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Synthesis and Properties of Fluorinated Ethers with Fluorobenzene Rings

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Since per- and polyfluorinated ethers display unique physiochemical properties[1] that make them invaluable in practical applications,[2,3] considerable effort has been devoted to their synthesis. While earlier attempts relied mainly on electrochemical fluorination,[4] extensive decomposition during this fluorination process makes it impractical to produce perfluorinated ethers on a large scale. It was not until 1966 that the first commercial perfluoroalkyl ether, poly(hexafluoropropene oxide), $C_3F_7O[CF(CF_3)CF_2O]_nC_2F_5$, was produced by Du Pont.[5,6] There are currently four commercially available perfluoroalkyl ether fluids[5−9] which are being used as vacuum pump oil,[10] as lubricants for magnetic recording media[11] and for space applications.[12−15] The major shortcoming of these perfluoroalkyl ethers is that they all contain at least one CF_2O segment in their backbones, which, when combined with the high free energy of formation of M−F bonds, renders these materials relatively unstable in the presence of metals, metal salts and oxides at elevated temperatures. Internal sectors with a pendant CF_3 group, such as those in Krytox, and alkoxy end groups adjacent to $-CF(CF_3)-$ are spared from, or are at least much more resistant to, the degradation process.[16] It is therefore of interest to study those fluorinated ethers whose structures do not contain the OCF_2 moiety.

Recently, we developed a very efficient way to synthesize fluorinated ethers by using siloxane derivatives of various fluoroalcohols.[17,18] In this work, we extend the strategy to obtain fluorinated ethers in order to determine their thermal stabilities under different conditions.

Results and Discussion

Nucleophilic displacement of a fluorine atom from polyfluoroarenes is used extensively with a variety of nucleophiles to obtain various substituted polyfluoroarenes.[19−25] However, while the sodium salt of 2,2,3,3-tetrafluorobutanediol can be used to attack the polyfluorobenzene ring to synthesize the corresponding substitution product, *viz.*,

$$\underset{\mathbf{1b}}{C_6F_5CN} + NaOCH_2CF_2CF_2CH_2ONa \xrightarrow{\text{diglyme}} \underset{\mathbf{3b}}{NCC_6F_4OCH_2CF_2CF_2CH_2OC_6F_4CN}$$

the reaction when run on a relatively large scale is sometimes very violent. Earlier we found that the disiloxane derivative of 2,2,3,3-tetrafluorobutanediol, (**2**), reacts smoothly with 1,2-diiodotetrafluorobenzene to give a cyclic product in the presence of fluoride ion with acetonitrile as solvent .[17] In contrast, when **2** is heated with substituted pentafluorobenzene in the presence of F^- with diglyme (DG) as solvent, the reaction invariably gives acyclic compounds as products.

$$\underset{\mathbf{1}}{C_6F_5X} + \underset{\mathbf{2}}{(CH_3)_3SiOCH_2CF_2CF_2CH_2OSi(CH_3)_3} \xrightarrow{\text{CsF/DG}} \underset{\mathbf{3}}{XC_6F_4OCH_2CF_2CF_2CH_2OC_6F_4X}$$

$$\mathbf{1}:\mathbf{2} = 2.5:1$$

X	C_6F_5X	$[XC_6F_4OCH_2(CF_2)]_2$	yield (%)	mp (°C)	bp (°C)
CF_3	**1a**	**3a**	77	70−72	326
CN	**1b**	**3b**	63	100−102	360 dec
F	**1c**	**3c**	75	82−85	317
NO_2	**1d**	**3d**	61	111−113	356 dec

All of these compounds are solids at room temperature. It is, however, of interest to note that some of the products from the reaction of the disiloxane derivative of 2,2,3,3,4,4-hexafluoropentanediol (**4**) with these polyfluorobenzenes are liquids at room temperature and have relatively high boiling points.

$$\underset{\mathbf{1}}{C_6F_5X} + \underset{\mathbf{4}}{(CH_3)_3SiOCH_2CF_2CF_2CF_2CH_2OSi(CH_3)_3} \xrightarrow{\text{CsF/DG}} \underset{\mathbf{5}}{XC_6F_4OCH_2CF_2CF_2CF_2CH_2OC_6F_4X}$$

$$\mathbf{1}:\mathbf{4} = 2.5:1$$

X	C_6F_5X	$(XC_6F_4OCH_2CF_2)_2CF_2$	yield (%)	mp (°C)	bp (°C)
CF_3	**1a**	**5a**	75	−40	327
CN	**1b**	**5b**	81	−25	>350 dec
F	**1c**	**5c**	71	61−63	310

In all these cases, the fluorine atom para to X is replaced by the alkoxide group. This is in agreement with previous results with other nucleophiles.[19] Although the stoichiometry of the

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Table 1. Thermal Stability of Compounds **5a**, **5b**, and **10** in the Presence of Metal Alloys and Lewis Acids

	color change temp (°C)				NMR change temp (°C)			
compd	M-50	Ti(4Al4Mn)	Al_2O_3	$AlCl_3$	M-50	Ti(4Al4Mn)	Al_2O_3	$AlCl_3$
5a	260	260	250	220	330	320	290	260
5b	240	240	230	200	310	310	280	260
10	230	230	210	190	260	260	240	210

reactions is 2:1, a slight excess of polyfluorobenzene is used to ensure optimum yields. In the case of hexafluorobenzene, however, use of an excess is essential to secure simple compounds **3c** and **5c**. Otherwise, higher molecular weight species are obtained according to the following scheme.

$$\underset{\mathbf{1c}}{C_6F_6} + \underset{n = 2,\ \mathbf{2};\ n = 3,\ \mathbf{4}}{(CH_3)_3SiOCH_2(CF_2)_nCH_2OSi(CH_3)_3} \xrightarrow{CsF/DG}$$

$$\underset{n = 2,\ \mathbf{3c};\ n = 3,\ \mathbf{5c}}{C_6F_5OCH_2(CF_2)_nCH_2OC_6F_5} +$$

$$\underset{n = 2,\ \mathbf{6};\ n = 3,\ \mathbf{7}}{C_6F_5OCH_2(CF_2)_nCH_2OC_6F_4OCH_2(CF_2)_nCH_2OC_6F_5}$$

$$\mathbf{1c}:\mathbf{2} \text{ or } \mathbf{4} = 2:1$$

When a 1:1 molar ratio of **1c** to **2** and **4** is used, compounds **6** and **7** are obtained in the ratio 59:44, respectively. In compounds **6** and **7**, one hexafluorobenzene ring is disubstituted at the para position to bridge the polyfluorinated diols. No further attempt was made at this point to extend the chain by replacing the para fluorine atom on either terminal C_6F_5 group.

In order to contrast the impact on the thermal stability of fluorinated ethers in the presence of a fluorinated benzene ring bonded to oxygen with those in which the pentafluorobenzene ring is separated from the ether link by a CH_2 unit, pentafluorobenzyl bromide was reacted with polyfluorinated diols **2** and **4**, viz.,

$$\underset{\mathbf{8}}{C_6F_5CH_2Br} + \underset{n = 2,\ \mathbf{2};\ n = 3,\ \mathbf{4}}{(CH_3)_3SiOCH_2(CF_2)_nCH_2OSi(CH_3)_3} \xrightarrow{CsF/DG}$$

$$\underset{n = 2,\ \mathbf{9};\ n = 3,\ \mathbf{10}}{C_6F_5CH_2OCH_2(CF_2)_nCH_2OCH_2C_6F_5}$$

$$\mathbf{8}:\mathbf{2} \text{ or } \mathbf{4} = 2.5:1$$

Compound **9** is a solid at room temperature while compound **10**, like **5a** and **5b**, is a liquid at room temperature.

All three liquids (**5a, 5b, 10**) have relatively high boiling points and wide liquid ranges. Their vapor pressures are less than 10 Torr below 200 °C. Preliminary thermal stability tests carried out by simply heating these liquids at various temperatures also indicates that compound **5a** is the most stable one among the three liquids. Changes in ^1H and ^{19}F NMR spectra occur at 330, 310, and 260 °C for compounds **5a**, **5b**, and **10**, respectively.

As mentioned above, per- and polyfluorinated ethers are usually vulnerable at high temperatures in the presence of metals and various Lewis acids. In general, various metals and Lewis acids have different effects on the thermal stabilities of fluorinated ethers. It is therefore of significance to examine the behavior of these liquids in the presence of different kinds of metals and Lewis acids. For present purposes, two alloys, M-50 stainless steel and Ti(4Al4Mn) alloy, and two Lewis acids, $AlCl_3$ and Al_2O_3, were selected for our study. The ASTM established procedure for thermal stability testing of different kinds of materials in the presence of metal was utilized. The results of these tests are listed in Table 1. Several conclusions can be drawn from Table 1. Compound **5a** is the most stable of the three liquids in all of these tests. Aluminum trichloride is most destructive to these polyfluorinated ethers in these cases. It should be pointed out that these are only initial results on the thermal stabilities of these liquids. No investigation was made to determine the mechanism of decomposition and the detailed structure of the decomposition products. Further work is required to scale up the preparation of the ethers and to perform complete physical and chemical property tests under a variety of conditions.

The thermal stabilities of compounds **9** and **10** are compared with their previously prepared analog $C_6F_5CH_2OCF_2CF_2OCH_2$-C_6F_5,[26] in which the CF_2 moiety is directly bonded to oxygen. The latter is found to be less stable than either **9** and **10**, its initial decomposition temperature being 40 °C lower than that of either one. Similar attempts to make the perfluorinated analogs by these reactions, however, failed to give the desired products. Further efforts are therefore needed to prepare these perfluorinated materials in order for their thermal stabilities to be assessed.

Experimental Section

Materials. CsF was oven dried and diglyme was distilled from sodium before use. $TMSOCH_2(CF_2)_2CH_2OTMS$ and $TMSOCH_2(CF_2)_3$-CH_2OTMS were prepared by reacting the corresponding polyfluorodiols with 1,1,1,3,3,3-hexamethyldisilazane in the presence of a catalytic amount of sacchrin. C_6F_5CN, $C_6F_5CF_3$, $C_6F_5NO_2$, $C_6F_5CH_2Br$, and C_6F_6 were used as received (PCR).

General Procedures. All reactions were performed under dry nitrogen atmosphere. Boiling points and melting points are uncorrected. A Perkin-Elmer Model 1710 infrared Fourier transform spectrometer equipped with an IBM PS/2 data station was used to record infrared spectra. ^{19}F and ^1H NMR spectra were obtained with a Bruker AC 200 Fourier transform NMR spectrometer by using $CDCl_3$ as solvent and TMS and CCl_3F as references. Mass spectra were obtained with a VG 7070HS mass spectrometer. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Reactions of $TMSOCH_2(CF_2)_2CH_2OTMS$ with $C_6F_5CF_3$—a Typical Procedure for the Preparation of Bis(polyfluoroaryl) ethers of Polyfluorodiols. To an oven-dried 50-mL Pyrex round-bottomed flask equipped with a magnetic stirrer were added 0.22 g (1.5 mmol) of CsF, 0.94 g (4 mmol) of $C_6F_5CF_3$, 0.61 g (2 mmol) of $TMSOCH_2(CF_2)_2$-CH_2OTMS, and 3 mL of diglyme under dry nitrogen. The mixture was heated and stirred at 80 °C for 12 h. After cooling to 25 °C, the product was extracted with 3 × 20 mL portions of ether. The ether extract was washed with water several times and dried over $MgSO_4$. Evaporation of the solvent under vacuum gave a solid crude product which was further purified by recrystallization.

Properties of $CF_3C_6F_4OCH_2(CF_2)_2CH_2OC_6F_4CF_3$ (3a). This compound is obtained in 77% yield, mp 70−72 °C, and bp 326 °C. Spectral data are as follows. IR (KBr): 1660 m, 1510 m, 1461 m, 1407 m,

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1377 s, 1344 s, 1286 s, 1237 s, 1186 s, 1156 s, 1111 s, 993 s, 957 m, 920 m, 877 m, 716 m cm^{-1}. ^{19}F NMR: δ −56.2 (6F, s, CF_3); 122.5 (4F, s, CH_2CF_2); −140.5 (4F, m, Ar−F); −155.1 (4F, m, Ar−F). ^{1}H NMR: δ 4.74 (t, J_{H-F} = 11.5 Hz, OCH_2). MS CI$^+$ [*m/e* (species) intensity]: 595 ($M^+ + 1$) 6.1; 594 (M^+) 29.3; 575 ($M^+ - F$) 13.8, 361 ($M^+ - CF_3C_6F_4O$) 100; 297 ($CF_3C_6F_4OCH_2CF_2^+$) 49.2; 247 ($CF_3C_6F_4OCH_2^+$) 36.1; 233 ($CF_3C_6F_4O^+$) 87.2; 217 ($CF_3C_6F_4^+$) 28.0; 205 ($CF_3C_6F_4O^+ - CO$) 47.5; 69 (CF_3^+) 33.5. Anal. Calcd for $C_{18}H_4F_{18}O_2$: C, 36.38; H, 0.67; F, 57.55. Found: C, 36.76; H, 0.68; F, 56.2.

Properties of $NCC_6F_4OCH_2(CF_2)_2CH_2OC_6F_4CN$ (3b). This compound is obtained in 63% yield, mp 100−102 °C, and bp 360 °C dec. Spectral data are as follows. IR (KBr): 2252, m, 1651 m, 1500 m, 1438 m, 1387, m, 1293, s, 1184, s, 1152 s, 1100, s, 995 s, 927 m cm^{-1}. ^{19}F NMR: δ −122.2 (4F, s, CH_2CF_2); −132.2 (4F, m, *o*-F to CN); −153.6 (4F, m, *m*-F to CN). ^{1}H NMR: δ 4.81 (t, $3J_{H-F}$ = 10.6 Hz, OCH_2). MS EI [*m/e* (species) intensity]: 509 ($M^+ + 1$) 6.5; 508 (M^+) 32.6; 318 ($M^+ - NCC_6F_4O$) 84.6; 254 ($NCC_6F_4OCH_2CF_2^+$) 31.6; 204 ($NCC_6F_4OCH_2^+$) 29.7; 191 ($NCC_6F_4OH^+$) 14.8; 190 ($NCC_6F_4O^+$) 100; 174 ($NCC_6F_4^+$) 16.3; 162 ($NCC_6F_4O^+ - CO$) 41.9. Anal. Calcd for $C_{18}H_4F_{12}N_2O_2$: C, 42.54; H, 0.79; N, 5.51; F, 44.86. Found: C, 42.37; H, 1.00; N, 5.09; F, 45.6.

Properties of $C_6F_5OCH_2(CF_2)_2CH_2OC_6F_5$ (3c). This compound is obtained in 75% yield, mp 82−85 °C, and bp 316.5 °C. Spectral data are as follows. IR (KBr): 1521.5 s, 1476 s, 1458 s, 1395 m, 1372, m, 1319, s, 1286 s, 1193 s, 1162 s, 1135 s, 1064, s, 1001, s, 955 s, 911 s cm^{-1}. ^{19}F NMR: δ −122.8 (4F, s, CH_2CF_2); −156.3 (4F, m, *m*-F); −161.1 (2F, m, *p*-F); −162.3 (4F, m, *o*-F). ^{1}H NMR: δ 4.60 (t, $^3J_{H-F}$ = 13.0 Hz, OCH_2). MS CI$^+$ [*m/e* (species) intensity]: 495 ($M^+ + 1$) 4.9; 494 (M^+) 27.6; 475 ($M^+ - F$) 1.0; 312 ($M^+ - C_6F_5O + 1$) 10.2; 311 ($M^+ - C_6F_5O$) 100; 247 ($C_6F_5OCH_2CF_2^+$) 1.4; 197 ($C_6F_5OCH_2^+$) 5.7; 184 ($C_6F_5O^+ + 1$) 8.1; 183 ($C_6F_5O^+$) 32.7; 155 ($C_6F_5O^+ - CO$) 8.0. Anal. Calcd for $C_{16}H_4F_{14}O_2$: C, 38.88; H, 0.82; F, 53.82. Found: C, 39.15; H, 0.97; F, 53.4.

Properties of $O_2NC_6F_4OCH_2(CF_2)_2CH_2OC_6F_4NO_2$ (3d). This compound is obtained in 61% yield, mp 111−113 °C, and bp 356 °C dec. Spectral data are as follows. IR (KBr): 2971, s, 1646 m, 1561, s, 1500 s, 1456 m, 1407, m, 1366, s, 1295, s, 1196, s, 1128 s, 1006, s, 950 s, 908 s cm^{-1}. ^{19}F NMR: δ −122.1 (4F, t, $^3J_{H-F}$ = 11.2 Hz, CH_2CF_2); −146.0 (4F, m, *o*-F to NO_2); −153.5 (4F, m, *m*-F to NO_2). ^{1}H NMR: δ 4.79 (t, $^3J_{H-F}$ = 11.5 Hz, OCH_2). MS CI$^+$ [*m/e* (species) intensity]: 550 ($M^+ + 2$) 17.6; 549 ($M^+ + 1$) 100; 548 (M^+) 21.1; 502 ($M^+ - NO_2$) 1.4; 338 ($M^+ - NO_2C_6F_4O$) 54.5; 274 ($NO_2C_6F_4OCH_2CF_2^+$) 6.9; 224 ($NO_2C_6F_4OCH_2^+$) 6.0; 210 ($NO_2C_6F_4O^+$) 1.6; 194 ($NO_2C_6F_4^+$) 3.4. Anal. Calcd for $C_{16}H_4F_{12}N_2O_6$: C, 35.05; H, 0.74; N, 5.11; F, 41.59. Found: C, 35.20; H, 0.91; N, 5.38; F, 42.0.

Properties of $CF_3C_6F_4OCH_2(CF_2)_3CH_2OC_6F_4CF_3$ (5a). This compound which boils at 327 °C is obtained in 75% yield. Spectral data are as follows. IR (film): 2967 m, 1667 m, 1505 m, 1458 m, 1432, m, 1403 m, 1347 s, 1312 s, 1239 s, 1170 s, 996 s, 958 s, 896 s, 876 m, 717 m cm^{-1}. ^{19}F NMR: δ −56.8 (6F, s, CF_3); −121.7 (4F, s, CH_2CF_2); −126.1 (2F, s, CF_2CF_2); −141.3 (4F, m, *o*-F to CF_3); −155.6 (4F, m, *m*-F to CF_3). ^{1}H NMR: δ 4.63 (t, J_{H-F} = 13.2 Hz, OCH_2). MS CI$^+$ [*m/e* (species) intensity]: 645 ($M^+ + 1$) 6.8; 644 (M^+) 38.7; 625 ($M^+ - F$) 17.6; 411 ($M^+ - CF_3C_6F_4O$) 27.0; 247 ($CF_3C_6F_4OCH_2^+$) 100; 233 ($CF_3C_6F_4O^+$) 13.4; 217 ($CF_3C_6F_4^+$) 23.5; 205 ($CF_3C_6F_4O^+ -$ CO) 18.3; 69 (CF_3^+) 25.6. Anal. Calcd for $C_{19}H_4F_{20}O_2$: C, 35.42; H, 0.63; F, 58.99. Found: C, 35.22; H, 0.70; F, 58.6.

Properties of $NCC_6F_4OCH_2(CF_2)_3CH_2OC_6F_4CN$ (5b). This compound which boils above 350 °C with decomposition is obtained in 81% yield. Spectral data are as follows. IR (film): 2971 m, 2247, m, 1652 m, 1507 m, 1457 m, 1403, m, 1320 s, 1153 s, 998 s, 756 m, 707 m cm^{-1}. ^{19}F NMR: δ −121.0 (4F, s, CH_2CF_2); −125.2 (2F, s, CF_2CF_2); −132.3 (4F, m, Ar−F); − 153.5 (4F, m, Ar−F). ^{1}H NMR: δ 4.79 (t, J_{H-F} = 13.2 Hz, OCH_2). MS CI$^+$ [*m/e* (species) intensity]: 559 ($M^+ + 1$) 8.7; 558 (M^+) 40.0; 368 ($M^+ - NCC_6F_4O$) 33.5; 348 ($M^+ - NCC_6F_4O - HF$) 4.1; 284 ($M^+ - NCC_6F_4OCH_2CF_2 - HF$) 10.3; 204 ($NCC_6F_4OCH_2^+$) 100; 191 ($NCC_6F_4OH^+$) 18.7; 190 ($NCC_6F_4O^+$) 33.8; 174 ($NCC_6F_4^+$) 21.5; 162 ($NCC_6F_4O^+ - CO$) 27.2. Anal. Calcd for $C_{19}H_4F_{14}N_2O_2$: C, 40.88; H, 0.72; F, 47.65; N, 5.02. Found: C, 40.65; H, 0.83; F, 47.6; N, 5.10.

Properties of $C_6F_5OCH_2(CF_2)_3CH_2OC_6F_5$ (5c). This compound is obtained in 71% yield, mp 61−63 °C, and bp 310 °C. Spectral data are as follows. IR (KBr): 1518.5 s, 1476 s, 1459 s, 1401 m, 1298 s, 1193 s, 1156 s, 1095 s, 1069, s, 1000, s, 762 s cm^{-1}. ^{19}F NMR: δ −121.4 (4F, s, CH_2CF_2); −125.6 (2F, s, CF_2CF_2); −156.2 (4F, m, *m*-F); −161.0 (2F, m, *p*-F); −162.4 (4F, m, *o*-F). ^{1}H NMR: δ 4.59 (t, $^3J_{H-F}$ = 13.5 Hz, OCH_2). MS CI$^+$ [*m/e* (species) intensity]: 545 ($M^+ + 1$) 19.6; 544 (M^+) 85.5; 525 ($M^+ - F$) 1.2; 506 ($M^+ - 2F$) 7.7; 362 ($M^+ - C_6F_5O + 1$) 15.8; 361 ($M^+ - C_6F_5O$) 100; 197 ($C_6F_5OCH_2^+$) 63.4; 184 ($C_6F_5O^+ + 1$) 23.0; 183 ($C_6F_5O^+$) 42.8; 155 ($C_6F_5O^+ - CO$) 15.2. Anal. Calcd for $C_{17}H_4F_{16}O_2$: C, 37.52; H, 0.74; F, 55.86. Found: C, 37.83; H, 0.81; F, 55.7.

Properties of $C_6F_5OCH_2(CF_2)_2CH_2OC_6F_4OCH_2(CF_2)_2CH_2OC_6F_5$ (6). This compound is formed in a ratio of 59:41 of $C_6F_5OCH_2(CF_2)_2CH_2OC_6F_5$ **(3c)** when hexafluorobenzene is reacted with $TMSOCH_2(CF_2)_2CH_2OTMS$ in a 1:1 molar ratio. No further attempt was made to separate **6** from **3c**. Spectral data unique to **6** are as follows. ^{19}F NMR: δ −156.6 (4F, m, C_6F_4). MS CI$^+$ [*m/e* (species) intensity]: 803 ($M^+ + 1$) 1.1; 802 (M^+) 4.1; 801 ($M^+ - 1$) 3.5; 620 ($M^+ - C_6F_5O + 1$) 2.0; 619 ($M^+ - C_6F_5O$) 9.1; 311 ($C_6F_5OCH_2CF_2CF_2CH_2^+$) 100.

Properties of $C_6F_5OCH_2(CF_2)_3CH_2OC_6F_4OCH_2(CF_2)_3CH_2OC_6F_5$ (7). This compound is formed at a ratio of 44:56 of $C_6F_5OCH_2(CF_2)_3CH_2OC_6F_5$ **(5c)** when hexafluorobenzene is reacted with $TMSOCH_2(CF_2)_3CH_2OTMS$ in a 1:1 molar ratio. No further attempt was made to separate **7** from **5c**. Spectral data unique to **7** are as follows. ^{19}F NMR: δ −156.7 (4F, m, C_6F_4). MS CI$^+$ [*m/e* (species) intensity]: 903 ($M^+ + 1$) 31.6; 902 (M^+) 73.5; 884 ($M^+ - F + 1$) 1.1; 865 ($M^+ - 2F + 1$) 1.3; 864 ($M^+ - 2F$) 7.3; 863 ($M^+ - 2F - 1$) 26.8; 719 ($M^+ - C_6F_5O$) 12.7; 718 ($M^+ - C_6F_5O - 1$) 52.7; 555 ($M^+ - C_6F_5OCH_2CF_2CF_2CF_2$) 2.3; 541 ($M^+ - C_6F_5OCH_2CF_2CF_2CF_2CH_2$) 4.5; 361 ($C_6F_5OCH_2CF_2CF_2CF_2CH_2^+$) 100.

Properties of $C_6F_5CH_2OCH_2(CF_2)_2CH_2OCH_2C_6F_5$ (9). This compound is obtained in 77% yield, mp 52 °C, and bp 316 °C. Spectral data are as follows. IR (film): 1658 m, 1505 s, 1458 m, 1435 m, 1376 m, 1310 s, 1187 s, 1138 s, 1057 s, 975 s, 940 s cm^{-1}. ^{19}F NMR: δ −122.3 (4F, s, CH_2CF_2); −143.1 (4F, m, *m*-F); −152.8 (2F, m, *p*-F); −161.8 (4F, m, *o*-F). ^{1}H NMR: δ 4.72 (4H, s, $C_6F_5CH_2$); 3.93 (4H, t, $^3J_{H-F}$ = 13.9 Hz, OCH_2). MS CI$^+$ [*m/e* (species) intensity]: 522 (M^+) 1.1, 504 ($M^+ - F + 1$) 10.0; 503 ($M^+ - F$) 46.8; 342 ($M^+ - C_6F_5CH_2 + 1$) 67.3; 341 ($M^+ - C_6F_5CH_2$) 57.8; 325 ($M^+ - C_6F_5CH_2O$) 4.3; 324 ($M^+ - C_6F_5CH_2O - 1$) 15.0; 311 ($M^+ - C_6F_5CH_2OCH_2$) 1.1; 292 ($C_6F_5CH_2OCH_2CF_2CF^+$) 16.0; 211 ($C_6F_5CH_2OCH_2^+$) 1.4; 197 ($C_6F_5CH_2O^+$) 33.0; 181 ($C_6F_5CH_2^+$) 100; 161 ($C_6F_5CH_2^+ -$ HF) 45.6.

Properties of $C_6F_5CH_2OCH_2(CF_2)_3CH_2OCH_2C_6F_5$ (10). This compound is obtained in 75% yield, bp 322 °C. Spectral data are as follows. IR (film): 2956, m, 1657 m, 1509.5 s, 1460 m, 1405 m, 1376 m, 1310 s, 1237 s, 1196 s, 1142.5 s, 1056 s, 975 s, 939 s cm^{-1}. ^{19}F NMR: δ −120.2 (4F, s, CH_2CF_2); −126.2 (2F, s, CF_2CF_2); −142.7 (4F, m, *m*-F); −153.0 (2F, m, *p*-F); −161.6 (4F, m, *o*-F). ^{1}H NMR: δ 4.71 (4H, s, $C_6F_5CH_2$); 3.95 (4H, t, $^3J_{H-F}$ = 13.8 Hz, OCH_2). MS CI$^+$ [*m/e* (species) intensity]: 554 ($M^+ - F + 1$) 4.9; 553 ($M^+ - F$) 22.9; 373 ($M^+ - C_6F_5CH_2 - F + 1$) 12.5; 357 ($M^+ - C_6F_5CH_2O - F + 1$) 3.3; 182 ($C_6F_5CH_2^+ + 1$) 8.1; 181 ($C_6F_5CH_2^+$) 100; 179 ($CH_2(CF_2)_3CH_2^+ + 1$) 9.0.

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