Reactions of 1,2-dichlorotetrafluorocyclobut-1-ene and 1,2-dichlorohexafluorocyclopent-1-ene with 2-mercaptoethanol and ethanedithiol and of their products

Qui-Chee Mir[a] and Jean'ne M. Shreeve[b,*]

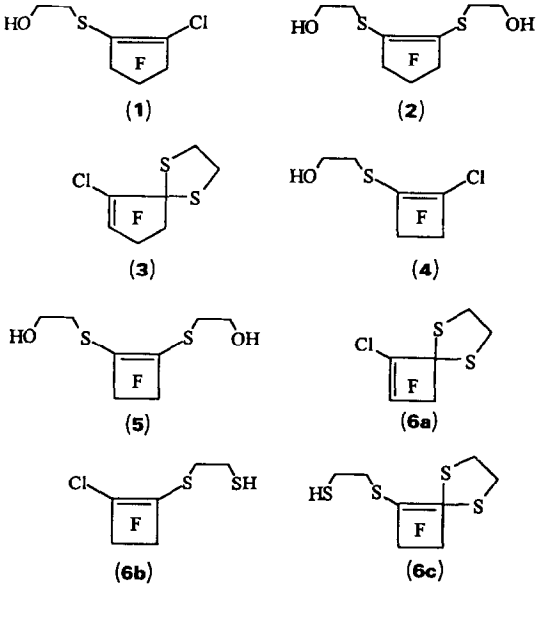
[a]*Department of Chemistry, Lanzhou University, Lanzhou, Gansu (China)*
[b]*Department of Chemistry, University of Idaho, Moscow, ID 83844 (USA)*

Abstract

1,2-Dichlorohexafluorocyclopent-1-ene and 1,2-dichlorotetrafluorocyclobut-1-ene in tetrahydrofuran solutions of 2-mercaptoethanol or 1,2-ethanedithiol and triethylamine give new mono- or di-substituted cycloolefins by displacement of one or two of the chlorine atoms at the double bond by $-SCH_2CH_2OH$ or $-SCH_2CH_2SH$ groups, respectively, as a function of the stoichiometry of the reactions. In several cases, the formation of spirocyclic compounds result via an intramolecular cyclization process with concomitant double-bond shift and loss of fluoride ion. Reactions of the spirocycles with nucleophiles, such as *N*-methylpiperazine, perfluoroglutaryl fluoride and phenylphosphonothionic chloride give rise to more highly substituted olefins and new macrofluoroheterocycles.

Introduction

Because of their varied uses in agrochemicals, pharmaceuticals and fluoropolymers [1–7], fluoroheterocycles attract considerable attention in both academia and industry. As part of our continued interest in this field [8–13], we now report the facile synthesis of polyfluoroheterocycles via displacement of vinyl halogens from polyfluorinated cyclic olefins followed by intramolecular cyclization with elimination of an allyl fluoride ion. In this regard, 1,2-dichlorotetrafluorocyclobut-1-ene and 1,2-dichlorohexafluorocyclopent-1-ene, when reacted with 2-mercaptoethanol, $HO(CH_2)_2SH$, and 1,2-ethanedithiol, $HS(CH_2)_2SH$, respectively, result in the formation of compounds **1–6**. Subsequent intramolecular cyclization of these products via elimination of fluoride ion, in the presence of a suitable base, e.g. triethylamine, gives rise to new mono or dispirocyclic compounds as indicated in eqns. (1)–(5). When ethylene glycol is reacted with decafluorocyclohexene, several bicyclic compounds are identified including the spiro derivative. In our studies with 2-mercaptoethanol and 1,2-ethanedithiol, all of the new bicyclic compounds appear to be spiro.

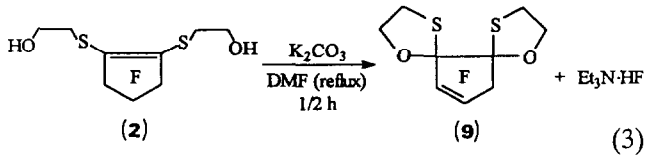


(1)

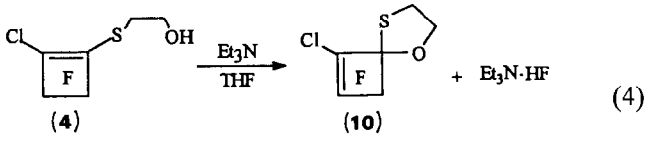
(2)

*Author to whom correspondence should be addressed.

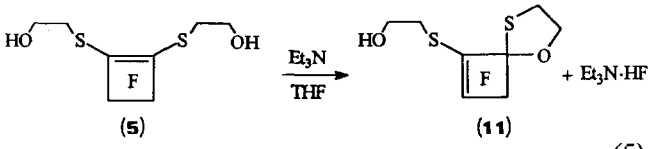
SSDI 0022-1139(93)05006-M



(2) (9) (3)

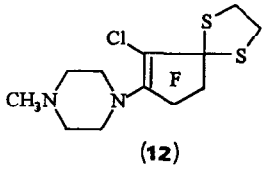


(4) (10) (4)

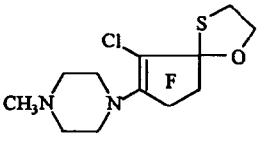


(5) (11) (5)

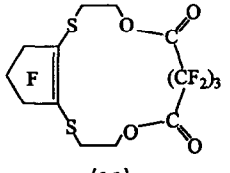
When the difunctional nucleophiles **2** and **5** are reacted with difunctional electrophiles such as perfluoroglutaryl fluoride, $FC(O)(CF_2)_3C(O)F$, or $PhP(S)Cl_2$, condensation reactions occur to yield compounds **14–17**. While this may prove to be a convenient way of synthesizing ether or thioether macrocycles, when polyamines are reacted with perfluoroglutaryl fluoride either the doubly-substituted chain products or polymeric materials are obtained [14]. However, triethanolamine, a polyalcohol, reacts with perfluoroglutary fluoride in a 1:1 ratio to give compound **18**.



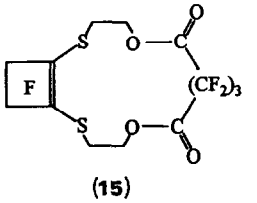
(12)



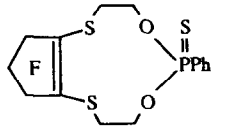
(13)



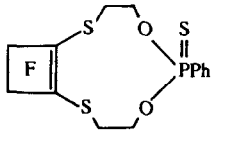
(14)



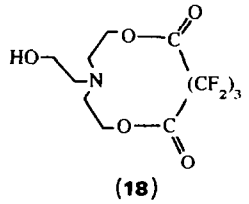
(15)



(16)



(17)



(18)

Compounds **3** and **7** undergo further nucleophilic attack at the vinyl carbon bonded to fluorine when reacted with a secondary amine, *N*-methyl piperazine, to produce compounds **12** and **13**.

Results and discussion

Cycloaddition via nucleophilic attack on fluorinated precursors plays an important role in the synthesis of fluoroheterocycles [15]. In an earlier study of the reactions of 1,2-dichloroperfluorocycloalk-1-enes (alkene = butene, pentene, hexene) with *N,N'*-dimethylethylenediamine, we reported that singly N-substituted products $H_3CNH(CH_2)_2N(CH_3)C{=}C(Cl)(CF_2)_nCF_2$ ($n=2$, 3) undergo intramolecular cyclization to produce spiro derivatives, $H_3CN(CH_2)_2N(CH_3)CC(Cl){=}CF(CF_2)_n$ ($n=1$, 2), with concomitant elimination of fluoride ion [8]. Polymerization rather than cyclization occurs in the case of the cyclobutene derivative of the diamine, $H_3CNH(CH_2)_2N(CH_3)C{=}C(Cl)CF_2CF_2$.

Intramolecular cyclization with concomitant β-elimination of an allyl fluoride ion in the presence of a suitable base may prove to be a convenient way of synthesizing fluoroheterocycles. In view of this, we reacted 1,2-dichloroperfluorocycloalk-1-enes-1 (alkene = butene, pentene) with the difunctional nucleophiles 2-mercaptoethanol, $HO(CH_2)_2SH$, and 1,2-ethanedithiol, $HS(CH_2)_2SH$, respectively. In the reactions of $HO(CH_2)_2SH$ with the chlorofluoroalkenes, depending on the stoichiometric ratio either singly [(1) and (4)] or doubly [(2) and (5)] substituted products are obtained. This is not unexpected, since it is well known that displacement of both chloride ions is possible when a strong nucleophilic reagent such as a mercaptide anion [16] is employed. In the presence of triethylamine, both five-membered ring compounds **1** and **2** convert readily into their spirocyclic components, **7** and **8**, respectively. This intramolecular cyclization proceeds more slowly with the four-membered ring derivatives. Complete conversion of compound **4** into **10**, or **5** into **11**, did not occur even after 2 weeks at 25 °C. However, in contrast to the cyclobutene derivative of the diamine, polymerization did not occur [8].

This intramolecular cyclization process involves substitution at a vinyl carbon with concomitant migration of the double bond. There is considerable precedence in the literature for spiro ring-formation reactions that involve displacement of the fluoride ion and ring fusion [17]. A similar cyclization mechanism involving the reaction of decafluorocyclohexene with ethylene glycol in the presence of potassium hydroxide has been described [18]. One of the disadvantages of the ethylene glycol/decafluorocyclohexene system is that the singly substituted product (2-hydroxyethyl ether) is not isolable

when using KOH as the base, although this species is postulated as an intermediate [18]. In later work, by using 2-acetoxyethanol in the reaction with decafluorocyclohexene in the presence of NaH, 1-(2-acetoxyethoxy)nonafluorocyclohexene was found in 38% yield, with octafluorocyclohex-2-enespiro-2'-dioxolan as the other major product (37%) arising from hydrolysis of the former compound [19]. The reaction pathway leading to these products is based on an addition–elimination sequence analogous to simple alcohol–perfluorocycloalkene reactions [20], i.e. nucleophilic attack at the double bond of the perfluoroolefin to eliminate fluoride ion. However, under basic conditions, the acetate is hydrolyzed generating an anion which subsequently attacks again at C-1 to form the spiro derivative quantitatively, in contrast with the attack by methoxide at C-2 of 1-methoxynonafluorocyclohexene. The overriding factor leading to the second attack at C-1 is the highly favored formation of the five-membered ring. Others have observed the formation of five-membered spiro rings in the reaction of 1-chlorononafluorocyclohexene with alkaline ethylene glycol [19, 21].

In our work, when ethanedithiol was reacted with the five-membered cyclic olefin $ClC{=}C(Cl)(CF_2)_2CF_2$, the likely intermediate, i.e. the 1-(SCH_2CH_2SH) derivative, was not observed and regardless of the reactant ratio only a singly substituted spiro derivative (**3**) was isolated. However, with the four-membered cyclic alkene $ClC{=}C(Cl)CF_2CF_2$, an inseparable mixture of either **6a** and **6b** or **6b** and **6c**, depending on the reaction ratio of 1:1 or 2:1 of dithiol to cyclic alkene, was obtained. Chambers and coworkers in their study of perfluorocycloalkenes with pyrocatechol and toluene-3,4-dithiol [22] demonstrate that because of the ability of sulfur (but not oxygen) to stabilize adjacent centers of negative charge, the two nucleophiles react via two different pathways leading to the formation of dissimilar products. Similarly, our study indicates that due to the greater polarizability of the electron pairs on sulfur, nucleophilic displacement of the vinyl chlorine at C-1 followed by attack of the thiolate anion again at C-1 occurs to form the spiro derivatives **3** and **6a**. Isolation of compound **6b** (but not the analogous cyclopentene derivative) is in keeping with our experience with the rates and products found for the reaction of $RN(H)CH_2CH_2N(H)R$ with dichlorotetrafluorocyclobutene and dichlorohexafluorocyclopentene [8].

It is interesting to note that double intramolecular cyclization does not occur to produce the dispiro derivative **9** when compound **2** is treated with excess triethylamine for an extended period of time at 25 °C. Heating **2** in THF for several days with K_2CO_3 only produced its monospiro derivative **8**. However, brief refluxing of **2** with K_2CO_3 in a more polar solvent with a higher boiling point, such as DMF, although resulting mainly in decomposition did produce a small amount of the dispiro derivative **9**. The carbon–carbon double bond infrared stretching mode of **9** was found to have shifted to a much higher frequency (1756 cm^{-1}) compared with that of the monospiro compound **8** (1656 cm^{-1}), which, in turn, is higher than 1543 cm^{-1} the stretching frequency of the parent molecule **2**. This increase in frequency supports the proposed change in atoms at the vinylic double bond from $^{S}\!\diagdown\!=\!\diagup^{S}$ to $^{S}\!\diagdown\!=\!\diagup^{F}$ to $^{F}\!\diagdown\!=\!\diagup^{F}$ which occurs in the conversion **2** → **8** → **9**.

As discussed earlier, since complete conversion of **5** into **11** did not occur, no attempts were made to make the analogous bispirocyclic derivative. The ^{19}F NMR spectra of **6a** and **6c** indicated that 1,2-addition of the dithiol with concomitant double bond shift may have occurred. The ^{19}F NMR spectra of the spiro derivatives **7**, **8**, **10**, **11** and **13** showed that their CF_2 groups are either AB or ABA'B'. In nearly every case, with the exception of **10** and **11**, i.e. for **3**, **6a**, **6c**, **7**, **8** and **9**, a ^{19}F NMR peak assigned to a vinylic fluorine atom occurred at higher field than δ −130 ppm. The infrared bands assigned to $\nu_{C=C}$ support the structure assignments, i.e. spiro ring formation.

When reacted with a secondary amine, *N*-methyl piperazine, compounds **3** and **7** underwent attack at the active sp^2 olefin carbon bonded to fluorine to displace fluoride ion and yield **12** and **13**, respectively. These structures are supported by the decrease in $\nu_{C=C}$ by ~60 cm^{-1} as the fluorine atom is replaced and by disappearance of the ^{19}F NMR resonance attributable to a vinyl fluorine.

The new macrofluoroheterocycles **14** and **15** are obtained as a result of 1:1 condensation reactions between the two difunctional nucleophiles **2** and **5**, and the difunctional electrophile perfluoroglutaryl fluoride. In contrast, when the latter was treated with *N*,*N'*-dimethylethylenediamine or *N*,*N'*-dimethyl-1,3-propanediamine, the 1:2 condensation reactions resulted in acyclic products, i.e. $HN(CH_3)(CH_2)_nN(CH_3)C(O)(CF_2)_3C(O)N(CH_3)(CH_2)_n(CH_3)NH$ ($n = 2, 3$) [8]. With piperazine or tris(2-aminoethyl)amine, perfluoroglutaryl fluoride reacted to form only polymeric materials [14]. Varying the reaction conditions, such as the concentration of the solutions, the sequence of adding the reactants, the nature of the solvents, etc. did not seem to change the reaction course and thus affect the nature of the products. However, when a milder electrophilic reagent such as *m*-phthalaldehyde was allowed to react with tris-(2-aminoethyl)amine, a 3:2 reaction resulting in an octaaza, bridged macrobicyclic ligand occurred [23]. Conversely, when perfluoroglutaryl fluoride reacted with a milder nucleophile such as a polyalcohol, e.g. triethanolamine, a 1:1 condensation product (**18**) was obtained. No 3:2, bridged, macrobicyclic product was formed in this case.

Based on the above observations, it seems only natural that when the new diols **2** and **5** were allowed to react with $PhP(S)Cl_2$ in the presence of triethylamine, 1:1 condensation reactions took place to give the macrocycles **16** and **17**, respectively. It is, however, interesting to note that when a nonfluorinated nucleophile, such as phosphodihydrazide, reacted with $PhP(S)Cl_2$ a 2:2 rather than a 1:1 macrocycle was produced [24]. Both macrocycles **16** and **17** tend to decompose at moderate temperatures (~50 °C). Purification, such as their separation from the amine salt ($Et_3N \cdot HCl$) and unreacted starting materials, was very difficult.

The recent literature is replete with the synthesis and specific binding ability of macroheterocycles. A 16-membered macrocyclic containing oxygen and sulfur is specific for Ag^+ [25], while a 15-membered macrocyclic ether containing amide and amine functional groups exhibits selectivity towards Pb^{2+} [26]. Some lipophilic cyclam derivatives take up Au^{3+} selectively [27]. The effects of size and substituents of macrocycles on the redox potentials of Pt complexes containing nitrogen or sulphur donor atoms have been studied [28].

We anticipate the coordinating ability of macrocycles **14** and **15** to be unique in view of the fact that the potential donor sites sulfur and oxygen are flanked by lipophobic fluorine-containing moieties. Although perfluorinated 18-crown-6 may have little use in complexing neutral species [29, 30], a large polyfluorinated heterocyclic ether actually traps an anion, i.e. a fluoride ion [31], rather than coordinating with cations. In the latter case, however, partial fluorination of the carbon segment between the coordinating oxygen nuclei is a necessary condition.

In conclusion, it is possible to synthesize and characterize a variety of spirocyclic compounds with sulfur or sulfur and oxygen in the spiro rings. The structures of the compounds isolated were based on spectral data and elemental analysis, and supported by the fact that the driving force to form five-membered rings is greater than that for six-membered rings. Small amounts of other possible isomers may also have formed but, if so, they were not found.

Experimental

General methods

All commercially available chemicals were of analytical reagent grade and used without further purification. They were 2-mercaptoethanol (Eastman Organic Chemical), 1,2-ethanedithiol (Aldrich), phenylphosphonothionic chloride (Aldrich), triethanolamine (Baker), 1,2-dichlorohexafluorocyclopent-1-ene (PCR), 1,2-dichlorotetrafluorocyclobut-1-ene (PCR) and perfluoroglutaryl fluoride (PCR). ^1H, ^{19}F and ^{31}P NMR spectra were obtained on a Bruker NR 200 Fourier-transform spectrometer employing $CDCl_3$ as the solvent and Me_4Si, CCl_3F and 85% H_3PO_4 as reference. Infrared spectra were recorded with a Perkin-Elmer model 1700 FT-IR spectrometer and mass spectra (CI) were obtained on a VG 7070SH mass spectrometer. Microanalyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. Melting points were obtained with a Thomas–Hoover apparatus.

General procedures for the preparation of compounds 1–6

In a typical reaction, 4 mmol of the chlorofluorocycloalkene, $ClC{=}C(Cl)(CF_2)_nCF_2$ ($n=1$, 2), were added slowly at 0 °C to a 10 ml THF solution containing a stoichiometric amount of 2-mercaptoethanol or ethanedithiol and triethylamine. (1:1:1 or 1:2:2). The reaction mixture was warmed slowly to 25 °C and stirred for several hours. After removal of THF, the reaction mixture was dissolved in $CHCl_3$ and washed with H_2O to remove the amine salt. The $CHCl_3$ layer was separated, concentrated and subjected to bulb-to-bulb distillation.

Compound **1** was obtained as a colorless liquid (70%) after distillation at 40 °C (1 Torr). Spectral data for **1**: IR (liquid, KBr) (cm^{-1}): 3347 9br, s); 2953 (m); 2885 (m); 1586 (s); 1327 (vs); 1284 (vs); 1255 (vs); 1201 (vs); 1141 (vs). ^1H NMR δ: 2.71 (br s, 1H); 3.26 (t, 2H, $J_{H-H}=6$ Hz) ppm. ^{19}F NMR δ: −106.7 (s, 2F); −112.5 (s, 2F); −129.2 (s, 2F) ppm. MS (CI) [*m/e* (species) intensity]: 288 ($^{37}M^+$) 17.9; 286 ($^{35}M^+$) 57.6; 271 ($^{37}M^+ - OH$) 32.9; 269 ($^{35}M^+ - OH$) 100. Analysis Calc. for $C_7H_5F_6ClSO$: C, 29.32; F, 39.79; H, 1.70%. Found: C, 29.93; F, 39.1; H, 2.07%.

Compound **2** was obtained as a colorless crystalline solid (m.p. 40–42 °C, 60%) after bulb-to-bulb distillation (70 °C, 0.6 Torr). Spectral data for **2**: IR (KBr) (cm^{-1}): 3318 (br s); 2949 (s); 2880 (s); 1543 (m); 1327 (s); 1250 (s); 1192 (s); 1132 (s); 1094 (s). ^1H NMR δ: 1.34 (s, 2H); 3.28 (b, 4H); 3.76 (b, 4H) ppm. ^{19}F NMR δ: −106.79 (s, 4F); −129.45 (s, 2F) ppm. MS (CI) [*m/e* (species) intensity]: 328 (M^+) 69.4; 311 ($M^+ - OH$) 22.5. Analysis: Calc. for $C_9F_6H_{10}O_2S_2$: C, 32.93; H, 3.05; F, 34.76%. Found: C, 33.22; H, 3.23; F, 34.5%.

Compound **3** was obtained as a colorless crystalline solid (m.p. 31 °C, 65%) after bulb-to-bulb distillation (45 °C, 0.5 Torr). Spectral data for **3**: IR (KBr) (cm^{-1}): 2937 (m); 2840 (m); 1689 (s); 1252 (vs); 1201 (vs); 1164 (vs); 1124 (vs). ^1H NMR δ: 3.39 (mult) ppm. ^{19}F NMR δ: −117.8 (mult, 2F); −118.2 (s, 2F); −138.4 (mult, 1F) ppm. MS (CI) [*m/e* (species) intensity]: 284 ($^{37}M^+$) 1.9; 282 ($^{35}M^+$) 7.5; 153 ($^{37}M^+ - C_3F_5$) 33.5; 151 ($^{35}M^+ - C_3F_5$) 100. Analysis: Calc. for $C_7H_4F_5ClS_2$: C, 29.73; F, 33.6; H, 1.42%. Found: C, 30.37; F, 34.1; H, 1.43%.

Compound **4** was obtained as a colorless oil (60%) after distillation at 45 °C (0.4 Torr). Spectral data for **4**: IR (liquid, KBr) (cm^{-1}): 3343 (br s); 2947 (m); 2886 (m); 1655 (m); 1327 (vs); 1293 (vs); 1256 (vs); 1121 (vs); 1067 (vs). ^1H NMR δ: 2.89 (br, 1H); 3.23 (t, 2H, $J_{H-H}=6$ Hz) ppm. ^{19}F NMR δ: −112.29 (mult, 2F); −114.95 (mult, 2F) ppm. MS (CI) [*m/e* (species) intensity]: 238 ($^{37}M^+$) 33.3; 236 ($^{35}M^+$) 100; 221 ($^{37}M^+ - OH$) 35.79; 219 ($^{35}M^+ - OH$) 100. Analysis: Calc. for $C_6H_5F_4ClSO$: C, 30.51; H, 2.11; F, 32.20%. Found: C, 30.64; H, 2.21; F, 31.7%.

Compound **5** was obtained as a viscous oil (40%) after bulb-to-bulb distillation (60 °C, 0.2 Torr). Spectral data for **5**: IR (liquid, KBr) (cm^{-1}): 3337 (br s); 2943 (m); 2882 (m); 1547 (w); 1311 (s); 1245 (s); 1158 (s); 1096 (s). ^1H NMR δ: 3.11 (s, 2H); 3.17 (t, 4H, $J_{H-H}=6$ Hz); 3.81 (t, 4H, $J_{H-H}=6$ Hz) ppm. ^{19}F NMR δ: −110.15 (s) ppm. MS (CI) [*m/e* (species) intensity]: 278 (M^+) 100; 261 ($M^+ - OH$) 22.4. Analysis Calc. for $C_8H_{10}F_4O_2S_2$: C, 34.53; H, 3.60; F, 27.34%. Found: C, 34.67; H, 3.71; F, 27.9%.

Compounds **6a** and **6b** were obtained as a mixture of colorless liquids after distillation at 40 °C (0.6 Torr). The relative ratio of **6a/6b** was approximately 2:1 as indicated from the ^1H and ^{19}F NMR spectral data of the mixture. Spectral data for the mixture: IR (liquid, KBr) (cm^{-1}): 2936 (m); 1717 (s); 1543 (w); 1354 (s); 1327 (s); 1281 (s); 1255 (s); 1177 (s); 1126 (s); 862 (s); 821 (s). ^1H NMR for $SCH_2^aCH_2^bSCC(Cl)=CFCF_2$ (**6a**) δ: 3.29 (b,c mult); 4.65 (a, dt, $J_{a-b}=9$ Hz, $J_{a-c}=6$ Hz) ppm. ^{19}F NMR for **6a** δ: −114.77 (d, 2F, $J_{F-F}=9.4$ Hz); −127.73 (t, 1F) ppm. ^{19}F NMR for **6a′** δ: −115.03 (d, 2F, $J_{F-F}=9.4$ Hz); −128.83 (t, 1F) ppm. ^1H NMR for $H^aS(CH_2^b)_2SC=C(Cl)CF_2CF_2$ (**6b**) δ: 1.40 (a, s); 3.29 (b, mult) ppm. ^{19}F NMR for **6b** δ: −112.80 (t, $J_{F-F}=9.0$ Hz); −113.96 (t) ppm. MS (CI) [*m/e* (species) intensity]: 255 ($^{37}M^+ + 1$ for **6b**) 3.12; 253 ($^{35}M^+ + 1$ for **6b**) 10.9; 235 ($^{37}M^+ + 1$ for **6a**)7.03; 233 ($^{35}M^+ + 1$ for **6a**) 19.87; 154 ($SCH_2CH_2SCCF_2^+$) 100. Compound **6a′** may result from the 1,2-addition of the dithiol with double-bond shift [19].

Compounds **6b** and **6c** were obtained as a mixture of pale yellow oils after bulb-to-bulb distillation at 60 °C (0.8 Torr). The relative ratio of **6b/6c** was roughly 1:2 as indicated from the ^1H and ^{19}F NMR spectral data of the mixture. Spectral data for the mixture: IR (liquid, KBr) (cm^{-1}): 2936 (s); 1667 (s); 1543 (m); 1361 (vs); 1280 (vs); 1257 (vs); 1219 (vs); 1175 (vs); 1136 (vs); 819 (vs). ^1H NMR for $SCH^aH^b-CH_2^cSCC(SCH_2^dCH_2^dSH^e)=CFCF_2$ (**6c**) δ: 1.65 (e, mult); 2.86 (d, mult); 3.29 (b,c, mult); 4.69 (a, dt, $J_{a-b}=9$ Hz, $J_{a-c}=6$ Hz) ppm. ^{19}F NMR for **6c** δ: −114.77 (d, 2F, $J_{F-F}=7.5$ Hz); −127.69 (t, 1F) ppm. ^{19}F NMR for **6c′** δ: −114.95 (d, 2F, $J_{F-F}=7.5$ Hz); −128.79 (t, 1F) ppm. MS (CI) [*m/e* (species) intensity]: 255 ($^{37}M^+ + 1$ for **6b**) 15.9; 253 ($^{35}M^+ + 1$ for **6b**) 37.9; 198 ($M^+ - S(CH_2)_2S$ for **6c**) 25.9; 170 ($M^+ - S_2(CH_2)_4$ for **6c**) 28.6. Compound **6c′** may result from the 1,2-addition of the dithiol with double-bond shift [19].

General procedures for the preparation of compounds 7, 8, 10 and 11

In a typical reaction, 2 mmol of **1**, **2**, **4** or **5** was added to a solution containing 5 ml of THF and 2.5 mmol of triethylamine. The reaction mixture was stirred at 25 °C for 6 (for **1** and **2**) to 14 (for **4** and **5**). After evaporation of the THF, the residue was dissolved in $CHCl_3$ and washed with H_2O. The $CHCl_3$ layer was separated, concentrated and purified by bulb-to-bulb distillation.

Compound **7** was obtained as a colorless liquid (80%) after distillation at 30 °C (0.3 Torr). Spectral data for **7**: IR (liquid, KBr) (cm^{-1}): 2955 (m); 2898 (m); 1697 (s); 1367 (s); 1305 (s); 1284 (s); 1271 (s); 1176 (s); 1132 (s). ^1H NMR for $OCH^aH^bCH_2^cSCC(Cl)=CF^XCF_2^{AA'}CF_2^{BB'}$ δ: 3.33 (c, mult); 4.06 (b, mult); 4.48 (a, mult) ppm. ^{19}F NMR (ABA′B′) δ: −112.42 (A, mult); −112.45 (A′, mult); −123.03 (B, t); −132.50 (B′, mult); −136.6 (X, dd) [$J_{A-B}=250$ Hz, $J_{A'-B'}=234$ Hz, $J_{A'-B}=J_{B-B'}=J_{B'-X}=11.3$ Hz, $J_{A'-X}=22.6$ Hz] ppm. MS (CI) [*m/e* (species) intensity]: 268 ($^{37}M^+$) 14.9; 266 ($^{35}M^+$) 42.6; 249 ($^{37}M^+ - F$) 33.3; 247 ($^{35}M^+ - F$) 89.9. Analysis: Calc. for $C_7H_4F_5ClSO$: C, 31.52; H, 1.5%. Found: C, 31.70; H, 1.5%.

Compound **8** was obtained as a colorless liquid (65%) after distillation at 55 °C (1 Torr). Spectral data for **8**: IR (liquid, KBr) (cm^{-1}): 3377 (br m); 2952 (m); 2859 (m); 1656 (s); 1349 (s); 1307 (s); 1271 (s); 1168 (s); 1084 (s). ^1H NMR for $OCH^aH^bCH_2^cSCC-(S(CH_2^d)_2OH^e)=CF^XCF_2^{AA'}CF_2^{BB'}$ δ: 2.47 (e, br); 3.24 (d, mult); 3.75 (c, t); 4.06 (b, mult); 4.48 (a, mult) [$J_{b-c}=12$ Hz, $J_{a-c}=J_{a-b}=6$ Hz] ppm. ^{19}F NMR (ABA′B′) δ: −112.09 (A, mult); −113.08 (A′, mult); −122.69 (B, mult); −133.74 (B′, mult); −138.32 (X, mult) [$J_{A-B}=250$ Hz, $J_{A'-B}=232$ Hz] ppm. MS (CI) [*m/e* (species) intensity]: 308 (M^+) 100; 291 ($M^+ - OH$) 100; 271 ($M^+ - OH - HF$) 37.

For compound **10**, after bulb-to-bulb distillation at 40 °C (1 Torr) a colorless liquid, i.e. a mixture of **10** (~40%, based on NMR peak area ratios) and unreacted **4**, was obtained. IR (liquid, KBr) (cm^{-1}): characteristic band of **10**: 1715 (s) (C=C). ^1H NMR for $OCH^a-H^bCH_2^cSCC(Cl)=CF^XCF_2^{AB}$ δ: 3.10 (c, mult); 3.97 (b, mult); 4.35 (a, mult) ppm. ^{19}F NMR (AB) δ: −107.2 (A, mult); −116.2 (X, mult); −120.7 (B, mult) [$J_{A-B}=188$ Hz] ppm.

Compound **11**, after bulb-to-bulb distillation at 60 °C (0.6 Torr) a colorless oil, i.e. a mixture of **11** (~40%, based on NMR peak area ratios) and unreacted **5**, was obtained IR (liquid, KBr) (cm^{-1}): characteristic bands

of **11**: 3345 (br s) (OH); 1673 (m) (C=C). ^{1}H NMR for $\overline{OCH^aH^bCH_2{}^cS}\underline{CC(S(CH_2{}^d)_2OH^e)=CF^XCF^AF^B}$ δ: 2.47 (e, br); 3.19 (d, mult); 3.87 (c, mult); 3.97 (b, mult); 4.36 (a, mult) ppm. ^{19}F NMR (AB) δ: −104.95 (A, mult); −118.11 (B, mult); −120.77 (X, mult) [J_{A-B} = 151 Hz] ppm.

Preparation of compound 9

A solution containing 15 ml of DMF, 1.2 mmol of compound **8** and excess K_2CO_3 was brought to reflux for ~0.5 h. After reaction had occurred, 15 ml of water and 10 ml of $CHCl_3$ were added to the resulting mixture. The oil layer was separated and washed with 5 ml of water. After removal of water and evaporation of $CHCl_3$, a bulb-to-bulb distillation at 60 °C (0.5 Torr) resulted in a colorless oil (10%). Spectral data for **9**: IR (liquid, KBr) (cm^{-1}): 2949 (m); 2893 (m); 1756 (s); 1393 (s); 1366 (s); 1270 (s); 1227 (s); 1202 (s). ^{1}H NMR for $\overline{OCH_2{}^aCH_2{}^bS}\underline{CCSCH_2{}^bCH_2{}^aOCF^X=CF^{X'}CF^AF^M}$ δ: 3.05 (b, mult); 4.25 (a, mult) ppm. ^{19}F NMR (AMX′) δ: −92.16 (A, t); −126.17 (M, t); −141.60 (X, t); −58.55 (X′, mult) [J_{A-M} = 243 Hz, J_{A-X} = $J_{A-X'}$ = 15 Hz, J_{M-X} = $J_{M-X'}$ = 11 Hz] ppm. MS (CI) [*m/e* (species) intensity]: 288 (M^+) 71.74; 269 ($M^+ - F$) 53.81; 200 ($M^+ - 2(CH_2CH_2O)$) 83.4. Analysis: Calc. for $C_9H_8F_4S_2O_2$: C, 37.5; H, 2.78; F, 26.39%. Found: C, 38.9; H, 3.07; F, 25.9%.

General procedures for the preparation of compounds 12 and 13

In a typical reaction, 1.0 mmol of **3** or **7** was added to 10 ml of a THF solution containing 2.2 mmol of *N*-methyl piperazine. The mixture was stirred at 25 °C for 3 d. After the usual work-up, the residue was subjected to either bulb-to-bulb distillation or recrystallization from $CHCl_3$.

Compound **12** was obtained as a colorless solid (60%, m.p. 62 °C) after recrystallization or distillation at 70 °C (0.5 Torr). Spectral data for **12**: IR (solid, KBr) (cm^{-1}): 2941 (m); 2891 (m); 2852 (m); 2803 (m); 1629 (s); 1305 (s); 1292 (s); 1279 (s); 1158 (s); 1108 (s); 1005 (s). ^{1}H NMR δ: 2.22 (s, 3H); 2.36 (mult, 4H); 3.28 (mult, 8H) ppm. ^{19}F NMR δ: −111.6 (mult, 2F); −118.1 (mult, 2F) ppm. MS (CI) [*m/e* (species) intensity]: 364 ($^{37}M^+$) 21.3; 362 ($^{35}M^+$) 63.7; 327 ($M^+ - Cl$) 100. Analysis: Calc. for $C_{12}H_{15}F_4ClS_2N_2$: C, 39.72; H, 4.14; F, 21.0%. Found: 39.73; H, 4.14; F, 21.8%.

Compound **13** was obtained as a colorless oil which crystallized slowly (75%, m.p. 58 °C) after distillation at 60 °C (0.5 Torr). Spectral data for **13**: IR (solid, KBr) (cm^{-1}): 2943 (m); 2889 (m); 2852 (m); 2800 (m); 1635 (s); 1417 (m); 1455 (m); 1306 (s); 1293 (s); 1279 (s); 1245 (s); 1220 (s); 1065 (m); 1038 (m); 1013 (s). ^{1}H NMR for $\overline{OCH^aH^bCH_2{}^cS}\underline{CC(Cl)=CN(CH_2{}^d)_2N(CH_3{}^f)(CH_2{}^e)_2CF^AF^BCF^{A'}F^{B'}}$ δ: 2.34 (f, s); 2.49 (e, mult); 3.18 (d, mult); 3.52 (c, mult); 4.07 (b, mult); 4.49 (a, mult) ppm. ^{19}F NMR (ABA′B′) δ: −103.89 (A, d); −116.11 (B, d); −112.46 (A′, d); −133.56 (B′, d) [J_{A-B} = 245 Hz, $J_{A'-B'}$ = 232 Hz, $J_{A-A'}$ = 11 Hz, $J_{B-B'}$ = 15 Hz, $J_{A-B'}$ = $J_{A'-B}$ = < 0.05 Hz] ppm. MS (CI) [*m/e* (species) intensity]: 349 ($^{37}M^+ + 1$) 15.0; 347 ($^{35}M^+ + 1$) 50.6; 311 ($M^+ - Cl$) 20.4. Analysis: Calc. for $C_{12}H_{15}F_4ClSON_2$: C, 41.56; H, 4.33; F, 21.93%. Found: C, 41.65; H, 4.33; F, 22.2%.

General procedures for the preparation of compounds 14, 15 and 18

In a typical reaction, 4.2 mmol of **2** or **5** or of triethanolamine was first dissolved in 30 ml of THF containing 1.0 g of Na_2CO_3. Perfluoroglutaryl fluoride (4.5 mmol) in 10 ml of THF was then added slowly via a dropping funnel to the above solution at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, then at 25 °C for another 16 h. After the usual work-up, distillation at 70 °C (2 Torr) afforded compound **14** as a white crystalline solid (48%, m.p. 67 °C). Spectral data for **14**: IR (solid, KBr) (cm^{-1}): 2965 (w); 1785 (s); 1775 (s); 1391 (s); 1327 (s); 1263 (s); 1244 (s); 1176 (s); 1160 (s); 1137 (s). ^{1}H NMR δ: 3.33 (t, J_{H-H} = 6 Hz); 4.50 (t) ppm. ^{19}F NMR δ: −106.44 (s, 4F); −117.56 (s, 4F); −125.94 (s, 2F); −129.73 (s, 2F) ppm. MS (CI) [*m/e* (species intensity]: 532 (M^+) 100; 516 ($M^+ - O$) 89.7. Analysis: Calc. for $C_{14}S_2O_4F_{12}H_8$: C, 31.58; H, 1.50; F, 42.9%. Found: C, 31.70; H, 1.68; F, 41.4%.

Compound **15** was obtained as a viscous oil (35%) after distillation at 70 °C (0.5 Torr). It crystallized slowly at 25 °C (m.p. 59–60 °C). Spectral data for **15**: IR (solid, KBr) (cm^{-1}): 2949 (w); 2882 (w); 1786 (s); 1549 (w); 1328 (s); 1244 (s); 1195 (s); 1143 (s); 1101 (s). ^{1}H NMR δ: 3.34 (t, J_{H-H} = 6 Hz); 4.51 (t) ppm. ^{19}F NMR δ: −110.43 (s, 4F); −118.14 (s, 4F); −125.26 (s, 2F) ppm. MS (CI) [*m/e* (species) intensity]: 428 (M^+ 58.6; 278 ($M^+ - (CF_2)_2CO_2(CH_2)_2S$) 35.4; 267 ($(CF_2)_3(CO_2)_2(CH_2)_2{}^+ + 1$) 100. Analysis Calc. for $C_{13}S_2O_4F_{10}H_8$: C, 36.44; H, 1.87%. Found: C, 33.17; H, 1.74%.

Compound **18** was obtained as a colorless grease (90%) after filtration and removal of THF from the filtrate. The grease gradually hardened to a waxy material. Spectral data for **18**: IR (KBr) (cm^{-1}): 3394 (br m); 2975 (m); 2878 (m); 1780 (s); 1680 (s); 1317 (vs); 1272 (vs); 1246 (vs); 1152 (vs); 1049 (vs). ^{1}H NMR δ: 1.77 (s, 2H); 3.17–4.00 (mult, 11 H) ppm. ^{19}F NMR (DMSO) δ: −114.7 (s, 4F); −122.45 (s, 2F) ppm. MS (CI) [*m/e* (species) intensity]: 354 ($M^+ + 1$) 35.5; 322 ($M^+ - CH_2OH$) 24.0; 195 ($M^+ - (CF_2)_2CO_2CH_2$) 100. Analysis: Calc. for $C_{11}F_6NO_5H_{13}$: F, 32.3%. Found: F, 32.4%.

General procedures for the preparation of compounds 16 and 17

In a typical reaction, 4.2 mmol of **2** or **5** was first dissolved in 10 ml of THF. A solution consisting of 9.0 mmol of triethylamine in 5 ml of THF and a solution consisting of 4.2 mmol of phenylphosphonothionic chloride in 5 ml of THF were then added simultaneously and slowly to the solution of **2** or **5** at 0 °C. The resulting mixture was stirred at 0 °C for 1 h and then at 25 °C for 24 h. After the usual work-up, **16** and **17** were both obtained as viscous yellow–brown oils which could not be purified by distillation or recrystallization. Spectral data for **16**: IR (liquid, KBr) (cm^{-1}): 2979 (m); 2946 (m); 1656 (w); 1544 (m); 1476 (m); 1440 (s); 1398 (m); 1328 (s); 1250 (s); 1195 (s); 910 (s); 877 (s); 852 (s). ^1H NMR δ: 3.45–4.15 (mult, 8H); 7.47–7.83 (mult, 5H) ppm. ^{19}F NMR δ: −105.5 (s, 4F); −129.3 (s, 2F) ppm. ^{31}P NMR δ: 88.11 ppm. MS (CI) [*m/e* (species) intensity]: 467 ($M^+ + 1$) 48.2; 387 ($M^+ - C_6H_7$) 22.2; 293 ($M^+ + 1 - C_5F_6$) 100. Spectral data for **17**: IR (liquid, KBr) (cm^{-1}): 2946 (m); 2884 (m); 1673 (m); 1590 (m); 1477 (m); 1462 (m); 1440 (m); 1350 (m); 1317 (s); 1245 (s); 1157 (s); 1068 (s); 1023 (s). ^1H NMR δ: 3.81 (mult, 4H); 4.38 (mult, 4H); 7.43–7.98 (mult, 5H) ppm. ^{19}F NMR δ: −114.2 (mult) ppm. ^{31}P NMR δ: 88.62 ppm. MS (CI) [*m/e* (species) intensity]: 417 ($M^+ + 1$) 100; 397 ($M^+ - F$) 100; 381 ($M^+ - F - O$) 45.8.

Acknowledgments

We are grateful to the National Science Foundation (CHE-9003509) and the Air Force Office of Scientific Research (91-0189) for support of this research. Q.-C.M. thanks Yakima Valley College for sabbatical leave.

References

1 R.E. Banks, *Organofluorine Chemicals and Their Industrial Applications,* E. Horwood, Chichester, 1979.
2 R.E. Banks, *Preparation, Properties and Industrial Applications of Organofluorine Compounds,* E. Horwood, Chichester, 1982.
3 R.L. Powell, *Eur. Pat. 127 365* (1984); [*Chem. Abs., 102* (1985) 65 005z].
4 Y. Kamitori, M. Hojo, M.R. Masuda, Y. Kawamura and X. Fang, *Heterocycles, 31* (1990) 5298.
5 R.A. Guenther and G. Gutman, *Eur. Pat. 366 483* (1990); [*Chem. Abs., 113* (1990) 116 136e].
6 Y. Kobayashi, R. Filler, K. Tanaka and K. Mitsuhashi, *J. Synth. Org. Chem., 45* (1987) 269.
7 K. Uneyama, F. Yamashita, K. Sugimoto and O. Morimoto, *Tetrahedron Lett., 31* (1990) 2717.
8 Q.C. Mir, R.L. Kirchmeier and J.M. Shreeve, *J. Org. Chem., 59* (1994) 173.
9 G. Sarwar, R.L. Kirchmeier and J.M. Shreeve, *Heteroatom. Chem., 1* (1990) 167.
10 H.-G. Mack, H. Oberhammer, J.M. Shreeve and X.-B. Xia, *J. Mol. Struct., 196* (1989) 57.
11 C.-Y. Guo, R.L. Kirchmeier and J.M. Shreeve, *J. Am. Chem. Soc., 113* (1991) 9000.
12 C.-Y. Guo, R.L. Kirchmeier and J.M. Shreeve, *J. Fluorine Chem., 52* (1991) 29.
13 O.D. Gupta, W.A. Kamil and J.M. Shreeve, *Inorg. Chem., 24* (1985) 2126.
14 Q.C. Mir, unpublished work.
15 M.J. Silvester, *Aldrichimica Acta, 24* (1991) No. 2, and references therein.
16 C.G. Krespan and D.C. England, *J. Org. Chem., 33* (1968) 1850.
17 W.H. Sharkey, *Fluorine Chem. Rev., 2* (1968) 1.
18 G. Camaggi and R. Stephens, *Tetrahedron, 22* (1966) 1189.
19 R.G. Plevey and D.J. Sparrow, *J. Chem. Soc., Perkin Trans. 1,* (1976) 573.
20 A.B. Clayton, J. Roylance, D.R. Sayers, R. Stephens and J.C. Tatlow, *J. Chem. Soc.,* (1965) 7358.
21 G. Gambaretto, M. Napoli and S. Gliozzi, *Ann.Chim. (Rome), 59* (1969) 702.
22 A.E. Bayliff, M.R. Bryce and R.D. Chambers, *J. Chem. Soc., Perkin Trans. 1,* (1987) 763.
23 R. Menif, J. Reibenspies and A.E. Martell, *Inorg. Chem., 30* (1991) 3446.
24 D. Colombo, A.M. Caminade and J.P. Majoral, *Inorg. Chem., 30* (1991) 3365.
25 M. Oue, K. Akama, K. Kimura, M. Tanaka and T. Shono, *J. Chem. Soc., Perkin Trans. 1,* (1989) 1675.
26 S. Kumar, R. Singh and S. Singh, *Indian J. Chem., 30B* (1991); [*Chem. Abs., 114* (1991) 258 413n].
27 E. Kimura, Y. Kurogi and T. Takahashi, *Inorg. Chem., 30* (1991) 4117.
28 D. Waknine, M.J. Heeg, J.F. Endicott and L.A. Ochrymowycz, *Inorg. Chem., 30* (1991) 3691.
29 W.-H. Lin, W.I. Bailey, Jr. and R.J. Lagow, *J. Chem. Soc. Chem. Commun.,* (1985) 1350.
30 R.J. Lagow and W.-H. Lin, *U.S. Pat. 4 570 004* (1986); [*Chem. Abs., 105* (1986) 172 519d].
31 W.B. Farnham, D.C. Roe, D.A. Dixon, J.C. Calabrese and R.L. Harlow, *J. Am. Chem. Soc., 112* (1990) 7707.