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Synthesis and Properties of 5-Chloro-4-nitropyrazoles

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Abstract—The nitration of 5-chloropyrazoles with a mixture of 100% nitric acid and 65% oleum or a mixture of 60% nitric acid and polyphosphoric acid gave substituted 5-chloro-4-nitropyrazoles in 45–91% yield. The nitration of 3-aryl-5-halopyrazoles was accompanied by introduction of a nitro group into the aromatic ring. 4-Chloropyrazoles failed to undergo nitration under these conditions. The reaction of 5-chloro-1,3-dimethyl-4-nitropyrazole with ethyl cyanoacetate in DMSO in the presence of K_2CO_3 led to the formation of ethyl 2-cyano-2-(1,3-dimethyl-4-nitro-1*H*-pyrazol-5-yl)acetate.

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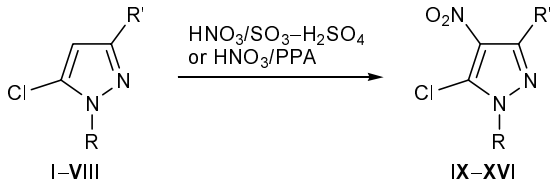
Heterocyclic compounds of the pyrazole series having functional substituents in the heteroring, including nitro-substituted pyrazoles, attract much interest from the synthetic viewpoint. Nitropyrazole derivatives are also used as dyes and intermediate products for the synthesis of biologically active compounds, e.g., antibiotics [1–4]. Of specific importance are pyrazoles containing both halogen atom and nitro group. We previously developed convenient methods for the preparation of 1-alkyl(aryl)-5-chloro(bromo)-pyrazoles by reactions of 2,2-dichloro(bromo)vinyl ketones with aryl- and alkylhydrazines and *N*,*N*-dimethylhydrazine [5–8]. The compounds thus obtained are promising as initial materials for the synthesis of insectoacaricides, dyes, and biologically active substances [9–11]. In continuation of our studies on the reactivity of halogen-substituted pyrazoles, in the present work we examined the nitration of 4- and 5-chloropyrazoles with a view to obtain derivatives with an activated halogen atom as intermediate products for the design of functionalized pyrazoles and heteroring assemblies.

Numerous methods for the synthesis of nitropyrazoles are known [1–4]; the scope of their application and nitration conditions depend on the substitution pattern and electron density distribution in the pyrazole ring. Musante [12] showed that 5-halopyrazoles having no substituent on the nitrogen can be nitrated with nitric acid (d = 1.52 g/cm^3) in 20% oleum. Zeller [13] proposed conditions for the nitration of 5-chloro-1,3-dimethylpyrazole, which were utilized in the large-scale preparation of 5-chloro-1,3-dimethyl-4-nitropyrazole, an intermediate product in the synthesis of medical agents. Nitration of other 1-substituted 4- and 5-chloropyrazoles was not studied.

We have found that 5-chloropyrazoles obtained from dihalovinyl ketones and hydrazines [5–8] do not give rise to nitration products on treatment with known nitrating agents under the conditions described in [1–4, 12, 13]. With the goal of obtaining halonitropyrazoles we tried mixtures of nitric and sulfuric acids with different concentrations, addition of oleum to the nitrating mixture, and other nitrating mixtures. We succeeded in effecting nitration of 1-alkyl(aryl)-3-alkyl(aryl)-5-chloropyrazoles **I**–**VIII** to the corresponding 1-alkyl-(aryl)-3-alkyl(aryl)-5-chloro-4-nitropyrazoles **IX**–**XVI** by the action of a large excess of a nitrating mixture consisting of 65% oleum and nitric acid (d =

Scheme 1.



I–VIII IX–XVI

I, **IX**, R = R' = Me; **II**, **X**, R = Me, R' = Pr; **III**, **XI**, R = Me, R' = *i*-Pr; **IV**, **XII**, R = Et, R' = Me; **V**, R = Et, R' = 4-$O_2NC_6H_4$; **XIII**, R = Et, R' = 2,4-$(O_2N)_2C_6H_3$; **VI**, **XIV**, R = C_7H_{15}, R' = Me; **VII**, **XV**, R = C_7H_{15}, R' = CF_3; **VIII**, **XVI**, R = 2,4-$(O_2N)_2C_6H_3$, R' = Pr.

1.51 g/cm^3) at a volume ratio of 2:1 on heating to 120–140°C (reaction time 8–10 h; method *a*; Scheme 1). Presumably, the drastic reaction conditions are determined by electron-withdrawing effect of the chlorine atom and protonation of pyrazole ring; both these factors deactivate the heteroring toward electrophilic substitution.

It is known that nitration of aryl-substituted pyrazoles under severe conditions is often accompanied by introduction of a nitro group into the aryl substituent [1–4]. In fact, the nitration of 5-chloro-1-ethyl-3-(4-nitrophenyl)pyrazole (**V**) under the above conditions gave 5-chloro-1-ethyl-3-(2,4-dinitrophenyl)-4-nitropyrazole (**XIII**).

Signals from protons in the nitrophenyl fragment (2'-H/6'-H and 3'-H/5'-H) of compound **V** were assigned on the basis of the 2D NOESY spectrum. The NOESY spectrum of **V** contained a cross peak from the proton resonating as a doublet at δ 8.04 ppm with proton in position *4* of the pyrazole ring. Therefore, the signal at δ 8.04 ppm was assigned to 2'-H/6'-H, and that located at δ 8.26 ppm, to 3'-H/5'-H. The carbon signals were assigned on the basis of the two-dimensional C–H correlation spectra, HMBC (Heteronuclear Multiple Bond Correlation using long-range couplings $^2J_{CH}$ and $^3J_{CH}$) and HSQC (Heteronuclear Single Quantum Correlation using direct coupling constants $^1J_{CH}$). Signals in the ^{1}H and ^{13}C NMR spectra of compounds **VIII**, **XIII**, and **XVI** were assigned by analogy with compound **V**, as well as using two-dimensional CH CORR HMBC and HSQC techniques.

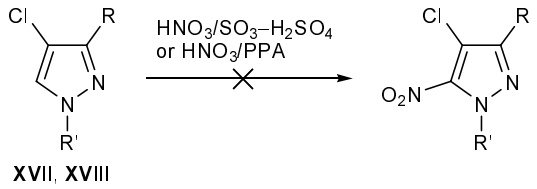
The proposed procedure for the nitration of 1-alkyl-(aryl)-3-alkyl(aryl)(trifluoromethyl)-5-chloropyrazoles to the corresponding 4-nitro derivatives with a mixture of nitric acid and oleum is characterized by a long reaction time and high temperature; moreover, it utilizes a very aggressive nitrating mixture which is inconvenient to handle with. Therefore, we continued search for a more convenient method for the preparation of chloronitropyrazoles and found that 5-chloro-4-nitropyrazoles can be obtained by nitrating 5-chloropyrazoles with a mixture consisting of 60% nitric acid and polyphosphoric acid (PPA) (method *b*). Here, a 2–2.2-fold amount of nitric acid and a large excess of PPA with respect to the initial pyrazole are required.

Comparison of the two procedures showed that method *b* is more advantageous. Both procedures ensured comparable yields of the final products, but the nitration with 60% HNO_3/PPA takes a shorter time (more than twofold) and occurs at a considerably lower temperature, and the nitrating agent is less aggressive. Presumably, excess polyphosphoric acid binds water which is present in nitric acid and is liberated during the process; as a result, the concentration of the nitrating species (NO_2^+) increases. On the other hand, it is obvious that the acidity of 60% HNO_3/PPA is much lower than the acidity of 100% HNO_3/65% oleum; therefore, weakly basic chloropyrazoles [14] are protonated to a lesser extent and are more reactive in electrophilic substitution.

Increase of the reaction time in the nitration with both nitrating mixtures led to sharp decrease in the product yield, and we failed to isolate 5-chloro-4-nitropyrazoles when the reaction mixture was heated for a time longer than 20 h. In this case, the reaction resulted in formation of unidentified compounds which (according to the IR spectra) contained carbonyl groups; the latter are likely to arise from oxidation of nitropyrazoles **IX**–**XVI**.

However, the proposed procedures for the nitration of 5-chloropyrazoles **I**–**VIII** (methods *a* and *b*) turned out to be inappropriate for the synthesis of 4-chloro-5-nitropyrazoles (Scheme 2). From the reaction mixtures obtained under analogous conditions, as well as on heating 1,3-dialkyl-4-chloropyrazoles [8] in nitrating mixtures at 20 to 150°C for 8 to 240 h, we isolated 50–60% of the initial 4-chloropyrazoles, while no corresponding nitration or oxidation products were detected.

Scheme 2.



XVII, **XVIII**

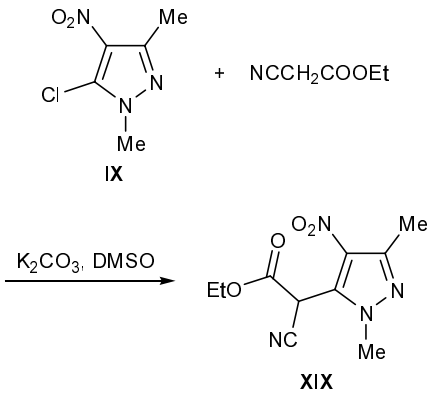
XVII, R = Pr, R' = Et; **XVIII**, R = Pr, R' = C_7H_{15}.

5-Chloro-4-nitropyrazoles **IX**–**XVI** are readily soluble in organic solvents, such as diethyl ether, chloroform, and ethanol. Their structure was confirmed by the IR and NMR spectra and elemental analyses. The IR spectra of **IX**–**XVI** lacked absorption in the region 3120–3130 cm^{-1}, which is typical of stretching vibrations of the C^4–H bond in the initial 5-chloropyrazoles, but strong broad absorption bands at 1525–1520 and 1350–1325 cm^{-1} were present in the spectra of pyrazoles **V**, **VIII**, and **IX**–**XVI** due to stretching vibrations of the nitro groups. Likewise, no 4-H signal typical of initial pyrazoles **I**–**VIII** (δ 6.60–6.90 ppm)

was observed in the ^{1}H NMR spectra of compounds **IX**–**XVI**.

The chlorine atom in 4- and 5-chloropyrazoles is inactive toward a number of C-nucleophiles. We obtained data demonstrating a high mobility of the halogen atom in the synthesized 5-chloro-4-nitropyrazoles; studies on their reactions with nucleophiles, ambident reagents, and difunctional nucleophiles are now in progress. Introduction of a nitro group into the 4-position of pyrazole ring activates the chlorine atom in position *5* to nucleophilic replacement, presumably as a result of stabilization of the negatively charged intermediate complex. 5-Chloro-1,3-dimethyl-4-nitropyrazole reacted with ethyl cyanoacetate in DMSO in the presence of K_2CO_3 to give 65% of ethyl 2-cyano-2-(1,3-dimethyl-4-nitro-1*H*-pyrazol-5-yl)acetate (**XIX**) (Scheme 3).

Scheme 3.



Thus we have developed procedures for the nitration of 5-chloropyrazoles to 5-chloro-4-nitropyrazoles and found that the nitration of 1-alkyl-3-alkyl(aryl or trifluoromethyl)-5-chloropyrazoles with 60% nitric acid in polyphosphoric acid occurs at a lower temperature and requires a shorter time than the reaction with a mixture of 100% nitric acid (d = 1.51 g/cm^3) and 65% oleum.

EXPERIMENTAL

The IR spectra were recorded in KBr on a Specord IR75 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-400 instrument at 400.13 and 100.61 MHz, respectively, using HMDS as internal reference. Pyrazoles **I**–**III**, **VI**, and **VII** were synthesized by the procedure described in [15].

5-Chloro-1-ethyl-3-methyl-1*H*-pyrazole (IV). 1,1-Dichlorobut-1-en-2-one, 1.39 g (0.01 mol), was added dropwise under stirring to a solution of 1.20 g (0.02 mol) of ethylhydrazine in 30 ml of anhydrous diethyl ether, and the mixture was stirred for 2–3 h. The precipitate of ethylhydrazinium chloride was filtered off, the filtrate was evaporated, and the residue was distilled under reduced pressure. Yield 0.96 g (66%), bp 54–56°C (12 mm), n_D^{20} = 1.4848. IR spectrum, ν, cm^{-1}: 3125 (=C–H), 2950 (C–H$_{aliph}$), 1510 (C=C), 770 (C–Cl). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.95 s (1H, 4-H), 4.09 t (2H, NCH_2, J = 7.2 Hz), 2.21 s (3H, CH_3), 1.38 t (3H, CH_3, J = 7.2 Hz). Found, %: C 50.05; H 6.17; Cl 24.48; N 19.58. $C_6H_9ClN_2$. Calculated, %: C 50.03; H 6.14; Cl 24.44; N 19.60.

5-Chloro-1-ethyl-3-(4-nitrophenyl)-1*H*-pyrazole (V). Ethylhydrazine, 0.6 g (0.01 mol), and triethylamine, 1.01 g (0.01 mol), were added dropwise to a solution of 2.46 g (0.01 mol) of 2,2-dichlorovinyl 4-nitrophenyl ketone in 20 ml of ethanol. The mixture was stirred for 3 h and poured into water, and the precipitate was filtered off, washed with water, and dried. Yield 2.29 g (91%), mp 116–117°C. IR spectrum, ν, cm^{-1}: 3135, 3070 (=C–H); 2990, 2969, 2930 (C–H$_{aliph}$); 1600 (C=N), 1510 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.22 d and 7.88 d (4H, C_6H_4, J = 1.0 Hz), 6.57 s (1H, 4-H), 4.24 q (2H, NCH_2, J = 7.2 Hz), 1.48 t (3H, CH_3, J = 7.2 Hz). Found, %: C 52.30; H 4.20; Cl 14.05; N 16.65. $C_{11}H_{10}ClN_3O_2$. Calculated, %: C 52.50; H 4.00; Cl 14.09; N 16.70.

5-Chloro-1-(2,4-dinitrophenyl)-3-propyl-1*H*-pyrazole (VIII). A mixture of 2.00 g (5.76 mmol) of 2,2-dichlorovinyl propyl ketone 2,4-dinitrophenylhydrazone [16] and 20 g of polyphosphoric acid was stirred for 20 min on heating at 130°C. The mixture was cooled and poured into water, and the precipitate was filtered off, washed with water until neutral reaction, and dried. Yield 1.59 g (90%), mp 73–75°C. IR spectrum, ν, cm^{-1}: 3090 (=C–H); 2960, 2940, 2875 (C–H$_{aliph}$); 1600 (C=N); 1545 (C=C); 1525, 1340 (NO_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.86 s (1H, 3'-H), 8.70 d (1H, 5'-H, ^3J = 8.8 Hz), 8.06 d (1H, 6'-H, ^3J = 8.8 Hz), 6.43 s (1H, 4-H), 2.57 t (2H, CH_2, J = 7.3 Hz), 1.66 m (2H, CH_2, J = 7.3 Hz), 0.93 t (3H, CH_3, J = 7.3 Hz). Found, %: C 46.36; H 3.45; Cl 11.52; N 18.09. $C_{12}H_{11}ClN_4O_4$. Calculated, %: C 46.39; H 3.57; Cl 11.41; N 18.03.

5-Chloro-1,3-dimethyl-4-nitro-1*H*-pyrazole (IX). *a*. Nitric acid (d = 1.51 g/cm^3), 4.5 ml, was slowly added dropwise to a mixture of 2.81 g (21.5 mmol) of 5-chloro-1,3-dimethyl-1*H*-pyrazole and 9 ml of 65% oleum. The mixture was heated for 10 h at 130°C,

cooled, poured into water, and made alkaline, and the precipitate was filtered off, washed with water until neutral reaction, and dried. Yield of compound **IX** 1.88 g (50%), mp 76°C.

b. 5-Chloro-1,3-dimethyl-1*H*-pyrazole, 0.65 g (5 mmol), was added dropwise to a mixture of 5 g of polyphosphoric acid and 1.15 ml of 60% nitric acid. The mixture was heated for 3 h at 85°C, poured into ice water, and neutralized with a saturated solution of Na_2CO_3 to a weakly acidic reaction. The precipitate was filtered off, washed with water, and dried. Yield 0.33 g (55%), mp 78°C. IR spectrum, ν, cm^{-1}: 2995, 2945 (C–H); 1525, 1350 (NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.84 (CH_3), 2.52 (CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.51 (CH_3), 37.03 (CH_3), 128.16 (C^4), 143.32 (C^5), 146.65 (C^3). Found, %: C 34.15; H 3.50; Cl 20.17; N 23.90. $C_5H_6ClN_3O_2$. Calculated, %: C 34.20; H 3.44; Cl 20.19; N 23.93.

5-Chloro-1-methyl-4-nitro-3-propyl-1*H*-pyrazole (X) was synthesized according to method *b* from 3 g (18.9 mmol) of 5-chloro-1-methyl-3-propyl-1*H*-pyrazole and 4.3 ml of 60% nitric acid in 10 g of polyphosphoric acid. The reaction mixture was heated for 3 h at 80°C. Yield 1.48 g (40%), mp 27°C. IR spectrum, ν, cm^{-1}: 2955, 2935, 2875 (C–H); 1525, 1350 (NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.75 (3H, CH_3), 2.72 t (2H, CH_2, J = 7.3 Hz), 1.55 m (2H, CH_2, J = 7.3 Hz), 0.84 t (3H, CH_3, J = 7.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 150.09 (C^5); 128.05 (C^3); 36.95 (NCH_3); 30.00, 21.01, and 13.76 (C_3H_7). Found, %: C 41.25; H 5.01; Cl 17.40; N 20.65. $C_7H_{10}ClN_3O_2$. Calculated, %: C 41.29; H 4.95; Cl 17.41; N 20.64.

5-Chloro-3-isopropyl-1-methyl-4-nitro-1*H*-pyrazole (XI) was synthesized according to method *a* from 0.40 g (2.5 mmol) of 5-chloro-3-isopropyl-1-methyl-1*H*-pyrazole, 0.13 ml of nitric acid (d = 1.51 g/cm^3) and 1.1 ml of 65% oleum. The reaction mixture was heated for 8 h at 120°C. Yield 0.41 g (81%), mp 53°C. IR spectrum, ν, cm^{-1}: 2975, 2930, 2870 (C–H); 1525, 1350 (NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.85 (CH_3), 3.57 m (1H, CH, J = 6.9 Hz), 1.28 d (6H, $2CH_3$, J = 6.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 155.05 (C^3), 138.98 (C^4), 128.27 (C^5), 37.12 (CH_3), 27.42 (CH), 21.01 ($2CH_3$). Found, %: C 41.25; H 5.01; Cl 17.38; N 20.61. $C_7H_{10}ClN_3O_2$. Calculated, %: C 41.29; H 4.95; Cl 17.41; N 20.64.

5-Chloro-1-ethyl-3-methyl-4-nitro-1*H*-pyrazole (XII). *a.* Compound **XII** was synthesized as described above for nitropyrazole **IX** from 0.58 g (4 mmol) of compound **IV**, 2.1 ml of nitric acid (d = 1.51 g/cm^3), and 3.15 ml of 65% oleum. The mixture was heated for 8 h at 120–140°C. Yield 0.45 g (60%), mp 32–34°C.

b. Following method *b*, from 0.38 g (3 mmol) of 5-chloro-1-ethyl-3-methyl-1*H*-pyrazole, 3 g of polyphosphoric acid, and 0.7 ml of 60% nitric acid (3 h at 85°C) we obtained 0.2 g (52%) of compound **XII** with mp 34°C. IR spectrum, ν, cm^{-1}: 3000, 2980, 2940 (C–H); 1530, 1350 (NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.12 q (2H, CH_2, J = 7.3 Hz), 2.44 (3H, CH_3), 1.38 t (3H, CH_3, J = 7.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 146.57 (C^3), 133.05 (C^4), 127.09 (C^5), 45.30 (CH_2), 14.62 (CH_3), 14.37 (CH_3). Found, %: C 38.10; H 4.30; Cl 18.72; N 22.15. $C_6H_8ClN_3O_2$. Calculated, %: C 38.01; H 4.25; Cl 18.70; N 22.16.

5-Chloro-3-(2,4-dinitrophenyl)-1-ethyl-4-nitro-1*H*-pyrazole (XIII) was synthesized according to method *a* from 0.11 g (0.44 mmol) of compound **V**, 0.02 ml of nitric acid (d = 1.51 g/cm^3), and 0.15 ml of 65% oleum; the reaction mixture was heated for 8 h at 120°C. Yield 0.121 g (83%), mp 128–130°C. IR spectrum, ν, cm^{-1}: 3095 (=C–H); 2980, 2935 (C–H_{aliph}); 1520, 1325 (NO_2); 1605 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.97 d (1H, 6'-H, ^4J = 2.3 Hz), 8.71 d.d (1H, 5'-H, ^4J = 2.3, ^3J = 8.5 Hz), 8.02 d (1H, 3'-H, ^3J = 8.5 Hz), 4.44 q (2H, CH_2, J = 7.4 Hz), 1.52 t (3H, CH_3, J = 7.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 164.77 ($C^{2'}$), 144.06 ($C^{4'}$), 135.30 ($C^{6'}$), 134.09 (C^3), 132.55 (C^4), 128.65 ($C^{5'}$), 123.05 (C^5), 120.84 ($C^{3'}$), 120.32 ($C^{1'}$), 46.88 (CH_2), 14.27 (CH_3). Found, %: C 38.96; H 2.15; Cl 10.45; N 20.70. $C_{11}H_8ClN_5O_6$. Calculated, %: C 38.67; H 2.36; Cl 10.38; N 20.50.

5-Chloro-1-heptyl-3-methyl-4-nitro-1*H*-pyrazole (XIV) was synthesized according to method *b* from 0.34 g (1.6 mmol) of 5-chloro-1-heptyl-3-methyl-1*H*-pyrazole and 0.15 g of 60% nitric acid in 1.5 g of polyphosphoric acid; the reaction mixture was heated for 3 h at 90°C. Yield 0.2 g (49%), n_D^{20} = 1.5076. IR spectrum, ν, cm^{-1}: 2955, 2925, 2855 (C–H); 1530, 1350 (NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.12 t (2H, CH_2, J = 7.4 Hz), 2.53 (3H, CH_3), 1.83 m (2H, CH_2), 1.29 m (8H, $4CH_2$), 0.86 t (3H, CH_3, J = 7.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 146.58 (C^3), 127.45 (C^5), 50.07 (CH_2), 31.57 (CH_2), 29.13 (CH_2), 28.69 (CH_2), 26.31 (CH_2), 22.52 (CH_2), 14.70 (CH_3), 13.95 (CH_3). Found, %: C 50.84; H 7.03; Cl 13.63; N 16.16. $C_{11}H_{18}ClN_3O_2$. Calculated, %: C 50.87; H 6.99; Cl 13.65; N 16.18.

5-Chloro-1-heptyl-4-nitro-3-trifluoromethyl-1*H*-pyrazole (XV) was synthesized according to method *b* from 0.33 g (1 mmol) of 5-chloro-1-heptyl-3-trifluoro-

methyl-1*H*-pyrazole, 3 g of polyphosphoric acid, and 0.25 ml of 60% nitric acid; the reaction mixture was heated for 11 h at 95°C. Yield 0.13 g (45%), dark very viscous substance. IR spectrum, ν, cm^{-1}: 2950, 2920, 2850 (C–H); 1535, 1350 (NO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.24 t (2H, CH_2, J = 7.5 Hz), 1.88 m (2H, CH_2), 1.29 m (8H, $4CH_2$), 0.86 t (3H, CH_3, J = 7.5 Hz). Found, %: C 41.95; H 5.01; Cl 11.25; F 17.87; N 15.25. $C_{11}H_{15}ClF_3N_3O_2$. Calculated, %: C 42.12; H 4.82; Cl 11.30; F 18.17; N 13.39.

5-Chloro-1-(2,4-dinitrophenyl)-4-nitro-3-propyl-1*H*-pyrazole (XVI). *a.* Compound **XVI** was synthesized from 1.04 g (3.3 mmol) of pyrazole **VIII** using 0.15 ml of nitric acid (d = 1.51 g/cm^3) and 1.15 ml of 65% oleum; the reaction mixture was heated for 8 h at 120°C. The product was isolated as a waxy material. Yield 0.53 g (45%).

b. By treatment of 0.28 g (0.9 mmol) of 5-chloro-1-(2,4-dinitrophenyl)-3-propyl-1*H*-pyrazole with 0.2 g of 60% nitric acid in 1.25 g of polyphosphoric acid at 100°C (reaction time 3 h) we obtained 0.25 g (78%) of compound **XVI**. IR spectrum, ν, cm^{-1}: 3090 (=C–H); 2955, 2925, 2875 ($C–H_{aliph}$); 1600 (C=N); 1525, 1340 (NO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 8.98 d (1H, 3-H, ^4J = 2.3 Hz), 8.70 d.d (1H, 5'-H, ^4J = 2.3, ^3J = 8.7 Hz), 7.93 d (1H, 6'-H, ^3J = 8.7 Hz), 2.96 t (2H, CH_2, J = 7.4 Hz), 1.73 m (2H, CH_2, J = 7.4 Hz), 0.98 t (3H, CH_3, J = 7.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 152.90 (C^3), 148.28 ($C^{2'}$), 145.42 ($C^{4'}$), 139.11 ($C^{1'}$), 134.40 (C^4), 131.10 ($C^{5'}$), 129.88 (C^5), 128.27 ($C^{3'}$), 121.43 ($C^{6'}$), 29.97 (CH_2), 20.46 (CH_2), 13.48 (CH_3). Found, %: C 40.50; H 2.85; Cl 10.0; N 19.65. $C_{12}H_{10}ClN_5O_6$. Calculated, %: C 40.52; H 2.83; Cl 9.97; N 19.69.

4-Chloro-1-ethyl-3-propyl-1*H*-pyrazole (XVII). Ethylhydrazine, 0.6 g (0.01 mol), and triethylamine, 1.01 g (0.01 mol), were added dropwise under stirring to a solution of 1.67 g (0.01 mol) of 1,2-dichlorovinyl propyl ketone in 30 ml of diethyl ether. The mixture was stirred for 1 h, the precipitate of triethylamine hydrochloride was filtered off, the filtrate was evaporated, and the residue was distilled under reduced pressure. Yield 1.29 g (75%), bp 70°C (5 mm), n_D^{20} = 1.4838. IR spectrum, ν, cm^{-1}: 3140, 3120 (=C–H); 2960, 2940, 2860 ($C–H_{aliph}$). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.27 s (1H, 5-H), 4.03 q (2H, CH_2, J = 7.3 Hz), 2.56 t (2H, CH_2, J = 7.5 Hz), 1.66 m (2H, CH_2, J = 7.5 Hz), 1.40 t (3H, CH_3, J = 7.3 Hz), 0.94 t (3H, CH_3, J = 7.5 Hz). Found, %: C 55.60; H 7.45; Cl 20.58; N 16.31. $C_8H_{13}ClN_2$. Calculated, %: C 55.65; H 7.59; Cl 20.53; N 16.22.

4-Chloro-1-heptyl-3-propyl-1*H*-pyrazole (XVIII) was synthesized as described above for compound **XVII** from 1.3 g (0.01 mol) of heptylhydrazine, 1.01 g (0.01 mol) of triethylamine, and 1.67 g (0.01 mol) of 1,2-dichlorovinyl propyl ketone. Yield 2.32 g (85%), bp 129°C (3 mm), n_D^{20} = 1.4823. IR spectrum, ν, cm^{-1}: 3120 (=C–H); 2950, 2920, 2850 ($C–H_{aliph}$); 1600 (C=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.26 s (1H, 5-H), 3.97 q (2H, CH_2, J = 7.1 Hz), 2.56 t (2H, CH_2, J = 7.4 Hz), 1.78 m (2H, CH_2, J = 7.1 Hz), 1.65 m (2H, CH_2, J = 7.4 Hz), 1.26 m (8H, $4CH_2$), 0.92 t (3H, CH_3, J = 7.4 Hz), 0.86 t (3H, CH_3, J = 7.1 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 149.23 (C^3); 127.06 (C^5); 107.98 (C^4); 52.76, 31.69, 30.39, 28.83, 27.86, 26.56, 22.59, 22.23 ($8CH_2$); 14.06, 13.84 ($2CH_3$). Found, %: C 64.35; H 10.50; Cl 14.63; N 11.55. $C_{13}H_{23}ClN_2$. Calculated, %: C 64.31; H 9.55; Cl 14.60; N 11.54.

Ethyl 2-cyano-2-(1,3-dimethyl-4-nitro-1*H*-pyrazol-5-yl)acetate (XIX). Preliminarily calcined and finely powdered potassium carbonate, 0.59 g (6 mmol), was added to a solution of 0.55 g (3 mmol) of compound **IX** and 0.34 g (3 mmol) of ethyl cyanoacetate in 20 ml of anhydrous DMSO. The mixture was stirred for 9 h at 70°C, cooled, diluted with 30 ml of water, and acidified with hydrochloric acid, and the precipitate was filtered off, washed with water, and dried. Yield 0.5 g (65%), mp 81–82°C. IR spectrum, ν, cm^{-1}: 3000, 2970, 2900 (C–H); 2250 (C≡N); 1745 (C=O); 1570, 1360 (NO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.16 s (1H, CH), 4.38 q (2H, CH_2, J = 7.17 Hz), 3.97 s (3H, CH_3), 2.56 s (3H, CH_3), 1.38 t (3H, CH_3, J = 7.17 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 161.28 (C=O), 146.38 (C^3), 130.28 (C^5), 116.00 (C^4), 111.50 (CN), 64.47 (CH_2), 38.12 (CH), 33.41 (CH_3), 30.66 (CH_3), 13.70 (CH_3). Found, %: C 47.60; H 4.82; N 22.23. $C_{10}H_{12}N_4O_4$. Calculated, %: C 47.62; H 4.80; N 22.21.

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