

Halogen displacement chemistry with silver and alkali metal salts: Preparation of SF₅-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

Received 7 March 2006; received in revised form 22 May 2006; accepted 7 June 2006

Available online 15 June 2006

Abstract

It has been found that treatment of SF₅-alkyl halides, especially SF₅(CH₂)₂Br, with silver salts such as CH₃C(O)OAg, *p*-CH₃C₆H₄SO₃Ag, CF₃SO₃Ag and AgNO₃ provides convenient pathways for preparing the following ester compounds: SF₅CH₂CH₂R (R = CH₃COO, TosO, CF₃SO₃, NO₃), SF₅(CH₂)₃OTos, and SF₅(CF₂)₄(CH₂)₂OAc. Important derivatives prepared from these esters include SF₅(CH₂)₂OH; SF₅(CF₂)₄(CH₂)₂OH. Several alkenes SF₅C(Br)=CH₂ and SF₅CH₂(COOCH₃)C=CHC(O)OCH₃ are obtained using silver salts. The use of alkali metal salts with SF₅(CH₂)₃Br is studied and yields SF₅(CH₂)₃I; also, a pathway has been developed that extends for SF₅(CH₂)₃– the chain by two-carbon atoms and also produces the first SF₅-containing malonic acid.

Published by Elsevier B.V.

Keywords: SF₅-esters; SF₅-alcohols; Pentafluorothio (SF₅); Silver and nucleophilic substituents; Sulfur hexafluoride derivatives

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 metal salts containing the SF₅-group. The reaction of AgF with SF₅CF=CF₂ gave the isolatable salt, Ag(SF₅CFCF₃)·CH₃CN [2]. The reaction of AgNO₃ and SF₅C≡CH produced a partially characterized SF₅C≡CAg salt [3]. The lithium salt, SF₅C≡CLi has been prepared in solution and was used to synthesize a number of interesting SF₅C≡CX (X = Hg, Cl, Br, I) compounds [4]. The MSF₅ salts (M = Ag, K, Rb, Cs, (CH₃)₄, Cs(18-crown-6)₂) were prepared from MF and SF₄ [5]. The alkali metal and silver salts can be used to prepare SF₅Cl [6]. Silver salts of SF₅-carboxylic acids have been prepared by reacting the corresponding acid with silver carbonate: SF₅CX₂C(O)OAg (X = H or F) [7–10]. The reaction

of the silver salts with halogens (X = Br, I) gave the corresponding SF₅CH₂Br [7,8] and SF₅CF₂I [9]. Several alkali metal salts of SF₅-carboxylic acids have also been reported [10,11]. We have now found that silver salt anions can replace the halide in various SF₅-alkyl halides thereby considerably expanding the range of reactivity of this readily available but poorly reactive class of SF₅-compounds. These method may be advantageously used to prepare SF₅-esters, alcohols, and alkenes. In some instances alkali metal salts may be used in lieu of silver salts.

2. Results and discussion

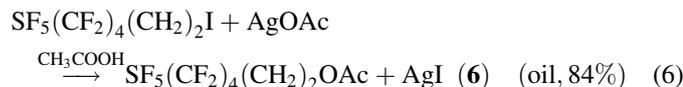
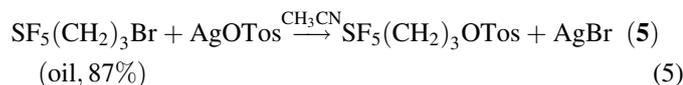
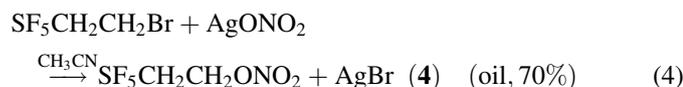
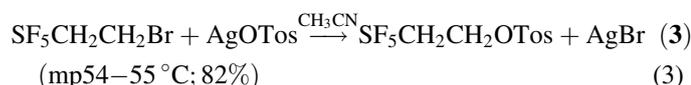
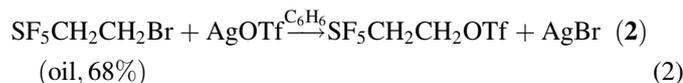
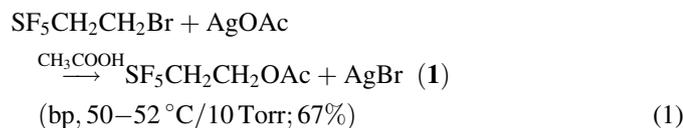
In general, previous attempts to replace the halogen (X = Br, Cl) in two-carbon SF₅-alkyl halides have resulted in either no reaction, elimination of XF or destruction of the SF₅-group; for example, treating SF₅CH₂CH₂Br with NaI resulted in the complete destruction of the SF₅-group [12]. The purpose of this study was to make direct use of the SF₅-alkyl bromides or iodides that are easily prepared using either SF₅Br or SF₅(CF₂)_{*n*}I. For the compound SF₅(CH₂)₃Br it was found that the Br could be easily replaced; this is in sharp contrast with SF₅(CH₂)₂Br. This study also afforded an improved method for making SF₅-fluoroalkyl alcohols in high yields and a new pathway for carbon chain extension in SF₅-systems. A safe and

* Corresponding author. Fax: +1 503 725 9525.

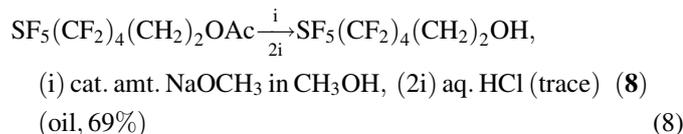
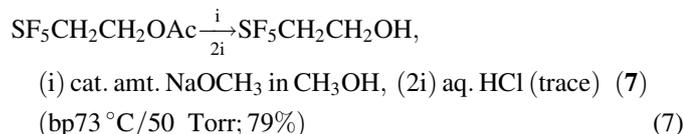
E-mail address: gardg@pdx.edu (G.L. Gard).

effective method for preparing SF₅CH₂CH₂Br is also given. This compound should not be prepared from SF₅Br and H₂C=CH₂ under pressure and heat as carbonization will occur [12].

The following SF₅-fluoroalkyl and SF₅-alkyl esters have been prepared by treatment of silver salts with the SF₅-fluoroalkyl and SF₅-alkyl iodide or bromides; all but SF₅CH₂CH₂OTos are new compounds. SF₅CH₂CH₂OTos was previously prepared from SF₅CH₂CH₂OH and *p*-CH₃C₆H₄SO₂Cl [13]:

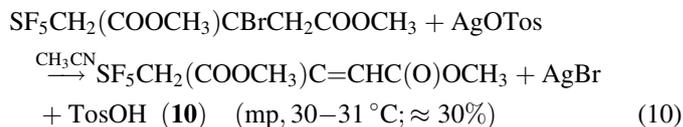
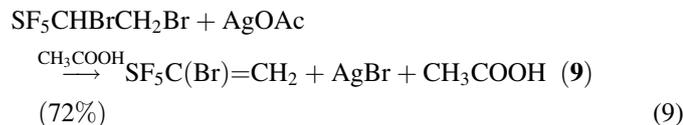


When the following SF₅-esters were transesterified, the corresponding alcohols were prepared in high yields:



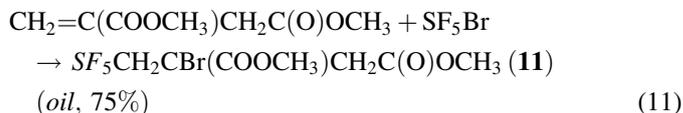
An important outcome of the above method is that SF₅-containing alcohols are readily prepared in high yields and purity. The alcohol SF₅CH₂CH₂OH was previously prepared from SF₅Cl and ketene followed by reduction of SF₅CH₂C(O)Cl with LiAlH₄ [13], while SF₅(CF₂)₂(CH₂)₂OH was prepared by the laborious lactam method [14].

An interesting observation was made when the following two SF₅Br-olefin adducts were treated with silver salts:

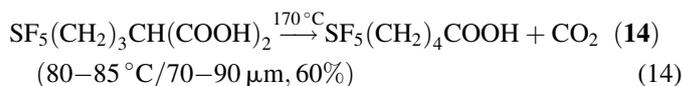
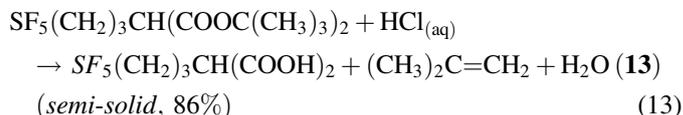
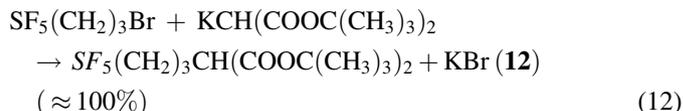


The silver salt acts as a base in these reactions with the formation of AgBr and the corresponding acid; when bromine is in the β-position to an acidic C–H bond, an elimination over substitution reaction is apparently favored.

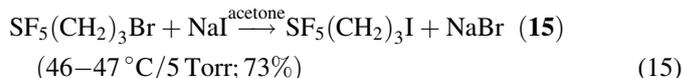
The starting SF₅-compound in reaction (10) was prepared by the following reaction which was carried out in CH₂Cl₂:



In addition to studying the chemistry of selected silver salts with SF₅ two-carbon halides, it was also of interest to look at SF₅ three-carbon halides. It was found that in SF₅(CH₂)₃Br the bromine could be substituted with tosyloxy and iodide. Therefore, the SF₅ three-carbon group is more stable and readily transferable. This stability should allow the use of alkali salts in preparing SF₅-containing derivatives. Of great importance was the development of a method for chain elongation in SF₅-alkanes. The following three-step reaction scheme clearly demonstrates this new procedure:



In contrast to SF₅(CH₂)₂Br, the three-carbon chain survived treatment with NaI:



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 SF₅-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 ¹⁹F NMR spectral data for all new compounds are given in Section 3. The compounds show a typical AB₄ splitting pattern in the ¹⁹F NMR spectrum for the SF₅-group. Except for SF₅(CF₂)₄(CH₂)₂OOCCH₃ (**6**), the axial fluorine (A) for the new SF₅-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 equatorial 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 SF₅-compounds are in excellent agreement with analogous SF₅-compounds [15].

3. Experimental

The reactant SF₅Br was prepared from SF₄, BrF₃, Br₂ and CsF via a method previously described by our laboratory [16]. The compounds SF₅(CH₂)₃Br [15], SF₅(CF₂)₄(CH₂)₂I [17] and SF₅CHBrCH₂Br [3] were prepared according to the literature method. SF₅CH₂CH₂Br 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: ¹⁹F Varian EM-390 (84.7 MHz) and ¹H General Electric (500 MHz) in CDCl₃ with CCl₃F and Si(CH₃)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. SF₅CH₂CH₂Br

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 SF₅Br 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 SF₅Br 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 SF₄ which would lead to etching of glass containers upon storage.

¹H NMR spectrum: δ₁ = 3.74 ppm, m, 2H (CH₂Br); δ₂ = 4.06, m, 2H (SF₅CH₂).

¹⁹F NMR spectrum: (AB₄-type) δ_A = 78.6 ppm, nine lines, 1F; δ_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(⁸¹Br, ⁷⁹Br)⁺; 127, 28, SF₅⁺; 109, 107, 97%, 100%, (M – SF₅)⁺; 89, 38, SF₃⁺; 70, 11,

SF₂⁺; 51, 2, SF⁺; 47, 52, (C₂H₄F)⁺, (SCH₂ + H)⁺; 28, 13, C₂H₄⁺; 27, 80, C₂H₃⁺; 26, 12, C₂H₂⁺.

3.2. SF₅CH₂CH₂OOCCH₃ (1)

SF₅CH₂CH₂Br (1.11 g, 4.72 mmol), CH₃COOAg (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).

¹H NMR spectrum: δ₁ = 4.49 ppm, t (each band shows signs of additional (pentet) splitting), J_t = 6.10 Hz, J_p ≈ 1 Hz, 2H (CH₂O); δ₂ = 3.91, t–p, J_t = 6.10, J_p = 7.85, 2H (SF₅CH₂); δ₃ = 2.10, s, 3H (CH₃CO).

¹⁹F NMR spectrum: (AB₄-type) δ_A = 80.3 ppm, nine lines, 1F; δ_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, (SF₄CH₂CH₂ + H)⁺; 133, SF₄C₂H⁺; 127, 8, SF₅⁺; 122, <1, SF₄CH₂⁺; 89, 11, SF₃⁺; 87, 11, CH₂CH₂OOCCH₃⁺; 70, 1, SF₂⁺; 61, 2, (SCH₂CH₂ + H)⁺; 47, 9, (SCH₂ + H)⁺; 43, 100, CH₃CO⁺.

Anal. calcd. for C₄H₇F₅O₂S: 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. SF₅CH₂CH₂OSO₂CF₃ (2)

SF₅CH₂CH₂Br (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.

¹H NMR spectrum: δ₁ = 4.86 ppm, t, J₁₂ = 6.0 Hz, 2H; δ₂ = 4.02, t–p, J_{SF₄CH₂} = 7.6, J = 6.0, 2H.

¹⁹F NMR spectrum: (AB₄-type) δ_A = 80.0 ppm, nine lines, 1F; δ_B = 66.0, skewed d, 4F, J_{AB} = 147 Hz; φ_{CF₃} = –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, (CF₃SO₂OCH₂ + 2H)⁺; 135, 9, C₂H₃SF₄⁺; 133, 9, CF₃SO₂⁺, C₂HSF₄⁺; 127, 27, SF₅⁺; 101, 16, CF₃S⁺; 99, 10, (C₂H₄SF₂ + H)⁺; 89, 29, SF₃⁺; 69, 100, CF₃⁺; 47, 44, (CH₂S + H)⁺.

High-resolution mass spectrum calcd. for ¹²C₃H₅¹⁹F₈³²S₂¹⁶O₃ (MH⁺): 304.95523. Found: 304.95322.

3.4. SF₅CH₂CH₂OTos (3)

SF₅CH₂CH₂Br (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 CH₂Cl₂. 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%.

¹H NMR spectrum: $\delta_1 = 4.40$ ppm, t, $J_t = 6.25$ Hz, 2H (CH₂O); $\delta_2 = 3.91$, t-p, $J_t = 6.25$, $J_p = 7.81$, 2H (SF₅CH₂); $\delta_3 = 2.10$, s, 3H (CH₃C₆H₄). $\delta = 7.38$, d, 2H; $\delta = 7.80$, d, 2H, $J = 8.20$ (toluyl).

¹⁹F NMR spectrum: (AB₄-type) $\delta_A = 81.4$ ppm, nine lines, 1F; $\delta_B = 66.2$, 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, SF₃CH₂CH₂O⁺; 107, 8, C₂H₃SO₃⁺; 91, 100, C₇H₇⁺; 89, 9, SF₃⁺; 77, 3, C₂H₂SF⁺; 65, 19, CH₂SF⁺; 51, 2, SF⁺; 39, C₃H₃⁺.

3.5. SF₅CH₂CH₂NO₃ (4)

SF₅CH₂CH₂Br (2.45 g, 10.4 mmol), 10 ml of CH₃CN and AgNO₃ (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 Na₂SO₄. The product was concentrated under vacuum; 1.63 g of a colorless, slightly oily product (72%) was obtained. Further distillation was not attempted.

¹H NMR spectrum: $\delta_1 = 4.88$ ppm, t, $J_t = 6.1$ Hz, 2H (CH₂O); $\delta_2 = 3.97$, t-p, $J_t = 6.1$, $J_p = 7.63$, 2H (SF₅CH₂).

¹⁹F NMR spectrum: (AB₄-type) $\delta_A = 81.0$ ppm, nine lines, 1F; $\delta_B = 66.0$, 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 - NO₂-H-F)⁺; 133, 5, SF₄C₂H⁺; 127, 12, SF₅⁺; 122, 6, SF₄CH₂⁺; 108, <1, SF₄⁺; 89, 20, SF₃⁺; 76, 4, SC₂H₄O⁺; 70, 4, SF₂⁺; 46, 100, NO₂⁺.

High-resolution mass spectrum calcd. for ¹²C₂H₅¹⁹F₅¹⁶O₃³²S¹⁴N (MH⁺): 217.99104. Found: 217.99087.

3.6. SF₅CH₂CH₂CH₂OTos (5)

SF₅CH₂CH₂CH₂Br (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 SF₅CH₂CH₂OTos and obtained as an oil (1.19 g) in 87% yield.

¹H NMR spectrum: $\delta_1 = 4.10$ ppm, t, $J_t = 5.7$ Hz, 2H (CH₂O); $\delta_2 = 2.28$, ≈t-t (broadened), $J \approx 5.7$, $J \approx 7.7$ Hz, 2H (C-CH₂-C); $\delta_3 = 3.72$, t-p (or septet), $J_t = 7.8$, $J_p = 7.8$, 2H (SF₅CH₂); $\delta_4 = 2.46$, s, 3H (CH₃C₆H₄); $\delta = 7.37$, d, 2H; $\delta = 7.78$, d, 2H, $J = 8.20$ (toluyl).

¹⁹F NMR spectrum: (AB₄-type) $\delta_A = 84.7$ ppm, nine lines, 1F; $\delta_B = 65.2$, 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 - SF₅)⁺; 185, 3, TosOCH₂⁺; 172, 14, TosOH⁺; 155, 100, Tos⁺; 127, 1, SF₅⁺; 107, 8, C₂H₃SO₃⁺; 91, 90, C₇H₇⁺; 89, 10, SF₃⁺; 77, 2, C₂H₂SF⁺; 65, 16, CH₂SF⁺; 51, 2, SF⁺; 41, 5, C₃H₅⁺; 39, 3, C₃H₃⁺.

High-resolution mass spectrum calcd. for ¹²C₁₀¹H₁₃¹⁹F₅¹⁶O₃³²S₂: 340.02263. Found: 340.02244.

3.7. SF₅CF₂CF₂CF₂CF₂CH₂CH₂OOCCH₃ (6)

SF₅CF₂CF₂CF₂CF₂CH₂CH₂I (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 CH₂Cl₂ was passed through 5 g of Kieselgel and after evaporation gave 0.72 g of a colorless oil (84%).

¹H NMR spectrum: $\delta_1 = 4.38$ ppm, t, $J_t = 6.71$ Hz, 2H (CH₂O); $\delta_2 = 2.45$, t-t, $J = 6.61$, $J = 18.3$ Hz, 2H (CF₂CH₂); $\delta_3 = 2.08$, s (CH₃CO).

¹⁹F NMR spectrum: (SF₅: AB₄-type) $\delta_A = 65.0$ ppm, nine lines, each line with triplet splitting, 1F; $\delta_B = 45.0$, skewed d, 4F, $J_{At} \approx 4.9$, $J_{AB} = 152$ Hz. CF₂: $\delta_3 = -116$, ≈p, $J = 18$ Hz, 2F (CF₂CH₂); $\delta_{4+5} = -125$, 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, $SF_3CF_2^+$; 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 $^{12}C_8^{1}H_7^{19}F_{13}^{16}O_2^{32}S$: 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].

1H NMR spectrum: $\delta_1 = 4.09$ ppm, t-p, $J_{12} = 6.0$ Hz, $J_{1SF_4} \approx 1$, 2H; $\delta_2 = 3.87$, t-p, $J = 6.0$, $J_{2SF_4} = 8.5$, 2H.

^{19}F NMR spectrum: (AB_4 -type) $\delta_A = 84.0$ ppm, nine lines, 1F; $\delta_B = 65.5$, 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.

1H NMR spectrum: $\delta_1 = 4.0$ ppm, t, $J_{12} = 6.4$ Hz, 2H (CH_2OH); $\delta_2 = 2.5$, 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) $\delta_A = 64.2$ ppm, nine lines (poorly resolved), 1F; $\delta_B = 44.6$, 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, $\ll 1\%$, $(M - H)^+$; 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 $^{12}C_6^{1}H_6^{19}F_{13}^{16}O^{32}S$ (MH): 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 -citrate (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 \times 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%.

1H NMR spectrum: $\delta_{12} = 3.82$, s, 3H; $\delta_{12} = 3.87$, s, 3H (CH_3); $\delta_3 = 5.26$, p, $J = 6.70$ Hz, 2H (CH_2SF_5); $\delta_4 = 7.07$, s, 1H ($CH=C$).

^{19}F NMR spectrum: (AB_4 -type) $\delta_A = 81.7$ ppm, nine lines, 1F; $\delta_B = 67.2$, 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**).

^1H 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, $J_{\beta 1\beta 2} = 14.7$, $J_{\text{SF}_4\beta 1} = 7.8$; $\delta_{\beta' 2} = 5.05$, d-p, $J_{\text{SF}_4\beta 1} = 8.2$, 1H; $\delta_{\text{CH}_3} = 3.75$, s, 3H; $\delta_{\text{CH}_3} = 3.88$, s, 3H.

^{19}F NMR spectrum: (AB_4 -type) $\delta_{\text{A}} = 82.5$ ppm, nine lines, 1F; $\delta_{\text{B}} = 67.8$, skewed d, 4F, $J_{\text{AB}} = 146$ Hz.

Mass spectrum (70 eV: ion (m/z), %, assignment): $R_t = 12.82$ min, 364, 366, <1%, M^+ ; 333, 335, 22, 22, ($M - \text{OCH}_3$) $^+$; 253, 14, ($M - \text{HBr} - \text{OCH}_3$) $^+$; 193, 195, 38, 38, ($M - \text{SF}_5\text{CH}_2 - \text{OCH}_3 + \text{H}$) $^+$; 157, 16, ($M - \text{SF}_5 - \text{Br} + \text{H}$) $^+$; 145, 21, $\text{SF}_4\text{C}_3\text{H}^+$; 127, 19, SF_5^+ ; 99, 53, ($\text{CH}_3\text{OOCCH}_2\text{CCH}_2 = \text{C}_5\text{H}_7\text{O}_2$) $^+$; 89, 12, SF_3^+ ; 71, $\text{C}_3\text{H}_5\text{O}_2^+$; 59, 100, $\text{C}_2\text{H}_3\text{O}_2^+$; 51, 6, SF^+ ; 39, 20, C_3H_3^+ .

High-resolution mass spectrum calcd. for $^{12}\text{C}_7\text{H}_{11}^{19}\text{F}_5$ $^{32}\text{S}^{16}\text{O}_4$ ^{79}Br (MH) $^+$: 364.9482. Found: 364.9497.

3.13. $\text{SF}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{COOC}(\text{CH}_3)_3)_2$ (**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. $\text{SF}_5(\text{CH}_2)_3\text{Br}$ (4.46 g, 17.9 mmol, in 10 ml of $(\text{CH}_3\text{OCH}_2)_2$) 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**).

^1H NMR spectrum: $\delta_{\text{CH}_3} = 1.47$, s, 18H; $\delta_{\alpha} = 3.15$, t, $J_{\alpha\beta} = 7.42$ Hz, 1H; $\delta_{\beta} = 1.85$, m, 2H; $\delta_{\gamma} = 1.98$, m, 2H; $\delta_{\delta} = 3.68$, t-p, $J_{\gamma\delta} = 8.01$, $J_{\text{B}\delta} = 8.20$, 2H.

^{19}F NMR spectrum: (AB_4 -type) $\delta_{\text{A}} = 85.2$, nine lines, 1F; $\delta_{\text{B}} = 64.5$, $J_{\text{AB}} = 148$ 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, ($M - (\text{CH}_3)_2\text{C} = \text{CH}_2 - \text{CH}_3$) $^+$; 273, 8, ($M - (\text{CH}_3)_3\text{CO} - 2\text{F}$) $^+$; 228, 2, ($\text{CH}_2\text{CH}(\text{COOC}(\text{CH}_3)_3)_2 - \text{H}$) $^+$; 145, 10, ($\text{C}_6\text{H}_8\text{O}_2\text{S} + \text{H}$) $^+$; 127, 3, SF_5^+ ; 115, 6, ($\text{CHCOOC}(\text{CH}_3)_3 + \text{H}$) $^+$; 89, 1, SF_3^+ ; 57, 100, C_4H_9^+ ; 41, 16, C_3H_3^+ .

3.14. $\text{SF}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{COOH})_2$ (**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 recrystallize 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) $\delta_{\text{A}} = 85.5$, nine lines, 1F; $\delta_{\text{B}} = 64.2$, $J_{\text{AB}} = 147.3$ Hz (AB_4 -system).

Anal. calcd. for $\text{C}_6\text{H}_9\text{F}_5\text{O}_4\text{S}$: C, 26.48; H, 3.33; S, 11.78. Found: C, 27.20; H, 3.22; S, 11.19.

3.15. $\text{SF}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ (**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.

^1H NMR spectrum: $\delta_{\alpha} = 2.43$ ppm, t, $J = 7.23$ Hz, 2H; δ_{β} , $\delta_{\gamma} = 1.70$, m, 2H and 1.97, m, 2H; $\delta_{\delta} = 3.68$, t-p, $J_{\text{B}\delta} = 8.20$, $J_{\gamma\delta} \approx 7$, 2H.

^{19}F NMR spectrum: (AB_4 -type) $\delta_{\text{A}} = 85.7$, nine lines, 1F; $\delta_{\text{B}} = 64.3$, $J_{\text{AB}} = 148$ 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%, ($M - \text{OH}$) $^+$; 127, 8, SF_5^+ ; 108, <1, SF_4^+ ; 101, 15, ($M - \text{SF}_5$) $^+$; 99, 10, ($M - \text{SF}_5 - 2\text{H}$) $^+$; 89, 22, SF_3^+ ; 83, 38, ($M - \text{SF}_5 - \text{OH} - \text{H}$) $^+$; 73, 7, $\text{C}_3\text{H}_5\text{O}_2^+$; 70, 6, SF_2^+ ; 59, C_2HO_2^+ ; 55, 100, $\text{C}_3\text{H}_3\text{O}^+$; 41, 29, C_3H_5^+ , C_2HO^+ .

Anal. calcd. for $\text{C}_5\text{H}_9\text{F}_5\text{O}_2\text{S}$: 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. $\text{SF}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$, 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 $\text{SF}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ (21 mmol) was added dropwise. A precipitate quickly formed and after 100 min the reaction was complete. The complex, $\text{NaI} \cdot (\text{CH}_3)_2\text{C} = \text{O}$ 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.

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

^{19}F NMR spectrum: (AB_4 -type) $\delta_{\text{A}} = 85.3$, nine lines, 1F; $\delta_{\text{B}} = 69.0$, $J_{\text{AB}} = 146.2$ 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. Tyrre, 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.