Preparation and Reactivity of Tris(trifluoromethylselanyl)carbenium $[(CF_3Se)_3C^+]$ and Trifluoromethylsulfanylacetic Acid Derivatives $[(CF_3S)_{3-n}CX_n(O)R]$☆

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Received April 26, 1996

Key Words: Trifluoromethylselanyl / Trifluoromethylsulfanyl / Acetic acid / Esters / Halides / Hexafluoroarsenate

Reaction pathways for the synthesis of the $(CF_3E)_3C$ moieties (E = Se, S) are described. $[(CF_3Se)_3C^+][AsF_6^-]$ was found to be a suitable synthon for the preparation of $(CF_3Se)_3C$ derivatives. It can be prepared either from $(CF_3Se)_4C$ or $(CF_3Se)_3CF$ and AsF_5 in liquid SO_2. Direct access to $(CF_3Se)_3CF$ was realized by the reaction of $FCBr_3$ with $Hg(SeCF_3)_2$. Treatment of $[(CF_3Se)_3C^+][AsF_6^-]$ with potassium halides provided $(CF_3Se)_3CX$ (X = F, Cl, Br). A different course took the reaction with KI, as $CF_3SeSeCF_3$ and $(CF_3Se)_2C{=}C(SeCF_3)_2$ were formed as main products. Minor amounts of $(CF_3Se)_3CC(SeCF_3)_3$ were formed which could be isolated and unambiguously characterized. Only two routes led to a threefold CF_3S-substituted acetic acid ester $(CF_3S)_3CC(O)OR$ [R = CH_3, $(CH_3)_3C$]: Metatheses between $(CF_3S)_2CBrC(O)OCH_3$ and $Hg(SCF_3)_2$ and metalation of $(CF_3S)_2CHC(O)OR$ [R = CH_3, $(CH_3)_3C$] with NaH followed by reaction with CF_3SCl. Other precursors such as $(CF_3S)_2CXC(O)OR'$ [X = H, Br; R' = Me_3Si, $(n\text{-}C_4H_9)_3Sn$] and $(CF_3S)_2CBrC(O)Y$ (Y = Cl, Br) were synthesized but could not be converted to the corresponding $(CF_3S)_3C$ derivatives. Attempts to hydrolyze $(CF_3S)_3CC(O)OR$ to $(CF_3S)_3CC(O)OH$ failed.

With the synthesis of $[(CF_3S)_3C^+][AsF_6^-]$ a building block for the preparation of compounds containing a $(CF_3S)_3C$ moiety became available. Thus it is nucleophilically attacked by halide ions such as F^-, Cl^-, Br^- leading to the formation of $(CF_3S)_3CX$ (X = F, Cl, Br) as stable colorless liquids in good yields. The reaction with I^- was of special interest. An excess of iodide reacts in liquid SO_2 with $[(CF_3S)_3C^+][AsF_6^-]$ to give good yields of $(CF_3S)_3CC(SCF_3)_3$[1] according to

$$2\,[(CF_3S)_3C^+][AsF_6^-] + 2\,KI \xrightarrow{20\,^\circ C/2\,d} (CF_3S)_3CC(SCF_3)_3 + I_2 + 2\,K[AsF_6]$$

This procedure provides a better access (86%) to the already known ethane derivative which was prepared by photolysis of $(CF_3S)_2C{=}S$ in 18% yield[2]. Attempts to synthesize the corresponding $(CF_3Se)_3CC(SeCF_3)_3$ by irradiation of $(CF_3Se)_2C{=}S$ and $CF_3Se(CF_3S)C{=}S$ with UV light gave only $CF_3S(CF_3Se)_2CC(SeCF_3)_2SCF_3$ and $(CF_3S)_2$-$CF_3SeCCSeCF_3(SCF_3)_2$, respectively[3].

The first problem to be solved was the synthesis of $[(CF_3Se)_3C^+][AsF_6^-]$ and its application as a synthon for the preparation of compounds with a $(CF_3Se)_3C$ moiety, especially $(CF_3Se)_3CC(SeCF_3)_3$. In addition, attempts were made to synthesize – besides the already known CF_3S-substituted acids $(CF_3S)_n(CH_{3-n}C(O)OH$ (n = 1[4], 2[5]) – the unknown $(CF_3S)_3CC(O)OH$ and some of its derivatives. Already known are $(CF_3S)_3CC(O)OC_2H_5$, $(CF_3S)_3CCN$, $(CF_3S)_3CC(O)NH_2$, and $(CF_3S)_3CC(O)NCO$[6].

Preparation and Chemical Reactions of Tris(trifluoromethylselanyl)methylium Hexafluoroarsenate (1)

Suitable starting materials for the preparation of **1** are $(CF_3Se)_4C$ and $(CF_3Se)_3CF$. They are prepared by metathesis between CBr_4 or CBr_3F and $Hg(SeCF_3)_2$ according to:

$$CBr_4 + 4\,Hg(SeCF_3)_2 \rightarrow (CF_3Se)_4C^{[3]} + 4\,CF_3SeHgBr$$
$$CBr_3F + 3\,Hg(SeCF_3)_2 \rightarrow (CF_3Se)_3CF + 3\,CF_3SeHgBr$$

Since less $Hg(SeCF_3)_2$ is needed for the preparation of $(CF_3Se)_3CF$ its application is superior to $(CF_3Se)_4C$. The reactions of $(CF_3Se)_3CF$ or $(CF_3Se)_4C$, with AsF_5 are carried out in liquid SO_2 and proceed almost quantitatively according to:

$$(CF_3Se)_3CF + AsF_5 \rightarrow \underset{\mathbf{1}}{[(CF_3Se)_3C^+][AsF_6^-]}$$

$$2\,(CF_3Se)_4C + 3\,AsF_5 \rightarrow \underset{\mathbf{1}}{2\,[(CF_3Se)_3C^+][AsF_6^-]} + CF_3SeSeCF_3 + AsF_3$$

Yellow **1** is stable at 20°C in the absence of nucleophiles but it reacts with KX (X = F, Cl, Br) in SO_2 at 20°C (16 h) to provide $(CF_3CSe)_3CX$ (**2**) in good yields. The colorless liquids are thermally less stable than the corresponding sulfur homologs and decompose slowly at 20°C with the formation of $CF_3SeSeCF_3$. **1** shows a completely different behavior towards KI. Instead of the expected $(CF_3Se)_3CI$ or $(CF_3Se)_3CC(SeCF_3)_3$ the main products are $(CF_3Se)_2C{=}C(SeCF_3)_2$ and $CF_3SeSeCF_3$ together with $KAsF_6$ and I_2. Only traces of $(CF_3Se)_3CC(SeCF_3)_3$ could be detected and finally also be isolated. Hexakis(trifluoro-

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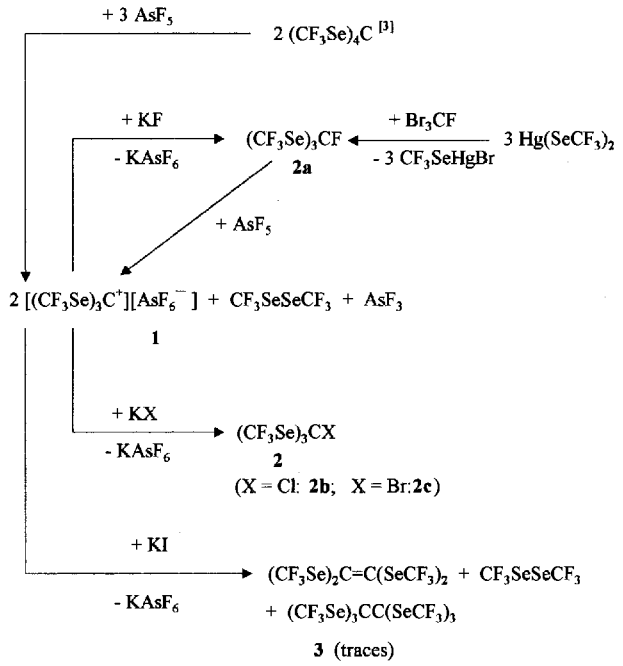
methylselanyl)ethane (**3**) does not dissociate homolytically in solution at 20°C reversibly into $(CF_3Se)_3C^•$ radicals in contrast to $(CF_3S)_3CC(SCF_3)_3$[2]. In Contrast to the sulfur analog, **3** does not show a $(CF_3Se)_3C^•$ peak in its mass spectrum[2]. Scheme 1 gives a summary of the new reactions described in this paper.

Scheme 1



Synthesis of $(CF_3S)_nCH_{3-n}C(O)OR$ Derivatives (n = 2, 3) and Their Hydrolysis Reactions

For a successful preparation of $(CF_3S)_3CC(O)OH$ and its derivatives the following strategies were pursued:

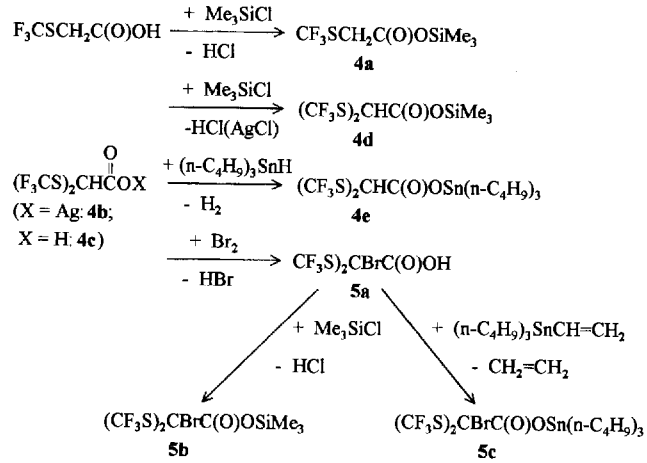
a) Preparation of $(CF_3S)_2CHC(O)OR$ [R = $SiMe_3$, $SnBu_3$, CH_3, $C(CH_3)_3$], metalation of the C–H bond with NaH followed by electrophilic substitution with CF_3SCl.

b) Bromination of $(CF_3S)_2CHC(O)OR$ affording $(CF_3S)_2BrCC(O)OR$ followed by nucleophilic substitution with $Hg(SCF_3)_2$, $AgSCF_3$, $(CH_3)_3SiSCF_3$ or *N*-trifluoromethylsulfanylsuccinimide.

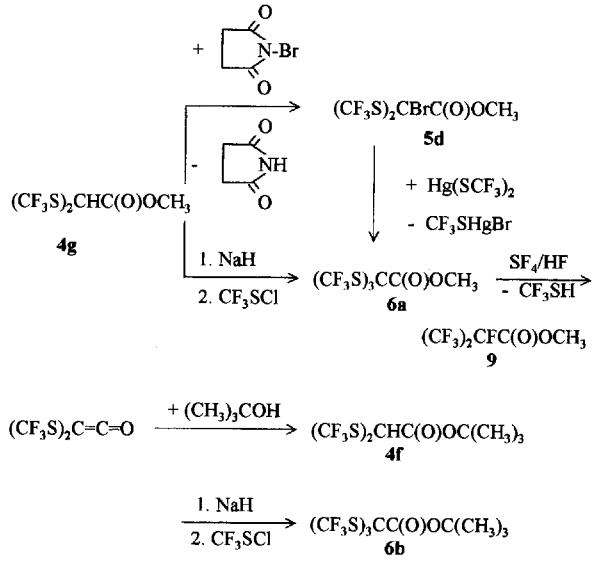
c) Hydrolysis of the synthesized esters.

The normal route to silyl esters **4a** and **4d** involves reaction of the acids $(CF_3S)_nCH_{3-n}C(O)OH$ (n = 1, 2) with $(CH_3)_3SiCl$, but the most convenient access to bis(trifluoromethylsulfanyl)acetic acid trimethylsilyl ester (**4d**) consists of the preparation of $(CF_3S)_2CHC(O)OAg$ (**4b**) and subsequent treatment with $(CH_3)_3SiCl$. Direct esterification of bis(trifluoromethylsulfanyl)acetic acid (**4c**) with $(CH_3)_3SiCl$ is troublesome since **4c** and **4d** have very similar boiling points and purification by distillation is tedious and time-consuming. The corresponding Bu_3Sn ester (**4e**) was prepared from (**4c**) and Bu_3SnH (see Scheme 2). The other two esters employed, bis(trifluoromethylsulfanyl)acetic acid methyl[13] (**4g**) and *tert*-butyl ester (**4f**), were obtained from $(CF_3S)_2C=C=O$ and ROH [R = CH_3, $(CH_3)_3C$]. Treatment of the esters **4d–g** with NaH and subsequently with CF_3SCl did not yield the expected compounds with **4d** and **4e**, but in the other two cases tris(trifluoromethylsulfanyl)-acetic acid methyl- (**6a**) and *tert*-butyl ester (**6b**) were formed (see Scheme 3).

Scheme 2



Scheme 3



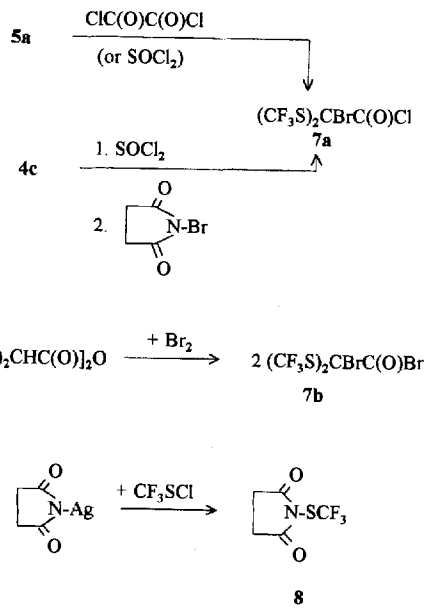
According to the second route $(CF_3S)_2CHC(O)OH$ could be brominated with bromine in the presence of PCl_3 as a catalyst to afford bromo-bis(trifluoromethylsulfanyl)acetic acid (**5a**) which was treated with $(CH_3)_3SiCl$ or $nBu_3SnCH=CH_2$ to furnish the corresponding esters **5b** and **5c** (see Scheme 2). Direct bromination of **4g** with *N*-bromosuccinimide (NBS) in CCl_4 gave $Br(CF_3S)_2CC(O)OCH_3$ (**5d**) in 85% yield (see Scheme 3). Bromination of **4f** with NBS under various reaction conditions failed. In all cases the starting compounds could be recovered. No nucleophilic substitution of $Br(CF_3S)_2CC(O)OR$ (R = $SiMe_3$, nBu_3Sn) was observed when $Hg(SCF_3)_2$, $AgSCF_3$, and Me_3SiSCF_3 were used. The reactions studied so far provided two suitable precursors for the synthesis of $(CF_3S)_3CC(O)OH$, namely

$(CF_3S)_3CC(O)OR'$ [R = CH_3, $C(CH_3)_3$]. Attempts to convert these two esters into the free acid by hydrolysis under acidic condition by varying the reaction parameters such as temperature, time, and concentrations yielded only the unchanged starting compounds. Attempts to pyrolyze $(CF_3S)_3CC(O)OC(CH_3)_3$ to $(CF_3S)_3C(O)OH$ and $(CH_3)_2C{=}CH_2$ failed as the ester was stable up to 225°C. At higher temperatures decomposition with cleavage of CF_3S groups occured.

Therefore, a new concept was applied: Preparation of $Br(CF_3S)_2CC(O)O(O)CR$ by reaction of $Br(CF_3S)_2C(O)Cl$ with RC(O)OM followed by nucleophilic substitution with $Hg(SCF_3)_2$. Hydrolyses should give the desired acid $(CF_3S)_3CC(O)OH$.

Chlorination of $Br(CF_3S)_2CC(O)OH$ with $SOCl_2$ or ClC(O)C(O)Cl gave $Br(CF_3S)_2CC(O)Cl$ in about 25% yield. Therefore, a more efficient method was applied. In a two-step reaction $(CF_3S)_2CHC(O)OH$ was first chlorinated with $SOCl_2$ to give $(CF_3S)_2CHC(O)Cl$ and then brominated with *N*-bromosuccinimide in the presence of HBr to furnish **7a** in 75% yield, but no reaction took place with RC(O)OM [M = Na, Ag; R = CH_3, CF_3, $(CF_3S)_2CH$]. An attempt to synthesize $(CF_3S)_3CC(O)Cl$ from $(CF_3S)_2CHC(O)Cl$ and *N*-trifluoromethylsulfanylsuccinimide prepared from silver succinimide and CF_3SCl failed as well. Bromination of $[(CF_3S)_2CHC(O)]_2O$ with bromine in CCl_4 yielded $(CF_3S)_2CBrC(O)Br$ (**7b**) which did not react with $Hg(SCF_3)_2$ (see Scheme 4). However, **6a** became available in almost quantitative yield by reaction of $Br(CF_3S)_2CC(O)OCH_3$ with $Hg(SCF_3)_2$ (see Scheme 3).

Scheme 4



Experimental

All experiments were carried out under argon in oven-dried glassware with strict exclusion of moisture. Volatile materials and solvents were manipulated in vacuo in a standard vacuum system with teflon-stemmed Young valves, solids in an argon glove box. Solvents were dried according to published procedures[7].

Microanalyses: Carlo-Erba Elementanalyser model 1106. – IR: Bruker IFS 66 FT, solids as KBr disks, liquids as capillary films and gases in a 10-cm cell with KBr windows. – NMR: Bruker WP 80 or AM 400. Standards used: $CFCl_3$ (^{19}F), $Si(CH_3)_4$ (^1H, ^{13}C, ^{29}Si), $(CH_3)_2Se$ (^{77}Se), $Sn(CH_3)_4$ (^{117}Sn); internal lock and solvent $CDCl_3$. Complex, incompletely resolved signals and higher-order spectra were classified as multiplets. – MS: Varian MAT CH5 (70 eV). – GC/MS: Hewlett-Packard 5989A, combined with a Hewlett-Packard 5890 (12.5-m capillary column covered with OV 1), 70 eV.

$Hg(SeCF_3)_2$[8], $(CF_3Se)_4C$[3], CF_3SCl[9], CF_3SSCF_3[10], $Hg(SCF_3)_2$[11], $AgSCF_3$[11], $CH_{3-n}(SCF_3)_nC(OC_2H_5)_3$[5c], $CH_{3-n}(SCF_3)_nC(O)OH$[5c], $(CF_3S)_2C{=}C{=}O$[5c], $(CH_3)_3SiSCF_3$[12], and $(CF_3S)_2CHC(O)OCH_3$[13] were prepared according to literature methods. The other starting materials used were commercially available and used without further purification.

Tris(trifluoromethylselanyl)methylium Hexafluoroarsenate (**1**): In a 200-ml Carius tube equipped with a teflon-stemmed Young valve and a magnetic stirring bar 0.8 g (1.3 mmol) of $(CF_3Se)_4C$ (dried with P_4O_{10}) was placed. Afterwards 0.35 g (2.0 mmol) of AsF_5 and 4 g of SO_2 as a solvent were condensed. The reaction mixture was stirred for 16 h at 20°C. Solvent and volatile products were removed in vacuo, leaving 0.8 g (95%) of **1** as a yellow powder.

An *alternative route* to **1** is the reaction of $(CF_3Se)_3CF$ with AsF_5 in SO_2. According to the procedure described above 1.0 g (2.1 mmol) of $(CF_3Se)_3CF$ was treated with 0.4 g (2.4 mmol) of AsF_5 in SO_2 at 20°C (16 h) to yield 1.1 g (80%) of **1**; m.p. 205°C. – IR: $\tilde{\nu}$ = 1208 cm^{-1} (m, br.), 1167 (m), 1087 (s), 817 (m), 740 (m), 700 (m), 575 (vw), 563 (w). – ^{13}C NMR (external standard: $CDCl_3$, solvent SO_2): δ = 119.1 (s), 127.8 [q, ^1J(C-F) = 345.2 Hz]. – ^{19}F NMR: δ = 30.2 (s). – ^{77}Se NMR: δ = 989 (m). – MS; *m/z* (%): 329 [$(CF_3Se)_2CF^+$] (100), 260 (17), 151 (65), 111 (60), 80 (15), 69 (95), 31 (17). – $C_4AsF_{15}Se_3$ (644.8): calcd. C 7.4; found C 7.3.

Fluorotris(trifluoromethylselanyl)methane (**2a**): The reaction was carried out in a 100-ml Carius tube equipped as described above. Into the tube 1.0 g (3.7 mmol) of Br_3CF and 5.6 g (11.3 mmol) of $Hg(SeCF_3)_2$ were filled, the mixture was then evacuated and sealed. It was heated at 80°C and stirred for 6 d, then separated by fractional condensation (three traps cooled to 0, −30, and −196°C). The fraction condensed at −30°C contained 1.0 g (60%) of **2a** with high purity.

An *alternative synthesis* is the reaction of 0.5 g (0.8 mmol) of **1** with 60 mg (1.0 mmo) of KF in 2.5 g of SO_2 carried out in a 20-ml Carius tube under analogous reaction conditions providing 0.3 g (80%) of **2a**. b.p. 45°C/10^{-3} Torr. – IR: $\tilde{\nu}$ = 1276 cm^{-1} (w), 1156 (s), 1088 (s), 731 (s), 418 (w). – ^{13}C NMR: δ = 82.1 [d, ^1J(C-F) = 370.0 Hz], 123.9 [q, ^1J(C-F) = 339.5 Hz]. – ^{19}F NMR: δ = −32.0 (d), −81.5 [dec, ^4J(F-F) = 7.9 Hz]. – ^{77}Se NMR: δ = 759 [md, ^2J(Se-F) = 52.7 Hz]. – MS; *m/z* (%): 329 [$(CF_3Se)_2CF^+$] (62), 241 (10), 160 (10), 149 (5), 111 (60), 80 (11), 69 (100). – $C_4F_{10}Se_3$ (474.9): calcd. C 10.1; found C 9.8.

Chlorotris(trifluoromethylselanyl)methane (**2b**): Similar to the reaction parameters described in the alternative syntheses described before 0.5 g (0.8 mmol) of **1** and 0.11 g (1.5 mmol) of KCl were allowed to react in liqud SO_2. The products were separated by fractional condensation at 0, −20, and −196°C. At −20°C **2b** was trapped as a colorless liquid with high purity. Byproducts such as $CF_3SeSeCF_3$, $(CF_3Se)_2C{=}C(SeCF_3)_2$, and $CF_3SeC|CSeCF_3$ were condensed at −196°C and identified by ^{19}F-NMR spectroscopy. Their δ values agreed with literature values. Yield: 0.18 g (45%).

As slow decomposition was already observed on standing at 20°C no boiling point culd be estimated. IR: $\tilde{\nu}$ = 2244 cm^{-1} (w), 1276 (m), 1165 (ws), 1081 (vs), 769 (w), 741 (s), 675 (m), 532 (w). – ^{13}C NMR: δ = 39.1 (s), 124.5 [q, ^1J(C-F) = 337.6 Hz]. – ^{19}F NMR: δ = −34.5 (s). – ^{77}Se NMR: δ = 824 (m). – MS; *m/z* (%): 457 [$(CF_3Se)_2CF^+$] (<1), 345 (23), 276 (2), 241 (4), 172 (6), 127 (45), 80 (10), 69 (100). – $C_4ClF_9Se_3$ (491.3): calcd. C 9.8, Cl 7.2; found: C 9.8, Cl 6.8.

Bromotris(trifluoromethylselanyl)methane (**2c**): As described before 0.5 g (0.8 mmol) of **1** was allowed to react with 140 mg (1.2 mmol) of KBr in liquid SO_2. At −20°C 0.35 g (84%) of **2c** condensed as an unstable colorless liquid at 20°C. IR: $\tilde{\nu}$ = 1274 cm^{-1} (w), 1147 (vs), 1062 (vs), 970 (w, br), 899 (w, br), 741 (s), 701 (w), 670 (w), 626 (w), 532 (w). – ^{13}C NMR: δ = 12.7 (s), 124.5 [q, ^1J(C-F) = 339.5 Hz]. – ^{19}F NMR: δ = −35.4 (s). – ^{77}Se NMR: δ = 848 (m). – MS; *m/z* (%): 457 [$(CF_3Se)_3C^+$] (1), 389/387 (14), 311 (4), 241/239 (20), 172/171 (14); 93 (13), 69 (100). – $C_4BrF_9Se_3$ (535.8): calcd. C 9.0; found C 9.1.

Hexakis(trifluoromethylselanyl)ethane (**3**): As described before 0.5 g (0.8 mmol) of **1** was treated with 0.15 g (0.9 mmol) of KI in 3 g of liquid SO_2 at 20°C for 48 h. The volatile products were fractioned on a standard vacuum system by using three traps, cooled to 0, −78, and −196°C. The fraction collected at −78°C consisted of a mixture of $(CF_3Se)_2C{=}C(SeCF_3)_2$ and $CF_3SeSeCF_3$. Both substances were unambiguously characterized by ^{19}F NMR and GC/MS. About 98% of $(CF_3Se)_2C{=}C(SeCF_3)_2$ were isolated. The solid residue in the Carius tube was sublimed at 65°C/10^{-3} Torr providing small amounts of a colorless powder characterized as **3**; m.p. 125°C. – IR: $\tilde{\nu}$ = 1199 cm^{-1} (m), 1141 (s), 1081 (vs), 1053 (sh), 738 (m), 640 (vw), 534 (vw). – ^{19}F NMR: δ = −33.4 (s). – MS; *m/z* (%): 765 [$(CF_3Se)_5C_2^+$] (18), 618 (80), 547 (21), 469 (21), 400 (23), 322 (42), 253 (28), 184 (77), 69 (100). – $C_8F_{18}Se_6$ (911.8): calcd. C 10.5; found C 10.4.

Trimethylsilyl Trifluoromethylsulfanylacetate (**4a**): In a 25-ml two-necked flask equipped with a reflux condenser, magnetic stirring bar, and a drying tube filled with $CaCl_2$ 4.0 g (25.0 mmol) of $CF_3SCH_2C(O)OH$ and 5.0 g (45.9 mmol) of Mc_3SiCl were placed and refluxed for 72 h. The end of the reaction was established by taking regularly probes which were analyzed by ^{19}F-NMR spectroscopy. The reaction mixture was fractionated in vacuo by using a Zinke apparatus. The pure ester was obtained as a colorless liquid. Yield 5.1 g (88%); b.p. 96°C/10 Torr. – IR: $\tilde{\nu}$ = 2966 cm^{-1} (m), 2907 (w), 1724 (m), 1312 (s), 1258 (s), 1201 (s), 1113 (vs), 946 (s), 850 (s), 724 (m), 697 (m). – ^1H NMR: δ = 0.32 (s, 9H, CH_3), 3.72 (s, 2H, CH_2). – ^{13}C NMR: δ = −0.53 [q, ^1J(C-H) = 120.2 Hz, 3 C], 33.4 [t, ^1J(C-H) = 141.1 Hz, 1 C], 130.3 [tq, ^1J(C-F) = 307.1 Hz, ^3J(C-H) = 5.7 Hz, 1 C], 167.6 [t, ^2J(C-H) = 5.7 Hz, C=O]. – ^{29}Si NMR: δ = 27.9 [dec, ^2J(Si-H) = 7.3 Hz]. – MS; *m/z* (%): 217 [$M^+ - CH_3$] (4), 143 (18), 117 (11), 96 (18), 77 (71), 73 (100), 69 (14). – $C_6H_{11}F_3O_2SSi$ (232.1): calcd. C 31.0, H 4.7, S 13.8; found C 30.3, H 4.6, S 13.4.

Silver Bis(trifluoromethylsulfanyl)acetate (**4b**): Neutralization of 4.4 g (16.9 mmol) of **4c** with 2.9 g (17.0 mmol) of a solution of $AgNO_3$ in 170 ml of H_2O provided after 30 min 5.1 g (82%) of **4b**; m.p. 125°C (dec.). – IR: $\tilde{\nu}$ = 1626 cm^{-1} (s), 1359 (s), 1151 (s), 1088 (s), 913 (w), 827 (w), 758 (m), 719 (m). – ^1H NMR (D_2O): δ = 7.2 (s). – ^{13}C NMR ($CDCl_3$): δ = 51.0 [d, ^1J(C-H) = 116 Hz], 128.7 [q, ^1J(C-F) = 309.0 Hz], 170.5 (s). – ^{19}F NMR: δ = 39.7 (s). – MS; *m/z* (%): 215 [$(CF_3S)_2CH^+$] (72), 145 (35), 115 (85), 69 (100), 45 (75). – $C_4HAgF_6O_2S_2$ (367.0): calcd. C 13.1, H 0.3, S 17.4; found C 12.8, H 0.4, S 17.5.

Trimethylsilyl Bis(trifluoromethylsulfanyl)acetate (**4d**): In an apparatus as described for the preparation of **4a** 4.5 g (17.2 mmol) of **4c** was allowed to react with 3.8 g (34.9 mmol) of Me_3SiCl at reflux temperature. After 12 h the mixture was separated by fractional distillation in vacuo giving 4.0 g (70%) of **4d** as a colorless liquid. This procedure was rather time-consuming as **4d** and **4c** have similar boiling points.

An *alternative route* is the reaction of 4.0 g (10.9 mmol) of **4b** with 2.4 g (11.0 mmol) of Me_3SiCl under similar reaction conditions. Yield: 3.3 g (91%); b.p. 62°C/5 Torr. – IR: $\tilde{\nu}$ = 2967 cm^{-1} (m), 2908 (w), 2262 (w), 1729 (s), 1418 (m), 1259 (vs), 1091 (vs), 952 (s), 847 (vs), 759 (s), 681 (m), 469 (m). – ^1H NMR: δ = 0.33 (s, 9H, CH_3), 5.10 (s, 1H, CH). – ^{13}C NMR: −0.79 [q, ^1J(C-H) = 122.0 Hz, 3 C, CH_3), 48.5 [d, ^1J(C-H) = 158.5 Hz, 1 C, CH], 129.2 [dq, ^1J(C-F) = 304.2 Hz, ^3J(C-H) = 3.8 Hz, 2 C, CF_3], 165.5 [d, ^2J(C-H) = 5.7 Hz, 1 C, C=O]. – ^{19}F NMR: δ = −41.3 (s). – ^{29}Si NMR: δ = 31.4 [dec, ^2J(Si-H) = 7.1 Hz]. – MS; *m/z* (%): 317 [$M^+ - CH_3$] (2), 117 (13), 77 (25), 73 (100), 69 (13). – $C_7H_{10}F_6O_2S_2Si$ (332.2): calcd. C 25.3, H 3.0, S 19.3; found C 25.4, H 3.3, S 19.7.

Tri(n-butyl)stannyl Bis(trifluoromethylsulfanyl)acetate (**4e**): In a 25-ml two-necked flask fitted with a magnetic stirring bar, reflux condenser and drying tube filled with $CaCl_2$, and a septum 1.5 g (5.8 mmol) of **4c** was placed and 1.7 g (5.8 mmol) of $(n\text{-}C_4H_9)_3SnH$ was added dropwise through the septum by means of a microsyringe in within 3 min. After H_2 evolution had ceased the mixture was stirred for 30 min. During this time colorless crystals of **4e** precipitated. Yield: 2.9 g (91%); m.p. 33°C. – IR: $\tilde{\nu}$ = 2960 cm^{-1} (s), 2733 (s), 2253 (m), 1880 (w), 1624 (s), 1466 (m), 1339 (m), 1122 (s), 1024 (s), 962 (m), 938 (m), 878 (m), 833 (m), 757 (m), 673 (m), 614 (m), 552 (m), 542 (m), 470 (m). – ^1H NMR: δ = 0.9 (m), 1.4 (m), 5.1 (s). – ^{13}C NMR: δ = 13.5 [tq, ^1J(C-H) = 124.0 Hz, ^2J(C-H) = 3.8 Hz, 3 C, CH_3], 17.1 [t, ^1J(C-H) = 125.9 Hz, 3 C, CH_2], 27.0 [t, ^1J(C-H) = 124.0 Hz, 3 C, CH_2], 27.5 [t, ^1J(C-H) = 122.1 Hz, 3 C, CH_2], 48.2 [d, ^1J(C-H) = 158.3 Hz, 1 C, CH], 129.1 [dq, ^1J(C-F) = 310.9 Hz, ^3J(C-H) = 5.7 Hz, 2 C, CF_3], 165.5 [d, ^2J(C-H) = 5.7 Hz, 1 C, CO]. – ^{19}F NMR: δ = −41.4 (s). – ^{119}Sn NMR: δ = 160 (m). – MS; *m/z* (%): 493 [$M^+ - C_4H_9$] (35), 291 (22), 253 (100), 177 (22), 69 (5), 57 (39), 29 (41). – $C_{16}H_{28}F_6O_2S_2Sn$ (548.8): calcd. C 35.0, H 5.7, S 11.7; found C 35.1, H 5.1, S 11.4.

tert-Butyl Bis(trifluoromethylsulfanyl)acetate (**4f**): In a 20-ml Carius tube equipped as described for **1** 0.5 g (6.8 mmol) of $(CH_3)_3COH$ and 1.8 g (7.4 mmol) of $(CF_3S)_2C{=}C{=}O$ were condensed one consecutively with stirring at 20°C (16 h). After fractional condensation (−20, −78, −196°C) **4f** condensed at −20°C analytically pure. Yield: 2.0 g (93%); b.p. 51°C/0.1 Torr. – IR: $\tilde{\nu}$ = 2987 cm^{-1} (m), 2940 (w), 1740 (s), 1480 (w), 1460 (w), 1373 (m), 1305 (m), 1263 (sh), 1098 (vs), 955 (w), 850 (m), 758 (m), 463 (w). – ^1H NMR: δ = 1.5 (s, 9H), 5.0 (s, 1H). – ^{13}C NMR: δ = 27.4 [mq, ^1J(C-H) = 131.6 Hz, 3 C, CH_3], 47.9 [d, ^1J(C-H) = 156.4 Hz, 1 C, CH], 85.6 (s), 128.9 [dq, ^1J(C-F) = 314.7 Hz, ^3J(C-H) = 5.7 Hz, 2 C, CF_3], 164.7 [d, ^2J(C-H) = 5.7 Hz, 1 C, CO]. – ^{19}F NMR: δ = −41.3 (s). – MS; *m/z* (%): 215 (18) [M^+], 69 (14), 59 (31), 57 (100). – $C_8H_{10}F_6O_2S_2$ (316.1): calcd. C 30.4, H 3.2, S 20.25; found C 29.9, H 2.9, S 19.5.

Bromobis(trifluoromethylsulfanyl)acetic Acid (**5a**) was prepared as described for **4a** by the reaction of 3.45 g (13.3 mmol) of **4c** with a solution of 0.8 ml (15.6 mmol) of Br_2 in 20 ml of C_6H_6 in the presence of a catalytical amount (0.1 ml) of PCl_3. After refluxing of the mixture for 72 h separation was accomplished by fractional condensation in a conventional vacuum apparatus. Among the three traps cooled to 0, −30, and −196°C **5a** condensed at 0°C as colorless crystals. Yield: 2.5 g (55%). Instead of PCl_3 also PBr_3

could be used as a catalyst but the yield decreased to 38%. Similar observations were made with CCl_4 as a solvent and PCl_3 or PBr_3 as a catalyst. The yield dropped to 30 or 32%, respectively; m.p. 48°C. – IR: $\tilde{\nu}$ = 3152 cm^{-1} (m, br.), 1729 (m), 1400 (w), 1253 (w), 1161 (m), 1098 (s), 758 (vw), 695 (w). – ^1H NMR: δ = 9.2 (s). – ^{13}C NMR: δ = 56.3 (s), 127.7 [q, ^1J(C-F) = 314.7 Hz], 169.0 (s). – ^{19}F NMR: δ = −40.3 (s). – MS; *m/z* (%): 295/293 [$(CF_3S)_2CBr^+$] (1), 259 (55), 239/237 (10), 215 (20), 145 (78), 101 (5), 76 (72), 69 (100), 63 (18), 44 (75). – $C_4HBrF_6O_2S_2$ (339.0): calcd. C 14.2, H 0.3, S 18.8; found C 14.0, H 0.2, S 18.8.

Trimethylsilyl Bromobis(trifluoromethylsulfanyl)acetate (**5b**): As described for **4a** a mixture of 2.0 g (5.9 mmol) of **5a** and 1.3 g (11.9 mmol) of Me_3SiCl was stirred at 50°C for 6 h. Fractional condensation of the mixture using traps cooled to 0, −30, and −196°C provided **5b** at 0°C with high purity. Yield: 2.0 g (83%); b.p. 53°C/2 · 10^{-1} Torr. – IR: $\tilde{\nu}$ = 3280 cm^{-1} (m, br.), 2965 (m), 2907 (w), 2245 (w), 1722 (vs), 1416 (m), 1279 (vs), 1091 (vs), 959 (s), 459 (vs), 733 (s), 678 (s), 617 (m), 464 (m), 443 (m). – ^1H NMR: δ = 0.38 (s), ^{13}C NMR: δ = −0.94 [q, ^1J(C-H) = 120.2 Hz, 3 C, CH_3], 59.5 (s, 1 C, CBr), 127.9 [q, ^1J(C-F) = 312.8 Hz, 2 C, CF_3], 163.7 (s, 1 C, CO). – ^{29}Si NMR: δ = 34.1 [dec, ^2J(Si-H) = 7.0 Hz]. – MS; *m/z* (%): 397/395 [$M^+ - CH_3$], 295/293 (2), 145 (30), 77 (30), 73 (100), 69 (55), 45 (43). – $C_7H_9BrF_6O_2S_2Si$ (411.1): calcd. C 20.4, H 2.2, S 15.6; found C 20.2, H 2.1, S 14.7.

Tri(n-butyl)stannyl Bromobis(trifluoromethylsulfanyl)acetate (**5c**): In a 10-ml two-necked flask equipped with magnetic stirring bar, reflux condenser and gas bubble counter 2.5 g (7.4 mmol) of **5a** was placed and the flask was sealed with a septum. As described for **4e** 2.3 g (7.4 mol) of $(n\text{-}C_4H_9)_3SnCH{=}CH_2$ was added dropwise at 20°C. After 5 minutes gas evolution ceased and a colorless precipitate formed. Yield: 4.0 g (85%); m.p. 38°C. – IR: $\tilde{\nu}$ = 3480 cm^{-1} (w), 2957 (s), 2923 (s), 2854 (s), 1768 (m), 1629 (m), 1457 (m), 1415 (m), 1378 (m), 1340 (m), 1293 (m), 1099 (m), 1023 (m), 961 (w), 876 (w), 790 (w), 758 (w), 668 (w), 602 (w), 511 (w). – ^1H NMR: δ = 1.3 (m), 1.4 (m). – ^{13}C NMR: δ = 13.6 [tq, ^1J(C-H) = 124.0 Hz, ^2J(C-H) = 3.8 Hz, 3 C, CH_3], 17.4 [t, ^1J(C-H) = 127.8 Hz, 3 C, CH_2], 27.0 [t, ^1J(C-H) = 125.9 Hz, 3 C, CH_2], 27.5 [t, ^1J(C-H) = 124.0 Hz, 3 C, CH_2], 60.3 (s, 1 C, CBr), 128.1 [q, ^1J(C-F) = 312.8 Hz, 2 C, CF_3], 167.4 (s, 1 C, CO). – ^{19}F-NMR: δ = −40.9 (s). – ^{119}Sn NMR: δ = 181 (m). – MS; *m/z* (%): 493 [$HC(SCF_3)_2CO_2Sn(C_4H_9)_2^+$] (5), 291 (12), 253 (61), 177 (38), 101 (5), 69 (20), 57 (58), 41 (58), 29 (100). – $C_{16}H_{27}BrF_6O_2S_2Sn$ (627.7): calcd. C 30.6, H 4.3, S 10.2; found C 30.7, H 4.6, S 9.2.

Methyl Bromobis(trifluoromethylsulfanyl)acetate (**5d**): As described for the preparation of **5c**, 1.6 g (5.8 mmol) of $(CF_3S)_2CHC(O)OCH_3$, 2.3 g (13.0 mmol) of *N*-bromosuccinimide and two drops of a 62% aqueous HBr in 10 ml of CCl_4 were refluxed for 40 h. The mixture was then fractionated into traps cooled to −25, −78, and −196°C. The condensate at −25°C contained 1.7 g (83%) of **5d** with high purity. b.p. 49°C/0.8 Torr. – IR: νÄ = 3469 cm^{-1} (w), 3015 (w), 2962 (m), 2267 (vw), 1748 (s), 1439 (s), 1260 (s), 1101 (vs), 1003 (s), 981 (m), 831 (m), 795 (w), 758 (s), 739 (w), 624 (m), 466 (m), 418 (m). – ^1H NMR: δ = 4.0 (s). – ^{13}C NMR: δ = 55.8 [q, ^1J(C-H) = 148.8 Hz, 1 C, CH_3], 57.1 (s, 1 C, CBr), 127.8 [q, ^1J(C-F) = 312.8 Hz, 2 C, CF_3], 165.0 (s, 1 C, CO). – ^{19}F NMR: δ = −40.6 (s). – MS; *m/z* (%): 295/293 [$(CF_3S)_2CBr^+$] (1), 273 (5), 145 (30), 69 (100), 59 (95). – $C_5H_3BrF_6O_2S_2$ (353.0): calcd. C 17.0, H 0.85, S 18.1; found C 17.3, H 0.70, S 18.6.

Methyl Tris(trifluoromethylsulfanyl)acetate (**6a**): In a 50-ml Carius tube equipped as described for the preparation of **1**, 3.0 g (8.5 mmol) of **5d** was mixed with 3.4 g (8.5 mmol) of $Hg(SCF_3)_2$ and the mixture was heated at 65°C for 16 h. The products were separated by fractional condensation (−5, −25, −78°C) giving 2.9 g (92%) of **6a** as the fraction collected at −25°C.

An *alternative synthesis* was carried out in a 100-ml three-necked flask equipped with a reflux condenser, and drying tube filled with $CaCl_2$, magnetic stirring bar, and gas inlet tube. To a suspension of 0.4 g (16.7 mmol) of NaH in 40 ml of ether, a solution of 3.0 g (11.0 mmol) of $(CF_3S)_2CHC(O)OCH_3$ in 10 ml of ether was dropped at 20°C. The mixture was stirred for 16 h at 20°C, cooled to −78°C and then 5.0 g (36.8 mmol) of CF_3SCl was condensed to this mixture. Afterwards the content was warmed stirring at 20°C during 16 h. Fractional condensation (−25, −78, −196°C) provided 1.0 g (25%) of **6a** collected at −25°C; b.p. 48°C/0.5 Torr. – IR: $\tilde{\nu}$ = 2964 cm^{-1} (w), 1776 (m), 1752 (s), 1438 (m), 1260 (s), 1163 (s), 1091 (s), 1004 (m), 920 (m), 828 (w), 759 (s), 651 (w), 544 (w), 474 (w), 447 (w). – ^1H NMR: δ = 3.95 (s). – ^{13}C NMR: δ = 54.4 [q, ^1J(C-H) = 150.7 Hz, 1 C, CH_3], 66.8 (s), 124.9 [q, ^1J(C-F) = 312.8 Hz, 3 C, CF_3], 164.0 (s, 1 C, CO). – ^{19}F NMR: δ = −38.5 (s). – MS, *m/z* (%): 315 [$(CF_3S)_3C^+$] (5), 273 (65), 145 (30), 69 (80), 59 (100). – $C_6H_3F_9O_2S_3$ (374.2): calcd. C 19.25, H 0.8, S 25.7; found C 19.0, H 0.5, S 26.6.

tert-Butyl Tris(trifluoromethylsulfanyl)acetate (**6b**): As described for the alternative synthesis of **6a**, **6b** was prepared from 4.5 g (14.2 mmol) of **4f**, 0.5 g (20.8 mmol) of NaH and 7.0 g (51.5 mmol) of CF_3SCl and purified analogously. Yield: 2.0 g (34%); b.p. 46°C/10^{-2} Torr. – IR: $\tilde{\nu}$ = 3447 cm^{-1} (w, br.), 2987 (vw), 1768 (m), 1740 (m), 1375 (m), 1262 (m), 1152 (s), 1093 (s), 757 (m). – ^1H NMR: δ = 1.5 (s). – ^{13}C NMR: δ = 27.1 [q, ^1J(C-H) = 127.8 Hz, 3 C, CH_3], 67.2 (s), 88.7 (s), 127.5 [q, ^1J(C-F) = 312.8 Hz, 3 C, CF_3], 162.4 (s). – ^{19}F NMR: δ = −38.0 (s). – MS; *m/z* (%): 315 [$(CF_3S)_3C^+$], (17) 215 (3), 145 (19), 69 (33), 57 (100). – $C_9H_9F_9O_2S_3$ (416.2): calcd. C 26.0, H 2.2, S 23.1; found C 26.3, H 2.1, S 22.6.

Bromobis(trifluoromethylsulfanyl)acetyl Chloride (**7a**): As described for **4a** 5.0 g (19.2 mmol) of **4e** and a solution of 9.0 g (76.0 mmol) of $SOCl_2$ in 5 ml of CCl_4 were refluxed for 12 h. Afterwards 4.1 g (23.0 mmol) of *N*-bromosuccinimide was added under inert gas. This mixture was heated at 85°C for 3 h and then separated by fractional condensation (−25, −45, −196°C). The fraction condensing at −45°C contained 4.5 g (66%) of pure **7a**, b.p. 40°C/1 Torr. – IR: $\tilde{\nu}$ = 1793 cm^{-1} (s), 1768 (s), 1163 (s), 1097 (vs), 1013 (s), 762 (s), 758 (s), 710 (s), 463 (m), 434 (m). – ^{13}C NMR: δ = 64.6 (s, 1 C, CBr), 127. 4 [q, ^1J(C-F) = 312.8 Hz, 2 C, CF_3], 167.9 (s, 1 C, CO). – ^{19}F NMR: δ = −39.6 (s). – MS; *m/z* (%): 295/293 [$(CF_3S)_2CBr^+$] (22), 279/277 (22), 251/249 (21), 242 (18), 231/229/227 (10), 145 (60), 101 (5), 69 (100). – $C_4BrClF_6OS_2$ (357.4): calcd. C 13.5, S 17.9, Cl 9.9; found C 13.1, S 17.5, Cl 10.1.

Bromobis(trifluoromethylsulfanyl)acetyl Bromide (**7b**): As described for **4a** a mixture of 3.0 g (6.0 mmol) of $[(CF_3S)_2CHC(O)]_2O$ and 2.9 g (18.0 mmol) of Br_2 dissolved in CCl_4 was refluxed for 24 h and subsequently separated by fractional condensation (−20, −50, −196°C). The trap cooled to −50°C contained 4.0 g (83%) of **7b**. Boiling point and elemental analytical data could not be determined as the substance decomposed already slowly at 20°C to $(CF_3S)_2C{=}C{=}O$ and bromine. IR: $\tilde{\nu}$ = 3510 cm^{-1} (w), 2989 (w), 2267 (w), 2138 (m), 1766 (s), 1166 (vs), 1096 (vs), 975 (s), 758 (s), 694 (s), 673 (s), 544 (m), 462 (s). – ^{13}C NMR: δ = 69.0 (s), 172.2 [q, ^1J(C-F) = 314.7 Hz], 164.0 (s). – ^{19}F NMR: δ = −39.3 (s). – MS; *m/z* (%): 295/293 [$(CF_3S)_2CBr^+$] (10), 242 (18), 215 (18), 145 (42), 69 (100), 44 (18), 28 (60).

N-(Trifluoromethylsulfanyl)succinimide (**8**): As described for **4a** to a suspension of 4.0 g (19.0 mmol) of silver succinimide in 15 ml

of ether 3.1 g of (23.0 mmol) CF_3SCl was condensed at −78°C. The mixture was allowed to slowly warm to 20°C (16 h) and was then left for 24 h at this temperature. After removal of the volatile products in vacuo the slightly grey residue was sublimed at 50°C/10^{-3} Torr to yield 3.2 g (85%) of **8**; m.p. 97°C. − IR: $\tilde{\nu}$ = 3402 cm^{-1} (w, br), 2951 (w), 1738 (vs), 1430 (m), 1298 (s), 1254 (s), 1229 (s), 1107 (vs), 1009 (vs), 935 (m), 817 (m), 760 (s), 659 (s), 587 (m), 572 (m), 469 (m). − ^{1}H NMR: δ = 2.9 (s). − ^{13}C NMR: δ = 28.4 [tt, ^1J(C-H) = 137.3 Hz, ^2J(C-H) = 5.1 Hz, 2 C, CH_2], 127.7 [q, ^1J(C-F) = 314.7 Hz], 174.4 (s, 2 C, CO). − ^{19}F NMR: δ = −48.4 (s). − MS; *m/z* (%): 200 [M^+] (20), 199 (95), 171 (21), 143 (20), 115 (18), 102 (59), 69 (48), 55 (100), 42 (20), 28 (99). − $C_5H_4F_3NO_2S$ (200.1): calcd. C 30.0, H 2.0, S 16.0, N 7.0; found C 30.0, H 1.9, S 14.8, N 7.4.

Methyl Fluorobis(trifluoromethylsulfanyl)acetate (**9**): In a 50-ml stainless steel autoclave equipped with a magnetic stirring bar and bursting plate 1.1 g (2.9 mmol) of **6a** and a solution of 2.0 g (100.0 mmol) of HF in 5 ml of CCl_4 were placed. Into this solution 1.0 g (9.3 mmol) of SF_4 was condensed at −78°C and the reaction vessel was heated at 110°C for 3 h. The mixture was filtered through NaF and the filtrate shaken with a saturated $NaHCO_3$ solution. The organic phase was separated and dried with $MgSO_4$. GC/MS indicated **9** in about 5% yield which was only characterized spectroscopically. − ^{1}H NMR: δ = 4.0 (s). − ^{19}F NMR: δ = −37.9 (d, 2 C, CF_3), −113.5 [sept, ^4J(F-F) = 9.8 Hz, 1 C, CF]. − MS; *m/z* (%): 292 [M^+] (1), 233 (7), 191 (53), 147 (17), 145 (7), 69 (60), 63 (43), 59 (100).

☆ Dedicated to Professor *Max Herberhold* on the occasion of his 60th birthday.

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