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Reactions of Iodoperfluoro-3-oxaundecylsulfonyl Fluoride with Halohydrocarbons through Organometallic Intermediates

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Iodoperfluoro-3-oxaundecylsulfonyl fluoride reacted with Cu, Zn, or Grignard reagent to produce the respective organometallic species, which was further reacted with halohydrocarbons 4-ClC_6H_4Br, 4-$CH_3C(O)C_6H_4Br$, $CH_2{=}CHCH_2Br$, and CH_3SiCl, to give derivatives of $R(CF_2)_8O(CF_2)_2SO_2F$ [R = 4-ClC_6H_4 (**7**), 4-$CH_3C(O)C_6H_4$ (**5**), $CH_2{=}CHCH_2$ (**3**), and CH_3Si (**13**)], in moderate yields. The compounds were characterized by NMR, infrared, and mass spectroscopy as well as elemental analyses. The addition product of trichlorosilane and **3** was reacted with sodium methoxide to give (12H,12H,13H,13H,14H,14H-hexahydroperfluoro-3-oxatetradecyl methylsulfonate) trimethoxysilane, [$(CH_3O)_3Si(CH_2)_3(CF_2)_8O(CF_2)_2SO_3Me$] (**11**).

Introduction

The sulfonyl fluorides have applications as ion exchange resins, as surfactants, and more recently as useful functionality in dye compositions.[1−5] Hence, there is continued interest in developing methods for synthesis of new compounds containing this functional group. Earlier, treatment of aryl halides with difluoroiodomethanefluorosulfonyl fluoride, ICF_2SO_2F, in the presence of copper in dimethylformamide (DMF) at 60−80 °C for 6−7 h gave high yields of the trifluomethylated aryl products, along with white copper(I) iodide.[6,7] Also, aroyl chloride reacted with ICF_2SO_2F in the presence of copper to give trifluoromethyl aryl ketones in moderate yields.[6,7]

$$ICF_2SO_2F + ArX \xrightarrow[60-80\ ^\circ C/6-7\ h]{Cu/DMF} ArCF_3 + SO_2$$

$$ICF_2SO_2F + ArCOCl \xrightarrow{Cu} ArCOCF_3 + ArCOF + HCF_2Cl + Cl$$

Polyfluoroalkoxysulfonyl fluorides are conveniently prepared from the reaction of sultones, $\overline{CFXCF_2OS}O_2$, with haloalkanes in the presence of a metal fluoride.[8,9] Reaction of a metal fluoride with the sultone generated the respective perfluoalkoxy salt, $FSO_2CF_2CF_2O^-M^+$, that subsequently reacted with several halocarbon substrates, as shown in Scheme 1. The products from these reactions were obtained in moderate yields.[8,9]

In these examples an oxo linkage of the perfluoroalkoxysulfonyl fluoride to the nonfluorinated or polyfluorinated organic groups is a common feature. The number of carbon atoms in the sultone and subsequently in the perfluoroalkoxysulfonyl fluoride is always fewer than four.[8,9] A longer perfluoroalkyl chain and a methylene linkage rather than an oxo linkage between the fluorinated and nonfluorinated components are useful for enhanced thermal properties of polyfluorinated organic compounds.[10] The polyfluoroalkoxysulfonyl fluorides derived from sultones do not have either of the two features, i.e., a long perfluoroalkyl chain or a methylene linkage to an organic group, except when benzyl halide was the starting material.[8,9] Synthesis of compounds containing C−C bonds from a methylene linkage between a perfluorooxaalkylsulfonyl fluoride and nonfluorinated organic groups may be achieved by starting from a haloperfluoroalkylsulfonyl fluoride, such as iodoperfluoro-3-oxaundecylsulfonyl fluoride (**1**), that contains a long perfluoroalkyl ether chain and is commercially available, and active halocarbons. Compound **1** is an excellent starting material that allows the exploration of cross coupling at the CF_2- moiety with nonfluorinated organic compounds through the use of traditional methods such as organometallic intermediates. Reactions involving Cu, Zn, or Grignard organometallic intermediates derived from haloperfluoroalkanes must be carefully temperature-controlled, and the S−F bond in the $-SO_2F$ functionality

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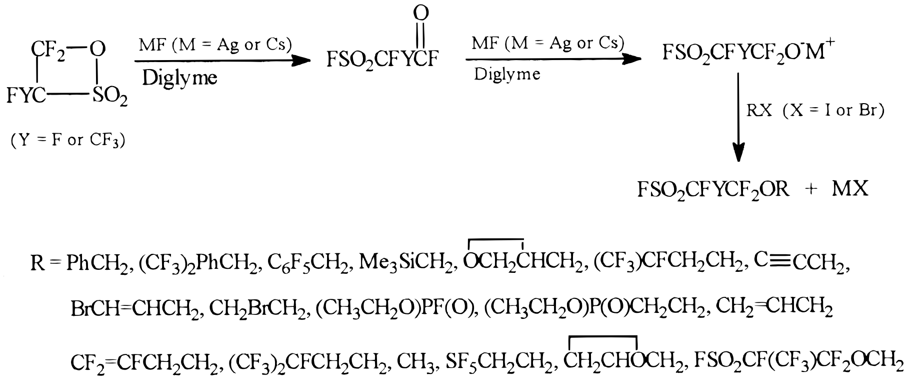
Scheme 1



of **1** is very sensitive to nucleophilic attack.[11,12] This paper extends the synthetic methodology of polyfluorooxaalkylsulfonyl fluorides via in situ organometallic intermediates.

Results and Discussion

The reactions of **1** with 2 equiv of Cu in DMSO resulted in a white organocopper(I) intermediate, which was either formed in the presence of another halocarbon compound or preformed in situ for further reaction.[13] The organocopper intermediate **2** formed in an almost quantitative conversion when reaction proceeded in either diethyl ether or dimethyl sulfoxide (DMSO) at about 80 °C for 48 h. The conversion was accompanied by a change in color from the shining brown of the copper-bronze powder to the white suspension of the Cu^I intermediate.[13] Addition of allyl bromide to **2** according to path A (Scheme 2) resulted in the formation of allyl-perfluoro-3-oxaundecylsulfonyl fluoride, **3**, in 40% yield.

When **2** was not preformed before attempting the reaction with allyl bromide, the allylic derivative did not form. For example, direct interaction between the two halides, **1** and $CH_2{=}CHCH_2Br$, in the presence of Cu followed path B and resulted in the diolefin $[CH_2{=}CHCH_2]_2$ (**4**) in more than 80% yield (based on the amount of starting allyl bromide) via a self-coupling reaction. Allyl bromide was obviously more reactive toward the copper-bronze powder than **1**.

The complete disappearance of the fluorine signal of ICF_2- at −59.6 ppm in the ^{19}F NMR spectra of derivatives was normally indicative of loss of the $I-CF_2$ bond and the subsequent formation of a CF_2-CH_2 linkage. In the ^{19}F NMR spectrum of **3**, the fluorine atoms of the $-SO_2F$ and $-CF_2$-OCF_2- groups have characteristic signals at 44.8 and −82.4 ppm, respectively. They were used to confirm the presence of the perfluorinated chain under our synthetic and workup conditions. In addition to elemental analysis, the molecular ion was observed in the mass spectrum at $m/e = 641$ as well as a signal at $m/e = 621$ ($M^+ - HF$) to characterize the compound. The ^1H and ^{13}C NMR spectra were also used for the characterization of **3**. The position and multiplicity of the γ-methylene protons changed from a doublet at 3.93 ppm in the spectrum of allyl bromide to a triplet of doublets at 2.80 ppm in **3** due to $^1H-^{19}F$ coupling.

Further evidence for formation of the $-CH_2-CF_2-$ bond was obtained from the evaluation of the $^{13}C\{^1H\}$ and $^{13}C\{F\}$ NMR spectra of **3**. The $^{13}C\{^1H\}$ NMR chemical shift for the methylene carbon in $-CH_2-Br$ was observed as a singlet at 33.1 ppm. After the transformation to $-CH_2-CF_2-$, the signal was shifted downfield, appeared as a triplet at 36.2 ppm, and was resolved into a singlet in the $^{13}C\{^{19}F\}$ spectrum, confirming the $-CF_2-CH_2-$ bond.

Two nonfluorinated haloaromatic substrates were reacted with **1** along path B to give the respective polyfluoro products **5** and **7**. With sustained stirring at about 80 °C the organocopper (I) intermediate that is formed in situ is simultaneously trapped by the aromatic halide. 4-Bromoacetophenone and 4-bromo-1-chlorobenzene reacted with **1** to give the respective products **5** and **7**, in 60−65% yields (Scheme 2).

Molecular ions were observed in the mass spectra of compounds **5** and **7** at $m/z = 718$ and $m/z = 710.5$, respectively. Styrene and allyl aromatic derivatives of **5** and **7** could serve as monomers for polymer synthesis, and attempts were made to derivatize both compounds.[10,12,14] In earlier literature, the acetyl substituent in 4-perfluoroalkyl-1-acetophenones was converted to the respective carbinol by the careful low-temperature introduction of common reducing agents such as sodium borohydride or lithium aluminum hydride.[12] However, the attempted reaction of **5** with either of these reagents did not produce the expected carbinol (Scheme 2).

The Grignard reagent $ClMgC_6H_4R_fSO_2F$ (**8**) formed in THF at −15 °C reacted with allyl bromide at −15 °C for 3 h to produce 4′-(perfluoro-3-oxaundecylsulfonyl fluoride)-1-allyl benzene (**9**), which was distilled at 97 °C/0.5 mm, in 52% yield. This compound was characterized on the basis of its elemental analysis, NMR, and high-resolution mass spectral data.

It was of interest to investigate the reaction of the organozinc(II) intermediate (**12**) with allyl bromide in order to obtain better yields in the synthesis of **3**. A clear colorless solution (1.0 M) of **12** was generated in situ by reaction of equimolar amounts of **1** and the Zn−Cu couple in dry THF at room temperature under nitrogen. The organozinc(II) compound **12** was stable at 25 °C and reacted with allyl bromide to produce **3** in about 60% yield.

Since alkoxy silane derivatives of polyfluorinated olefins do demonstrate good surface modification properties, it was thought worthwhile to extend our work in this direction.[13,14] Therefore, we found that reaction of equimolar amounts of **3** with trichlorosilane gave trichloro(12H,12H,13H,13H,14H,14H-hexahydroperfluoro-3-oxatetradecylsulfonyl fluoride)silane, $Cl_3Si(CH_2)_3(CF_2)_8O(CF_2)_2SO_2F$ (**10**) as a white waxy solid, bp 108

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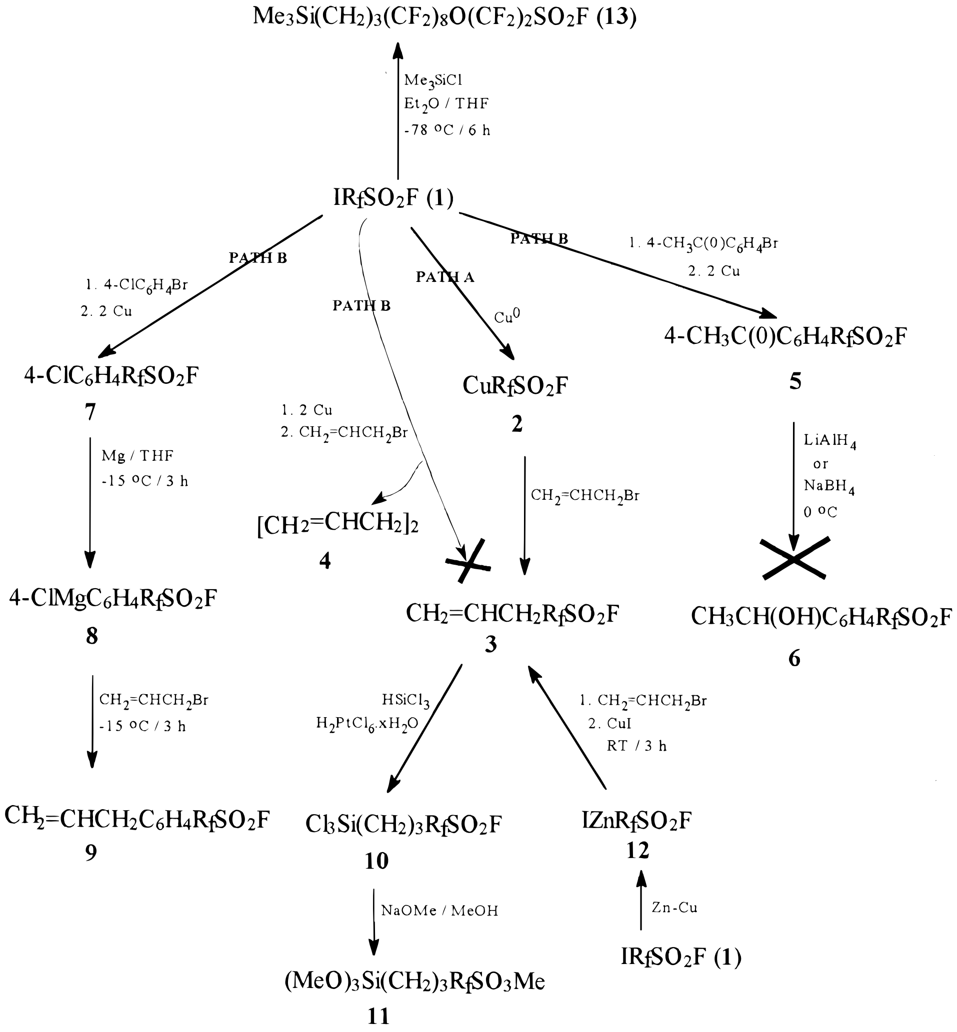
Scheme 2



$R_fSO_2F = (CF_2CF_2)_4OCF_2CF_2SO_2F$

°C/3 mm, in 85% yield. Compound **10** was very moisture sensitive, hydrolyzing to form fluorinated siloxanes. NMR spectroscopy confirmed that the addition reaction had occurred by hydrosilylation. Careful addition of sodium methoxide to **11** in methanol gave the colorless liquid (12H,12H,13H,13H,14H,-14H-hexahydroperfluoro-3-oxatetradecylsulfonyl fluoride) trimethoxysilane, [$(CH_3O)_3Si(CH_2)_3(CF_2)_8O(CF_2)_2SO_3Me$] (**11**) (bp 95 °C/0.6 mm), in 72% yield. The surface properties of **11** are under study.

Hydrolysis with concentrated HCl at −50 °C of the product formed by addition of ethylmagnesium bromide to a mixture of **1** and Me_3SiCl in a 3:1 tetrahydrofuran:diethyl ether solvent mixture at −78 °C resulted in the formation of $Me_3Si(CF_2CF_2)_4OCF_2CF_2SO_2F$ (**13**). Compound **13** was surprisingly stable and distilled without decomposition at 98 °C/ 0.25 mm in 44% yield. The formation of Me_3SiF instead of **13** was a likely possibility because of the driving force of the Si−F bond. Also, the $-SO_2F$ functional group contains a polar S−F bond that is susceptible to nucleophiles. This may explain the low yield obtained and also show that the reactivity of the $-SO_2F$ functionality with Grignard reagent is controllable at low temperatures.

Elemental analysis and a combination of evidence from its ^1H, ^{13}C, ^{19}F, and ^{29}Si and $^{29}Si\{F\}$ NMR and mass spectra aided in the characterization of compound **13**. The ^{29}Si NMR was particularly useful, showing a triplet at 9.3 ppm resulting from $^2J_{Si-F}$ coupling with the neighboring $Si-CF_2$ fluorine atoms ($^2J_{Si-F} = -57.5$ Hz). The coupling constant falls within the −14 to −91 Hz range reported for $^2J_{Si-F}$ in the literature.[15] The fluorine-decoupled $^{29}Si\{F\}$ NMR spectrum of **13** showed only a single band at the same frequency. The molecular ion was observed in the mass spectrum of **13** at $m/e = 672$, as well as other characteristic signals for fragments such as 599 [$M^+ - Me_3Si$], 489 [$M^+ - CF_2CF_2SO_2F$], 183 [$CF_2CF_2SO_2F^+$], and 73 [Me_3Si^+]. This compound was synthesized as a thermally stable reagent with potential for transfer of perfluoro-3-oxadecylsulfonyl fluoride to organic substrates by a mechanism similar to the one involved in the well-known nucleophilic transfer of CF_3^- from Me_3SiCF_3.[16] Its usefulness for this function is currently being evaluated.

Experimental Section

General. The solvents [tetrahydrofuran (THF), diethyl ether, and dichloromethane] were dried with sodium and distilled over purple solution of benzophenone. Dimethyl sulfoxide (DMSO) was dried over

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calcium hydride. A standard Schlenk line system was used for handling the reactions under anaerobic (dry nitrogen) conditions. All reactions and manipulations were carried out in an atmosphere of dry nitrogen. Infrared spectra were recorded on a Bio-Rad FTS 3000 Excalibur series infrared spectrometer as neat liquids between KBr plates. ^{1}H, ^{13}C or [^{13}C{F}], ^{19}F, and ^{29}Si NMR spectra were obtained on a Bruker AMX NMR instrument (200, 300, or 500 MHz) at 200, 50, 188, and 59 MHz, respectively, by using $CDCl_3$ as locking solvent except where otherwise indicated. Chemical shifts were reported with respect to Me_4Si or $CFCl_3$. Routine mass spectra (EI) were obtained from a Finnigan GCQ spectrometer. High-resolution mass data were obtained on a JEOL JMS-AX505HA mass spectrometer connected with a Hewlett-Packard HP 6890 series GC system. The chemicals were purchased from Aldrich and used without further purification.

General Procedures. Path A: Procedure for 3. The mixture of iodoperfluoro-3-oxaundecylsulfonyl fluoride (**1**) (15 g, 20.69 mmol) and a brown dispersion of copper-bronze (2.64 g, 41.58 mmol) in dry diethyl ether was carefully stirred and warmed gently to 80 °C in a 100 mL three-neck flask fitted with a reflux condenser and nitrogen gas inlet. Over a 48 h period a white suspension of the fluorinated organocopper(I) intermediate (**2**) formed in situ. A 10 mL diethyl ether solution of allyl bromide (1.75 g, 22.72 mmol) was added dropwise from a syringe while an anaerobic reaction atmosphere was maintained. The reaction of allyl bromide with **2** was spontaneous, and the flask contents turned dirty green while stirring continued at the same temperature for 6 h. After cooling, diethyl ether was evaporated under vacuum. Fractional distillation of the crude product gave allylperfluoro-3-oxaundecylsulfonyl fluoride (**3**) as a clear colorless liquid (bp 88 °C/0.25 mm) in 40% yield. IR: 1276 cm^{-1} $\nu_a(CH_2{=}CH)$ and 1182 cm^{-1} $\nu_s(CH_2{=}CH)$. NMR ($CDCl_3$): ^{1}H, δ 2.73−2.92 ($CH_2{=}CHCH_2-$, 2H, td), 5.24−5.33 ($CH_2{=}CHCH_2-$, 2H, d), and 5.68−6.23 ppm ($CH_2{=}CHCH_2-$, 1H, m); ^{13}C, δ 35.7, 108−117 (m), 119.4, and 127.9 ppm; ^{19}F, δ +44.9, −82.7, −83.5, −113.8, −122.5, −126.0, and −138.0 ppm. MS (EI) (*m*/*z*, species, %): 640, M$^+$, 45; 183, $CF_2CF_2SO_2F$, 35; and 119, CF_3CF_2, 100. Elemental anal. Calcd for $C_{13}H_5O_3F_{21}S$: C, 23.21; H, 1.34; S, 4.76. Found: C, 23.09; H, 1.38; S, 4.64.

Data for Compound 4. In the attempt to synthesize **3** by path B (see Scheme 2), 1,5-hexadiene distilling at 60 °C was the unexpected product.[17]

IR: 1828 cm^{-1} $\nu_a(CH_2{=}CH)$ and 993−911(br) cm^{-1}. $\nu_s(CH_2{=}CH)$. NMR ($CDCl_3$): ^{1}H, δ 2.43−2.67 ($CH_2{=}CHCH_2-$, 4H, td), 5.24−5.33 ($CH_2{=}CHCH_2-$, 4H, d), and 5.68−6.23 ppm ($CH_2{=}CHCH_2-$, 2H, m); ^{13}C, δ 21.6, 119.1, and 132.4 ppm. MS (EI) (*M*/*z*, species, %): 82, M$^+$, 100.

Path B. Procedure for 5 and 7. Preparation of 4′-(Perfluoro-3-oxaundecylsulfonyl fluoride)acetophenone, $CH_3C(O)C_6H_4(CF_2)_8O(CF_2)_2SO_2F$ (5). A mixture of iodoperfluoro-3-oxaundecylsulfonyl fluoride (**1**) (7.25 g, 10.0 mmol), 4′-bromoacetophenone (2.01 g, 10.03 mmol), copper-bronze powder (1.28 g, 20.16 mmol), and 20 mL of DMSO was stirred and heated at 80 °C for 48 h in a two-neck 50 mL flask fitted with a nitrogen inlet three-way stopcock and a reflux condenser. Excess copper-bronze was separated from the crude product by centrifuge and filtration. Freon 113 (20 mL) was added to the stirring mixture at room temperature and followed by a mixture of 15 mL of diethyl ether and 15 mL of water. Most of the DMSO was moved into the aqueous phase and separated from the organic phase after 5 min. The combined organic phase was washed twice with 10 mL of water, dried over anhydrous magnesium sulfate, and then evaporated under reduced pressure. Fractional distillation gave the product, 4′-(perfluoro-3-oxaundecylsulfonyl fluoride)acetophenone, $CH_3C(O)C_6H_4(CF_2)_8O(CF_2)_2SO_2F$ (**5**), as a clear, colorless liquid (bp 125 °C/0.30 mm) in 65% yield. IR: 3137 cm^{-1} $\nu(CH_3)$, 1717 cm^{-1} $\nu(C{=}O)$, and 1585 cm^{-1} ν(Ph). NMR ($CDCl_3$): ^{1}H, δ 2.51 ($CH_3C(O)C_6H_4-$, 3H, s), 7.55−7.59 and 7.94−7.98 ($CH_3C(O)C_6H_4-$, 4H, dd); ^{13}C, δ 25.9, 102−122 (m), 127.0, 128.2, 132.8, 139.7, and 196.4 ppm; ^{19}F, δ +44.9, −82.7, −83.5, −113.8, −122.5, −126.0, and −138.0 ppm. MS (EI) (*M*/*z*, species, %): 718, M$^+$, 40; 703, M$^+$ − CH_3, 45; 535, M$^+$ − $CF_2CF_2SO_2F$, 25; 183, $CF_2CF_2SO_2F$, 35; and 119, CF_3CF_2, 100. Elemental anal. Calcd for $C_{18}H_7O_4F_{21}S$: C, 30.08; H, 0.98. Found: C; 29.94; H; 0.93.

Characteristic Data for Compound 7: distilled at bp 115 °C/0.25 mm in 62%. IR: 1585 cm^{-1} ν(Ph). NMR ($CDCl_3$): ^{1}H, δ 7.55−7.59 and 7.94−7.98 (ClC_6H_4-, 4H, dd); ^{13}C{^{1}H}, δ 102−122 (m), 128.0, 130.1, 133.0 (t), and 141 ppm; ^{19}F, δ +44.9, −82.7, −83.5, −113.8, −122.5, −126.0, and −138.0 ppm. MS (EI) (*M*/*z*, species, %): 710.5, M$^+$, 45; 183, $CF_2CF_2SO_2F$, 30; and 119, CF_3CF_2, 100. Elemental anal. Calcd for $C_{16}H_4O_3ClF_{21}S$: C, 27.02; H, 0.56; S, 4.50. Found: C, 26.85; H, 0.52; S, 4.37.

Preparation of 4′-(Perfluoro-3-oxaundecylsulfonyl fluoride)-1-allylbenzene, $H_2C{=}CHCH_2C_6H_4(CF_2)_8O(CF_2)_2SO_2F$ (9). In a 250 mL three-neck flask fitted with a magnetic stirrer, dropping funnel, reflux condenser, and nitrogen inlet three-way stopcock were placed magnesium turnings (0.9 g, 38.5 mmol) and sufficient THF to cover the turnings. This was activated by adding 10 drops of 1,2-dibromoethane. THF (50 mL) was added and a small amount of 4′-chloro-1-(perfluoro-3-oxaundecylsulfonyl fluoride)benzene (**7**). The appearance of a brown color indicated that Grignard reagent formation had commenced. The flask was cooled to −15 °C, and a solution of 10.8 g (15 mmol) of **7** in 25 mL of THF was added slowly over 3 h. The reaction mixture was subsequently stirred at −15 °C for another 3 h. The conversion of the chlorobenzene was monitored by removing small aliquots, hydrolyzing, and examining the disappearance of its signal from the GC chromatogram. An excess of allyl bromide (4.25 g, 35 mmol) was slowly added to the Grignard reagent over 30 min while a −15 °C temperature was maintained. The mixture was stirred under this condition for another 3 h and allowed to warm to 0 °C. An ice-cooled mixture of 40 mL of Freon 113 and 10 mL of a saturated solution of ammonium chloride was added. The combined organic layer was separated, washed twice with 30 mL portions of water at 0 °C, and dried over anhydrous magnesium sulfate. 4′-(Perfluoro-3-oxaundecylsulfonyl fluoride)-1-allylbenzene, $H_2C{=}CHCH_2C_6H_4(CF_2)_8O(CF_2)_2SO_2F$ (**9**), was obtained as a clear colorless liquid, bp 97 °C/0.5 mm, in 52% yield. IR: 1268 $\nu_a(CH_2{=}CH)$, 1187 $\nu_s(CH_2{=}CH)$, and 1589 cm^{-1} ν(Ph). NMR ($CDCl_3$): ^{1}H, δ 2.68−2.82 ($CH_2{=}CHCH_2-$, 2H, t), 5.27−5.29 ($CH_2{=}CHCH_2-$, 2H, d), and 5.64−6.18 ppm ($CH_2{=}CHCH_2-$, 1H, m); ^{13}C{^{1}H}, δ 27.2, 102−121 (m), 119.3, 128.1, 129.0, 130.2, 131.7, and 134.1 ppm; ^{19}F, δ +44.9, −82.7, −83.5, −113.8, −122.5, −126.0, and −138.0 ppm. MS (EI) (*M*/*z*, species, %): 716, M$^+$, 38; 675, M$^+$ − $CH_2{=}CHCH_2$, 43; 533, M$^+$ − $CF_2CF_2SO_2F$, 15; 183, $CF_2CF_2SO_2F$, 63; and 119, CF_3CF_2, 100. Elemental anal. Calcd for $C_{19}H_9O_3F_{21}S$: C, 31.83; H, 1.26. Found: C, 31.66; H, 1.14.

Preparation of (12H,12H,13H,13H,14H,14H-Hexahydroperfluoro-3-oxatetradecylsulfonyl fluoride)trichlorosilane,[$Cl_3Si(CH_2)_3(CF_2)_8O(CF_2)_2SO_2F$] (10). Allylperfluoro-3-oxaundecylsulfonyl fluoride (**3**) (3.2 g, 5.0 mmol), trichlorosilane (0.68 g, 5.02 mmol), and two drops of a 0.1 M solution of chloroplatinic acid in methanol were placed in a 100 mL reactor glass ampule and sealed under a vacuum. The mixture was allowed to react at 90 °C for 72 h. The tube was cooled to −195 °C in liquid nitrogen, broken carefully at the tip, and its contents quickly poured into a dry two-neck 100 mL flask connected by a stopcock to a nitrogen inlet valve. The white powdery solid product, $Cl_3Si(CH_2)_3(CF_2)_8O(CF_2)_2SO_2F$ (**10**), was distilled (bp 108 °C/0.3 mm) in 85% yield. NMR ($CDCl_3$): ^{1}H, δ 1.15−1.89 ($Si(CH_2)_3-$, 6H, br); ^{13}C, δ 9.8, 15.3, 21.2, and 102−122 (m) ppm; ^{19}F, δ +44.9, −82.7, −83.5, −113.8, −122.5, −126.0, and −138.0 ppm; ^{29}Si{^{1}H}, δ 10.7 (s). MS (EI) (*M*/*z*, species, %): 776, M$^+$, 30; 593, M$^+$ − $CF_2CF_2SO_2F$, 37; 183, $CF_2CF_2SO_2F$, 44; and 113, CF_3CF_2, 100. Elemental anal. Calcd for $C_{13}H_6O_3Cl_3F_{21}SSi$: C, 20.12; H, 0.84. Found: C, 20.27; H, 0.89.

Preparation of (12H,12H,13H,13H,14H,14H-Hexahydroperfluoro-3-oxatetradecylsulfonyl fluoride)trimethoxysilane, [$(CH_3O)_3Si(CH_2)_3(CF_2)_8O(CF_2)_2SO_3CH_3$] (11). Thirty milliliters of a Freon 113 solution of $Cl_3Si(CH_2)_3(CF_2)_8O(CF_2)_2SO_2F$ (**10**) (2.33 g, 3.0 mmol) was stirred in a 50 mL two-neck flask connected with a three-way stopcock for nitrogen gas inlet. To this was added 12 mL of a methanolic solution of 1.0 M sodium methoxide at 0 °C, and stirring was continued for 1 h at room temperature. The sodium salts produced were filtered off,

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(17) (a) Pouchert, C. J., Behnke, J., Eds. *The Aldrich Library of ^{1}H and ^{13}C FT-NMR Spectra*, 1st ed.; 1998; Vol. 43A. (b) Pouchert, C. J., Ed. *The Aldrich Library of FT-IR Spectra*, 1st ed.; Aldrich Chemical Company, Inc.: Milwaukee, WI, 1985; Vol. 1, p 29A.

and fractional distillation gave the colorless liquid product $(CH_3O)_3Si(CH_2)_3(CF_2)_8O(CF_2)_2SO_3CH_3$ (**11**) (bp 115 °C/0.6 mm) in 72% yield. IR: 3032 cm^{-1} $\nu(CH_3O)$. NMR $(CDCl_3)$: ^1H, δ 0.44 $(CH_3O)_3Si-$, 9H, s), 0.49 $(-S-CH_3$, 3H, s), and 1.15−1.89 $(Si(CH_2)_3-$, 6H, br); ^{13}C, δ 1.3, 1.6, 8.4, 13.8, 20.5, and 102−122 (m) ppm; ^{19}F, δ +44.9, −82.7, −83.5, −113.8, −122.5, −126.0, and −138.0 ppm; $^{29}Si\{^1H\}$, δ 9.9 (s). MS (EI) (*M*/*z*, species, %): 774, M^+, 27; 579, $M^+ - CF_2CF_2SO_3CH_3$, 19; 195, $CF_2CF_2SO_3CH_3$, 40; and 119, CF_3CF_2, 100. Elemental anal. Calcd for $C_{17}H_{18}O_7F_{20}SSi$: C, 26.36; H, 2.33. Found: C, 26.22; H, 2.19.

Preparation of $CH_2{=}CHCH_2(CF_2)_8O(CF_2)_2SO_2F$ (3) via the Organozinc(II) Intermediate (12). The zinc−copper couple (0.69 g, 10.0 mmol) and a magnetic stir bar were placed in a three-neck 50 mL flask fitted with a nitrogen inlet stopcock, a reflux condenser, and a dropping funnel.[18] An iodoperfluoro-3-oxaundecylsulfonyl fluoride (**1**) (7.25 g, 10.0 mmol) solution in 15 mL of THF was added dropwise with vigorous stirring at 25 °C to initiate the reaction, which was accompanied by a temperature rise. Careful addition of **1** over a period of 1 h was done to maintain constant temperature. The mixture was further stirred at room temperature for 2 h to generate the organozinc(II) intermediate in situ, and the mixture was filtered through a Schlenk filter into a clean two-neck 50 mL flask fitted with a nitrogen inlet stopcock and a stir bar to give a 1 M solution of **2**. Copper(I) iodide (1.90 g, 10.0 mmol) and 5 mL of a THF solution of allyl bromide (1.45 g, 12.0 mmol) were added to the stirring THF solution of the organozinc(II) intermediate, and the mixture was stirred at the same temperate for another 2 h. The appearance of a dirty green color was indicative of halide oxidation of CuI to form the copper(II) salt. A mixture of Freon 113 (15 mL) and diethyl ether (10 mL) was then added to the contents of the flask, followed by 15 mL of water. The combined organic phase was separated from the aqueous phase, washed twice with 10 mL of water, and dried over anhydrous magnesium sulfate. The product, allylperfluoro-3-oxaundecylsulfonyl fluoride (**3**), was obtained by fractional distillation, bp 88 °C/0.25 mm, in 60% yield. Analysis and characterization were essentially the same as described earlier for **3**.

Preparation of Trimethylsilyl(perfluoro-3-oxaundecylsulfonyl fluoride), $(CH_3)_3SiCF_2(CF_2)_7O(CF_2)_2SO_2F$ (13). A perfluoro-3-oxadecylsulfonyl fluoride (15.0 g, 20.69 mmol) solution in a mixture of THF/diethyl ether (260 mL/120 mL) in a three-neck 500 mL flask connected with a nitrogen inlet stopcock, a dropping funnel, and a mechanical stirrer was cooled to −78 °C, and 8.5 mL of 3 M ethylmagnesium bromide (25.5 mmol) was slowly added at this temperature. The reaction mixture was then allowed to gradually warm to −60 °C, maintained at this temperature for 6 h, and allowed to slowly warm to −50 °C in the last hour. Ten milliliters of concentrated hydrochloric acid was added to hydrolyze the active magnesium at −50 °C with stirring. The cold contents of the flask was then poured into the mixture composed of 150 mL of 2 N hydrochloric acid, 250 mL of diethyl ether, and 30 mL of Freon 113. The organic phase was separated and dried over magnesium sulfate. The solvents were removed by evaporation under reduced pressure, and fractional distillation gave trimethylsilyl(perfluoro-3-oxaundecylsulfonyl fluoride) (**13**) as a clear colorless distillate, bp 98 °C/0.25 mm, 44% yield. NMR $(CDCl_3)$: ^1H, δ 0.27 $(CH_3Si-$, 9H, s); ^{13}C, δ 1.1 and 102−122 (m) ppm; ^{19}F, δ +44.9, −82.7, −83.5, −113.8, −122.5, −126.0, and −138.0 ppm; $^{29}Si\{^1H\}$, δ 9.3 (t), $^2J_{Si-CF2} = 57.5$ Hz $[^{29}Si\{^{19}F\} = 9.3$ (s)]. MS (EI) (*M*/*z*, species, %): 672, M^+, 60; 703, $M^+ - CH_3$, 45; 489, $M^+ - CF_2CF_2SO_2F$, 16; 183, $CF_2CF_2SO_2F$, 30; and 119, CF_3CF_2, 100. Elemental anal. Calcd for $C_{13}H_9O_3F_{21}SSi$: C, 23.21; H, 1.34; S, 4.76. Found: C, 23.36; H, 1.28; S, 4.86.

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