

New fluoroalkenes and alcohol with pentafluoro- λ^6 -sulfanyl (SF_5) terminal groupings

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Abstract

The synthesis of new compounds that contain both a terminal pentafluoro- λ^6 -sulfanyl (SF_5) group and an alkene or alcohol functional group is reported. Five new SF_5 containing alkenes and one new SF_5 containing alcohol were prepared: $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ (1), $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ (2), $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ (3), $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}=\text{CH}_2$ (4), $\text{SF}_5(\text{CF}_2\text{CF}_2)_2\text{CH}=\text{CH}_2$ (5) and $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ (6). These compounds are useful as monomers or as intermediates in the preparation of polymers, polymer surface coatings, and surfactants. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Pentafluorosulfanyl; Alkene; Alcohol; Synthesis; NMR spectroscopy; Mass spectrometry

1. Introduction

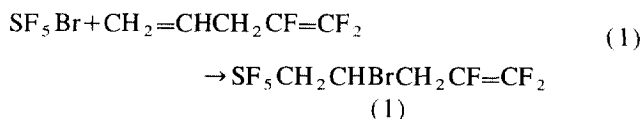
Long-chain fluoroalkyl compounds have many important applications including use as surface-active and surface treatment agents. Many commercially available fluoroalkyl compounds contain terminal trifluoromethyl groups as well as functional groups tailored to meet the needs of specific application. Replacement of the terminal trifluoromethyl group with a terminal pentafluoro- λ^6 -sulfanyl (SF_5) group in new polymers, polymer surface coatings, and surfactants can lead to materials with unique chemical and physical properties. These properties include high dielectric strength, high thermal stability, high chemical resistance, low refractive index and low surface free energy [1–6].

In a continuing effort to prepare new organic derivatives of SF_6 , we have synthesized five new SF_5 containing alkenes and one new alcohol: $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ (1), $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ (2), $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ (3), $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}=\text{CH}_2$ (4), $\text{SF}_5(\text{CF}_2\text{CF}_2)_2\text{CH}=\text{CH}_2$ (5) and $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ (6). Several of the new compounds (3–6) were prepared from the recently reported synthetically versatile SF_5 -containing β -(perfluoroalkyl)ethyl iodides [7]. The new fluoroalkenes can be used as monomers in the preparation of SF_5 -containing homo- or copolymers or as intermediates for further synthetic transformations. SF_5 -containing acrylate monomers and

polymers, phosphate esters and polyethers illustrate several of the applications possible for the new SF_5 -containing alcohol.

2. Results and discussion

Compound 1 was synthesized by the thermally induced radical addition of SF_5Br to the diolefin $\text{CH}_2=\text{CHCH}_2\text{CF}=\text{CF}_2$.

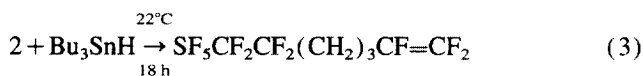
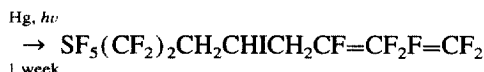
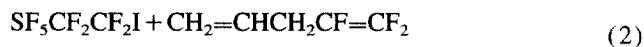


In general, SF_5Br additions to alkenes are regioselective reactions with the addition of SF_5Br occurring at the vinyl group in preference to the trifluorovinyl group. The addition of the SF_5 radical to the terminal CH_2 of the vinyl group forms the most stable SF_5 -containing alkyl radical [8]. There was no indication of the isomer containing a terminal bromine or the product resulting from SF_5Br addition to the electron-poor fluoroalkene in the reaction. The yield of compound 1 was much higher when the reaction was carried out in a Pyrex-glass vessel (91%) instead of a stainless-steel vessel (23%).

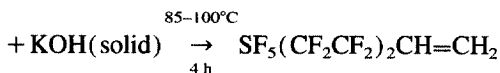
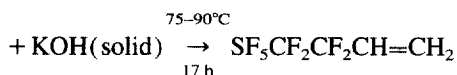
Perfluoroalkyl iodides are versatile materials for the preparation of many fluorinated intermediates including carboxylic acids, sulfonyl chlorides, and β -(perfluoroalkyl)ethyl iodides. The reaction of perfluoroalkyl iodides with alkenes

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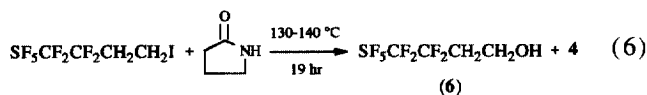
is useful for chainlength extension as well as functionalization of the perfluoroalkyl iodides. These addition reactions are induced by heat, light, free-radical initiators, or transition-metal catalysts [9–13]. We have recently reported the reactions of $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ with acetylene, alkenes and fluoroalkenes [7]. The reactions are catalyzed by mercury and irradiated with a halogen lamp. Since these mercury-catalyzed photochemical reactions are carried out in Pyrex-glass vessels it is unlikely that mercury photosensitization is occurring. The appearance of mercury iodides in the reaction vessel would suggest that the catalytic effect is due to the prevention of primary recombination of the fluoroalkyl radical and the iodine atom as postulated by Haszeldine [9]. Compound **2** was prepared in 74% yield by the mercury-catalyzed regioselective addition of $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ to a diolefin. Reduction of compound **2** using tributyltin hydride led to the fluoroalkene **3** in 61% yield.



Dehydroiodination of β -(perfluoroalkyl)ethyl iodides can be accomplished by several different methods; in the case of the SF_5 -containing iodides, the use of solid KOH to prepare compounds **4** and **5** proved to be a very effective method [10,11]. The alkenes were produced in high yield (83–85%) and were easily removed from the solid KOH matrix by vacuum transfer.



The preparation of β -(perfluoroalkyl)ethyl alcohols from the corresponding iodides can be accomplished by various reagents including fuming sulfuric acid, *N*-methylformamide, a mixture of *N,N*-dimethylformamide and water, or lactams [14–21]. The lactam method avoids the handling problems associated with oleum and the toxicity concerns of the formamides [20,21]; for these reasons it was used to prepare the new alcohol **6**. Reaction of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ with a seven-fold excess of 2-pyrrolidinone, at elevated temperatures, gave compound **6** in 48% yield; compound **4** was produced as a byproduct (15%).



The compounds **1–6** were characterized by a combination of elemental analysis; ^1H -, ^{13}C - and ^{19}F -NMR spectroscopy; IR- spectroscopy; and GC-MS. The infrared spectra for all compounds exhibit strong absorption bands between 832–885 cm^{-1} due to the S–F stretching modes of the SF_5 group. One of the SF_5 group deformation modes occurs between 603–605 cm^{-1} with medium to strong intensity. The C=C stretching vibration in fluoroalkenes **1–3** exhibit a large shift to higher frequencies due to the electronegative fluorines. The band appeared as a medium to strong absorption between 1801–1802 cm^{-1} . Alkenes **4** and **5** have weak absorption bands at 1652–1654 cm^{-1} corresponding to the vinyl C=C stretching vibration.

The ^1H -, ^{13}C - and ^{19}F -NMR spectral data for all compounds can be found in Tables 1 and 2. The compounds show a typical AB_4 splitting pattern in the ^{19}F -NMR spectrum for the SF_5 -group. The axial fluorine (A) appears as a distorted pentet (or nine-line pattern) and the equatorial fluorines (B) as a doublet of multiplets. The SF_5 -group of compound **1** is attached to a methylene carbon resulting in a downfield shift of the AB_4 pattern compared to compounds **2–6** which contain the SF_5 -group attached to a CF_2 -carbon. Compounds **1–3** have chemical shifts and coupling constants for the fluorines of the vinyl group in good agreement with other trifluorovinyl derivatives [22]. The ^1H - and ^{13}C -NMR chemical shifts and coupling constants for all compounds agree with the values found for alkenes and alcohols of similar chemical structure [23,24].

GC-MS analysis was performed on all compounds except **3** and **5**. The major mass spectral peaks are presented in Section 3. Typical fragmentation peaks, including SF_5^+ (m/z 127), SF_3^+ (m/z 89), and SF^+ (m/z 51), were observed for all compounds. Compound **1** exhibits a molecular ion peak while compounds **2** and **6** have $[\text{M} - \text{H}]^+$ peaks. The mass spectrum for **1** contains a molecular ion peak and a $[\text{M} + 2]^+$ peak in the expected ratio for a bromine containing compound. The loss of iodine ($[\text{M} - \text{I}]^+$, m/z 349) is indicated in the spectrum of **2**. The spectrum of **6** contains the common alcohol fragmentation peak CH_2OH^+ (m/z 31) as the base peak.

3. Experimental details

3.1. Materials

SF_5Br , $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ and $\text{SF}_5(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{I}$ (where $n=1,2$) were prepared according to literature methods [7,25]. $\text{CF}_2=\text{CFCH}_2\text{CH}=\text{CH}_2$ was obtained from Dr. D.J. Burton (Univ. of Iowa) and was used without further purification. 2-pyrrolidinone (99%) and tributyltin hydride

Table 1
¹H- and ¹⁹F-NMR data for new compounds

Compound	a	b	c	d	e	f	g	h	i	j
1	81.6 (m) $J_{a,b} = 154.5$	65.6 (d,m) $J_{e,f} = 20.2$	4.24 (m) $J_{f,g} = 114$	3.52 (m) $J_{f,h} = 33$	4.08 (m) $J_{g,h} = 82$	-174.6 (d,d,t)	-121.2 (d,d)	-102.4 (d,d)		
2	65.2 (p,t) $J_{a,b} = 146.8$	44.7 (d,p) $J_{a,c} = 3.77$	-96.3 (p) $J_{b,c} = 15.1$	d - 112.7 (d,m) d' - 115.1 (d,m) $J_{b,d} = 11.3$	2.92 (m) $J_{d,d'} = 269.2$	4.48 (tt) $J_{h,i} = 113$	2.92 (m) $J_{h,j} = 33.4$	-176.1 (d,d,d,d)	-120.9 (d,d,t) $J_{g,h} = 10.8$	-102.9 (d,d) $J_{i,j} = 79.0$
3	64.6 (p,t) $J_{a,b} = 145.1$ $J_{h,i} = 113.9$	43.5 (d,p) $J_{a,c} = 4.68$ $J_{h,j} = 33.9$	-96.3 (p) $J_{b,c} = 15.0$ $J_{i,j} = 88.5$	-116.2 (m) $J_{b,d} = 13.9$	2.19 (d,d) $J_{d,e} = 18.0$	1.93 (p) $J_{e,f} = 7.8$	2.42 (d,m) $J_{f,g} = 7.6$	-176.9 (d,d,t) $J_{g,h} = 22.2$	-125.7 (d,d,t) $J_{g,i} = 7.5$	-106.4 (d,d,t) $J_{e,j} = 3.8$
4	67.2 (p,m) $J_{a,b} = 141.1$	44.7 (d,p) $J_{a,c} = 5.6$	-97.1 (p,t) $J_{b,c} = 14.1$	-115.0 (m) $J_{c,d} = 9.9$	5.8 (m)	6.0 (m)		6.1 (m)		
5	63.5 (p,t) $J_{a,b} = 144.9$	44.3 (d,p) $J_{b,c} = 15$	-94.2 (p)	-122.4 (m)	-123.2 (m)	-114.3 (m)	5.9 (m)			
6	65.0 (p,t) $J_{a,b} = 146.0$	43.9 (d,p) $J_{a,c} = 4.3$	-96.5 (p) $J_{b,c} = 14.2$	-115.0 (m) $J_{b,d} = 13.6$	2.39 (tt) $J_{d,e} = 18.8$	3.94 (t) $J_{e,f} = 6.4$	3.83 (s)			

Chemical shifts in ppm relative to CFCl₃ or (CH₃)₄Si.

Coupling Constants in Hz; s = singlet, d = doublet, t = triplet, p = pentet, m = multiplet.

- 1 F¹⁹SE¹⁹C¹⁹H₂¹⁹C¹⁹H¹⁹BrC¹⁹H₂¹⁹C¹⁹F¹⁹=C¹⁹F¹⁹F¹⁹ (f and h are *cis*).
 2 F¹⁹SE¹⁹C¹⁹F₂¹⁹C¹⁹F¹⁹F¹⁹C¹⁹H₂¹⁹C¹⁹H¹⁹C¹⁹F¹⁹=C¹⁹F¹⁹F¹⁹ (h and j are *cis*).
 3 F¹⁹SE¹⁹C¹⁹F₂¹⁹C¹⁹F¹⁹C¹⁹H₂¹⁹C¹⁹H¹⁹C¹⁹F¹⁹=C¹⁹F¹⁹F¹⁹ (h and j are *cis*).
 4 F¹⁹SE¹⁹C¹⁹F₂¹⁹C¹⁹F¹⁹C¹⁹H₂¹⁹C¹⁹H¹⁹=C¹⁹H₂¹⁹.
 5 F¹⁹SE¹⁹C¹⁹F₂¹⁹C¹⁹F¹⁹C¹⁹F₂¹⁹C¹⁹H₂¹⁹=C¹⁹H₂¹⁹.
 6 F¹⁹SE¹⁹C¹⁹F₂¹⁹C¹⁹F¹⁹C¹⁹H₂¹⁹C¹⁹H₂¹⁹OH¹⁹.

Table 2
¹³C-NMR (decoupled) data for new compounds

Compound	α	β	γ	δ	ε	ζ	η
1	76.2 (p) $J_{\alpha,b} = 14.0$ $J_{e,g} = 288.1$	40.5 (d) $J_{\beta,i} = 2.7$ $J_{e,h} = 288.6$	35.0 (d) $J_{\gamma,t} = 21.3$	126.0 (d,d,d) $J_{\delta,t} = 234.7$	154.5 (d,d,d) $J_{\delta,g} = 53.0$	$J_{\delta,h} = 53.1$	$J_{e,i} = 45.0$
2	121.7 (t,m) $J_{\alpha,c} = 301.8$ $J_{\xi,d} = 20.1$	117.5 (t,t) $J_{\beta,c} = 30.2$ $J_{\eta,h} = 40.2$	42.2 (t) $J_{\beta,d} = 261.6$ $J_{\eta,i} = 291.7$	11.5 (s) $J_{\gamma,d} = 21.1$ $J_{\eta,j} = 259.0$	37.4 (d) $J_{e,h} = 21.1$	127.5 (d,d,d) $J_{\xi,h} = 231.4$	154.3 (d,d,d) $J_{\xi,i} = 50.3$
3	122.4 (t,m) $J_{\alpha,c} = 305.9$ $J_{\xi,d} = 20.1$	118.0 (t,t) $J_{\beta,c} = 30.8$ $J_{\eta,h} = 40.2$	30.8 (t) $J_{\beta,d} = 256.5$ $J_{\eta,i} = 286.7$	16.9 (s) $J_{\gamma,d} = 22.6$ $J_{\eta,j} = 256.5$	24.9 (d) $J_{e,h} = 21.1$	127.8 (d,d,d) $J_{\xi,h} = 241.4$	153.8 (d,d,d) $J_{\xi,i} = 55.3$
4	123.2 (t,t,p) $J_{\alpha,b} = 25.0$	114.9 (t,t) $J_{\alpha,c} = 305.8$	126.6 (m) $J_{\alpha,d} = 38.5$	126.1 (s) $J_{\beta,c} = 30.3$	$J_{\beta,d} = 254.8$		
5	121.3 (t,t,p) $J_{\alpha,b} = 27.0$ $J_{\delta,c} = 31.3$	111.9 (t,p) $J_{\alpha,c} = 311.3$ $J_{\delta,t} = 253.6$	111.4 (t,p) $J_{\alpha,d} = 36.4$	114.9 (t,t) $J_{\beta,c/e} = 34$	125.8 (m) $J_{\beta,d} = 267.9$	125.8 (s) $J_{\gamma,d/t} = 32$	$J_{\gamma,e} = 271.9$
6	122.5 (t,m) $J_{\alpha,c} = 305.2$	118.3 (t,t) $J_{\beta,c} = 30.9$	35.1 (t) $J_{\beta,d} = 256.6$	55.4 (s) $J_{\gamma,d} = 21.6$			

Chemical shifts in ppm relative to (CH₃)₄Si.

Coupling constants in Hz; s = singlet, d = doublet, t = triplet, p = pentet, m = multiplet.

1 F^aSF₄^bC^cH₂^cC^βH^dBrC^γH₂^cC^δF^e=C^fF^gF^h (f and h are *cis*).

2 F^aSF₄^bC^cF₂^cC^βF₂^dC^γH₂^cC^δHⁱC^eH₂^cC^fH^j=C^gF^hFⁱ (h and j are *cis*).

3 F^aSF₄^bC^cF₂^cC^βF₂^dC^γH₂^cC^δH₂^cC^eH₂^cC^fH^j=C^gF^hFⁱ (h and j are *cis*).

4 F^aSF₄^bC^cF₂^cC^βF₂^dC^γH^e=C^fH₂^g.

5 F^aSF₄^bC^cF₂^cC^βF₂^dC^γF₂^cC^δF₂^eC^fH^g=C^hH₂ⁱ.

6 F^aSF₄^bC^cF₂^cC^βF₂^dC^γH₂^cC^δH₂^eOH^f.

(97%) were purchased from Aldrich and used as received. Mercury (triply distilled), carbon tetrachloride and potassium hydroxide (Pellets, 85%) were used as received.

3.2. General methods

NMR-spectra were recorded with a Varian EM-390 spectrometer operating at 84.67 MHz for ¹⁹F-analysis; a Bruker AMX-400 spectrometer operating at 400 MHz for ¹H-analysis, 100.6 MHz for ¹³C-analysis and 376.5 MHz for ¹⁹F-analysis. CDCl₃ was used as the solvent for all NMR samples; (CH₃)₄Si and CFCl₃ were used as internal standards. The IR-spectra were obtained between potassium bromide plates using a Perkin Elmer System 2000 FT-IR operating at 2 cm⁻¹ resolution or a Perkin Elmer PE 1600 operating at 4 cm⁻¹. Elemental analyses were determined by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. Mass spectra were measured via a Hewlett-Packard HP5890 series II gas chromatograph (25 m, DB-5 column) with a HP5970 mass selective detector operating at 70 eV.

3.3. Synthesis of SF₅CH₂CHBrCH₂CF=CF₂ (1)

3.3.1. Stainless steel reaction vessel

Into a 75 ml Hoke stainless steel vessel equipped with a Whitey stainless steel valve, 16.15 g (78 mmol) of SF₅Br

and 8.97 g (73.5 mmol) of CH₂=CHCH₂CF=CF₂ were condensed at -196°C. The reaction mixture was held at room temperature (≈ 22°C) for 24 h, then heated to 50°C with occasional shaking for 1 week. Distillation of the product at reduced pressure gave 5.61 g (23% yield) of compound 1; boiling point (b.p.), 58°C at 16 mm Hg.

3.3.2. Pyrex-glass reaction vessel

Into a 2 l Pyrex-glass vessel cooled to -196°C, 1.84 g (15.1 mmol) of CH₂=CHCH₂CF=CF₂ and 3.54 g (17.1 mmol) of SF₅Br were condensed. The vessel was maintained at room temperature for 18 h. Distillation at reduced pressure gave 4.52 g (91% yield) of compound 1.

The infrared spectrum exhibited the following bands (cm⁻¹): 2976 (w), 1802 (s), 1425 (m), 1302 (s), 1273 (m), 1243 (m), 1198 (m), 1174 (m), 1129 (m), 1103 (s), 1027 (w), 845 (vs), 825 (vs), 785 (w), 659 (w), 641 (w), 603 (w), 571 (m).

MS *m/z* (rel. abund., species): 330 (3, [M(⁸¹Br)]⁺), 328 [M(⁷⁹Br)]⁺, 141 (52, SF₅CH₂⁺), 140 (16, SF₅CH⁺), 127 (18, SF₅⁺), 122 (10, C₂F₃C₃H₅⁺), 121 (51, C₂F₃C₃H₄⁺), 113 (11, SF₃C₂⁺), 101 (45, SF₃C⁺), 95 (100, C₂F₃CH₂⁺), 89 (24, SF₃⁺), 81 (2, ⁸¹Br⁺, C₂F₃⁺), 79 (1, ⁷⁹Br⁺), 77 (38, C₃H₃F₂⁺), 75 (13, C₃HF₂⁺), 72 (12, C₄H₅F⁺), 71 (10, C₄H₄F⁺), 70 (11, SF₂⁺), 69 (54, CF₃⁺), 51 (26, SF⁺), 45 (10, C₂H₂F⁺), 39 (17, C₃H₃⁺), 27 (21, C₂H₃⁺).

3.4. Synthesis of $SF_5CF_2CF_2CH_2CHICH_2CF=CF_2$ (2)

To a 130 ml Pyrex-glass Carius tube equipped with a Kontes Teflon stopcock, two drops (≈ 0.5 g) of mercury and 5.13 g (15 mmol) of $SF_5CF_2CF_2I$ were added. The Carius tube was cooled to $-196^\circ C$, evacuated, and 1.76 g (14 mmol) of $CH_2=CHCH_2CF=CF_2$ was condensed into the vessel. The vessel was irradiated for 7 days (with shaking 5 times in 24 h) using a halogen lamp (Sylvania Capsylite Halogen Par 38) maintained at a distance of 12–18 in. An additional 0.088 g (0.7 mmol) of the diolefin was added after the fourth day of irradiation. After the irradiation period the volatile materials were removed from the reaction vessel by vacuum transfer into a round bottom flask cooled to $-196^\circ C$. The viscous liquid remaining in the reaction vessel was removed by washing four times with 5 ml portions of carbon tetrachloride. Distillation of the washing solution was performed to remove the carbon tetrachloride. The remaining liquid was combined with the contents of the round bottom flask and distilled at reduced pressure to give 5.10 g (74% yield) of compound 2; b.p., 86.5 – $88^\circ C$ at 14 mm Hg.

The infrared spectrum exhibited the following bands (cm^{-1}): 2967 (vw), 2930 (vw), 2894 (vw), 1802 (m), 1427 (w), 1377 (vw), 1359 (w), 1307 (m,br), 1249 (m), 1201 (s), 1166 (m), 1124 (s), 1085 (m), 997 (w), 963 (vw), 926 (w), 881 (vs), 837 (s), 821 (m), 783 (vw), 751 (m), 684 (w), 605 (m), 576 (w), 540 (vw), 522 (w), 512 (vw).

Analysis: Calc. for $C_7H_5F_{12}IS$: C, 17.66; H, 1.06; F, 47.9%; Found: C, 17.91; H, 1.11; F, 48.1%.

MS m/z (rel. abund., species): 475 (6, $[M-H]^+$), 349 (23, $[M-I]^+$, $[M-SF_5]^+$), 221 (33, $C_7F_7H_4^+$), 201 (27, $C_7F_6H_3^+$), 177 (73, $SF_5CF_2^+$), 151 (29, $C_6F_4H_3^+$), 127 (85, SF_5^+ , I^+ , $C_2F_4C_2H_3^+$), 121 (61, $C_5F_3H_4^+$), 113 (35, $C_2F_4CH^+$), 109 (32, $C_4F_3H_4^+$), 100 (64, $C_2F_4^+$), 95 (100, $C_2F_3CH_2^+$), 89 (42, SF_3^+), 77 (62, $CF_2C_2H_3^+$), 69 (68, CF_3^+), 51 (39, SF^+).

3.5. Synthesis of $SF_5CF_2CF_2CH_2CH_2CH_2CF=CF_2$ (3)

To a 25 ml three-neck flask equipped with a Teflon-coated stirring bar, dropping funnel, nitrogen inlet, and a water cooled condenser attached to a $-78^\circ C$ trap and a drying tube containing Drierite was added 4.55 g (9.6 mmol) of compound 2. The flask was flushed with nitrogen, cooled to $-20^\circ C$, and 3.33 g (11.4 mmol) of tributyltin hydride was added via the dropping funnel over a 1 h period. After the addition of tributyltin hydride the reaction vessel was flushed with nitrogen and allowed to warm to room temperature over an 18 h period. Distillation of the reaction mixture gave 2.03 g (60% yield) of compound 3; b.p., 55.5 – $58^\circ C$ at 14 mm Hg.

The infrared spectrum exhibited the following bands (cm^{-1}): 2968 (w), 2929 (w), 2894 (vw), 2856 (vw), 1801 (m), 1772 (w), 1559 (vw), 1492 (vw), 1467 (w), 1440 (w), 1390 (w), 1364 (vw), 1303 (m), 1254 (m), 1202 (s), 1139 (m), 1118 (m), 1009 (m), 974 (w), 924 (m), 881

(vs), 833 (s), 791 (m), 744 (m), 705 (vw), 682 (m), 640 (vw), 605 (m), 574 (w), 547 (w), 535 (w), 483 (vw), 449 (vw), 417 (vw).

Analysis: Calc. for $C_7H_6F_{12}S$: C, 24.00; H, 1.73; F, 65.1; S, 9.16%; Found: C, 24.35; H, 1.80; F, 64.8; S, 8.97%.

3.6. Synthesis of $SF_5CF_2CF_2CH=CH_2$ (4)

A mortar and pestle was used to grind 7.35 g (131 mmol) of KOH pellets into a fine powder. The KOH powder was placed in a 50 ml Carius tube equipped with a Teflon-coated stirring bar and a Kontes Teflon stopcock. Addition of 6.83 g (17.9 mmol) of $SF_5CF_2CF_2CH_2CH_2I$ resulted immediately in a light yellowish-brown liquid. The reaction vessel was cooled to $-196^\circ C$ and evacuated. After heating at 75 – $90^\circ C$ for 17 h a clear, colorless liquid was removed from the reaction vessel in vacuo and collected in a $-196^\circ C$ trap. Distillation of the liquid at atmospheric pressure gave 3.85 g (85% yield) of compound 4; b.p., 74 – $75^\circ C$.

The infrared spectrum exhibited the following bands (cm^{-1}): 3118 (w), 3103 (w), 3062 (w), 3014 (w), 1940 (w), 1652 (w), 1563 (w), 1494 (w), 1423 (ms), 1297 (w), 1264 (m), 1234 (ms), 1200 (s), 1151 (s), 1118 (s), 1093 (ms), 1021 (m), 980 (ms), 970 (ms), 937 (m), 879 (vs), 832 (vs), 819 (vs), 743 (ms), 729 (m), 683 (m), 658 (w), 648(w), 603 (s), 574 (ms), 541 (w), 517 (m), 465 (w), 440 (w), 416 (w).

Analysis: Calc. for $C_4H_3F_9S$: C, 18.90; H, 1.19; F, 67.3; S, 12.62%; Found: C, 19.10; H, 1.27; F, 67.4; S, 12.30%.

MS m/z (rel. abund., species): 127 (12, SF_5^+ , $C_4H_3F_4^+$), 100 (4, $C_2F_4^+$), 89 (10, SF_3^+ , $C_4H_3F_2^+$), 77 (74, $C_3H_3F_2^+$), 75 (4, $C_3HF_2^+$), 69 (6, CF_3^+), 51 (28, SF^+ , CHF_2^+), 32 (25, $^{32}S^+$, CHF^+), 31 (14, CF^+), 28 (100, $C_2H_4^+$), 27 (16, $C_2H_3^+$), 14 (11, CH_2^+).

3.7. Synthesis of $SF_3(CF_2CF_2)_2CH=CH_2$ (5)

The synthesis of compound 5 is similar to that for compound 4 reported above (Section 3.6). 5.60 g (100 mmol) of finely ground KOH and 5.04 g (10.5 mmol) of $SF_5(CF_2CF_2)_2CH_2CH_2I$ were placed in a Carius tube. The reaction vessel was cooled to $-196^\circ C$, evacuated, and heated at 85 – $100^\circ C$ for 4 h. Removal of the clear, colorless liquid in vacuo and subsequent distillation gave 3.08 g (83% yield) of compound 5; b.p., 105 – $107^\circ C$ at 500 mm Hg.

The infrared spectrum exhibited the following bands (cm^{-1}): 3103 (vw), 3062 (vw), 3016 (vw), 1938 (vw), 1654 (w), 1504 (vw), 1423 (m), 1318 (w), 1297 (w), 1223 (s), 1176 (s), 1151 (s), 1106 (m), 1090 (m), 1019 (m), 1000 (m), 982 (m), 968 (m), 948 (m), 885 (vs), 812 (m), 790 (s), 758 (s), 730 (s), 708 (m), 685 (m), 641 (w), 604 (s), 579 (m), 538 (w), 507 (w), 443 (w), 417 (w).

Analysis: Calc. for $C_6H_3F_{13}S$: C, 20.35; H, 0.85; F, 69.74; S, 9.05%; Found: C, 19.84; H, 0.48; F, 70.00; S, 9.63%.

3.8. Synthesis of $SF_5CF_2CF_2CH_2CH_2OH$ (**6**)

Into a 50 ml Pyrex-glass Carius tube equipped with a Teflon coated stirring bar and a Kontes Teflon stopcock, 9.74 g (25.5 mmol) of $SF_5CF_2CF_2CH_2CH_2I$ and 14.44 g (170 mmol) of 2-pyrrolidinone were added. The vessel was cooled to $-196^\circ C$ and evacuated. After heating to $130\text{--}140^\circ C$ for 19 h, distillation at reduced pressure using a 15 cm Vigreux column gave 3.32 g (48% yield) of **6**; b.p., $64\text{--}64.5^\circ C$ at 13 mm Hg. In addition, 0.99 g (15% yield) of the dehydroiodination product **4** was collected.

The infrared spectrum exhibited the following bands (cm^{-1}): 3649 (vw), 3369 (m, br), 2965 (w), 2909 (w), 1767 (vw), 1482 (vw), 1445 (vw), 1431 (w), 1399 (w), 1371 (w), 1335 (vw), 1307 (w), 1260 (w), 1196 (s), 1119 (s), 1051 (m), 1009 (m), 962 (w), 875 (vs), 833 (s), 804 (s), 760 (vw), 739 (m), 716 (w), 682 (m), 645 (vw), 605 (s), 574 (m), 550 (w), 529 (w), 486 (vw), 455 (w), 428 (w).

Analysis: Calc. for $C_4H_5F_9SO$: C, 17.65; H, 1.85; F, 62.8%; Found: C, 17.73; H, 1.86; F, 63.2%.

MS m/z (rel. abund., species): 271 (0.1, $[M - H]^+$), 127 (6, SF_5^+ , $C_2F_4C_2H_3^+$), 113 (14, $C_2F_4CH^+$), 105 (18, $C_4F_3^+$), 95 (22, $C_2F_3CH_2^+$, $CF_2C_2H_4OH^+$), 89 (28, SF_3^+ , $C_2F_2C_2H_3^+$), 77 (26, $CF_2C_2H_3^+$), 69 (11, CF_3^+), 64 (12, $CF_2CH_2^+$), 51 (11, SF^+ , CHF_2^+), 31 (100, CF^+ , CH_2OH^+), 29 (16, $C_2H_5^+$).

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