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Insertion of Fluoroalkenes into Activated C—H Bonds for the Preparation of Polyfluorinated Sulfanes, Alcohols, and Acyclic and Cyclic Ethers

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Free radical addition reactions of tetrahydrothiophene, pentamethylene sulfide, and 1,4-thioxane with various cyclic and acyclic per- and polyfluorinated olefins are readily initiated by di-*tert*-butyl peroxide, providing a convenient route for synthesizing cyclic sulfanes with fluorinated side groups. Tetrahydrothiophene reacts with hexafluoropropene, perfluoroallylbenzene, perfluorocyclobutene, and 1,2-dichlorotetrafluorocyclobutene in the presence of catalytic amounts of the peroxide to give the corresponding addition products $CH_2CH_2CH_2SCHCF_2CHFCF_3$ (**1**), $CH_2CH_2CH_2SCHCF_2CHFCF_2C_6F_5$ (**2**), $CH_2CH_2CH_2SCHCFCHFCF_2CF_2$ (**3**), and $CH_2CH_2CH_2SCHCClCHClCF_2CF_2$ (**4**), respectively. Pentamethylene sulfide reacts analogously with hexafluoropropene to give $CH_2CH_2CH_2CH_2SCHCF_2CHFCF_3$ (**8**). Reaction of 1,4-thioxane with hexafluoropropene or perfluoroallylbenzene gives a mixture of two products, $OCH_2CH_2SCH_2CHCF_2CHFCF_3$ (**9**) and $SCH_2CH_2OCH_2CHCF_2CHFCF_3$ (**10**) or $OCH_2CH_2SCH_2CHCF_2CHFCF_2C_6F_5$ (**11**) and $SCH_2CH_2OCH_2CHCF_2CHFCF_2C_6F_5$ (**12**), respectively. Fluorinated alcohols $C_6F_5CF_2CHFCF_2C(CH_3)_2OH$ (**15**), $C_6F_5CF_2CHFCF_2CH(CH_3)OH$ (**16**), and $C_6F_5CF_2CHFCF_2CH_2OH$ (**17**) are prepared by reacting perfluoroallylbenzene with the corresponding alcohols. When **15** is reacted with pentafluorobenzonitrile in the presence of potassium carbonate, an unexpected cyclic ether **19** is obtained as the major product in addition to $C_6F_5CF_2CHFCF_2C(CH_3)_2OC_6F_5CN$ (**18**). Alcohols **15**−**17** can be cyclized by heating with potassium carbonate to give fluorinated cyclic ethers **19**−**21**. The X-ray crystal structures of acyclic ether **18** and cyclic ether **19** are given. Compound **18** crystallizes in the tetragonal system, space group $P4(2)/n$, with $a = 18.471(0)$ Å, $b = 18.471(0)$ Å, $c = 11.702(0)$ Å, $V = 3992.5(9)$ Å^3, $D_{calc} = 1.768$ mg/m^3, $Z = 8$, and $R = 0.0617$. Compound **19** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 8.103(3)$ Å, $b = 8.790(3)$ Å, $c = 9.832(3)$ Å, $\alpha = 66.25(4)°$, $\beta = 72.01(3)°$, $\gamma = 80.19(4)°$, $V = 608.7(4)$ Å^3, $D_{calc} = 1.845$ mg/m^3, $Z = 2$, and $R = 0.0346$.

Introduction

Recently we reported the introduction of fluorinated side chains into 18-crown-6 by the free radical addition of the cyclic ether to fluorinated olefins and the crystal structure of one of these fluoroalkyl-substituted crown ether complexes with lanthanum triflate.[1] Since fluoroalkyl groups often play important roles in many aspects of chemistry, it is of significance to extend this free radical technique beyond alcohols and cyclic ethers to other heterocyclic compounds to enhance the utility of this reaction.

Free radical addition reactions of ethers and alcohols with fluoroolefins have been studied extensively,[2−5] and there are also limited reports on free radical additions of amines to fluoroolefins.[6] No report, however, to the best of our knowledge, has appeared on free radical initiated addition of sulfides to fluoroolefins. Free radical addition of methanethiol and trifluoromethanethiol to fluoroolefins under the influence of X-ray or UV radiation was reported[7] with the thiyl radical, RS$^•$, as the reactive intermediate in these cases. For ethers and alcohols, the α-ethereal and α-hydroxyalkyl radicals, $^•$C(R)-HOR′ and $^•$C(R)HOH, are the respective reactive intermediates.

In previous work, we have found that fluorinated ethers containing fluorobenzene rings exhibited useful thermal properties.[8] To further these studies fluorinated alcohols that contain fluorobenzene rings are prepared using the free radical addition technique mentioned above. We also extended this technique to the addition of cyclic sulfides to various fluorinated cyclic and acyclic olefins. Tetrahydrofuran is used in some cases under the same reaction conditions to compare the reactivity of sulfides and ethers in free radical addition to fluorinated olefins. The behavior of 1,4-thioxane, which possesses both ether and sulfide moieties, appears to differ from that of the mono-heteroatom rings.

Results and Discussion

In the presence of catalytic amounts of di-*tert*-butyl peroxide, tetrahydrothiophene adds across the double bond of fluorinated

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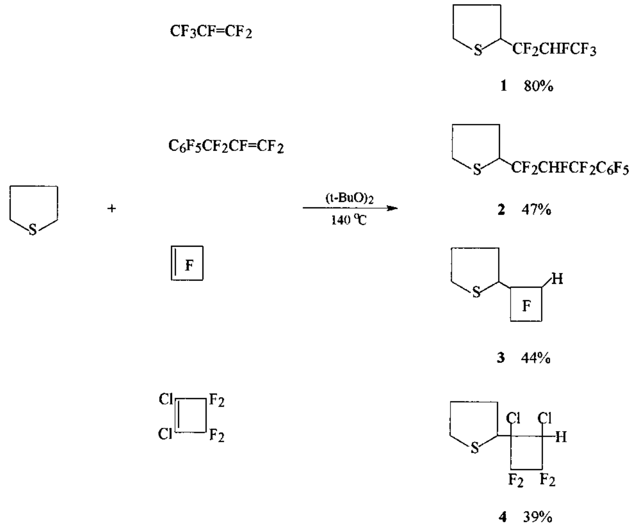
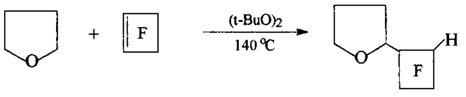
olefins to give the corresponding fluoroalkylated tetrahydrothiophenes in moderate to good yields.

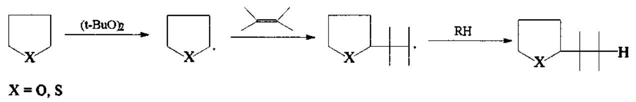


In the reaction of ethers with fluoroolefins, it is believed that oxygen plays an important role in stabilizing the intermediate free radical. A similar effect is expected here for the sulfur atom in stabilizing the free radical on the α carbon. In order to compare the relative significance of this stabilizing influence for different heteroatoms (sulfur vs oxygen in this case), tetrahydrofuran is reacted with perfluorocyclobutene under the same conditions used for tetrahydrothiophene

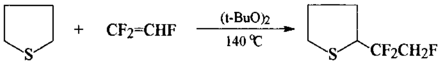


5 71%

Better yields are achieved in the case of tetrahydrofuran than with tetrahydrothiophene, as has been reported previously.[1,4,5] Tetrahydrofuran is obviously more effective than tetrahydrothiophene with respect to free radical addition to fluorinated olefins under the conditions we used. However, it is difficult to evaluate the relative reactivity simply from the different yields of these two reactions because, in the case of tetrahydrothiophene, more unidentified high-boiling residue is formed. The different yields of tetrahydrofuran vs tetrahydrothiophene in such reactions could result from the different stabilities of these two reagents under the reaction conditions applied. The reaction mechanism for both tetrahydrothiophene and tetrahydrofuran is depicted as follows:



Reaction of tetrahydrothiophene with trifluoroethylene gives almost exclusively the unidirectional addition product as is observed in the case of tetrahydrofuran.[1,4,5] This agrees with the observation that the free radical α to oxygen is nucleophilic with only the more electrophilic end of the double bond being attacked.



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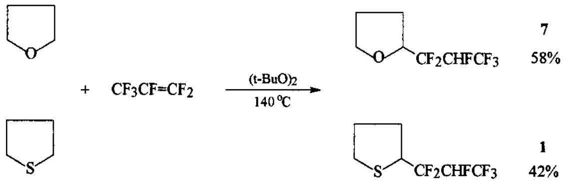
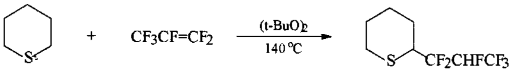
Competitive reactions between tetrahydrothiophene and tetrahydrofuran are studied by reacting an equimolar mixture of each with hexafluoropropene. The ^{19}F NMR spectrum shows that a higher yield of addition product is obtained with tetrahydrofuran (**7**:**1** = 58:42). Again, the lower yield of tetrahydrothiophene addition product can be attributed to its lower stability under the reaction conditions.

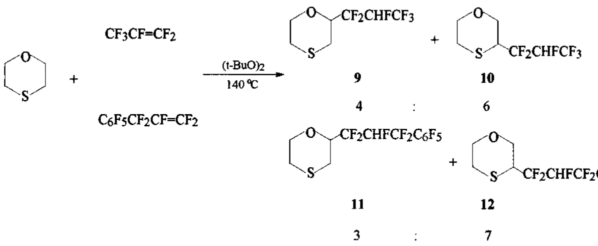


Pentamethylene sulfide behaves in the same manner as tetrahydrothiophene in its reaction with fluoroolefins, e.g.,



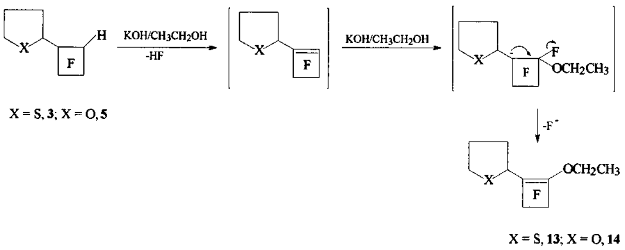
8 56%

When 1,4-thioxane, in which both oxygen and sulfur atoms are present in the ring, is reacted with hexafluoropropene and perfluoroallylbenzene, mixtures of products with the fluoroalkyl chain either adjacent to sulfur or to oxygen are obtained.



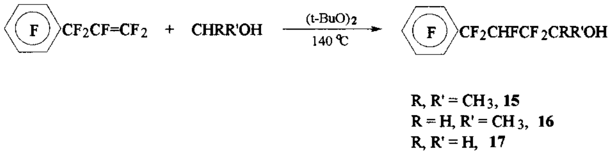
On the basis of NMR, it is possible to estimate the relative amounts of the products. However, current efforts to separate these compounds are not successful. It is interesting to note that given the opportunity for addition to occur either adjacent to the oxygen or the sulfur atoms in these cases, the majority of the product obtained has the fluoroalkyl group bonded to the carbon α to the latter. Although the total yields in these reactions are lower than the yields found either in the case of tetrahydrofuran or tetrahydrothiophene, possibly due to the decomposition of 1,4-thioxane under our reaction conditions, it is apparent that the carbon atom α to sulfur is more reactive with respect to free radical addition to fluoroolefins.

Dehydrofluorinations of both **3** and **5** with potassium hydroxide in ethanol give ethoxy substituted olefins, shown as follows:

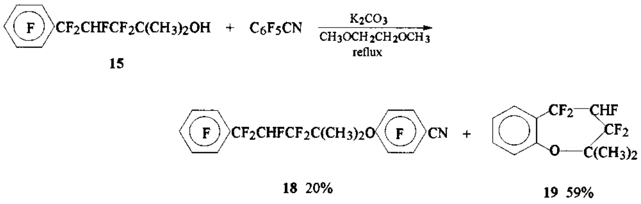


Although the intermediate fluoroolefin is not isolated, it is reasonable to believe that such an olefin is formed along the reaction pathway. The fluorine atom on the double bond is susceptible to nucleophilic attack via an addition—elimination mechanism.

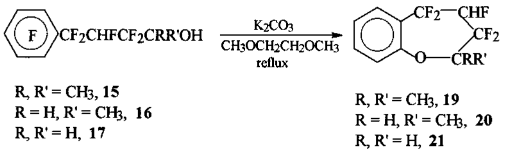
Fluorinated alcohols that contain the fluorobenzene moiety can be obtained by reacting perfluoroallylbenzene with various alcohols in the presence of di-*tert*-butyl peroxide.



It is rather unexpected that intramolecular cyclization is the dominant process (up to 59%) in the reaction of **15** with pentafluorobenzonitrile. Although it has been shown that fluorinated tertiary alcohols usually do not attack fluorobenzene rings when potassium carbonate is used as the base, with some more reactive species, such as pentafluorobenzonitrile, these nucleophilic displacement reactions do occur.[9,10] The expected product **18** from intermolecular attack is obtained in only 20% yield.



Cyclization occurs when the fluorinated alcohols are heated in the presence of potassium carbonate and in the absence of pentafluorobenzonitrile; i.e., intramolecular nucleophilic attack on the fluorinated benzene ring by the alkoxide group results in the formation of the fluorinated cyclic ether in high yield.



Compound **19** is distilled under vacuum and solidifies slowly (about 1 week) at 25 °C. The crystal structures of both **18** and **19** are determined at −80 °C. The X-ray crystal parameters are listed in Table 1. In compound **18**, the two perfluorobenzene rings are nearly perpendicular to each other. The C—O bond lengths of the ether oxygen atom bound to the benzene ring in both the acyclic and cyclic ethers are identical (1.363(4) Å in **18** and 1.368(2) Å in **19**). It is interesting to note that all of the bond angles along the aliphatic backbone in **18** are smaller than the corresponding angles in **19** with the exception of the C—O—C bond angles [C(10)—O(1)—C(13), 121.3(3)°; C(10)—O(1)—C(1), 118.2(2)°]. Table 2 lists some selected bond lengths and bond angles of **18** and **19**. Figure 1 and Figure 2 show the structures of **18** and **19**, respectively, at a 30% thermal ellipsoids level.

In summary, insertion of fluorinated olefins into activated C—H bonds under free radical conditions was used successfully to prepare fluoroalkylated sulfides, fluorinated alcohols that contain fluorobenzene rings, and fluorinated ethers. The reaction of sulfides with fluoroolefins follows the same pattern as that observed in the case of ethers. It appears that sulfides are slightly more reactive than ethers with respect to free radical reactions with fluorinated olefins.

Table 1. X-ray Crystallographic Parameters for **18** and **19**

	compound **18**	compound **19**
	Crystal Data	
empirical formula	$C_{19}H_7F_{14}NO$	$C_{12}H_7F_9O$
fw	531.3	338.2
color, habit	colorless, block	colorless, block
cryst size (mm)	0.10 × 0.25 × 0.35	0.15 × 0.3 × 0.4
cryst syst	tetragonal	triclinic
space group	$P4_2/n$	$P\bar{1}$
unit cell dimens		
a (Å)	18.471(2)	8.102(3)
b (Å)	18.471(2)	8.790(3)
c (Å)	11.702(2)	9.832(3)
α (deg)	90.00	66.24(4)
β (deg)	90.00	72.01(3)
γ (deg)	90.00	80.19(4)
vol (Å^3)	3992.5(9)	608.7(4)
Z	8	2
ρ_{calc} (mg/m^3)	1.768	1.845
F(000)	2096	336
abs coeff (mm^{-1})	0.200	0.210
	Data Collection	
temp (K)	193(2)	193(2)
2θ range (deg)	3.1−46.5	4.7−53.8
index ranges	$-19 \le h \le 20$	$-10 \le h \le 10$
	$-15 \le k \le 20$	$-11 \le k \le 7$
	$-11 \le l \le 12$	$-12 \le l \le 11$
no. of data collctd	15344	3182
no. of unique reflcns	2864	2210
no. of reflcns with $I > 2\sigma(I)$	2256 ($R_{int} = 0.0471$)	2088 ($R_{int} = 0.0222$)
T_{max}/T_{min}	0.996/0.872	0.990/0.867
extincn coeff.	0.0008(2)	0.043(4)
	Solution and Refinement on F^2	
params refined	345 (0 restraints)	228 (0 restraints)
final R indices (2σ data)		
R	0.0617	0.0346
R_w	0.0853	0.0849
final R indices (all data)		
R	0.0854	0.0367
R_w	0.0926	0.0867
goodness-of-fit, S (F^2)	1.204	1.062
largest diff peak (e Å^{-3})	0.13	0.27
largest diff hole (e Å^{-3})	−0.1	−0.15

Table 2. Selected bond Lengths and Bond Angles for **18** and **19**

18		**19**	
	Bond Lengths		
O(1)−C(13)	1.363(4)	O(1)−C(1)	1.368(2)
O(1)−C(10)	1.467(4)	O(1)−C(10)	1.458(2)
C(10)−C(9)	1.535(5)	C(10)−C(9)	1.532(2)
C(9)−C(8)	1.529(5)	C(9)−C(8)	1.523(3)
C(8)−C(7)	1.533(5)	C(8)−C(7)	1.526(3)
C(7)−C(1)	1.514(5)	C(7)−C(6)	1.506(2)
	Bond Angles		
C(13)−O(1)−C(10)	121.3(3)	C(1)−O(1)−C(10)	118.2(2)
O(1)−C(10)−C(9)	102.8(3)	O(1)−C(10)−C(9)	105.0(2)
C(8)−C(9)−C(10)	116.7(3)	C(8)−C(9)−C(10)	120.5(2)
C(9)−C(8)−C(7)	115.3(3)	C(9)−C(8)−C(7)	118.3(2)
C(1)−C(7)−C(8)	114.2(3)	C(6)−C(7)−C(8)	116.0 (2)

Experimental Section

Materials. Tetrahydrothiophene, pentamethylene sulfide, and 1,4-dithioxane (Aldrich) are freshly distilled before use. Tetrahydrofuran (Aldrich) is distilled from sodium/benzophenone. Hexafluoropropene, trifluoroethylene, hexafluorocyclobutene, 1,2-dichlorotetrafluorocyclobutene (PCR), perfluoroallylbenzene (BNFL), and di-*tert*-butyl peroxide (Aldrich) are used as received.

General Procedures. Volatile liquids are handled in a Pyrex vacuum system equipped with a Heise−Bourdon tube gauge and a

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(9) Zhang, Y.-F.; Kirchmeier, R. L; Shreeve, J. M. Unpublished results.
(10) Patel, N. R.; Chen, J.; Zhang, Y.-F.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1994**, *33*, 5463.

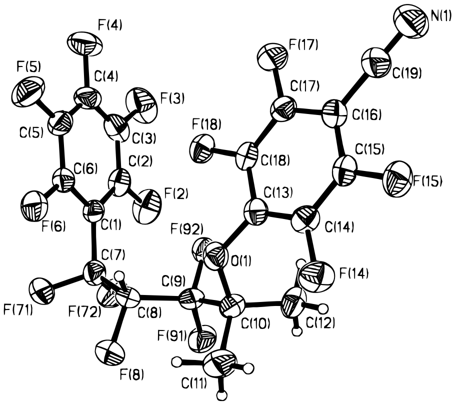

Figure 1. Molecular structural diagram of **18** with thermal ellipsoids at 30% probability level.

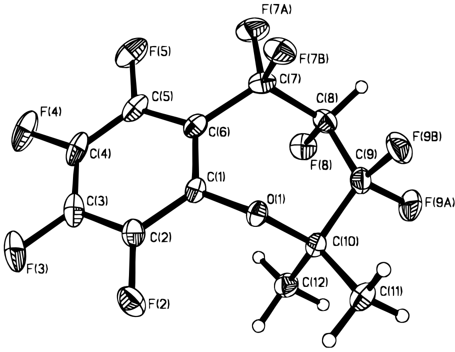

Figure 2. Molecular structural diagram of **19** with thermal ellipsoids at 30% probability level.

Televac thermocouple gauge. Conventional *PVT* techniques are used to quantitate volatile starting materials and products. All reactions are conducted in Hoke stainless steel vessels. Products are separated either by low-temperature trap-to-trap distillation under dynamic vacuum or by fractional distillation. Infrared spectra are recorded on a Perkin-Elmer Model 1710 infrared Fourier transform spectrometer. The ^{19}F and ^{1}H NMR spectra are obtained with a Bruker AC 200 Fourier transform NMR spectrometer using $CDCl_3$ as solvent. Mass spectra are obtained with a VG 7070HS mass spectrometer. Elemental analyses are performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany, and National Chemical Consulting, Inc., Tenafly, NJ.

Reactions of Tetrahydrothiophene with Fluorinated Olefins in the Presence of Di-*tert*-butyl Peroxide. To a 120-mL stainless steel vessel that contains approximately 3 mmol of di-*tert*-butyl peroxide are added a molar excess of tetrahydrothiophene and 10 mmol of fluorinated olefin, either by syringe or by vacuum transfer. After being evacuated at −196 °C, the vessel is heated at about +140 °C for 12 h. The products are then separated under dynamic vacuum or distilled under vacuum.

Properties of $\overline{SCH_2CH_2CH_2C}HCF_2CHFCF_3$ (1). This compound is obtained in 80% yield. Spectral data are as follows. IR (film): 2954 s, 2871 m, 1447 s, 1388 vs, 1339 s, 1287 vs, 1196 vs, 1099 vs, 1059 s, 1030 s, 1016 s, 848 s cm^{-1}. ^{1}H NMR: δ 1.97−2.29 (4H, m, CH_2-CH_2), 2.85−2.95 (2H, m, SCH_2), 3.71−3.94 (1H, overlap of two multiplets, SCH), 4.84−5.24 (1H, overlap of two multiplets, CHF) ppm. ^{19}F NMR: δ −74.4 (3F, s, CF_3), −113.1 (2F/2, d−d, $^{3}J_{H-F}$ = 11.3 Hz, diastereoisomeric CF_2), −115.1, −123.3 (2F/2, AB pattern, $^{2}J_{H-F}$ = 253.3 Hz, diastereoisomeric CF_2), −198.1, −199.2 (1F, d−m, $^{2}J_{F-F}$ = 43.3 Hz, diastereoisomeric CHF) ppm. MS (CI$^+$) [*m*/*e* (species) intensity]: 239 (M$^+$ + 1) 82.6; 238 (M$^+$) 19.0; 219 (M$^+$ − F) 100; 199 (M$^+$ − F − HF) 13.7; 87 (M$^+$ − C_3F_6H) 67.3. Anal. Calcd for $C_7H_8F_6S$: C, 35.29; H, 3.39; F, 47.9; S, 13.46. Found: C, 35.27; H, 3.24; F, 47.7; S, 13.78.

Properties of $\overline{SCH_2CH_2CH_2C}HCF_2CHFCF_2C_6F_5$ (2). This compound is obtained in 47% yield, bp 87−89 °C/0.5 Torr. Spectral data are as follows. IR (film): 2950 s, 2869 s, 1657 s, 1530 s, 1510 s, 1446 s, 1426 s, 1354 s, 1329 s, 1287 s, 1202 s, 1121 s, 1087 s, 997 s, 853 s cm^{-1}. ^{1}H NMR: δ 1.95−2.19 (4H, m, CH_2CH_2), 2.88 (2H, m, SCH_2), 3.85−3.95 (1H, m, SCH), 5.20 (1H, d−d−q, $^{2}J_{H-F}$ = 44.0 Hz, $^{3}J_{F-F}$ = 11.0, 11.0 Hz, CFH) ppm. ^{19}F NMR: δ −99.6, −103.6 (2F/2, AB pattern, $^{2}J_{F-F}$ = 286.2 Hz, diastereoisomeric CF_2), −99.7, −102.7 (2F/2, AB pattern, $^{2}J_{F-F}$ = 282.5 Hz, diastereoisomeric CF_2), −111.7 (2F/2, m, diastereoisomeric CF_2), −114.4, −121.3 (2F/2, AB pattern, $^{2}J_{F-F}$ = 259.9 Hz, diastereoisomeric CF_2), −139.1(2F, m, *m*-F), −148.3 (1F, m, *p*-F), −160.2 (2F, m, *o*-F), −208.9 (1F, m, CHF) ppm. MS (CI$^+$) [*m*/*e* (species) intensity]: 387 (M$^+$ + 1) 2.5; 367 (M$^+$ − F) 13.1; 366 (M$^+$ − HF) 3.9; 348 (M$^+$ − 2F) 3.0; 347 (M$^+$ − F − HF) 10.0; 327(M$^+$ − F − 2HF) 14.4; 326 (M$^+$ − 3HF) 11.5; 307 (M$^+$ − F − 3HF) 13.3; 137 ($C_4H_7SCF_2^+$) 4.9; 109 ($C_2H_3SCF_2^+$) 12.2; 87 ($C_4H_7S^+$) 47.1; 55 ($C_4H_7^+$) 100. Anal. Calcd for $C_{13}H_8F_{10}S$: C, 40.42; H, 2.09. Found: C, 40.83; H, 2.20.

Properties of $\overline{SCH_2CH_2CH_2C}H\underline{CFCHFCF_2C}F_2$ (3). This compound is obtained in 44% yield. Spectral data are as follows. IR (film): 2946 s, 2869 m, 1446 s, 1407 s, 1343 s, 1292 s, 1241 s, 1186 s, 1089 vs, 1049 s, 1010 s, 981 s, 962 s, 914 s, 856 s, 780 s cm^{-1}. ^{1}H NMR: δ 1.92−2.24 (4H, m, CH_2CH_2), 2.80−2.86 (2H, m, SCH_2), 3.70−3.84 (1H, m, SCH), 4.98−5.43 (1H, m, CFH) ppm. ^{19}F NMR: δ −121.0, −133.4 (2F/2, AB pattern, $^{2}J_{F-F}$ = 231.6 Hz, diastereoisomeric CF_2), −121.4, −133.0 (2F/2, AB pattern, $^{2}J_{F-F}$ =231.6 Hz, diastereoisomeric CF_2), −125.9, −129.2 (2F, overlap of AB patterns, CF_2), −180.9, −182.5 (1F, t, $^{3}J_{F-F}$ = 15.1, diastereoisomeric CF), −198.0, −199.7 (1F, d, $^{2}J_{H-F}$ = 49.0 Hz, diastereoisomeric CFH) ppm. MS (CI$^+$) [*m*/*e* (species) intensity]: 251 (M$^+$ + 1) 100; 250 (M$^+$) 18.7; 231 (M$^+$ − F) 16.9; 211 (M$^+$ − F − HF) 6.9; 191 (M$^+$ − F − 2HF) 10.0; 87 ($C_4H_7S^+$) 77.7; 55 ($C_4H_7^+$) 37.7. Anal. Calcd for $C_8H_8F_6S$: C, 38.40; H, 3.32; F, 45.6; S, 12.81. Found: C, 38.45; H, 3.46; F, 45.2; S, 12.90.

Properties of $\overline{SCH_2CH_2CH_2C}H\underline{CClCHClCF_2C}F_2$ (4). This compound is obtained in 39% yield. Spectral data are as follows. IR (film): 2959 s, 2872 m, 1584 m, 1542 m, 1448 s, 1324 s, 1255.5 s, 1121 s, 863 s cm^{-1}. ^{1}H NMR: δ 1.86−1.92 (4H, m, CH_2CH_2), 3.11 (2H, t, $^{3}J_{H-H}$ = 6.8 Hz, SCH_2), 3.51−3.57 (2H, m, overlap of SCH and ClCH) ppm. ^{19}F NMR: δ −112.5 (2F, t, $^{3}J_{F-F}$ = 20.8 Hz, CF_2), −115.0 (2F, t, $^{3}J_{F-F}$ = 20.9 Hz, CF_2) ppm. MS (CI$^+$) [*m*/*e* (species) intensity]: 286/284/282 (M$^+$) 2.3/10.8/18.2; 267/265/263 (M$^+$ − F) 10.4/40.9/69.3; 249/247 (M$^+$ − Cl) 22.7/46.6; 207/205 (M$^+$ − Cl − C_3H_6) 7.1/18.2; 175/173 (M$^+$ − Cl − C_3H_6S) 18.6/64.2; 138 (M$^+$ − 2Cl − C_3H_6S) 24.5; 87 ($C_4H_7S^+$) 40.8, 55 ($C_4H_7^+$) 100. Anal. Calcd for $C_8H_8F_4Cl_2S$: C, 34.04; H, 2.85. Found: C, 34.45; H, 2.79.

Reaction of Tetrahydrofuran with Hexafluorocyclobutene. This reaction is performed by using the procedure as decribed above for tetrahydrothiophene.

Properties of $\overline{OCH_2CH_2CH_2C}H\underline{CFCHFCF_2C}F_2$ (5). This compound is obtained in 71% yield. Spectral data are as follows. IR (film): 2966 s, 2884 m, 1466 m, 1409 s, 1343 s, 1300 s, 1246 s, 1197 s, 1084 s, 1049 s, 1014 s, 949 s, 877 s cm^{-1}. ^{1}H NMR: δ 1.80−2.16 (4H, m, CH_2CH_2), 3.84 (2H, m, OCH_2), 4.22−4.41 (1H, m, OCH), 4.99−5.38 (1H, m, CFH) ppm. ^{19}F NMR: δ −120.9, −134.1 (2F/2, AB pattern, $^{2}J_{F-F}$ = 233.5 Hz, diastereoisomeric CF_2), −121.1, −134.3 (2F/2, AB pattern, $^{2}J_{F-F}$ = 231.6 Hz, diastereoisomeric CF_2), −128.0, −128.7 (2F, s, CF_2), −180.9, −188.4 (1F, m, CF), −195.4, −197.7 (1F, d, $^{2}J_{H-F}$ = 50.8 Hz, diastereoisomeric CFH) ppm. MS (CI$^+$) [*m*/*e* (species) intensity]: 235 (M$^+$ + 1) 13.7; 233 (M$^+$ − 1) 3.6; 217 (M$^+$ − O − H) 8.4; 197 (M$^+$ − O − H − HF) 4.4; 71($C_4H_7O^+$) 100. Anal. Calcd for $C_8H_8F_6O$: C, 41.04; H, 3.44; F, 48.68. Found: C, 41.27; H, 3.33; F, 48.5.

Properties of $\overline{SCH_2CH_2CH_2C}HCF_2CH_2F$ (6). This compound is obtained in 23.4% yield. Spectral data are as follows. IR (film): 2957 s, 2870 m, 1548 m, 1447 s, 1310 s, 1244 s, 1167 vs, 1098 s, 910 s, 857 s cm^{-1}. ^{1}H NMR: δ 2.02−2.12 (4H, m, CH_2CH_2), 2.84 (2H, m, SCH_2), 3.73−3.82 (1H, m, SCH), 4.34−4.69 (2H, m, CFH_2) ppm. ^{19}F NMR (high resolution): δ −109.7, −117.4 (2F, AB pattern, $^{2}J_{F-F}$ = 257.0 Hz; A, d−t, $^{3}J_{F-F}$ = 13.2 Hz, $^{3}J_{H-F}$ = 13.2 Hz; B, d−d−t, $^{3}J_{H-F}$ = 9.4, 16.9 Hz, $^{3}J_{F-F}$ = 15.1 Hz, CF_2), −194.2 (1F, t−t, $^{2}J_{H-F}$ = 46.1

Hz, $^3J_{F-F}$ = 15.1 Hz, CH_2F) ppm. MS (EI^+) [*m/e* (species) intensity]: 171 ($M^+ + 1$) 2.1; 170 (M^+) 26.9; 87($C_4H_7S^+$) 100; 60 ($C_2H_4S^+$) 12.8. Anal. Calcd for $C_6H_9F_3S$: C, 42.34; H, 5.33; F, 33.49; S, 18.84. Found: C, 42.47; H, 5.13; F, 34.0; S, 18.67.

Properties of $SCH_2CH_2CH_2CHCF_2CHFCF_3$ (7). The properties of this compound are the same as those reported in the literature.[1]

Reactions of Pentamethylene Sulfide and 1,4-Thioxane with Fluorinated Olefins. These reactions are accomplished as described above for the reactions of olefins with tetrahydrothiophene.

Properties of $SCH_2CH_2CH_2CH_2CHCF_2CHFCF_3$ (8). This compound is obtained in 56% yield. Spectral data are as follows. IR (film): 2931 s, 2852 m, 1443 s, 1385 s, 1339 s, 1287 s, 1202 s, 1102 s, 1059 s, 1035 m, 844 m, cm^{-1}. ^{1}H NMR (mixture of diastereoisomers): δ 1.42−1.54 (2H, m, CH_2) 1.64−2.08 (4H, m, CH_2CH_2), 2.47−2.70 (2H, m, SCH_2), 2.99−3.23 (1H, m, SCH), 4.88−5.47 (1H, m, CFH) ppm. ^{19}F NMR: δ −74.0, −74.4 (3F, d−d−t, $^3J_{F-F}$ = 11.3 Hz, $^4J_{H-F}$ = 11.3 Hz, $^4J_{F-F}$ = 5.6 Hz, diastereoisomeric CF_3), −112.9, −116.3 (2F, m, diastereoisomeric CF_2), −205.9, −208.9 (1F, d−m, $^2J_{F-F}$ = 43.3 Hz, diastereoisomeric CHF) ppm. MS (CI^+) [*m/e* (species) intensity]: 253 ($M^+ + 1$) 66.7; 252 (M^+) 100; 251 ($M^+ - 1$) 29.6; 233 ($M^+ - F$) 81.7; 213 ($M^+ - F - HF$) 18.9; 101 (($M^+ - C_3HF_6$) 74.5.

Properties of $OCH_2CH_2SCH_2CHCF_2CHFCF_3$ (9) and $SCH_2CH_2OCH_2CHCF_2CHFCF_3$ (10). These two compounds are obtained as a mixture in 27% total yield, bp 73−77 °C/2 Torr. Attempts to separate them failed. Spectral data of the mixture of isomers are as follows. IR (film): 2964 s, 2867 s, 1746 s, 1661 s, 1458 s, 1387 s, 1284 s, 1191 s, 1110 s, 884 s, 863 s cm^{-1}. ^{1}H NMR: δ 2.21−2.61 (m, CH_2SCH_2), 2.82−3.16 (m, CF_2CHSCH_2), 3.67−3.91 (m, SCH), 3.95−4.13 (m, CH_2OCH_2), 4.20−4.47 (m, OCH), 4.87−5.61 (m, overlap of two CFH peaks) ppm. ^{19}F NMR: δ −73.2 to −75.4 (overlap of isomers, CF_3), −110.6 to −111.0 (m, diastereoisomeric $SCHCF_2$), −114.5, −115.8 (AB pattern, $^2J_{F-F}$ = 263.6 Hz, diastereoisomeric $SCHCF_2$), −121.0, −123.1 (AB pattern, $^2J_{F-F}$ = 273.0 Hz, diastereoisomeric $OCHCF_2$), −126.4, −127.6 (AB pattern, $^2J_{F-F}$ = 269.3 Hz, diastereoisomeric $OCHCF_2$), −210.7 (d−m, $^2J_{H-F}$ = 43.3 Hz, diastereoisomeric $SCHCF_2CHF$), −214.5 (d−q, $^2J_{H-F}$ = 43.3 Hz, $^3J_{F-F}$ = 11.3 Hz, diastereoisomeric $SCHCF_2CHF$), −213.8 (d−m, $^2J_{H-F}$ = 43.3 Hz, diastereoisomeric $OCHCF_2CHF$), −218.9 (d−q, $^2J_{H-F}$ = 43.3 Hz, $^3J_{F-F}$ = 9.4 Hz, diastereoisomeric $OCHCF_2CHF$) ppm. MS (CI^+) [*m/e* (species) intensity]: 255 ($M^+ + 1$) 100; 254 (M^+) 20.9; 253 ($M^+ - 1$) 10.2; 235 ($M^+ - F$) 36.6; 215 ($M^+ - F - HF$) 16.0; 211 ($M^+ - C_2H_4O + 1$) 40.8; 103 ($M^+ - C_3F_6H$) 51.6; 89 ($C_3H_5OS^+$) 15.0; 87 ($C_4H_7S^+$) 19.6.

Properties of $OCH_2CH_2SCH_2CHCF_2CHFCF_2C_6F_5$ (11) and $SCH_2CH_2OCH_2CHCF_2CHFCF_2C_6F_5$ (12). These two compounds are obtained as a mixture in 27% combined yield, bp 102−109 °C/0.5 Torr. Several attempts to separate them were unsuccessful. Spectral data of the mixture of isomers are as follows. IR (film): 2963 s, 2865 s, 1748 s, 1659 s, 1505 s, 1456 s, 1425 s, 1328 s, 1092 s, 864 s, 835 s cm^{-1}. ^{1}H NMR: δ 2.23−2.50 (m, CH_2SCH_2), 2.81−3.14 (m, CF_2CHSCH_2), 3.69−3.89 (m, SCH), 3.93−4.09 (m, CH_2OCH_2), 4.23−4.41 (m, OCH), 4.99−5.75 (m, overlap of two CFH peaks) ppm. ^{19}F NMR: δ −97.7 to −106.6 (overlap of AB patterns of isomers, $C_6F_5CF_2$), −120.1, −120.8 (m, diastereoisomeric $SCHCF_2$), −119.7, −121.2 (AB pattern, $^2J_{F-F}$ = 273.0 Hz, diastereoisomeric $OCHCF_2$), −124.9, −127.0 (AB pattern, $^2J_{F-F}$ = 271.2 Hz, diastereoisomeric $OCHCF_2$), −139.0 to −139.4 (m, *m*-F), −148.0 to −148.6(m, *p*-F), −160.1 to −160.6 (m, *o*-F), −208.3, −210.6 (d−m, $^2J_{H-F}$ = 37.7 Hz, diastereoisomeric $SCHCF_2CHF$), −211.0, −214.0 (d−m, $^2J_{H-F}$ = 39.5 Hz, diastereoisomeric $OCHCF_2CHF$) ppm. MS (CI^+) [*m/e* (species) intensity]: 403 ($M^+ + 1$) 18.2; 402 (M^+) 44.9; 401 ($M^+ - 1$) 4.7; 383 ($M^+ - F$) 13.7; 359 ($M^+ + 1 - OCH_2CH_2$) 4.2; 103 ($M^+ - C_6H_5CF_2CHFCF_3$) 100; 89 ($C_3H_5OS^+$) 2.0; 87 ($C_4H_7S^+$) 2.9.

Dehydrofluorination of 3 and 5 To Form $SCH_2CH_2CH_2CHC{=}C(OCH_2CH_3)CF_2CF_2$ (13) and $OCH_2CH_2CH_2CHC{=}C(OCH_2CH_3)CF_2CF_2$ (14). Dehydrofluorinations are carried out by reacting **3** and **5** with potassium hydroxide in refluxing ethanol. After cooling to room temperature, the reaction mixtures are poured into water and extracted with diethyl ether. Removal of the ether gives the crude products that are distilled to give olefins **13** and **14**.

Properties of $SCH_2CH_2CH_2CHC{=}C(OCH_2CH_3)CF_2CF_2$ (13). This compound is obtained in 53% yield. Spectral data are as follows. IR (film): 2942 s, 2868 m, 1696 s, 1534 s, 1502 s, 1481 s, 1445 s, 1418 s, 1395 s, 1338 s, 1240 s, 1199 s, 1088 s, 1043 s, 982 s cm^{-1}. ^{1}H NMR: δ 1.01 (3H, t, $^3J_{H-H}$ = 6.7 Hz, CH_3), 1.58−1.85 (4H, m, CH_2-CH_2), 2.49−2.74 (2H, m, SCH_2), 3.74−3.83 (1H, m, SCH), 3.88 (2H, q, $^3J_{H-H}$ = 6.7 Hz, OCH_2CH_3) ppm. ^{19}F NMR: δ −111.4 (1F, $^4J_{H-F}$ = 9.0 Hz), −111.7 (2F, s), −115.4 (2F, s, CF_2) ppm. MS (EI^+) [*m/e* (species) intensity]: 256 (M^+) 10.8; 227 ($M^+ - C_2H_5$) 8.3; 87($C_4H_7S^+$) 63.9; 60 ($C_2H_4S^+$) 100.

Properties of $OCH_2CH_2CH_2CHC{=}C(OCH_2CH_3)CF_2CF_2$ (14). This compound is obtained in 59% yield. Spectral data are as follows. IR (film): 2989 s, 2878 s, 1682 s, 1626 s, 1435 s, 1396 s, 1309 s, 1236 s, 1197 s, 1092 s, 1039 s, 988 s cm^{-1}. ^{1}H NMR: δ 1.38 (3H, t, $^3J_{H-H}$ = 8.0 Hz, CH_3), 1.88−2.16 (4H, m, CH_2CH_2), 3.73−3.97 (2H, m, OCH_2), 4.26 (2H, q, $^3J_{H-H}$ = 8.0 Hz, OCH_2CH_3), 4.57−4.64 (1H, m, OCH) ppm. ^{19}F NMR: δ −111.6 (2F, m, CF_2), −115.4 (2F, s, CF_2) ppm. MS (CI^+) [*m/e* (species) intensity]: 239 ($M^+ - 1$) 2.3; 221 ($M^+ - F$) 85.9; 212 ($M^+ + 1 - C_2H_5$) 5.3; 195 ($M^+ - OC_2H_5$) 20.6; 193 ($M^+ + 1 - C_2H_5 - F$) 41.2; 71($C_4H_7O^+$) 100.

Reactions of Perfluoroallylbenzene with Alcohols in the Presence of Di-*tert*-butyl Peroxide. To a 120-mL stainless steel vessel that contains approximately 2.5 mmol di-*tert*-butyl peroxide are added an excess of the alcohol and 10 mmol perfluoroallylbenzene. The vessel is evacuated at −196 °C, sealed, and heated at about +140 °C for 12 h. After cooling to room temperature, the excess alcohol is removed under vacuum and the residue is distilled to give the crude product. Further purification is accomplished by column chromatography on silica gel with hexane/ethyl acetate (80/20) as eluent.

Properties of $C_6F_5CF_2CHFCF_2C(CH_3)_2OH$ (15). This compound is obtained in 76% yield. Spectral data are as follows. IR (film): 3447 br, 2996 m, 1657 m, 1506 s, 1426 m, 1329 s, 1085 s, 997 s, 887 s cm^{-1}. ^{1}H NMR: δ 1.32 (3H, d, $^4J_{H-F}$ = 3.5 Hz, CH_3), 1.36 (3H, s, CH_3), 2.41 (1H, br, OH), 4.09−4.27 (1H, m, OCH), 5.35 (1H, d−d−t, $^2J_{H-F}$ = 44.0 Hz, $^3J_{F-F}$ = 18.0, 10.0 Hz, CHF) ppm. ^{19}F NMR: δ −101.4, −102.2 (2F, AB pattern, $^2J_{F-F}$ = 301.3 Hz, $C_6F_5CF_2$), −122.7, −126.4 (2F, AB pattern, $^2J_{F-F}$ = 274.9 Hz, CH_2CF_2), −139.4 (2F, m, *m*-F), −148.9 (1F, m, *p*-F), −160.6 (2F, m, *o*-F), −203.7 (1F, d, $^2J_{H-F}$ = 42.7, CHF) ppm. MS (CI^+) [*m/e* (species) intensity]: 341 ($M^+ - OH$) 15.8; 321 ($M^+ - OH - HF$) 21.6; 319 ($M^+ - F - HF$) 10.7; 303 ($M^+ - 2F - OH$) 33.6; 299 ($M^+ - 2HF - F$) 16.8; 279 ($M^+ - 3HF - F$) 16.6; 217 ($C_7F_7^+$) 66.7; 59 ($C_3H_7O^+$) 100. Anal. Calcd for $C_{12}H_8F_{10}O$: C, 40.24; H, 2.25. Found: C, 40.11; H, 2.20.

Properties of $C_6F_5CF_2CHFCF_2CH(CH_3)OH$ (16). This compound is obtained in 64% yield. Spectral data are as follows. IR (film): 3415 br, 2997 m, 1657 m, 1531 s, 1509 s, 1459 m, 1426 m, 1385 m, 1353 m, 1330 s, 1190 s, 1094 s, 997 s cm^{-1}. ^{1}H NMR: δ 1.32, 1.33 (3H, diastereoisomers, d, $^3J_{H-H}$ = 6.6 Hz, CH_3), 2.28, 2.41 (1H, diastereoisomers, br, OH), 4.09−4.27 (1H, m, OCH), 5.00−5.49 (1H, m, CHF) ppm. ^{19}F NMR: δ −99.5, −104.2 (2F/2, AB pattern, $^2J_{F-F}$ = 274.9 Hz, $C_6F_5CF_2$), −100.7, −102.7 (2F/2, AB pattern, $^2J_{F-F}$ = 276.8 Hz, $C_6F_5CF_2$), −120.6, −124.4 (2F/2, AB pattern, $^2J_{F-F}$ = 269.3 Hz, CH_2-CF_2), −125.1, −130.8 (2F/2, AB pattern, $^2J_{F-F}$ = 273.0 Hz, CH_2CF_2), −139.5 (2F, m, *m*-F), −148.6 (1F, m, *p*-F), −160.5 (2F, m, *o*-F), −210.4, −211.5 (1F, diastereoisomers, d, $^2J_{H-F}$ = 47.1, 43.1 Hz, CHF) ppm. MS (EI^+) [*m/e* (species) intensity]: 344 (M^+) 4.5; 325 ($M^+ - F$) 6.3; 305 ($M^+ - F - HF$) 8.5; 279 ($M^+ - F - C_2H_5O$) 34.1; 217 ($C_7F_7^+$) 100; 167 ($C_6F_5^+$) 11.5. Anal. Calcd for $C_{11}H_6F_{10}O$: C, 38.39; H, 1.76; F, 55.20. Found: C, 38.47; H, 1.98; F, 55.1.

Properties of $C_6F_5CF_2CHFCF_2CH_2OH$ (17). This compound is obtained in 65% yield. Spectral data are as follows. IR (film): 3372 s, 2963 s, 1657 s, 1531 s, 1510 s, 1427 s, 1330 s, 1201 s, 1095 s, 997 s, 872 s, 787 s cm^{-1}. ^{1}H NMR: δ 1.81 (1H, br, OH), 3.76 (2H, m, OCH_2), 4.79−5.22 (1H, m, CHF) ppm. ^{19}F NMR: δ −101.4, −102.7

(2F, AB pattern, $^2J_{F-F}$ = 274.9 Hz, $C_6F_5CF_2$), −117.9, −121.6 (2F, AB pattern, $^2J_{F-F}$ = 274.9 Hz, CH_2CF_2), −139.4 (2F, m, *m*-F), −148.1 (1F, m, *p*-F), −160.1 (2F, m, *o*-F), −200.1 (1F, d, $^2J_{H-F}$ = 39.5 Hz, CHF) ppm. MS (CI^+) [*m*/*e* (species) intensity]: 330 (M^+) 14.2; 311 ($M^+ - F$) 25.8; 291 ($M^+ - F - HF$) 51.0; 271 ($M^+ - F - 2HF$) 100; 253 ($M^+ - 3HF - OH$) 42.7; 217 ($C_7F_7^+$) 42.3. Anal. Calcd for $C_{10}H_4F_{10}O$: C, 36.38; H, 1.22; F, 57.55. Found: C, 36.27; H, 1.30; F, 57.60.

Reaction of $C_6F_5CF_2CHFCF_2C(CH_3)_2OH$ (15) with Pentafluorobenzonitrile in the Presence of Potassium Carbonate. Into a 50 mL three-necked flask equipped with a magnetic stirrer, a reflux condenser and a nitrogen inlet are added 1.17 g (3.3 mmol) of alcohol 17, 0.7 g (3.6 mmol) of pentafluorobenzonitrile, 1 g (7.2 mmol) of potassium carbonate, and 10 mL of ethylene glycol dimethyl ether under a nitrogen atmosphere. After being stirred at 25 °C for 10 h, the reaction mixture is poured into water and extracted with diethyl ether. Removal of the ether gives a mixture of **18** and **19**. Pure **18** and **19** are obtained by column chromatography (silica gel, hexane/ethyl acetate = 80/20) in 59 and 20% yields, respectively.

Properties of $C_6F_5CF_2CHFCF_2C(CH_3)_2OC_6F_4CN$ (18). This compound is obtained in 59% yield, mp 75−77 °C. Spectral data are as follows. IR (KBr plate): 3010 w, 2248 m, 1661 m, 1511 s, 1440 m, 1400 m, 1382 m, 1328 s, 1213 s, 1177 s, 1146 s, 1099 s, 993 s, 917 s cm^{-1}. ^1H NMR: 1.45 (3H, s, CH_3), 1.59 (3H, s, CH_3), 5.62 (1H, d−m, $^2J_{H-F}$ = 42.9 Hz, CHF) ppm. ^{19}F NMR: δ −101.8 (2F, m, $C_6F_5CF_2$), −120.1, −123.8 (2F, AB pattern, $^2J_{F-F}$ = 279.6 Hz, CH_2CF_2), −132.5 (2F, m, Ar−F), −139.5 (2F, m, Ar−F), −148.2 (3F, m, overlap of Ar−F), −160.2 (2F, m, Ar−F). −204.1 (1F, d−m, $^2J_{H-F}$ = 42.4 Hz, CHF) ppm. MS (EI^+) [*m*/*e* (species) intensity]: 532 ($M^+ + 1$) 1.0; 341 ($M^+ - OC_6F_4CN$) 2.2; 340 ($M^+ - OC_6F_4CN - 1$) 9.7; 232 ($M^+ - C_9HF_{10}$) 13.8; 217 ($C_7F_7^+$) 64.7; 191 ($NCC_6F_4O^+ + 1$) 48.2; 91 ($C_4H_5F_2^+$) 100. Anal. Calcd for $C_{19}H_7F_{14}NO$: C, 42.96; H, 1.33; F, 50.07. Found: C, 43.08; H, 1.42; F, 49.5. The X-ray crystal structure of **18** is presented in Figure 1.

Properties of 1,2-$\overline{C_6F_4CF_2CHFCF_2C(CH_3)_2O}$ (19). This compound is obtained in 20% yield, bp 88 °C/0.5 Torr, mp 40−42 °C. Spectral data are as follows. IR (film): 3008 m, 2956 m, 1612 s, 1522.5 s, 1498 s, 1411 s, 1399 m, 1379 s, 1366 s, 1345 s, 1322 s, 1220 s, 1189 s, 1142 s, 1096 s, 1073.5 s, 1014.5 s, 1000.5 s, 878 s, 856 s cm^{-1}. ^1H NMR: 1.32 (3H, s, CH_3), 1.60 (3H, s, CH_3), 5.01 (1H, d−d−d−d, $^2J_{H-F}$ = 46.0 Hz, $^3J_{H-F}$ = 8.0, 8.0, 16.0 Hz, CHF) ppm. ^{19}F NMR: δ −92.8, −104.3 (2F, AB pattern, $^2J_{F-F}$ = 295.0 Hz, $C_6F_5CF_2$), −109.6, −113.6 (2F, AB pattern, $^2J_{F-F}$ = 266.2 Hz, CH_2CF_2), −140.4 (2F, m, a-F), −149.5 (1F, m, c-F), −153.4 (2F, m, b-F), −157.9 (2F, m, d-F), −203.9 (1F, br, CHF) ppm. Anal. Calcd for $C_{12}H_7F_9O$: C, 42.62; H, 2.09; F, 50.56. Found: C, 42.34; H, 2.13; F, 50.4. The X-ray crystal structure of **19** is given in Figure 2.

Cyclization of Alcohols 15−17. Polyfluorinated alcohols **15**−**17** form cyclic ethers **19**−**21** when heated with potassium carbonate. Compound **19** is formed in 71% yield. These products are separated by using column chromatography.

Properties of 1,2-$\overline{C_6F_4CF_2CHFCF_2CH(CH_3)O}$ (**20**). This compound is obtained as a mixture of diastereoisomers in 80% total yield, bp 97 °C/1 Torr. The two pairs of enantiomers can be separated by column chromatography (silica gel; eluent, hexane/ethyl acetate = 80/20). Spectral data are as follows. IR (mixture of diatereoisomers, film): 3008 w, 2999 w, 1646 m, 1525 s, 1499 s, 1452 m, 1414 m, 1391 m, 1324 s, 1219 s, 1153 s, 1218 s, 1135 s, 1081 s, 1021 s, 1000 s cm^{-1}. ^1H NMR (first portion from column): δ 1.60 (3H, d, $^3J_{H-H}$ = 6.6, CH_3), 4.08, 4.19 (1H, d−q, $^3J_{H-H}$ = 6.6 Hz, $^3J_{H-F}$ = 21.8 Hz, OCH), 5.06 (1H, d−d−d−d, $^2J_{H-F}$ = 45.2 Hz, $^3J_{H-F}$ = 5.4, 9.1, 15.9 Hz, CHF) ppm. ^{19}F NMR (first portion from column): δ −95.5, −102.8 (2F, AB pattern, $^2J_{F-F}$ = 303.2 Hz, $C_6F_5CF_2$), −111.7, −124.9 (2F, AB pattern, $^2J_{F-F}$ = 278.7 Hz, CH_2CF_2), −139.4 (2F, m, a-F), −148.5 (1F, m, c-F), −154.6 (2F, m, b-F), −158.2 (2F, m, d-F), −208.4 (1F, m, CHF) ppm. ^1H NMR (second portion from column): δ 1.54 (3H, d−d, $^3J_{H-H}$ = 6.6, $^4J_{H-F}$ = 1.6, CH_3), 4.39(1H, m, OCH), 5.01 (1H, d−m, $^2J_{H-F}$ = 45.4 Hz, CHF) ppm. ^{19}F NMR (second portion from column): δ −92.1, −95.2 (2F, AB pattern, $^2J_{F-F}$ = 305.1 Hz, $C_6F_5CF_2$), −106.8, −124.8 (2F, AB pattern, $^2J_{F-F}$ = 281.5 Hz, CH_2CF_2), −138.1 (2F, m, a-F), −149.1 (1F, m, c-F), −155.4 (2F, m, b-F), −160.2 (2F, m, d-F), −205.5 (1F, d−m, $^2J_{H-F}$ = 45.2, CHF) ppm. MS (mixture of diastereoisomers) (EI^+) [*m*/*e* (species) intensity]: 325 ($M^+ + 1$) 5.6; 324 (M^+) 50.8; 285 ($M^+ - F - HF$) 6.4; 284 ($M^+ - 2HF$) 34.0; 266 ($M^+ - F - 2HF$) 12.4; 265 ($M^+ - 3HF$) 32.4; 215 ($C_7F_6O^+ + 1$) 74.3; 214 ($C_7F_6O^+$) 55.8; 199 ($C_7F_6^+ + 1$) 15.8; 198 ($C_7F_6^+$) 24.2; 148 ($C_6F_4^+$) 10.1; 117 ($C_5F_3^+$) 32.2; 77 ($C_3H_3F_2^+$) 100.

Properties of 1,2-$\overline{C_6F_4CF_2CHFCF_2CH_2O}$ (21). This compound is obtained in 61% yield, bp 89 °C/1 Torr. Spectral data are as follows. IR (film): 2937 m, 1646 s, 1526 s, 1500 s, 1450 m, 1394, 1356 s, 1297 m, 1255 m, 1218 s, 1158 s, 1083 s, 1037 s, 983 m cm^{-1}. ^1H NMR: δ 4.15, 4.52 (2H, AB pattern, $^2J_{H-H}$ = 13.0 Hz; A, d−d, $^3J_{H-F}$ = 6.0 Hz, $^4J_{H-F}$ = 10.0 Hz; B, d−d−d, $^3J_{H-F}$ = 6.0, 2.0 Hz, $^4J_{H-F}$ = 20.0 Hz, CH_2), 5.50 (1H, d−d−d−d−d, $^2J_{H-F}$ = 46.0 Hz, $^3J_{H-F}$ = 7.0, 7.0, 7.0, 7.0 Hz, CHF) ppm. ^{19}F NMR: δ −93.9, −101.3 (2F, AB pattern, $^2J_{F-F}$ = 298.5 Hz, $C_6F_5CF_2$), −110.7, −113.0 (2F, AB pattern, $^2J_{F-F}$ = 288.1 Hz, CH_2CF_2), −138.7 (2F, m, a-F), −148.1 (1F, m, c-F), −154.3 (2F, m, b-F), −157.9 (2F, m, d-F), −206.8 (1F, d, $^2J_{H-F}$ = 45.2, CHF) ppm. MS (EI^+) [*m*/*e* (species) intensity]: 311 ($M^+ + 1$) 6.5; 310 (M^+) 100; 291 ($M^+ - F$) 9.9; 280 ($M^+ - CH_2O$) 12.9; 215 ($C_7F_6O^+ + 1$) 19.4; 214 ($C_7F_6O^+$) 45.6; 199 ($C_7F_6^+ + 1$) 29.2; 198 ($C_7F_6^+$) 38.9; 148 ($C_6F_4^+$) 10.1; 117 ($C_5F_3^+$) 28.4.

Crystallography. Suitable crystals of **18** and **19** for diffraction studies are obtained by slow recrystallization from hexane solutions of **18** and **19** over a period of 3 months for **18** at 4 °C and 1 week for **19** at 25 °C. The X-ray diffraction data for compounds **18** and **19** are collected with SMART software by using a Siemens three-circle platform equipped with a monochromated Mo Kα (λ = 0.710 73 Å) radiation from a fine-focus tube. The *X*-axis on this platform is fixed at 54.74°, and the diffractometer is equipped with a CCD detector maintained at about −54 °C. The cell constants are initially determined by the least squares refinement of 60 frames collected at 10 s intervals by using the SMART software and finally by the least squares refinement of all the observed reflections by SAINT software. A complete hemisphere of data is scanned on ω (0.3°) with a run time of 10 or 30 s/frame at the detector resolution of 512 × 512 pixels. A total of 1271 frames are collected in three sets, and a final set of 50 frames, identical to the first 50 frames, is also collected to determine crystal decay. The frames are then processed on a SGI-Indy workstation using the SAINT software to give the *hkl* file corrected for Lp/decay. The structures are solved by the direct method using the SHELXTL-86 program and refined by the least squares method on F^2, SHELXTL-93, incorporated in SHELXTL-PC V 5.03. All non-hydrogen atoms are refined anisotropically by full-matrix least squares to minimize $\sum w(F_o - F_c)^2$. The hydrogen atoms are located from the difference electron density map and are included in the refinement process in an isotropic manner. Details of the data collection, solution, and refinement for **18** and **19** are given in Table 1.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic thermal parameters, and hydrogen coordinates for **18** and **19** (18 pages). Ordering information is given on any current masthead page.

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