Received **september 2000**

Synthesis of partially fluorinated organic compounds with the use of perfluoro-2-methyl-2-pentene and phenol derivatives.

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Introduction of fluorine atoms into organic molecules has brought to generation of series of new specific properties that are widely used in creation of up-to-date materials [1,2]. That considerably stimulates intensive development of the chemistry of fluorine-containing organic compounds that was caused by demands of technique and modern medicine. The class of bioactive compounds has been of growing interest after discovery of biological activity growth when fluorine atoms and perfluoroalkyl groups are introduced into bioactive compounds. Fluorine-containing intermediate products has been widely used for creation of both medicines and bioactive substances for agriculture [3,4].

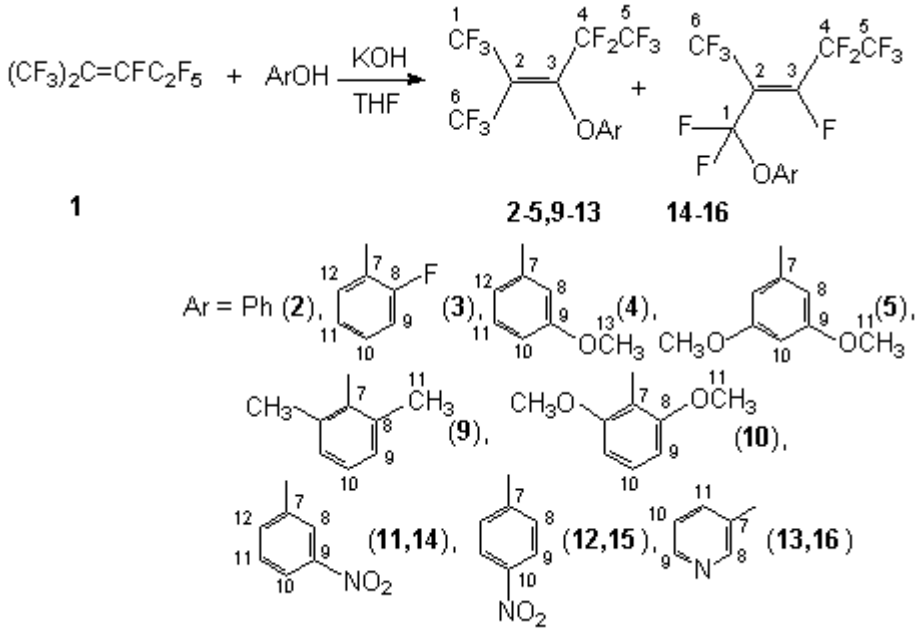
Fluorine-containing diphenyl ethers and phenoxy-containing compounds take an important place among commercially used herbicides. One of approaches to synthesize compounds of this class is based on reactions of nucleophilic replacement of fluorine atoms with O-nucleophilic reagents in internal perfluoroolefins. Thus, it was shown that interaction of dimer and trimer of hexafluoropropylene in the presence of triethylamine [5,6] or sodium phenolate [7] results in formation of products of replacement of fluorine atoms at the double bond. Majority of aromatic compounds containing the OH group under conditions of catalysis with bases is effective O-nucleophilic reagents. The reactions resulting in the products of replacement of fluorine atoms at the internal double bond were described: between paracreosol and dimer or trimer of hexafluoropropylene [8], N-(4-hydroxyphenyl)acetamine and dimer of hexafluoropropylene [9], 3-oxybenzodioxane and trimer of hexafluoropropylene [10], methyl ether of 4-oxybenzoic acid and tetrafluoroethylene pentamer [11] .

This work is aimed to the synthesis of partially fluorinated alkenaryl ethers based on perfluoro-2-methyl-2-pentene (**1**) and various derivatives of phenol with the purpose to

determine influence of fluorine atoms on biological activity of this class of compounds and intermediate products. It is essential to produce by a way of direct fluorination completely fluorinated alkylcyclohexyl ethers used as high-temperature heat carriers and dielectrics.

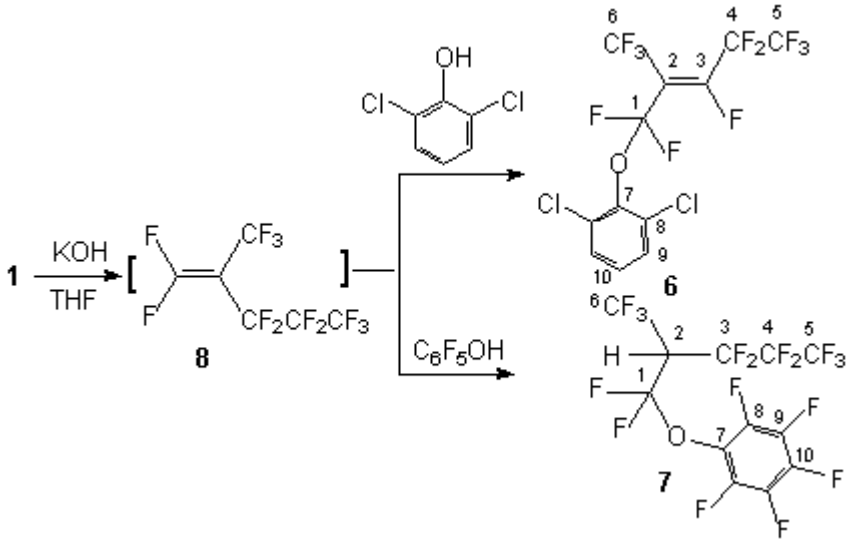
It is known that when N-nucleophilic reagents react with internal perfluoroolefins in the presence or absence of bases, the isomerization of the starting perfluoroolefins takes place. In the case of perfluoro-2-methyl-2-pentene there is formed perfluoro-2-methyl-1-pentene as an intermediate product, its terminal double bond contains extremely a nucleophilically labile fluorine atom. This condition can considerably influence the direction of the further attack of the nucleophilic reagent and can result in products of a different structure. Thus, another task is arisen: to study the influence of the nucleophilic reagent used and conditions of the process taken into account the properties of the starting internal perfluoroolefin.

Earlier it was shown that the interaction of phenol and compound **1** in the presence of KOH in tetrahydrofurane resulted in formation of [3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethyl-oxypropenyl[benzene (**2**), a product of a formal replacement of the fluorine atom at the double bond.



Scheme1

We have determined that the interaction of compound **1** and phenols containing electron donating substituents (2-fluorophenol, 3-metoxyphenol, 3,5-dimetoxyphenol) does not change the character of product formation, there are formed compounds (3-5) respectively. At the same time the reactions of compound **1** with 2,6-dichlorophenol and pentafluorophenol under the same conditions give (1,1,3,4,4,5,5,5-octafluoro-2-trifluoromethyl pent-2-enyloxy)-2,6-dichlorobenzene **6** and (1,1,3,3,4,4,5,5,5-nonafluoro-2-trifluoromethylphenoxy)-pentafluorobenzene **7** respectively. One of explanations of that is the replacement of the fluorine atom in terminal olefin **8** formed from olefin **1** under action of the base.

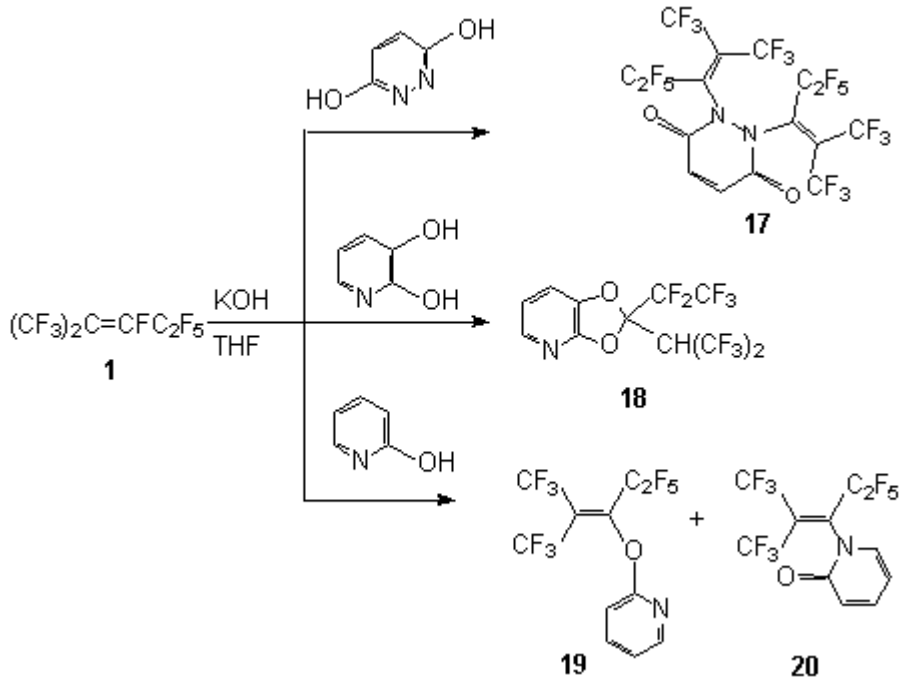


Scheme 2

Such a behavior of these phenols probably is a consequence of the presence of the chlorine and fluorine atoms at the 2- and 6-positions and due to low reactivity of the respective phenolate anions. But the reaction of compound **1** with 2,6-dimethyl-phenol and 2,6-dimethyloxyphenol results in the formation of compounds **9** and **10** despite considerable space requirements. At the same time these results can not be explained by only electron donating properties of the substituents because in the case of interaction of compound **1** with 3-nitrophenol and 4-nitrophenol there are formed mixtures both of the product of fluorine replacement at the internal multiple bond and of the product of fluorine replacement at the terminal bond of intermediate olefin **8** (compounds **11,12,14,15** respectively). The formation of compounds **14** and **15** is caused by a difference in rates of nucleophilic attack of phenoxy-anion to the carbon atom of the double bond and the rate of isomerization of olefin **1**.

It is reasonable to expect a similar behavior in the reaction of compound **1** with 3-oxypyridine also, a mixture of compounds **13** and **16** is formed.

It was shown that in case of the presence of two OH-groups the reaction involved the two groups with formation of the product of replacement of the fluorine atom at the double bond (compound **17**). Thus, interaction of compound **1** and pyridazine-3,6-diol in the presence of KOH in tetrahydrofuran gives 1,5-bis[3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethylprepenyl]1,2-dihydropyradizine-3,6-dion **17**, whereas the reaction with 2,3-dioxypyridine gives 2-pentafluoroethyl-2(2,2,2-trifluoro-1-trifluoromethyl-ethyl)-[1,3]dioxolo[4,5-b] pyridine **18**.



Scheme 3

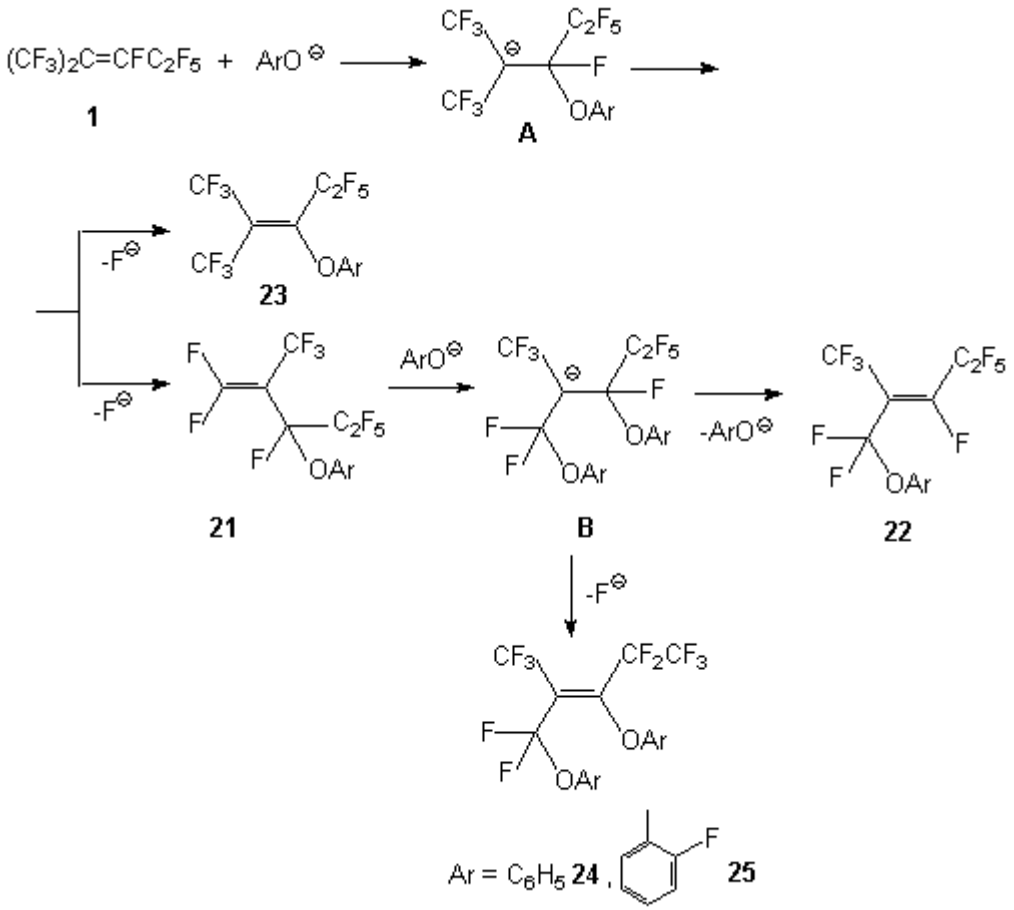
In the case of reaction of compound **1** with 2-oxypyridine ,as it should be expected, a mixture of 2[3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethyl-propenyloxy]pyridine **19** and 1[3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethyl-propenyl]1H-pyridine-2-on **20** is formed. That may be explained by the attack of the double bond of olefin1 by O- and N-nucleophilic centers.

The reaction of compound **1** with phenol begins by the attack of O-nucleophilic center of the reagent towards the carbon atom of the internal double bond following by generation of intermediate carbanion **A** stabilized by two CF_3 groups. Further transformations of the latter may proceed at the expense of elimination of the fluoride ion both from the CF fragment and from the CF_3 group. Comparing thermodynamical stability of the end products, it turned out that the elimination of the fluoride ion from the CF fragment and formation of the product containing phenoxy substituent at the a position to the double bond is more preferable. Prevailing formation of perfluoroolefin **2** in the reaction of compound **1** and sodium phenolate should then be ascribed to kinetic control.

However, it must not be ruled out a different way to form compounds **14-16** which may consist in the formation of compound **21** from intermediate carbanion **A**. In fact, authors [5] have determined the formation of olefin **2**1 in the reaction between compound **1** and phenol and have isolated such an olefin.

The fluorine atoms at the terminal double bond in olefin **21** are more sensitive to the action of nucleophilic reagents comparing with fluorine mobility at the internal double bond of olefin **1**. The interaction of olefin **21** with phenolate anion gives intermediate carbanion B. In it stabilization of negative carbanion under action of phenoxy group (OAr) is less effective and there are two ways of stabilization of this carbanion: elimination of the fluoride ion from the CF fragment that brings to reaction products **24** and **25** or elimination of the phenoxy-anion leading to the formation of compound **22**

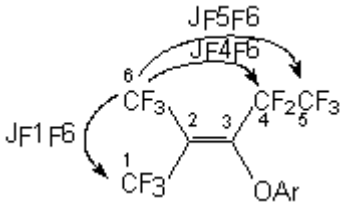
This way is observed exclusively for ArO=OC_6F_5,$OC_6H_3Cl_2$2 - 2,6; for other phenols containing, for example, NO_2 group in the benzene ring a mixture of compounds of **22** and **23** type is formed.



Scheme 4.

From our point of view, the way through intermediate formation of carbanion **B** via olefin **21** seems possible.

The structure of new compounds described above has been determined on the basis of the data of IR, ^1H, ^{13}C and ^{19}F NMR spectra (Table 1) and mass spectrometry (Table 2). The IR spectra of these compounds show vibrations of the double bond at 1647 cm^{-1}. The ^1H NMR spectrum exhibits signals from hydrogen atom of the aromatic ring in the range characteristic for phenols. In the ^{19}F NMR spectrum the chemical shift and thin structure of the signals correspond to analogs described earlier (see, for example, for phenol[5]), the constants are as follows: J_{F1F6} is up to 10.7, J_{F4F6} is up to 23.2, J_{F5F6} is up to 4.0 Hz.



For compounds of **22** type the ^{13}C and ^{19}F NMR spectra exhibit signals of fluorine and

coupling are characteristic for a double bond and fluorine at it.

Conclusion.

The reaction way for internal perfluoroolefin 1 is determined by the nature of the substituent in the phenyl fragment , that provides a possibility to synthesize partially fluorinated arylalkenyl ethers.

Experimental

The ^{19}F NMR (ppm) spectra were recorded on a Bruker WP 200SY spectrometer (188.324 MHz) with C6F6 in CDCl3 as the internal standard. The ^{13}C NMR (ppm) spectra were recorded on a Bruker-400 spectrometer (100.614 MHz) with Me_4Si (0.00) as the internal standard in $CDCl^3$ (J_{CH} was not measured). The IR spectra were recorded on a Bruker IFS66 spectrometer (5% in CCl_4). The GC-MS spectra were obtained at 70 eV under electron impact mode and reported as m/z index on a CM spectrometer Funnigan 8200. The mass spectra were determined on a liquid chromatograph Hewlett Packard G 1800A, GCD system with a GC electronic ionization detector and using a 30mm capillary column 0.25 mm covered with a 0.2 μk polymer coating of 5% of diphenyl / 95% of 1,4-dimethylsiliconate (HP-5), helium as a gas, 1 mL/min, the temperature of the column was 280^oC. The yield, boiling point and HRMS data of the new compounds are given in Table 1 and Table 2 shows the data of the ^1H, ^{13} C and ^{19}F NMR spectra.

General synthesis procedure

Compound **1** was added dropwise (10.7g, 36 mmol) to a suspension of KOH (2g, 36mmoles) in anhydrous THF (20 mL) at stirring at room temperature and cooled to 0^oC. 2-Fluorophenol (4g,36 mmol) was then added in small portions for 15 minutes at stirring, after aging at stirring for 1 hour at 0^oC the temperature was raised to room temperature and everything was stirred for another hour and then for 2 hours at 45^oC. The reaction mixture was poured into water (100mL), neutralized with diluted hydrochloric acid, extracted with CH_2Cl_2 (3x30mL) and dried over $MgSO_4$. After distillation of the solvent the residue was distilled in vacuum to produce 2-trifluoromethyl-3-orto-fluorophenoxy-1,1,1,4,4,5,5,5-octafluoropropent-2-en (2).

The work has been executed at financial support of STEPI grant (South Korea,2000) and innovational grant N47, 2000 of the Siberian branch of the Russian academy of Science.

Table 1. ^1H , ^{13}C and ^{19}F NMR Data of the Partly-fluorinated Products

Compound	^{1}H NMR	^{13}C NMR,δ_C (J_{C-F})	^{19}F NMR, δ_F				
			F^1	F^3	F^4	F^5	F^6
3	7/00	109.9 (C^4, $^1J_{CF}$= 264.8; $^2J_{CF}$=	106.6	30.2[a]	50.2	81.6	103.3

		40.1), 117.4 (C^9, $^2J_{CF}$= 18.2), 118.1 (C^5, $^1J_{CF}$=? , $^2J_{CF}$= 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)					
4	7.06; 6.54; 6.45; 3.55; 6.58	110.3 (C^4, $^1C_{CF}$= 264.9; $^2J_{CF}$= 40.1), 118.4 (C^5, $^1J_{CF}$=287.7; $^2J_{CF}$= 35.1), 120.3 (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
5	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
6	7.27 (H^9), 7.26 (H^{10})	128.6 (C^8), 128.9 (C^9), 142.5 (C^{10}), 148.3 (C^7), 160.4 (C^1, $^1J_{CF}$ = 309.4)	102.5	37.6	55.6	82.4	108.0
7	4.17	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),	b c	39.1	53.1	83.4	102.8

		143.2 (C^8, $^1J_{CF}$= 256.1; $^2J_{CF}$= 8.9)					
9	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
10	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, $^1J_{CF}$= 274.7), 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
11	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
12	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),151.1 (C^3, $^2J_{CF}$= 29.6), 160.3 (C^{10})	106.6		51.5	81.6	103.4
13	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;	107.2		51.9	82.3	103.7

		$^{2}J_{CF}$= 36),119.3 (C^{6}, $^{1}J_{CF}$= 286.7), 119.9 (C^{1},$^{1}J_{CF}$= 286.7), 121.6 (C^{2}, $^{2}J_{CF}$= 24.6),122.3 (C^{10}), 122.5 (C^{11}), 137.9 (C^{9}),145.9 (C^{8}), 151.8 (C^{3}, $^{2}J_{CF}$= 34.2),153 (C^{7})					
14	8.59; 8.46; 7.28;7.28		108.5	51.1	38.9	83.8	107.5
15	7.41; 8.28		106.9	50.8	38.4	83.6	107.0
17	7.46; 7.26	109.3 (C^{4}, $^{1}J_{CF}$= 264.8; $^{2}J_{CF}$= 39.5),116.1 (C^{2}, $^{2}J_{CF}$= 28.2), 117.7 (C^{5},$^{1}J_{CF}$= 288.2; $^{2}J_{CF}$= 31.5), 118.9 (C^{6},$^{1}J_{CF}$= 275.4), 119 (C^{5}, $^{1}J_{CF}$= 259.2; $^{2}J_{CF}$=30.3), 119.5 (C^{1}, $^{1}J_{CF}$= 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}, $^{2}J_{CF}$= 28.5), 158.1(C^{3}, $^{2}J_{CF}$= 18.9)	106.3		55.0	82.7	103.1
18	7.83; 7.31; 7.01;4.83	51.6 (C^{7}, $^{2}J_{CF}$= 37.9), 106.7 (C^{6}, $^{2}J_{CF}$=28.8), 109.4 (C^{7}, $^{1}J_{CF}$= 265.2; $^{2}J_{CF}$=36.3), 116.1 (C^{5}), 117.9 (C^{8}, $^{1}J_{CF}$=287.1; $^{2}J_{CF}$= 39), 118.4 ($C^{11,12}$, $^{1}J_{CF}$=285.1), 119.2 (C^{6}), 137.3 (C^{3}), 141(C^{4}), 155.4 (C^{2})	d				
19	8.02; 7.60; 6.95;6.88	110.2 (C^{4}, $^{1}J_{CF}$= 264.3; $^{2}J_{CF}$= 39.6),110.5 (C^{10}), 118.5 (C^{5}, $^{1}J_{CF}$= 287.9;$^{2}J_{CF}$= 35.3), 120 (C^{6}, $^{1}J_{CF}$= 243),120.4 (C^{1}, $^{1}J_{CF}$= 235.2), 120.6 (C^{9}),121.9 (C^{11}), 122.8 (C^{2}, $^{2}J_{CF}$= 35),129.9 (C^{8}), 162.4 (C^{7})	106.6		51.5	82.5	103.2
24	7.11; 6.95; 6.45		108.8		38.8	83.7	107.6
25	6.93		108.6	32.6[a]	39.0	83.9	107.7

Note : [a] F in benzene ring;

[b] 98.5 and 97.8 (F^1) AB-system J_{FF} = 145.4;

[c] 12.6 (F^8), 7.3 (F^{10}), 0.9 (F^9) (F benzene ring);

[d] 102.5 ($F^{11,12}$) 39.1 (F^8) 84.2 (F^9)

Table 2. Yields, Boiling-points and HRMS Data of the Partly-fluorinated Products

Compound	Yeld, %	b.p. , ^oC/Torr	Found , amu	Formula	Calculated, amu	Mass-spectrum, m/z (I_{otn},%)
2	70	69-71/19	374.0162	$C_{12}H_5F_{11}O$	374.0165	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)
3	75	36-37/3	392.0054	$C_{12}H_4F_{12}O$	392.0074	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)
4	71	61-62/2	404.0273	$C_{13}H_7F_{11}O_2$	404.0270	404$[M]^+$ (75.36), 385 $[M-F]^+$ (16.63), 335 [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)
5	68	82-83/2.5	434.0371	$C_{14}H_9F_{11}O_3$	434.0376	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)
6	75	82-84/1	441.9402	$C_{12}H_3F_{11}Cl_2O$	441.9385	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)
7	40	50-51/3	483.9733	$C_{12}HF_{17}O$	483.9756	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 [illegible]

						$[CF_3]^+$ (93.82)51 $[CHF_2]^+$ (22.22)
9	61	58-59/3	402.0483	$C_{14}H_9F_{11}O$	402.0477	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)
10	79	84-86/2	434.0371	$C_{14}H_9F_{11}O_3$	434.0376	0376 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)
11	69	91-92/2.5	419.0008	$C_{12}H_4F_{11}NO_3$	419.0015	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)
12	55	96-97/2.5	418.9999	$C_{12}H_4F_{11}NO_2$	419.0015	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 $[M\text{-}C_2F_5]^+$ (4.58), 254 $[M\text{-}C_2F_5\text{-}NO_2]^+$ (9.86), 235$[M\text{-}C_2F_5\text{-}NO_2\text{-}F]^+$ (17.19), 122 $[C_6H_4NO_2]^+$ (12.56), 119 $[C_2F_5]^+$ (17.98), 76 $[C_6H_4]^+$ (36.89), 69 $[CF_3]^+$(17.38), 46 $[NO_2]^+$ (1.90), 50 $[CF_2]^+$(19.40)
17	76	69-70/1	671.9769	$C_{16}H_2F_{22}N_2O_2$	671.9765	672 $[M]^+$ (9.38), 653 $[M\text{-}F]^+$ (41.62),603 $[M\text{-}CF_3]^+$ (100), 553 $[M\text{-}C_2F_5]^+$ (8.06), 503 $[M\text{-}C_2F_5\text{-}CF_2]^+$ (82.56),391 $[M\text{-}C_6F_{11}]^+$ (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)
18	93	46-47/3	391.0061	$C_{11}H_4F_{11}NO_2$	391.0066	391 $[M]^+$ (27.98), 372 $[M\text{-}F]^+$ (0.60),272 $[M\text{-}C_2F_5]^+$ (100), 252 $[M\text{-}C_2F_5\text{-}HF]^+$ (5.77), 203 $[M\text{-}C_2F_5\text{-}CF_3]^+$ (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)
19	50	68-70/2	356.0126	$C_{11}H_4F_{10}NO$[a]	356.0133	356 $[M\text{-}F]^+$ (5.87), 306 $[M\text{-}CF_2]^+$ (58.37), 287 $[M\text{-}CF_3]^+$ (0.58), 237$[M\text{-}C_2F_5]^+$ (7.76), 206 $[M\text{-}(CF_2)_2\text{-}C]^+$ (3.99), 119

						$[C_2F_5]^+$ (0.97), 78 $[C_5H_5N]^+$ (100), 69 $[CF_3]^+$ (7.16), 51 $[C_4H_4]^+$ (20.13)
24	33	76-77/7	448.0475	$C_{18}H_{10}F_{10}O_2$	448.0521	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)
25	25	79-80/7	484.0339	$C_{18}H_8F_{12}O_2$	484.0333	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)

Note : [a] For $[M-F]^+$

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