1,1,3,3-Tetraoxopolyfluoro-1,3-dithiacycloalkanes. $\overline{CH_2SO_2(CF_2)_nSO_2}$ (n = 2−5) and 2-Substituted Derivatives

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Received August 3, 1994[⊗]

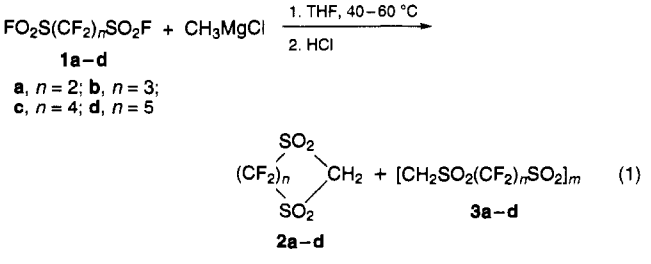
1,1,3,3-Tetraoxopolyfluoro-1,3-dithiacycloalkanes $\overline{CH_2SO_2(CF_2)_nSO_2}$ (n = 2−5) are synthesized by the reaction of α,ω-bis(fluorosulfonyl)perfluoroalkanes $FO_2S(CF_2)_nSO_2F$ with methylmagnesium chloride or bromide. Depending on reaction conditions, α,ω-bis(methylsulfonyl)perfluoroalkanes $CH_3SO_2(CF_2)_nSO_2CH_3$ and probable oligomeric products $[CH_2SO_2(CF_2)_nSO_2]_m$ are also observed. 2-Substituted products $\overline{RCHSO_2(CF_2)_nSO_2}$ (R = CH_3, C_6H_5) are obtained using RCH_2MgCl. The structures of the phenyl derivatives **5a** (n = 2) and **5b** (n = 3) were obtained by single-crystal X-ray diffraction analysis.

Introduction

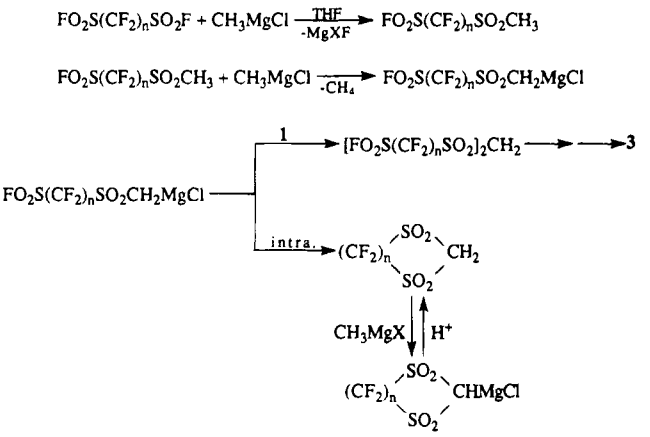
Compounds containing two geminal sulfonyl groups were first synthesized nearly 100 years ago,[1] but for a long time the number of examples were small and they were not well investigated. Cyclic geminal disulfones are usually obtained by oxidizing 1,3-dithiocycloalkanes, which are prepared by treatment of α,ω-dithiaalkanes with carbonyl compounds,[2] or by the reaction of α,ω-dihalogenoalkanes with sodium thiosulfate followed by reaction with carbonyl compounds.[3] Recently, the ring-substituted 1,1,3,3-tetraoxo-1,3-dithiacycloalkanes have been prepared.[4] Fluorinated analogues of $(RSO_2)_2CH_2$ have been reported and were shown to be very strong hydrocarbon acids.[5] As part of an exploratory program to develop new fluorinated acids as potential electrolytes for phosphoric acid-based fuel cells, the preparation of fluorinated cyclic sulfones was of interest. Herein we report the synthesis of several examples of these heterocycles of varying ring size. As expected, the compounds are highly acidic and the methylene carbon is easily functionalized to give 2-substituted derivatives.

Results and Discussion

1,1,3,3-Tetraoxopolyfluoro-1,3-dithiacycloalkanes $\overline{SO_2(CF_2)_nSO_2CH_2}$ are synthesized in moderate yields from the reaction of α,ω-bis(fluorosulfonyl)perfluoroalkanes $FO_2S(CF_2)_nSO_2F$ (**1**) with methylmagnesium chloride using tetrahydrofuran as a solvent. In all these reactions probable oligomeric products $[CH_2SO_2(CF_2)_nSO_2]_m$ (**3**) are also observed in varying amounts. Compounds **3** have not been unequivocally identified, and only limited data are presented for these products.



Scheme 1



The yields of **2c,d** are low, due to the unfavorable seven- and eight-membered rings compared to the five- and six-membered rings in **2a,b**. The yields of **2a,b** are 50−60%, compared to only 10−20% for **2c,d**. The products **2** are white crystalline solids, which can be easily sublimed in vacuo. They are highly acidic with $pK_1 \simeq 1$ in H_2O. The second ionizable hydrogen is estimated to have $pK_2 \simeq 20$.

The synthesis of **2** involves a sequence of reactions in which $FO_2S(CF_2)_nSO_2CH_3$ is an intermediate. The acidic α-hydrogen is easily abstracted by the Grignard reagent CH_3MgCl, forming methane and $FO_2S(CF_2)_nSO_2CH_2MgCl$. The latter then undergoes an intramolecular cyclization, forming **2**, or intermolecular reactions with itself, other intermediates, or **1**, forming probable oligomeric products **3** as shown in Scheme 1. The methane observed in these reactions was not quantitated. In the proposed Scheme 1, a third equivalent of Grignard reagent is consumed in the facile transmetalation of the very acidic α-hydrogen in **2**, giving $\overline{SO_2(CF_2)_nSO_2CHMgCl}$. Treatment with 3N HCl forms **2**.

The formation of **2** in these reactions is strongly dependent on reaction conditions. For example, when **1c** was added slowly to methylmagnesium chloride/THF, **2c** was obtained in 22%

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1994.

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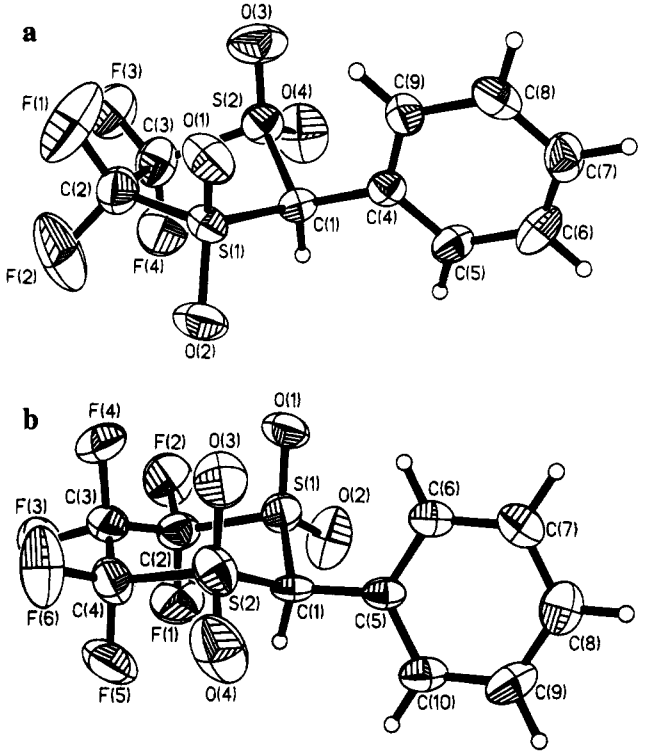

Figure 1. Thermal ellipsoid plots (50% probability) showing the atom-labelling scheme used for (a) **5a** and (b) **5b**.

yield; if the Grignard reagent was added dropwise to **1c**/THF, only oligomeric products **3** were observed even at −50 °C. In this manner the concentration of the bis(fluorosulfonyl) complex **1c** is higher than that of CH_3MgCl, and intermolecular reactions are more facile, resulting in the formation of **3.**

When other Grignard reagents such as ethylmagnesium bromide or benzylmagnesium bromide were used to react with **1a** and **1b**, the 2-substituted 1,1,3,3-tetraoxopolyfluoro-1,3-dithiacycloalkanes **4** and **5** were obtained. Compound **1c** was

$$\mathbf{1a,b} + RCH_2MgBr \rightarrow \overbrace{SO_2(CF_2)_nSO_2CHR}^{\mathbf{4a,b,\ 5a,b}} \quad (2)$$

$$\mathbf{4},\ R = CH_3;\ \mathbf{5},\ R = C_6H_5$$

also treated with C_2H_5MgBr but no $\overbrace{SO_2(CF_2)_4SO_2CHCH_3}$ was formed under similar conditions. Benzylmagnesium bromide reacts smoothly with **1a** and **1b**, giving higher yields of **5a** (81%) and **5b** (72%) with little or no oligomeric products. These reactions form bibenzyl $(C_6H_5CH_2)_2$ (~15%) as a byproduct which may arise from a radical reaction process. Both **5a** and **5b** are highly crystalline. The X-ray structures of **5a** and **5b** are shown in Figure 1. Both samples crystallize in the monoclinic space group $P2_1/c$, with one molecule per asymmetric unit. The five-membered ring has a puckered conformation; the six-membered ring adopts a chair conformation, with the phenyl ring located in an equatorial position. The crystal data, atomic coordinates, and distances and angles are given in Tables 1−3.

The ^{19}F NMR spectra of **4** and **5** are very different from those of **2a,b**. For example, the ^{19}F NMR of the six-membered ring **2b** is an apparent first-order spectrum with two resonances for the methylene groups in the ratio of 1:2. For **4b**, the spectrum consists of two second-order A−B patterns in a ratio 1:2.

The observed bands can be analyzed as two AB spectra due to the nonequivalent axial and equatorial fluorines of each CF_2 group (CCF_2C) and ($-CF_2S$)] in molecule **4b**. The assignment of the spectrum is based upon the assumption that equatorial fluorines (B) are generally more highly shielded than axial fluorines (A).[6,7] For CF_2S $\Delta\nu_{AB}$ = 1533 Hz (18.3 ppm) and the coupling constant $^2J_{AB}$ = 274 Hz. For the CF_2C group $\Delta\nu_{A'B'}$ = 1031 Hz (12.2 ppm) and $^2J_{A'B'}$ = 287 Hz.

Table 1. Crystal Data

	5a	**5b**
formula	$C_9H_6O_4F_4S_2$	$C_{10}H_6O_4F_6S_2$
fw	318.26	368.27
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	12.802(4)	16.392(5)
b, Å	6.030(1)	5.756(1)
c, Å	15.465(5)	15.623(5)
β, deg	95.48(2)	115.03(2)
V, Å3	1188.4(7)	1335.7(7)
Z	4	4
D_{calc}, g cm^{-3}	1.78	1.83
μ, mm^{-1}	0.51	0.49
transm coeff	0.81−1.00	0.86−1.00
no. of obsd data ($I > 3\sigma(I)$)	1368	1516
$R(F_o)^a$	0.0657	0.0410
$R_w(F_o)^b$	0.0809	0.0502

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	y	z	$U_{eq}{}^a$
		Compound **5a**		
S(1)	8767(1)	1714(3)	2172(1)	36(1)
S(2)	7288(1)	3998(3)	944(1)	45(1)
F(1)	8958(6)	−222(9)	684(4)	110(3)
F(2)	10187(4)	1963(12)	1064(4)	105(3)
F(3)	8441(4)	3090(10)	−332(3)	82(2)
F(4)	9128(4)	5414(8)	617(3)	78(2)
O(1)	8251(3)	−332(8)	2265(4)	54(2)
O(2)	9637(3)	2390(9)	2770(3)	56(2)
O(3)	6685(4)	2072(11)	763(3)	72(2)
O(4)	6921(5)	6158(11)	713(4)	81(3)
C(1)	7818(5)	3981(11)	2069(4)	32(2)
C(2)	9172(6)	1762(14)	1047(5)	56(3)
C(3)	8555(6)	3507(14)	499(5)	56(3)
C(4)	6996(5)	3881(11)	2700(4)	32(2)
C(5)	6918(5)	5620(12)	3271(4)	41(2)
C(6)	6159(6)	5601(14)	3837(5)	55(3)
C(7)	5468(5)	3861(13)	3849(4)	48(3)
C(8)	5545(5)	2134(14)	3287(4)	48(3)
C(9)	6313(5)	2111(12)	2699(4)	40(2)
		Compound **5b**		
S(1)	3072(1)	6426(2)	4874(1)	46(1)
S(2)	1631(1)	7578(2)	5519(1)	51(1)
F(1)	1954(2)	3510(4)	3692(2)	76(1)
F(2)	2386(2)	6322(5)	3062(2)	84(1)
F(3)	593(2)	6317(5)	2706(2)	80(1)
F(4)	1348(2)	9343(4)	3436(2)	81(1)
F(5)	635(2)	4537(5)	4296(2)	80(1)
F(6)	119(2)	8060(6)	4053(2)	104(2)
O(1)	3259(2)	8838(5)	4878(2)	62(1)
O(2)	3739(2)	4732(6)	4990(2)	77(1)
O(3)	1850(2)	9969(5)	5531(2)	69(1)
O(4)	1239(2)	6687(7)	6100(2)	82(2)
C(1)	2593(2)	5760(6)	5700(2)	35(1)
C(2)	2104(3)	5781(8)	3727(3)	52(2)
C(3)	1223(3)	7079(7)	3528(3)	53(2)
C(4)	853(3)	6782(8)	4280(3)	57(2)
C(5)	3283(2)	5914(6)	6714(2)	35(1)
C(6)	3847(2)	7831(6)	7050(3)	42(1)
C(7)	4476(3)	7897(7)	7991(3)	49(2)
C(8)	4535(3)	6089(8)	8590(3)	51(2)
C(9)	3972(3)	4196(7)	8259(3)	53(2)
C(10)	3349(3)	4092(7)	7322(3)	45(2)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Distances (Å) and Angles (deg)

Distances

5a		5b	
S(1)−O(1)	1.413(5)	S(1)−O(1)	1.421(3)
S(1)−O(2)	1.437(5)	S(1)−O(2)	1.418(4)
S(1)−C(1)	1.825(6)	S(1)−C(1)	1.812(4)
S(1)−C(2)	1.861(8)	S(1)−C(2)	1.861(3)
S(2)−O(3)	1.408(7)	S(2)−O(3)	1.420(3)
S(2)−O(4)	1.419(7)	S(2)−O(4)	1.412(4)
S(2)−C(1)	1.806(6)	S(2)−C(1)	1.811(4)
S(2)−C(3)	1.846(9)	S(2)−C(4)	1.868(4)

Angles

5a		5b	
O(1)−S(1)−O(2)	121.5(3)	O(1)−S(1)−O(2)	121.1(2)
O(1)−S(1)−C(1)	110.4(3)	O(1)−S(1)−C(1)	111.2(2)
O(2)−S(1)−C(1)	108.1(3)	O(2)−S(1)−C(1)	107.8(2)
O(1)−S(1)−C(2)	106.5(4)	O(1)−S(1)−C(2)	107.1(2)
O(2)−S(1)−C(2)	109.2(3)	O(2)−S(1)−C(2)	106.4(2)
C(1)−S(1)−C(2)	98.6(3)	C(1)−S(1)−C(2)	101.2(2)
O(3)−S(2)−O(4)	123.0(4)	O(3)−S(2)−O(4)	121.6(2)
O(3)−S(2)−C(1)	109.6(3)	O(3)−S(2)−C(1)	111.1(2)
O(4)−S(2)−C(1)	109.5(3)	O(4)−S(2)−C(1)	107.0(2)
O(3)−S(2)−C(3)	106.1(4)	O(3)−S(2)−C(4)	108.0(2)
O(4)−S(2)−C(3)	109.6(4)	O(4)−S(2)−C(4)	106.2(2)
C(1)−S(2)−C(3)	95.4(3)	C(1)−S(2)−C(4)	100.8(2)

Koshar[5] observed a strong solvent effect in the Grignard reactions with trifluoromethanesulfonyl fluoride leading to $(CF_3SO_2)_2CH_2$. The results observed in this work are similar. As mentioned above, the major product is the cyclic compound for **1a,b** and the oligomeric products for **1c,d** when the reactions are carried out in THF. If diethyl ether is used as a solvent however, the major products with **1b,c** are α,ω-bis(methylsulfonyl)perfluoroalkanes **6** and compounds **2**. For example, **1c**

$$\mathbf{1b,c} + CH_3MgCl \xrightarrow{Et_2O} CH_3SO_2(CF_2)_nSO_2CH_3 + \underset{\mathbf{6b,c}}{\mathbf{2b,c}} \quad (3)$$

was treated with methylmagnesium chloride in diethyl ether at room temperature, giving **6c** (64%) and **2c** (22%). Under the same conditions, **1b** afforded **2b** (67%) and **6b** (8%); if the reaction was carried out at −40 to −50 °C, the yield of **6b** increased to 85%. Tetrahydrofuran is known to be more basic than diethyl ether and more readily forms coordination complexes with organometallic compounds.[8] This property apparently facilitates the transmetalation to form $FSO_2(CF_2)_nSO_2CH_2MgCl$, leading to products **2** and **3** (Scheme 1). In diethyl ether this reaction is obviously less favorable. The effects of solvent and temperature on the products and yields of reactions are summarized in Table 4.

Summary

Reactions of α,ω-bis(fluorosulfonyl)perfluoroalkanes with Grignard reagents in ether solvents provide routes to novel fluorinated, cyclic α,β-disulfones and α,ω-bis(methylsulfonyl)-perfluoroalkanes. These compounds are useful hydrocarbon acids which provide routes to a variety of new inorganic and organic derivatives which will be the subject of forthcoming publications.

Experimental Section

General Considerations. α,ω-Bis(fluorosulfonyl)perfluoroalkanes **1** were obtained from 3M Co. The Grignard reagents were obtained from Aldrich. Infrared spectra were obtained using a Perkin-Elmer 1430 spectrometer with a 7500 data station. ^{19}F and ^1H NMR were recorded on either a JEOL FX-90Q or an IBM NR 200 AF spectrometer using $CFCl_3$ or TMS as internal standard. Mass spectra EI and CI (CH_4) were obtained using a Hewlett-Packard 5985B GC-MS system operating at 70 eV and direct solids inlet techniques. All the melting points were taken on a Mel-Temp melting point apparatus and are uncorrected.

Table 4. Summary of Reactions of **1** with CH_3MgCl

reactant	solvent	temp, °C	products	yield, %
1a	THF	40−60	**2a**	60
			3a	21
1b	THF	40−60	**2b**	58
			3b	23
1b	Et_2O	22	**2b**	67
			6b	8
1b	Et_2O	−50	**2b**	5
			6b	85
1c	THF	40−60	**2c**	22
			3c	60
1c	THF	40−60	**3c**	90[a]
1c	Et_2O	22	**2c**	22
			6c	64
1d	THF	40−60	**2d**	11
			3d	60

[a] The Grignard reagent was added to **1c**.

X-ray Crystallographic Analysis. Intensity data for compounds **5a** and **5b** were measured at 21 ± 1°C by using $\omega/2\theta$ scans ($2\theta_{max}$ = 50°) on a Nicolet R3mV diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). An empirical absorption correction based on azimuthal scans of several moderately intense reflections was applied to the data for both compounds, as were Lorentz and polarization corrections; however, the intensities of three check reflections measured periodically throughout data collection indicated no need for a decay correction. The structures were solved by direct methods and refined by using full-matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in calculated positions (d_{C-H} = 0.96 Å) with a refined group thermal parameter (U = 0.037(7) Å^2 for **5a**; U = 0.049(4) Å^2 for **5b**). Structure solution, refinement, and the calculation of derived results were performed with the SHELXTL[9] package of computer programs. Neutral atom scattering factors were those of Cromer and Waber,[10] and the real and imaginary anomalous dispersion corrections were those of Cromer.[11]

Syntheses. Typical procedures for the preparation of **2** and **4**, **5** were carried out as follows.

1,1,3,3-Tetraoxo-4,4,5,5-tetrafluoro-1,3-dithiacyclopentane (2a). In a 250 mL flask equipped with a condenser, thermometer, magnetic stirrer bar, and a dropping funnel was placed 55 mL of a 3 M solution of methylmagnesium chloride in tetrahydrofuran. 1,2-Bis(fluorosulfonyl)tetrafluoroethane (**1a**) (13.3 g, 0.05 mol) was added dropwise while the temperature was kept at 40 °C. After the addition was completed (4 h), the reaction mixture was heated for 6 h at 50−60 °C, cooled to 22 °C, and hydrolyzed by slowly adding 50 mL of 3 N HCl. The organic layer was removed, and the aqueous layer was extracted twice with ether (20 mL). The combined organic layers were evaporated to dryness under vacuum. The resulting solid was sublimed under high vacuum to give 6.3 g of a white solid. Recrystallization from CH_2Cl_2 gave pure **2a** (5.9 g, 52%).

2a: mp = 91 °C; IR (solid, KCl) 2984 (m), 2915 (m), 1451 (w), 1391 (vs), 1350 (s), 1348 (s), 1274 (m), 1211 (vs), 1132 (s), 955 (m), 915 (m), 859 (m), 791 (m), 724 (m), cm^{-1}; ^{19}F NMR [$(CD_3)_2CO$] δ −118.2 (s); ^1H NMR δ 5.80 (s); MS (CI) *m/z* 243 (MH^+, 100%); MS (EI) *m/z* 178 ($M^+ - SO_2$, 100%).

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(10) Cromer, D. T.; Waber, J. C. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.
(11) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

The solid remaining after sublimation was dissolved in 20 mL of THF, and the solution was filtered. The filtrate was poured into 100 mL of benzene, and the resulting precipitated solid was filtered off and dried under vacuum, giving product **3a** (1.8 g, 20%).

3a, $[SO_2(CF_2)_2SO_2CH_2]_n$: mp > 287 °C; IR (solid, KCl) 2994 (m), 2928 (m), 1480 (m), 1400 (s), 1208 (s), 1140 (s), 1090 (m), 830 (m), 680 (m), 590 (m) cm^{-1}; ^{19}F NMR [$(CD_3)_2CO$] δ −116.8 (s, CF_2); ^1H NMR δ 5.75 (broad, $-CH_2-$).

1,1,3,3-Tetraoxo-4,4,5,5,6,6-hexafluoro-1,3-dithiacyclohexane (2b). **1b** (15.8 g, 0.05 mol) was treated as above with CH_3MgCl/THF (0.16 mol) affording **2b** (8.2 g, 58%) and **3b** (3.2 g, 23%).

2b: mp = 150 °C; IR (KCl, solid) 2963 (m), 2900 (m), 1397 (vs), 1343 (s), 1279 (m), 1260 (m), 1225 (vs), 1193 (s), 1154 (s), 1084 (m), 1059 (m), 997 (m), 904 (s), 842 (s), 771 (m), 746 (m), 642 (m), 611 (m) cm^{-1}; ^{19}F NMR [$(CD_3)_2CO$] δ −126.0 (2F, m), −121.6 (4F, t), $^3J_{FF}$ = 8.0 Hz; ^1H NMR δ 6.0 (s); MS *m/z* (CI) 293 (MH^+, 100%); MS (EI) *m/z* 228 ($M^+ - SO_2$, 100%).

3b: mp > 280 °C; IR (KCl, solid) 2990 (m), 2928 (m), 1400 (s), 1280 (m), 1200 (s), 1110 (s), 1092 (m), 950 (m), 830 (m), 692 (s), 600 (m) cm^{-1}; ^{19}F NMR [$(CD_3)_2CO$] δ −118.0 (s, CF_2S), −122.5 (s, CF_2C), 2:1; ^1H NMR δ 5.80 (broad, CH_2).

1,1,3,3-Tetraoxo-4,4,5,5,6,6,7,7-octafluoro-1,3-dithiacycloheptane (2c). **1c** (18.3 g, 0.05 mol) was treated with 0.15 mol of CH_3MgCl/THF to give **2c** (3.4 g, 22%) and **3c** (10.2 g, 60%).

2c: mp = 132 °C; IR (KCl, solid) 2980 (m), 2905 (m), 1459 (m), 1403 (vs), 1386 (vs), 1338 (s), 1234 (s), 1202 (vs), 1169 (vs), 1139 (s), 1106 (s), 1020 (s), 974 (s), 876 (s), 819 (m), 764 (m), 626 (m) cm^{-1}; ^{19}F NMR [$(CD_3)_2CO$] δ −121.7 (4F, m, CF_2C), −113.3 (4F, m, CF_2S); ^1H NMR δ 5.78 (s); MS (CI) *m/z* 343 (MH^+, 100%), MS (EI) *m/z* 278 ($M^+ - SO_2$, 100%).

3c: mp > 290 °C; IR (solid, KCl) 2995 (m), 2927 (m), 1482 (m), 1400 (s), 1204 (s), 1141 (s), 1085 (m), 826 (m), 678 (m) cm^{-1}; ^{19}F NMR (CD_3CN) δ −109.8 (s, CF_2S), −119.2 (s, CF_2C), 1:1; ^1H NMR δ 5.77 (broad, CH_2).

1,1,3,3-Tetraoxo-4,4,5,5,6,6,7,7,8,8-decafluoro-1,3-dithiacyclooctane (2d). **1d** (20 g, 0.055 mol) reacted with 0.18 mol of CH_3MgCl/THF giving **2d** (4.3 g, 11%) and **3d** (11.8 g, 60%).

2d: mp = 137 °C; IR (KCl, solid) 2993 (m), 2925 (m), 1460 (s), 1386 (vs), 1203 (s, broad), 1142 (vs), 1106 (s), 1043 (m), 884 (m), 814 (m), 680 (m), 644 (m), 611 (m) cm^{-1}; ^{19}F NMR [$(CD_3)_2CO$] δ −107.3 (4F, CF_2S), −119.5 (4F, CF_2CF_2S), −120.5 (2F, CCF_2C); ^1H NMR (CD_3CN) δ 5.85 (s); MS (CI) *m/z* 393 (MH^+, 100%).

3d: mp > 292 °C; IR (solid, KCl) 2995 (m), 2928 (m), 1480 (m), 1402 (s), 1204 (s), 1147 (s), 1185 (m), 826 (m), 678 (m), 590 (m) cm^{-1}; ^{19}F NMR [$(CD_3)_2CO$] δ −104.3 (CF_2S), −116.0 (CF_2CF_2S), −120.0 (CCF_2C), 2:2:1; ^1H NMR (CD_3CN) δ 5.80 (CH_2, broad).

1,3,3,3-Tetraoxo-2-methyl-4,4,5,5-tetrafluoro-1,3-dithiacyclopentane (4a). **1a** (5.3 g, 0.02 mol) was treated with 33 mL (0.065 mol) of EtMgCl in THF, forming **4a** (2.97 g, 58%).

4a: mp = 56 °C; IR (solid, KCl) 3022 (m), 2948 (m), 1448 (m), 1379 (vs), 1283 (m), 1212 (vs), 1169 (s), 1133 (vs), 1054 (m), 963 (m), 917 (s), 743 (m), 716 (s), 647 (m), 609 (m), 580 (m) cm^{-1}; ^{19}F NMR [$(CD_3)_2CO$] δ −118.2; ^1H NMR δ 1.95 (3H, d), 5.91 (1H, q); MS (CI) *m/z* 257 (MH^+, 100%), MS (EI) *m/z* 257 (MH^+, 1%), 148 ($(CF_2)_2SO^+$, 2.4%), 100 ($C_2F_4^+$, 100%), 92 ($CH_3CHSO_2^+$, 78%).

1,1,3,3-Tetraoxo-2-methyl-4,4,5,5,6,6-hexafluoro-1,3-dithiacyclohexane (4b). **1b** (10.4 g, 0.033 mol) reacted with 0.1 mol of EtMgCl in THF to give **4b** (5.0 g, 60%).

4b: mp 111 °C; IR (KCl, solid) 3015 (m), 2941 (m), 1445 (m), 1392 (s), 1372 (vs), 1262 (m), 1231 (m), 1208 (s), 1192 (s), 1155 (vs), 1050 (m), 991 (m), 904 (m), 726 (s), 608 (m), 504 (m) cm^{-1}; ^{19}F NMR [$(CD_3)_2CO$] δ A′ −119.5, B′ −131.7 (2F, CF_2C), A −111.2, B −131.7 (4F, CF_2S), $^2J_{A'B'}$ = 287, $^2J_{AB}$ = 274 Hz; ^1H NMR δ 2.09 (3H, d), 6.45 (1H, q), ^3J = 7.0 Hz; MS (CI) *m/z* 307 (MH^+, 100%), MS (EI) *m/z* 242 ($M^+ - SO_2$, 1.1%), 150 ($C_3F_6^+$, 5.9%), 100 ($C_2F_4^+$, 100%), 92 ($CH_3CH^+SO_2$, 20%) 76 (CH_3CH^+SO, 22.4%).

1,1,3,3-Tetraoxo-2-phenyl-4,4,5,5-tetrafluoro-1,3-dithiacyclopentane (5a). **1a** (6.6 g, 0.025 mol) reacted with 40 mL of 2 M benzylmagnesium chloride in THF, giving **5a** (6.5 g, 81%).

5a: mp = 134 °C; IR (KCl, solid) 2921 (m), 1490 (m), 1450 (m), 1383 (vs), 1277 (m), 1218 (s), 1180 (s), 1163 (m), 1133 (m), 962 (m), 919 (m), 856 (m), 790 (m), 695 (m), 678 (m), 625 (m) cm^{-1}; ^{19}F NMR [$(CD_3)_2C{=}O$] δ A −114.9, B −119.2, $^2J_{AB}$ = 227 Hz; ^1H NMR (CD_3Cl) δ 7.61−7.74 (5H, m), 5.75 (1H, s); MS (CI) *m/z* 318 (M^+, 1.7%), 190 ($M^+ - 2SO_2$, 8.1%), 154 ($C_6H_5CH^+SO_2$, 43.4%), 121 ($C_6H_5CS^+$, 3.3%), 107 ($C_6H_3S^+$, 100%); MS (EI) *m/z* 318 (M^+, 16.9%), 190 ($M^+ - 2SO_2$, 11%), 154 ($C_6H_5CHSO_2^+$, 117.6%), 140 ($M^+ - 2SO_2 - CF_2$, 15%), 90 ($C_6H_5CH^+$, 100%), 77 ($C_6H_5^+$, 11.9%), 63 ($C_5H_3^+$, 15.1%).

The byproduct $(C_6H_5CH_2)_2$, 1.1 g (15%): mp = 52 °C. ^1H NMR (CD_3Cl) δ 2.90 (s), (4H, CH_2), 7.25 (10H, m).

1,1,3,3-Tetraoxo-2-phenyl-4,4,5,5,6,6-hexafluoro-1,3-dithiacyclohexane (5b). **1b** (7.9 g, 0.025 mol) was treated with 50 mL of 2 M benzylmagnesium chloride in THF to give **5b** (6.7 g, 72%).

5b: mp = 156 °C; IR (KCl, solid) 2919 (m), 1490 (m), 1451 (m), 1390 (vs), 1377 (s), 1286 (m), 1207 (m), 1186 (s), 1163 (s), 1150 (s), 1059 (m), 987 (m), 907 (m), 852 (m), 799 (m), 694 (m), 654 (m) cm^{-1}; ^{19}F NMR [$(CD_3)_2CO$] δ A′ −117.7, B′ −132.9 (2F, CF_2C), A −108.9, B −131.8 (4F, CF_2S), $^2J_{A'B'}$ = 286, $^2J_{AB}$ = 278 Hz; ^1H NMR (CD_3Cl) δ 7.26−7.82 (5H, m), 5.81 (1H, s); MS (CI) *m/z* 369 (MH^+, 1.1%), 368 (M^+, 3.0%), 240 ($M^+ - 2SO_2$, 4.2%), 140 ($M^+ - 2SO_2 - C_2F_4$, 44%), 121 ($C_6H_5CS^+$, 4%), 107 ($C_6H_3S^+$, 100%); MS (EI) *m/z* 368 (M^+, 1.9%), 240 ($M^+ - 2SO_2$, 1.6%), 140 ($M^+ - 2SO_2 - C_2F_4$, 100%), 90 ($C_6H_5CH^+$, 58.2%), 77 ($C_6H_5^+$, 28.8%), 63 ($C_5H_3^+$, 33.9%).

The byproduct $(C_6H_{15}CH_2)_2$ 1.4 g (16%) was also isolated.

1,3-Bis(methylsulfonyl)hexafluoropropane (6b). **1b** (3.1 g, 0.01 mol) was treated with methylmagnesium chloride (13 mL, 0.04 mol) in diethyl ether at −50 °C to give **6b** (2.6 g, 85%) and **2b** (0.15 g, 5%).

6b: mp = 129 °C; IR (KCl, solid) 3009 (w), 2961 (m), 2900 (w), 1395 (s), 1342 (s), 1260 (m), 1221 (s), 1188 (s), 1154 (s), 1126 (m), 1057 (m), 991 (m), 903 (m), 842 (m), 771 (m), 692 (m), 643 (m) cm^{-1}; ^{19}F NMR ($CDCl_3$) δ 114.2 (4F, CF_2S), −119.4 (2F, CF_2C); ^1H NMR δ 3.20 (s); MS (CI) *m/z* 309 (MH^+, 78.8%), 293 ($M^+ - CH_3$, 100%), 229 ($M^+ - SO_2CH_3$, 4.0%). MS (EI) *m/z* 150 ($C_3F_6^+$, 5.9%), 131 ($C_3F_5^+$, 32.8%), 119 ($C_2F_5^+$, 8.2%), 100 ($C_2F_4^+$, 100%), 79 ($CH_3SO_2^+$, 6.2%), 63 (CH_3SO^+, 10.1%), 62 ($CH_2{=}SO^+$, 58.8%), 48 (SO^+, 6.4%).

1,4-Bis(methylsulfonyl)octafluorobutane (6c). **1c** (9.2 g, 0.025 mol) was treated with methylmagnesium chloride (34 mL, 0.1 mol) in Et_2O at room temperature to give **2c** (1.1 g, 22%) and **6c** (5.7 g, 64%).

6c: mp = 156 °C; IR (KCl, solid) 3029 (m), 3007 (m), 2926 (m), 1343 (vs), 1314 (s), 1193 (s), 1168 (s), 1139 (vs), 1098 (s), 958 (m), 783 (m), 660 (m) cm^{-1}; ^{19}F NMR (CD_3CN) δ −113.8 (4F, CF_2S), −119.6 (4F, CCF_2C); ^1H NMR δ 3.32 (s); MS (CI) *m/z* 359 (MH^+, 100%); MS (EI) *m/z* 358 (M^+, 2.6%), 294 ($M^+ - SO_2$, 10.5%), 279 ($M^+ - SO_2 - CH_2$, 19.9%), 131 ($C_3F_5^+$, 14.5%), 100 ($C_2F_4^+$, 34.2%), 79 ($CH_3SO_2^+$, 90.7%), 69 (CF_3^+, 11.2%), 64 (SO_2^+, 6.8%), 63 (CH_3SO^+, 100%).

Preparation of Oligomer 3c. To a 100 mL flask containing 7.3 g (0.02 mol) of **1c** was added dropwise 20 mL of 3 M methylmagnesium chloride in THF at 22 °C. After addition was complete (1 h), the reaction mixture was stirred for 6 h and then hydrolyzed with 20 mL of 3 N HCl. The organic layer was separated from the mixture, and the solvent was removed under vacuum. The resulting solid was dried under vacuum and then dissolved in 30 mL of THF, the solution was filtered, and the filtrate was poured into 200 mL of benzene. The resulting solid was filtered off and dried to give **3c** (6.7 g, 91%). A weighed portion of the solid was dissolved in H_2O, and the solution was titrated with 0.10 M NaOH to a phenolphthalein end point. This gave a value of the equivalent weight at 440. Assuming the oligomer is $(CH_3)FSO_2(CF_2)_4[SO_2CH_2SO_2(CF_2)_4]_nSO_2(CF_2)_4SO_2F(CH_3)$, then whether the end groups are FSO_2 or CH_3SO_2, the value of $\bar{n}$ is ca. 6.2.

Acknowledgment. The financial support of this research by the Gas Research Institute (Contract No. 5084-260-1086) is gratefully acknowledged. We thank Dr. Fred Behr of 3M Co. for samples of the α,ω-bis(fluorosulfonyl)perfluoroalkanes.

Supplementary Material Available: Complete listings for **5a** and **5b** of crystallographic data, anisotropic thermal parameters, hydrogen atom coordinates, and bond distances and angles (7 pages). Ordering information is given on any current masthead page.

IC940907W