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5-FLUORO-SUBSTITUTED PYRAZOLES

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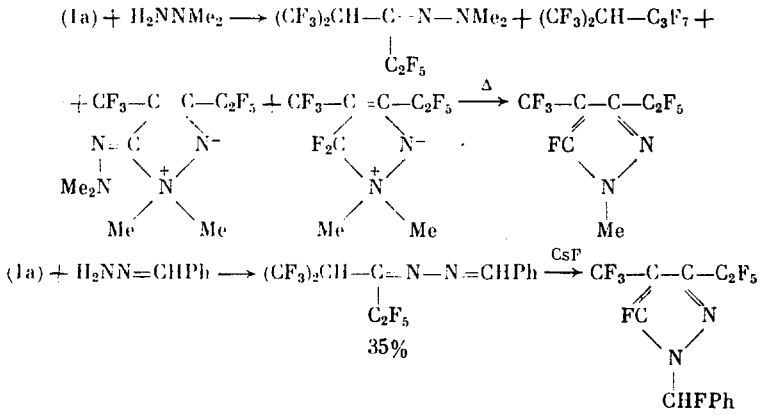
UDC 542.91:547.773.1

A preparative method was developed for the synthesis of 5-fluoro-substituted pyrazoles by the reaction of fluoroolefins with substituted hydrazines in the presence of triethylamine. The fluorine atom at the C^5 position of the pyrazoles obtained is readily substituted by O-, N-, and S-nucleophiles with the formation of 5-alkoxy-, amino-, mercapto-substituted fluoroalkylpyrazoles.

5-Fluoro-substituted pyrazoles are obtained in a low yield by the reaction of the readily available perfluoro-2-methyl-2-pentene (Ia) with N,N-dimethylhydrazine [1] or benzaldehyde hydrazone [2].



The authors of [3] used the difficultly obtained perfluoroalkyl alkyl ketones as the starting compounds.

The present work is devoted to the study of the reaction of monosubstituted hydrazines with perfluoro-2-methyl-2-pentene and 1-ethoxyperfluoroisobutylene (Ib) in order to develop a preparative method for the synthesis of 5-fluoro-substituted pyrazoles and to study their reactivity.

It was found that in the reaction of olefins (Ia, b) with phenylhydrazine in the presence of triethylamine, 3-pentafluoroethyl- (IVa)* and 3-ethoxy-1-phenyl-4-trifluoromethyl-5-fluoropyrazole (IVb) are formed in about 90% yield.

*This compound was previously reported in [4, 5].

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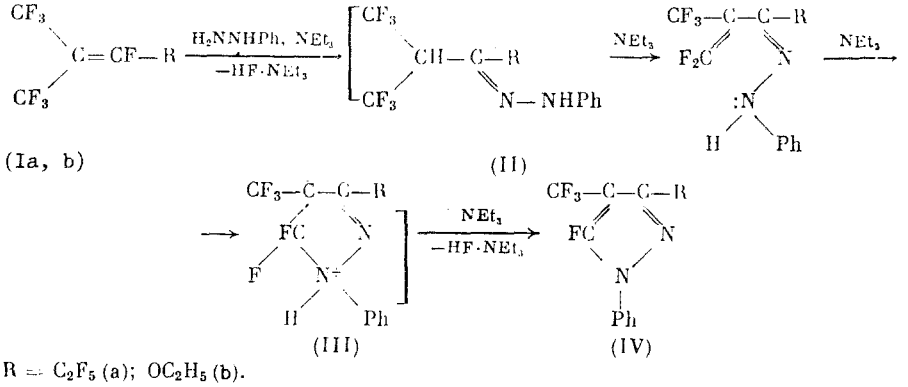
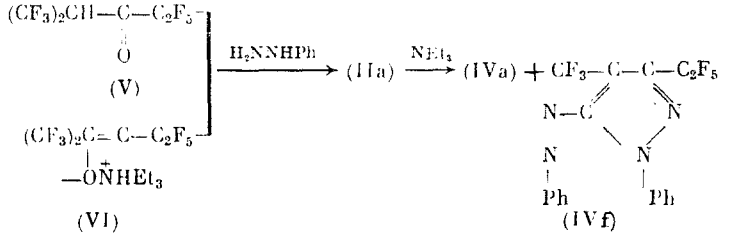


(Ia, b) (II) (III) (IV)

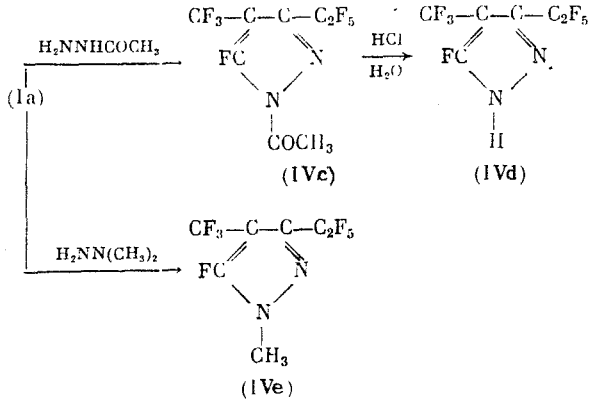
R = C_2F_5 (a); OC_2H_5 (b).

The formation of pyrazoles (IVa, b) clearly involves dehydrofluorination of an intermediately formed phenylhydrazone (II) and cyclic betaine (III), for which another two moles of triethylamine are consumed. The formation of pyrazoles (IV) from phenylhydrazone (II) was confirmed by a special experiment. Thus, in the reaction of phenylhydrazine with hexafluoroisopropyl pentafluoroethyl ketone (V) or its triethylammonium salt (VI), first phenylhydrazone (IIa) and then pyrazole (IVa) were obtained. Pyrazole (IVa) was also obtained from ketone (V) and phenylhydrazine in the triethylamine medium without separation of (IIa); 1-phenyl-3-pentafluoroethyl-4-trifluoromethyl-5-phenylazopyrazole (IVf) was also obtained in this reaction in a yield of about 20%



(V) (VI) (IVf)

The reaction of olefin (Ia) with N-acetylhydrazine proceeds in a similar way and leads to the formation of 1-acetyl-3-pentafluoroethyl-4-trifluoromethyl-5-fluoropyrazole (IVc), which in an acid medium readily hydrolyzes into 1-hydro-3-pentafluoroethyl-4-trifluoromethyl-5-fluoropyrazole (IVd)

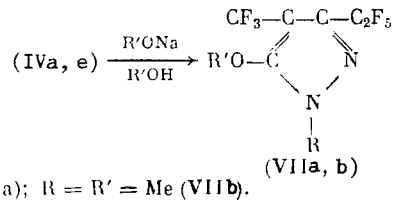


(Ia) (IVc) (IVd) (IVe)

The conditions found were also extended to the reaction of N,N dimethylhydrazine with olefin (Ia), where 1-methyl-3-pentafluoroethyl-4-trifluoromethyl-5-fluoropyrazole (IVe), previously described in [1], was obtained in a quantitative yield.

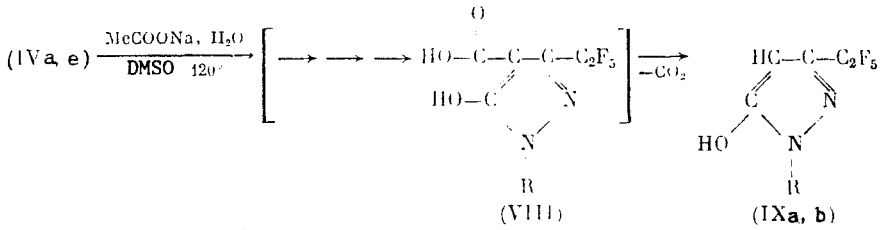
Thus, the use of equimolar amounts of fluoroolefin, hydrazine and three moles of triethylamine in the reaction makes it possible to carry out the reaction as predetermined with the tendency of formation of only one reaction product and the avoidance of formation of byproducts, as was the case in [1].

The pyrazoles obtained are adequate starting compounds in subsequent reactions of nucleophilic substitution of a fluorine atom in the 5-position of pyrazole. Thus, pyrazoles (IVa, e) react readily (mainly at 20°C) with alkali metal alcoholates resulting in the formation of 5-alkoxy-substituted fluoroalkylpyrazoles (VIa, b).



R = Ph; R′ = C_2H_5 (VIIa); R = R′ = Me (VIIb).

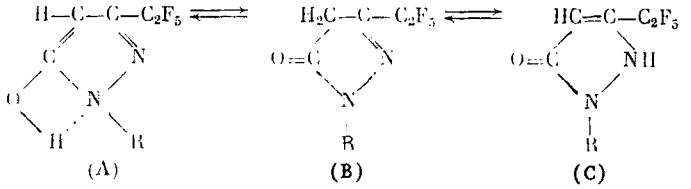
It was found that under more rigorous conditions, in the presence of a weak nucleophile such as the anion acetate in a dimethyl sulfoxide medium, pyrazoles (IVa, e) convert into 1-phenyl- and 1-methyl-3-pentafluoroethyl-4-hydro-5-hydroxypyrazoles (IX)



R = Ph (IXa), Me (IXb).

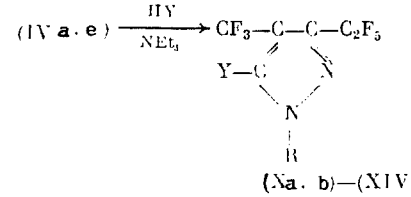
The formation of pyrazoles (IXa, b) clearly involves the hydrolysis in (IVa, e), first of a fluorine atom, and then of the trifluoromethyl group with subsequent decarboxylation of the intermediate acid (VIII), as happens, for example, in the case of perfluoro(2-methyl-2-pentenoyl) fluoride [6].

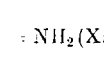
For compounds (IXa, b) the presence of three tautomers (A), (B), (C) (cf. [7]) is possible



On the basis of IR spectral data, where the absorption regions characteristic for the amine (C) and amide (B) groups are absent, structure (A) was ascribed to compounds (IXa, b) (ν of a bound OH, 2200-2800 cm^{-1}). This is not contradicted by the PMR spectral data (DMSO), which indicates three types of proton signals: the C_6H_5 (or CH_3), OH, and CH groups with integral intensity 5(3):1:1. In taking the spectra of comopunds (IXa, b) in aminic type solvents (triethylamine), the character and the number of signals do not change, which indicates the formation of a stable chelate structure of the enol form (A).

Pyrazoles (IVa, e) react under mild conditions with compounds containing amino groups, whereby 5-amino-substituted pyrazoles (Xa, b)-(XIV) are formed in good yield (Table 1)

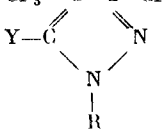


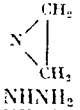
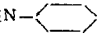
R = Me, Y = NH_2 (Xa),  (XIa); NH—NH_2 (XIIa); R = Ph, Y = NH_2 (Xb), (XIb);

HN— (XIII), HN—CH_2CO_2Et (XIV).

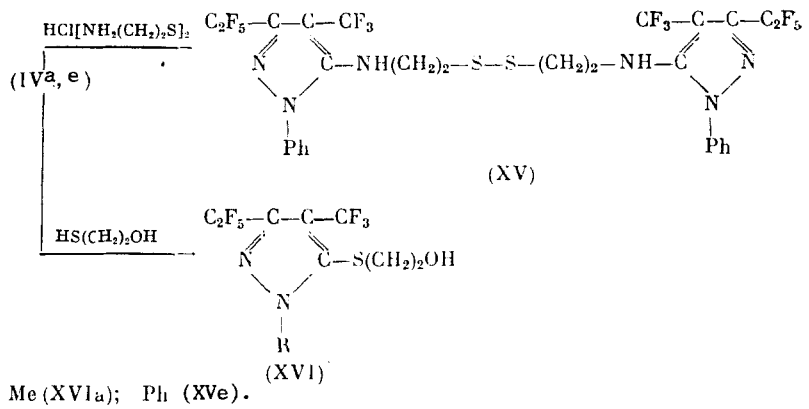
In the reaction of pyrazole (IVa) with di(2-aminoethyl)disulfide, bis[2-(1-phenyl-3-pentafluoroethyl-4-trifluoromethylpyrazol-5-ylamino)ethyl] disulfide (XV) is formed

TABLE 1. 1-Methyl (or Phenyl)-3-pentafluoroethyl-4-trifluoromethyl-5-substituted Pyrazoles $CF_3^3-C-C-CF_2^2-CF_3^1$



Compound	R	Y	Bp, °C (p, mm Hg) mp, °C	Yield, %	Found, %				Empirical formula	Calculated, %				^{19}F NMR (δ, ppm, CF_3COOH)					PMR (δ, ppm)
					C	H	F	N		C	H	F	N	CF_3^1	CF_2^2	CF_3^3	Ph(5H)	Me(3H)	
(Xa)	CH_3	H_2N	88–90° (3)	51	30,48	2,04	—	15,64	$C_7H_5F_8N_3$	29,69	1,78		14,84	‡ −22,2	6,6	33,3		‡ 3,48	4,7 s (2H)
(Xb)	C_6H_5	H_2N *	110° (3)	71	41,98	2,11	—	11,95	$C_{12}H_7F_8N_3$	41,75	2,04	–	12,17	−23,1	6,0	33,3	7,33		4,36 (2H) ‡
(XIa)	CH_3		Oil	64	34,80	2,22	—	13,56	$C_9H_7F_8N_3$	34,96	2,28	–	13,59	−26,2	4,4	30,6		3,79	2,36 s (4H) **
(XIb)	C_6H_5		92–94°	75	45,27	2,45	—	11,09	$C_{14}H_9F_8N_3$	45,20	2,42	–	11,30	26,0	3,8	30,3	7,3		2,0 (4H) ‡
(XIIa)	CH_3	$NHNH_2$	90° (3)	77	28,26	2,07	—	18,91	$C_7H_6F_8N_3$	28,20	2,03	–	18,79	−22,6	6,4	33,5		3,8	5,7 (1H); 4,07 (2H)
(XIIb)	C_6H_5	$NHNH_2$	62–64°	78	39,89	2,13	—	15,76	$C_{12}H_8F_8N_4$	40,00	2,22	–	15,50	***	4,8	31,8			
(XIII)	C_6H_5	HN– 	Oil †	81	50,50	4,16	36,25	–	$C_{18}H_7F_8N_3$	50,59	3,99	35,59		−24,2 −23,8	5,3	32,2; 31,8	7,6 ‡		3,87 (HN); 2,78 (CH); 1,75 (10H)
(XIV)	C_6H_5	$HN-CH_2CO_2Et$	110–112° (3)	70	44,89	3,28	35,17	9,75	$C_{16}H_{12}F_8N_3O_2$	44,56	3,04	35,24	9,74	−25,11	4,67	31,35	7,25		4,87 (HN); 3,93 q (OCH_2); 3,4 (CH_2N); 0.99 t (CH_3)

*Heating in autoclave for 10 h at 90°C.
†Purified on a column with Al_2O_3 (neutral), eluent) hexane.
‡Solvent CCl_4.
**Solvent $CDCl_3$.
***Solvent $CHCl_3$.



R = Me (XVIa); Ph (XVe).

1-Methyl- and 1-phenyl-3-pentafluoroethyl-4-trifluoromethyl-5-(2-hydroxyethylthio) pyrazoles (XVIa, e) were obtained under similar conditions from pyrazoles (IVa, e) and mercaptoethanol. The structure of the compounds obtained was confirmed by the IR, ^1H and ^{19}F NMR, and mass spectral data.

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra (δ, ppm) were obtained on a "Perkin-Elmer R-32" spectrometer (90 MHz and 84.6 MHz) with reference to TMS and CF_3COOH, respectively, as external standards; the IR spectra on a UR-20 spectrophotometer; and the mass spectra on a "Varian MAT-8" chromato-mass spectrometer (energy of ionizing electrons 70 eV); the m/z and tentative assignments are given.

1-Phenyl-3-pentafluoroethyl-4-trifluoromethyl-5-fluoropyrazole (IVa). a) A mixture of 3.38 g (30 mmoles) of phenylhydrazine, 10 g (100 mmoles) of NEt_3 and 20 ml of dry CH_3CN was added dropwise, with stirring and at −50 to −40°C to 9.3 g (30 mmoles) of olefin (Ia). The cooling was then removed, the mixture was allowed to stand at ∿20°C for 1 h, then was poured into water, the organic layer was separated, washed with water, a 10% solution of HCl, and water again, dried over $MgSO_4$ and distilled. Yield, 9.7 g (90%) of (IVa), bp 67-69°C (3 mm). Found: C 41.68; H 1.88; N 8.34%. $C_{12}H_5F_9N_2$. Calculated: C 41.38; H 1.44; N 8.05%. IR spectrum (ν, cm^{-1}): 1490, 1525, 1600 and 1620 s (unsaturated bonds). Mass spectrum, m/z: 343 M^+, 324 $(M - F)^+$. ^{19}F NMR spectrum (δ, ppm): −20.6 m (3F), +6.45, t.m (3F), 34.2 q.m (2F), 45 q.m (F). PMR spectrum (δ, ppm): 7.25 m (C_6H_5).

b) A 0.9 g portion (8.3 mmoles) of phenylhydrazine was added dropwise to 1.8 g (6 mmoles) of ketone (V) in 10 ml of $(C_2H_5)_2O$, and then 1.43 g (14 mmoles) of NEt_3 in 10 ml of ether was added. The reaction mixture was allowed to stand at 20°C for 12 h, then was washed with a 10% solution of HCl, water, dried over $MgSO_4$, the ether was removed on a rotary evaporator, and the residue was distilled. Yield, 1.2 g (58%) of (IVa), bp 67-68°C (3 mm), which with respect to the ^{19}F NMR data and to the boiling point was identical with an authentic sample, and 0.56 g (20%) of (IVf), bp 62°C (3 mm). Found: C 50.01; H 2.44; N 12.80; F 35.56%. $C_{18}H_{10}F_8N_4$. Calculated: C 49.99; H 2.30; N 12.90; F 35.23%. IR spectrum (ν, cm^{-1}): 1430-1480 w, 1500, 1560, 1600 s (unsaturated bonds), 3090 w (CH). ^{19}F NMR spectrum ($(CH_3)_2CO$, δ, ppm): −23.1, t.m (3F), +4.7 t.m (3F), 31.2 q.m (2F).

c) A 6 g portion (50 mmoles) of phenylhydrazine was added dropwise at −30°C, with stirring, to a mixture of 22.5 g (56 mmoles) of ketone salt (VI) in 50 ml of dry monoglyme, and then 5.2 g (51 mmoles) of NEt_3 in 10 ml of monoglyme was added. The temperature was raised to ∿20°C, and after 2 h, the mixture was diluted with water, the organic layer was washed with a 10% solution of HCl and water, dried over $MgSO_4$ and distilled. Yield, 11.8 g (60%) (IVa), bp 68-70°C (4 mm).

d) A 2 ml portion of dry NEt_3 was added at 0°C to 1 g of phenylhydrazone (IIa), the mixture was allowed to stand for 30 min at 20°C, then was washed with a 10% solution of HCl and washed, dried and distilled. Yield 0.6 g (66%) of (IVa), bp 68-70°C (3 mm).

1-Phenyl-3-ethoxy-4-trifluoromethyl-5-fluoropyrazole (IVb). In a similar way as in (a), a mixture of 2.4 g (22 mmoles) of phenylhydrazine and 7 g (69 mmoles) of NEt_3 was added dropwise to 5 g (22 mmoles) of olefin (Ib) in 10 ml of C_2H_5OH. Yield, 5.5 g (90%) of (IVb), bp 98-99°C (1 mm). Found: C 52.89; H 3.84; N 10.21%. $C_{12}H_{10}F_4N_2O$. Calculated: C 52.55:

H 3.86; N 10.21%. PMR spectrum (δ, ppm, CCl_4): 1.25 t (3H), 4.18 q (2H), 7.0-7.3 m (5H). ^{19}F NMR spectrum (δ, ppm, CCl_4): −21.7 d.m (3F), +42.5 q.m (2F, $J_{CF_3/F}$ = 11.2 Hz.

1-Acetyl- and 1-Hydro-3-pentafluoroethyl-4-trifluoromethyl-5-fluoropyrazoles (IVc, d). a) In a similar way as in (a), a mixture of 5.3 g (71 mmoles) of N-acetylhydrazine, 40 ml (210 mmoles) of NEt_3 and 100 ml of $(C_2H_5)_2O$ was added dropwise to 21.4 g (71 mmoles) of (Ia). The mixture was allowed to stand for 4 h at 20°C, the solvent was removed on a rotary evaporator, and the residue was dstilled. Yield, 13.3 g (60%) of (IVc), bp 88-89°C (3 mm). Found: N 8.63%. $C_8C_3F_9N_2O$. Calculated: N 8.91%. Mass spectrum, m/z: 272 $(M-COCH_3)^+$, 263 $(M-COCH_3, F)^+$, 203 $(M-COCH_3, CF_3)^+$, 119 $(C_2F_5\ N)$, 69 (F_3^+), 43 $(COCH_3^+)$. ^{19}F NMR spectrum (δ, ppm): −21.8 m (3F), 6.8 (3F), 35.0 (2F), 53.5 (1F); at −78°C, a liquid was collected in a trap, from which after washing with a 10% of HCl and water, and drying and distillation, 2 g (10%) of (IVd) was obtained, bp 158-160°C. Found: C 27.32; H 0.68; N 11.06%. $C_6HF_9N_2$. Calculated: C 26.47; H 0.37; N 10.60%. ^{19}F NMR spectrum (δ, ppm): −20.1 m (3F), 8.42 m (3F), 37.4 m (2F), 48.5 m (F). Mass spectrum, m/z: 272 $(M)^+$.

b) A mixture of 1 g of (IVc) and 2 ml of 36% HCl was stirred for 30 min at 20°C. After washing with water and drying, 0.6 g of (IVd) was obtained, bp 159°C (69%).

1-Methyl-3-pentafluoroethyl-4-trifluoromethyl-5-fluoropyrazole (IVe). A mixture of 3 ml (51 mmoles) of NEt_3, 1 g (17 mmoles) of dimethylhydrazine and 15 ml of $(C_2H_5)_2O$ was added dropwise with stirring, at −50 to −40°C to 5 g (17 mmoles) of olefin (Ia). Cooling was then removed, the mixture was allowed to stand for 12 h, and the triethylamine hydrofluoride precipitate was separated. After removal of the solvent on a rotary evaporator and holding the residue for 3 h at 120°C, the reaction mixture was distilled. Yield, 4.3 g (90%) of (IVe), bp 35-36°C (3 mm). Found: C 29.11; H 1.20; N 9.89%. $C_7H_3F_9N_2$. Calculated, C 29.38; H 1.06; N 9.79%. ^{19}F NMR spectrum (δ, CF_3COOH: −26.6 (eF), 6.89 (3F), 34.67 (2F), 49.10 (1F) (cf. [1]).

1-Phenyl-3-pentafluoroethyl-4-trifluoromethyl-5-ethoxypyrazole (VIIa). A 1.7 g portion (5 mmoles) of pyrazole (IVa) was added to a solution of 0.15 g (6.3 mmoles) of Na in 30 ml of absolute C_2H_5OH. The mixture was allowed to stand overnight at 20°C, and after distillation 1.2 g (66.7%) of (VIIa) was obtained, bp 128-130°C (3 mm). Found: C 44.49; H 2.72; F 41.56%. $C_{14}H_{10}F_8N_2O$. Calculated: C 44.93; H 2.69; F 40.62%. ^{19}F NMR spectrum (δ, ppm): −22.2 m (3F), 5.78 m (3F), 32.9 m (2F). PMR spectrum (δ, ppm): 1.45 t (3H), 4.21 q (2H), 7.0 (5H).

1-Methyl-3-pentafluoroethyl-4-trifluoromethyl-5-methoxypyrazole (VIIb). A 4.7 g portion (16.4 mmoles) of pyrazole (IVe) was added to a solution of 0.38 g (16.5 mmoles) of Na in 30 ml of absolute MeOH. The reaction mixture was boiled for 6 h, the precipirate was filtered off, the solvent was removed on a rotary evaporator, and the residue was distilled. Yield, 2.8 g (60%) of (VIIb), bp 57°C (3 mm). Found: C 32.94; H 2.24; F 51.13%. $C_8H_6F_8N_2O$. Calculated: C 32.23; H 2.03; F 50.98%. ^{19}F NMR spectrum (δ, ppm): −22.0 t.m (3F), 6.22 t.m (3F), 32.9 q.m (2F). PMR spectrum (δ, ppm, CCl_4): 3.76 (3H, OCH_3), 4.0 (3H, NCH_3).

1-Phenyl-3-pentafluoroethyl-4-hydro-5-hydroxypyraozle (IXa). A 5 g portion (14 mmoles) of pyrazole (IVa) was added to a mixture of 2.93 g (22 mmoles) of sodium acetate dihydrate, 2 ml of H_2O and 12 ml of DMSO, and the mixture was heated for 8 h at 100°C with stirring. The precipitate was filtered, the mother liquor was washed with water, the organic layer was dried over $MgSO_4$ and distilled in vacuo (3 mm) on a boiling water bath to give 1.7 g of a fraction, bp 70-72°C (3 mm) (unreacted pyrazole). The residue was subjected to sublimation. Yield, 1.93 g (72.5%) of (IXa), mp 147-149°C. Found: C 47.37; H 2.47; N 9.83%. $C_{11}H_7F_5N_2O$. Calculated: C 47.50; H 2.51; N 10.01%. Mass spectrum, m/z (I, %): 278 (76.9) M^+, 209 (11.1) $(M-CF_3)^+$, 159 (3.0) $(M-C_2F_5)^+$; 105 (20.9) PhN_2^+; 91 (17.1) PhN^+, 77 (100) Ph^+, 50 (6.2) CF_2^+. ^{19}F NMR spectrum (δ, ppm, DMSO): 7.32 (3F), 36.7 (2F). PMR spectrum (δ, ppm, DMSO): 7.5 (5H), 6.0 (1H, OH), 2.5 (1H, CH).

1-Methyl-3-pentafluoroethyl-4-hydro-5-hydroxypyrazole (IXb). In a similar way, from 5.7 g of pyrazole (IVe), 8.1 g of CH_3COONa, 10 ml of H_2O, 70 ml of DMSO, 3.1 g (72%) of (IXb) was obtained, bp 120°C (3 mm). Found: C 33.70; H 1.98; N 13.03%. $C_6H_4F_5N_2O$. Calculated: C 33.34; H 2.33; N 12.97%. ^{19}F NMR spectrum (δ, ppm, DMSO): 5.55 (3F), 33.8 (2F). PMR spectrum (δ, ppm, DMSO): 5.0 (1H), 3.8 (3H), 2.55 (1H).

5-Amino-substituted Pyrazoles (Xa, b)-(XIV). Typical Experiment. Equimolar amounts of pyrazole, an amino compound, triethylamine in monolgyme were held at 20°C or were heated at the boiling point of the solvent for several hours (a ^{19}F NMR monitoring for the absence of

the initial pyrazole), and then the reaction mixture was diluted with water, the organic layer was separated, washed with water, dried and distilled. The yields and physicochemical characteristics of the compounds (Xa,b)-(XIV) obtained are given in Table 1.

Bis[2-(1-phenyl-3-pentafluoroethyl-4-trifluoromethylpyrazol-5-ylamino)ethyl] Disulfide (XV). A mixture of 0.9 g (4 mmoles) of di-(2-aminoethyl) disulfide hydrochloride, 3 ml of H_2O, 5 ml of NEt_3, 10 ml of monoglyme, and 2.8 g (8.0 mmoles) of pyrazole (IVa) was allowed to stand at 20°C for 12 h. The reaction mixture was then diluted with water, extracted with diethyl ether, the ether solution was washed with water, dried over $MgSO_4$, and the solvent was removed on a rotary evaporator. Yield, 2.9 g of a transparent oil, which was purified on a column with Al_2O_3 (neutral) (carrier 5/40 mixed with super S, eluent CCl_4). Yield. 2.1 g (61%) of (XV). Found: F 38.43; S 7.87%. $C_{28}H_{20}F_{16}N_6S_2$. Calculated: F 37.62; S 7.78%. ^{19}F NMR spectrum (δ, ppm, CCl_4), −24.2 m (3F), 4.2 br. s (3F), 31 br. q (2F). PMR spectrum (δ, ppm, CCl_4): 7.7 (10H), 4.5 t (2H, 2NH), 3.3 q ($2CH_2N$), 2.6 t (2H, CH_2S).

1-Methyl-3-pentafluoroethyl-4-trifluoromethyl-5-(2-hydroxyethylthio)pyrazole (XVIa). In a similar way as in the preceding experiment, from 4.4 g (15 mmoles) of (IVe), 1.6 g (16 mmoles) of NEt_3 in 5 ml of absolute monoglyme and 1.25 g (15 mmoles) of mercaptoethanol, 3.3 g (62.6%) of (XVIa) was obtained, bp 123-124°C (3 mm). Found: C 31.47; H 2.41; N 8.04%. $C_9H_8N_2SO$. Calculated: C 31.40; H 2.34; N 8.14%.

1-Phenyl-3-pentafluoroethyl-4-trifluoromethyl-5-(2-hydroxyethylthio)pyrazole (XVIe). In a similar way as in the preceding experiment, from 1.6 g (46 mmoles) of pyrazole (IVa), 0.6 g (60 mmoles) of NEt_3 and 0.9 g (115 mmoles) of mercaptoethanol in 10 ml of toluene, 1.6 g (85%) of (XVIe) was obtained, bp 150-152°C (3 mm). Found: C 41.5; H 2.51; S 7.76%. $C_{14}H_{10}F_8N_2OS$. Calculated: C 41.13; H 2.46; S 7.88%. ^{19}F NMR spectrum (δ, ppm, CCl_4): −23.2 t.q (3F), 4.45 m (3F), 31.2 q.q (2F), integral intensity 3:3:2.

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