An examination of Table VII shows that, on the average, aluminum chloride forms slightly stronger complexes than gallium chloride. For donors using N or O (hard bases)[38,39] alumium chloride forms bonds about 10 kcal/mol stronger than the gallium chloride bonds. Equilibrium measurements of gallium chloride and aluminum chloride with substituted anilines in ether also show that aluminum chloride is a slightly better acid toward these bases.[40] For donors using S or Cl^- as the bridging group (softer bases), the two acids form bonds of about the same strength (±3 kcal/mol). These regularities hold even though the actual values of the bond energies vary from 26 to 83 kcal/mol. This regularity can be used to predict bond energies where steric effects are small. For instance, Greenwood and Perkins[31] gave $\Delta H_f(g) = -34$ kcal/mol for the gallium chloride–piperidine complex. One would, therefore, predict that $-\Delta H_f(g)$ for the aluminum chloride complex was -44 ± 5 kcal/mol.

The slight preference of $GaCl_3$ for softer bases compared to $AlCl_3$ indicates that $GaCl_3$ is a softer acid than $AlCl_3$, as expected. The small difference between the two means that they have about the same acid strength. It is the similarity in acids strengths, together with the small difference in their preferences for hard bases, which allows predictions to be made.

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Perfluorocarboxylato Disulfides and Methylsilanes

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The reaction of disulfur dichloride, S_2Cl_2, with silver perfluorocarboxylates gives substituted disulfides, $(R_fCO_2S)_2$, where R_f = CF_3, C_2F_5, C_3F_7. They are thermally unstable and decompose to $(R_fCO)_2O$, SO_2, and S. Compounds of the general formula $(R_fCO_2)_nSi(CH_3)_{4-n}$, where $n = 1, 2, 3$ and R_f = CF_3, C_2F_5, C_3F_7, have been prepared similarly by reaction with the corresponding chloromethylsilanes. Infrared, nmr, and mass spectra as well as elemental analyses are reported for these new compounds.

Many perfluorocarboxylates or, at least, trifluoroacetates are known. However, none has been reported for group VI elements with the exception of chromium.[1,2] It was of interest to attempt the preparation of compounds containing sulfur to compare their stabilities with those of their carboxylate analogs. The tetrakis(trifluoroacetates), $(CF_3COO)_4M$, of several group IV elements have been prepared.[3] Silicon tetrakis(trifluoroacetate) was obtained from the reaction of silicon tetrachloride with trifluoroacetic acid in benzene solution.

In this work, bis(perfluorocarboxylato) disulfides, $(R_fCO_2S)_2$, where R_f = CF_3, C_2F_5, C_3F_7, and perfluorocarboxylatomethylsilanes of the general formula $(R_fCO_2)_nSi(CH_3)_{4-n}$ where n = 1, 2, 3, and R_f = CF_3, C_2F_5, C_3F_7, have been prepared by the reactions of silver perfluorocarboxylates with disulfur dichloride and the corresponding chloromethylsilanes.

Experimental Section

Apparatus.—A standard Pyrex high-vacuum system was used for handling volatile materials and for separating volatile products by trap-to-trap distillation. Reactions were carried out in 125-ml Pyrex bulbs fitted with 4-mm Teflon stopcocks (Fischer and Porter Co.). Kel-F No. 90 stopcock grease (3M Co.) was used on all ground joints.

Infrared spectra (Table I) were recorded with a Beckman IR5A spectrophotometer or a Perkin-Elmer Model 621 grating infrared spectrophotometer. Spectra of gases were obtained by introducing the vapors into a Pyrex cell with a path length of 100 mm and KBr windows. Spectra of liquids were taken after the liquids were placed between KBr windows in a dry box. High-resolution ^{19}F nmr spectra (Table II) were recorded with a Varian Model HA-100 spectrometer operating at 94.1 Mc and ^1H nmr spectra were recorded with an A-60 nmr spectrometer. The compounds were sealed in Pyrex tubes with CCl_3F and tetramethylsilane as internal references. Mass spectra were obtained with a Hitachi Perkin-Elmer Model RMU-6E spectrometer operating at an ionization potential of 70 eV. Elemental analyses (Table III) were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany, or by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. Molecular weights were determined by Regnault's method with a calibrated bulb equipped with a Teflon stopcock.

Reagents.—Silver salts of the perfluorocarboxylic acids were obtained from Fisher Scientific Co. and Peninsular ChemResearch, Inc. They were ground to fine powders and dried overnight under dynamic vacuum. S_2Cl_2 (Eastman Kodak Co.) was purified by distillation. The fraction with a boiling point range of 133–134° was used. $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, and CH_3SiCl_3 (Wilshire Chemical Co.) were dried over molecular sieves.

General Preparation.—All of the compounds were prepared by the same method. In a typical reaction, $(CH_3)_3SiCl$ (5.60

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TABLE I

INFRARED SPECTRAL DATA FOR PERFLUOROCARBOXYLATO DISULFIDES AND METHYLSILANES

$(CF_3CO_2S)_2$[a]	1812 m, 1326 m, 1238 s, 1196 s, 1117 w, 1049 s, 998 w, 865 w, 731 m, 622 m
$(C_2F_5CO_2S)_2$[a]	1780 s, 1330 s, 1279–1163 vs, b, 1130–1101 vs, b, 1010–968 vs, b, 809 m, 728 s, 654 s
$(C_3F_7CO_2S)_2$[a]	1765 s, 1670 m,[b] 1353 w,[b] 1338 m, 1273 m,[b] 1217 vs, 1193 m, 1158 m, 1120 s, 1088 s, 967 s, 929 m, 810 w, 787 m, 754 w, 703 m, 641 w, 589 w, 518 vw
$CF_3CO_2Si(CH_3)_3$	2964 m, 2900 vw, 1774 s, 1378 s, 1257 vs, 1160 vs, 1066 w, 873 w,[b] 840 w, 753 m, 719 m, 693 w,[b] 638 w,[b] 630 m, 474 m
$(CF_3CO_2)_2Si(CH_3)_2$	2966 w, 2913 w, 1797 s, 1783 s, 1369 s, 1274 s,[b] 1268 s, 1181 vs, 1133 vs, 885 s, 835 s, 820 s, 745 w, 717 m, 650 vw, 570 w, 514 vw
$(CF_3CO_2)_3SiCH_3$	2964 vw, 1810 s, 1800 s, 1360 m, 1280 w, 1193 s, 1125 vs, 906 m, 810 w, 716 m, 655 w, 580 w
$C_3F_7CO_2Si(CH_3)_3$	2958 m, 2900 w, 1766 s, 1333 w,[b] 1316 s, 1260 s, 1226 vs, 1188 s, 1151 vs, 1130 s, 1066 s, 1030 s, 962 m, 930 m, 843 vs, 810 m, 743 m, 712 m, 615 w, 588 w, 535 w
$(C_3F_7CO_2)_2Si(CH_3)_2$[a]	2969 w, 1770 s, 1340 m,[b] 1310 m, 1268 s, 1200 vs, 1188 s, 1146 s, 1122 s, 1083 s, 1033 w, 967 s, 933 m, 831 m, 798 m, 710 m, 630 w, 592 w, 524 vw
$(C_3F_7CO_2)_3SiCH_3$[a]	1790 s, 1353 m, 1300 s, 1200 vs, 1191 vs, 1138 vs, 1127 s,[b] 1080 s, 1024 vw, 969 s, 936 s, 870 m, 800 m, 752 m, 709 m, 640 w, 625 w, 594 vw, 582 vw, 526 w, 500 vw[b]
$C_2F_5CO_2Si(CH_3)_3$	2970 s, 2908 vw, 1768 s, 1360 m, 1320 s, 1256 s, 1228 vs, 1198 s, 1163 vs, 1067 vs, 1035 vs, 850 vs, 819 s, 755 m, 720 m, 612 w, 589 w, 535 w
$(C_2F_5CO_2)_2Si(CH_3)_2$[a]	2963 w, 1770 s, 1360 m, 1315 s, 1270 s, 1218 vs, 1190 s,[b] 1166 vs, 1098 m, 1027 vs, 820 s, 714 m, 581 w, 532 vw
$(C_2H_5CO_2)_3SiCH_3$[a]	2922 vw, 1790 s, 1352 s, 1298 vs, 1120 vs, 1163 s,[b] 1142 vs, 1026 vs, 882 s, 810 s, 798 s, 755 w, 724 s, 585 m, 541 m

[a] Liquid phase. [b] Shoulder.

TABLE II

NMR SPECTRAL DATA FOR PERFLUOROCARBOXYLATO DISULFIDES AND METHYLSILANES

	ϕ^*, ppm			$J_{CF_3-\alpha\text{-}CF_2}$, cps	$\delta(^1H)$, ppm
	CF_3	α-CF_2	β-CF_2		
$(CF_3CO_2S)_2$	74.23 (s)				
$(C_2F_5CO_2S)_2$	83.37 (t)	120.38 (q)		1.7	
$(C_3F_7CO_2S)_2$	81.34 (t)	117.79 (q)	127.01 (s)	8.8	
$(CH_3)_3SiO_2CCF_3$	77.01 (s)				0.384 (s)
$(CH_3)_2Si(O_2CCF_3)_2$	76.76 (s)				0.699 s)
$CH_3Si(O_2CCF_3)_3$	76.58 (s)				0.991 (s)
$(CH_3)_3SiO_2CC_2F_5$	83.65 (t)	121.90 (q)		1.3	0.384 (s)
$(CH_3)_2Si(O_2CC_2F_5)_2$	83.55 (t)	122.16 (q)		1.2	0.699 (s)
$CH_3Si(O_2CC_2F_5)_3$	83.56 (t)	122.30 (q)		1.6	0.991 (s)
$(CH_3)_3SiO_2CC_3F_7$	81.63 (t)	119.89 (q)	127.80 (s)	8.6	0.384 (s)
$(CH_3)_2Si(O_2CC_3F_7)_2$	81.53 (t)	119.78 (q)	127.47 (s)	8.6	0.699 (s)
$CH_3Si(O_2CC_3F_7)_3$	81.56 (t)	119.65 (q)	127.36 (s)	8.6	0.991 (s)
$(CF_3CO)_2O$	75.99 (s)				
$(C_2F_5CO)_2O$	83.45 (t)	122.00 (q)		1.5	
$(C_3F_7CO)_2O$	81.39 (t)	119.46 (q)	127.03 (s)	8.7	

TABLE III

ELEMENTAL ANALYSES OF PERFLUOROCARBOXYLATO DISULFIDES AND METHYLSILANES

	Theoret %			Theoret mol wt	Exptl %			Exptl mol wt
	C	F	S (H)		C	F	S (H)	
$(CF_3CO_2S)_2$	16.55	39.28	22.10	...	16.64	39.25	21.99	...
$(C_2F_5CO_2S)_2$	18.47	48.70	16.44	...	18.64	48.87	16.29	...
$(C_3F_7CO_2S)_2$	19.61	54.26	13.06	...	19.06	52.90	12.81	...
$(CH_3)_3SiO_2CCF_3$	32.28	30.53	4.89	186.2	32.48	30.6	5.01	188.6
$(CH_3)_2Si(O_2CCF_3)_2$	25.36	40.11	2.13	284.2	25.41	40.3	2.12	285.2
$CH_3Si(O_2CCF_3)_3$	22.00	44.47	0.79	382.2	22.52	44.1	0.88	383.1
$(CH_3)_3SiO_2CC_2F_5$	30.51	40.25	3.81	236.2	30.37	40.8	3.66	239.3
$(CH_3)_2Si(O_2CC_2F_5)_2$	25.01	49.45	1.57	384.2	25.14	48.5	1.63	385.9
$CH_3Si(O_2CC_2F_5)_3$	22.57	53.55	0.57	532.2	22.57	53.3	0.56	532.5
$(CH_3)_3SiO_2CC_3F_7$	29.37	46.50	3.15	286.2	29.32	46.0	3.06	288.3
$(CH_3)_2Si(O_2CC_3F_7)_2$	24.80	54.93	1.25	...	24.87	54.7	1.30	...
$CH_3Si(O_2CC_3F_7)_3$	22.89	58.48	0.44	...	22.87	57.2	0.47	...

mmol) was condensed onto a slight excess of silver trifluoroacetate (5.65 mmol) at −196°, and the reaction bulb was allowed to warm to 25°. A color change of the salt indicated that reaction occurred below room temperature. After the mixture was shaken overnight, the volatile products were removed under vacuum and distilled trap-to-trap to give trimethyl(trifluoroacetato)silane in essentially quantitative yield. The yields of all the new compounds are greater than 90%. In the preparations of bis(perfluorocarboxylato) disulfides, small amounts of the corresponding acid anhydrides and SO_2 were observed.

Trimethyl(trifluoroacetato)silane also was prepared in 80% yield by the reaction of anhydrous trifluoroacetic acid with trimethylchlorosilane. However, reaction of trifluoroacetic acid with methyltrichlorosilane resulted in the formation of only traces of $(CF_3COO)_3SiCH_3$.

Thermal Decomposition of Bis(trifluoroacetato) Disulfide.—When $(CF_3COOS)_2$ (90.1 mg) was held at 40° for 12 hr, SO_2 (9.8 mg), $(CF_3CO)_2O$ (65.6 mg), and S (14.7 mg) were obtained after trap-to-trap separation. Experimental (calculated) percentages of products are: SO_2, 10.89 (11.03); S, 16.42 (16.55); $(CF_3CO)_2$, 72.59 (71.42), based on the equation

$$2(CF_3COOS)_2 \longrightarrow 2(CF_3CO)_2O + SO_2 + 3S$$

Hydrolysis of Bis(trifluoroacetato) Disulfide.—An excess of H_2O was condensed onto $(CF_3COOS)_2$ (86.3 mg). The hydrolysis products formed [SO_2 (9.6 mg), CF_3COOH (67.6 mg), and S (14.5 mg)] support the equation

$$2(CF_3COOS)_2 + 2H_2O \longrightarrow 4CF_3COOH + SO_2 + 3S$$

Results and Discussion

All of the new compounds are colorless, water-sensitive liquids at room temperature. The bis(perfluorocarboxylato) disulfides are thermally unstable and precipitate sulfur when they remain at room temperature for about 2 weeks. (This is consistent with the low stability of the carboxylato analogs.) They decompose rapidly and completely at 40° to perfluorocarboxylic anhydrides, sulfur, and sulfur dioxide and in contact with water to perfluorocarboxylic acids, sulfur, and sulfur dioxide. In contrast, the silanes are all stable at 100° and many were not decomposed even at temperatures in excess of 300°.

The infrared assignments for the disulfides follow the interpretation of the spectrum of $CF_3CO_2SCF_3$.[4] The carbonyl stretching absorptions reveal the strong inductive effect of the fluoroalkyl group, since a marked shift to lower frequency occurs from $(CF_3CO_2S)_2$ (ν 1812 cm^{-1}) to $(C_2F_5CO_2S)_2$ (ν 1780 cm^{-1}) to $(C_3F_7CO_2S)_2$ (ν 1765 cm^{-1}).

In the case of the perfluorocarboxylatomethylsilanes, detailed assignments of the trifluoroacetates are based on the interpretation of the infrared spectra of trifluoroacetic acid[5] and of metal trifluoroacetates[1] and the Raman spectrum of sodium trifluoroacetate.[6]

In an investigation of the C=O stretching band, Sartori and Weidenbruch[3] noted the progressive trend to lower frequency as the ionic character of a compound increased from $Si(O_2CCF_3)_4$ (ν 1815 cm^{-1}) to $Sn(O_2CCF_3)_4$ (ν 1750 cm^{-1}). A similar trend is also found in the series of $Ge(O_2CCF_3)_4$ (ν 1800 cm^{-1}), $CH_3Ge(O_2CCF_3)_3$ (ν 1770 cm^{-1}), $(CH_3)_2Ge(O_2CCF_3)_2$ (ν 1755 cm^{-1}),[7] and $(CH_3)_3GeO_2CCF_3$ (ν 1750 cm^{-1}).[8] In our work the trend again appears in the following series: $CH_3Si(O_2CCF_3)_3$ (ν 1800 cm^{-1}), $(CH_3)_2Si(O_2CCF_3)_2$ (ν 1790 cm^{-1}), $(CH_3)_3SiO_2CCF_3$ (ν 1774 cm^{-1}); $CH_3Si(O_2CC_2F_5)_3$ (ν 1790 cm^{-1}), $(CH_3)_2Si(O_2CC_2F_5)_2$ (ν 1770 cm^{-1}), $(CH_3)_3SiO_2CC_2F_5$ (ν 1768 cm^{-1}); $CH_3Si(O_2CC_3F_7)_3$ (ν 1790 cm^{-1}), $(CH_3)_2Si(O_2CC_3F_7)_2$ (ν 1770 cm^{-1}), $(CH_3)_3SiO_2CC_3F_7$ (ν 1766 cm^{-1}). The CO absorption frequency decreases as the perfluoroalkyl group changes from CF_3 to C_2F_5 to C_3F_7 and as the perfluorocarboxy groups are substituted by methyl groups. The former is a result of the decreased inductive effect of the perfluoroalkyl group and the latter is due to an increase in the polarity of the bonds to the remaining perfluorocarboxy groups.[7]

In the ^{19}F nmr spectra, the F–F coupling constants are in agreement with those reported in similar compounds.[9] Comparison of the chemical shifts of disulfides with those of anhydrides shows that the α-F atom resonances of the disulfides are shifted slightly to lower field. A downfield shift could result from the availability of empty low-lying sulfur orbitals to accept electrons thus decreasing the effective electron density associated with the α-F atoms. The appropriate area ratios are observed in every case. Nmr spectra of $(R_fCO_2)_nSi(CH_3)_{4-n}$ exhibit two major trends. First, the methyl group(s) attached to silicon tend to shift the ^{19}F resonance absorption to higher field (about 0.2 ppm per methyl group for α-F). Second, perfluorocarboxy group substitution causes the ^1H resonance to shift to lower field by about 0.3 ppm per perfluorocarboxy group. No effect on the ^1H spectrum is observed when the perfluorocarboxy group is changed from trifluoroacetoxy to pentafluoropropionoxy to heptafluorobutyroxy. No H–F coupling is observed.

In the mass spectra of the three disulfides, molecular ion peaks and fragments larger than the respective acyl moiety do not contribute to the spectra. For $(C_3F_7CO_2S)_2$, the *m/e* 64 (S_2^+, SO_2^+) species is the predominant peak; while for $(CF_3CO_2S)_2$ and $(C_2F_5CO_2S)_2$, CF_3^+ and $C_2F_5^+$ are the base peaks. Fragmentation patterns for all compounds contain some ions derived from rearrangement, *e.g.*, CFO^+, CF_2O^+, CF_3O^+, $C_2F_2O^+$, $C_2F_5O^+$, and $C_3F_7O^+$. For the silanes, when $n = 1$ or 2, the base peak is the species having *m/e* 77 corresponding to $(CH_3)_2SiF^+$, and when $n = 3$, the base peak is *m/e* 81 corresponding to $CH_3SiF_2^+$. This indicates that abstraction of fluorine by silicon is favored and agrees with the work of Miller[10] on pentafluorophenyl derivatives. The parent peak appears only in $CF_3CO_2Si(CH_3)_3$ (*m/e* 186) and $C_3F_7CO_2Si(CH_3)_3$ (*m/e* 286). The perfluoroacyl and perfluoroalkyl group peaks are found in every case and are increasingly intense as n becomes greater.

Sulfur dichloride with CF_3COOAg, C_2F_5COOAg, C_3F_7COOAg, or CF_3COOH failed to yield the monosulfide analogs, $(R_fCOO)_2S$. When these silver salts were treated with SCl_2 in a 2:1 ratio under the same conditions that have been described for the preparation of disulfides, only SO_2, anhydrides, and sometimes traces of perfluoroacyl chlorides were obtained after trap-to-trap or gas chromatographic (Kel-F no. 3 oil on Chromosorb P) separations. A very exothermic reaction occurred when a 1:1 ratio of CF_3CO_2Ag to SCl_2 was tried. After 30 min, separation yielded CF_3COCl (60%) and a trace of $(CF_3CO)_2O$, SO_2, and $SOCl_2$ as well as an unidentified yellow liquid. The ir spectrum of the yellow liquid is similar to trifluoroacetic anhydride except for an additional strong peak at 934 cm^{-1}. Work is continuing on this reaction.

Attempts to break the S–S bond by chlorination of bis(trifluoroacetato) disulfide with chlorine were made. Bis(trifluoroacetato) disulfide and Cl_2 in the ratios 1.2:1, 1:1.6, and 1:5 were used. After separation of the reaction mixture, the presence of CF_3COCl, $(CF_3CO)_2O$, SO_2, and a trace of CF_3Cl was shown by ir analysis. Unreacted chlorine which remained in all but the first reaction was identified also.

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