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Halogen displacement chemistry with silver and alkali metal salts: Preparation of SF_5-esters, alcohols, aliphatic olefins, acids and an iodide

R.W. Winter, G.L. Gard *

Department of Chemistry, Portland State University, Portland, OR 97207, United States

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Abstract

It has been found that treatment of SF_5-alkyl halides, especially $SF_5(CH_2)_2Br$, with silver salts such as $CH_3C(O)OAg$, p-$CH_3C_6H_4SO_3Ag$, CF_3SO_3Ag and $AgNO_3$ provides convenient pathways for preparing the following ester compounds: $SF_5CH_2CH_2R$ (R = CH_3COO, TosO, CF_3SO_3, NO_3), $SF_5(CH_2)_3OTos$, and $SF_5(CF_2)_4(CH_2)_2OAc$. Important derivatives prepared from these esters include $SF_5(CH_2)_2OH$; $SF_5(CF_2)_4(CH_2)_2OH$. Several alkenes $SF_5C(Br)=CH_2$ and $SF_5CH_2(COOCH_3)C=CHC(O)OCH_3$ are obtained using silver salts. The use of alkali metals salts with $SF_5(CH_2)_3Br$ is studied and yields $SF_5(CH_2)_3I$; also, a pathway has been developed that extends for $SF_5(CH_2)_3$– the chain by two-carbon atoms and also produces the first SF_5-containing malonic acid.
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1. Introduction

The use of silver salts in chemistry often allows one to obtain derivatives that cannot be prepared by other means. This method allows the transfer of various groupings either to or from silver salts. A recent survey covering the preparation and reaction of perfluoroorganosilver(I) compounds has been published [1]. There are several reports in the literature that describe either the formation or use of silver and alkali metals salts containing the SF_5-group. The reaction of AgF with $SF_5CF=CF_2$ gave the isolatable salt, $Ag(SF_5CFCF_3)\cdot CH_3CN$ [2]. The reaction of $AgNO_3$ and $SF_5C\equiv CH$ produced a partially characterized $SF_5C\equiv CAg$ salt [3]. The lithium salt, $SF_5C\equiv CLi$ has been prepared in solution and was used to synthesize a number of interesting $SF_5C\equiv CX$ (X = Hg, Cl, Br, I) compounds [4]. The MSF_5 salts (M = Ag, K, Rb, Cs, $(CH_3)_4$, Cs(18-crown-6)$_2$) were prepared from MF and SF_4 [5]. The alkali metal and silver salts can be used to prepare SF_5Cl [6]. Silver salts of SF_5-carboxylic acids have been prepared by reacting the corresponding acid with silver carbonate: $SF_5CX_2C(O)OAg$ (X = H or F) [7–10]. The reaction of the silver salts with halogens (X = Br, I) gave the corresponding SF_5CH_2Br [7,8] and SF_5CF_2I [9]. Several alkali metal salts of SF_5-carboxylic acids have also been reported [10,11]. We have now found that silver salt anions can replace the halide in various SF_5-alkyl halides thereby considerably expanding the range of reactivity of this readily available but poorly reactive class of SF_5-compounds. These method may be advantageously used to prepare SF_5-esters, alcohols, and alkenes. In some instances alkali metal salts may be used in lieu of silver salts.

2. Results and discussion

In general, previous attempts to replace the halogen (X = Br, Cl) in two-carbon SF_5-alkyl halides have resulted in either no reaction, elimination of XF or destruction of the SF_5-group; for example, treating $SF_5CH_2CH_2Br$ with NaI resulted in the complete destruction of the SF_5-group [12]. The purpose of this study was to make direct use of the SF_5-alkyl bromides or iodides that are easily prepared using either SF_5Br or $SF_5(CF_2)_nI$. For the compound $SF_5(CH_2)_3Br$ it was found that the Br could be easily replaced; this is in sharp contrast with $SF_5(CH_2)_2Br$. This study also afforded an improved method for making SF_5-fluoroalkyl alcohols in high yields and a new pathway for carbon chain extension in SF_5-systems. A safe and

* Corresponding author. Fax: +1 503 725 9525.
E-mail address: gardg@pdx.edu (G.L. Gard).

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effective method for preparing $SF_5CH_2CH_2Br$ is also given. This compound should not be prepared from SF_5Br and $H_2C{=}CH_2$ under pressure and heat as carbonization will occur [12].

The following SF_5-fluoroalkyl and SF_5-alkyl esters have been prepared by treatment of silver salts with the SF_5-fluoroalkyl and SF_5-alkyl iodide or bromides; all but $SF_5CH_2CH_2OTos$ are new compounds. $SF_5CH_2CH_2OTos$ was previously prepared from $SF_5CH_2CH_2OH$ and *p*-$CH_3C_6H_4SO_2Cl$ [13]:

$$SF_5CH_2CH_2Br + AgOAc \xrightarrow{CH_3COOH} SF_5CH_2CH_2OAc + AgBr \quad (\mathbf{1})$$
$$(bp, 50{-}52\,^{\circ}C/10\,Torr; 67\%) \qquad (1)$$

$$SF_5CH_2CH_2Br + AgOTf \xrightarrow{C_6H_6} SF_5CH_2CH_2OTf + AgBr \quad (\mathbf{2})$$
$$(oil, 68\%) \qquad (2)$$

$$SF_5CH_2CH_2Br + AgOTos \xrightarrow{CH_3CN} SF_5CH_2CH_2OTos + AgBr \quad (\mathbf{3})$$
$$(mp54{-}55\,^{\circ}C; 82\%) \qquad (3)$$

$$SF_5CH_2CH_2Br + AgONO_2 \xrightarrow{CH_3CN} SF_5CH_2CH_2ONO_2 + AgBr \quad (\mathbf{4}) \quad (oil, 70\%) \qquad (4)$$

$$SF_5(CH_2)_3Br + AgOTos \xrightarrow{CH_3CN} SF_5(CH_2)_3OTos + AgBr \quad (\mathbf{5})$$
$$(oil, 87\%) \qquad (5)$$

$$SF_5(CF_2)_4(CH_2)_2I + AgOAc \xrightarrow{CH_3COOH} SF_5(CF_2)_4(CH_2)_2OAc + AgI \quad (\mathbf{6}) \quad (oil, 84\%) \qquad (6)$$

When the following SF_5-esters were transesterified, the corresponding alcohols were prepared in high yields:

$$SF_5CH_2CH_2OAc \xrightarrow[2i]{i} SF_5CH_2CH_2OH,$$
$$(i)\ cat.\ amt.\ NaOCH_3\ in\ CH_3OH,\ (2i)\ aq.\ HCl\ (trace) \quad (\mathbf{7})$$
$$(bp73\,^{\circ}C/50\ \ Torr; 79\%) \qquad (7)$$

$$SF_5(CF_2)_4(CH_2)_2OAc \xrightarrow[2i]{i} SF_5(CF_2)_4(CH_2)_2OH,$$
$$(i)\ cat.\ amt.\ NaOCH_3\ in\ CH_3OH,\ (2i)\ aq.\ HCl\ (trace) \quad (\mathbf{8})$$
$$(oil, 69\%) \qquad (8)$$

An important outcome of the above method is that SF_5-containing alcohols are readily prepared in high yields and purity. The alcohol $SF_5CH_2CH_2OH$ was previously prepared from SF_5Cl and ketene followed by reduction of $SF_5CH_2C(O)Cl$ with $LiAlH_4$ [13], while $SF_5(CF_2)_2(CH_2)_2OH$ was prepared by the laborious lactam method [14].

An interesting observation was made when the following two SF_5Br–olefin adducts were treated with silver salts:

$$SF_5CHBrCH_2Br + AgOAc \xrightarrow{CH_3COOH} SF_5C(Br){=}CH_2 + AgBr + CH_3COOH \quad (\mathbf{9})$$
$$(72\%) \qquad (9)$$

$$SF_5CH_2(COOCH_3)CBrCH_2COOCH_3 + AgOTos \xrightarrow{CH_3CN} SF_5CH_2(COOCH_3)C{=}CHC(O)OCH_3 + AgBr + TosOH \quad (\mathbf{10}) \quad (mp, 30{-}31\,^{\circ}C; \approx 30\%) \qquad (10)$$

The silver salt acts as a base in these reactions with the formation of AgBr and the corresponding acid; when bromine is in the β-position to an acidic C–H bond, an elimination over substitution reaction is apparently favored.

The starting SF_5-compound in reaction (10) was prepared by the following reaction which was carried out in CH_2Cl_2:

$$CH_2{=}C(COOCH_3)CH_2C(O)OCH_3 + SF_5Br \rightarrow \mathit{SF}_5CH_2CBr(COOCH_3)CH_2C(O)OCH_3 \quad (\mathbf{11})$$
$$(\mathit{oil}, 75\%) \qquad (11)$$

In addition to studying the chemistry of selected silver salts with SF_5 two-carbon halides, it was also of interest to look at SF_5 three-carbon halides. It was found that in $SF_5(CH_2)_3Br$ the bromine could be substituted with tosyloxy and iodide. Therefore, the SF_5 three-carbon group is more stable and readily transferable. This stability should allow the use of alkali salts in preparing SF_5-containing derivatives. Of great importance was the development of a method for chain elongation in SF_5-alkanes. The following three-step reaction scheme clearly demonstrates this new procedure:

$$SF_5(CH_2)_3Br + KCH(COOC(CH_3)_3)_2 \rightarrow \mathit{SF}_5(CH_2)_3CH(COOC(CH_3)_3)_2 + KBr \quad (\mathbf{12})$$
$$(\approx 100\%) \qquad (12)$$

$$SF_5(CH_2)_3CH(COOC(CH_3)_3)_2 + HCl_{(aq)} \rightarrow \mathit{SF}_5(CH_2)_3CH(COOH)_2 + (CH_3)_2C{=}CH_2 + H_2O \quad (\mathbf{13})$$
$$(\mathit{semi\text{-}solid}, 86\%) \qquad (13)$$

$$SF_5(CH_2)_3CH(COOH)_2 \xrightarrow{170\,^{\circ}C} SF_5(CH_2)_4COOH + CO_2 \quad (\mathbf{14})$$
$$(80{-}85\,^{\circ}C/70{-}90\,\mu m, 60\%) \qquad (14)$$

In contrast to $SF_5(CH_2)_2Br$, the three-carbon chain survived treatment with NaI:

$$SF_5(CH_2)_3Br + NaI \xrightarrow{acetone} SF_5(CH_2)_3I + NaBr \quad (\mathbf{15})$$
$$(46{-}47\,^{\circ}C/5\,Torr; 73\%) \qquad (15)$$

The infrared spectra for the new compounds exhibit strong absorption bands in the 800–900 cm^{-1} range due to the S–F stretching modes of the SF_5-group. The C–H stretching bands were located near 3000 cm^{-1}. The carbonyl stretching band for compounds **1**, **6**, **11**, **12**, and **14** is located in the range 1714–1752 cm^{-1}.

The mass spectral peaks contained, for some of the compounds, a parent ion but all compounds had peaks supporting the assigned structures.

The ^1H and ^{19}F NMR spectral data for all new compounds are given in Section 3. The compounds show a typical AB_4 splitting pattern in the ^{19}F NMR spectrum for the SF_5-group. Except for $SF_5(CF_2)_4(CH_2)_2OOCCH_3$ (**6**), the axial fluorine (A) for the new SF_5-acids and esters appears as a nine line pattern

and is located in the range 80–86 ppm; for (**6**) the axial fluorine appears at 65.0 ppm. The equatioral fluorines (B), except for (**6**), appear as a doublet of multiplets in the range of 64–66 ppm; for (**6**) the axial fluorine is found at 45.0 ppm. The values for these compounds and for the remaining SF_5-compounds are in excellent agreement with analogous SF_5-compounds [15].

3. Experimental

The reactant SF_5Br was prepared from SF_4, BrF_3, Br_2 and CsF via a method previously described by our laboratory [16]. The compounds $SF_5(CH_2)_3Br$ [15], $SF_5(CF_2)_4(CH_2)_2I$ [17] and $SF_5CHBrCH_2Br$ [3] were prepared according to the literature method. $SF_5CH_2CH_2Br$ was first prepared by Merrill [18]. We have modified his method in order to prepare larger amounts in a safe and facile manner.

The infrared spectra of the reactants and products were obtained on a Perkin-Elmer 2000 FTIR spectrometer operating at 1.0 cm^{-1} resolution using KBr windows. The NMR spectroscopy values were obtained by use of the following instruments: ^{19}F Varian EM-390 (84.7 MHz) and ^{1}H General Electric (500 MHz) in $CDCl_3$ with CCl_3F and $Si(CH_3)_4$ as internal standards. Gas chromatography–mass spectroscopy (GC–MS) results were obtained using a Hewlett-Packard HP5890 mass selective detector (operating at 70 eV) and a DB5, 30 m column; the temperature profile used was 50 °C for 2 min, then 11 °C min^{-1} up to 280 °C. The HRMS values were determined on a Kratos MS 50TC; chemical ionization with methane.

3.1. $SF_5CH_2CH_2Br$

An acid-washed and very dry 3 l surge-vessel with a cylindrical extension at one end (finger) and a Teflon stopcock at the other end was charged by vacuum-condensation (liquid nitrogen) with ethylene and then SF_5Br so that their combined pressure at room temperature would be 1 atm (a slight excess of ethylene was used). The vessel was slowly warmed to room temperature; a reaction was noticed by a wetting of the walls, fog formation and a steady increase of the volume of liquid collecting in the cylindrical finger of the vessel. After several hours, the product is transferred into a cold-trap. If the vessel had been properly dried and the SF_5Br was of good quality, the product would be pure and obtained in practically quantitative yield. However, it is recommended that the product (bp = 108 °C) is distilled because of the frequent presence of trace quantities of SF_4 which would lead to etching of glass containers upon storage.

^{1}H NMR spectrum: $\delta_1 = 3.74$ ppm, m, 2H (CH_2Br); $\delta_2 = 4.06$, m, 2H (SF_5CH_2).

^{19}F NMR spectrum: (AB_4-type) $\delta_A = 78.6$ ppm, nine lines, 1F; $\delta_B = 67.4$, skewed d–m, 4F, $J_{AB} = 150$ Hz.

Infrared spectrum (KBr): 3059, vw; 3030, vw; 2983, vw; 1752, vs; 141434, w–m; 1314, w; 1279, w; 1223, w–m; 1145, 977, w–m; 927, w–m; 828 (vs with sh at 828); 584, vs.

Mass spectrum (70 eV: ion (*m*/*z*), %, assignment): $R_t = 2.31$ min, 236, 234, 5%, 5%, $M(^{81}Br, ^{79}Br)^+$; 127, 28, SF_5^+; 109, 107, 97%, 100%, $(M - SF_5)^+$; 89, 38, SF_3^+; 70, 11, SF_2^+; 51, 2, SF^+; 47, 52, $(C_2H_4F)^+$, $(SCH_2 + H)^+$; 28, 13, $C_2H_4^+$; 27, 80, $C_2H_3^+$; 26, 12, $C_2H_2^+$.

3.2. $SF_5CH_2CH_2OOCCH_3$ (**1**)

$SF_5CH_2CH_2Br$ (1.11 g, 4.72 mmol), CH_3COOAg (0.90 g, 5.4 mmol) and 10 ml of glacial acetic acid were heated in a 25 ml round bottom flask containing a stirring bar to reflux for 5 days. AgBr was filtered off, the filtrate was poured into 100 ml of water and the product extracted with ether (1× 20, 2× 10 ml). Distillation affords 0.68 g of a colorless liquid, bp = 50–52 °C/10 Torr, yield = 67%. The time of refluxing could be halved by adding about 1 g of potassium acetate for every 6 g of silver acetate (to increase the solubility of silver acetate).

^{1}H NMR spectrum: $\delta_1 = 4.49$ ppm, t (each band shows signs of additional (pentet) splitting), $J_t = 6.10$ Hz, $J_p \approx 1$ Hz, 2H (CH_2O); $\delta_2 = 3.91$, t–p, $J_t = 6.10$, $J_p = 7.85$, 2H (SF_5CH_2); $\delta_3 = 2.10$, s, 3H (CH_3CO).

^{19}F NMR spectrum: (AB_4-type) $\delta_A = 80.3$ ppm, nine lines, 1F; $\delta_B = 66.0$, skewed d, 4F, $J_{AB} = 148$ Hz.

Infrared spectrum (KBr): 3034, w; 2986, w; 1752, vs; 1720, sh, s; 1466, sh, m; 1419, m; 1393, m; 1371, m–s; 1310, w; 1286, sh, m–s; 1241, s–vs; 1084, br, w–m; 1051, s; 1004, w; 978, w–m; 944, w; 839, vs; 812, s; 712, w; 635, w–m; 604, m; 586, w–m; 565, w–m; 553, m.

Mass spectrum (70 eV: ion (*m*/*z*), %, assignment): $R_t = 4.33$ min, 137, 1, $(SF_4CH_2CH_2 + H)^+$; 133, $SF_4C_2H^+$; 127, 8, SF_5^+; 122, <1, $SF_4CH_2^+$; 89, 11, SF_3^+; 87, 11, $CH_2CH_2OOCCH_3^+$; 70, 1, SF_2^+; 61, 2, $(SCH_2CH_2 + H)^+$; 47, 9, $(SCH_2 + H)^+$; 43, 100, CH_3CO^+.

Anal. calcd. for $C_4H_7F_5O_2S$: C, 22.43; H, 3.29; F, 44.4; S, 14.97. Found: C, 22.72; H, 3.32; F, 44.0; S, 14.91.

3.3. $SF_5CH_2CH_2OSO_2CF_3$ (**2**)

$SF_5CH_2CH_2Br$ (4.15 g, 17.7 mmol) and silver triflate (6.65 g, 25.9 mmol) in 50 ml of benzene were heated in a 30 ml Carius tube in an oil bath at 115–120 °C for a total of 3 weeks; a gradual darkening occurred during heating. AgBr was filtered (2.63 g, 79%) and the benzene evaporated (rotary evaporator); the product was taken up in 50 ml of methylene chloride (a salt is precipitated) and passed through 5 g of Kieselgel and after re-evaporation, 3.63 g (68%) of a brown clear, oily compound was obtained, and found to be virtually pure by GC–MS analysis. When (**2**) is distilled under high vacuum a colorless oil is found; at ambient temperatures a yellow cast is quickly formed.

^{1}H NMR spectrum: $\delta_1 = 4.86$ ppm, t, $J_{12} = 6.0$ Hz, 2H; $\delta_2 = 4.02$, t–p, $J_{SF_4CH_2} = 7.6$, $J = 6.0$, 2H.

^{19}F NMR spectrum: (AB_4-type) $\delta_A = 80.0$ ppm, nine lines, 1F; $\delta_B = 66.0$, skewed d, 4F, $J_{AB} = 147$ Hz; $\varphi_{CF_3} = -75$, s, 3F.

Infrared spectrum (KBr): 3037, w; 2986, w; 1752, w–m; 1420, vs; 1339, vw; 1277, sh, w; 1248, s–vs; 1219, s–vs; 1145, s–vs; 1084, w–m; 1054, vw; 1006, s; 975, s; 926, m–s; 898, sh, m; 834, vs; 795, m–s; 755, m–s; 706, vw; 676, w; 641, sh, m; 615, s; 591, m; 579, w–m; 566, m; 554, m–s; 526, m.

Mass spectrum (70 eV: ion (*m*/*z*), %, assignment): R_t = 4.13 min, 177, 2, $(M - SF_5)^+$; 165, 4, $(CF_3SO_2OCH_2 + 2H)^+$; 135, 9, $C_2H_3SF_4^+$; 133, 9, $CF_3SO_2^+$, $C_2HSF_4^+$; 127, 27, SF_5^+; 101, 16, CF_3S^+; 99, 10, $(C_2H_4SF_2 + H)^+$; 89, 29, SF_3^+; 69, 100, CF_3^+; 47, 44, $(CH_2S + H)^+$.

High-resolution mass spectrum calcd. for $^{12}C_3H_5{}^{19}F_8{}^{32}S_2{}^{16}O_3$ (MH^+): 304.95523. Found: 304.95322.

3.4. $SF_5CH_2CH_2OTos$ (**3**)

$SF_5CH_2CH_2Br$ (8.01 g, 34.1 mmol), silver tosylate (15.0 g, 35.8 mmol) and acetonitrile (20 ml) were heated in a 30 ml Carius tube in a boiling water bath for 9 h. AgBr was filtered away and the filtrate was poured into water (100 ml); the product was extracted with ether (3× 30 ml). The solvent was removed and the crude product passed through 20 g of Kieselgel in CH_2Cl_2. The solvent was removed and 9.05 g of an oil was obtained; the oil slowly solidified. mp = 54–55 °C, reported, 56 °C [13]. Yield = 81.5%.

^{1}H NMR spectrum: δ_1 = 4.40 ppm, t, J_t = 6.25 Hz, 2H (CH_2O); δ_2 = 3.91, t–p, J_t = 6.25, J_p = 7.81, 2H (SF_5CH_2); δ_3 = 2.10, s, 3H ($CH_3C_6H_4$). δ = 7.38, d, 2H; δ = 7.80, d, 2H, J = 8.20 (toluyl).

^{19}F NMR spectrum: (AB_4-type) δ_A = 81.4 ppm, nine lines, 1F; δ_B = 66.2, skewed d, 4F, J_{AB} = 146 Hz.

Mass spectrum (70 eV: ion (*m*/*z*), %, assignment): R_t = 15.71 min, 326, 31, M^+; 172, 2, $TosOH^+$; 155, 87, $(M - TosO)^+$; 133, 5, $SF_3CH_2CH_2O^+$; 107, 8, $C_2H_3SO_3^+$; 91, 100, $C_7H_7^+$; 89, 9, SF_3^+; 77, 3, $C_2H_2SF^+$; 65, 19, CH_2SF^+; 51, 2, SF^+; 39, $C_3H_3^+$.

3.5. $SF_5CH_2CH_2NO_3$ (**4**)

$SF_5CH_2CH_2Br$ (2.45 g, 10.4 mmol), 10 ml of CH_3CN and $AgNO_3$ (6.8 g, 140.5 m.f.w.) were heated in a 30 ml Carius tube at 100 °C for 5 h. After filtration, the filtrate was poured into 100 ml of water, and the product was extracted with ether (3× 20 ml). The combined extracts were washed once with 10 ml of water and then dried over Na_2SO_4. The product was concentrated under vacuum; 1.63 g of a colorless, slightly oily product (72%) was obtained. Further distillation was not attempted.

^{1}H NMR spectrum: δ_1 = 4.88 ppm, t, J_t = 6.1 Hz, 2H (CH_2O); δ_2 = 3.97, t–p, J_t = 6.1, J_p = 7.63, 2H (SF_5CH_2).

^{19}F NMR spectrum: (AB_4-type) δ_A = 81.0 ppm, nine lines, 1F; δ_B = 66.0, skewed d, 4F, J_{AB} = 146 Hz.

Infrared spectrum (KBr): 3039, w–m; 2987, w; 2917, w–m; 2666, w–vw; 2560, w; 2385, w; 2257, w; 1652, vs; 1465, m; 1437, m; 1419, m–s; 1388, w; 1335, w–m; 1284, s; 1227, w; 1216, w; 1083, w–m; 1071, w–m; 1030, m; 1000, m; 898, sh, m; 837, vs; 756, m; 737, w; 706, w; 674, w; 648, br, w; 605, w–m; 587, w–m; 565, w–m; 550, w–m.

Mass spectrum (70 eV: ion (*m*/*z*), %, assignment): R_t = 3.78 min, 151, <1%, $(M - NO_2–H–F)^+$; 133, 5, $SF_4C_2H^+$; 127, 12, SF_5^+; 122, 6, $SF_4CH_2^+$; 108, <1, SF_4^+; 89, 20, SF_3^+; 76, 4, $SC_2H_4O^+$; 70, 4, SF_2^+; 46, 100, NO_2^+.

High-resolution mass spectrum calcd. for $^{12}C_2H_5{}^{19}F_5{}^{16}O_3{}^{32}S^{14}N$ (MH^+): 217.99104. Found: 217.99087.

3.6. $SF_5CH_2CH_2CH_2OTos$ (**5**)

$SF_5CH_2CH_2CH_2Br$ (1.00 g, 4.0 mmol), silver tosylate (2.10 g, 7.2 mmol) and acetonitrile (10 ml) were heated in 30 ml Carius tube in a boiling water bath for 9 h. The product was isolated as described for $SF_5CH_2CH_2OTos$ and obtained as an oil (1.19 g) in 87% yield.

^{1}H NMR spectrum: δ_1 = 4.10 ppm, t, J_t = 5.7 Hz, 2H (CH_2O); δ_2 = 2.28, ≈t–t (broadened), $J \approx 5.7$, $J \approx 7.7$ Hz, 2H (C–CH_2–C); δ_3 = 3.72, t–p (or septet), J_t = 7.8, J_p = 7.8, 2H (SF_5CH_2); δ_4 = 2.46, s, 3H ($CH_3C_6H_4$); δ = 7.37, d, 2H; δ = 7.78, d, 2H, J = 8.20 (toluyl).

^{19}F NMR spectrum: (AB_4-type) δ_A = 84.7 ppm, nine lines, 1F; δ_B = 65.2, skewed d, 4F, J_{AB} = 150 Hz.

Infrared spectrum (KBr): 3068, vw; 3040, vw; 2975, w; 2925, w; 2865, vw; 1599, 1496 w–m; 1471, w–m; 1450, w–m; 1434, w–m; 1399, w–m; 1361 (s with sh at 1389); 1308, w–m; 1295, w–m; 1252, w; 1215, w; 1191, s; 1178, s; 1120, w; 1098, m; 1076, w; 1042, vw; 1019, w–m; 985, w–m; 934, s; 831 (vs with sh at 868); 816, vs; 770, w–m; 742, m; 702, vw; 686, w–m; 663, s; 633, s; 600, s.

Mass spectrum (70 eV: ion (*m*/*z*), %, assignment): R_t = 17.2 min, 340, 22, M^+; 213, <1, $(M - SF_5)^+$; 185, 3, $TosOCH_2^+$; 172, 14, $TosOH^+$; 155, 100, Tos^+; 127, 1, SF_5^+; 107, 8, $C_2H_3SO_3^+$; 91, 90, $C_7H_7^+$; 89, 10, SF_3^+; 77, 2, $C_2H_2SF^+$; 65, 16, CH_2SF^+; 51, 2, SF^+; 41, 5, $C_3H_5^+$; 39, 3, $C_3H_3^+$.

High-resolution mass spectrum calcd. for $^{12}C_{10}{}^1H_{13}{}^{19}F_5{}^{16}O_3{}^{32}S_2$: 340.02263. Found: 340.02244.

3.7. $SF_5CF_2CF_2CF_2CF_2CH_2CH_2OOCCH_3$ (**6**)

$SF_5CF_2CF_2CF_2CF_2CH_2CH_2I$ (1.00 g, 2.1 mmol), silver acetate (0.40 g, 2.4 mmol) and 3 ml of glacial acetic acid were heated (116 °C) for 30 min in a 10 ml round bottom flask. After filtration (0.496 g AgI), the product was isolated as above, except that methylene chloride was used to extract the aqueous phase. The crude product dissolved in CH_2Cl_2 was passed through 5 g of Kieselgel and after evaporation gave 0.72 g of a colorless oil (84%).

^{1}H NMR spectrum: δ_1 = 4.38 ppm, t, J_t = 6.71 Hz, 2H (CH_2O); δ_2 = 2.45, t–t, J = 6.61, J = 18.3 Hz, 2H (CF_2CH_2); δ_3 = 2.08, s (CH_3CO).

^{19}F NMR spectrum: (SF_5: AB_4-type) δ_A = 65.0 ppm, nine lines, each line with triplet splitting, 1F; δ_B = 45.0, skewed d, 4F, $J_{At} \approx 4.9$, J_{AB} = 152 Hz. CF_2: $\delta_3 = -116$, ≈p, J = 18 Hz, 2F (CF_2CH_2); $\delta_{4+5} = -125$, m, 4F; $\delta_6 = -96$, ≈p, $J_p \approx 16$, 2F; J_{6A} not resolved.

Infrared spectrum (KBr): 2976, w; 2917, vw; 1752, s; 1479, vw; 1463, w; 1431, w; 1397, vw; 1327, w–m; 1222, s; 1198, sh, m–s; 1170, m; 1148, s; 1108, w–m; 1074, w–m; 1053, w–m; 1014, w; 967, vw; 959, vw; 883, vs; 821, w; 789, m; 752, w–m; 742, w–m; 732, w; 722, w; 710, w; 695, m; 685, w–m; 668, vw; 603, w; 585, vw.

Mass spectrum (70 eV: ion (*m/z*), %, assignment): R_t = 6.91 min, 414, 4, M^+; 394, 3, $(M - HF)^+$; 227, 10, $SF_5CF_2CF_2^+$; 177, 2, $SF_5CF_2^+$; 127, 5, SF_5^+; 95, 10, $(CF_2CH_2CH_2O + H)^+$; 89, 10, SF_3^+; 77, 14, $CF_2C_2H_3^+$; 73, 13, $C_3H_2FO^+$; 69, 8, CF_3^+; 51, 3, SF^+; 43, 100, CH_3CO^+.

High-resolution mass spectrum calcd. for $^{12}C_8{}^1H_7{}^{19}F_{13}{}^{16}O_2{}^{32}S$: 413.99592. Found: 413.99567.

3.8. $SF_5CH_2CH_2OH$ (7)

A solution of $SF_5CH_2CH_2OOCCH_3$ (2.50 g, 11.7 mmol) in methanol (10 ml) was made weakly alkaline (pH 9–10) by adding dropwise a solution of Na in methanol (15 mg/ml). After standing at ambient temperature for 18 h the solution was neutralized by adding a drop of dil. HCl (6N); methanol and methyl acetate were removed by distillation at atmospheric pressure. The product (1.58 g, 79%) was obtained by distillation at 73 °C/50 Torr. The literature boiling point is 77 °C/49 Torr [17].

^{1}H NMR spectrum: δ_1 = 4.09 ppm, t–p, J_{12} = 6.0 Hz, $J_{1SF_4} \approx 1$, 2H; δ_2 = 3.87, t–p, J = 6.0, J_{2SF_4} = 8.5, 2H.

^{19}F NMR spectrum: (AB_4-type) δ_A = 84.0 ppm, nine lines, 1F; δ_B = 65.5, skewed d, 4F, J_{AB} = 144 Hz.

Mass spectrum (70 eV: ion (*m/z*), %, assignment): R_t = 2.67 min, 171, $\ll$1%, $(M - H)^+$; 152, 6, $(M - HF)^+$; 151, 10, $(M - H–HF)^+$; 127, 17, SF_5^+; 122, 63, $SF_4CH_2^+$; 89, 100, SF_3^+; 70, 15, SF_2^+; 65, 7, $SFCH_2^+$; 51, 4, SF^+; 45, 92, SCH^+, $C_2H_5O^+$; 44, $C_2H_4O^+$; 43, $C_2H_3O^+$; 31, 40, CH_2OH^+; 29, 23, $C_2H_5^+$, COH^+; 27, $C_2H_3^+$.

3.9. $SF_5CF_2CF_2CF_2CF_2CH_2CH_2OH$ (8)

A solution of $SF_5CF_2CF_2CF_2CF_2CH_2CH_2OOCCH_3$ (0.50 g, 1.21 mmol) in 5 ml of methanol (≈170 mmol) was made alkaline by adding dropwise a solution of 1.6 mg Na in 1 ml of methanol. The reaction was completed after 1 h. A drop of HCl (6N) was then added and the solvent removed; the residue was taken up in methylene chloride and passed through a short column of Kieselgel. The solvent was removed by evaporation; 0.31 g (69%) of the pure compound (oil) was found.

^{1}H NMR spectrum: δ_1 = 4.0 ppm, t, J_{12} = 6.4 Hz, 2H (CH_2OH); δ_2 = 2.5, t–t–t, J_{23} = 19.0, J_{12} = 6.4, $J_{24} \approx 0.8$ (poorly resolved), 2H, CF_2CH_2).

^{19}F NMR spectrum: (AB_4-type) δ_A = 64.2 ppm, nine lines (poorly resolved), 1F; δ_B = 44.6, skewed d, 4F, J_{AB} = 142 Hz (broad F_A-signal, needed for determination of J_{AB}, allowed for little accuracy). CF_2: $\delta_3 = -116$, not resolved, 2F (CF_2CH_2); $\delta_{4+5} = -125$, not resolved, 4F; $\delta_6 = -96$, not resolved, 2F.

Infrared spectrum (KBr): 2976, w; 2917, vw; 1752, s; 1479, sh, vw; 1463, w; 1431, w; 1397, vw; 1372, w–m; 1222, s; 1198, m–s, sh; 1170, m; 1148, s–vs; 1108, w–m; 1074, w–m; 1053, w–m; 1014, w; 967, vw; 959, vw; 883, vs; 822, w; 789, w–m; 762, w–m; 742, w–m; 722, w; 709, w; 695, w–m; 684, w–m; 668, w; 603, w.

Mass spectrum (70 eV: ion (*m/z*), %, assignment): 371, <1%, $(M - H)^+$; 252, 5, $(M - HF)^+$; 195, 11, $(M - SF_5CF_2)^+$; 175, 9, $(M - HF–SF_5CF_2)^+$; 157, 6, $C_5H_2F_5^+$; 145, 10, $C_4H_2F_5^+$; 131, 15, $C_3F_5^+$; 127, 18, SF_5^+; 119, 20, $(C_2F_4 + F)^+$; 100, 12, $C_2F_4^+$; 95, 57, $CF_2CH_2CH_2OH^+$; 89, 29, SF_3^+; 77, $CF_2CH_2CH^+$; 69, 16, CF_3^+; 65, $(CF_2CH_2 + H)^+$; 51, 9, SF^+; 31, 100, CH_2OH^+.

High-resolution mass spectrum calcd. for $^{12}C_6{}^1H_6{}^{19}F_{13}{}^{16}O^{32}S$ (*M*H): 372.99318. Found: 372.99306.

3.10. $SF_5CBr{=}CH_2$ (9)

Silver acetate (5.3 g, 0.032 f.w.), 4.81 g of $SF_5CHBrCH_2Br$ (4.81 g, 0.0153 mol) and glacial acetic acid (15 ml) were refluxed in a 50 ml round bottom flask for 4 days. The cooled supernatant portion was poured into water (20 ml) producing 2.6 g of pure 1-SF_5–1-Br–ethylene; yield was 72%. A sample for analysis was obtained by preparative gas chromatography on an SE-30 column, length 3 m, at 140 °C. The infrared spectrum of this compound was identical to that of an authentic sample of $SF_5CBr{=}CH_2$ [3].

3.11. Dimethyl SF_5-citraconate (10)

Dimethyl α-bromo-α-(SF_5-methyl) succinate (1.12 g, 3.07 mmol, **11**), silver tosylate (7.63 g, 27.3 mmol) and 15 ml of acetonitrile were heated in a 30 ml Carius tube at 110–120 °C for 5 h. After filtration and pouring the filtrate into water (100 ml), the product was extracted with ether (3× 30 ml). The ether was distilled away and the product (0.84 g) was heated under dynamic vacuum in a short-path distillation unit and condensed in a cooled receiving flask to give 0.61 g of a partially crystalline product. The product was then recrystallized from cyclohexane at +4 °C; mp = 30–31 °C. Yield = 70%.

^{1}H NMR spectrum: δ_{12} = 3.82, s, 3H; δ_{12} = 3.87, s, 3H (CH_3); δ_3 = 5.26, p, J = 6.70 Hz, 2H (CH_2SF_5); δ_4 = 7.07, s, 1H (CH=C).

^{19}F NMR spectrum: (AB_4-type) δ_A = 81.7 ppm, nine lines, 1F; δ_B = 67.2, skewed d, 4F, J_{AB} = 150 Hz.

Infrared spectrum (KBr): 3054, w; 3009, w–vw; 2962, w–m; 2850, vw; 1738, 1734, vs; 1653, w–m; 1440, s, sh at 1459, 1428; 1368, m; 1287, s–vs; 1254, m; 1240, s; 1205, s–vs; 1185, m–s; 1101, m–s; 1069, vw; 1022, m–s; 981, vw; 937, w–m; 921, w–m; 863, s–vs; 846, vs; 827, vs; 791, s–vs; 751, vw.

Mass spectrum (70 eV: ion (*m/z*), %, assignment): 252, 100%, $(M - CH_3OH)^+$; 157, 30, $(M - SF_5)^+$; 145, 35, $(M - SF_5 + 2H)^+$; 127, 8, SF_5^+; 117, 14, $C_7HO_2^+$; 98, 20, $(C_5H_6O_2)^+$; 89, 20, SF_3^+; 59, 35, $COOCH_3^+$.

Anal. calcd. for $C_7H_9F_5O_4S$: C, 29.58; H, 3.19; F, 33.43. Found: C, 29.88; H, 3.35; F, 33.3%.

3.12. Dimethyl α-bromo-α-(SF_5-methyl) succinate (11)

Dimethyl itaconate (6.33 g, 40.0 mmol), methylene chloride (25 ml) and SF_5Br (8.77 g, 42.4 mmol) were heated together at 69–72 °C for 20 h in a 75 ml steel bomb vessel. Distillation of the mixture under reduced pressure gave 10.94 g (75%) of a light-tan oily product (**11**); bp = 85–95 °C/0.5–1 Torr. The compound was used for preparing compound (**10**).

^{1}H NMR spectrum: $\delta_{\beta 1}$ = 3.75 ppm, d, 1H; $\delta_{\beta 2}$ = 3.88, d, 1H, $J_{\beta 1\beta 2}$ = 18.6 Hz (CH_2CO); $\delta_{\beta' 1}$ = 4.70, d–p, 1H, $J_{\beta 1\beta 2}$ = 14.7, $J_{SF_4\beta 1}$ = 7.8; $\delta_{\beta' 2}$ = 5.05, d–p, $J_{SF_4\beta 1}$ = 8.2, 1H; δ_{CH_3} = 3.75, s, 3H; δ_{CH_3} = 3.88, s, 3H.

^{19}F NMR spectrum: (AB_4-type) δ_A = 82.5 ppm, nine lines, 1F; δ_B = 67.8, skewed d, 4F, J_{AB} = 146 Hz.

Mass spectrum (70 eV: ion (*m/z*), %, assignment): R_t = 12.82 min, 364, 366, <1%, M^+; 333, 335, 22, 22, $(M - OCH_3)^+$; 253, 14, $(M - HBr–OCH_3)^+$; 193, 195, 38, 38, $(M - SF_5CH_2–OCH_3 + H)^+$; 157, 16, $(M - SF_5–Br + H)^+$; 145, 21, $SF_4C_3H^+$; 127, 19, SF_5^+: 99, 53, $(CH_3OOCCH_2CCH_2{=}C_5H_7O_2)^+$; 89, 12, SF_3^+; 71, $C_3H_3O_2^+$; 59, 100, $C_2H_3O_2^+$; 51, 6, SF^+; 39, 20, $C_3H_3^+$.

High-resolution mass spectrum calcd. for $^{12}C_7H_{11}{}^{19}F_5{}^{32}S^{16}O_4{}^{79}Br$ $(MH)^+$: 364.9482. Found: 364.9497.

3.13. $SF_5CH_2CH_2CH_2CH(COOC(CH_3)_3)_2$ (**12**)

$KOC(CH_3)_3$ (2.28 g, 19.5 mmol) was added to 50 ml of ethyleneglycol dimethylether in a 100 ml round bottom flask and stirred for ≈0.5 h; di-*t*-butyl malonate (4.00 g, 18.5 mmol) was added and stirring continued in a water bath for 0.25 h. $SF_5(CH_2)_3Br$ (4.46 g, 17.9 mmol, in 10 ml of $(CH_3OCH_2)_2$) was added dropwise to this solution over a 0.5 h period. After 1.5 h, an additional 0.10 g of $KOC(CH_3)_3$ was added; this addition was repeated again after 1.5 h. The solution was yellow and after 0.25 h was filtered; the solvent was removed under vacuum, leaving behind 7.03 g of a yellowish oil that was used in preparing compound (**13**).

^{1}H NMR spectrum: δ_{CH_3} = 1.47, s, 18H; δ_α = 3.15, t, $J_{\alpha\beta}$ = 7.42 Hz, 1H; δ_β = 1.85, m, 2H; δ_γ = 1.98, m, 2H; δ_δ = 3.68, t–p, $J_{\gamma\delta}$ = 8.01, $J_{B\delta}$ = 8.20, 2H.

^{19}F NMR spectrum: (AB_4-type) δ_A = 85.2, nine lines, 1F; δ_B = 64.5, J_{AB} = 148 Hz (AB_4-system).

Infrared spectrum (KBr): 3004, m; 2981, s; 2938, m; 2894, sh, w; 1726, vs; 1478, m; 1460, m; 1413, w; 1394, m–s; 1370, s–vs; 1349, m; 1296, s; 1284, s; 1256, s–vs; 1164, sh, s–vs; 1142, vs; 1072, m; 1041, m; 973, w; 929, vw; 877, s–vs; 838, vs; 740, w–m; 684, vw; 660, vw; 629, m–s; 596, m; 568, m.

Mass spectrum (70 eV: ion (*m/z*), %, assignment): R_t = 14.52 min, 313, 5, $(M - (CH_3)_2C{=}CH_2–CH_3)^+$; 273, 8, $(M - (CH_3)_3CO–2F)^+$; 228, 2, $(CH_2CH(COOC(CH_3)_3)_2–H)^+$; 145, 10, $(C_6H_8O_2S + H)^+$; 127, 3, SF_5^+; 115, 6, $(CHCOOC(CH_3)_3 + H)^+$; 89, 1, SF_3^+; 57, 100, $C_4H_9^+$; 41, 16, $C_3H_3^+$.

3.14. $SF_5CH_2CH_2CH_2CH(COOH)_2$ (**13**)

The crude di-*t*-butyl γ-SF_5-propylmalonate (**12**) from the previous reaction (7.03 g, ≤17.9 mmol) was heated with 25 ml of concentrated HCl at 70–80 °C for 70 min in a 50 ml round bottom flask; gas evolution was apparent even at the warm-up stage. The solution was kept in an ice-bath for 1 h, and the crystalline precipitate filtered away. In an attempt to re-crystallize from a warm aqueous acetone solution, gas evolution and formation of an insoluble oil occurred. The oil (3.51 g) was recovered and after 1 week solidified. The filtrate was extracted with CH_2Cl_2 (3× 15 ml), leaving 0.69 g of solid after concentration. This solid was crystallized twice from CH_2Cl_2.

Analysis of the product by GC–MS showed that compound (**13**) was not stable in the gas chromatography unit (heated injection block) and had decomposed to product (**14**).

^{19}F NMR spectrum: (AB_4-type) δ_A = 85.5, nine lines, 1F; δ_B = 64.2, J_{AB} = 147.3 Hz (AB_4-system).

Anal. calcd. for $C_6H_9F_5O_4S$: C, 26.48; H, 3.33; S, 11.78. Found: C, 27.20; H, 3.22; S, 11.19.

3.15. $SF_5CH_2CH_2CH_2CH_2COOH$ (**14**)

The combined impure malonic acid fractions from the previous step (3.8 g) were heated in a 25 ml distillation flask (oil-bath) with stirring to 167 °C. Initially, bubbling was observed at 140 °C, and then heating was continued from 140 to 167 °C over a 20 min period; the reaction was then heated at 167 °C for 10 min. Distillation under a dynamic vacuum at 80–85 °C (70–40 μm) gave 2.10 g of a colorless oily liquid.

^{1}H NMR spectrum: δ_α = 2.43 ppm, t, J = 7.23 Hz, 2H; δ_β, δ_γ = 1.70, m, 2H and 1.97, m, 2H; δ_δ = 3.68, t–p, $J_{B\delta}$ = 8.20, $J_{\gamma\delta} \approx 7$, 2H.

^{19}F NMR spectrum: (AB_4-type) δ_A = 85.7, nine lines, 1F; δ_B = 64.3, J_{AB} = 148 Hz (AB_4-system).

Infrared spectrum (KBr): 2974, vb–m; 1714, vs; 1467, w–m; 1433, m; 1418, m; 1290, m; 1266, m; 1240, w; 1212, m; 1157, w–m; 1083, w–m; 915, sh, m; 870, sh, s–vs; 825, vs; 751, m; 690, m; 683, s.

Mass spectrum (70 eV: ion (*m/z*), %, assignment): R_t = 9.66 min, 211, <1%, $(M - OH)^+$; 127, 8, SF_5^+; 108, <1, SF_4^+; 101, 15, $(M - SF_5)^+$; 99, 10, $(M - SF_5–2H)^+$; 89, 22, SF_3^+; 83, 38, $(M - SF_5–OH–H)^+$; 73, 7, $C_3H_5O_2^+$; 70, 6, SF_2^+; 59, $C_2HO_2^+$; 55, 100, $C_3H_3O^+$; 41, 29, $C_3H_5^+$, C_2HO^+.

Anal. calcd. for $C_5H_9F_5O_2S$: C, 26.32; H, 3.98; F, 41.63; S, 14.05. Found: H, 26.24; H, 3.86; F, 41.3; S, 14.15.

3.16. $SF_5CH_2CH_2CH_2I$, γ-SF_5-propyl iodide (**15**)

Into a 100 ml flask, 10.2 g of NaI (68 mmol) and 75 ml of acetone were added. The flask was wrapped with Al-foil and 5.10 g of $SF_5CH_2CH_2CH_2Br$ (21 mmol) was added dropwise. A precipitate quickly formed and after 100 min the reaction was complete. The complex, $NaI{\cdot}(CH_3)_2C{=}O$ was filtered away by suction filtration, washed with cold acetone, and the filtrate poured into 0.4 l of ice-water. The product was extracted with 1× 75, 2× 20 ml of CH_2Cl_2, and the combined extracts were washed with water (1× 80 ml). The extract was dried (Na_2SO_4). Distillation resulted in 4.42 g (73%) of product, bp = 46–47 °C/5 Torr.

^{1}H NMR spectrum: δ_α = 3.20, t, $J_{\alpha\beta}$ = 6.64 Hz, 2H; δ_β = 2.43, t–t, J = 6.64, $J_{\beta\gamma}$ = 7.81, 2H; δ_γ = 3.78, t–p, j = 7.81, $J_{B\gamma}$ = 8.20, 2H.

^{19}F NMR spectrum: (AB_4-type) δ_A = 85.3, nine lines, 1F; δ_B = 69.0, J_{AB} = 146.2 Hz (AB_4-system).

Infrared spectrum (KBr): 2971, w–m; 2928, w; 2877, vw; 1447, m–s; 1429, m–s; 1362, w; 1309, w; 1288, m; 1231, s–vs; 1182, m; 1134, w; 1064, w; 1001, w–m; 969, w; 934, w–m; 871,

vs; 762, m–s; 739, sh, w–m; 706, w; 687, w; 645, m–s; 630, s–vs; 589, m–s; 569, m–s; 645, m; 511, w–m.

Mass spectrum (70 eV: ion (*m*/*z*), %, assignment): R_t = 6.92 min, 296, 82%, M^+; 169, 73, $(M - I)^+$; 141, 14, $SF_5CH_2^+$; 127, 29, SF_5^+, I^+; 109, 8, SF_4^+; 89, 1, SF_3^+; 70, 8, SF_2^+; 61, 24, $C_2H_5S^+$; 59, 10, $C_2H_3S^+$; 51, 2, SF^+; 41, 100, $C_3H_5^+$; 39, 22, $C_3H_3^+$.

High-resolution mass spectrum calcd. for $^{12}C_3H_6{}^{19}F^{127}I^{32}S$: 295.91557. Found: 295.91552.

References

[1] W. Tyrra, D. Naumann, J. Fluorine Chem. 125 (2004) 823.
[2] R.E. Noftle, W.B. Fox, J. Fluorine Chem. 9 (1977) 219.
[3] F.W. Hoover, D.D. Coffman, J. Org. Chem. 29 (1964) 3567.
[4] J. Wessel, H. Hartl, K. Seppelt, Chem. Ber. 119 (1986) 453.
[5] R. Winter, R. Dodean, G.L. Gard, in: V.A. Soloshonok (Ed.), Fluorine Containing Synthons, ACS Symposium Series #911, Oxford University Press/American Chemical Society, Washington, DC, 2005, pp. 87–119.
[6] C.W. Tullock, D.D. Coffman, E.L. Muetterties, J. Am. Chem. Soc. 86 (1964) 357.
[7] G. Kleemann, K. Seppelt, Chem. Ber. 112 (1979) 1140.
[8] G. Kleemann, K. Seppelt, Angew. Chem. 90 (1978) 547.
[9] R.A. Bekker, B.L. Dyatkin, I.L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim. 12 (1970) 2738.
[10] R.N. Haszeldine, F. Nyman, J. Chem. Soc. (1956) 2684.
[11] J.C. Hansen, P.M. Savu, United States 5,286,352 (1994), $SF_5(CF_2)_4CO_2Li$;
P.G. Nixon, Ph.D. Thesis, Portland State University, 1999 ($SF_5(CH_2)_2CO_2Li$).
[12] In-house work done at Portland State University.
[13] J. Wessel, G. Kleemann, K. Seppelt, Chem. Ber. 116 (1983) 2399.
[14] P.G. Nixon, J. Renn, R.J. Terjeson, Y.S. Choi, R. Winter, G.L. Gard, J. Fluorine Chem. 91 (1998) 13.
[15] R. Winter, G.L. Gard, J. Fluorine Chem. 102 (2000) 79.
[16] R. Winter, R.J. Terjeson, G.L. Gard, J. Fluorine Chem. 89 (1998) 105.
[17] P.G. Nixon, J. Mohtasham, R. Winter, G.L. Gard, B. Twamley, J.M. Shreeve, J. Fluorine Chem. 125 (2004) 553.
[18] C. Merrill, Ph.D. Thesis, University of Washington, 1962.