Hydroxy- and alkoxymethylation of polyfluoroalkyl pyrazoles*

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A synthetic route to 1-hydroxy- and 1-alkoxymethyl-3-polyfluoroalkylpyrazoles *via* regioselective *N*-hydroxy- and alkoxymethylation of *N*-unsubstituted pyrazoles with paraformaldehyde has been proposed. The alkoxyalkylation of polyfluoroalkylpyrazoles proceeds in aqueous-alcohol medium, whereas hydroxymethylation requires anhydrous conditions.

Key words: polyfluoroalkylpyrazoles, paraformaldehyde, *N*-hydroxy- and alkoxymethylation, regioselectivity.

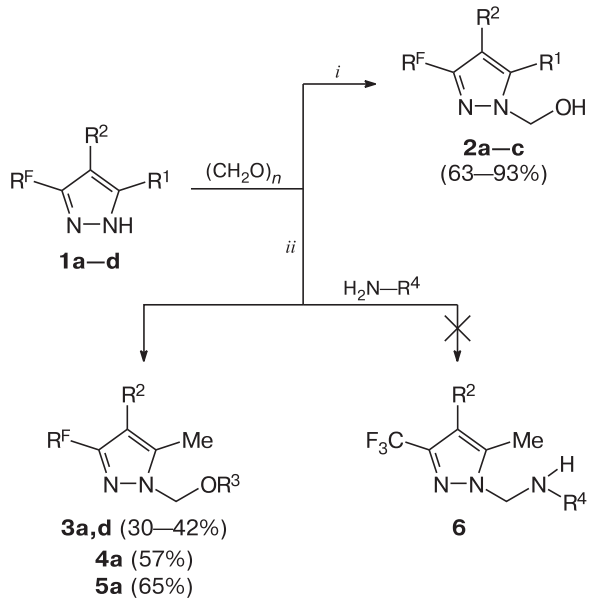
The enormous data on biological properties of pyrazoles allows one to designate them as promising objects for the modification that opens the way to obtain bioactive molecules.[1—8] This is the cause of an inexhaustible interest of chemists to the synthesis and modification of pyrazoles. According to the SciFinder® search system, more than 40 reviews on synthesis and properties of pyrazoles and their derivatives have been published only during the last five years.

Fluorinated pyrazoles deserve special attention because of their potential use in pharmacy and agrochemistry. Due to unique properties of the fluorine atom,[9,10] fluorinated derivatives display distinctive physico-chemical and biological properties making them promising molecules for formulating novel medical preparations or special-purpose materials.[10—16] Thus, a series of known medicines and agrochemicals comprise (trifluoromethyl)pyrazole moiety.[17] Among them, an anti-inflammatory drug *celebrex* (*celecoxib*), veterinary antiarthritic drug *mavacoxib* (*trocoxil*), as well as anticoagulant preparation *razaxaban*[18] being currently under clinical investigation, fungicide *pentiopirad,*[19] and herbicide *fluazolat*[20] are worth mentioning.

Here, we have studied the possibility to modify polyfluorinated pyrazoles **1** *via* reactions with paraformaldehyde. Non-fluorinated 1-hydroxymethylpyrazoles[21,22] obtained in result of such transformations were used as building blocks to construct acyclic nucleosides,[23] various ligands, and metal complexes including those promising for practical applications, *e.g.*, Zn^{II} complexes of *N*,*N*-bis-(1*H*-pyrazolyl-1-methyl)arylamines showing high catalytic activity in polymerization of methylacrylate.[24]

It was found that reac tions of polyfluoroalkylpyrazoles **1a—c** with paraformaldehyde carried out according to a previously described procedure [24] in methylene chloride in the absence of an acid afford 1-hydroxymethylsubstituted compounds **2a—c** in 5 days (Scheme 1). However, in absolute ethanol saturated with dried hydrogen chloride,

Scheme 1



i. CH_2Cl_2, Δ or abs. EtOH, HCl gas, Δ; *ii*. R^3OH, HCl, 80—90 °C.

Compound	R^F	R^1	R^2	Products	R^3
1a,**2a**	CF_3	Me	4-MeC_6H_4N=N	**3a**	Et
				4a	Bu^n
				5a	Hex
1b, **2b**	CF_3	Ph	H	—	—
1c, **2c**	$H(CF_2)_2$	Ph	H	—	—
1d	C_3F_7	Me	4-$MeOC_6H_4N$=N	**3d**	Et

R^4 = CH_2Ph, CH_2CO_2H

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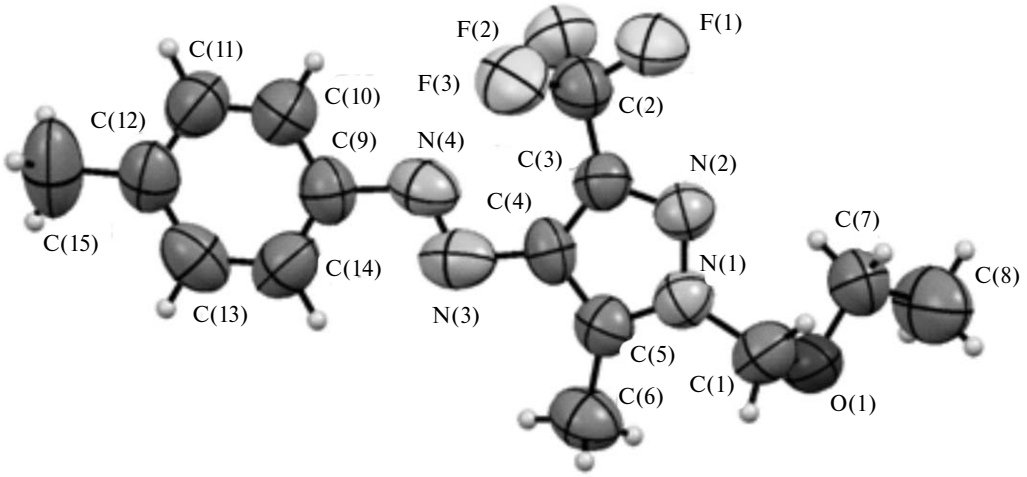


Fig. 1. General view of a molecule of **3a**.

these reactions proceed far more rapidly (in 4 h), according to the TLC data, and in nearly quantitative yields.

Compounds **2a**—**c** are unstable and decompose to give starting pyrazoles **1a**—**c** during purification by column chromatography.

Further, we have investigated the possibility of aminomethylation of polyfluoroalkyl pyrazoles **1** *via* the Mannich reaction with paraformaldehyde and amines. A heterocycle having the NH-center is known to act in these reactions either as a substrate capable of reacting with paraformaldehyde or as an amine component.[25] First, we proposed that pyrazoles **1** can act as substrates. However, it turned out that 4-aryldiazenylpyrazole **1a** reacting with benzylamine, taken as an amine component, remains unchanged under the classical Mannich reaction conditions (acidic catalysis, ethanol), whereas reaction with glycine under the same conditions produces 3-trifluoromethyl-1-ethoxymethylpyrazole **3a** rather than an expected *N*-aminomethyl pyrazole **6** (*see* Scheme 1). Changing the reaction conditions, namely, replacement a solvent for acetonitrile, did not produce an aminomethylation product. The molecule of a solvent (ethanol) seemed to act as a substrate when forming the product **3a**, whereas pyrazole **1a** reacted as an amine component. Ethoxymethylation of pyrazole **1d** was carried out in refluxing EtOH with paraformaldehyde in the presence of hydrochloric acid without an amine, thus affording pyrazole **3d**. Moderate yields in these reactions are defined by an incomplete conversion of the substrate. Prolonging the reaction time resulted in the formation of unidentifiable mixtures.

By the example of reactions of 4-aryldiazenylpyrazole **1a** with butanol and hexanol it was shown that alkoxymethylation discovered by us can be applied to obtain other 1-alkoxymethylpyrazoles **4a** and **5a** (see Scheme 1). Here, as the alcohol carbon chain length increases, the reaction time is reduced, and the product yields are improved.

Unsymmetrical polyfluoroalkylpyrazoles **1** have two competitive nucleophilic centers, namely, N(1) and N(2), capable of reacting with electrophilic reagents to give two regioisomeric 3-R^F- and 5-R^F-pyrazoles. Actually, as we have demonstrated earlier, methylation[26] and alkylation[27,28] of pyrazoles **1** proceed on both centers with predomination of a particular isomer depending on the reaction conditions, however, melting the pyrazoles together with (2-acetoxyethoxy)methylacetate,[28] as well as ribosylation[29] proceeds regioselectively on the N(1) center.

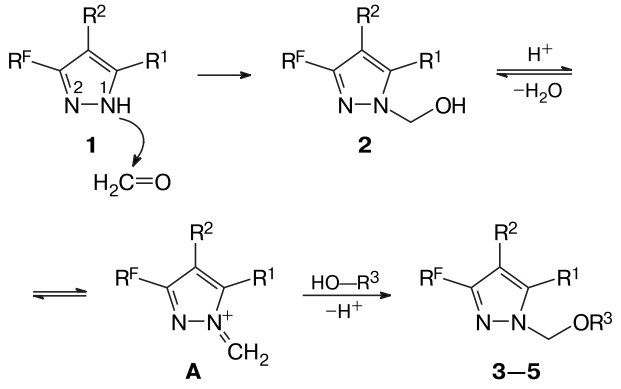
We have found that hydroxy- and alkoxymethylation of polyfluoroalkylpyrazoles **1** with paraformaldehyde proceed regioselectively on the N(1) atom to give 3-R^F-pyrazoles **2a**—**c**, **3a**,**d**, **4a**, and **5a**. In this case, when studying the reaction mixture by the GC-MS, the formation of an alternative 5-R^F-isomer was not observed. Regioisomeric structure of pyrazoles **2a**—**c**, **3a**,**d**, **4a**, and **5a** was detected by the ^{19}F NMR spectroscopy data. Thus, in their ^{19}F NMR spectra, the CF_3 signals were observed in the same region ($\delta_F \approx 99.3$—100.0), as those for the starting pyrazoles **1a**,**b** ($\delta_F \approx 99.6$—100.3); similarly, the signals of the fluorine atoms of α-CF_2 groups in products **3c** (δ_F 48.6) and **3d** (δ_F 52.2) were observed in the same regions as those for *N*-unsubstituted pyrazoles **1c** (δ_F 48.9) and **1d** (δ_F 52.3).

For pyrazole **3a**, X-ray diffraction analysis has been performed, also confirming its 3-CF_3-isomeric structure (Fig. 1).

Regioselectivity of the reactions under consideration may result from the preferable existence of pyrazoles **1** in a tautomeric form with a "pyrrole" nitrogen atom at a nonfluorinated substituent.[26] As a result, an addition of formaldehyde proceeds on the N(1) atom affording 1-hydroxymethyl-3-R^F-pyrazoles **2**. The latter can eliminate the OH group in an aqueous acid forming an intermediate carbocation **A**, which adds to an alcohol to yield 1-alkoxymethylated pyrazoles **3**—**5** (Scheme 2).

To summarize, we have discovered the reaction of regioselective *N*-alkoxymethylation of polyfluoroalkyl pyrazoles with paraformaldehyde in an aqueous-alcoholic medium, whereas under absolute (anhydrous) conditions

Scheme 2



the reaction is terminated at the step of 1-hydroxymethylated pyrazole formation.

Experimental

IR spectra were recorded on a «Perkin Elmer Spectrum One» IR-Fourier spectrometer in 4000—400 cm^{-1} range using Attenuated Total Reflection technique. NMR spectra were recorded on a Bruker DRX-400 spectrometer (^1H, 400 MHz, relatively $SiMe_4$, ^{19}F, 376 MHz, relatively C_6F_6) and on a Bruker Avance-500 spectrometer (^1H, 500 MHz, relatively $SiMe_4$, ^{19}F, 470 MHz, relatively C_6F_6), using $CDCl_3$ as the main solvent, unless noted otherwise. Elemental analyses (C, H, N) were performed using an elemental analyzer Perkin Elmer PE 2400, series II. Melting points were measured in opened capillaries on a Stuart SMP30 apparatus. Column chromatography was performed on a silica gel, grade 60 (0.063—0.2 mm), supplied by Alfa Aesar.

Single crystals of pyrazole **3a** were obtained by crystallization from chloroform. X-ray studies were performed on a Xcalibur 3 automatic diffractometer equipped with a CCD-detector (graphite monochromator, λ(Cu-Kα) = 1.54184 Å, φ/ω-scan technique, temperature 295(2) K). The absorption correction was done analytically using a multifaceted crystal model on a CrysAlis RED 1.171.29.9 software. Crystal structures were solved by direct method and refined by the full matrix least square method on F^2 using the SHELXTL software package.[30] Non-hydrogen atoms were refined in anisotropic approximation; hydrogen atoms were placed in geometrically calculated positions and included into the refinement using a rider model with dependent isotropic thermal parameters.

The main crystallographic data for compound **3a** and certain experimental data are given in Table 1.

Synthesis of pyrazoles 1a—d (general procedure). Hydrazine hydrate (1 mL, 12 mmol) and glacial acetic acid (10 mL) were added to a solution of 1,3-diketone (10 mmol) in EtOH (20 mL), and the resulting reaction mixture was heated under reflux for 8 h. On completion of the reaction water was added, the precipitate was filtered and recrystallized from 50% EtOH. Physicochemical characteristics of pyrazoles **1a**,[28] **1b**,[31] and **1c**[32] are consistent with the literature data.

3-Heptafluoropropyl-4-[(4-methoxyphenyl)diazenyl]-5-methyl-1*H*-pyrazole (1d). Dark-orange powder, 78% yield, m.p. 142—144 °C. IR, ν/cm^{-1}: 3170 (NH); 1610, 1582 (C=C, C=N); 1180—1250 (C—F). NMR ^1H, δ: 2.61 (s, 3 H, 5-Me); 3.88 (s, 3 H, OMe); 6.97—7.00 (m, 2 H, H_m, C_6H_4); 7.79—7.81 (m, 2 H, H_o, C_6H_4). NMR ^{19}F, δ: 35.55 (m, 2 F, β-CF_2); 52.30 (m, 2 F, α-CF_2); 81.5 (t, 3 F, CF_3, J = 9.4 Hz). Found (%): C, 43.88; H, 2.75; N, 14.36. $C_{14}H_{11}F_7N_4O$. Calculated (%): C, 43.76; H, 2.89; N, 14.58.

Table 1. Crystallographic data and X-ray data for compound **3a***

Parameter	**3a**
Formule	$C_{15}H_{17}F_3N_4O$
Molecular weight	326.32
Syngony	Triclinic
Space group	$P\bar{1}$
a/Å	8.966(11)
b/Å	10.390(5)
c/Å	10.623(11)
α/deg	110.55(7)
β/deg	100.54(9)
γ/deg	110.82(7)
V/Å^3	810.7(13)
Z	2
d_{calc}/g cm^{-3}	1.337
μ/mm^{-1}	0.950
Total number of reflections	9004
Number of independent reflections	2742
R_1-factor	0.062
The number of refined parameters	211

* Complete crystallographic data for compound **3a** are available on https://www.ccdc.cam.ac.uk/structures (CCDC 1586571).

Synthesis of 1-hydroxymethyl pyrazoles 2a—c. Method *A*. A mixture of pyrazole **1a,b,c** (1.5 mmol) and paraformaldehyde (0.15 g) in CH_2Cl_2 (15 mL) was heated to reflux for 5 days. Unreacted paraformaldehyde was filtered off, and the filtrate was concentrated.

Method *B*. Dried hydrogen chloride was bubbled through absolute ethanol for 20 min. Pyrazole **1a—c** (1.5 mmol) and paraformaldehyde (0.15 g) were added, and the reaction mixture was heated to reflux under argon for 4 h. Unreacted paraformaldehyde was filtered off, and the filtrate was concentrated. Compounds **2a—c** were recrystallized from 2 : 1 hexane—chloroform mixture.

1-(1-Hydroxymethyl)-5-methyl-4-[(4-methylphenyl)diazenyl]-3-trifluoromethyl-1*H*-pyrazole (2a). Yellow powder, 78% yield (according to method ***A***), 93% (according to method ***B***), m.p. 146—147 °C. IR, ν/cm^{-1}: 3299 (OH); 1605, 1583 (C=C, C=N); 1167—1143 (C—F). NMR ^1H, δ: 2.43 (s, 3 H, C_6H_4—Me); 2.73 (s, 3 H, 3-Me); 5.62 (s, 2 H, CH_2); 7.28—7.30 (m, 2 H, H_m, C_6H_4); 7.75—7.77 (m, 2 H, H_o, C_6H_4). NMR ^{19}F, δ: 99.93 (s, CF_3). Found (%): C, 52.24; H, 4.29; N, 18.67. $C_{13}H_{13}F_3N_4O$. Calculated (%): C, 52.35; H, 4.39; N, 18.78.

1-(1-Hydroxymethyl)-5-phenyl-3-trifluoromethyl-1*H*-pyrazole (2b). White powder, 74% yield (according to method ***A***), 92% (according to method ***B***), m.p. 94—96 °C. IR, ν/cm^{-1}: 3312 (OH); 1603, 1587 (C=C, C=N); 1197—1132 (C—F). NMR ^1H, δ: 5.59 (s, 2 H, CH_2); 6.64 (s, 1 H, H(4)); 7.50—7.63 (m, 5 H, Ph). NMR ^{19}F, δ: 99.53 (s, CF_3). Found (%): C, 54.43; H, 3.72; N, 11.43. $C_{11}H_9F_3N_2O$. Calculated (%): C, 54.55; H, 3.75; N, 11.57.

1-(1-Hydroxymethyl)-5-phenyl-3-(1,1,2,2-tetrafluoroethyl)-1*H*-pyrazole (2c). White powder, 63% yield (according to method ***A***), 90% (according to method ***B***), m.p. 96—98 °C. IR, ν/cm^{-1}: 3305 (OH); 1607, 1581 (C=C, C=N); 1205—1145 (C—F). NMR ^{1}H, δ: 4.27 (t, 1 H, OH, J = 7.4 Hz); 5.58 (d, 2 H, CH_2, J = 6.9 Hz); 6.11 (tt, 1 H, $H(CF_2)_2$, J = 53.5 Hz, J = 3.6 Hz); 6.65 (s, 1 H, H(4)); 7.49—7.63 (m, 5 H, Ph). NMR ^{19}F, δ: 26.04 (dt, 2 F, HCF_2, J = 53.5 Hz, J = 6.3 Hz); 48.6 (td, 2 F, CF_2, J = 6.3 Hz, J = 3.9 Hz). Found (%): C, 52.11; H, 3.63; N, 10.01. $C_{12}H_{10}F_4N_2O$. Calculated (%): C, 52.56; H, 3.68; N, 10.22.

Synthesis of 1-alkoxymethyl pyrazoles 3a,d, 4a, and 5a. A mixture of pyrazole **1a,d** (0.45 mmol), paraformaldeldehyde (0.35 g) in a corresponding alcohol (10 mL) with 0.3 mL of concentrated HCl was heated at 80—90 °C for 2—5 days (monitoring by TLC). The reaction mixture was evaporated, products **3a,d, 4a,** and **5a** were isolated by column chromatography, eluent: chloroform—ehtylacetate, 10 : 1.

1-Ethoxymethyl-3-trifluoromethyl-5-methyl-4-[(4-methylphenyl)diazenyl]-1*H*-pyrazole (3a). Yellow powder, 30% yield, m.p. 79—81 °C. IR, ν/cm^{-1}: 1610, 1583 (C=C, C=N); 1187—1142 (C—F). NMR ^{1}H, δ: 1.19 (t, 3 H, $OCH_2\underline{Me}$, J = 7.0 Hz); 2.42 (s, 3 H, C_6H_4—$\underline{Me}$); 2.70 (s, 3 H, 3-Me); 3.59 (q, 2 H, $OC\underline{H}_2Me$, J = 7.0 Hz); 5.52 (br. s, 2 H, CH_2); 7.28—7.30 (m, 2 H, H_m, C_6H_4); 7.75—7.76 (m, 2 H, H_o, C_6H_4). NMR ^{19}F, δ: 100.0 (s, CF_3). Found (%): C, 55.13; H, 5.21; N, 17.11. $C_{15}H_{17}F_3N_4O$. Calculated (%): C, 55.21; H, 5.25; N, 17.17.

1-Ethoxymethyl-3-heptafluoropropyl-5-methyl-4-[(4-methoxyphenyl)diazenyl]-1*H*-pyrazole (3d). Orange oil, 42% yield. IR, ν/cm^{-1}: 1603, 1585 (C=C, C=N); 1257—1209 (C—F). NMR ^{1}H, δ: 1.17 (t, 3 H, $OCH_2\underline{Me}$, J = 7.0 Hz); 2.67 (s, 3 H, 3-Me); 3.56 (q, 2 H, $OC\underline{H}_2Me$, J = 7.0 Hz); 3.88 (s, 3 H, OMe); 5.55 (s, 2 H, CH_2); 6.98—7.00 (m, 2 H, H_m, C_6H_4); 7.81—7.83 (m, 2 H, H_o, C_6H_4). NMR ^{19}F, δ: 35.64 (m, 2 F, β-CF_2); 52.23 (m, 2 F, α-CF_2); 81.7 (t, 3 F, CF_3, J = 9.3 Hz). Found (%): C, 46.37; H, 3.81; N, 12.42. $C_{17}H_{17}F_7N_4O_2$. Calculated (%): C, 46.16; H, 3.87; N, 12.67.

1-Butoxymethyl-5-methyl-4-[(4-methylphenyl)diazenyl]-3-trifluoromethyl-1*H*-pyrazole (4a). Crystallizing orange oil, 57% yield. IR, ν/cm^{-1}: 1609, 1587 (C=C , C=N); 1237—1172 (C—F). NMR ^{1}H, δ: 0.88 (t, 3 H, $O(CH_2)_3\underline{Me}$, J = 7.4 Hz); 1.33 (m, 2 H, $OCH_2CH_2C\underline{H}_2Me$); 1.53 (m, 2 H, $OCH_2C\underline{H}_2CH_2Me$); 2.43 (s, 3 H, C_6H_4—$\underline{Me}$); 2.70 (s, 3 H, 3-Me); 3.52 (t, 2 H, $OC\underline{H}_2(CH_2)_2Me$, J = 6.5 Hz); 5.53 (s, 2 H, CH_2); 7.29 (d, 2 H, H_m, C_6H_4, J = 8.2 Hz); 7.76 (d, 2 H, H_o, C_6H_4, J = 8.2 Hz). NMR ^{19}F, δ: 100.0 (s, CF_3). Found (%): C, 57.82; H, 6.10; N, 16.00. $C_{17}H_{21}F_3N_4O$. Calculated (%): C, 57.62; H, 5.97; N, 15.81.

1-Hexyloxymethyl-5-methyl-4-[(4-methylphenyl)diazenyl]-3-trifluoromethyl-1*H*-pyrazole (5a). Orange oil, 65% yield. IR, ν/cm^{-1}: 1608, 1582 (C=C, C=N); 1227—1162 (C—F). NMR ^{1}H, δ: 0.89 (t, 3 H, $O(CH_2)_5\underline{Me}$, J = 6.8 Hz); 1.34 (m, 6 H, $OCH_2CH_2(C\underline{H}_2)_3Me$); 1.58 (m, 2 H, $OCH_2C\underline{H}_2(CH_2)_3Me$); 2.43 (s, 3 H, C_6H_4—$\underline{Me}$); 2.70 (s, 3 H, 3-Me); 3.52 (t, 2 H, $OC\underline{H}_2(CH_2)_4Me$, J = 6.6 Hz); 5.52 (s, 2 H, CH_2); 7.28 (d, 2 H, H_m, C_6H_4, J = 8.3 Hz); 7.76 (d, 2 H, H_o, C_6H_4, J = 8.3 Hz). NMR ^{19}F, δ: 100.0 (s, CF_3). Found (%): C, 59.63; H, 6.47; N, 14.72. $C_{19}H_{25}F_3N_4O$. Calculated (%): C, 59.67; H, 6.59; N, 14.65.

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