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Journal of Fluorine Chemistry 107 (2001) 23–30

JOURNAL OF FLUORINE CHEMISTRY

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New SF_5-long chain carbon systems

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Received 26 June 2000; accepted 8 August 2000

Abstract

A new SF_5-terminated perfluoroalkyl thiol — $SF_5(CF_2)_6CH_2CH_2SH$ — and a symmetric SF_5-terminated dialkyl disulfide — $[SF_5CH–CH(CH_2)_8S]_2$ — were synthesized from the corresponding SF_5-terminated precursors. The chemistry employed in the preparation of the disulfide encompasses high yield pathways for the preparation of new SF_5-long chain derivatives. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Long carbon chains with pentafluoro-λ^6-sulfanyl (SF_5) groups; Thiol; Disulfide

1. Introduction

Perfluorinated alkyl thiols and disulfides terminated in the apolar $–CF_3$ group have been widely reported as alternative components to hydrocarbon-based constituents for self-assembled organic monolayers (SAMs) commonly used for surface modification of metals [1–10]. Perfluoroalkyl SAM chains provide both unambiguous chemical markers for modern high resolution surface analytical methods (e.g. X-ray photoelectron spectroscopy, secondary ion mass spectrometry) as well as extremely apolar, non-wetting surfaces interesting for various technologies. Work to-date has shown that CF_3-terminated perfluoroalkyl thiols and disulfides form high quality SAMs on noble or coinage metal supports, with highly organized surfaces exhibiting high apolar character consistent with arrays comprising the $–CF_3$ terminal group [11]. While interest in non-wetting, lubricating or apolar, unreactive SAM interfacial chemistry has focused primarily on perfluoroalkyl surface species, recent reports on another fluorinated interfacial chemistry — the perfluoroalkyl pentafluoro-λ^6-sulfanyl terminal group ($–(CF_2)_nSF_5$) [12,13] — provide a new, unexplored alternative for surfaces providing analogous interfacial properties to more conventional perfluoroalkyl thiols, in addition to interesting new surface analytical chemistry.

Unusual properties unique to gaseous SF_6 are largely retained in its organic derivatives [14–17]. High chemical and thermal stability and dielectric capacity known for SF_6 have also been shown for SF_5-small molecule adducts. Yet, less is known about bulk solid materials properties from SF_5-derivatized materials. Cast films of acrylate monomers containing SF_5 terminal groups were shown to enrich surfaces of photopolymerized matrices of aliphatic acrylic comonomers to high non-stoichiometric levels, imparting apolar, non-wetting surface properties comparable to those known for common $–CF_2$-containing polymer surfaces (e.g. FEP, PTFE) [12]. Alkylsilane monolayer films terminated in $SF_5(CF_2)_n–$ groups ($n = 2$ or 4) were also recently reported to exhibit high aqueous contact angles comparable to CF_3-terminated perfluoroalkyl silanes [13]. Both these studies provide evidence that the SF_5 group holds interesting potential as an alternative to more generic perfluorocarbons in thin film applications, although its lateral packing ability due to bulky pentafluoro sulfanyl bonding geometry in the central SF_5 sulfur atom may hinder film lateral organization [13].

In this contribution, new asymmetric sulfur-terminated long-chain hydrocarbon derivatives containing the perfluoroalkyl-SF_5 or alkyl-SF_5 terminal groups and sulfur or disulfide anchoring groups at the opposing ends were synthesized and characterized. A future report will describe use of these materials as perfluoroalkyl SF_5-terminated self-assembled alkylthiol and SF_5-dialkyl disulfide monolayers on polycrystalline gold substrates.

2. Results and discussion

In order to prepare unique new SAM surfaces containing arrays of apolar SF_5 groups, new long-chain asymmetric

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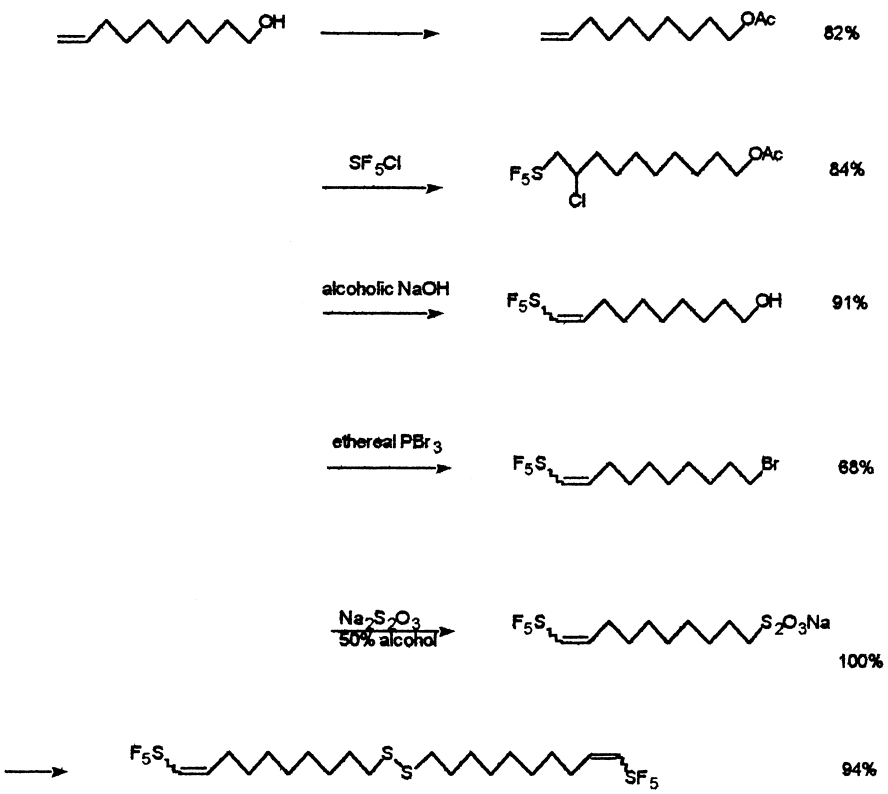
PII: S0022-1139(00)00340-7



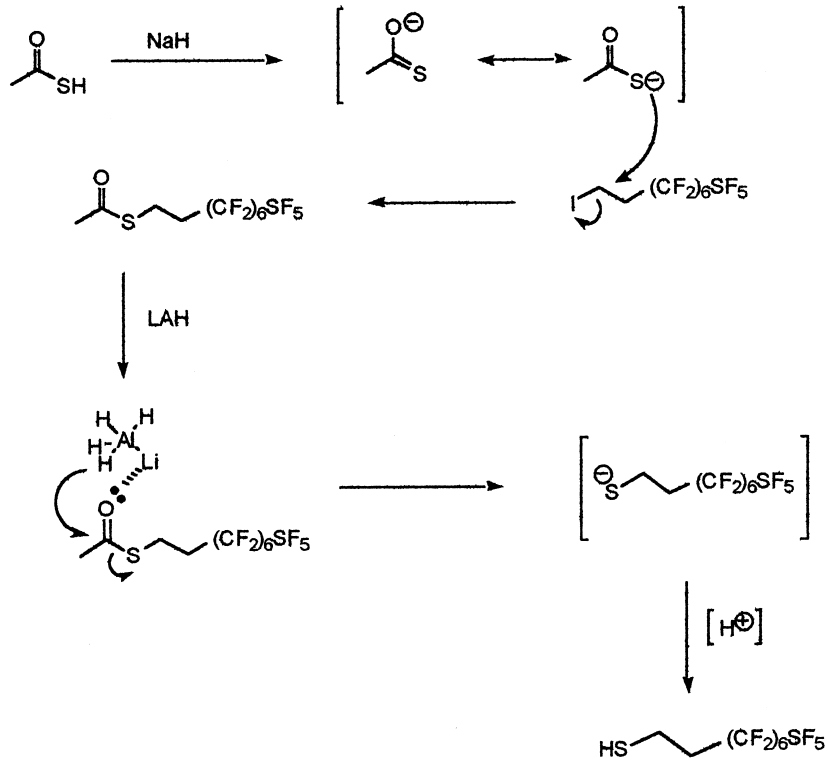
Scheme 1. Synthetic route to the symmetric SF_5 dialkyl disulfide.

hydrocarbon and fluorocarbon derivatives terminated with the SF_5 group at one end and a suitable sulfur anchor group (disulfide or thiol) at the other end were synthesized. Initially, a completely saturated hydrocarbon chain was envisioned for both systems; but only $SF_5(CH_2)_4Cl$ was known [18]. We have previously studied the preparation of these compounds via the addition of SF_5Br or SF_5Cl to a terminal olefin followed by reduction with now readily available tin hydride reagents [13,19]. In preliminary experiments, SF_5Cl was added to 1-hexene, with the production of 1-SF_5-2-Cl-hexane in the common direction of addition, while SF_5Br was too reactive and only BrF-adducts were found (via GC analysis). Additionally, neither infrared nor ^{19}F NMR analysis showed any detectable amount of the desired SF_5-aliphatic derivative. Addition of SF_5Cl to a double bond in the presence of a hydroxy group is possible, but with 9-decanol, only a 21% yield of the desired adduct was obtained. This alcohol was converted to its acetate derivative since esters are neutral moieties in such additions. SF_5Cl added, in this case, in high yield to provide the expected product, 10-SF_5-9-Cl-decyl-1-acetate.

We thus established that the addition of SF_5Cl to terminal olefins is a useful reaction for the introduction of the SF_5-group at the end of a chain. This was previously shown for propylene [20]. The intended reduction of 10-SF_5-9-Cl-decyl-1-acetate with the tin reagent was unsuccessful. However, base treatment led cleanly to 10-SF_5-9-decen-1-ol (91%). The alcohol was converted to the bromide with PBr_3, which in turn was converted to the Bunte salt where some care was necessary. When one equivalent of sodium thiosulfate was used, not all the bromide was consumed; with a slight excess, the formation of a by-product was observed (based on its mass spectrum, this could be bis-(9-decenyl) disulfide). The reaction was then conducted with one equivalent of sodium thiosulfate, the mixture dried and the residue repeatedly extracted with *n*-heptane, in order to remove the unreacted $SF_5CH{=}CH(CH_2)_8Br$. The remaining mixture consisted of the Bunte salt, sodium bromide and some sodium thiosulfate. In order to effect conversion to the desired disulfide end product, the Bunte salt was treated with iodine [21]; the disulfide product was then extracted with diethyl ether. If the recovered 10-SF_5-9-decenyl bromide starting material (~25%) was subtracted from the original amount, the disulfide final product was obtained in 94% yield. The entire reaction pathway to the SF_5-terminated dialkyl disulfide (overall yield 41%) is shown in Scheme 1. In Scheme 1, it is noteworthy to point out that the SF_5 group was stable towards a number of reactive reagents.

The SF_5-perfluoroalkyl thiol was synthesized from the corresponding SF_5-perfluoroalkyl iodide precursor [22,23].[1] Scheme 2 shows the mechanism proposed to accomplish this synthesis via reduction of the thiolacetate with $LiAlH_4$ (LAH). This method has been shown to produce

[1] In-house work done at Portland State University.



Scheme 2. Reduction mechanism of the thioacetate precursor to the SF_5-terminated perfluoroalkylthiol.

the analogous CF_3-terminated perfluoroalkyl thiols from corresponding iodides efficiently [10]. NMR and GC–MS methods confirm product formation.

The ^1H NMR spectra of the compounds from each step in Scheme 1 show little difference but are in agreement with the structural and chemical changes occurring from step to step. The chemical shift for the terminal CH_2-group moves in going from the acetate, alcohol, bromide and thiosulfate, to the disulfide, in agreement with the general chemical shift-range for these substituents. The SF_5-terminus, is not affected by these changes and retains a constant appearance as a broad multiplet between 6.3 and 6.9 ppm in the dehydrochlorinated compounds and two multiplets at about 3.9 (SF_5CH_2) and 4.3 (CHCl) ppm in the SF_5Cl-adducts, in the latter cases, assignment was by integration. The olefinic protons in the dehydrochlorinated compounds could not be individually assigned. The vinylic resonances were neither resolved at 100 nor at 400 MHz but it was apparent that both major and minor species were present (assumed to be *cis*- and *trans*-isomerides). These were assigned on grounds of chemical shift arguments and the absence of a signal at ~4 ppm expected if the HCl-elimination had occurred in both directions (9, 10 and 8, 9) such that the SF_5-group would have been in an allylic position in one isomer. Previously, two products were found (isolated in the ratio 11:89) from the dehydrochlorination of 1-SF_5-2-Cl-propane; products were assigned as propenylsulfurpentafluoride and as allylsulfurpentafluoride [20]. The reasoning was based upon the expectation that, had SF_5Cl added to give 1-SF_5-2-Cl-propane, two dehydrochlorination products were possible, while the isomer, 2-SF_5-1-Cl-propane, would yield only a single product, 2-SF_5-propene. Other workers have found that in the dehydrochlorination of 1-SF_5-2-Cl-propane, *cis*- and *trans*-propenylsulfurpentafluoride are formed (separation on a spinning band column gives a mixture of 21% of *cis*- + *trans*-, and 79% of mostly *trans*-compound) and the allyl compound is detected in trace amounts [24]. Furthermore, none of the allylic product in the dehydrochlorination of 3-SF_5-4-Cl-cyclopentanol was found [25]. Hence, the SF_5-group is always positioned adjacent to the double-bond.

The ^{19}F NMR spectrum of the dehydrochlorinated products shows two AB_4-resonances which are different in the B_4-portion only, in the ratio of ~88:12. This ratio is approximately carried through the reaction sequence to the final disulfide. The signals lie very close and in the same region as found for propenylsulfurpentafluoride [24] ($\delta_{B4} = 61.6$ ppm for *trans* and $\delta_{B4} = 64.1$ ppm for *cis*), while only a very small chemical shift difference was seen for δ_A in the two forms. In our products, $\delta_{B4}^{major} = 62.8-63.2$ ppm and $\delta_{B4}^{minor} = 65.3-65.6$ ppm, ratio ~88:12. Since it was not possible to separate the isomers, the published values for *cis*- and *trans*-propenylsulfur pentafluoride were used to assign our major component as the *trans*-compound and the minor component as the *cis*-compound [24].

Table 1
GC–MS data for $[SF_5CH{=}CH(CH_2)_8S]_2$[a]

Fragment	Major band (%)	Minor band (%)	Mass
M^+	100	92	594
$M^+(^{13}C)$	24	19.5	595
$(m/2\text{-}SF_5\text{-}2H)^+(^{13}C)$	6	8.4	170
$(m/2\text{-}SF_5\text{-}2H)^+$	59	72	169
SF_5^+	7.1	8.7	127
$C_9H_5^+$	9.6	10.5	113
SF_4^+	1.4	–	108
$C_8H_5^+$	16.3	16.7	101
$C_7H_{13}^+$	9.6	14.8	97
$SF_2C_2H^+$, $C_7H_{11}^+$	50.7	52.0	95
$C_7H_9^+$	11.9	17.2	93
SF_3^+	7.9	15.3	89
$C_6H_{15}^+$, $C_7H_3^+$	45.8	60.0	87
$C_6H_{13}^+$	9.5	12.9	85
$C_6H_9^+$	41.7	55.2	81
$C_6H_7^+$	17.3	25.9	79
$SC_3H_5^+$	16.2	26.8	73
$SC_3H_3^+$	8.7	10.5	71
SF_2^+, $C_5H_{10}^+$	3.1	2.9	70
$C_5H_9^+$	25.8	28.6	69
$C_5H_7^+$	39.0	51.1	67
$SC_2H_3^+$ $(SC_2H_2^+ + H)^+$	21.0	24.9	59
SC_2H^+	29.6	32.0	57
$C_4H_7^+$	82.7	100.0	55
$C_4H_5^+$	11.2	17.3	53
SF, $C_4H_3^+$	1.1	–	51

[a] GC–MS: $R_t = 22.16$ (major component); 22.37 (minor component); area 1:area 2 = 82.2:17.8.

The disulfide final product should exist as three geometric isomers not expected to be distinguished by NMR analysis as its constituent halves should behave as independent entities with the same appearance prior to forming the disulfide bond. The ratio of the two B_4-portions of the ^{19}F NMR spectrum in the disulfide was 89.5:10.5. In agreement with this, its GC–MS spectrum (see Table 1) shows two bands with a ratio of 17.8:82.2, rather close to the expected distribution $(\text{i.e.}(1.05(\text{form a}) + 8.95(\text{form b}))^2)$ yielding approximately 1 aa + 19 ab + 80 bb (where (a) and (b) are either *cis*- or *trans*-forms, and the ^{19}F NMR-spectral integration ratio of the disulfide was used to derive the coefficients) of the coupled product. Using the above assignment for the major component (*trans*-form), the disulfide would then comprise 80% of the *trans–trans* structure.

The most apparent feature change in the NMR spectra of $F_5S(CF_2)_6CH_2CH_2X$ (X = I, $SOC(O)CH_3$, and SH) is that the methylene hydrogens β to the first fluorinated methylene group, show the following changes for the proton (δ) values: 3.25 ppm for –I, ~2.3 for $-SC(O)CH_3$, and 2.72 for –SH compounds, respectively. The chemical shifts and relative integration values, for both the fluorine and hydrogen substituents, are in excellent agreement with literature results and strongly support the characterization of both the thiolacetate and thiol derivatives [22,23].

3. Experimental

3.1. Materials

Acetic anhydride and 9-decenol were purchased from Aldrich Chemical Company and used as received. Methylene chloride (Burdick and Jackson, high purity grade), hexane (J.T. Baker), diethyl ether (J.T. Baker, anhydrous), sodium hydroxide, sodium thiosulfate (Merck), and sodium sulfate (EM Science, anhydrous, GR) were used as received. Compounds $SF_5(CF_2CF_2)_nCH{=}CH_2$ and $SF_5(CF_2CF_2)_nCH_2CH_2I$ ($n = 3$) were prepared as previously described [22,23].

3.2. General bulk characterization methods

NMR spectra were obtained using either a Varian EM-390 spectrometer operating at 84.67 MHz for ^{19}F analysis, or a Varian Inova 300 instrument operating at 282 MHz for ^{19}F analysis or 300 MHz for ^1H analysis, or a Bruker AMX-400 spectrometer operating at 400 MHz for ^1H analysis, 376.5 MHz for ^{19}F analysis. $CDCl_3$ was used as the solvent for NMR samples; $(CH_3)_4Si$ and $CFCl_3$ were used as internal standards. Bulk infrared (FTIR) spectra were obtained between potassium bromide plates using a Perkin-Elmer System 2000 FT-IR operating at 2 cm^{-1} resolution. Mass spectra were measured via a Hewlett-Packard HP 5890 series II gas chromatograph (25 m, DB-5 column held at 50°C for 4 min. then increased to 18°C min^{-1} to 280°C) with a HP 5970 mass selective detector operating at 70 eV. Elemental analyses of each product were determined by Beller Mikroanalytisches Laboratorium (Göttingen, Germany).

3.3. Synthesis of symmetric dialkyldisulfide $[SF_5CH{=}CH(CH_2)_8S]_2$

3.3.1. 9-Decenyl-1-acetate

In a 125 ml, Erlenmeyer flask were stirred 24.82 g 9-decenol, 50 ml acetic anhydride and 10 drops of conc. H_2SO_4 until the temperature reached 60°C from the liberated heat of reaction. The mixture (covered) was then kept in a water bath at ambient temperature for 12 h, poured onto ice, allowed to hydrolyze overnight and extracted with 3×50 ml CH_2Cl_2. The combined extracts were washed with 100 ml sat. $NaHCO_3$ solution until CO_2 evolution ceased. Evaporation of the solvent gave the product that distilled at 72–83°C (0.2–0.3 mm Hg; main fraction) [26–28], Yield: 25.88 g (82%).[2]

[2] The compound 9-decenyl-1-acetate is reported repeatedly in the literature with a variety of inconsistent boiling points and ranges. While our boiling range (72–83°C at 0.2–0.3 Torr) is comparable with one report [26] (120–125°C at 14 mm Hg), other values (60–65°C at 8 Torr) [27] and (160°C at 9 Torr) [28] are disparate. We found that this compound is difficult to distill with a tendency to flood the column, which might explain the differing reported values.

^{1}H NMR spectrum: $\delta_1 = 1.1$–2.3 (1.33 and 2.07 ppm(s); 17.3H), $\delta_2 = 4.10$(t; 2H, $J = 6.4$ Hz; CH_2OAc), $\delta_3 = 4.9$–6.2 (m, 3H, CH=CH_2), $\delta_1 = 2.02$(s; CH_3CO), $\delta_2 = 4.05$ (t; $J = 6.5$ Hz; CH_2OAc), $\delta_3 = 4.75$–6.10 (m; 3H, CH=CH_2) [29]. Infrared spectrum: $\nu_{C=O}$: 1743 cm^{-1}; $\nu_{C=C}$: 1642 cm^{-1}; $\nu_{C=O}$: 1750 cm^{-1}; $\nu_{C=C}$: 1645 cm^{-1} [27]. A double-bond vibration at 1642 cm^{-1} with additional bands at 994 and 910 cm^{-1}, is observed, consistent with terminal olefins [30]. No evidence was found for any isomerization. Refractive index: $n_D^{25} = 1.4350$, lit. value is 1.4350, [31]; GC–MS:$R_t = 10.9$ min., single peak; 138 = $(M-CH_3COOH)^+$, 4%, 43 = $(CH_3CO)^+$, 100%.

3.3.2. 2-Chloro-1-SF_5-hexane

Into a 75 ml Hoke stainless steel reaction vessel was added 4.16 g (49.5 mmol) of 1-hexene. The vessel was then cooled to −196°C, evacuated and warmed to room temperature. This freeze-thaw process was repeated twice more to remove air from the vessel. After cooling to −196°C, 3.53 g (21.7 mmol) of SF_5Cl was condensed into the vessel and then heated at 55–60°C for 47 h. Distillation at reduced pressure provided 4.77 g (89% yield) of $SF_5CH_2CHCl(CH_2)_3CH_3$; bp 55–57°C at 10 mm Hg. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz): $\delta = 0.93$ ppm, t; $J = 7.2$ Hz, 3.0 H (CH_3); $\delta = 1.2$–2.0 ppm, several m, 6.4 H, (–$(CH_2)_3$–; $\delta = 3.94$ ppm, m, 2.1 H; ($SF_5C\overline{H}_2$). $\delta = 4.34$ ppm, m, 1.0H, ($C\overline{H}Cl$). Infrared spectrum: 3030, vw; 2964, s; 2937, s; 2878, s; 2868, s; 2739, vw; 1470, m; 1464, m; 1436, m; 1429, m; 1418, m; 1384, w; 1360, vw; 1345, vw; 1318, w; 1278, w; 1247, w; 1239, w; 1193, m; 1108, w; 1077, w; 1022, m; 976, m; 954, s; 938, s; 875, vs; 845, vs; 825, vs; 751, w; 735, w; 718, w; 701, m; 695, m; 673, w; 661, w; 636, s; 620, s; 598, s; 573, m; 565, s; 530, w; 520, w. ^{19}F NMR spectrum ($CDCl_3$, $CCl_3F = 0$): AB_4-spectrum [12,13], $\varphi_A = 83.30$ ppm(9 lines, 1.0 F); $\varphi_B = 66.0$ ppm (skewed d, 4.0 F); $J_{AB} = 146.2$ Hz, $J_{FAH1} = 7.9$ Hz.

GC–MS: $R_t = 6.25$ min., single peak: (*m/z*, species, % abundance): 127, SF_5^+, 9%; 89, SF_3^+, 16%; 84, $C_6H_{12}^+$, 5%; 83, $C_6H_{11}^+$, 80%; 82, $C_6H_{10}^+$, 27%; 81, $C_6H_9^+$, 7%; 74, $(C_3H_5S+H)^+$, 10%; 73, $C_3H_5S^+$, 7%; 70, $C_5H_{10}^+$, 3%; 69, $C_5H_9^+$, 3%; 68, $C_5H_8^+$, 2%; 67, $C_5H_7^+$,32%; 63, CSF^+, 5%; 62, ?, 7; 57, $C_4H_9^+$, 41; 56, $C_4H_8^+$, 12%; 55, $C_4H_7^+$, 98%; 54, $C_4H_6^+$, 7%; 53, $C_4H_5^+$, 14%; 51, SF^+, 5%;43, $C_3H_7^+$, 30%; 42, $C_3H_6^+$, 44%; 41, $C_3H_5^+$, 100%; 40, $C_3H_4^+$, 5%; 39, $C_3H_3^+$, 34%; 29, $C_2H_5^+$, 48%; 28, $C_2H_4^+$, 9%; 27, $C_2H_3^+$, 40%; 26, $C_2H_2^+$, 4%; 15, CH_3^+, 4%.

Elemental analysis: calculated for $C_6H_{12}ClF_5S$: C, 29.21; H, 4.91; S, 13.00; F, 38.51%. Found: C, 29.32; H, 4.96; S, 13.84; F, 38.80%.

3.3.3. 9-Chloro-10-SF_5-decanol

To a 75 ml Hoke stainless steel bomb tube was added 4.93 g (31.6 mmol) of 9-decen-1-ol. The vessel was chilled (−196°C), evacuated, and 5.37 g (33.0 mmol) of SF_5Cl was condensed into it. After warming to room temperature, the vessel was heated at 65°C for 17 h. The product was distilled at reduced pressure to provide 2.13 g (21% yield) of $SF_5CH_2CHCl(CH_2)_8OH$; bp 95–97°C at 0.04 mm Hg.

^{19}F NMR spectrum ($CDCl_3$, $CCl_3F = 0$): AB_4-spectrum [13,14], $\varphi_A = 83.10$ ppm (9 lines, 1.0 F); $\varphi_B = 65.9$ ppm (skewed d, 4.0 F); $J_{AB} = 146.0$ Hz.

Infrared spectrum (cm^{-1}): 3624, vw,br; 3362, m,br; 3023, vw; 2933, s; 2859, s; 1734, vw; 1467, m; 1434, m; 1417, w; 1376, w; 1319, w; 1252, w; 1194, w; 1103, w; 1059, m; 951, m; 933, m; 875, vs; 846, vs; 826, vs; 770, w; 725, w; 695, w; 673, w; 659, w; 636, m; 619, m; 598, s; 573, m; 564, m.

GC–MS: $R_t = 12.61$ min. (and several small additional peaks nearby, probably due to reaction of the compound in the injection port), (*m/z*, species, related abundance): 137, $C_{10}H_{17}^+$, 6%; 127, SF_5^+, 3%; 109, $C_8H_{13}^+$, 19%; 95, $C_7H_{11}^+$, 23%; 89, SF_3^+, 11%; 87, $C_5H_{10}OH^+$, 5%; 83, $C_6H_{11}^+$, 18%; 82, $C_6H_{10}^+$, 6%; 81, $C_6H_9^+$, 32%; 79, $C_6H_7^+$, 7%; 73, $C_4H_8OH^+$, 7%; 71, $C_5H_{11}^+$, 5%; 70, SF_2^+, $C_5H_{10}^+$, 16%; 69, $C_5H_9^+$, 47; 68, $C_5H_8^+$, 19%; 67, $C_5H_7^+$, 34%; 59, $C_3H_6OH^+$, 9%; 57, $C_4H_9^+$, 13%; 56, $C_4H_8^+$, 26%; 55, $C_4H_7^+$, 88; 54, $C_4H_6^+$, 19%; 53, $C_4H_5^+$, 16%; 51, SF^+, $C_4H_3^+$,4%; 45, $C_2H_4OH^+$, 5%; 44, CS^+, 5%; 43, $C_3H_7^+$, 33%; 42, $C_3H_6^+$, 43%; 41, $C_3H_5^+$, 100%; 40, $C_3H_4^+$, 9%; 39, $C_3H_3^+$, 34%; 31, CH_2OH^+, 98%; 29, $C_2H_5^+$, 41%; 28, $C_2H_4^+$, 11%; 27, $C_2H_3^+$, 33%.

Elemental analysis: calculated for $C_{10}H_{20}ClF_5OS$: C, 37.67; H, 6.34; S, 10.06; F, 29.80%. Found: C, 38.33; H, 6.20; S, 9.82; F, 29.50%.

3.3.4. 9-Chloro-10-SF_5-decyl-1-acetate

Into a 75 ml steel bomb tube containing 21.0 g (106 mmol) of 9-decenyl acetate was condensed at −196°C 18.3 g (113 mmol) of SF_5Cl and the container was then allowed to reach ≈0°C (∼1.5 h), and kept in an ice bath in a beaker overnight (the ice melted). A check of the gas pressure (by expanding into a space with attached manometer) showed that the pressure was still high. It was then heated for 2 days at ∼90°C (oil bath); gas chromatography-mass spectrometry showed that only a trace of olefin remained. Distillation afforded 31.96 g (84%) of a colorless oil, boiling range 116–128°C at 11–14 mm Hg.

^{1}H NMR spectrum (90 MHz): $\delta_1 = 1.36$–2.00 (broad multiplet, 14 H), $\delta_2 = 2.07$(s; CH_3C=O, 3H), $\delta_3 = 3.8$–4.3 m, $C\overline{H}_2OAc + SF_5C\overline{H}_2$, (4H); $\delta_4 = 4.3$–4.6 m, $C\overline{H}Cl$, (1H). ^{19}F NMR spectrum: AB_4-spectrum, $\varphi_A = 83.83$ ppm (9 lines, 1.0 F); $\varphi_B = 66.33$ ppm (skewed d, 4.0 F); $J_{AB} = 154.8$ Hz.

Infrared spectrum (cm^{-1}): 3022, vw; 2934, s; 2860, m; 1739, s-vs; 1467, w-m; 1437, w-m; 1418, w; 1389, w-m; 1367, m; 1245, vs; 1040, m; 955, vw; 933, w-m; 874, s-vs; 846, vs; 827, vs; 725, w; 693, w; 635, m-s; 618, m; 597, m-s; 571, w; 564, m. GC-MS: $R_t = 13.6$ min., single peak: 361 = $(M(^{35}Cl)^+ + H)$: <1%; 43 = (CH_3CO^+): 100%.

Elemental analysis: calculated for $C_{12}H_{22}ClF_5O_2S$, C, 39.95; H, 6.15; F, 26.3; S, 8.89. Found, C, 39.89; H, 6.39; F, 24.6; S, 8.25%.

3.3.5. 10-SF_5-9-Decen-1-ol

To a solution of 7.5 g (0.1875 mol) NaOH in 200 ml of ethyl alcohol, 30.70 g (0.085 mol) of $SF_5CH_2CHCl(CH_2)_8OAc$ was added dropwise with stirring within 5 min. A precipitate formed almost instantly and slight warming was observed. After 1 h, more alcohol (~50 ml) was added to facilitate stirring; a gas chromatogram showed that complete reaction had occurred. The insoluble material (NaCl and NaOAc solids) was suction filtered off, and the filtrate concentrated to ~50 and 100 ml of water was added to dissolve the precipitated salts. The lower layer was drained in a separatory funnel, and the remaining aqueous phase extracted with $CHCl_3$ (1 × 50 ml). This extract was combined with the initially collected lower layer; chloroform was removed at low pressure, and the residue was fractioned at 17 micro reduced pressure (dynamic vacuum) to yield: (1) initial fraction (room temperature to 98°C, 3.77 g, colorless oil); (2) main fraction (98–108°C, 18.16 g, colorless oil); (3) tail fraction (108–90°C, 1.15 g, yellowish oil).The initial and main fractions were pure (by gas chromatography), while the third fraction contained an impurity and was discarded. Yield (fractions 1 + 2): 21.93 g (91.3%).

^{1}H NMR spectrum: $\delta_1 = 1.2-2.5$ (three broad features: $\delta_A = 1.36$, $\delta_B = 1.80$, $\delta_c = 2.23$; 15.00 H); $\delta_2 = 3.71$ (t; $J = 6.0$ Hz; 1.98 H); $\delta_3 = 6.3-6.9$ (multiplet centered at 6.57; 1.65 H, olefinic); no distinction between *cis*- and *trans*-isomers could be made. ^{19}F NMR spectrum: 2 SF_5-groups; only one axial-fluorine resonance. AB_4-spectrum, $\varphi_{A1} = \varphi_{A2} = 84.97$ (9 lines, 1.0 F); $\varphi_{B1} = 63.22$, $\varphi_{B2} = 65.32$ (skewed doublets, $\varphi_{B1} + \varphi_{B2}$: 4.0 F; $\varphi_{B1} : \varphi_{B2} = 89.6$: 10.4%); $J_{AB1} = 151.0$ Hz, $J_{AB2} = 151.5$ Hz; i.e. two forms, 1 and 2, were distinguishable.

Infrared spectrum (cm^{-1}): 3345 m, br; 2933, s-vs;. 2860, s; 1653, w; 1466, w-m; 1438, w-m; 1375, w; 1317, w; 1251, vw; 1203, vw; 1057, w-m; 963, w-m; 946, wsh; 895, s; 840, vs; 749, m-w; 721, m; 645, m; 600, m; 570, m-w.

GC-MS: $R_t = 11.91$ min., single peak, (*m/z*, species, related abundance,): 180, $SF_5C_4H_5^+$, 0.24%; 148, $SF_4C_3H_4^+$, 1.4%; 127, SF_5^+, 0.63%; 108, SF_4^+, 2.50%; 89, SF_3^+, 5.70%; 85, $C_6H_{11}^+$, 7.8%; 82, $C_6H_{10}^+$, 11.2%; 79, $C_6H_7^+$, 10.6%; 71, $SC_3H_3^+$, 25.0%; 70, SF_2^+, 6.13%; 69, SC_3H^+, $C_5H_9^+$, 27.3%; 68, SC_3^+, $C_5H_8^+$, 18.0%; 67, $C_5H_7^+$: 44.6%; 59, $SC_2H_3^+$, $C_4H_{11}^+$, 11.6%; 57, SC_2H^+, 14.3%; 56, $C_4H_8^+$, SC_2^+, 26.7%; 55, $C_4H_7^+$, 100.0%; 54, $C_4H_6^+$, 15.0%; 52, $C_4H_4^+$, 1.8%; 51, SF^+, 3.10%.

Elemental analysis: calculated for $C_{10}H_{19}F_5OS$, C, 42.54; H, 6.78; F, 33.7; S, 11.36. Found: C, 44.26; H, 6.97; F, 29.3; S, 11.08%.

3.3.6. 1-Bromo-10-SF_5-9-decene (SF_5–CH=CH(–CH_2)$_8$–Br)

$F_5SCH{=}CH(CH_2)_8OH$ (16.00 g, 56.7 mmol) was dissolved in 100 ml of diethyl ether in a 250 ml round bottom flask. After cooling in an ice-bath, 8.60 g (31.7 mmol) of PBr_3 was added dropwise with stirring at such a rate that temp. ≤5°C. After approximately 30 min., the ice was melted and stirring was continued for 2 h. The mixture was hydrolyzed by adding small pieces of ice with stirring. The ether layer was then drained. However, GC–MS indicated insufficient conversion and hence, the mixture was re-brominated after aqueous washing, shaking with saturated $NaHCO_3$ solution, drying with Na_2SO_4, filtering and removing the ether (leaving 17.76 g of an oil). This was dissolved in 25 ml of ether, and 11.00 g (40.6 mmol) of PBr_3 was added dropwise with cooling (temp. ≤10°C). After attaining room temperature, the solution contained ~3% of the starting material (GC–MS) after 14 h. of reaction time. Accordingly, the mixture was stirred for 3 more days, then hydrolyzed cautiously with small pieces of ice, then 50 ml of water. The two phases were separated (funnel), the upper (ether) layer washed with water (2 × 25 ml), then stirred with solid $NaHCO_3$ (1 h), dried (Na_2SO_4), and filtered by suction. After ether removal, 17.76 g of an oil remained, GC–MS ($R_t = 12.51$ min.) showed only one component; distillation under dynamic vacuum and over the temperature range 81–91°C gave a clear colorless oil (13.40 g, yield = 68%).

^{1}H NMR spectrum: $\delta_1 = 1.2$–2.5 (3 broad features: $F_5SCH{=}CH{-}((\underline{CH_2})_{\overline{7}})CH_2Br$ $\delta_a = 1.37$; $\delta_b = 1.9$, broadened triplet; $J \sim 6.5$ Hz; $\delta_c = 2.2$; (a + b + c = 14.3 H); $\delta_2 = 3.45$ (t; $J = 6.68$ Hz; 2.04 H, $C\overline{H}_2Br$); $\delta_3 = 6.25$–6.9 (broadened feature; centered at 6.57; 1.70 H, olefinic). ^{19}F NMR spectrum: 2 SF_5-groups, only one axial-fluorine resonance. AB_4-spectrum, $\varphi_A = \varphi_{A1} = \varphi_{A2} = 84.85$ (9 lines, 1.0 F); $\varphi_{B1} = 62.85$, $\varphi_{B2} = 65.2$ (skewed doublets, $\varphi_{B1} + \varphi_{B2} = 4.0$ F); $J_{AB} = 150.6$ Hz; B1:*B*2 ≈ 88:12.

Infrared spectrum (cm^{-1}): 3082, w-w; 3008, wsh;. 2933, vs-s; 2859, s; 1652, w-m; 1466, m; 1440, m; 1433, mw,sh; 1373, vw; 1355, vw; 1341, vw; 1304, wsh; 1248, w; 1221, wsh; 1150, vw; 960, m; 892, s-vs; 842, vs; 748, w-m; 721, m; 692, vw; 645, m-s; 599, m-s; 570, m; 486, vw; 457, vw.

GC-MS (intensity of bromine fragments is sum of $^{79}Br + {}^{81}Br$, single peak at 12.51 min) 325, 327, 0.6%, M^+; 161, 162, 163,164, 1:1:1:1, 12%, $C_6H_{10}Br^+$, $C_6H_{11}Br^+$; 148,150, $C_5H_9Br^+$, 23.5%; 137, $C_{10}H_{17}^+$, 22.6%; 135, $C_{10}H_{15}^+$, $SF_2C_5H_5^+$, 12%; 134, 136, $C_4H_7Br^+$, 6.2%; 127, SF_5^+, 1.1%; 121, SF_4CH^+, 2.0%; 109, $SF_2C_3H_3^+$, 7.8%; 108, SF_4^+, 0.9%; 97, $C_7H_{13}^+$, 10.5%; 95, $SF_2C_2H^+$, $C_7H_{11}^+$, 27.4%; 89, SF_3^+, 6.0%; 88, SFC_3H^+, 1.9%; 85, $C_6H_{13}^+$, 1.6%; 84, $C_6H_{12}^+$, 1.6%; 83, $C_6H_{11}^+$, SF_2CH^+,14.7%; 82, $C_6H_{10}^+$, 8.0%; 81, $C_6H_9^+$, 28.2%; 80, $C_6H_8^+$, 1.7%; 79, $C_6H_7^+$, 4.8%; 77, $C_6H_5^+$, 2.0%; 73, C_6H^+, $SC_3H_5^+$, 6.7%; 71, $SC_3H_3^+$, 2.0%; 69, $C_5H_9^+$: 51.0%; 68, SC_3^+, $C_5H_8^+$, 9.0%; 67, $C_5H_7^+$, 24.0%; 65, $C_5H_4^+$, 3.4%; 59, $C_4H_{11}^+$, $SC_2H_3^+$,14.5%; 57, SC_2H^+, 18.2%; 56, SC_2^+, $C_4H_8^+$: 14.1%; 55, $C_4H_7^+$, 100.0%; 54, $C_4H_6^+$, 12.6%; 53, $C_4H_5^+$, 14.6%; 51, SF^+, $C_4H_3^+$, 2.6%.

Elemental analysis: calculated for $C_{10}H_{18}BrF_5S$, C, 34.79; H, 5.26; Br, 23.15; F, 27.5; S, 9.29. Found: C, 35.55; H, 5.21; F, 26.2; S, 8.34%.

3.3.7. Bunte Salt, $SF_5CH{=}CH(CH_2)_8S_2O_3Na$, and final product $[SF_5CH{=}CH(CH_2)_8S]_2$

$F_5SCH{=}CH(CH_2)_8Br$ (2.70 g, 7.83 mmol) and $Na_2S_2O_3$ (1.23 g, 7.79 mmol) were refluxed in 10 ml of 50% ethanol for 1 h, the mixture becoming clear after ca. 45 min. The solution was poured into a beaker, and the solvent was allowed to evaporate overnight. A white, waxy solid was obtained. After vacuum drying, 3.73 g (theoretical yield = 3.93 g) were obtained and stirred overnight with 50 ml of *n*-heptane and suction-filtered. Gas chromatography of the extract showed it to contain some bromide starting material. The procedure was repeated twice more with 40 ml *n*-heptane each for 2 h, respectively. While the second extract contained a small amount of $F_5SCH{=}CH(CH_2)_8Br$, the third extract was entirely free of starting material (by GC). The dried residue, a bright white powder (3.20 g), should have comprised a mixture of the desired Bunte salt $F_5SCH{=}CH(CH_2)_8S_2O_3Na$, with NaBr and $Na_2S_2O_3$. The weight difference of 0.73 g compared to the theoretical yield was assumed to be entirely due to unreacted $F_5SCH{=}CH(CH_2)_8Br$, and was subtracted in calculating the theoretical yield. This Bunte salt–NaBr–$Na_2S_2O_3$mixture (3.2 g) was dissolved in 50 ml of distilled water, forming a soapy solution, and stirred overnight with 0.76 g of iodine. To the decolored, milky solution was added another 0.24 g of I_2 and stirred for 4 h.; some iodine remained. Extraction with ether (1×50, 3×30 ml) and washing the combined ether extracts with 30 ml of water containing ≈0.05 g of Na_2SO_3 provided a colorless solution, slightly turbid. The ether layer was washed with water (3×30 ml), and after removal of the ether (rotary evaporator), the resulting milky oil was dried under high vacuum yielding 1.60 g of a nearly colorless heavy oil (yield = 94% based on recovered $F_5SCH{=}CH(CH_2)_8Br$ starting material).

^{1}H NMR spectrum: $\delta_1 = 1.1{-}2.4$ (3 broad features, structureless; $\delta_A = 2.02$, $\delta_B = 1.73$, $\delta_C = 2.2$; 14 H); $\delta_2 = 2.72$(t; $J = 6.82$ Hz; $\underline{CH_2}$ S; 2.07 H); $\delta_3 = 6.59$ (center of a broad feature; 1.87 H). ^{19}F NMR spectrum (in ether): 2 SF_5-groups; only one axial-fluorine resonance. AB_4-spectrum, $\varphi_{A1} = \varphi_{A2} = 84.85$(9 lines, 1.0 F); $\varphi_{B1} = 62.85$, $\varphi_{B2} = 65.55$ (skewed doublets, 4.0 F; $\varphi_{B1} : \varphi_{B2} = 89.5 : 10.5$); $J_{AB1} = 150.8$, $J_{AB2} = 150.6$.

Infrared spectrum (cm^{-1}, film on NaCl): 3084, vw; 2930, s; 2837, s-m; 1651, w-m; 1468, w-m; 1445, w-m; 1372, w-vw; 1350, w-vw; 1306, w-vw; 1277, vw; 1251, w-vw; 1130, vw; 1074, vw; 964, w-m; 893, s-vs; 839, vs; 750, w-m; 721, w-m; 644, m-s; 599, m-s; 568, w-m.

Elemental analysis: calculated for $C_{20}H_{36}F_{10}S_4$: C, 40.39; H, 6.10; F, 31.9; S, 21.56: Found: C, 41.36; H, 6.47; F; 34.0; S, 22.00%.

3.4. Synthesis of perfluoroalkylthiol $SF_5(CF_2)_6CH_2CH_2SH$

3.4.1. 3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-8-(pentafluorothio)-octyl-1-thioacetate ($SF_5(CF_2)_6(CH_2)_2$–S–C(O)CH_3)

To a 250 ml round bottom flask 0.075 g NaH (0.124 g, ∼50% dispersion, ∼3.1 mmol), was suspended in 40 ml dry THF while cooled to 0°C. After cooling, 0.253 g thiol acetic acid (3.32 mmol, 3 eq) was added dropwise over 15 min with stirring under N_2 atmosphere. The reaction mixture was stirred for 45 additional minutes at 0°C, then cooled to −78°C (dry ice/acetone) before adding 0.500 g (1.04 mmol) of the $SF_5(CF_2)_6(CH_2)_2I$ precursor. The solution was slowly warmed to 25°C and stirred overnight. The reaction was quenched with 20 ml water, and extracted with 1,1,2-trichlorotrifluoroethane (3×20 ml), the organic layer was washed with saturated $Na_2S_2O_3$, dried over Na_2SO_4 and evaporated to yield a yellow oil which was used without further purification. Yield: 0.436 g, >95%.

^{1}H NMR spectrum ($CDCl_3$ ppm): $\delta_1 = 2.2$–2.4 (overlapping peaks, $F_5S(CF_2)_6\,\underline{CH_2}\,CH_2SC(O)\underline{CH_3}$, 5H), $\delta_2 = 3.0$(t, $F_5S(CF_2)_6CH_2\ \underline{CH_2}\ SC(O)CH_3$, 2H) ^{19}F NMR ($CDCl_3$ ppm): $\varphi_A = 63.9$(pentet, –$\overline{F}$ F_4S–CF_2–, 1F), $\varphi_B = 44.8$(d, multiplet $F\overline{F}_4SCF_2$, 4F), multiple features, $\varphi_{(CF2)n} = -94.5$(m, 2F), −115.4 (m, 2F), −121.5 to −122.0, −122.8, −123.8 (all broad, 2F).

3.4.2. 3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-8-(pentafluorothio)-1-mercaptooctane ($SF_5(CF_2)_6(CH_2)_2SH$)

To a 50 ml round bottom flask, 0.040 g lithium aluminum hydride (LAH) was added and suspended in 20 ml dry THF. The suspension was cooled to −78°C and $SF_5(CF_2)_6(CH_2)_2SC(O)CH_3$ was added slowly over 45 min. After 20 min the reaction was monitored by TLC and showed all thioester had been consumed. The reaction was quenched with methanol, and stirred at −78°C for 20 min, when the reaction mixture was warmed to RT and transferred to a separatory funnel containing 50 ml DI water. The product was extracted with CH_2Cl_2 (4×30 ml), the organic layers were combined and dried with Na_2SO_4 followed by rotary evaporation to yield a clear oil.

^{1}H NMR ($CDCl_3$ ppm): $\delta_1 = 2.72$(q, $CH_2\underline{CH_2}SH$ 2H) $\delta_2 = 2.48$– 2.48 (m, –$(CF_2)_6\underline{CH_2}CH_2SH$, 2H), $\delta_3 = 1.56$ (t, CH_2CH_2–S$\underline{H}$ 1H) ^{19}F NMR ($CDCl_3$ ppm): $\varphi_A = 63.9$ (pentet, $\underline{F}F_4S$–CF_2–, 1F), $\varphi_B = 44.8$ (d, multiple $F\underline{F}_4S$–CF_2, 4F), multiple features, $\varphi_{(CF2)} = -94.5$(m, 2F), −114.4 (m, 2F), −121.5 to −122.0, −122.8, −123.7 (all broad, 2F).

Acknowledgements

We are grateful for the support from the National Science Foundation grants CHE-9632815 (GG) and DMR-9596023 (DWG), the Petroleum Research Foundation (ACS-PRF #31099-AC1, GG), a 3M Faculty Fellowship (DWG), and a DuPont Research Award (DWG) and NIH grant RR 01296 from the National Center for Research Resources (DGC) for support of this work.

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