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Insertion of γ-SO_3 into Perfluoroalkyl- and Polyfluoroalkoxysilanes

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The reactions of γ-SO_3 with the silanes $R_fSi(CH_3)_3$ [R_f = CF_3 (**1**), C_6F_5 (**2**), $CF_2{=}CF$ (**3**), $CF_2{=}CFCH_2CH_2$ (**8**), and $R_fSi(n\text{-}C_3H_7)_3$ [R_f = $CF_2{=}CF$ (**7**), $CF_2{=}CFCH_2CH_2$ (**9**)] are reported. Several of the expected silyl sulfonates $R_fSO_2OSi(CH_3)_3$ [(R_f = CF_3 (**4**), C_6F_5 (**5**), $CF_2{=}CF$ (**6**)] are isolated. The polyfluoroalkenyltin compound $CF_2{=}CFCH_2CH_2Sn(CH_3)_3$ (**10**) is prepared, and also reacted with γ-SO_3; however, the tin sulfonate does not form. With fluorinated siloxanes $R_fOSi(CH_3)_3$ [R_f = $(CF_3)_2CH$ (**11**), $(CF_3)_2C(CH_3)$ (**12**), $(CF_3)_2C(C_6H_5)$ (**13**), CF_3CH_2 (**14**), $(CF_3)_3C$ (**15**), $(CH_2CF_2)_2$ (**16**)] reactions with γ-SO_3 give the respective silyl sulfate esters $R_fOSO_2OSi(CH_3)_3$ in yields up to 85%. The acids $CF_2{=}CFSO_3H$ (**25**) and $(HO_3SOCH_2CF_2)_2$ (**26**) are easily obtained by the hydrolysis of **6** and **22**, respectively. The compounds prepared in this study are characterized by ^1H, ^{19}F and ^{29}Si NMR, IR and mass spectrometry.

Introduction

Perfluoroalkanesulfonic acid esters, and in particular (perfluoroalkyl)silanesulfonates, are highly reactive Lewis acids and silylating reagents. They find wide application in synthetic organic chemistry,[1,2] and are commonly used as catalysts for many types of reactions,[3−5] as precursors for the preparation of surfactants, sulfonic acids and their derivatives,[6] and as strong silylating reagents.[7−9] To date, only a limited number of this interesting and highly useful class of compounds have been prepared.[1,2,10−12]

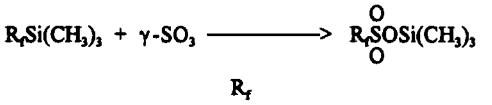
The most often reported method for the synthesis of fluorinated silyl sulfonates is the reaction of fluorosulfonic acids with alkylsilyl chlorides.[2,11,13] It is also well known that (fluoroalkyl)silanesulfonates are obtained from the reactions between silicon halides and silver sulfonates,[1] and from perfluoroalkyl anhydrides and hexamethyldisilazane.[14] Trimethylsilanesulfonates of polyfluorobenzenesulfonic acids are prepared via the sulfonation of polyfluorobenzenes with SO_3 followed by hydrolysis and reaction with trimethylsilyl chloride.[15]

As early as 1958, others reported the reactions of $SO_3$with a variety of organic silanes, as well as with organogermanium, -tin, and -lead compounds.[16−20] The highly electrophilic nature of SO_3 results in insertion reactions into M−C as well as M−O (M = Si, Ge, Sn, Pb) bonds under very mild conditions to leave the organic portion of the molecule intact. With nonfluorinated silyl halides,[17,19] siloxanes,[20] alkoxysilanes,[20] and aminosilanes,[17] the respective silanesulfonate or silyl sulfate esters are formed in high yields.

In this paper, we report the reactions of per- and polyfluoroalkyl-, alkenyl-, and -alkoxysilanes with SO_3. The reactions are generally synthetically useful, and provide an easy route to the preparation of a large variety of fluorinated silyl sulfate esters and silanesulfonates.

Results and Discussion

Perfluoroorganosilanes react readily with γ-SO_3 under very mild reaction conditions (−196 °C to 25 °C over 1 h in Freon 113).



$$R_fSi(CH_3)_3 + \gamma\text{-}SO_3 \longrightarrow R_f\overset{O}{\underset{O}{S}}OSi(CH_3)_3$$

	R_f	
1	CF_3	**4**
2	C_6F_5	**5**
3	$CF_2{=}CF$	**6**

Products **4**−**6** are stable colorless liquids that fume on exposure to air and react vigorously with water. They are formed in yields ranging from 69−83%.

In contrast to the reactions of other fluoroalkenes with γ-SO_3 to give β-fluorosultones,[21] the only product isolated from the reaction of **3** with SO_3 is the linear insertion product **6**. No evidence was found for the formation of a sultone from this vinylsilane. When $CF_2{=}CFSi(n\text{-}C_3H_7)_3$ (**7**) is reacted with γ-SO_3, neither a linear insertion product nor a β-sultone is formed. When excess γ-SO_3 is reacted with **6**, a β-sultone is not isolated, but nonvolatile materials which contain CF_3 and SO_2F functional groups (identified by ^{19}F NMR and infrared analysis) are found.

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When $CF_2{=}CFCH_2CH_2X$ [$X = Si(CH_3)_3$ (**8**), $Si(n\text{-}C_3H_7)_3$ (**9**), $Sn(CH_3)_3$ (**10**)] are combined with γ-SO_3, mixtures of products are obtained. Spectral analysis of these mixtures (infrared, NMR, mass spectral) indicates that both ring formation (sultone) and linear insertion reactions (silane(stannane)sulfonate) occur with all three polyfluoroalkenyl substrates. Infrared analysis shows typical carbonyl and symmetric and antisymmetric SO_2 stretching vibrations (1780 cm^{-1}, and 1450−1190 cm^{-1}, respectively). In the NMR spectra, ABX patterns are observed for the vinylic fluorine atoms, as well as the expected low field shifts in the CH_2 resonance region that result from linear SO_3 insertion. Sultone ring fluorine resonances (−80 to −90 ppm (CF_2O) and −145 to −150 ppm (CF)) are also readily apparent in the NMR spectra of the product mixtures. Mass spectral data are consistant with the formation of both β-sultones and silyl(stannyl)sulfonates from these substrates. Attempts to isolate and purify the compounds present in these mixtures result only in decomposition.

We find that poly and perfluoroorganosilylsulfuric acid esters are generally formed in excellent yield (up to 85%) by reacting γ-SO_3 with a wide variety of fluorinated siloxanes.

$$R_fOSi(CH_3)_3 + \gamma\text{-}SO_3 \xrightarrow[\text{-196 °C -> 25 °C}]{\text{Freon 113}} R_fOSO_2OSi(CH_3)_3$$

1 h

	R_f			R_f	
11	$(CF_3)_2CH$	**17**	**14**	CF_3CH_2	**20**
12	$(CF_3)_2C(CH_3)$	**18**	**15**	$(CF_3)_3C$	**21**
13	$(CF_3)_2C(C_6H_5)$	**19**	**16**	$\text{-}(CH_2CF_2)_2$	**22**

Products **17** through **22** are highly moisture sensitive, fuming distillable liquids. Although SO_3 is difficult to remove from the products formed, elemental analysis of the sulfonic acid esters **19**, **20**, and **22** indicates that SO_3 is absent. Purification by low temperature distillation, as well as the concomitant formation of bis-trimethylsilylsulfonate during the reaction provide for the preparation of pure products by this route.

With perfluoroalkoxysilanes, only **15** gives a sulfuric acid ester on reaction with γ-SO_3. With either $(CF_3)_2C(C_6F_5)OSi(CH_3)_3$ (**23**) or $(CF_3)_2CFOSi(CH_3)_3$ (**24**), SO_3 forms only decomposition products, e.g., $CF_3Si(CH_3)_3$, $(CH_3)_3SiF$, etc. In contrast to the nonfluorinated sulfuric acid esters reported earlier,[16−20] the per and polyfluorinated analogues that we have prepared are much less stable. Many of these undergo partial decomposition on standing at room temperature in glass over several days.

In their infrared spectra, both the sulfonic and sulfuric acid esters show typical antisymmetric SO_2 stretching vibrations around 1400 cm^{-1} and symmetric vibrations at approximately 1200 cm^{-1}. In all cases, the proton NMR spectra for the SO_3 insertion products show characteristic downfield shifts for the $(CH_3)_3Si$ group (from 0.1 to 0.25 ppm). A 3 ppm downfield shift is also observed in the ^{19}F NMR spectra of the fluorine atom that is alpha to the SO_3 in these compounds.

For **6**, the vinyl fluorine ABX resonance patterns are shifted more than 20 ppm downfield. The coupling constant between CF_a and CF_b of the CF_2 group in **6** decreases from 88 Hz to 34 Hz on insertion of SO_3.

A most useful tool for monitoring the progress of the SO_3 insertion reactions is ^{29}Si NMR. While the ^{29}Si chemical shifts for the silanes $R_fSi(CH_3)_3$ fall in the range from −5 to +5 ppm, the sulfonic acid esters give rise to ^{29}Si resonances around 40 ± 4 ppm. These results compare well with the chemical shift data reported for nonfluorinated siloxy-sulfur containing compounds.[22] The alkoxysilane starting materials ^{29}Si NMR resonances are found to occur in the region from 20 to 29 ppm. These shifts are also in good agreement with the values reported for nonfluorinated analogues.[22,23] With the exception of compound **8**, increasing fluorine content results in a consistantly larger downfield shift of the ^{29}Si resonances.[6,24,25] These shifts observed for both the sulfonic and sulfuric acid esters lie in the range from 39 to 43 ppm.

Generally, chemical ionization mass spectra give $M^+ - CH_3$ as the heaviest mass fragment observable for the silanes, silanesulfonates and silyl sulfates. However, molecular ions were observed in the spectra for **4**, **6**, **8**, **9**, and **20**. For the sulfonic and sulfuric acid esters, peaks at 80 (SO_3^+), 81 (HSO_3^+), 64 (SO_2^+) and 65 (HSO_2^+) are quite prominent.

The reactions of two compounds, **6** and **22**, with water give $CF_2{=}CFSO_3H$ (**25**) and $(HO_3SOCH_2CF_2)_2$ (**26**) respectively, in 70% yield. Interestingly, the vinyl group in $CF_2{=}CFSi(CH_3)_3$ (**3**) remains intact through sulfonation to give $CF_2{=}CFSO_3Si(CH_3)_3$(**6**), and hydrolysis to give $CF_2{=}CFSO_3H$ (**25**) under the reaction conditions used.

The preparation of unusual, and potentially highly useful polyfluorinated sulfonic acids by such a simple, and generally high yield technique, provides an extemely easy entrance into the synthesis of fluorinated sulfonic and/or sulfuric acids. The precursors are readily available or can be easily synthesized. The preparation of these materials by other methods is fraught with difficulties, particularly the preparation of pure polyfluorinated sulfonic acids.

Experimental Section

Materials. The starting materials $CF_3Si(CH_3)_3$ (**1**), $C_6F_5Si(CH_3)_3$ (**2**), $CF_2{=}CFSi(CH_3)_3$ (**3**) and $CF_2{=}CFSi(n\text{-}C_3H_7)_3$ (**7**) are synthesized by the literature methods.[26,27] The compounds CF_3Br, $CF_2{=}CFBr$, C_6F_5Br (PCR), $(n\text{-}C_3H_7)_3SiCl$, SO_3 (EM), $(CH_3)_3SnCl$, $(CH_3)_3SiCl$, and $CF_2{=}CFCH_2CH_2Br$ (Aldrich) are used as received.

General Procedures. Gases and volatile liquids are transferred and measured in a Pyrex glass vacuum line equipped with a Televac thermocouple and a Heise Bourdon tube gauge. Infrared spectra are recorded with a Perkin-Elmer Model 1710 FT-IR spectrometer in 10-cm gas cells or between KBr plates. A VG 7070HS mass spectrometer is used to obtain mass spectral data, and ^1H and ^{19}F NMR spectra are obtained with a Bruker AC 200 Fourier transform spectrometer operating at frequencies of 200.13 and 188.31 MHz, respectively. Chemical shifts upfield from $CFCl_3$ for fluorine are assigned negative values. The ^{29}Si NMR shifts are recorded with a IBM-NR 300 Fourier transform NMR spectrometer operating at 59.62 MHz with tetramethylsilane as reference. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Properties of $CF_2^{a,b}{=}CF^cSi(C_3H_7)_3$ (7). Previously unreported spectral data for (**7**)[27] are as follows. IR (film): 2960 vs, 2872 s, 1719 vs, 1475 m, 1463 m, 1410 m, 1377 m, 1281 vs, 1207 m, 1125 s, 1069 s, 1031 m, 1007 m, 896 m, 846 m, 810 m, 756 m, 716 m cm^{-1}. ^{19}F NMR: δ −87.0 (a, dd), −116.8 (b, dd), −197.8 (c, dd), $J_{a-b} = 68.5$ Hz, $J_{a-c} = 25.0$ Hz, $J_{b-c} = 117.0$ Hz. ^1H NMR: δ 0.67 (CH_2Si, m), 0.95 (CH_3, t), 1.4 (CH_2, m), $J_{CH_2-CH_3} = 7.1$ Hz.

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Preparation of $CF_2=CFCH_2CH_2R$ (R = $Si(CH_3)_3$ (8), $Si(n\text{-}C_3H_7)_3$ (9), and $Sn(CH_3)_3$ (10)). To a mixture of 30 mL of anhydrous ether and 0.5 g (0.02 mol) of Mg (activated with iodine) is added dropwise 4.0 g (0.021 mol) of $CF_2=CFCH_2CH_2Br$ at 20 °C with vigorous stirring. Stirring is continued for 6 h after addition of the alkene is complete. Then 0.021 mol of $(CH_3)_3SiCl$, $(CH_3)_3SnCl$ and $(n\text{-}C_3H_7)_3SiCl$ is added, and the mixture is stirred overnight. The ether layer is decanted from the solid residue and after removal of ether under vacuum, followed by distillation, a 52% yield of $CF_2=CFCH_2CH_2Si(CH_3)_3$ (**8**), a 41% yield of $CF_2=CFCH_2CH_2Si(n\text{-}C_3H_7)_3$ (**9**), and a 67% yield of $CF_2=CFCH_2CH_2Sn(CH_3)_3$ (**10**) are obtained. Compound (**8**) was identified by comparing its properties with the properties in the literature[27,28] (e.g., the material we prepared boils at 112 °C, and the literature value is 112−114 °C). Spectral data obtained for $CF_2^{a,b}=CF^c$-$CH_2^{d,e}CH_2Si(n\text{-}C_3H_7)_3$ (**9**) are as follows. IR (film): 2979 vs, 2938 s, 2872 s, 1799 vs, 1490 m, 1480 w, 1445 m, 1383 m, 1352 m, 1303 vs, 1246 vs, 1174 s, 1158 s, 1122 vs, 1087 s, 995 w, 866 w cm^{-1}. ^{19}F NMR: δ −106.2 (a, dd), −126.6 (b, dd), −175.4 (c, m), $J_{a-b} = 88.5$ Hz, $J_{a-c} = 30.1$ Hz, $J_{b-c} = 114.8$ Hz. ^1H NMR: δ 0.78 ($SiCH_2$, m), 0.96 (CH_3, m), 1.45 (CH_2, m), 1.6 (f, g, m), 2.3 (d, e, m). MS (EI) [*m/e* (species) intensity]: 267 (M^+) 0.8, 176 ($(C_3H_7)_3SiF^+$) 10.1, 133 ($(C_3H_7)_2SiF^+$) 100, 109 ($M^+ - Si(C_3H_7)_3$) 49.9, 91 ($C_3H_7SiF^+ + 1$) 83.2, 81 ($C_2F_3^+$) 49.7, 63 ($C_2F_2H^+$) 78.3. Spectral data obtained for $CF_2^{a,b}=CF^cCH_2^{d,e}CH_2^fSn(CH_3)_3$ (**10**) are as follows. IR (film): 2979 m, 2936 m, 2872 m, 1798 vs, 1245 vs, 1194 m, 1174 s, 1121 s, 1087 m, 784 vs cm^{-1}. ^{19}F NMR: δ −106.5 (a, dd), −125.0 (b, dd), −175.1 (c, m), $J_{a-b} = 84.7$ Hz, $J_{a-c} = 35.2$ Hz, $J_{b-c} = 108.6$ Hz. ^1H NMR: δ 0.59 ($Si(CH_3)_3$, s), 1.03 (d, e, m), 3.3 (f, g, m), $^2J_{^{119}Sn-H} = 56.0$ Hz. MS (CI) [*m/e* (species) intensity] (correct isotope ratios are observed): 257 ($M^+ - CH_3 - H$) 3.3, 229 ($M^+ + 1 - C_3H_9$) 67.6, 165 ($Sn(CH_3)_3^+ + 1$) 100, 109 ($M^+ - Sn(CH_3)_3$) 73.2, 95 ($CF_2=CFCH_2^+$) 96.7, 81 ($C_2F_3^+$) 49.8. Anal. Calcd for $C_7H_{13}F_3Sn$: C, 30.77; H, 4.76. Found: C, 30.47; H, 4.80.

Preparation and Properties of $R_fOSi(CH_3)_3$ (R_f = $(CF_3)_2CH$ (11), $(CF_3)_2C(CH_3)$ (12), $(CF_3)_2C(C_6H_5)$ (13), CF_3CH_2 (14)), and $(CF_2CH_2OSi(CH_3)_3)_2$ (16). These siloxanes are prepared by a modified literature method.[29] The alcohol, and hexamethyldisilazane (in a ratio of 1 to 0.8, respectively) are placed in a 50 mL flask fitted with a reflux condenser and a magnetic stirrer. The mixture is refluxed with stirring for 12 h. Distillation gives 50 to 80% yields of the corresponding siloxanes. Siloxanes **11**, **14**, and **16** were identified by comparison of spectral data with that previously published.[12,29−31] Spectral data obtained for $(CF_3)_2C(CH_3)OSi(CH_3)_3$ (**12**) (bp 99 °C) are as follows. IR (film): 3014 m, 2965 s, 2907 m, 1463 s, 1410 m, 1390 s, 1310 vs, 1299 vs, 1150 vs, 1122 vs, 1080 vs, 1007 vs, 935 s, 857 vs, 761 vs, 702 vs, 632 s, 621 m, 554 m cm^{-1}. ^{19}F NMR: δ −79.8 (CF_3, q), $J_{CF_3-CH_3} = 1.0$ Hz. ^1H NMR: δ 0.21 (CH_3Si, s), 1.57 (CH_3, m). MS (EI) [*m/e* (species) intensity]: 181 ($M^+ - Si(CH_3)_3$) 0.6, 147 ($C_4F_5H_4^+$) 25.4, 143 ($C_4F_5^+$) 51.4, 123 ($C_4F_3H_2O^+$) 96.0, 115 ($C_5H_{11}OSi^+$) 82.3, 95 ($C_3F_3H_2^+$) 19.9, 77 ($(CH_3)_2SiF^+$) 100, 73 ($(CH_3)_3Si^+$) 91.2. Previously unreported spectral data for $(CF_3)_2C(C_6H_5)OSi(CH_3)_3$ (**13**)[32] (bp 29 °C/0.03 Torr) are as follows. IR (film): 3070 w, 2909 w, 1961 w, 1890 w, 1813 w, 1605 w, 1502 m, 1453 m, 1412 m, 1323 s, 1300 vs, 1257 vs, 1209 vs, 1153 vs, 1109 m, 1084 s, 1039 m, 970 vs, 945 vs, 920 s, 879 vs, 850 vs, 814 m, 762 vs, 746 m, 715 vs, 696 s, 664 s, 633 m cm^{-1}. ^{19}F NMR: δ −73.9 (CF_3, s). ^1H NMR: δ 0.26 (CH_3, s), 7.4−7.7 (C_6H_5, m). MS (EI) [*m/e* (species) intensity]: 301 ($M^+ - CH_3$) 2.9, 247 ($M^+ - CF_3$) 3.5, 205 ($C_9F_4H_5O^+$) 100, 177 ($(CH_3)_3SiOC_6H_4^+$) 49.2, 158 ($M^+ - (CH_3)_3SiOCF_3$) 8.5, 127 ($C_7F_2H_5^+$) 38.4, 105 ($C_6H_5CO^+$) 40.1, 77 ($C_6H_5^+$) 56.8, 73 ($(CH_3)_3Si^+$) 27.5.

Preparation of $(CF_3)_3COSi(CH_3)_3$ (15) and $(CF_3)_2C(C_6F_5)OSi(CH_3)_3$ (23). Into a mixture of 1.0 g (0.017 mol) of KF and 4 mL of acetonitrile in a 50 mL flask equipped with a magnetic stirrer and a Teflon stopcock are condensed 0.015 mol of $(CF_3)_2C=O$ and 0.015 mol of the appropriate silane (either $CF_3Si(CH_3)_3$ or $C_6F_5Si(CH_3)_3$). The mixture is allowed to warm to room temperature and stirred vigorously for 15 h. After all volatile materials are removed, 0.02 mol of $(CH_3)_3SiCl$ was added. Reaction occurred at room temperature in 2 h to give a 73% yield of $(CF_3)_3COSi(CH_3)_3$(**15**) and a 38% yield of $(CF_3)_2C(C_6F_5)OSi(CH_3)_3$ (**23**) after distillation. The IR and NMR data obtained for **15** and **23** agree well with the previously published spectral data.[33−39]

General Procedure for the Preparation of Sulfonates and Sulfates from Silanes and Siloxanes. Into a round-bottomed flask equipped with a Teflon stopcock and a magnetic stirrer is placed 0.026 mol of freshly distilled SO_3 in Freon 113. While holding the flask at −196 °C, air is removed and 0.02 mol of the appropriate silane or siloxane is condensed into the flask. The reaction mixture is allowed to warm slowly to room temperature. After 15 to 30 min, all volatile materials are removed under vacuum. Low temperature vacuum distillation gives the desired sulfonates and sulfates in yields ranging from 70 to 85%. In most cases, hexamethyldisiloxane and bis(trimethylsilyl) sulfate are identified as byproducts. It should be noted that many of the reactions are very exothermic, and an ice bath may be necessary to control the reaction.

Properties of $CF_3SO_2OSi(CH_3)_3$ (4), and $C_6F_5SO_2OSi(CH_3)_3$ (5). (Trimethylsilyl)trifluoromethanesulfonate (**4**) and (trimethylsilyl)pentafluorobenzenesulfonate (**5**) are prepared in 83 and 69% yields, respectively, by the reaction of the appropriate silane with freshly distilled SO_3 as described above. The infrared and NMR (^{19}F, ^1H and ^{29}Si) spectral data obtained for these compounds are in good agreement with the spectral data reported in the literature.[10,11,15,23,34]

Properties of $CF_2^{a,b}=CF^cSO_2OSi(CH_3)_3$ (6). Spectral data obtained for $CF_2=CFSO_2OSi(CH_3)_3$ (**6**) (bp 48 °C/0.03 Torr, 72% yield) are as follows. IR (film): 2970 w, 1759 s, 1442 s, 1391 s, 1262 vs, 1246 vs, 1195 vs, 1085 s, 974 s, 855 vs, 769 m, 613 s cm^{-1}. ^{19}F NMR: δ −88.0 (a, dd), −95.0 (b, dd), −176.5 (c, dd), $J_{a-b} = 34.4$ Hz, $J_{a-c} = 40.2$ Hz, $J_{B-C} = 116.5$ Hz. ^1H NMR: δ 0.43 (CH_3, s). ^{29}Si NMR: δ 36.2 (s). MS (CI) [*m/e* (species) intensity]: 235 ($M^+ + 1$) 1.6, 219 $M^+ - CH_3$) 15.3, 147 ($C_2F_3SO_2H^+ + 1$) 100, 93 ($(CH_3)_3SiF^+ + 1$) 89.1, 77 ($(CH_3)_2SiF^+$) 82.0, 75 ($(CH_3)_2SiO^+ + 1$) 51.0, 73 ($(CH_3)_3Si^+$) 95.0, 65 ($SO_2^+ + 1$) 91.2.

Properties of $(CF_3)_2CHOSO_2OSi(CH_3)_3$ (17). Spectral data obtained for $(CF_3)_2CHOSO_2OSi(CH_3)_3$ (**17**) (bp = 26 °C/0.025 Torr, 79% yield) are as follows. IR (KBr disk): 2977 m, 1370 vs, 1245 vs, 1112 vs, 980 vs, 857 vs, 769 s, 737 m, 689 vs, 613 s, 543 m, 530 m cm^{-1}. ^{19}F NMR: δ −73.8 (CF_3, d), $J_{CH-CF_3} = 6.95$ Hz. ^1H NMR: δ 0.4 ($SiCH_3$, s), 5.16 (CH, spt). ^{29}Si NMR: δ 42.3 (s). MS (EI) [*m/e* (species) intensity]: 305 ($M^+ - CH_3$) 1.0, 225 ($C_6FH_{10}O_4SSi^+$) 4.4, 169 ($(CH_3)_3SiOSO_2O^+$) 42.1, 151 ($(CF_3)_2CH^+$) 7.3, 147 ($CF_3CHOSO^+ + 1$) 100, 129 (CF_3COS^+) 98.0, 101 ($C_2F_4H^+$) 68.2, 99 ($CF_3CHO^+ + 1$) 97.0, 97 (CF_3CO^+) 24.8, 93 ($(CH_3)_3SiF^+ + 1$) 95.0, 73 ($(CH_3)_3Si^+$) 87.0. Anal. Calcd for $C_6F_6H_{10}O_4SSi$: C, 22.51; H, 3.12; S, 10.01. Found: C, 22.80; H, 3.22; S, 9.80.

Properties of $(CF_3)_2C(CH_3)OSO_2OSi(CH_3)_3$ (18). Spectral data obtained for $(CF_3)_2C(CH_3)OSO_2OSi(CH_3)_3$ (**18**) (bp 31 °C/0.025 Torr, 85% yield) are as follows. IR (KBr disk): 3028 w, 2973 m, 2911 w, 1461 s, 1386 vs, 1304 vs, 1245 vs, 1127 s, 1088 s, 995 s, 867 vs, 769 m, 754 m, 703 s, 651 m, 611 s, 538 s, 499 m cm^{-1}. ^{19}F NMR: δ −77.6 (CF_3, q). ^1H NMR: δ 0.4 (CH_3Si, s), 2.02 (CH_3, spt), $J_{CF_3-CH_3} = 1.0$ Hz. ^{29}Si NMR: δ 41.2 (s). MS (CI) [*m/e* (species) intensity]: 281 ($M^+ - CH_3 - 2F$) 5.0, 183 ($(CF_3)_2C(CH_3)OH^+ + 1$) 16.3, 163 ($(CF_3)CF_2C(CH_3)O^+ + 1$) 43.7, 147 ($(CH_3)_3SiOSi(CH_3)_2^+$) 26.9, 143 ($(CF_2)_2CCH_3O^+$) 77.0, 123 ($C_2H_3SO_4^+$) 7.1, 115 ($C_3F_4H_3^+$) 100, 113 ($CF_3C(CH_3)OH^+$) 49.7, 81 ($SO_3^+ + 1$) 5.7, 77 ($(CH_3)_2SiF^+$) 98.0, 73 ($(CH_3)_3Si^+$) 55.0, 69 (CF_3^+) 26.2, 65 ($SO_2^+ + 1$) 53.1.

Properties of $(CF_3)_2C(C_6H_5)OSO_2OSi(CH_3)_3$ (19). Spectral data obtained for $(CF_3)_2C(C_6H_5)OSO_2Si(CH_3)_3$ (**19**) (bp 63 °C/0.02 Torr,

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82% yield) are as follows. IR (KBr disk): 3072 w, 2969 m, 1503 m, 1455 s, 1403 vs, 1236 vs, 1057 s, 976 vs, 947 s, 862 vs, 825 vs, 628 s, 553 m, 516 m. ^{19}F NMR: δ −70.7 (CF_3, d), $J_{CF_3-CH} = 11.3$ Hz. ^{1}H NMR: δ 0.46 ($SiCH_3$, s), 7.44−7.74 (C_6H_5, m). ^{29}Si NMR: δ 40.7 (s). MS (CI) [*m/e* (species) intensity]: 327 ($M^+ - CF_3$) 0.5, 244 ($(CF_3)_2C(C_6H_5)O^+ + 1$) 6.8, 227 ($(CF_3)_2CC_6H_5^+$) 100, 205 ($C_8F_4H_5$-CO^+) 75.1, 175 ($CF_3(C_6H_5)CO^+ + 1$) 94.8, 147 ($(CH_3)_3SiOSi(CH_3)_2^+$) 31.8, 105 ($C_6H_5CO^+$) 89.1, 77 ($C_6H_5^+$) 55.0, 73 ($(CH_3)_3Si^+$) 33.4. Anal. Calcd for $C_{12}F_6H_{14}O_4SSi$: C, 36.36; H, 3.53; S, 8.09. Found: C, 36.24; H, 3.57; S, 7.90.

Properties of $CF_3CH_2OSO_2OSi(CH_3)_3$ (20). Spectral data obtained for $CF_3CH_2OSO_2OSi(CH_3)_3$ (**20**) (bp 28 °C/0.015 Torr, 80% yield) are as follows. IR (KBr disk): 2975 m, 1388 vs, 1287 vs, 1263 s, 1187 vs, 1058 s, 973 s, 824 vs, 796 s, 689 m, 662 m, 623 m, 577 s, 549 m cm^{-1}. ^{19}F NMR: δ −74.5 (CF_3, t), $J_{CF_3-CH_2} = 6.7$ Hz. ^{1}H NMR: δ 0.43 ($SiCH_3$, s), 4.6 (CH_2, d). ^{29}Si NMR: δ 41.3 (s); MS (CI) [*m/e* (species) intensity]: 253 ($M^+ + 1$) 0.8, 181 ($M^+ + 2 - Si(CH_3)_3$) 1.1, 147 ($CF_3CH_2OSO^+$) 51.2, 101 ($CF_3CH_2OH^+ + 1$) 14.7, 81 ($SO_3^+ + 1$) 83.6, 77 ($Si(CH_3)_2F^+$) 86.1, 73 ($(CH_3)_3Si^+$) 100. Anal. Calcd for $C_5F_3H_{11}O_4SSi$: C, 23.81; H, 4.36; S, 12.71. Found: C, 23.91; H, 4.16; S, 12.36.

Properties of $(CF_3)_3COSO_2OSi(CH_3)_3$ (21). Decomposition of $(CF_3)_3COSO_2OSi(CH_3)_3$ (**21**) occurs rapidly at room temperature to give $(CH_3)_3SiF$, $(CH_3)_3SiCF_3$, $(CH_3)_3SiOSO_2OSi(CH_3)_3$ and an unidentified nonvolatile residue. Spectral data obtained for **21** are as follows. IR (KBr disk): 2972 s, 2911 m, 1423 vs, 1252 vs, 1103 s, 995 vs, 859 vs, 748 s, 730 m, 681 m, 623 s, 580 s, 552 s, 458 m cm^{-1}. ^{19}F NMR: δ −70.1 (CF_3, s). ^{1}H NMR: δ 0.43 (CH_3Si, s). ^{29}Si NMR: δ 43.6 (s).

Properties of $[(CH_3)_3SiOSO_2OCH_2CF_2]_2$ (22). Spectral data obtained for $[(CH_3)_3SiOSO_2OCH_2CF_2]_2$ (**22**) (bp = 155 °C/0.02 Torr, 69% yield) are as follows. IR (KBr disk): 2971 m, 1456 m, 1387 vs, 1263 vs, 1145 s, 1051 vs, 1024 vs, 972 vs, 844 vs, 770 s, 687 m, 592 m, 572 m, 522 m cm^{-1}. ^{19}F NMR: δ −121.3 (CF_2, s). ^{1}H NMR: δ 0.28 ($(CH_3)_3Si$, s), 4.5 (CH_2, m). ^{29}Si NMR: δ 39.7 (s). MS (CI) [*m/e* (species) intensity]: 295 ($(CH_3)_3SiOSO_2OCHCF_2CF_2CH^+$) 7.8, 281 ($(CH_3)_2CH_2SiOSO_2OCHCF_2CF_2^+$) 24.6, 267 ($(CH_3)_2SiOSO_2$-$OCHCF_2CF_2^+$) 1.1, 221 ($C_4F_4HO_4S^+$) 43.0, 207 ($CHCF_2CF_2CH_2OSO_2^+$) 26.9, 147 ($(CH_3)_3SiOSi(CH_3)_2^+$) 100, 125 ($OCH_2CFCF_2CH_2^+$) 18.5, 74 ($(CH_3)_3Si^+ + 1$) 64.3. Anal. Calcd for $C_{10}F_4H_{22}O_8S_2Si_2$: C, 25.74; H, 4.71; S, 13.74. Found: C, 24.64; H, 4.75; S, 13.09.

Preparation and Properties of $CF_2{=}CFSO_3H$ (25). The reaction of $CF_2{=}CFSO_2OSi(CH_3)_3$ (**6**) (0.05 mol) with excess water is carried out in a 50 mL round-bottomed flask at room temperature. The aqueous layer is separated from $(CH_3)_3SiOSi(CH_3)_3$, the water is removed, and the acid **25** is obtained in 72% yield. Spectral data obtained for $CF_2^{a,b}{=}CF^cSO_3H$ (**25**) are as follows: ^{19}F NMR: δ −94.9 (a, dd), −101.5 (b, dd), −176.3 (c, dd), $J_{a-b} = 58.2$ Hz, $J_{a-c} = 38.5$ Hz, $J_{b-c} = 118.6$ Hz. ^{1}H NMR: δ 12.2 (s). MS (CI) [*m/e* (species) intensity]: 163 ($M^+ + 1$) 12.1, 145 ($M^+ - OH$) 4.0, 81 ($CF_2{=}CF^+$) 100, 65 ($SO_2^+ + 1$) 99.0, 64 (SO_2^+) 98.0, 63 (CFS^+) 98.0.

Preparation and Properties of $[HO_3SOCH_2CF_2]_2$ (26). When the silyl sulfate $[(CH_3)_3SiOSO_2OCH_2CF_2]_2$ (**22**) (0.05 mol) is treated with excess water, a rapid exothermic reaction occurs to give $(CH_3)_3SiOSi$-$(CH_3)_3$and the acid (**26**) (isolated from the aqueous layer in 68% yield). Spectral data obtained for **26** are as follows. ^{19}F NMR: δ −123.7 (CF_2, t), $J_{CF_2-CH_2} = 1.9$ Hz. ^{1}H NMR: δ 3.9 (CH_2, t), 8.8 (OH, s). MS (CI) [*m/e* (species) intensity]: 305 ($M^+ - OH$) 3.5, 207 ($CHCF_2CF_2$-$CH_2OSO_2^+$) 81.3, 125 ($CH_2CFCF_2CH_2O^+$) 27.5, 111 ($CFCF_2CH_2O^+$) 34.1, 81 ($SO_3^+ + 1$) 100.

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