REACTION OF PERFLUORINATED NITRILES WITH BENZ- AND TEREPHTHALAMIDOXIMES FOR THE ISOLATION OF MIXED 1,2,4-OXADIAZOLES

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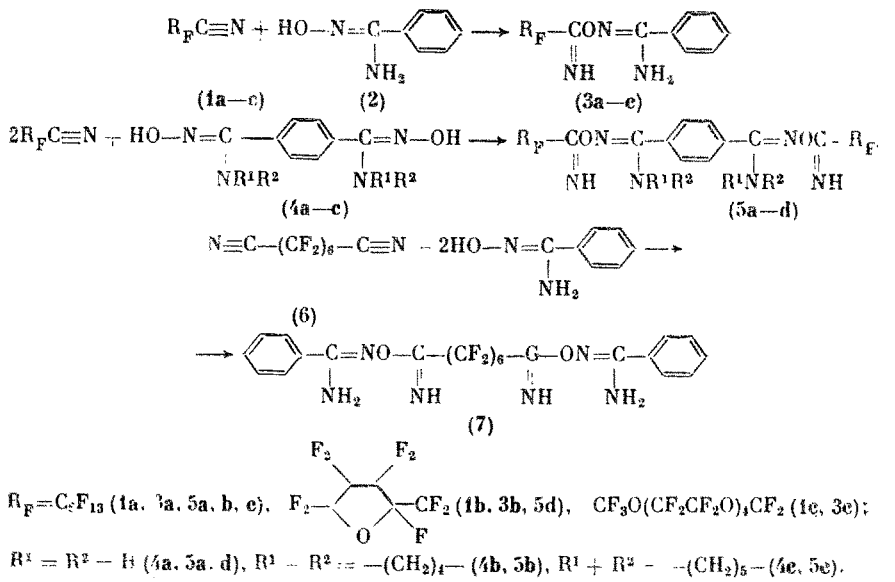
The reaction of perfluorinated nitriles with benz- and terephthalamidoximes afforded amidoximimidates which can form mixed 1,2,4-oxadiazoles in high yield under mild conditions by the action of acid fluorides of perfluorocarboxylic acids. The structure of the compounds obtained was confirmed by the methods of ^{13}C, ^{19}F, and ^{1}H NMR, and by IR spectroscopy.

Keywords: *nitriles, terephthalamidoximes, acid fluorides, amidoximimidates, 1,2,4-oxadiazoles, structure.*

The method for the isolation of fluorinated imidates, based on the reaction of perfluorinated nitriles with alcohols and phenols in the presence of strong bases, is known [1, 2]. We observed the formation of similar iminoester structures by the reaction of different perfluorinated nitriles with benzamidoxime and unsubstituted and substituted terephthalamidoximides:



The character of the reaction described by us is probably more like the interaction of perfluorinated nitriles and strong bases such as aromatic amidines [3].

If, in the case of the reaction of perfluorinated nitriles with N,N-substituted amidoximes, the correctness of the final presented structures of the imidates is not in doubt and is confirmed by different physicochemical methods (^{1}H, ^{19}F, and ^{13}C NMR, and IR spectroscopy), then the following two alternative variants are possible when unsubstituted amidoximes are utilized in the indicated reaction:

*Deceased.

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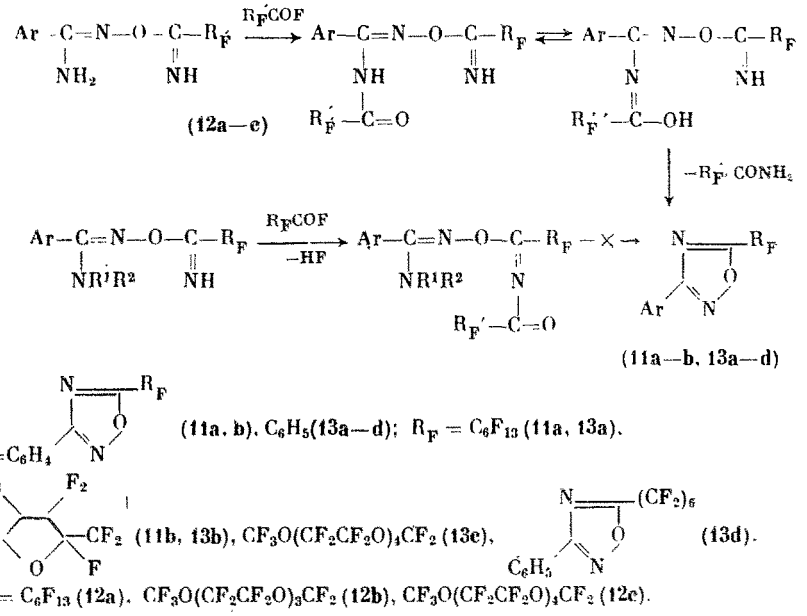
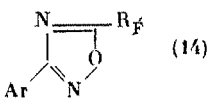
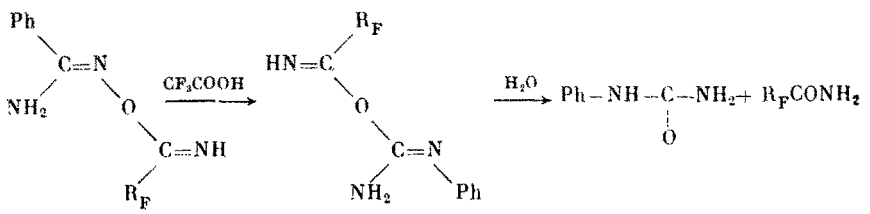


The only side reaction observed is the formation of 3-10% of the 1,2,4-oxadiazole **14** and the corresponding amide R_FCONH_2 by the acylation of **12b**, and up to 30% on the treatment of **12a**.



The cyclization of the amidoximimidate **3a** by trifluoroacetic anhydride leads to **13a** and 3-phenyl-5-trifluoromethyl-1,2,4-oxadiazole (**15**) in equal proportions.

The action of moist trifluoroacetic acid on the amidoximimidates at room temperature is accompanied by rearrangement analogous to the Tiemann reaction [5], with the formation of phenyl-substituted urea:

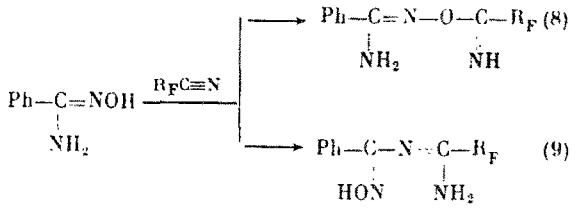


Therefore, our described method for the isolation of mixed 1,2,4-oxadiazoles from unsubstituted amidoximimidates and acid fluorides of perfluorocarboxylic acids differs favorably from the method of [6], since the reaction proceeds under mild conditions and with high yields. It is possible to obtain the quantitative formation of the oxadiazole by utilizing the acid fluoride in the same fluorocarbon chain as exists for the amidoximimidate.

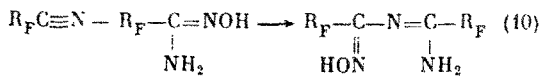
EXPERIMENTAL

The ^{19}F, ^{1}H, and ^{13}C NMR spectra were taken on the Bruker AC-200P spectrometer at 188.31, 200.13, and 50.324 MHz, correspondingly. The internal standards were $CFCl_3$ and TMS. The solvents were $(CD_3)_2CO$, $CDCl_3$, C_5D_5N, and Freon-113. The IR spectra were taken on the Specord M-80 instrument using tablets of NaCl or a thin layer.

Benzamidoxime (2). This compound was obtained according to the method of [7]; it had mp 77.0-78.0°C (alcohol–water) (literature data: 79.0-80.0°C). The PMR spectrum (δ, ppm, $CDCl_3$) was as follows: 9.71 s (OH), 7.60 m (H_o), 7.33 m ($H_{m,p}$), and 4.96 s (NH_2). The ^{13}C NMR spectrum (δ, ppm, $CDCl_3$) was as follows: 152.62 s (C=N), 129.84 s (C_p), 128.53 s (C_o), 125.84 s (C_m), and 127.30 (C_{ips}) IR spectrum (ν, cm^{-1}): 915 (OH), 1580 (C–C arom.), 1640 (C=N), 3190 br. (OH), and 3355 and 3444 (NH_2).



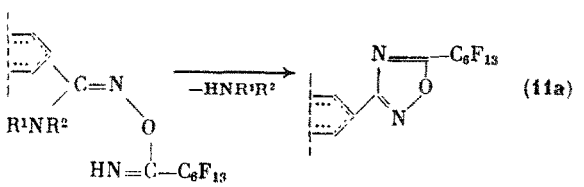
In particular, for the reaction of perfluoronitriles with unsubstituted perfluorinated amidoximes, the authors [4] postulate the formation of the corresponding imidoylamidoxime **10**:



In our case, the proposition concerning the formation of the imidate **8** is confirmed by the following data of the IR spectroscopy: 1) the absence of the absorption band of the free OH group in the region of 3600-3700 cm^{-1}; 2) the absence of the broad absorption band in the near-IR spectral region, corresponding with the intermolecular hydrogen bond; 3) the absence of the broadened absorption band in the range of 900-1000 cm^{-1}, characteristic of the stretching vibrations of the NH_2 group (3150 and 3300 cm^{-1}); 5) the presence of a narrow single band in the region of 3500 cm^{-1}, characteristic of the NH group adjoining the fluorinated radical.

Therefore, it can be concluded on the basis of the spectral data that the reaction of the unsubstituted benz- and terephthalamidoximes with perfluorinated nitriles proceeds at the oxime group.

An interesting feature of the reaction described is the fact that the interaction of perfluoronitrile with N,N-substituted terephthalamidoximes is accompanied by the formation of small amounts of mixed 1,2,4-oxadiazoles.



The phenomenon indicated is possible in the case when a part of the molecules of the amidoximimidate has a configuration conducive to ring formation. The amine isolated as a result of the reaction is bound by the perfluorinated nitrile in the form of the substituted amidine.

A very convenient method for the observation of the course of the reaction and for quantitative determinations is the method of ^{19}F NMR spectroscopy, since the CF_2 group situated in the α position to the functional group has a specific chemical shift (CS). Thus, for the α-CF_2 group in perfluorinated substituted amidines, the CS is equal to -108.0 ppm (determined from the spectra of standard compounds). For the mixed 1,2,4-oxadiazole **11a** this shift comprises -112.6 ppm. For the amidoximimidates **5b** and **5c** it comprises -116.5 to -118.8 ppm. The signals of the remaining CF_2 groups occur at a higher field, and occupy the region of -120.0 to -127.0 ppm.

The determination of the content of these compounds in the reaction mixture does not present difficulty since it corresponds with the ratio of the integral intensities of the signals of the α-CF_2 groups in the ^{19}F NMR spectrum.

The very mild conditions of the reaction studied by us and the high yields of the amidoximimidates should be noted.

As was already noted, the amidoximimidates are able to undergo ring closure to 1,2,4-oxadiazoles under certain conditions with the cleavage of amine. However, attempts to carry out thermal cyclization (by boiling in toluene) led to retrodecomposition of the unsubstituted amidoximimidate to the initial components — the amidoxime and the perfluoronitrile, and the substituted imidate did not undergo any changes under these conditions.

We undertook the attempt to utilize chemical methods of cyclodeamination, and obtained high yields of mixed 1,2,4-oxadiazoles by the treatment of unsubstituted amidoximimidates with acid fluorides of perfluorocarboxylic acids. Taking into account that a similar effect could not be obtained on substituted amidoximimidates, the following reaction scheme was suggested:

TABLE 1. Physicochemical Characteristics of the Compounds Obtained

Compound	Yield %	mp, °C (solvent) or bp, °C	Found/Calculated, %				Empirical formula
			C	H	F	N	
3a	99	132.5–133.0 (Chloroform)	34.89 / 34.92	1.69 / 1.66	52.04 / 51.35	8.70 / 8.73	$C_{14}H_8F_{13}N_3O$
3b	96	72.0–73.0 (Freon-113)	38.16 / 38.14	1.92 / 1.96	41.65 / 41.81	10.04 / 10.26	$C_{13}H_8F_9N_3O_2$
3c	98	69.0–70.0 (Acetone)	28.39 / 28.38	1.03 / 1.05	52.57 / 52.43	5.44 / 5.52	$C_{18}H_8F_{21}N_3O_6$
5a	98	178.0 (dec.)	29.72 / 29.86	1.05 / 1.13	55.14 / 55.88	9.68 / 9.50	$C_{22}H_{10}F_{26}N_6O_2$
5b	84	171.0(dec.) (Acetonitrile)	36.40 / 36.29	2.18 / 2.22	50.07 / 49.80	8.30 / 8.47	$C_{30}H_{22}F_{26}N_6O_2$
5c	72	125.0–131.0 (Tetrachloro-methane)	37.48 / 37.65	2.61 / 2.55	48.17 / 48.43	8.35 / 8.23	$C_{32}H_{26}F_{26}N_6O_2$
5d	94	172.0 (dec.) (Chloroform)	33.01 / 32.43	1.22 / 1.35	47.01 / 46.22	11.50 / 11.35	$C_{20}H_{16}F_{18}N_6O_4$
7	99	174.0–176.0 (Ether)	42.28 / 42.31	2.60 / 2.56	36.38 / 36.54	13.60 / 13.46	$C_{22}H_{16}F_{12}N_6O_2$
11a	85 a 80 b	120.5–121.0 (Acetonitrile)	31.12 / 31.06	0.51 / 0.47	58.38 / 58.12	6.47 / 6.59	$C_{22}H_4F_{26}N_4O_2$
11b	97a,c	64.5–65.0 (Methanol)	33.84 / 33.99	0.55 / 0.57	48.17 / 48.44	7.80 / 7.93	$C_{20}H_4F_{18}N_4O_4$
13a	99b,c	38.0–39.0 (Methanol)	36.32 / 36.21	1.11 / 1.08	53.02 / 53.23	5.98 / 6.03	$C_{14}H_5F_{13}N_2O$
13b	69a,b 81b,c	239.0–240.5	39.72 / 39.80	1.23 / 1.28	43.48 / 43.63	7.20 / 7.14	$C_{16}H_5F_9N_2O_2$
13c	100 d	250.0–251.0	28.95 / 29.03	0.61 / 0.67	53.75 / 53.63	3.59 / 3.76	$C_{18}H_5F_{21}N_2O_6$
13d	96b,c	121.5–122.5 (Methanol)	44.68 / 44.75	1.66 / 1.69	38.38 / 38.64	9.60 / 9.43	$C_{22}H_{10}F_{12}N_4O_2$

Notes. a) Cyclization of **12a**. b) Cyclization of **12b**. c) Determined from the data of ^{19}F NMR spectroscopy. d) Cyclization of **12c.**

Terephthalamidoxime (4a). This compound was obtained analogously to **2**. Yield 91%; mp 257.0-258.0°C (alcohol–water). PMR spectrum (δ, ppm, C_5D_5N): 12.14 s (OH), 8.25 s (H arom.), and 6.63 s (NH_2). ^{13}C NMR spectrum (δ, ppm, C_5D_5N): 151.96 s (C=N), 135.14 s (C_{ips}), 126.06 s ($C_{o,m}$). IR spectrum (ν, cm^{-1}): 928 (OH), 1596 (C–C arom.), 3220 br. (OH), 3356 and 3448 (NH_2).

Bis-(N,N-tetramethylene)terephthalamidoxime (4b) (General Method). To the suspension of 1.6 g (10 mmoles) of terephthalnitrile oxide (obtained by the treatment of terephthalaldehyde oxime with NaOCl in water at 0°C for 0.5 h) in 30 ml of CCl_4 at 0°C was slowly added the solution of 1.42 g (20 mmoles) of pyrrolidine in 15 ml of CCl_4. The reaction mass was stirred for 1 h at 20°C; the solvent was removed *in vacuo*. After recrystallization from methanol, the yield of **4b** obtained was 2.78 g (92%) (mixture of isomers); mp 234.0-238.0°C. Found, %: C 63.45; H 7.20; N 19.06. $C_{16}H_{22}N_4O_2$. Calculated, %: C 63.58; H 7.28; N 18.54. PMR spectrum (δ, ppm, C_5D_5N): 11.06 s, 11.62 s (OH), 7.84 s, 7.75 s (H arom.), 3.61 t, 3.18 t (α-CH_2–), 1.62 m (β-CH_2–). ^{13}C NMR spectrum (δ, ppm, C_5D_5N): 129.94 s (C_{ips}), 129.10 s, 127.85 s ($c_{o,p}$), 50.76 s, 48.34 s (α-CH_2–), 25.72 s, 25.00 s (β-CH_2–). IR spectrum (ν, cm^{-1}): 960 and 980 (OH), 1516 (C–C arom.), 1620 (C=N), 2872 and 2972 (CH_2), 3292 br. (OH).

Bis-(N,N-pentamethylene)terephthalamidoxime (4c). This compound was obtained analogously to **4b**. mp 108.0-108.5°C (ether); yield 87%. Found, %: C 65.61; H 7.94; N 16.63. $C_{18}H_{26}N_4O_2$. Calculated, %: C 65.45; H 7.88; N 16.97. PMR spectrum (δ, ppm, $CDCl_3$): 7.49 s (H arom.), 3.28 m, 3.02 m (α-CH_2–), 1.61 m (β, γ-CH_2–). IR spectrum (ν, cm^{-1}): 956 (OH), 1624 (C=N), 2852 and 2932 (CH_2), 3208 br. (OH).

O-(Perfluoroalkanimidoyl)benzamidoximes (3a-c) (General Method). To a solution of 10 mmoles of **2** in 40 ml of ether at 20°C were added 11 mmoles of **1**. The mixture was stirred for 1 h. The solvent was removed *in vacuo*. After recrystallization, the corresponding **3a-c** were isolated. Some physicochemical characteristics are presented in Table 1.

3a. IR spectrum (ν, cm^{-1}): 1100-1300 (CF), 1590 (C−C arom.), 1635 and 1680 (C=N)$_3$ 3160 and 3298 (NH_2), 3492 (NH). PMR spectrum [δ, ppm, $(CD_3)_2CO$]: 9.34 s (NH), 7.85 m (H_o), 7.51 ($H_{m,p}$), 6.56 s (NH_2). ^{19}F NMR spectrum [δ, ppm, $(CD_3)_2CO$]: −115.72 s (α-CF_2). ^{13}C NMR spectrum (δ, ppm; J_{C-F}, Hz, C_5D_5N): 159.04 s (PhC=N), 154.56 t (C=N, *J* 24.7), 132.18 s and 131.57 s (C_p), 129.20 s and 128.85 s (C_o), 127.92 s and 126.55 s (C_m), 129.54 s (C_{ips}).

3b. IR spectrum (ν, cm^{-1}): 1100-1300 (CF), 1597 (C−C arom.), 1636 and 1685 (C=N), 3155 and 3296 (NH_2), 3478 (NH). PMR spectrum (δ, ppm, $COCl_3$): 9.02 s (NH), 7.67 m (H_o), 7.48 m ($H_{m,p}$), 5.40 s (NH_2). ^{19}F NMR spectrum (δ, ppm, $CDCl_3$): −82.99 q (OCF_2), −115.59 q (α-CF_2), −121.52 s (OCF), −125.40 to −135.98 (CF_2-CF_2).

3c. IR spectrum (ν, cm^{-1}): 1100-1300 (CF), 1600 (C−C arom.), 1640 and 1690 (C=N), 3150 and 3295 (NH_2), 3480 (NH). PMR spectrum [δ, ppm, $(CD_3)_2CO$]: 9.18 s (NH), 7.72 m (H_o), 7.46 m ($H_{m,p}$), 6.54 s (NH_2). ^{19}F NMR spectrum [δ, ppm; J_{C-F}, Hz, $(CD_3)_2CO$]: −74.52 t (α-CF_2, *J* 9.09). ^{13}C NMR spectrum [δ, ppm; J_{C-F} Hz $(CD_3)_2CO$]: 158.41 s (PhC=N), 154.39 t (C=N, *J* 32.2), 131.68 s and 129.84 s (C_p), 129.21 s and 128.20 s (C_o), 127.56 s and 126.30 s (C_m). 128.83 s (C_{ips}).

O,O′-Perfluorohexanedicarbamidoyl-bis(benzamidoxime (7). This compound was obtained analogously to **3**. The physicochemical characteristics are presented in Table 1. PMR spectrum [δ, ppm, $(CD_3)_2CO$ + C_5D_5N]: 8.35 m and 8.03 m (H_o), 7.45 m and 7.36 m ($H_{m,p}$). ^{19}F NMR spectrum [δ, ppm, $(CD_3)_2CO$ + C_5D_5N]: 8.35 m and 8.03 m (H_o), 7.45 m and 7.36 m ($H_{m,p}$). ^{19}F NMR spectrum [δ, ppm, $(CD_3)_2CO$ + C_5D_5N]: −115.58 s (α-CF_2), −120.98 s and −121.51 s (β,γ-CF_2). IR spectrum (ν, cm^{-1}): 1100-1250 (CF), 1600 (C−C arom.), 1644 and 1688 (C=N), 3160 and 3304 (NH_2), 3500 (NH).

Bis(O-perfluoroalkanimidoyl)terphthalamidoximes (5a, d) (General Method). To the solution of 10.6 mmoles of **4a** in 20 ml of pyridine at 20°C were added 21.5 mmoles of **1**, and the mixture was stirred for 1 h. The precipitated residue of **5** was filtered off, washed with pyridine, and dried *in vacuo*. The physicochemical characteristics of the compounds obtained are presented in Table 1.

5a. IR spectrum (ν, cm^{-1}): 1100-1280 (CF), 1592 (C−C arom.), 1644 and 1688 (C=N), 3172 and 3304 (NH_2), 3496 (NH).

5d. IR spectrum (ν, cm^{-1}): 1100-1300 (CF), 1592 (C−C arom.), 1640 and 1685 (C=N), 3165 and 3302 (NH_2), 3488 (NH). PMR spectrum (δ, ppm, C_5D_5N): 10.06 s (NH), 8.20 m (H arom.). ^{19}F NMR spectrum (δ, ppm, C_5D_5N) −83.30 s (OCF_2), −114.77 s (α-CF_2), −120.47 s (OCF), −123.73 to −135.14 (CF_2-CF_2).

Reaction of 4b with the Nitrile of Perfluorohexanecarboxylic Acid. To the suspension of 1.82 g (6 mmoles) of **4b** in 50 ml of pyridine at 20°C were added 4.55 g (13.2 mmoles) of **1a**, and the mixture was stirred for 3 h. The solvent was removed *in vacuo*. After the addition of 50 ml of methanol, the precipitated residue of 0.5 g (10%) of **11a** was filtered off. To the concentrated filtrate were added 35 ml of acetonitrile. The precipitated residue of **5b** was separated and dried *in vacuo*. The physicochemical characteristics are presented in Table 1.

5b. IR spectrum (ν, cm^{-1}): 1100-1300 (CF), 1690 (C=N), 2878 and 2965 (CH_2), 3265 (NH). The PMR spectrum (δ, ppm, $CDCl_3$): 8.59 s (NH), 7.17 s (H arom.), 3.15 s (α-CH_2), 1.81 s (β-CH_2). ^{19}F NMR spectrum (δ, ppm, $CDCl_3$): −116.95 s and −118.82 s (α-CF_2). ^{13}C NMR spectrum (δ, ppm, $CDCl_3$): 164.49 s (PhC=N), 132.88 s (C_{ips}), 128.52 s and 127.25 s (C arom.), 51.24 s and 48.00 s (α-CH_2), 25.32 s and 25.03 s (β-CH_2).

Reaction of 4c with the Nitrile of Perfluorohexanecarboxylic Acid. To the suspension of 1.65 g (5 mmoles) of **4c** in 50 ml of ether at 20°C were added 4.49 g (13 mmoles) of **1a**, and the mixture was stirred for 24 h. The ether was removed *in vacuo*, and 50 ml of methanol were added. The precipitated residue of 1.05 g (25%) of **11a** was filtered off. To the concentrated filtrate were added 30 ml of CCl_4, and the precipitated residue of **5c** was separated and dried *in vacuo*. The physicochemical characteristics are presented in Table 1.

5c. IR spectrum (ν, cm^{-1}): 1100-1250 (CF), 1565 and 1690 (C=N), 2860 and 2958 (CH_2), 3275 (NH). PMR spectrum (δ, ppm, $CDCl_3$): 8.96 s and 8.74 s (NH), 7.60 s and 7.29 s (H arom.), 3.37 br.s and 3.24 br.s (α-CH_2), 1.66 br.s (β,γ-CH_2). ^{19}F NMR spectrum (δ, ppm, $CDCl_3$): −116.54 s and −117.06 s (α-CF_2).

3-Phenyl-5-perfluoroalkyl-1,2,4-oxadiazoles (13a-c) (General Method). To the solution of 10 mmoles of **3** in pyridine were added 12 mmoles of the corresponding **12** (see Table 1), and the mixture was heated for 2 h at 65°C. The pyridine was removed *in vacuo*. Methanol was added while the mixture was cooled with ice. The precipitated residue of **13a** was filtered off, recrystallized, and dried *in vacuo*. For the isolation of **13b** and **13c**, methanol was added to he concentrated reaction mass.

After prolonged standing, the lower layer was separated, and the solvent residues were removed *in vacuo*. The physicochemical characteristics are presented in Table 1.

13a. PMR spectrum (δ, ppm, $CDCl_3$): 8.14 m (H_o) and 7.56 m ($H_{m,p}$). ^{19}F NMR spectrum (δ, ppm, $CDCl_3$): −80.48 s (CF_3), −112.60 s (α-CF_2), −121.84 to −122.45 [$(CF_2)_3$], −125.83 s ($\underline{CF_2}-CF_3$).

13b. PMR spectrum (δ, ppm, $CDCl_3$): 8.15 m (H_o) and 7.55 m ($H_{m,p}$). ^{13}C NMR spectrum (δ, ppm, $CDCl_3$): 169.41 s (PhC=N), 142.72 s (C_{ips}), 132.28 s (C_p), 129.10 s (C_o), 127.76 s (C_m). ^{19}F NMR spectrum (δ, ppm, $CDCl_3$): −83.04 s (OCF_2), −111.85 q (α-CF_2), −121.40 s (OCF), −121.90 to −135.44 ($\underline{CF_2}-CF_2$).

13c. PMR spectrum (δ, ppm, $CDCl_3$): 8.12 m (H_o) and 7.54 m ($H_{m,p}$). ^{13}C NMR spectrum (δ, ppm, $CDCl_3$): 169.26 s (PhC=N), 132.22 s (C_p), 129.08 s (C_o), 127.69 s (C_m). ^{19}F NMR spectrum (δ, ppm, $CDCl_3$): −55.44 s (OCF_3), −68.24 s (α-OCF_2), −88.20 to −88.75 (OCF_2CF_2), −90.76 s ($\underline{CF_2}OCF_3$).

1,6-Bis(3-phenyl-1,2,4-oxadiazol-5-yl)perfluorohexane (13d). This compound was obtained analogously to **13a-c**. The physicochemical characteristics are presented in Table 1. PMR spectrum (δ, ppm, C_5D_5N): 8.17 m (H_o) and 7.47 m ($H_{m,p}$). ^{19}F NMR spectrum (δ, ppm, C_5D_5N): −112.80 s (α-CF_2), −121.6 s and −121.83 s (β,γ-CF_2). ^{13}C spectrum (δ, ppm, C_5D_5N): 164.64 s (PhC=N), 132.93 s (C_p), 129.76 s (C_o), 128.17 s (C_m).

1,4-Bis(5-perfluoroalkyl-1,2,4-oxadiazol-3-yl)benzenes (11a, b). These compounds were obtained analogously to **13**. Some physicochemical characteristics are presented in Table 1.

11a. PMR spectrum (δ, ppm, $C_2F_3Cl_3$): 8.28 s (H arom.)., ^{19}F NMR spectrum (δ, ppm, $C_2F_3Cl_3$): −80.50 s (CF_3), −112.25 m (α-CF_2), −120.35 to −122.00 [$(CF_2)_3$], −125.13 s ($\underline{CF_2}-CF_3$). ^{13}C NMR spectrum (δ, ppm, $C_2F_3Cl_3$): 169.71 s (PhC=N), 129.84 s (C_{ips}), 129.28 s ($C_{o,m}$).

11b. PMR spectrum (δ, ppm, $CDCl_3$): 8.31 s (H arom.). ^{13}C NMR spectrum (δ, ppm, $CDCl_3$): 169.27 s (PhC=N), 129.10 s ($C_{o,m}$). ^{19}F NMR spectrum (δ, ppm, $CDCl_3$): −82.89 s (OCF_2), −111.74 q (α-CF_2), −121.26 s (OCF), −124.45 to −135.29 (CF_2-CF_2).

Reaction of 3a with Trifluoroacetic Anhydride. Trifluoroacetic anhydride (4.73 g, 22.5 mmoles) was added to 40 ml of pyridine, and the mixture was stirred for 15 min. Then the solution of 4.33 g (9 mmoles) of **3a** in 35 ml of pyridine was added. The reaction mass was stirred for 5 h at 20°C. According to the data of the ^{19}F NMR spectroscopy, the reaction mixture contains equal amounts of **13a** and **15**; identification was carried out using the spectra of a standard substance.

15. PMR spectrum (δ, ppm, $CDCl_3$): 8.12 m (H_o), 7.55 m ($H_{m,p}$). ^{19}F NMR spectrum (δ, ppm, $CDCl_3$): −65.15 s (CF_3).

Reaction of 3a with Trifluoroacetic Acid. The compound **3a** (4.81 g, 10 mmoles) was dissolved in 15 ml of CF_3COOH containing up to 5% of moisture. The mixture was stirred for 3 h at 20°C. The acid was removed from the reaction mass *in vacuo*. The perfluorohexanecarboxylic amide was sublimed *in vacuo*, and the residue was recrystallized from water. The yield of 1.1 g (81%) of phenylurea with mp 146.0-147.0°C (literature data 147°C [8]) was obtained. Found, %: C 61.71; H 5.91; N 20.44. $C_7H_8N_2O$. Calculated, %: C 61.76; H 5.88; N 20.59.

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