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CHEMICAL PROPERTIES OF DERIVATIVES OF N-DIFLUOROMETHYL- AND N-2-H-TETRAFLUOROETHYLPYRAZOLES

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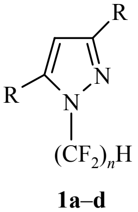
Nitration, chlorination, bromination, and iodination reactions have been investigated for pyrazole derivatives containing a difluoromethylene fragment directly on a nitrogen atom. Conditions have been found for introducing a cyano group into the nucleus of N-2-H-tetrafluoroethylpyrazole and converting it into carboxyl or tetrazole functions.

Keywords: N-2-H-tetrafluoroethyl- and N-difluoromethylpyrazole, cyanation, halogenation, nitration.

Pyrazole derivatives enter into the composition of many compounds possessing high biological activity. Several of them, containing fluorinated groupings, are used as medicinal preparations [1] and pesticides [2].

Compounds containing a difluoromethylene fragment linked directly with the nitrogen atom have been little studied up to the present. Trialkylamines containing the α-difluoromethylene fragment are hydrolytically unstable [3-5] as a result of the electron-donating influence of the unshared electron pair of nitrogen. However in the case of nitrogen heterocycles such compounds are significantly more stable, since the nitrogen electron pair is involved in the π–conjugation of the heterocyclic ring. Difluoromethyl and 2H-tetrafluoroethyl derivatives of pyrrole [5], imidazole, benzimidazole [6-8], triazole, 3,5-dimethyl-, and 3-carbethoxypyrazole [9, 10] have been synthesized previously.

Recently we investigated [11] the chemical properties of N-2-H-tetrafluoroethyl derivatives of pyrrole and imidazole, and found conditions for nitrating, halogenating, and acylating such compounds. As a continuation of investigations in this area we have studied the chemical properties of N-difluoromethyl and N-2H-tetrafluoroethylpyrazoles **1a-d.**



1a–d

a R = H, **b** R = Me, **c** R = H, **d** R = Me; **a**, **b** n = 1, **c**, **d** n = 2

Difluoromethylation of pyrazole, and of 3,5-dimethylpyrazole was carried out in aqueous dioxane medium by the action of chlorodifluoromethane and alkali. N-Difluoromethylpyrazole **1a** proved to be an extremely volatile compound. It forms an azeotropically boiling mixture with water and diethyl ether. It is

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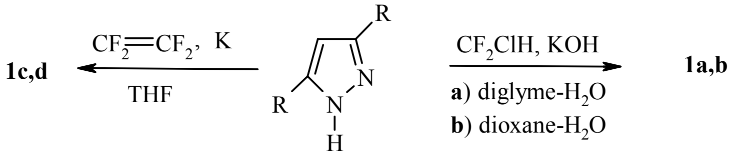
appreciably soluble in water as a result of which it was not successfully isolated in the pure state. Preparing compound **1a** in a preparative yield succeeded on carrying out the difluoromethylation in a more highly boiling solvent, diglyme at 90-100°C with simultaneous distillation of the desired product. After a second fractional distillation pure pyrazole **1a** was obtained in 68% yield. In contrast the isolation of N-difluoromethyl-3,5-dimethylpyrazole **1b** from an aqueous dioxane medium did not present experimental difficulties.

Compound **1d** was obtained previously [9] in an autoclave at 150°C in 42% yield. The use of an autoclave and high pressures on working with tetrafluoroethylene is dangerous since it may lead to an explosion [12]. Carrying out the tetrafluoroethylating reaction in aqueous acetone medium, as was described for imidazole derivatives [8], does not give the expected products.

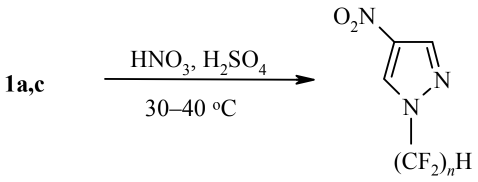
We found that tetrafluoroethylation of pyrazole and 3,5-dimethylpyrazole occurs on passing tetrafluoroethylene into a solution of the initial heterocycle in THF containing 5 mol % of the potassium derivative. The reaction proceeds at atmospheric pressure at 35-45°C.



The yield of compound **1c** did not exceed 45% since significant loss occurs on separating it from THF. Compound **1d** was obtained in 75% yield. The synthesized N-difluoromethyl- and N-2–H-tetrafluoroethylpyrazoles are fully accessible compounds and were selected by us as models for studying the chemical properties of pyrazole derivatives containing a difluoromethylene group at the nitrogen atom.

Previously [11] we were unsuccessful in carrying out nitration of N-2-H-tetrafluoroethylimidazole by the action of a mixture of sulfuric and nitric acids, since on solution in the nitrating mixture an imidazolium salt is formed and the heterocyclic nucleus is deactivated towards electrophilic substitution reaction.

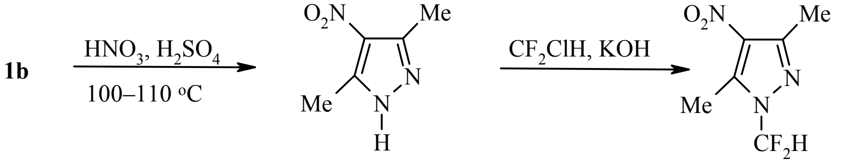
The polyfluoroalkylpyrazoles **1a-d** are weaker bases than the analogous imidazole derivatives, consequently the corresponding pyrazolium salts are formed with more difficulty, and nitration of the polyfluoroalkylpyrazoles **1a,c** unsubstituted in the nucleus occurs under milder conditions (at 30-40°C) at position 4 with the formation of compounds **2a,c**. In their ^1H NMR spectra the highest field signal (~6.5 ppm) of the pyrazole ring was absent, and the remaining ring protons were displayed as singlets, which proves unequivocally the occurrence of reaction at position 4.



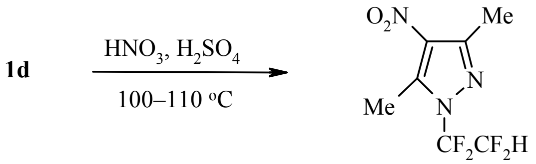
2a,c

On attempting the nitration of 3,5-dimethylpyrazole derivatives under these conditions unexpectedly the initial compounds were isolated. The presence of the methyl groups increases the basicity, which leads to a higher stability for the pyrazolium salt and deactivation of the heterocyclic nucleus.

The nitration of compounds **1b,d** under more forcing conditions, at 100-110°C, leads in the case of **1b** to hydrolysis of the difluoromethyl group with the formation of 3,5-dimethyl-4-nitropyrazole [13]. The nitro derivative **2b** was synthesized by the difluoromethylation of this compound. In the case of compound **1d** the tetrafluoroethyl group was not affected even under such forcing conditions, because it is more stable towards acid hydrolysis than the difluoromethyl group, as a result of which product **2d** was obtained in good yield.



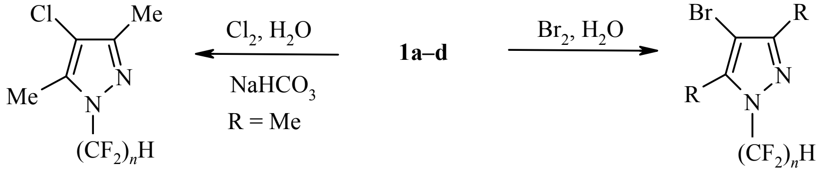
2b



2d

It is known that the pyrazole ring is less sensitive towards the action of halogens than imidazole and pyrrole. Bromination of N-arylpyrazoles with bromine leads to the preparation of monobromo derivatives at position 4 [14]. We have shown that under the action of an equimolar amount of bromine in water at room temperature compounds **1a-d** also form only the 4-bromo derivatives **3a-d**.

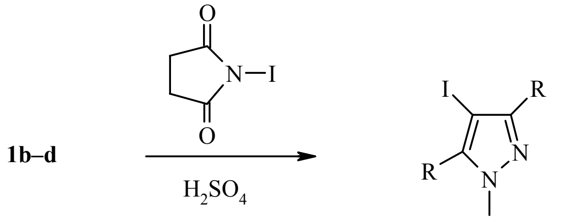
Compounds **1b,d**, containing methyl groups in the pyrazole nucleus, are converted under the action of an excess of chlorine into the corresponding chloro derivatives **4b,d**. The reactions took place at room temperature in an aqueous suspension of sodium bicarbonate. Neither the methyl nor the difluoromethyl groups were affected by this. However the chlorination under these conditions of compound **1c**, containing no methyl groups on the ring, leads to a complex mixture of products difficult to identify.



4b,d

3a–d

Iodination of N-alkylpyrazoles occurs under the action of iodine [15]. However compounds **1a-d**, as a result of deactivation of the heterocyclic nucleus by the electron-withdrawing fluorinated group, were not iodinated under these conditions. To intruduce an iodine atom into the molecule of compounds **1b-d** we used N-iodosuccinimide in sulfuric acid, which has been used for the iodination of aromatic compounds [16]. As a result the 4-iodo derivatives **5b-d** were obtained in high yield.



5b–d

Unlike N-tetrafluoroethyl-2-bromoimidazole, in which attempts to replace a halogen atom by a cyano group by the action of copper cyanide led to resinification [11], replacement of the iodine atom by a cyano group in compound **5c** occurs in high yield with the formation of nitrile **6c**. In the case of compound **5b,**

TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %				^{1}H NMR spectrum, δ, ppm (*J*, Hz)	^{19}F NMR spectrum, δ, ppm (*J*, Hz)	mp, °C	bp, °C (mm Hg)	Yield, %
		C	H	N	Br (I)					
1	2	3	4	5	6	7	8	9	10	11
1a	$C_4H_4F_2N_2$	41.06 40.69	3.92 3.41	23.33 23.72		6.44 (1H, s, CH); 7.20 (1H, t, J = 60, CHF_2); 7.65 (1H, s, CH); 7.81 (1H, d, J = 4, CH)	-93.89 (2F, d, J = 60, CHF_2)		85-87 (760)	65
1b	$C_6H_8F_2N_2$	49.13 49.31	5.33 5.52	19.06 19.17		2.14 (3H, s, CH_3); 2.35 (3H, s, CH_3); 5.95 (1H, s, CH); 7.64 (1H, t, J = 60, CHF_2)	-93.66 (2F, d, J = 60, CHF_2)		142-144 (760)	72
1c	$C_5H_4F_4N_2$	35.95 35.72	2.62 2.40	16.56 16.67		6.44-6.47 (1H, m, CH); 6.53 (1H, tt, $^2J_{H-F}$ = 53, $^3J_{H-F}$ = 4.7, CHF_2); 7.67 (1H, s, CH); 7.86 (1H, d, J = 4, CH)	-99.79 (2F, s, CF_2); -138.22 (2F, d, J = 53, CHF_2)		108-110 (760)	43
2a	$C_4H_3F_2N_3O_2$	29.44 29.46	2.31 1.85	24.98 25.77		7.58 (1H, t, J = 60, CHF_2); 8.20 (1H, s, CH); 9.02 (1H, s, CH)	-97.24 (2F, d, J = 60, CHF_2)		87-90 (20)	50
2b	$C_6H_7F_2N_3O_2$	37.52 37.70	3.79 3.70	22.00 21.98		2.48 (3H, s, CH_3); 2.77 (3H, s, CH_3); 7.87 (1H, t, J = 60, CHF_2)	-95.07 (2F, d, J = 60, CHF_2)	51-53		68
2c	$C_5H_3F_4N_3O_2$	28.14 28.18	1.41 1.42	19.96 19.72		6.53 (1H, tt, $^2J_{H-F}$ = 53, $^3J_{H-F}$ = 4.7, CHF_2); 8.27 (1H, s, CH); 8.80 (1H, s, CH)	-102.09 (2F, s, CF_2); -139.72 (2F, d, J = 53, CHF_2)		100-101 (20)	63
2d	$C_7H_7F_4N_3O_2$	34.92 34.87	2.82 2.93	17.30 17.43		2.51 (3H, s, CH_3); 2.84 (3H, s, CH_3); 6.65 (1H, tt, $^2J_{H-F}$ = 53, $^3J_{H-F}$ = 4.7, CHF_2)	-97.09 (2F, s, CF_2); -137.02 (2F, d, J = 53, CHF_2)		106-108 (20)	57
3a	$C_4H_3BrF_2N_2$	23.97 24.39	1.51 1.52		40.55 40.56	7.58 (1H, t, J = 60, CHF_2); 7.79 (1H, s, CH); 8.33 (1H, s, CH)	-96.60 (2F, d, J = 60, CHF_2)		42-43 (20)	71
3b	$C_6H_7BrF_2N_2$	32.13 32.02	3.33 3.14		35.74 35.51	2.18 (3H, s, CH_3); 2.40 (3H, s, CH_3); 7.57 (1H, t, J = 60, CHF_2)	-95.53 (2F, d, J = 60, CHF_2)		60-62 (20)	75
3c	$C_5H_3BrF_4N_2$	24.54 24.31	1.59 1.22		33.09 32.35	6.48 (1H, tt, $^2J_{H-F}$ = 53, $^3J_{H-F}$ = 4.7, CHF_2); 7.68 (1H, s, CH); 7.88 (1H, s, CH)	-100.09 (2F, s, CF_2); -137.45 (2F, d, J = 53, CHF_2)		49-50 (20)	68

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11
3d	$C_7H_7BrF_4N_2$	$\frac{30.31}{30.57}$	$\frac{2.80}{2.56}$		$\frac{28.60}{29.05}$	2.35 (3H, s, CH_3); 2.49 (3H, s, CH_3); 6.56 (1H, tt, $^2J_{H-F}$ = 53, $^3J_{H-F}$ = 4.7, CHF_2)	-100.12 (2F, s, CF_2); -137.65 (2F, d, J = 53, CHF_2)		87-90 (20)	50
4b*	$C_6H_7ClF_2N_2$	$\frac{39.75}{39.91}$	$\frac{3.75}{3.91}$			2.19 (3H, s, CH_3); 2.37 (3H, s, CH_3); 7.27 (1H, t, J = 60, CHF_2)	-95.07 (2F, d, J = 60, CHF_2)		68-69 (70)	60
4d*	$C_7H_7ClF_4N_2$	$\frac{36.77}{36.46}$	$\frac{2.92}{3.06}$			2.39 (3H, s, CH_3); 2.52 (3H, s, CH_3); 6.63 (1H, tt, $^2J_{H-F}$ = 53, $^3J_{H-F}$ = 4.7, CHF_2)	-100.22 (2F, s, CF_2); -138.05 (2F, d, J = 53, CHF_2)		57-59 (50)	63
5b	$C_6H_7IF_2N_2$				$\frac{(45.90)}{(46.65)}$	2.33 (3H, s, CH_3); 2.55 (3H, s, CH_3); 6.58 (1H, tt, $^2J_{H-F}$ = 53, $^3J_{H-F}$ = 4.7, CHF_2)	-97.98 (2F, d, J = 60, CHF_2	16-18	84-85 (20)	67
5c	$C_5H_3IF_4N_2$				$\frac{(43.06)}{(43.17)}$	6.48 (1H, tt, $^2J_{H-F}$ = 53, $^3J_{H-F}$ = 4.7, CHF_2); 7.68 (1H, s, CH); 7.88 (1H, s, CH)	-97.95 (2F, s, CF_2); -138.04 (2F, d, J = 53, CHF_2)		56-58 (15)	75
5d	$C_7H_7IF_2N_2$				$\frac{(38.80)}{(39.41)}$	2.32 (3H, s, CH_3); 2.46 (3H, s, CH_3); 6.57 (1H, tt, $^2J_{H-F}$ = 53, $^3J_{H-F}$ = 4.7, CHF_2)	-97.64 (2F, s, CF_2); -137.24 (2F, d, J = 53, CHF_2)		93-94 (20)	79
6b	$C_7H_7F_2N_3$	$\frac{48.61}{49.11}$	$\frac{3.96}{4.12}$	$\frac{24.12}{24.55}$		2.34 (3H, s, CH_3); 2.58 (3H, s, CH_3); 7.36 (1H, t, J = 60, CHF_2)	-95.11 (2F, d, J = 60, CHF_2)	53-55		20
6c	$C_6H_3F_4N_3$	$\frac{37.45}{37.32}$	$\frac{1.40}{1.57}$	$\frac{22.04}{21.76}$		6.48 (1H, tt, $^2J_{H-F}$ = 53, $^3J_{H-F}$ = 4.7, CHF_2); 7.95 (1H, s, CH); 8.43 (1H, s, CH)	-98.84 (2F, s, CF_2); -138.22 (2F, d, J = 53, CHF_2)	30-32		80
7*[2]	$C_6H_4F_4N_6$	$\frac{30.59}{30.52}$	$\frac{1.85}{1.71}$	$\frac{35.68}{35.59}$		6.59 (1H, tt, $^2J_{H-F}$ = 53, $^3J_{H-F}$ = 4.7, CHF_2); 8.07 (1H, s, CH); 8.75 (1H, s, CH)	-98.56 (2F, s, CF_2); -138.85 (2F, d, J =53, CHF_2)	162-164		95
8	$C_6H_4F_4N_2O_2$	$\frac{33.49}{33.98}$	$\frac{1.90}{2.11}$	$\frac{13.66}{13.21}$		6.52 (1H, tt, $^2J_{H-F}$ = 53, $^3J_{H-F}$ = 4.7, CHF_2); 7.90 (1H, s, CH); 8.43 (1H, s, CH)	-98.22 (2F, s, CF_2); -138.17 (2F, d, J = 53, CHF_2)	107-109		63

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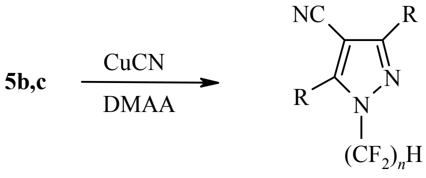
* **4b**, found, %: Cl 20.02. Calculated, %: Cl 19.63. **4d**, found, %: Cl 15.77. Calculated, %: Cl 15.37.

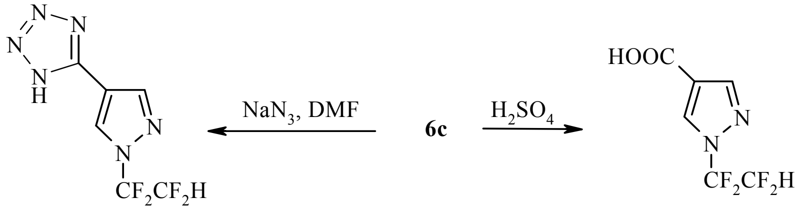
*[2] NMR spectra were taken in DMSO-d_6.

containing two methyl groups, replacement of the iodine atom by a nitrile group is hindered as a result of their donating and steric effects. The reaction occurs in boiling dimethylacetamide during 20 h in ~20% yield with the formation of compound **6b**.



6b,c

The nitrile group in compound **6c** may be converted into a tetrazole by the action of sodium azide in DMF, or hydrolyzed to a carboxyl by the action of sulfuric acid without destruction of the tetrafluoroethyl fragment, with the formation of compounds **7** and **8**.



7 **8**

We have therefore investigated the electrophilic substitution reaction of pyrazoles containing a difluoromethyl fragment at the nitrogen atom and have found conditions for nitration, halogenation, and cyanation of such compounds.

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were recorded on a Varian VXR 300 (300 MHz) instrument, internal standards were TMS and trichlorofluoromethane. The IR spectra were obtained on a UR 20 instrument in KBr disks.

N-Difluoromethylpyrazole (1a). A solution of pyrazole (6.8 g, 100 mmol) in diglyme (30 ml) was placed in a three-necked flask fitted with a bubbler for introducing gas, a thermometer, and an efficient fractionating column with a Würtz head connected to a downward condenser. Potassium hydroxide (11.4 g, 200 mmol) in water (10 ml) was added with stirring. A stream of chlorodifluoromethane was passed with vigorous stirring, gradually increasing the temperature in the reaction mixture to 90-100°C. The desired product containing water and solvent is distilled out. The reaction is stopped when the vapor temperature in the Würtz head reaches 90°C. The collected crude product was dried with $MgSO_4$ and subjected to fractional distillation, collecting the fraction of bp 85-87°C.

N-Difluoromethyl-3,5-dimethylpyrazole (1b). Chlorodifluoromethane was bubbled with vigorous stirring through a solution of 3,5-dimethylpyrazole (9.6 g, 100 mmol) in a mixture of dioxane (30 ml), water (20 ml), and KOH (17.1 g, 300 mmol) at 40-45°C until gas was no longer absorbed (~4 h). Water (150 ml) was added, the precipitated oil was extracted with ether (3 × 50 ml), the ether extract was washed with water (3 × 50 ml), and dried over $MgSO_4$. The ether was distilled off, and the residue distilled collecting the fraction with bp 142-144°C.

N-2-H-Tetrafluoroethylpyrazole (1c). Potassium metal (0.2 g, 5 mmol) was added to a solution of pyrazole (6.8 g, 100 mmol) in anhydrous THF (30 ml). After solution of the metal a current of tetrafluoroethylene was passed through with vigorous stirring for 20-25 h at such a rate that the gas was completely absorbed, maintaining the temperature of the reaction mixture at 35-45°C. The THF was distilled off with an efficient fractionating column, and the fraction of bp 90-110°C was collected. The crude product, containing solvent as contaminant, was stirred with water (20 ml) and ether (20 ml), and extracted. The ether layer was separated, dried over $MgSO_4$, and the ether was distilled off at atmospheric pressure with a fractionating column. The residue was redistilled, collecting the fraction of bp 107-112°C.

N-2-H-Tetrafluoroethyl-3,5-dimethylpyrazole (1d) was obtained analogously to compound **1c**. After distillation of THF the residue was redistilled in vacuum. The data corresponded with those described in [8].

N-Difluoromethyl-4-nitropyrazole (2a). Pyrazole **1a** (1.18 g, 10 mmol) was added with stirring to a mixture of H_2SO_4 ($d = 1.84$) (3 ml) and HNO_3 ($d = 1.52$) (2 ml). The reaction mixture was stirred for 3 h at 30-40°C, and left overnight. The mixture was poured onto ice, neutralized with sodium carbonate solution, extracted with ether (3 × 20 ml), the ether extract was washed with water (3 × 50 ml), dried over $MgSO_4$, the ether distilled off, and the residue distilled in vacuum.

N-Difluoromethyl-3,5-dimethyl-4-nitropyrazole (2b). Chlorodifluoromethane was bubbled with vigorous stirring through a solution of 3,5-dimethyl-4-nitropyrazole (1.4 g, 10 mmol) in a mixture of dioxane (10 ml), water (7 ml), and KOH (2.9 g, 50 mmol) at 40-45°C until the end of gas absorption (~4 h). Water (50 ml) was added, the precipitated crystals were filtered off, dried in the air, and crystallized from hexane.

N-2-H-Tetrafluoroethyl-4-nitropyrazole (2c) was obtained analogously to compound **2a**.

N-2-H-Tetrafluoroethyl-3,5-dimethyl-4-nitropyrazole (2d). Pyrazole **1d** (1.96 g, 10 mmol) was added with stirring to a mixture of H_2SO_4 ($d = 1.84$) (3 ml), HNO_3 ($d = 1.52$) (2 ml), and 10% oleum (0.5 ml). The reaction mixture was stirred for 3 h at 100-110°C, and left overnight. The mixture was then treated analogously to compound **2a**.

N-Polyfluoroalkyl-4-bromopyrazoles (3a-d). Bromine (3.2 g, 20 mmol) was added with vigorous stirring to a mixture of the appropriate compound **1a-d** (20 mmol) and water (20 ml), and the mixture stirred at room temperature until decoloration of the reaction mixture. The mixture was extracted with ether (3 × 20 ml), the ether extract was washed with water (3 × 50 ml), with 2% $NaHSO_3$ solution (50 ml), and once again with water (50 ml). The extract was dried over $MgSO_4$, the ether distilled off, and the residue distilled in vacuum.

N-Difluoromethyl-4-chloro-3,5-dimethylpyrazole (4b). Sodium bicarbonate (1.68 g, 20 mmol) was added with vigorous stirring to a mixture of pyrazole **1b** (2.92 g, 20 mmol) and water (30 ml), and the mixture stirred at room temperature while passing a current of chlorine until saturation (~30 min). The mixture was extracted with ether (3 × 20 ml), the ether extracts washed with water (3 × 50 ml), with 2% $NaHSO_3$ solution (50 ml), and once again with water (50 ml). The extract was dried over $MgSO_4$, the ether distilled off, and the residue redistilled in vacuum.

N-2-H-Tetrafluoroethyl-4-chloro-3,5-dimethylpyrazole (4d) was obtained analogously.

N-Difluoromethyl-4-iodo-3,5-dimethylpyrazole (5b). N-Iodosuccinimide (4.75 g, 21 mmol) was added with stirring to a solution of pyrazole **1b** (2.9 g, 20 mmol) in 90% H_2SO_4 (15 ml). The mixture was stirred at 30-35°C until the appearance of an intense color of iodine, then poured onto ice, and extracted with ether (3 × 20 ml). The combined ether extract was washed with water (3 × 50 ml), with 5% $NaHSO_3$ solution (50 ml), and once again with water (50 ml). The solution was dried over $MgSO_4$, the ether distilled off and the residue distilled in vacuum.

N-2-H-Tetrafluoroethyl-4-iodopyrazole (5c) and N-2H-Tetrafluoroethyl-4-iodo-3,5-dimethylpyrazole (5d) were obtained analogously.

N-Difluoromethyl-4-cyano-3,5-dimethylpyrazole (6b). Copper(I) cyanide (2.7 g, 30 mmol) was added to a solution of pyrazole **5b** (2.9 g, 20 mmol) in anhydrous dimethylacetamide (15 ml). The reaction mixture was boiled with stirring for 20 h. Water (100 ml) was then added, the product was extracted with ether, and separated chromatographically (silica gel MN-Kieselgel-60, eluent chloroform, R_f 0.8).

N-2-H-Tetrafluoroethyl-4-cyanopyrazole (6c) was obtained analogously. Reaction time was 2 h. After extraction with ether the product was not chromatographed, but was crystallized from pentane by freezing out.

N-2-H-Tetrafluoroethyl-4-(5-tetrazolyl)pyrazole (7). Sodium azide (0.22 g, 35 mmol) and NH_4Cl (0.15 g, 2.7 mmol) were added to a solution of cyanopyrazole **6c** (0.58 g, 3 mmol) in anhydrous DMF (5 ml). The reaction mixture was stirred at 120-135°C for 12 h, and the solvent was distilled off in vacuum. Water (20 ml) was added to the residue, and the solution was acidified with HCl to pH 2-3. The precipitated solid was filtered off, and crystallized from aqueous methanol.

N-2-H-Tetrafluoroethyl-4-carboxypyrazole (8). A solution of cyanopyrazole **6c** (0.58 g, 3 mmol) in 50% H_2SO_4 (3 ml) was heated at 100-110°C for 3 h. Water (10 ml) was added and the mixture partially neutralized with ammonia to pH 2-3. The mixture was maintained at 0°C for 4 h, the precipitated crystals were filtered off, and dried in the air.

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