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Synthesis of Partially Fluorinated Organic Compounds from Perfluoro-2-methyl-2-pentene and Phenol Derivatives

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Abstract — The reactions of perfluoro-2-methyl-2-pentene with substituted phenols and some heterocyclic compounds containing OH group result in the substitution of the fluorine atom either exclusively at the internal multiple bond or at the terminal multiple bond of perfluoro-2-methyl-1-pentene formed by isomerization of the starting perfluoroolefin in the course of the reaction. The reaction pathway depends on the reaction conditions, base used, and substituents in the benzene ring. The structures of the compounds were confirmed by ^{1}H, ^{13}C, and ^{19}F NMR and IR spectroscopy.

Introduction of fluorine atoms imparts to organic molecules new specific properties, which are widely used in the development of modern materials [1, 2]. Perfluorinated dialkyl ethers are resistant to heat and oxidants and have low freezing points. The viscosity characteristics, lubricating properties, and electrophysical parameters of these compounds make them valuable [1]. Fluorinated intermediates found wide use in the synthesis of drugs and bioactive substances for agriculture [3, 4].

A prominent place among herbicides is occupied by fluorinated diphenyl ethers and compounds containing phenoxy group. One of synthetic routes to these compounds is based on nucleophilic substitution of fluorine atoms in internal perfluoroolefins with O-nucleophiles. The majority of aromatic compounds containing OH group are effective O-nucleophiles under the conditions of base catalysis. The reactions of the hexafluoropropene dimer and trimer with phenol in the presence of triethylamine [5, 6] (or with sodium phenolate [7], or with *p*-cresol [8]), of the hexafluoropropene dimer with *N*-(4-hydroxyphenyl)-acetamide [9], of the hexafluoropropene trimer with 3-hydroxybenzodioxane [10], and of the tetrafluoroethene pentamer with methyl 4-hydroxybenzoate [11] yield products of fluorine substitution at the internal double bond.

Our goal was to develop simple routes to partially fluorinated alkenyl aryl ethers derived from available perfluoro-2-methyl-2-pentene **I** and various phenol derivatives. These ethers can be used as intermediates in the synthesis of perfluorinated alkyl cyclohexyl ethers by direct fluorination. The latter products, in turn, show promise as high-temperature heat carriers, dielectrics, and lubricants.

It is known that internal perfluoroolefins, when treated with N-nucleophilic agents in the presence of bases or without them, isomerize into terminal perfluoroolefins. Perfluoro-2-methyl-2-pentene **I** can isomerize into perfluoro-2-methyl-1-pentene **II** whose terminal double bond contains a labile fluorine atom. As a result, the reaction pathway can change, with the formation of products of different structure.

It was shown previously that the reaction of phenol with **I** in the presence of KOH in THF yields (3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethylpropenyloxybenzene **III**, the product of formal substitution of fluorine at the double bond (Scheme 1).

With phenols containing electron-donor substituents (2-fluorophenol, 3-methoxyphenol, 3,5-dimethoxyphenol), compound **I** reacts similarly to give **IV**–**VI**, respectively. Some heterocyclic compounds containing the OH group at the heteroring also react similarly. The reactions of **I** with 2-hydroxybenzimidazole and 2-hydroxybenzothiazole under the same conditions yield fluorine replacement products **VII** and **VIII**, respectively. At the same time, the reactions of **I** with 2,6-dichlorophenol and pentafluorophenol under the same conditions yield (1,1,3,4,4,5,5,5-octafluoro-2-trifluoromethylpent-2-enyloxy)-2,6-dichlorobenzene **IX** and (1,1,3,3,4,4,5,5,5-nonafluoro-2-trifluo-

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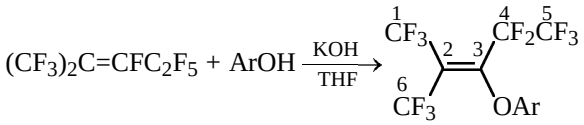
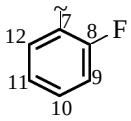
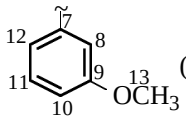
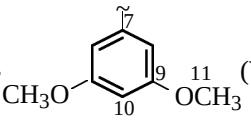
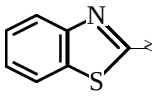
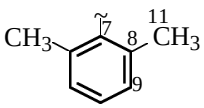
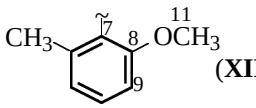
Scheme 1.

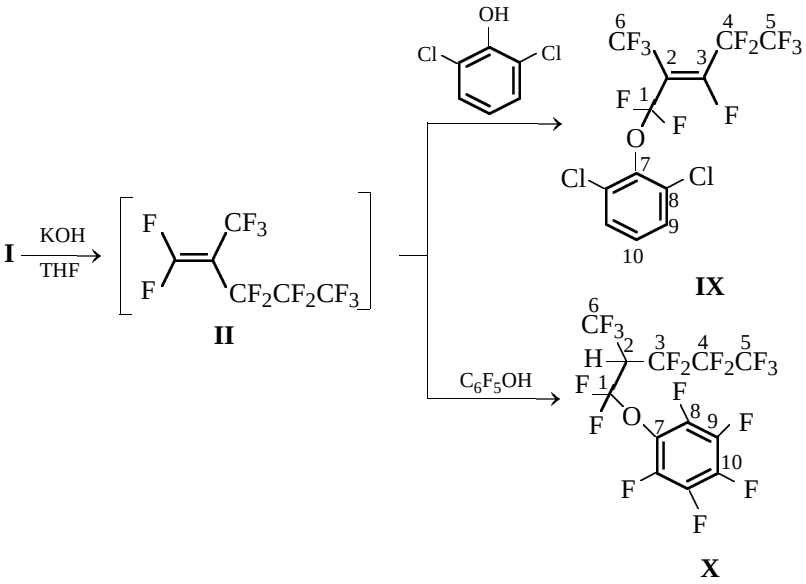


III–VIII, XI, XII

Ar = Ph (**III**),  (**IV**),  (**V**),  (**VI**),  (**VIII**),  (**XI**),  (**XII**).

romethylpentyloxy)pentafluorobenzene **X**, respectively (Scheme 2). This can be accounted for by the replacement of the fluorine atom in terminal olefin **II** formed by isomerization of **I** effected by a base.

Scheme 2.



II

IX

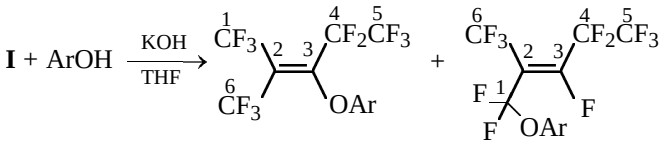
X

Such a behavior of these phenols may be due to 2,6-disubstitution of the benzene ring with the chlorine and fluorine atoms and to the low reactivity of the corresponding phenolate ions. However, the reaction of **I** with 2,6-dimethylphenol and 2,6-dimethoxyphenol yields compounds **XI** and **XII**, despite considerable steric shielding of the reaction center. At the same time, our results cannot be attributed solely to the electron-donor properties of the substituents, since the reactions of **I** with 3-nitrophenol, 4-nitrophenol, and 3-hydroxypyridine yield mixtures of fluorine replacement products **XIII** + **XVI**, **XIV** + **XVII**, and **XV** + **XVIII**, respectively (Scheme 3).

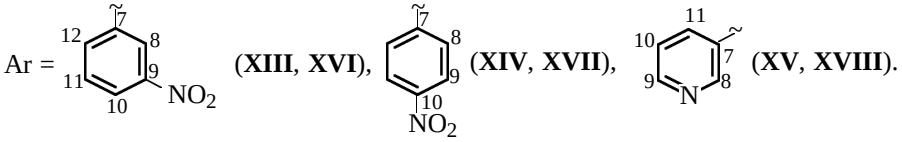
Formation of **XVI**–**XVIII** is apparently associated with different rates of nucleophilic substitution of the fluorine atom at the multiple bond in **I** with the phenoxide anion and of isomerization of **I** into **II**.

In compounds containing two nucleophilic centers, each of them can attack the carbon atom of the multiple bond, either with formation of the substitution products or with the subsequent intramolecular cycli-

Scheme 3.



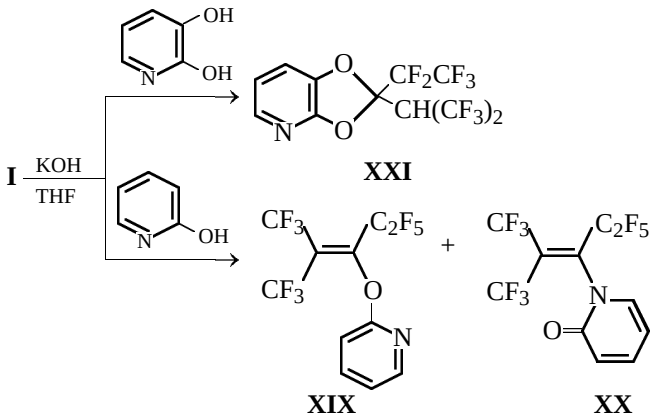
XIII–XV **XVI–XVIII**



(**XIII**, **XVI**), (**XIV**, **XVII**), (**XV**, **XVIII**).

zation of the heterocyclic system (Scheme 4). The reaction of **I** with 2-hydroxypyridine, as expected, yields a mixture of 2-(3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethylpropenyloxy)pyridine **XIX** and 1-(3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethylpropenyl)-1*H*-pyridin-2-one **XX**. This may be due to the attack of the double bond of **I** with O- and N-nucleophilic centers. The reaction of **I** with 2,3-dihydroxypyridine in the presence of KOH in THF yields 2-pentafluoroethyl-2-(2,2,2-trifluoro-1-trifluoromethylethyl)[1,3]dioxolo[4,5-*b*]pyridine **XXI**.

Scheme 4.



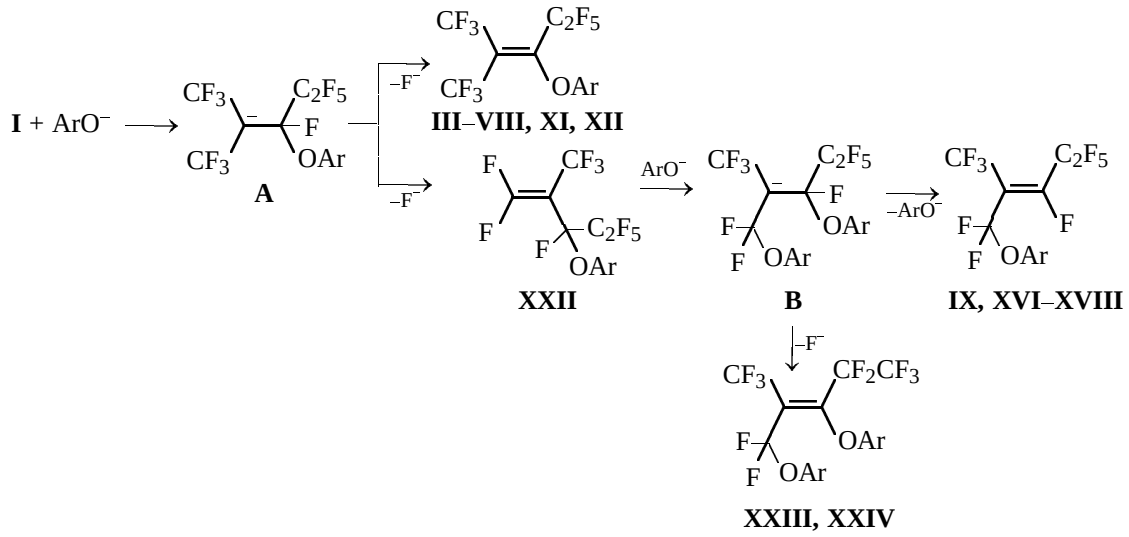
XXI

XIX **XX**

The reaction of **I** with phenol starts with the attack of the O-nucleophilic center of the reagent at the carbon atom of the double bond to give intermediate carbanion **A** (Scheme 5) stabilized with two CF_3 groups. Further transformations of carbanion **A** can involve elimination of the fluoride ion from either CF or CF_3 group. The former pahtway is thermodynamically preferable; it yields perfluoroalkenes **III**–**VIII** containing the phenoxy substituent at the double bond. The preferential formation of perfluoroolefin **II** in the reaction of **I** with sodium phenolate should be accounted for by the kinetic control of the reaction. However, we also should not rule out another reaction pathway, involving transformation of carbanion **A** into compound **XXII** [5] whose reaction with the phenolate anion yields intermediate carbanion **B**. In this species, stabilization of the negative charge with the phenoxy group OAr is less efficient, and carbanion **B** is stabilized either by elimination of the fluoride anion from the CF group with the formation of **XXIII** and **XXIV**, or by elimination of the phenoxide anion with the formation of **XVI**–**XVIII**. This pathway is realized exclusively at ArO = $OC_6H_3Cl_2$-2,6; the reactions with other phenols, in particular, with those containing the NO_2 group at the benzene ring, and with hydroxypyridine yields compounds **IX** and **XVI**–**XVIII**.

The reaction of **I** with pyridazine-3,6-diol is more complex. In the presence of KOH in THF, 1,2-bis-(3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethyl-

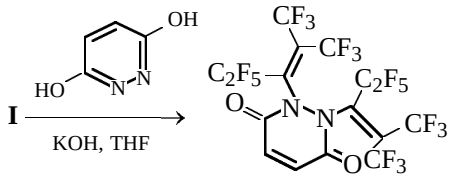
Scheme 5.



Ar = 2,6-$C_2C_6H_3$ (**IX**), 3-$NO_2C_6H_4$ (**XII**), 4-$NO_2C_6H_4$ (**XVII**), 3-pyridyl (**XVIII**), C_6H_5 (**XXIII**), 2-FC_6H_5 (**XXIV**).

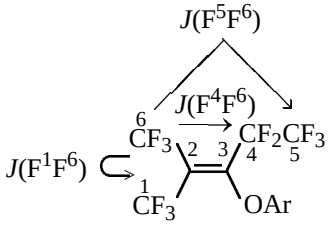
propenyl)-1,2-dihydropyridazine-3,6-dione **XXV**is formed intead of the expected ether (Scheme 6).

Scheme 6.



XXV

The structures of the compounds prepared were confirmed by the mass (Table 1), ^{1}H, ^{13}C, and ^{19}F NMR, and IR spectra (Table 2). The IR spectra of these compounds contain a C=C vibration band at 1647 cm^{-1}. The ^{1}H NMR spectra contain signals of aromatic ring protons with the characteristic chemical shifts. The ^{19}F NMR spectra contain signals with the characteristic chemical shifts and coupling constants: $J(F^1F^6)$ up to 10.7, $J(F^4F^6)$ up to 23.2, and $J(F^5F^6)$ up to 4.0 Hz.



The ^{13}C and ^{19}F NMR spectra of **XVI**–**XVIII** contain signals of the F and C atoms of the C=CF group.

EXPERIMENTAL

The IR spectra (5% solutions in CCl_4) were taken on a Bruker IFS-66 IR Fourier spectrometer. The ^{19}F NMR spectra were recorded on a Bruker WP-200SY spectrometer (188.324 MHz), and the ^{13}C NMR spectra, on a Bruker 400 spectrometer (100.614 MHz) (internal references C_6F_6, TMS); the constants J_{CH} were not determined. The mass spectra (electron impact, 70 eV) were recorded on a Finnigan-8200 device and on a chromatograph with a mass-selective detector (Hewlett–Packard G-1800A, GCD system). In the latter case, we used a 30 000 × 0.25 mm column with HP-5 stationary phase (5% diphenyl- and 95% dimethylsiloxane units, coating thickness 0.25 μm); the carrier gas was He (1 ml min^{-1}), and the vaporizer temperature, 280°C. The column temperature program was as follows: 50°C, 2 min; heating to 280°C, 10 deg min^{-1}; and 280°C, 5 min. All the reactions were monitored by ^{19}F NMR. The reaction mixtures were analyzed with an LKhM-72 chromatograph (15% SE, SKTF-803 : QF-1, Chromosorb-W, 4000 × 4-mm column).

The characteristics of the compounds synthesized are given in Table 1.

Reactions of perfluoro-2-methyl-2-pentene I with substituted phenols. *a*. A 10.7-g portion of **I** was added dropwise with vigorous stirring at 0°C to a suspension of 2 g of KOH in 20 ml of anhydrous THF. Then 4 g of 2-fluorophenol was added dropwise with stirring over a period of 15 min. The mixture was stirred for 1 h at 0°C, 1 h at room temperature,

Table 1. Yields, boiling points, and mass-spectrometric data for partially fluorinated aryl alkenyl ethers

Comp. no.	Yield, %	bp, °C (*p*, mm Hg)	Mass spectrum, *m/z* (I_{rel}, %)	Found *M*	Formula	Calculated *M*
III	70	69–71 (19)	374 $[M]^+$ (24.64), 355 $[M - F]^+$ (2.98), 305 $[M - CF_3]^+$ (24.38), 285 $[M - CF_3 - HF]^+$ (3.19), 255 $[M - C_2F_5]^+$ (0.80), 236 $[M - C_2F_5 - F]^+$ (1.10), 186 $[M - CF_3 - C_2F_5]^+$ (10.69), 119 $[C_2F_5]^+$ (2.30), 93 $[C_6H_5O]^+$ (2.19), 77 $[C_6H_5]^+$ (100), 69 $[CF_3]^+$ (7.06), 51 $[CHF_2]^+$ (16.42)	374.0162	$C_{12}H_5F_{11}O$	374.0165
IV	75	36–37 (3)	392 $[M]^+$ (75.76), 373 $[M - F]^+$ (7.74), 353 $[M - F - HF]^+$ (27.14), 323 $[M - CF_3]^+$ (40.56), 303 $[M - CF_3 - HF]^+$ (10.97), 281 $[M - C_6H_4FO]^+$ (0.78), 273 $[M - C_2F_5]^+$ (2.07), 119 $[C_2F_5]^+$ (26.77), 111 $[C_6H_4FO]^+$ (31.07), 100 $[CF_2{=}CF_2]^+$ (0.88), 95 $[C_6H_4F]^+$ (100), 75 $[C_6H_4F - HF]^+$ (40.14), 69 $[CF_3]^+$ (33.31)	392.0054	$C_{12}H_4F_{12}O$	392.0074
V	71	61–62 (2)	404 $[M]^+$ (75.36), 385 $[M - F]^+$ (16.63), 335 $[M - CF_3]^+$ (95.65), 266 $[M - 2CF_3]^+$ (4.76), 124 $[C_6H_8O_2]^+$ (2.72), 119 $[C_2F_5]^+$ (2.40), 107 $[C_6H_7O_2]^+$ (34.26), 92 $[C_6H_4O]^+$ (36.90), 69 $[CF_3]^+$ (8.72)	404.0273	$C_{13}H_7F_{11}O_2$	404.0270
VI	68	82–83 (2.5)	434 $[M]^+$ (50.34), 415 $[M - F]^+$ (17.41), 365 $[M - CF_3]^+$ (100), 315 $[M - C_2F_5]^+$ (0.54), 246 $[M - CF_3 - C_2F_5]^+$ (46.74), 138 $[C_8H_9O_2]^+$ (0.76), 119 $[C_2F_5]^+$ (1.40), 107 $[C_7H_7O]^+$ (8.52), 69 $[CF_3]^+$ (12.10)	434.0371	$C_{14}H_9F_{11}O_3$	434.0376
IX	75	82–84 (1)	442 $[M]^+$ (54.87), 423 $[M - F]^+$ (12.06), 323 $[M - C_2F_5]^+$ (78.46), 281 $[M - C_6H_3Cl_2]^+$ (0.94), 161 $[C_6H_3Cl_2O]^+$ (7.67), 145 $[C_6H_3Cl_2]^+$ (100), 119 $[C_2F_5]^+$ (4.73), 109 $[C_3H_3Cl_2]^+$ (35.97), 69 $[CF_3]^+$ (15.06)	441.9402	$C_{12}H_3F_{11}Cl_2O$	441.9385
X	40	50–51 (3)	484 $[M]^+$ (26.15), 465 $[M - F]^+$ (22.22), 445 $[M - HF - F]^+$ (19.99), 365 $[M - C_2F_5]^+$ (3.45), 301 $[M - C_6F_5O]^+$ (3.72), 281 $[M - C_6F_5O - HF]^+$ (11.01), 277 $[M - C_6F_5 - 2HF]^+$ (5.48), 233 $[C_6F_5OCF_2]^+$ (66.40), 184 $[C_6F_5OH]^+$ (100), 167 $[C_6F_5]^+$ (69.09), 119 $[C_2F_5]^+$ 93 $[CF_3CC]^+$ (7.80), 69 $[CF_3]^+$ (93.82) 51 $[CHF_2]^+$ (22.22)	483.9733	$C_{12}HF_{17}O$	483.9756
XI	61	58–59 (3)	402 $[M]^+$ (39.63), 383 $[M - F]^+$ (4.69), 333 $[M - CF_3]^+$ (4.69), 283 $[M - C_2F_5]^+$ 214 $[M - CF_3 - C_2F_5]^+$ (1.92), 121 $[C_6H_3O(CH_3)_2]^+$ (2.70), 105 $[C_8H_9]^+$ (100), 91 $[C_7H_6]^+$ (6.28), 69 $[CF_3]^+$ (4.37)	402.0483	$C_{14}H_9F_{11}O$	402.0477
XII	79	84–86 (2)	434 $[M]^+$ (100), 415 $[M - F]^+$ (14.13), 315 $[M - C_2F_5]^+$ (1.08), 281 $[M - C_8H_9O]^+$ (0.75), 265 $[M - C_8H_9]^+$ (51.60), 153 $[C_8H_9O_3]^+$ (51.60), 137 $[C_8H_9O]^+$ (0.84), 119 $[C_2F_5]^+$ (0.83), 69 $[CF_3]^+$ (4.96)	434.0371	$C_{14}H_9F_{11}O_3$	434.0376
XIII	69	91–92 (2.5)	419 $[M]^+$ (100), 400 $[M - F]^+$ (6.01), 373 $[M - NO_2]^+$ (16.98), 350 $[M - CF_3]^+$ (19.63), 330 $[M - CF_3 - HF]^+$ (22.44), 304 $[M - CF_3 - NO_2]^+$ (17.78), 300 $[M - C_2F_5]^+$ (2.39), 235 $[M - 2CF_3 - NO_2]^+$ (13.50), 122 $[C_6H_5NO_2]^+$ (14.01), 119 $[C_2F_5]^+$ (15.52), 69 $[CF_3]^+$ (17.43)	419.0008	$C_{12}H_4F_{11}NO_3$	419.0015
XIV	55	96–97 (2.5)	419 $[M]^+$ (100), 400 $[M - F]^+$ (3.19), 373 $[M - NO_2]^+$ (11.83), 354 $[M - F - NO_2]^+$ (17.64), 350 $[M - CF_3]^+$ (4.75), 304 $[M - CF_3 - NO_2]^+$ (10.82), 300 $[M - C_2F_5]^+$ (4.58), 254 $[M - C_2F_5 - NO_2]^+$ (9.86), 235 $[M - C_2F_5 - NO_2 - F]^+$ (17.19), 122 $[C_6H_4NO_2]^+$ (12.56), 119 $[C_2F_5]^+$	418.9999	$C_{12}H_4F_{11}NO_2$	419.0015

Table 1. (Contd.)

Comp. no.	Yield, %	bp, °C (*p*, mm Hg)	Mass spectrum, *m/z* (I_{rel}, %)	Found *M*	Formula	Calculated *M*
XIV			(17.98), 76 $[C_6H_4]^+$ (36.89), 69 $[CF_3]^+$ (17.38), 46 $[NO_2]^+$ (1.90), 50 $[CF_2]^+$ (19.40)			
XVIII	93	46–47 (3)	391 $[M]^+$ (27.98), 372 $[M - F]^+$ (0.60), 272 $[M - C_2F_5]^+$ (100), 252 $[M - C_2F_5 - HF]^+$ (5.77), 203 $[M - C_2F_5 - CF_3]^+$ (0.72), 119 $[C_2F_5]^+$ (4.90), 109 $[C_5H_3NO_2]^+$ (0.83), 93 $[C_5H_4NO]^+$ (28.84), 69 $[CF_3]^+$ (15.38) 65 $[C_5H_5N]^+$ (22.64)	391.0061	$C_{11}H_4F_{11}NO_2$	391.0066
XIX	50	68–70 (2)	356 $[M - F]^+$ (5.87), 306 $[M - CF_2]^+$ (58.37), 287 $[M - CF_3]^+$ (0.58), 237 $[M - C_2F_5]^+$ (7.76), 206 $[M - (CF_3)_2C]^+$ (3.99), 119 $[C_2F_5]^+$ (0.97), 78 $[C_5H_5N]^+$ (100), 69 $[CF_3]^+$ (7.16), 51 $[C_4H_4]^+$ (20.13)	356.0126[a]	$C_{11}H_4F_{10}NO$[a]	356.0133[a]
XXIII	33	76–77 (7)	448 $[M]^+$ (6.63), 355 $[M - OC_6H_5]^+$ (32.55), 335 $[M - C_6H_5OH - F]^+$ (5.36), 259 $[M - F - C_6H_5 - C_6H_5O]^+$ (16.10), 119 $[C_2F_5]^+$ (0.70), 94 $[C_6H_5OH]^+$ (84.85), 77 $[C_6H_5]^+$ (100), 69 $[CF_3]^+$ (1.23)	448.0475	$C_{18}H_{10}F_{10}O_2$	448.0521
XXIV	25	79–80 (7)	484 $[M]^+$ (10.20), 465 $[M - F]^+$ (0.52), 389 $[M - C_6H_4F]^+$ (0.47), 373 $[M - C_6H_4FO]^+$ (71.01), 353 $[M - C_6H_4FO - HF]^+$ (16.28), 161 $[C_6H_4FOCF_2]^+$ (1.25), 119 $[C_2F_5]^+$ (1.84), 111 $[C_6H_4FO]^+$ (4.21), 95 $[C_6H_4F]^+$ (100), 75 $[C_6H_4F - HF]^+$ (21.27), 69 $[CF_3]^+$ (9.56)	484.0339	$H_{18}H_8F_{12}O_2$	484.0333
XXV	76	69–70 (1)	672 $[M]^+$ (9.38), 653 $[M - F]^+$ (41.62), 603 $[M - CF_3]^+$ (100), 553 $[M - C_2F_5]^+$ (8.06), 503 $[M - C_2F_5 - CF_2]^+$ (82.56), 391 $[M - C_6F_{11}]^+$ (0.51), 281 $[C_6F_{11}]^+$ (2.30), 119 $[C_2F_5]^+$ (11.44), 100 $[CF_2{=}CF_2]^+$ (1.64), 80 $[C_4H_4N_2]^+$ (30.77), 69 $[CF_3]^+$ (36.94), 52 $[C_4H_4]^+$ (12.10)	671.9769	$C_{16}H_2F_{22}N_2O_2$	671.9765

[a] For $[M - F]^+$.

Table 2. ^1H, ^{13}C, and ^{19}F NMR spectra of partially fluorinated alkyl alkenyl ethers

Comp. no.	^1H NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz)	^{19}F NMR spectrum, δ_F, ppm				
			F^1	F^3	F^4	F^5	F^6
IV	7.00	109.9 (C^4, $^1J_{CF}$ 264.8, $^2J_{CF}$ 40.1), 117.4 (C^9, $^2J_{CF}$ 18.2), 118.1 (C^5, $^1J_{CF}$ = J_{CF} 35.2), 118.2 (C^{10}), 120.3 (C^1, $^1J_{CF}$ 275.4), 120.7 (C^6, $^1J_{CF}$ 276.2), 121.2 (C^2, $^2J_{CF}$ 25.8), 124.4 (C^{11}), 124.8 (C^{12}) 144.4 (C^7, $^2J_{CF}$ 10.8), 151.9 (C^8, $^1J_{CF}$ 248.9), 153.7 (C^3, $^2J_{CF}$ 30)	106.6	30.2[a]	50.2	81.6	103.3
V	7.06, 6.54, 6.45, 3.55, 6.58	110.3 (C^4, $^1J_{CF}$ 264.9, $^2J_{CF}$ 40.1), 118.4 (C^5, $^1J_{CF}$ 287.7, $^2J_{CF}$ 35.1), 20.3 (C^6, $^1J_{CF}$ 274.8), 120.5 (C^1, $^1J_{CF}$ 277), 121.5 (C^2, $^2J_{CF}$ 33.8), 153 (C^3, $^2J_{CF}$ 28.9)	106.9	–	51.5	82.1	103.6
VI	6.19,6.16, 3.58	54.8 (C^{11}), 94.6 (C^8), 96.5 (C^{10}), 110.2 (C^4, $^1J_{CF}$ 265.2, $^2J_{CF}$ 39.7), 118.3 (C^5, $^1J_{CF}$ 287.6, $^2J_{CF}$ 34.9), 120.2 (C^6, $^1J_{CF}$ 275), 120.4 (C^1, $^1J_{CF}$ 277.7), 121.6 (C^3, $^2J_{CF}$ 29.5), 152.8 (C^2, $^2J_{CF}$ 28.3), 158.7 (C^7), 162 (C^9)	107	–	51.5	82.6	103.6

Table 2. (Contd.)

Comp. no.	^{1}H NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ_C, ppm (J_{CF}, Hz)	^{19}F NMR spectrum, δ_F, ppm				
			F^1	F^3	F^4	F^5	F^6
IX	7.27 (H^9), 7.26 (H^{10})	–	102.5	39.1	53.1	83.4	108
X	4.17	128.6 (C^8), 128.9 (C^9), 142.5 (C^{10}), 148.3 (C^7), 160.4 (C^1, $^1J_{CF}$ 309.4) 52.0 (C^2, $^2J_{CF}$ 15.4), 109.0 (C^4, $^1J_{CF}$ 268.3, $^2J_{CF}$ 38.2), 109.5 (C^1, $^1J_{CF}$ 287.5), 113.4 (C^3, $^1J_{CF}$ 266.9, $^2J_{CF}$ 33.8), 118.2 (C^5, $^1J_{CF}$ 287.4, $^2J_{CF}$ 30.2), 120.9 (C^6, $^1J_{CF}$ 287.5), 124.5 (C^7), 138.7 (C^9, $^1J_{CF}$ 266.4, $^2J_{CF}$ 5.6), 141.4 (C^{10}, $^1J_{CF}$ 245.9, $^2J_{CF}$ 13.1), 143.2 (C^8, $^1J_{CF}$ 256.1, $^2J_{CF}$ 8.9)	[a] [b]	37.6	55.6	82.4	102.8
XI	6.85, 2.13	16.4 (C^{11}), 109.2 (C^2, $^2J_{CF}$ 35.5), 110.6 (C^4, $^1J_{CF}$ 265, $^2J_{CF}$ 38.5), 118.8 (C^5, $^1J_{CF}$ 288, $^2J_{CF}$ 35.2), 120.6 (C^6, $^1J_{CF}$ 275.1), 121.3 (C^1, $^1J_{CF}$ 253.7), 126.3 (C^8), 127.9 (C^{10}), 129.9 (C^9), 153.1 (C^7), 157 (C^3, $^2J_{CF}$ 36)	108.1	–	50.6	83.1	104.6
XII	7.02, 6.54, 3.74	53.1 (C^{11}), 55.6 (C^{11}), 104.8 (C^9), 109.9 (C^4, $^1J_{CF}$ 263.4, $^2J_{CF}$ 39.1), 118.2 (C^5, $^1J_{CF}$ 287.8, $^2J_{CF}$ 35.3), 120.5 (C^6, $^1J_{CF}$ 274.7), 120.7 (C^1, $^1J_{CF}$ 74.7), 125.4 (C^{10}), 127.3 (C^3, $^1J_{CF}$ 17.2), 134.9 (C^7), 149.6 (C^8), 156.4 (C^3, $^2J_{CF}$ 27.4)	107	–	49.5	81.8	103.4
XIII	8.98, 7.95, 7.67, 7.47	109.9 (C^4, $^1J_{CF}$ 265.2, $^2J_{CF}$ 40.2), 111.2 (C^{11}), 117.9 (C^5, $^1J_{CF}$ 287.9, $^2J_{CF}$ 35), 119.6 (C^6, $^1J_{CF}$ 270.2), 119.9 (C^1, $^1J_{CF}$ 278.3), 120 (C^8), 120.7 (C^{10}), 124 (C^2, $^2J_{CF}$ 30.8), 130.5 (C^{12}), 149 (C^9), 151.4 (C^3, $^2J_{CF}$ 28.4), 156 (C^7)	106.8	–	51.8	82.4	103.7
XIV	9.33–9.28, 7.19–7.14	109.7 (C^4, $^1J_{CF}$ 265.5, $^2J_{CF}$ 40.1), 115.3 (C^8), 117.6 (C^5, $^1J_{CF}$ 288, $^2J_{CF}$ 35.1), 119.3 (C^6, $^1J_{CF}$ 276.1), 119.7 (C^1, $^1J_{CF}$ 277.4), 125.4 (C^9), 126 (C^2, $^2J_{CF}$ 17.6), 144.2 (C^7), (C^3, $^2J_{CF}$ 29.6), 160.3 (C^{10})	106.6	–	51.5	81.6	103.4
XV	8.51, 8.41, 7.39, 7.23	109.6 (C^4, $^1J_{CF}$ 265.2, $^2J_{CF}$ 39.8), 117.6 (C^5, $^1J_{CF}$ 287.9, $^2J_{CF}$ 36), 119.3 (C^6, $^1J_{CF}$ 286.7), 119.9 (C^1, $^1J_{CF}$ 286.7), 121.6 (C^2, $^2J_{CF}$ 24.6), 122.3 (C^{10}), 122.5 (C^{11}), 137.9 (C^9), 145.9 (C^8), 151.8 (C^3, $^2J_{CF}$ 34.2), 153 (C^7)	107.2	–	51.9	82.3	103.7
XVI	8.59, 8.46, 7.28, 7.28	–	108.5	51.1	38.9	83.8	107.5
XVII	7.41, 8.28	–	106.9	50.8	38.4	83.6	107.0
XVIII	7.83, 7.31, 7.01, 4.83	51.6 (C^7, $^2J_{CF}$ 37.9), 106.7 (C^6, $^2J_{CF}$ 28.8), 109.4 (C^7, $^1J_{CF}$ 265.2, $^2J_{CF}$ 36.3), 116.1 (C^5), 117.9 (C^8, $^1J_{CF}$ 287.1, $^2J_{CF}$ 39), 118.4 ($C^{11,12}$, $^1J_{CF}$ 285.1), 119.2 (C^6), 137.3 (C^3), 141 (C^4), 155.4 (C^2)	[c]				
XIX	8.02, 7.60, 6.95, 6.88	110.2 (C^4, $^1J_{CF}$ 264.3, $^2J_{CF}$ 39.6), 110.5 (C^{10}), 118.5 (C^5, $^1J_{CF}$ 287.9, $^2J_{CF}$ 35.3), 120 (C^6, $^1J_{CF}$ 243), 120.4 (C^1, $^1J_{CF}$ 235.2), 120.6 (C^9), 121.9 (C^{11}), 122.8 (C^2, $^2J_{CF}$ 35), (C^8), 162.4 (C^7)	106.6	51.5	–	82.5	103.2
XXIII	7.11, 6.95, 6.45	–	108.8	–	38.8	83.7	107.6
XXIV	6.93	–	108.6	32.6[d]	39.0	83.9	107.7
XXV	7.46, 7.26	109.3 (C^4, $^1J_{CF}$ 264.8, $^2J_{CF}$ 39.5), 116.1 (C^2, $^2J_{CF}$ 28.2), 117.7 (C^5, $^1J_{CF}$ 288.2, $^2J_{CF}$ 31.5), 118.9 (C^6, $^1J_{CF}$ 275.4), 119 (C^5, $^1J_{CF}$ 259.2, $^2J_{CF}$ 30.3), 119.5 (C^1, $^1J_{CF}$ 277.1), 126.3 (C^{12}), 127.3 (C^{12}), 133.6 (C^{11}), 134.6 (C^{11}), 151.5 ($C^{7,10}$), 158 (C^2, $^2J_{CF}$ 28.5), 158.1 (C^3, $^2J_{CF}$ 18.9)	106.3	–	55.0	82.7	103.1

[a] 98.5 and 97.8 ppm (F^1), *AB* system, J_{FF} 145.4 Hz. [b] 12.6 (F^8), 7.3 (F^{10}), 0.9 ppm (F^9) (F atoms in the benzene ring). [c] 102.5 ($F^{11,12}$), 39.1 (F^8), 84.2 ppm (F^9). [d] F atoms in the benzene ring.

and 2 h at 45°C. Then the mixture was poured into water (100 ml) and neutralized with dilute HCl; the reaction products were extracted with CH_2Cl_2 (3 × 30 ml), and the extract was dried over $MgSO_4$. The solvent was distilled off, and the residue was distilled in a vacuum to obtain 2-trifluoromethyl-3-*o*-fluorophenoxy-1,1,1,4,4,5,5,5-octafluoropent-2-ene **III**.

b. A 3.33-mmol portion of 2-hydroxybenzimidazole or 2-hydroxybenzothiazole was added with vigorous stirring at 0°C to a solution of 1 g of **I** and 1.01 g of triethylamine in 30 ml of acetonitrile. The mixture was stirred for 1 h at 0°C, 1 h at 25°C, and 2 h at 40°C. Then the mixture was poured into water, the products were extracted with CH_2Cl_2 (3 × 30 ml), and the extract was dried over $CaCl_2$. The solvent was distilled off, and the residue was dried in a vacuum and recrystallized from CH_2Cl_2.

2-(3,3,3-Trifluoro-1-pentafluoroethyl-2-trifluoromethylpropenyloxy)-1*H*-benzimidazole VII. Yield 56%, yellow crystals, mp 57–58°C. IR spectrum, ν, cm^{-1}: 3040, 1762, 1487, 1201, 1033. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.00–7.06 m (2H), 7.28 d.d (2H, *J* 3.6, 5.8 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 51.0 m (2F), 81.3 d (3F, *J* 9.7 Hz), 100.2 q (3F, *J* 10.4 Hz), 104.6 m (3F). Mass spectrum, *m/z* (I_{rel}): 419 (80) $[M]^+$, 373 (16), 350 (23), 304 (30).

2-(3,3,3-Trifluoro-1-pentafluoroethyl-2-trifluoromethylpropenyloxy)benzothiazole VIII. Yield 76%, yellow crystals, mp 48–50°C. IR spectrum, ν, cm^{-1}: 3095, 1698, 1474, 1193. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.27–7.48 m (4H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 52.0 m (2F), 82.1 q (3F, *J* 9.5 Hz), 100.2 q (3F, *J* 10.6 Hz), 104.6 m (3F). Mass spectrum, *m/z* (I_{rel}, %): 431 (76) $[M]^+$, 362 (99).

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REFERENCES

1. *Novoe v tekhnologii soedinenii ftora* (Fluorine Compounds. Modern Techonology and Application), Ishikawa, N., Ed., Moscow: Mir, 1984.
2. *Organofluorine Chemistry, Principles and Commercial Applications*, Banks, R.E., Smart, B.E., and Tatlow, J.C., Eds., New York: Plenum, 1994.
3. *Organofluorine Compounds in Medicinal Chemistry and Biomedical Applications*, Filler, R., Kobayashi, Y., and Yagupolskii, L.M., Eds., Amsterdam: Elsevier, 1993.
4. Welch, J.T. and Eswarakrishnan, S., *Fluorine in Bioorganic Chemistry*, New York: Wiley, 1991.
5. Maruta, M. and Ishikawa, N., *J. Fluorine Chem.*, 1979, vol. 13, no. 5, p. 421.
6. Ishikawa, N. and Nagashima, A., *Bull. Chem. Soc. Jpn.*, 1976, vol. 49, no. 2, p. 502.
7. Makarov, K.N., Gervits, L.L., Cheburkov, Yu.A., and Knunyants, I.L., *J. Fluorine Chem.*, 1977, vol. 10, no. 4, p. 323.
8. Sereda, S.V., Antipin, M.Yu., Gervits, L.L., and Struchkov, Yu.T., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, no. 11, p. 1549.
9. JPN Patent 62-178551, 1987, *Chem. Abstr.*, 1988, vol. 108, 55648w.
10. JPN Patent 08 41 045, 1996, *Chem. Abstr.*, 1996, vol. 124, 343275v.
11. UK Patent 1366691, 1974, *Ref. Zh. Khim.*, 1975, 18N197P.