it possible to synthesize also 4-halogeno-substituted nitropyrazolecarboxylic acids **3b,c** obtained earlier by other procedures, *viz.*, by nitration of the corresponding 4-halogenopyrazole-3-carboxylic acids in oleum.[6] It should be noted that nitropyrazolecarboxylic acids **3a—c** are important intermediates for the synthesis, therefrom, of a number of compounds with various biological activities.[7,8] We developed a method of reduction of the nitro group with hydrazine in water in the presence of the Raney nickel resulting for the first time in amino acids (**4a,b**) nonsubstituted at the nitrogen atom of the ring. The classical methods of reduction using hydrazine in ethanol do not lead to the desired product because of low solubility of hydrazinium salts of compound **3** in ethanol. The method of catalytic reduction over the Raney nickel or Pd/C in various organic solvents is also inapplicable because amines that formed are not soluble in the solvents pointed and are adsorbed on the catalyst that leads to considerable decrease in its activity.

Carboxylic acid **3a** smoothly undergoes esterification with methanol in the presence of thionyl chloride to give methyl ester **5**, which gives amide **6** in high yield under the action of aqueous ammonia.

We studied the Hofmann rearrangement of amide **6**. It was found that upon the reaction in water a mixture of

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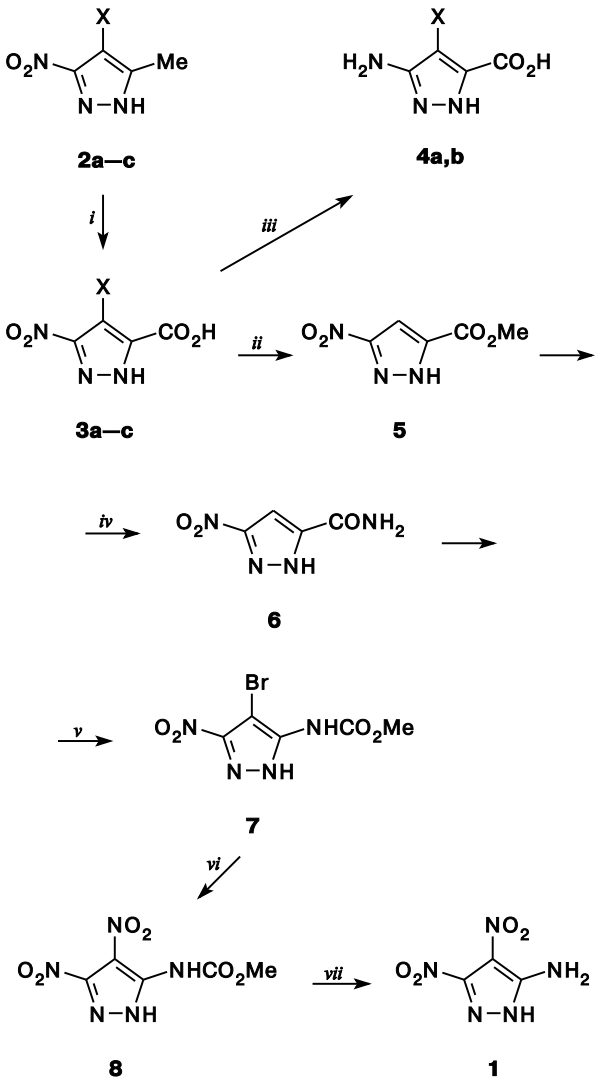
Scheme 1



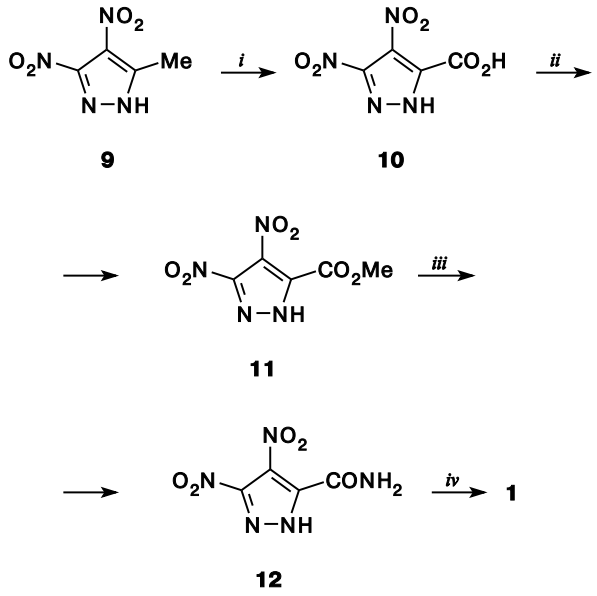
X = H (**a**), Cl (**b**), Br (**c**)

i. Na_2CrO_7/H_2SO_4, 60 °C, 8 h; *ii*. $SOCl_2$, MeOH, Δ, 8 h; *iii*. N_2H_4/H_2O, Ni Raney, 60 °C, 8 h; *iv*. $NH_3 \cdot H_2O$, 25 °C, 8 h; *v*. 1) KOH, Br_2, 1 h, 2) HCl; *vi*. H_2SO_4/HNO_3, 25 °C, 2 h; *vii*. 1) KOH/H_2O, 60 °C, 8 h, 2) H_2SO_4.

compounds formed containing no 3(5)-amino-5(3)-nitropyrazole. Under milder conditions (in methanol, at −30 °C), the formation of the carbamate group was accompanied by simultaneous bromination at the free position 4 of the pyrazole ring. Bromonitrocarbamate **7** undergoes nitrodebromination with a sulfuric-nitric acid nitrating mixture under mild conditions with formation of 3,4-dinitrocarbamate **8** in moderate yield. The removal of the methoxycarbonyl group was carried out by alkaline hydrolysis using the procedure that was employed by us for the synthesis of 4-amino-3,5-dinitropyrazole,[9] which is isomeric to dinitropyrazole **1**.

Yet another possible version of the synthesis of pyrazole **1** can be based on methylpyrazole containing two nitro groups in the ring, *viz.*, 3,4-dinitro-5-methylpyrazole (**9**),[10] as the starting compound (Scheme 2).

Scheme 2



i. 1) KOH, $KMnO_4$, 60 °C, 8 h, 2) H_2SO_4; *ii*. $SOCl_2$, MeOH, Δ, 8 h; *iii*. $NH_3 \cdot H_2O$, 25 °C, 8 h; *iv*. 1) NaOH, Br_2, 50 °C, 2 h, 2) HCl.

In fact, we found that dinitropyrazole **9** can be smoothly oxidized with potassium permanganate in water to form dinitro acid **10**. We synthesized the corresponding dinitro ester **11** and amide **12** using the same procedures as for mononitro ester **5** and amide **6**. It turned out that dinitro amide **12** is more appropriate compound for the synthesis of the target aminopyrazole **1**, since, in contrast to mononitro amide **6**, in this case the Hofmann rearrangement proceeds in water with formation of aminopyrazole **1** in high yield and the alternative path *via* intermediate dinitro carbamate **8** is not required.

Thus, we developed the general procedure for the synthesis of aminonitro- and aminodinitropyrazoles (see also Refs 4, 5, 11), the key step of which is the Hofmann rearrangement of nitro- and dinitropyrazolecaboxamides.

The structures of all compounds mentioned were established by IR and NMR spectroscopy and confirmed by data from mass spectrometry and elemental analysis. The presence of hydrogen-containing substituents followed from the ^1H NMR spectra, whereas the structures of nitrogen-carbon framework were determined based on the chemical shifts in the ^{13}C, $^{14(15)}N$ NMR spectra and $^{13}C—^1H$ and $^{15}N—^1H$ coupling constants through different number of bonds. The presence of one or several nitro groups in the molecule leads to broadening of the signals

for carbon atoms bound to the nitro group in the ^{13}C NMR spectra due to the quadrupole effect of the ^{14}N atom of the nitro group. Therefore, the ^{13}C NMR spectra were recorded under the conditions of heteronuclear triple resonance $^{13}C\{^1H,^{14}N\}$, *viz.*, the observation of ^{13}C nuclei at the broadband decoupling with ^1H and the selective decoupling with ^{14}N nuclei of the nitro groups.[12,13] It allowed us to observe a narrow signal for the carbon atom C—NO_2, long-range $^{13}C—^1H$ coupling constants and, generally, to correlate the signal for the nitro group in the $^{14(15)}N$ NMR spectrum with the signals for the carbon atoms in the ^{13}C NMR spectrum.

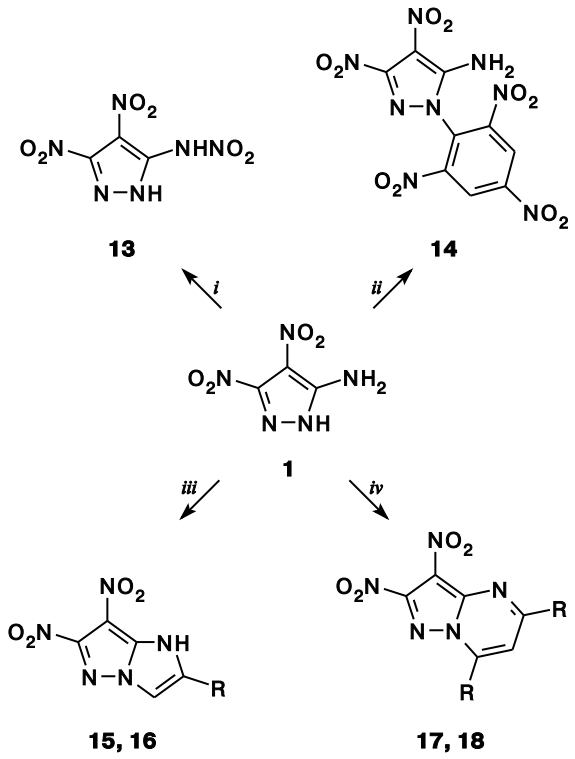
Let us consider in detail the elucidation of the structure of compound **1**. Only one signal for the carbon atom assigned to that bound to the NH_2 group is observed at δ 148.72 in the standard ^{13}C NMR spectrum. The $^{13}C\{^1H,^{14}N\}$ NMR spectrum contained additionally two signals for the carbon atoms bound to the NO_2 groups at δ 150.21 and 109.08. It is known[14,15] that in the ^{13}C NMR spectra of 3(5),4-dinitropyrazoles the order of the signals for carbon atoms (C—NO_2) is as follows: C(3) > C(5) > C(4). Therefore, one can suppose that pyrazole **1** exists, at least in the solution, mainly in the form of 5-amino-3,4-dinitropyrazole.

The protonation site of pyrazole **1** was established using ^{15}N NMR spectroscopy. Five signals at δ −22.05 (C(4)NO_2), −23.30 (C(3)NO_2), −108.32 (N(2)), −210.37 (N(1)), and −315.96 (t, NH_2, J = 91.9 Hz) were observed in the ^{15}N NMR spectrum of compound **1**. The signals for the N(2) atom displaced to the greatest degree (by 84 ppm) upon addition of concentrated sulfuric acid (δ −192.64, −193.25 (N(1), N(2))). This is evidence of the protonation of the pyrazole ring, as in the case of other 3(5)-aminopyrazoles,[16] rather than the amino group, despite the presence of two nitro groups in the ring.

The acidity and basicity constants of pyrazole **1** in water at 20 °C were determined spectrophotometrically. The values obtained (pK_a = 6.34, pK_{BH^+} = −7.12) indicate that pyrazole **1** as the NH acid is similar to carbonic acid (pK_{a_1} = 6.35) and, despite the presence of the amino group, is extremely weak base similar to 3,4-dinitropyrazole (pK_{BH^+} = −8.06). Since protonation of pyrazole **1** proceeds at the nitrogen atom of the ring, the "intrinsic" basicity of the amino group is even lower in this compound.

Despite the reduced basicity of the amino group, aminodinitropyrazole **1** smoothly undergoes nitration under the action of acetyl nitrate in trifluoroacetic acid to produce nitramine **13** (Scheme 3). This fact follows from the ^{15}N NMR spectrum: the signals at δ −40.57 and −207.82 corresponding to the NH—NO_2 fragment are observed. Similar direction of the reaction toward the nitration of the amino group has already been observed by us in the case of nitration of 3(5)-amino-4-nitropyrazole. Apparently, this is determined by the protonation of the nitrogen ring atom of compound **1**.[5]

Scheme 3



R = Me (**15**,**18**), Ph (**16**), H (**17**)

i. HNO_3/Ac_2O, 0 °C, 2 h; *ii*. LiOMe/MeOH, picryl chloride, 25 °C, 2 h; *iii*. NaOH/DMF, $BrCH_2COR$, Δ, 2—4 h; *iv*. $MeCO_2H$, $CH_2(COR)_2$, Δ, 8 h.

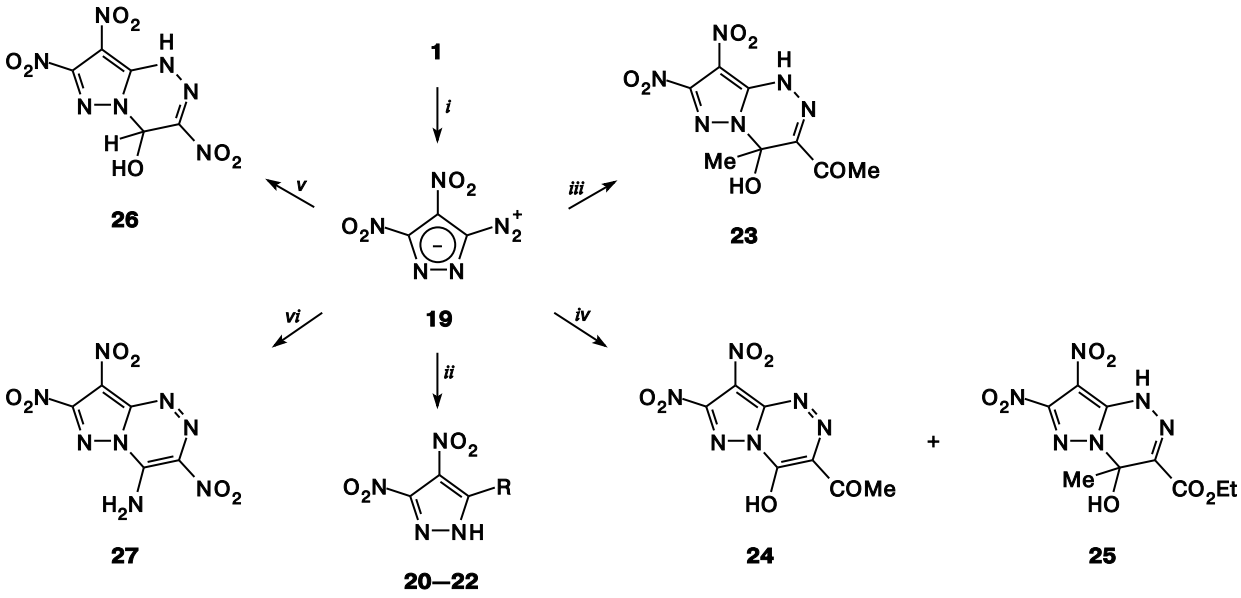
Arylation of the lithium salt of pyrazole **1** with picryl chloride affords 5-amino-3,4-dinitro-1-picrylpyrazole (**14**).

The presence of a vicinal NH fragment and the NH_2 group in pyrazole **1** allows annulation of heterocycles. Thus reaction of compound **1** with α-bromo ketones in an alkaline medium results in hitherto unknown imidazo-[1,2-*b*]pyrazole dinitroderivatives **15** and **16**. Dinitropyrazole **1** also smoothly reacts with the simplest β-dicarbonyl compounds, *viz.*, malonaldehyde acetal and acetylacetone, under conditions of acid catalysis to yield pyrazole[5,1-*a*]pyrimidine dinitroderivatives **17** and **18**.

We succeeded in diazotization of aminodinitropyrazole **1** without application of special procedures despite low basicity of the amino group. As in the case of 4-amino-3,5-dinitropyrazole,[9] which is isomeric to compound **1**, the corresponding diazodinitropyrazole **19** is formed as a result of the treatment of pyrazole **1** with sodium nitrite in 20% H_2SO_4 at 0—5 °C; it occurs in the form of betaine (Scheme 4). This is a quite stable compound, its decomposition begins at 110 °C.

Reactions of diazopyrazole **19** with nucleophiles, *viz.*, the halide and azide ions and some carbanions, were studied by us in detail. Diazopyrazole **19** reacts with nucleophiles in a conventional manner, *viz.*, either azocoupling

Scheme 4



R = Br (**20**), N_3 (**21**), Cl (**22**)

i. 20% $H_2SO_4/NaNO_2$, 0—5 °C, 2 h; *ii*. **20**: 40% HBr/KBr, 0—5 °C, 1 h, 25 °C, 7 h; **21**: NaN_3/H_2O, 0—5 °C, 1 h; **22**: HCl/CuCl, 0—5 °C, 1 h, 25 °C, 7 h; *iii*. 1) $NaCH(COMe)_2/H_2O$, 25 °C, 10 h, 2) H_2SO_4; *iv*. 1) $NaCH(CO_2Et)COMe/H_2O$, 25 °C, 10 h, 2) H_2SO_4; *v*. $NaC(CHO)_2NO_2/H_2O$, 25 °C, 10 h, 2) H_2SO_4; *vi*. 1) $NaCH(CN)NO_2/H_2O$, 25 °C, 2 h, 2) H_2SO_4.

or nucleophilic substitution of the diazo group takes place. Thus the corresponding dinitropyrazoles **20** and **21** are formed under the action of the bromide and azide ions. In the case of the chloride ion, addition of CuCl is required for the substitution of the diazo group (see Scheme 4).

Azocoupling of diazopyrazole **19** with active methylene carbonyl compounds resulted in dinitropyrazolo-[5,1-*c*][1,2,4]triazines **23—27** (see Scheme 4). The formation of compounds **24** and **25** corresponding to two directions of cyclization is observed. It should be noted that under the reaction conditions aromatization of the ring occurs not in all cases, which follows from the presence of the signals for both the OH (δ 6.8—8.0), and NH groups (δ 12—13) in the ^{1}H NMR spectrum. Mass spectra shows intensive peaks of the ions $[M^+ - H_2O]$ of the corresponding aromatization products of compounds **23**, **24**, and **26**.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200, Bruker WM-250, Bruker AC-300, and Bruker DRX-500 instruments at 295 K (if other temperature is not pointed). The ^{1}H and ^{13}C chemical shifts are referred to $SiMe_4$, the chemical shifts of ^{15}N are referred to $MeNO_2$, high-field chemical shifts are given with the minus sign. IR spectra were measured on a Specord M-80 instrument in KBr pellets, UV spectra were recorded on a Specord UV—Vis instrument, mass spectra were obtained on Kratos MS-30 and Finnigan MAT INCOS 50 mass spectrometers (direct sample inlet, electron impact, ionization energy of 70 eV). The reaction course and purity of synthesized compounds were monitored by TLC on Silufol UV-254. Elemental analysis was carried out on a Perkin Elmer Series II 2400 instrument.

5-Amino-3,4-dinitropyrazole (1). ***A.*** Carbamate **8** (10 g, 0.043 mol) was added to a solution of KOH (7.23 g, 0.13 mol) in H_2O (100 mL). The reaction mixture was stirred for 7 h at 60—70 °C, cooled to ~20 °C, and acidified with 20% H_2SO_4 to pH 2—3. It was extracted with ethyl acetate (3×50 mL), the extract was dried with $MgSO_4$, and the solvent was removed *in vacuo*. The product was recrystallized from H_2O. The yield was 5 g(67%).

B. Bromine (3.1 mL, 0.06 mol) was added dropwise to a solution of NaOH (12 g, 0.3 mol) in H_2O (100 mL) at 0—5 °C, then amide **12** (10 g, 0.05 mol) was added portionwise and the reaction mixture was stirred for 40 min at 0—5 °C. Then it was heated to 55—60 °C and kept for 2 h, cooled to 10 °C and acidified with concentrated HCl to pH 2—3. The precipitate that formed was filtered off, washed with water, and recrystallized from H_2O. The yield was 5.4 g (62%). M.p. 197—199 °C (with decomp.) (*cf.* Ref. 3). ^{13}C NMR ($(CD_3)_2CO$) (*cf.* Ref. 3), δ: 109.80 (t, C(4), J = 4 Hz); 148.65 (C(5)); 150.21 (C(3)). ^{15}N NMR ($(CD_3)_2CO$) (*cf.* Ref. 3), δ: −315.96 (t, NH_2, J = 91.9 Hz); −210.37 (N(1)); −108.32 (N(2)); −23.30 ($C(3)NO_2$); −22.05 ($C(4)NO_2$). ^{15}N NMR (H_2SO_4 (75%) + $(CD_3)_2SO$ (25%)), δ: −322.48 (NH_2); −193.25, −192.64 (N(1), N(2)); −38.22 ($C(3)NO_2$); −29.87 ($C(4)NO_2$). UV, λ/nm (ε): H_2O 356 (6290); NaOH 409 (5900); H_2SO_4 332 (2992).

3-Nitropyrazole-5-carboxylic acids 3 (general procedure). Nitropyrazole **2** (0.18 mol) was dissolved in concentrated H_2SO_4

(300 mL) and $Na_2Cr_2O_7 \cdot 2H_2O$ (53 g, 0.27 mol) was added dropwise to this solution, temperature being maintained at 60—65 °C. The reaction mixture was kept at this temperature for 8 h, poured into ice (1 kg), extracted with ethyl acetate (3×250 mL). The organic layer was washed with water, dried with $MgSO_4$, the solvent was removed *in vacuo*, and the residue was recrystallized from H_2O.

3-Nitropyrazole-5-carboxylic acid (3a). The yield was 25 g (88%), m.p. 174—175 °C. Found (%): C, 30.88; H, 2.09; N, 26.86. $C_4H_3N_3O_4$. Calculated (%): C, 30.58; H, 1.92; N, 26.75. ^{1}H NMR ($(CD_3)_2SO$), δ: 14.6 (br.s, 1 H, OH); 10.6 (br.s, 1 H, NH); 7.25 (s, 1 H, H(4)). ^{13}C NMR ($(CD_3)_2SO$), δ: 159.3 (CO); 156.2 (C(3)); 137.4 (C(5)); 104.5 (d, C(4), J = 188.97 Hz). ^{14}N NMR ($(CD_3)_2SO$), δ: −19.54 (C(3)NO_2). IR, ν/cm^{-1}: 1696 (CO); 1536, 1336 (NO_2). MS, m/z: 157 $[M]^+$.

4-Chloro-3-nitropyrazole-5-carboxylic acid (3b). The yield was 22.41 g (65%), m.p. 189—190 °C. Found (%): C, 25.24; H, 1.10; Cl, 18.63; N, 22.05. $C_4H_2ClN_3O_4$. Calculated (%): C, 25.08; H, 1.05; Cl, 18.51; N, 21.94. ^{13}C NMR ($(CD_3)_2SO$), δ: 158.52 (CO); 151.28 (C(3)); 134.61 (C(5)); 107.81 (C(4)). IR, ν/cm^{-1}: 1725 (CO); 1536, 1340 (NO_2). MS, m/z: 193, 191 (1 : 3) $[M]^+$.

4-Bromo-3-nitropyrazole-5-carboxylic acid (3c). The yield was 24.21 g (57%), m.p. 201—202 °C. Found (%): C, 20.55; H, 1.03; Br, 33.92; N, 17.97. $C_4H_2BrN_3O_4$. Calculated (%): C, 20.36; H, 0.85; Br, 33.86; N, 17.81. ^{13}C NMR ($(CD_3)_2SO$), δ: 158.67 (CO); 153.17 (C(3)); 136.14 (C(5)); 92.29 (C(4)). IR, ν/cm^{-1}: 1708 (CO); 1560, 1296 (NO_2). MS, m/z: 235, 237 (1 : 1) $[M]^+$.

3-Aminopyrazole-5-carboxylic acids 4 (general procedure). Hydrazine hydrate (10 g, 0.2 mol) was added to a solution of nitro acid **3a,b** (0.08 mol) in H_2O (200 mL), the solution was heated to 60 °C, and freshly prepared Raney Ni was slowly added over 3 h. The reaction mixture was kept at this temperature for 3 h, then cooled, the solids were filtered off, and the solution was acidified with conc. HCl to pH 4. The precipitate that formed was filtered off, recrystallized from water, and dried at 100 °C for 4 h.

3-Aminopyrazole-5-carboxylic acid (4a). The yield was 7.6 g (75%), m.p. 245—246 °C. Found (%): C, 38.00; H, 4.05; N, 33.23 $C_4H_5N_3O_2$. Calculated (%): C, 37.80; H, 3.97; N, 33.06. ^{13}C NMR ($(CD_3)_2SO$) , δ: 162.15 (CO); 152.80; 138.29; 92.30. IR, ν/cm^{-1}: 1690 (CO); 1535, 1329 (NO_2). MS, m/z: 127 $[M]^+$.

3-Amino-4-chloropyrazole-5-carboxylic acid (4b). The yield was 8.43 g (55%), m.p. 287—288 °C. Found (%): C, 30.09; H, 2.71; Cl, 22.25; N, 26.12. $C_4H_4ClN_3O_2$. Calculated (%): C, 29.74; H, 2.50; Cl, 21.95; N, 26.01. ^{13}C NMR ($(CD_3)_2SO$), δ: 160.92 (CO); 151.22; 132.33; 95.45. IR, ν/cm^{-1}: 1708 (CO); 1560, 1296 (NO_2); 840 (CCl). MS, m/z: 163, 161 (1 : 3) $[M]^+$.

Methyl nitropyrazole-5-carboxylates (general procedure). Acid **4a** (**10**) (0.10 mol) was dissolved in MeOH (100 mL) and $SOCl_2$ (8 mL, 0.11 mol) was added dropwise. The reaction mixture was refluxed for 3 h, the solvent was removed *in vacuo* and the products were used without additional purification for subsequent tranformations.

Methyl 3-nitropyrazole-5-carboxylate (5). The yield was 16.42 g (96%), m.p. 135—136 °C (H_2O) (*cf.* Ref. 8: m.p. 138 °C). Found (%): C, 35.21; H, 3.04; N, 24.77. $C_5H_5N_3O_4$. Calculated (%): C, 35.10; H, 2.95; N, 24.56. ^{1}H NMR ($(CD_3)_2SO$), δ: 14.83 (br.s, 1 H, NH); 7.35 (s, 1 H, H(4)); 3.88 (s, 3 H, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 158.28 (q, CO, J = 4.2 Hz); 155.82 (d, C(3), J = 5.1 Hz); 135.65 (d, C(5), J = 5.8 Hz); 104.47 (d, C(4), J = 189.64 Hz); 52.48 (q, Me, J = 148.25 Hz). ^{14}N NMR ($(CD_3)_2SO$), δ: −22.90 (C(3)NO_2). IR, ν/cm^{-1}: 1712 (CO); 1532, 1344 (NO_2); 1232 (COOMe). MS, m/z: 171 $[M]^+$.

Methyl 3,4-dinitropyrazole-5-carboxylate (11). The yield was 19.66 g (91%), m.p. 59—60°C (H_2O). Found (%): C, 26.43; H, 2.57; N, 24.46. $C_5H_4N_4O_6 \cdot 0.5\ H_2O$. Calculated (%): C, 26.68; H, 2.24; N, 24.89. ^{1}H NMR ($(CD_3)_2CO$), δ: 4.32 (s, 3 H, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 156.24 (CO); 145.73 (C(3)); 130.34 (C(5)); 127.8 (C(4)), 53.48 (CH_3). IR, ν/cm^{-1}: 1720 (CO); 1525, 1328 (NO_2). MS, m/z: 216 $[M]^+$.

Nitropyrazole-5-carboxamides (general procedure). Ester **5** (**11**) (0.08 mol) was added to 25% aqueous ammonia (200 mL) at 20 °C, the reaction mixture was stirred until complete dissolution and kept for 24 h. The solvent was removed *in vacuo*, the residue was suspended in H_2O (20 mL) and acidified with 20% H_2SO_4 to pH ~1. The suspension was stirred for an additional 30 min, the precipitate was filtered off, washed with H_2O, and dried in air.

3-Nitropyrazole-5-carboxamide (6). The yield was 10.61 g (85%), m.p. 244 °C (H_2O). Found (%): C, 31.11; H, 2.84; N, 36.02. $C_4H_4N_4O_3$. Calculated (%): C, 30.78; H, 2.58; N, 35.86. ^{1}H NMR ($(CD_3)_2SO$), δ: 14.66 (br.s, 1 H, NH); 8.16 (s, 1 H), 7.75 (s, 1 H, $CONH_2$); 7.56 (s, 1 H, H(4)). ^{13}C NMR ($(CD_3)_2SO$), δ: 158.97 (CO); 155.86 (C(3)); 139.54 (C(5)); 101.84 (d, C(4), J = 188.0 Hz). IR, ν/cm^{-1}: 1690, 1672 (CO); 1525, 1350 (NO_2). MS, m/z: 156 $[M]^+$.

3,4-Dinitropyrazole-5-carboxamide (12). The yield was 14.47 g (90%), m.p. 187—188 °C (EtOH). Found (%): C, 24.10; H, 1.55; N, 34.90. $C_4H_3N_5O_5$. Calculated (%): C, 23.89; H, 1.50; N, 34.83. ^{1}H NMR ($(CD_3)_2SO$), δ: 8.35 (br.s, 2 H, $CONH_2$). ^{13}C NMR ($(CD_3)_2SO$), δ: 157.5 (CO); 147.3 (C(3)); 137.5 (C(5)); 129.4 (C(4)). IR, ν/cm^{-1}: 1690, 1672 (CO); 1535, 1340 (NO_2). MS, m/z: 201 $[M]^+$.

Methyl *N*-(4-bromo-3-nitropyrazol-5-yl)carbamate (7). Bromine (1.3 mL, 0.025 mol) was added dropwise to a solution of KOH (5.25 g, 0.094 mol) in MeOH (50 mL) at −30 °C, then amide **6** (2.1 g, 0.013 mol) was added portionwise, and the mixture was stirred for 30 min at this temperature. Then it was heated to 55 °C and kept for 1 h, cooled to ~20 °C, the solvent was removed *in vacuo*, the residue was suspended in H_2O (15 mL) and acidified with conc. HCl to pH ~3. The precipitate that formed was filtered off, washed with H_2O, and dried in air. The yield was 1.2 g (35%), m.p. 201 °C (MeOH). Found (%): C, 22.90; H, 2.06; Br, 30.37; N, 21.36. $C_5H_5BrN_4O_4$. Calculated (%): C, 22.66; H, 1.90; Br, 30.15; N, 21.14. ^{1}H NMR ($(CD_3)_2SO$), δ: 14.0 (br.s, 1 H, NH); 9.5 (br.s, 1 H, CONH); 3.75 (s, 3 H, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 154.25 (CO); 151.30 (C(3)); 138.81 (C(5)); 83.52 (C(4)); 52.69 (q, Me, J = 147.65 Hz). IR, ν/cm^{-1}: 1690 (CO); 1525, 1328 (NO_2); 1208 (COOMe). MS, m/z: 264, 266 (1 : 1) $[M]^+$.

Methyl *N*-(3,4-dinitropyrazol-5-yl)carbamate (8). Nitric acid (d = 1.5 g cm^{-3}) (2 mL, 0.048 mol) was added to a solution of carbamate **7** (2 g, 7.5 mmol) in 92.5% H_2SO_4 (d = 1.826 g cm^{-3}) (15 mL, 0.24 mol) at 25—35 °C, and the mixture was stirred for 2 h at this temperature, then it was poured onto ice (60 g). The precipitate that formed was filtered off, washed with water, and dried in air. The yield was 1.2 g (69%), m.p. 188—190 °C (EtOH). Found (%): C, 26.30; H, 2.26; N, 30.58. $C_5H_5N_5O_6$. Calculated (%): C, 25.98; H, 2.18; N, 30.30. ^{1}H NMR ($(CD_3)_2SO$), δ: 3.76 (s, 3 H, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 153.35 (CO);

150.30 (C(3)); 149.25 (C(5); 130.20 (C(4)); 52.51 (q, Me, J = 150.1 Hz). IR, ν/cm^{-1}: 1700 (CO); 1560, 1360 (NO_2); 1232 (COOMe). MS, m/z: 231 $[M]^+$.

3,4-Dinitropyrazole-5-carboxylic acid (10). 3,4-Dinitro-5-methylpyrazole **9** (51.6 g, 0.3 mol) was added to a solution of KOH (16.8 g, 0.3 mol) in H_2O (850 mL), the mixture obtained was heated to 60 °C, $KMnO_4$ (124 g, 0.78 mol) was added portionwise at this temperature. Then the reaction mixture was kept for an additional 5 h at 60 °C, cooled, acidified with 20% H_2SO_4 to pH 2—3, extracted with ethyl acetate (4×100 mL). The organic layer was dried with $MgSO_4$, the solvent was removed *in vacuo*, and the residue was recrystallized from 50% aqueous ethanol. The yield was 47.3 g (78%), m.p. 194 °C (with decomp.). Found (%): C, 23.64; H, 1.12; N, 27.81. $C_4H_2N_4O_6$. Calculated (%): C, 23.77; H, 1.00; N, 27.72. ^{13}C NMR (CD_3CN), δ: 155.20 (CO_2H); 148.0 (C(3)); 130.10 (C(5)); 128.0 (C(4)). IR, ν/cm^{-1}: 3150 (NH); 1725 (CO); 1572, 1339 (NO_2). MS, m/z: 202 $[M]^+$.

5-Nitramino-3,4-dinitropyrazole (13). Nitric acid (d = = 1.5 g cm^{-3}) (3.3 mL, 0.08 mol) was added dropwise to a suspension of compound **1** (0.79 g, 0.005 mol) in CF_3CO_2H (5 mL) at 0 °C. Ac_2O (1 mL, 0.01 mol) was added to the solution that formed, this mixture was stirred for 2 h at 0—2 °C. The precipitate that formed was filtered off, washed with water, and dried in air. The yield was 0.7 g (69%), decomp. temp. 123 °C. Found (%): C, 16.68; H, 1.10; N, 38.69. $C_3H_2N_6O_6$. Calculated (%): C, 16.52; H, 0.92; N, 38.54. ^{13}C NMR ($(CD_3)_2SO$), δ: 149.23 (C(3)); 135.03 (C(5)); 117.42 (C(4)). ^{15}N NMR ($(CD_3)_2SO$), δ: −207.82, −187.42 (N(1)), N—NO_2); −40.57 (N—NO_2); −27.37 (C(3)NO_2, C(4)NO_2). IR, ν/cm^{-1}: 3152, 3132, 2940 (NH); 1560, 1376, 1344 (NO_2). MS, m/z: 218 $[M]^+$.

5-Amino-3,4-dinitro-1-(2,4,6-trinitrophenyl)pyrazole (14). A solution of LiOMe in MeOH (1 M, 2.9 mL) and picryl chloride (0.79 g, 3 mmol) were added to a solution of pyrazole **1** (0.5 g, 2.9 mmol) in MeOH (30 mL), the mixture obtained was kept for 24 h at ~20 °C. The organic solvent was removed *in vacuo*, the residue was crystallized from 50% aqueous ethanol. The yield was 0.8 g (72%), m.p. 168—169 °C. Found (%): C, 28.40; H, 1.13; N, 29.34. $C_9H_4N_8O_{10}$. Calculated (%): C, 28.14; H, 1.05; N, 29.17. ^{1}H NMR ($(CD_3)_2CO$), δ: 9.47 (s, 2 H, H(3′), H(5′)); 8.11 (br.s, 2 H, NH_2). ^{13}C ($(CD_3)_2CO$), δ: 151.88 (C(3)); 150.40 (C(2′), C(6′)); 150.20 (C(4′)); 148.88 (C(5)); 127.52 (t, C(1′), J = 7.0 Hz); 126.40 (dd, (C(3′), C(5′), J = 160.0 Hz, J = 5.0 Hz); 109.70 (t, C(4), J = 3.5 Hz). ^{15}N NMR ($(CD_3)_2CO$), δ: −312.43 (t, NH_2, J = 93.2 Hz); −227.46 (N(1)); −109.47 (N(2)); −26.01, −25.0 (C(3)NO_2, C(4)NO_2); −23.07, −22.25 ($(NO_2)_{Pic}$). IR, ν/cm^{-1}: 3160, 3128 (NH); 1530, 1376, 1350 (NO_2). MS, m/z: 384 $[M]^+$.

Dinitroimidazo[1,2-*b*]pyrazoles (general procedure). Sodium hydroxide (0.42 g, 10.5 mmol) was added to a solution of pyrazole **1** (10 mmol) in methanol (30 mL), the mixture obtained was stirred for 30 min, then the solvent was removed *in vacuo*. The precipitate was dissolved in DMF (30 mL), and an α-bromoketone (12 mmol) was added to the solution. The mixture was kept for 2 h at 140—145 °C, cooled and poured into water (150 mL). It was extracted with ethyl acetate (3S40 mL), the organic layer was washed with water, dried with $MgSO_4$, and the solvent was removed *in vacuo*.

2-Methyl-6,7-dinitroimidazo[1,2-*b*]pyrazole (15). The yield was 1.48 g (70%), decomp. temp. 201 °C (MeOH—H_2O). Found (%): C, 34.30; H, 2.47; N, 33.31. $C_6H_5N_5O_4$. Calculated (%): C, 34.13; H, 2.39; N, 33.17. ^{1}H NMR ($(CD_3)_2SO$), δ: 12.40 (br.s, 1 H, NH); 7.58 (s, 1 H, H(3)); 2.48 (s, 3 H, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 150.10; 134.44; 122.22 (d, J = 200 Hz); 110.40 (dq, J = 11.4 Hz, J = 6.7 Hz); 106.96; 10.16 (q, Me, J = 131.2 Hz). IR, ν/cm^{-1}: 1516, 1344 (NO_2). MS, m/z: 211 $[M]^+$.

6,7-Dinitro-2-phenylimidazo[1,2-*b*]pyrazole (16). The yield was 1.61 g (59%), decomp. temp. 224 °C (DMF—H_2O). Found (%): C, 48.60; H, 2.66; N, 25.95. $C_{11}H_7N_5O_4$. Calculated (%): C, 48.36; H, 2.58; N, 25.63. ^{1}H NMR ($(CD_3)_2SO$), δ: 13.85 (br.s, 1 H, NH); 8.58 (s, 1 H, H(3)); 7.90 (m, 2 H, H_{Ph}); 7.48 (m, 3 H, H_{Ph}). ^{13}C NMR ($(CD_3)_2SO$), δ: 150.14; 135.91; 135.00; 129.20 (d, J = 162.3 Hz); 128.84 (d, J = 161.3 Hz); 127.64; 125.96 (d, J = 160.6 Hz); 110.52; 106.73 (d, J = 205.3 Hz). IR, ν/cm^{-1}: 1520, 1340 (NO_2). MS, m/z: 273 $[M]^+$.

Dinitropyrazolo[1,5-*a*]pyrimidines (general procedure). Malonaldehyde bis(dimethyl acetal) or acetylacetone (3 mmol) was added to a suspension of pyrazole **1** (3 mmol) in 2 M HCl (6 mL) at 50—60 °C. The reaction mixture was kept at this temperature for 1 h, then it was cooled to ~25 °C. the precipitate that formed was filtered off, washed with H_2O, and dried over P_2O_5.

2,3-Dinitropyrazolo[1,5-*a*]pyrimidine (17). The yield was 0.53 g (91%), m.p. 146 °C (MeOH). Found (%): C, 34.80; H, 1.53; N, 33.71. $C_6H_3N_5O_4$. Calculated (%): C, 34.46; H, 1.45; N, 33.49. ^{1}H NMR ($(CD_3)_2SO$), δ: 9.32 (dd, 1 H, H(7), J = 7.1 Hz, J = 1.7 Hz); 9.21 (dd, 1 H, H(5), J = 4.3 Hz, J = 1.7 Hz); 7.80 (dd, 1 H, H(6), J = 7.1 Hz, J = 4.3 Hz). ^{13}C NMR ($(CD_3)_2SO$), δ: 159.09 (ddd, C(5), J = 185.6 Hz, J = 6.0 Hz, J = 2.5 Hz); 153.42 (C(2)); 143.52 (C(3a)); 139.20 (ddd, C(7), J = 197.0 Hz, J = 4.5 Hz, J = 6.0 Hz); 115.81 (ddd, C(6), J = 177.2 Hz, J = 9.4 Hz, J = 2.7 Hz); 113.40 (C(3)). ^{14}N NMR ($(CD_3)_2SO$), δ: −25.5, −28.2 (C(2)NO_2, C(3)NO_2). IR, ν/cm^{-1}: 1520, 1350 (NO_2). MS, m/z: 209 $[M]^+$.

5,7-Dimethyl-2,3-dinitropyrazolo[1,5-*a*]pyrimidine (18). The yield was 0.42 g (63%), m.p. 138 °C (MeOH). Found (%): C, 40.72; H, 3.09; N, 29.67. $C_8H_7N_5O_4$. Calculated (%): C, 40.51; H, 2.97; N, 29.53. ^{1}H NMR ($(CD_3)_2SO$), δ: 7.53 (q, 1 H, H(6), J = 1.0 Hz); 2.85 (d, 3 H, C(7)Me, J = 1.0 Hz); 2.76 (s, 3 H, C(5)Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 169.59 (dq, C(5), J = 2.2 Hz, J = 6.7 Hz); 153.14 (C(2)); 149.60 (dq, C(7), J = 3.3 Hz, J = 6.6 Hz); 143.23 (C(3a)); 115.90 (dqq, C(6), J = 172.0 Hz, J = 3.4 Hz, J = 3.4 Hz); 113.60 (C(3)); 25.39 (q, C(5)$\underline{C}H_3$, J = 129.3 Hz); 16.45 (q.d, C(7)$\underline{C}H_3$, J = 131.2 Hz, J = 3.2 Hz). ^{15}N NMR ($(CD_3)_2SO$), δ: −168.10 (qd, N(8), J = 4.7 Hz, J = 2.5 Hz); −122.80 (N(1)); −110.17 (q, N(4), J = 3.2 Hz); −26.89 (C(3)NO_2); −23.72 (C(2)NO_2). IR, ν/cm^{-1}: 1520, 1350 (NO_2). MS, m/z: 237 $[M]^+$.

5-Diazo-3,4-dinitropyrazole (19). A solution of $NaNO_2$ (0.6 g, 9 mmol) in ice water (2 mL) was added dropwise with stirring to a suspension of compound **1** (1.00 g, 6 mmol) in 20% H_2SO_4 (12 mL) at 0—5 °C, the reaction mixture was kept at this temperature for 2 h. The precipitate that formed was filtered off, washed with cold water, and dried *in vacuo* over P_2O_5. The yield was 0.95 g (89%), decomp. temp. 110 °C. Found (%): C, 19.73; N, 45.85. $C_3N_6O_4$. Calculated (%): C, 19.58; N, 45.66. ^{13}C NMR ($(CD_3)_2CO$), δ: 147.9 (CNO_2); 129.6 (C(4)); 118.2 (CN_2^+). ^{14}N NMR ($(CD_3)_2CO$), δ: −156.0 ($\nu_{1/2}$ = 70 Hz, N_2^+); −32.9 ($\nu_{1/2}$ = 25 Hz, C(4)NO_2), −27.2 ($\nu_{1/2}$ = 40 Hz, C(3)NO_2). IR, ν/cm^{-1}: 2250 (N_2^+); 1525, 1350 (NO_2). MS, m/z: 184 $[M]^+$.

5-Bromo-3,4-dinitropyrazole (20). Potassium bromide (1.19 g, 10 mmol) was added to a solution of compound **19**

(0.93 g, 5 mmol) in 40% HBr (10 mL) at 0—5 °C, the reaction mixture was stirred for 1 h. The temperature of the reaction mixture was allowed to rise to ~25 °C spontaneously and kept for an additional 7 h. It was extracted with ether (3×20 mL), the organic layer was washed with water, and dried with $MgSO_4$. The solvent was removed *in vacuo*, the residue was recrystallized from CCl_4. The yield was 1.0 g (84%), m.p. 118—120 °C. Found (%): C, 15.37; H, 0.51; Br, 34.04; N, 23.57. $C_3HBrN_4O_4$. Calculated (%): C, 15.21; H, 0.43; Br, 33.72; N, 23.64. ^{13}C NMR ($(CD_3)_2CO$), δ: 150.03 (C(3)); 126.94 (C(4)); 116.65 (C(5)). ^{14}N NMR ($(CD_3)_2CO$), δ: −178.12 (N(1)); −29.53, −27.86 ($C(3)NO_2$, $C(4)NO_2$). IR, ν/cm^{-1}: 1510, 1320 (NO_2). MS, *m/z*: 236, 238 (1 : 1) $[M]^+$.

5-Azido-3,4-dinitropyrazole (21). A solution of NaN_3 (0.64 g, 0.01 mol) in ice water (12 mL) was added dropwise with stirring to a solution of compound **19** (0.93 g, 0.005 mol) in water (10 mL) at 0—5 °C, the reaction mixture was kept at this temperature for 1 h. The precipitate that formed was filtered off, washed with cold water, and dried *in vacuo* over P_2O_5. It was recrystallized from dichloroethane. The yield was 0.65 g (65%), decomp. temp. 125—126 °C (*cf.* Ref. 3: decomp. temp. 125 °C).

5-Chloro-3,4-dinitropyrazole (22). A solution of compound **19** (0.93 g, 0.005 mol) in conc. HCl (10 mL) was added with stirring at 0—5 °C to a solution of CuCl (1 g, 0.01 mol) in conc. HCl (4 mL), the reaction mixture was stirred for 1 h. The temperature of the reaction mixture was allowed to rise to ~25 °C spontaneously and kept for an additional 7 h. It was extracted with ether (3×20 mL), the organic layer was washed with water, and dried with $MgSO_4$. The solvent was removed *in vacuo*, the residue was recrystallized from CCl_4. The yield was 0.8 g (83%), m.p. 110—112 °C. Found (%): C, 18.90; H, 0.53; Cl, 19.04; N, 29.28. $C_3HClN_4O_4$. Calculated (%): C, 18.72; H, 0.52; Cl, 18.42; N, 29.10. ^{13}C NMR ($(CD_3)_2CO$), δ: 149.62 (C(3)); 130.62 (C(5)); 124.21 (C(4)). ^{14}N NMR ($(CD_3)_2CO$), δ: −178.43 (N(1)); −29.46, −27.32 ($C(3)NO_2$, $C(4)NO_2$). IR, ν/cm^{-1}: 1520, 1340 (NO_2). MS, *m/z*: 194, 192 (1 : 3) $[M]^+$.

Cyclization of betaine 19 with active methylene compounds (general procedure). A suspension of betaine **19** (1 g, 5.4 mmol) in H_2O (8 mL) was added at 5—10 °C to a solution of a salt of an active methylene compound (11 mmol) in H_2O (5 mL). The reaction mixture was kept at this temperature for 1 h, then the temperature was allowed to rise to ~25 °C and the reaction mixture was kept for an additional 12 h. The precipitate that formed was filtered off, suspended in H_2O (15 mL) and acidified with 10% H_2SO_4 to pH = 1.

6-Acetyl-7-hydroxy-7-methyl-2,3-dinitro-4,7-dihydropyrazolo[5,1-*c*][1,2,4]triazine (23). The reaction was carried out with $NaCH(COCH_3)_2$. The solution was extracted with ether (3×10 mL), the organic layer was washed with water, and dried with $MgSO_4$, the solvent was removed *in vacuo*. The yield was 1.1 g (77%), m.p. 176—178 °C (dichloroethane). Found (%): C, 34.41; H, 3.03; N, 29.68. $C_8H_8N_6O_6$. Calculated (%): C, 33.81; H, 2.84; N, 29.57. ^1H NMR ($(CD_3)_2SO$), δ: 12.07 (br.s, 1 H, NH); 6.81 (br.s, 1 H, OH); 2.44 (s, 3 H, COMe); 2.27 (s, 3 H, C(7)Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 195.51 (q, CO, J = 6.8 Hz); 149.20 (C(2)); 142.84 (q, C(6), J = 3.4 Hz); 136.37 (d, C(3a), J = 10.5 Hz); 108.99 (C(3)); 81.04 (q, C(7), J = 4.8 Hz); 26.61 (q, Me, J = 129.9 Hz); 24.69 (q, C(7)$\underline{C}H_3$, J = 131.6 Hz). ^{15}N NMR ($(CD_3)_2SO$), δ: −244.07 (d, N(4), J = 114.4 Hz); −198.75 (N(8)); −110.52 (N(1)); −59.67 (N(5)); −26.56, −25.97 ($C(2)NO_2$), $C(3)NO_2$). IR, ν/cm^{-1}: 3450 (NH); 3340 (OH); 1690 (CO); 1525, 1352 (NO_2). MS, *m/z*: 284 $[M]^+$, 266 $[M^+ - H_2O]$.

6-Acetyl-7-hydroxy-2,3-dinitropyrazolo[5,1-*c*][1,2,4]triazine (24) and ethyl 7-hydroxy-7-methyl-2,3-dinitro-4,7-dihydropyrazolo[5,1-*c*][1,2,4]triazine-3-carboxylate (25). The reaction was carried out with $NaCH(CO_2Et)COCH_3$. The precipitate of compound **24** was filtered off, washed with cold water, and dried over P_2O_5. The yield of compound **24** was 0.5 g (37%), m.p. 252—254 °C (dichloroethane). Found (%): C, 31.51; H, 1.62; N, 31.48. $C_7H_4N_6O_6$. Calculated (%): C, 31.35; H, 1.50; N, 31.34. ^1H NMR ($(CD_3)_2SO$), δ: 13.00 (br.s, 1 H, OH); 2.60 (s, 3 H, Me). ^{13}C NMR ($(CD_3)_2SO$), δ: 192.85 (q, CO, J = 6.2 Hz); 151.41 (C(2)); 144.75; 141.74; 139.61; 110.49 (C(3)); 27.74 (q, Me, J = 129.0 Hz). ^{14}N NMR ($(CD_3)_2SO$), δ: −28.64 ($C(2)NO_2$), $C(3)NO_2$). IR, ν/cm^{-1}: 3230 (OH); 1760 (CO); 1520, 1325 (NO_2). MS, *m/z*: 268 $[M]^+$.

The mother liquor was extracted with ether (3×10 mL), the organic layer was washed with water, dried with $MgSO_4$, and the solvent was removed *in vacuo*. The yield of compound **25** was 0.6 g (38%), m.p. 176—178 °C (dichloroethane). Found (%): C, 34.56; H, 3.30; N, 26.84. $C_9H_{10}N_6O_7$. Calculated (%): C, 34.40; H, 3.21; N, 26.75. ^1H NMR ($(CD_3)_2SO$), δ: 12.10 (br.s, 1 H, NH); 7.10 (br.s, 1 H, OH); 4.36 (q, 2 H, CH_2, J = 7.0 Hz); 2.30 (s, 3 H, Me); 1.35 (q, 3 H, $CH_2C\underline{H}_3$, J = 7.0 Hz). ^{13}C NMR ($(CD_3)_2SO$), δ: 162.22 (t, CO, J = 3.1 Hz); 149.50 (C(2)); 138.20 (t, C(6), J = 3.4 Hz); 136.59 (d, C(3a), J = 10.8 Hz); 109.60 (C(3)), 81.07 (q, C(7), J = 4.6 Hz); 62.49 (tq, CH_2, J = 149.0 Hz, J = 4.4 Hz); 25.11 (q, Me, J = 131.0 Hz); 14.32 (q.t, $CH_2\underline{C}H_3$, J = 128.2 Hz, J = 2.4 Hz). IR, ν/cm^{-1}: 3400 (NH); 3250 (OH); 1710 (CO); 1530, 1320 (NO_2). MS, *m/z*: 314 $[M]^+$, 296 $[M^+ - H_2O]$.

4,7-Dihydro-2,3,6-trinitropyrazolo[5,1-*c*][1,2,4]triazin-4-ol (26). The reaction was carried out with $NaC(CHO)_2NO_2$. The reaction mixture was extracted with ether (3×10 mL), the organic layer was washed with water, and dried with $MgSO_4$, the solvent was removed *in vacuo*. The yield was 1.3 g (88%), m.p. 187 °C (dichloroethane). Found (%): C, 22.13; H, 1.15; N, 36.02. $C_5H_3N_7O_7$. Calculated (%): C, 21.99; H, 1.11; N, 35.90. ^1H NMR ($(CD_3)_2SO$), δ: 12.75 (br.s, 1 H, NH); 8.02 (br.s, 1 H, OH); 7.22 (s, 1 H). ^{13}C NMR ($(CD_3)_2SO$), δ: 149.72 (C(2)); 144.97 (C(6)); 136.27 (C(3a)); 110.42 (C(3)); 72.88 (d, C(7), J = 178.18 Hz). IR, ν/cm^{-1}: 3350 (NH); 1530, 1340 (NO_2). MS, *m/z*: 273 $[M]^+$, 255 $[M^+ - H_2O]$.

7-Amino-2,3,6-trinitropyrazolo[5,1-*c*][1,2,4]triazine (27). The reaction was carried out with $NaCH(CN)NO_2$. The precipitate that formed was filtered off, washed with cold water, and dried over P_2O_5. The yield was 1.27 g (95%), m.p. 242 °C (CH_3CN). Found (%): C, 22.39; H, 0.81; N, 42.05. $C_5H_2N_8O_6$. Calculated (%): C, 22.23; H, 0.75; N, 41.89. ^{13}C NMR ($(CD_3)_2SO$), δ: 153.69; 144.47; 140.91; 140.01; 93.30. ^{15}N NMR ($(CD_3)_2SO$), δ: −184.68; −124.12; −64.35; −29.15 ($C(6)NO_2$); −26.82 ($C(3)NO_2$); −20.23 ($C(2)NO_2$). IR, ν/cm^{-1}: 3230 (OH); 1520, 1325 (NO_2). MS, *m/z*: 270 $[M]^+$.

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