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Tetrakis (perfluoropropyl)tin and other perfluoropropyltin compounds: synthesis, characterization and reactivity ☆

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Abstract

The n-perfluoropropyltin compounds $(C_3F_7)_4Sn$, $(C_3F_7)_3SnCH_3$, $(C_3F_7)_2SnR_2$ (R = CH_3 and $CH{=}CH_2$), $(C_3F_7)_2(R)SnCl$ (R = CH_3 and $CH{=}CH_2$) and $C_3F_7(C_6H_5)_2SnCl$ were prepared by the reaction of C_3F_7MgX (X = Cl or Br) with the appropriate organotin halide. A novel 1:1 adduct was formed between $(C_3F_7)_4Sn$ and 1,10-phenanthroline. Bromine cleavage of $(C_3F_7)_2Sn(CH{=}CH_2)_2$ gave $(C_3F_7)_2SnBr_2$. $(C_3F_7)_4Sn$ was found to be remarkably stable toward cleavage by Br_2, HCl and $SnCl_4$.

Keywords: Tin; Fluorocarbons

1. Introduction

Very few homoleptic perfluoroorganotin compounds are known: $(CF_2=CF)_4Sn$ [1], $(C_6F_5)_4Sn$ [2] and, in the alkyl series, only $(CF_3)_4Sn$ have been prepared [3]. More usual, and easier to prepare, are mixed species, $R_xSn(C_nF_{2n+1})_{4-x}$ (R = alkyl, aryl, H, halide, $x = 1$–3, $n = 1$–4), but here most of the work has centered on the CF_3–tin derivatives [4], in part because they are useful CF_2 transfer agents [4a,5].

The higher perfluoroalkyltin compounds also should be of interest. While $(CH_3)_3SnCF_3$ decomposes thermally at about 150°C [4a], Cullen et al. [5f] reported that $(CH_3)_3SnC_2F_5$ survived heating at 200°C for 72 h, and the perfluoroisopropyl analog, $(CH_3)_3SnCF(CF_3)_2$, also showed high thermal stability. Thus the higher perfluoroalkyltin compounds have considerable thermal stability and do not undergo facile β-elimination to give an organotin fluoride and a perfluoroolefin.

In addition to the few $R_3SnC_nF_{2n+1}$ compounds that are known [4b] even fewer $R_2Sn(C_nF_{2n+1})_2$ compounds have been reported [6] and, to the best of our knowledge, $RSn(C_nF_{2n+1})_3$ compounds are unknown.

Although diverse special (non-Grignard) methods have been used in the synthesis of CF_3-substituted organotin compounds [4] the higher perfluoroalkyltin compounds were mainly prepared by the Grignard procedure (Eq. (1)) [7]:

$$R_nSnX_{4-n} + (4-n)C_3F_7MgY \rightarrow R_nSn(C_3F_7)_{4-n} + (4-n)MgXY \qquad (1)$$

These reactions had to be carried out at low temperature since perfluoroalkylmagnesium reagents decompose rapidly at room temperature [8]. The higher perfluoroalkyltin compounds have also been prepared using the Barbier procedure in which the perfluoroalkyl halide is added to a mixture of the organotin halide and magnesium in tetrahydrofuran at room temperature [6a].

Since organotin compounds of type $(C_nF_{2n+1})_4Sn$ and $RSn(C_nF_{2n+1})_3$ ($n > 1$) appeared to be unknown and since they might have interesting properties, we undertook a brief investigation aimed at the synthesis of tetrakis(perfluoropropyl)tin and other perfluoropropyltin compounds. (In this discussion we deal only with $CF_3CF_2CF_2$–tin compounds and we write the n-perfluoropropyl group as C_3F_7.)

2. Results and discussion

The best procedure of several tried for the synthesis of $(C_3F_7)_4Sn$ involved the use of performed C_3F_7MgCl

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☆ Dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University.

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(prepared via the reaction of $^{i}PrMgCl$ with C_3F_7I [9]) with tin tetrachloride, initially at −78°C, with warming to −40°C. The initial product of the reaction of 8 molar equivalents of C_3F_7MgCl with one of $SnCl_4$ in diethyl ether was a mixture of $(C_3F_7)_4Sn$ and perfluoropropyltin chlorides, $(C_3F_7)_nSnCl_{4-n}$. Treatment of this mixture with more C_3F_7MgCl gave pure $(C_3F_7)_4Sn$ in 19% yield after recrystallization.

Tetrakis(perfluoropropyl)tin is a colorless solid (b.p. 86°C at 25 Torr, m.p. 32°C). In comparison, $(n\text{-}C_3H_7)_4Sn$ melts at −109.2°C and has a b.p. of 110°C at 9 Torr. $(C_3F_7)_4Sn$ is poorly soluble in organic solvents except for aliphatic hydrocarbons such as pentane and hexane. It is thermally stable at least to 180°C and has high kinetic stability, surviving prolonged (24 h) heating at 120°C in sealed tubes with water (toluene-d_8 emulsion) and $SnCl_4$ and Br_2 in hexane. In contrast, $(n\text{-}C_3H_7)_4Sn$ reacts readily with $SnCl_4$ (redistribution) and Br_2 (Sn–C cleavage).

Tetrakis(perfluoropropyl)tin forms a solid 1 : 1 adduct with 1,10-phenanthroline. Such Lewis acid behavior undoubtedly is the result of strong electron withdrawal from tin by the four electronegative C_3F_7 groups. The ^{19}F NMR spectrum of the adduct shows two singlets of equal intensity due to the α-CF_2 groups which are accompanied by satellite signals arising from spin–spin coupling to the adjacent ^{117}Sn and ^{119}Sn nucleus. These and all other Sn–F coupling constants of C_3F_7–Sn compounds prepared in this study were not resolved, despite all attempts to obtain better spectra. Hence the Sn–F coupling constants mentioned are averaged $^{117/119}Sn$–^{19}F coupling constants. The observation of two α-CF_2 signals is indicative of different environments for each pair of C_3F_7 groups. The two different geminal Sn–F spin–spin coupling constants of 317.2 and 447.6 Hz indicate that the σ-electron density in the bonds involving the first two C_3F_7 groups is decreased compared with uncomplexed $(C_3F_7)_4Sn$ ($J_{Sn-F} = 390$ Hz). Therefore, these two C_3F_7 substituents are expected to be *cis* to one another in the plane of the donor atom(s). The second set of C_3F_7 substituents is then expected to be in the *trans* configuration perpendicular to this plane. The dependence of the geminal Sn-element spin–spin coupling constant on the position of the substituent bearing the element in hypervalent organotin compounds has been thoroughly investigated for alkyl (in particular, CH_3)-substituted organotin complexes where the element is H [10]. Unfortunately, X-ray diffraction quality crystals of $(C_3F_7)_4Sn \cdot$ 1,10-phenanthroline could not be grown and its poor solubility precluded measurement of its solution ^{119}Sn NMR spectrum. Thus the coordination number of Sn in this complex remains uncertain.

Tetrakis(perfluoropropyl)tin did not form an isolable complex with pyridine. A slightly upfield shifted and broadened signal for the $SnCF_2$ fluorine atoms in the ^{19}F NMR spectrum of $(C_3F_7)_4Sn$ in a hexane solution containing pyridine possibly gave an indication of a weak interaction and, in fact, pyridine may activate the hydrolysis of $(C_3F_7)_4Sn$. Prolonged contact of such a solution with moist air resulted in hydrolytic cleavage of one C_3F_7 group (giving C_3F_7H) and in the separation of fine needles of $[(C_3F_7)_3Sn]_2O \cdot n\text{-}C_5H_5N$. A similar perfluoroalkyl–Sn hydrolytic cleavage, apparently induced by pyridine, has been reported by Chambers et al. [11] for $(CH_3)_2(CF_3)SnCl$.

Some mixed bis- and tris(perfluoroalkyl)hydrocarbyltin compounds were also prepared. The reaction of an excess of C_3F_7MgCl with CH_3SnCl_3 at −40°C gave a mixture of about 30 mol% of the desired product and about 60 mol% of $(C_3F_7)_2(CH_3)SnCl$ in good yield. Further treatment of this mixture with more C_3F_7MgCl gave pure $(C_3F_7)_3SnCH_3$, but the final pure product yield was only 11%. This procedure was not successful for complete perfluoroalkylation of $CH_2{=}CHSnCl_3$. The partial alkylation product, $(C_3F_7)_2(CH_2{=}CH)SnCl$ was isolated in high yield. Further treatment of the latter with an excess of C_3F_7MgCl led to the formation of $(C_3F_7)_3SnCH{=}CH_2$ to only a minor extent (< 10% yield, as estimated by ^{19}F NMR spectroscopy). When additional C_3F_7MgCl treatment was not employed in the case of CH_3SnCl_3, the partial perfluoroalkylation product, $(C_3F_7)_2(CH_3)SnCl$, was obtained in 49% yield.

Better product yields were obtained in reactions of C_3F_7MgBr (via $CH_3MgBr + C_3F_7I$) with R_2SnBr_2 compounds. Such a reaction with $(CH_2{=}CH)_2SnBr_2$ at −30°C gave $(C_3F_7)_2Sn(CH{=}CH_2)_2$ in 46% yield. By the same procedure, using $(CH_3)_2SnBr_2$, an 82% yield of $(C_3F_7)_2$-$Sn(CH_3)_2$ was obtained. Multiple treatments with C_3F_7MgBr were not required. Finally, attempted preparation of $(C_3F_7)_2Sn(C_6H_5)_2$ was not successful; the only product obtained was $C_3F_7(C_6H_5)_2SnCl$ in 43% yield.

High kinetic stability was observed also for CH_3-containing perfluoropropyltin compounds, $(C_3F_7)_3SnCH_3$, $(C_3F_7)_2Sn(CH_3)_2$ and $(C_3F_7)_2(CH_3)SnCl$. For instance, $(C_3F_7)_2Sn(CH_3)_2$ is stable toward Br_2 at 120°C, even on UV irradiation, conditions which result in CF_3–Sn cleavage in the case of $(CF_3)_4Sn$. It is inert toward Cl_2 and gaseous HCl at room temperature, toward refluxing CF_3CO_2H and toward $SnCl_4$ at 120°C, reagents which react readily with the hydrocarbyl analog, $(C_2H_5)_2Sn(CH_3)_2$ [12]. When Cl_2 is bubbled into gently refluxing $(C_3F_7)_2Sn(CH_3)_2$ in daylight, methyl group chlorination (giving $(C_3F_7)_2(CH_3)SnCH_2Cl$) is competitive with Sn–C cleavage. However, even after 1 h of chlorination at 180–190°C, much of the starting material remains unreacted. Although (chloromethyl)tin compounds have been known for a long time [13], this, to the best of our knowledge, is the first example of Sn–CH_3 to Sn–CH_2Cl chlorination.

The vinyl derivative $(C_3F_7)_2Sn(CH{=}CH_2)_2$, as expected, is more reactive than $(C_3F_7)_2Sn(CH_3)_2$. It reacts slowly and selectively with Br_2 in dichloromethane at room temperature to give first $(C_3F_7)_2(CH_2{=}CH)SnBr$ and then $(C_3F_7)_2SnBr_2$. The latter can be isolated as a heavy, colorless liquid. Chlorine, on the other hand, does not react selectively, cleaving both vinyl and perfluoropropyl groups even at low temperature.

This study has shown that perfluoropropyltin compounds are fairly stable thermally and very stable kinetically, much more so than their hydrocarbyl analogs. Based on these properties, this class of organotin compounds might find some useful applications. However, further work aimed at developing improved syntheses of perfluoroalkyltin compounds is necessary.

3. Experimental section

3.1. General comments

All experiments involving air- or moisture-sensitive compounds were carried out in an argon atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl prior to use, and pentane and hexane from calcium hydride. Pyridine was dried over KOH, filtered, distilled and stored over molecular sieves. Chlorine was dried by passing it through a solution of P_2O_5 in concentrated H_2SO_4. Tetramethyltin, methyltin trichloride and perfluoropropyl iodide were obtained from commercial sources; other organotin starting materials were prepared by standard literature procedures.

^{1}H, ^{13}C, ^{19}F and ^{119}Sn NMR spectra were recorded using a Varian VXR-300 NMR spectrometer, except for the ^{119}Sn NMR spectrum of $(C_3F_7)_4Sn$, which was recorded using a Varian VXR-500 instrument. Mass spectra were determined using a Hewlett-Packard HP 5971 MSD GC–MS instrument or a Finnigan MAT 8200 mass spectrometer. Assignments of peaks refer to the ^{120}Sn isotope of the Sn isotope cluster. Analyses for C, H and N were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and those for Sn by Galbraith Laboratories, Knoxville, TN, USA.

3.2. General procedure

All reactions were carried out in three-necked, round-bottomed flasks of appropriate size that were equipped with a low-temperature thermometer, a pressure-equalizing addition funnel (or a rubber septum for addition of reactants by syringe) and an argon inlet–outlet tube. The reaction mixtures were stirred magnetically or with an overhead stirrer. Low temperatures were maintained by the appropriate dry-ice–solvent bath.

Suspensions of C_3F_7MgCl and C_3F_7MgBr in diethyl ether were prepared by *slow* addition of a solution of $^{i}PrMgCl$ and CH_3MgBr, respectively, in Et_2O to an Et_2O solution of C_3F_7I at −60 to −70°C. After the addition had been completed, the reagent solution was allowed to equilibrate at −70°C for 1 h.

3.3. Tetrakis(perfluoropropyl)tin

In a typical reaction, 3.8 g (14.6 mmol) of $SnCl_4$ were added slowly by syringe to a stirred suspension of C_3F_7MgCl (from 34.8 g (0.118 mol) of C_3F_7I and 0.12 mol of $^{i}PrMgCl$) in 200 ml of Et_2O at −70°C. The $SnCl_4 \cdot OEt_2$ adduct precipitated immediately. On completion of the addition, the reaction mixture was allowed to warm to −40°C and was stirred at this temperature for 2 h. During this period, the heavy $SnCl_4 \cdot OEt_2$ complex precipitate was replaced by a light-weight, white slurry. The reaction mixture was left to warm to room temperature overnight. Subsequently, diethyl ether was removed by distillation at atmospheric pressure. The residue was trap-to-trap distilled in vacuum into a receiver cooled with liquid nitrogen. Redistillation at reduced pressure (15 cm Vigreux column) gave first a low-boiling fraction containing solvent and ^{i}PrI and then 5.2 g of a colorless liquid boiling over the range 80–100°C at 55 Torr. A heavier liquid layer separated from the distillate. The distillate (by ^{19}F NMR) contained about 50 mol% of $(C_3F_7)_4Sn$ and incompletely perfluoroalkylated products. Reaction of the distillate with an excess of C_3F_7MgCl using the procedure described above gave, after recrystallization from hexane at −20°C, 2.2 g (19%) of $(C_3F_7)_4Sn$, b.p. 86°C/25 Torr, m.p. 32°C. ^{13}C NMR (neat): δ_C 109 (t of m, $^{1}J_{CF} = 287$ Hz, β-CF_2), 118 (q of t, $^{1}J_{CF} = 256$ Hz, $^{2}J_{CF} = 38$ Hz, CF_3), 130.5 (t of t, $^{1}J_{CF} = 309$ Hz, $^{2}J_{CF} = 57$ Hz, α-CF_2). ^{19}F NMR (hexane): δ_F −118.4 (β-CF_2), −102.5 ($^{2}J_{SnF} = 386.9$ Hz, α-CF_2), −89.9 (CF_3). ^{119}Sn NMR (neat): δ_{Sn} −284 (see Fig. 1). EIMS (*m/z*, relative intensity (%)), 677 (2, $(C_3F_7)_3SnCF_2^+$), 627 (2, $(C_3F_7)_3Sn^+$), 477 (2, $(C_3F_7)_2SnF^+$), 139 (82, SnF^+), 131 (100, $C_3F_5^+$). Anal. Calc. for $C_{12}F_{28}Sn$: C, 18.13; Sn, 14.93. Found: C, 17.82; Sn, 15.55%.

1,10-Phenanthroline adduct

A solution of 26 mg (0.13 mmol) of 1,10-phenanthroline monohydrate in THF was added to 100 mg (0.13 mmol) of $(C_3F_7)_4Sn$. Recrystallization of the solid product which formed from THF–hexane gave 110 mg (87%) of $(C_3F_7)_4Sn \cdot$ 1,10-phen, microcrystalline, white powder, decomp. range 140–180°C. ^{19}F NMR (THF): δ_F C_3F_7 set 1: −122.0 (β-CF_2), −106.2 ($J_{SnF} = 317.2$ Hz, α-CF_2), −80.0 (CF_3); C_3F_7 set 2: −123.1 (β-CF_2), −111.3 ($J_{SnF} = 447.6$ Hz, α-CF_2), −80.6 (CF_3). FAB-MS (matrix = 3-$O_2NC_6H_4CH_2OH$) (*m/z*, relative intensity (%)): 807

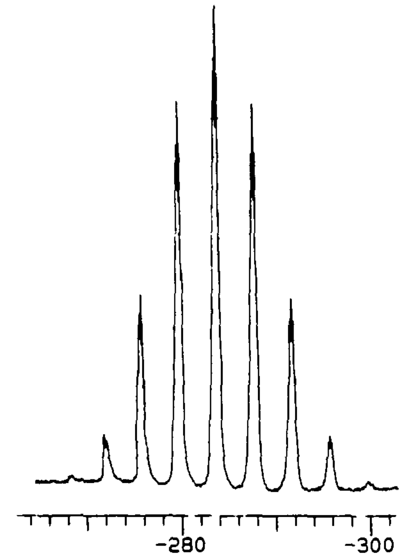

Fig. 1. 186.4 MHz ^{119}Sn NMR spectrum of neat $(C_3F_7)_4Sn$ at 35°C (a nonet of nonets, with $^3J_{Sn-F} = 15$ Hz, if $^4J_{Sn-F} = 0$).

(100, $(C_3F_7)_3Sn \cdot C_{12}H_8N_2^+$), 655 (25, $(C_3F_7)_2SnF \cdot C_{12}H_8N_2^+$). Anal. Calc. for $C_{24}H_8N_2F_{28}Sn$: C, 29.57; H, 0.83; N, 2.87. Found: C, 29.96; H, 0.94; N, 3.21%.

3.4. *Tris (perfluoropropyl)methyltin*

The same procedure was used in the reaction of C_3F_7MgCl (from 28.4 mmol each of C_3F_7I and ^{i}PrMgCl) with 1.4 g (5.8 mmol) of CH_3SnCl_3 in 50 ml of Et_2O. A crude product (2.4 g) was obtained which (by ^{19}F NMR) contained about 60 mol% of $(C_3F_7)_2(CH_3)SnCl$ and less than 30 mol% of $(C_3F_7)_3SnCH_3$. This product was treated twice with an excess of C_3F_7MgCl. Extraction of the product with $CHCl_3$ at −20°C and subsequent distillation gave 400 mg (11%) of $(C_3F_7)_3SnCH_3$, b.p. 89°C/50 Torr. ^{19}F NMR ($CDCl_3$): δ_F −120.8 (β-CF_2), −108.7 ($^2J_{SnF} = 308.4$ Hz, α-CF_2), −80.1 (CF_3). ^{119}Sn NMR (neat): δ_{Sn} −131 (sept). ^{13}C NMR ($CDCl_3$): δ_c 1.09 ($J_{SnH} = 66.0$ Hz, CH_3). Anal. Calc. for $C_{10}H_3F_{21}Sn$: C, 18.74; H, 0.47. Found: C, 18.95: H, 0.59%.

3.5. *Bis(perfluoropropyl)methyltin chloride*

The same procedure was used in a single treatment of 3.1 g (12.9 mmol) of CH_3SnCl_3 with C_3F_7MgCl (from 28.4 mmol each of ^{i}PrMgCl and C_3F_7I) in 50 ml of Et_2O. A colorless liquid was obtained by distillation at reduced pressure: 3.2 g (49%), b.p. 93°C/75 Torr. ^{19}F NMR ($CDCl_3$): δ_F −121.3 (β-GF_2), −113.2, −113.5 ($J_{SnF} = 358$ and 368 Hz, respectively, α-CF_2, diastereotopic C_3F_7 groups), −79.8 (CF_3). ^{119}Sn NMR (neat): δ_{Sn} −42(quin). ^{13}C NMR ($CDCl_3$): δ_C 1.2 ($^2J_{SnH} = 67.8$ Hz, CH_3). GC–MS (m/z, relative intensity (%)): 339 (12, $C_3F_7(CH_3)SnCl^+$), 180 (30, CH_3SnFCl^+), 155 (32, $SnCl^+$), 131 (100, $C_3F_5^+$). Anal. Calc. for $C_7H_3F_{14}ClSn$: C, 16.58; H, 0.6. Found: C, 17.14; H, 0.73%.

3.6. *Bis(perfluoropropyl)vinyltin chloride*

Using the standard procedure described above, reaction of 1.0 g (4 mmol) of $CH_2=CHSnCl_3$ with C_3F_7MgCl (from 14.5 mmol each of ^{i}PrMgCl and C_3F_7I) in 50 ml of Et_2O gave 2.0 g (96%) of $(C_3F_7)_2(CH_2=CH)SnCl$, b.p. 93°C/75 Torr. ^{19}F ($CDCl_3$): δ_F −121.3 (β-CF_2), −111.8, −111.9 ($J_{SnF} = 347$ and 378.7 Hz, respectively, α-CF_2, diastereotopic C_3F_7 groups), −79.9 (CF_3). ^{119}Sn NMR (neat): δ_{Sn} −132 (quin). Anal. Calc. for $C_8H_3F_{14}ClSn$: C, 18.5; H, 0.58. Found: C, 18.59; H, 0.75%.

3.7. *Bis(perfluoropropyl)dimethyltin*

The standard procedure was used in the reaction of 3.1 g (10 mmol) of $(CH_3)_2SnBr_2$ and C_3F_7MgBr (from 33.8 mmol each of CH_3MgBr and C_3F_7I in Et_2O at −70°C). The standard work-up gave 4.0 g (82%) of $(C_3F_7)_2Sn(CH_3)_2$, b.p. 73°C/45 Torr. ^{19}F NMR ($CDCl_3$): δ_F −121.6 (β-CF_2), −116.1 ($J_{SnF} = 394.8$ Hz, α-CF_2), −79.7 (CF_3). ^{119}Sn NMR (neat): δ_{Sn} −22.8 (quin). ^{13}C NMR ($CDCl_3$): δ_C 0.76 ($J_{SnH} = 61.5$ Hz, CH_3). GC–MS (m/z, relative intensity(%)): 473 (2, $(C_3F_7)_2SnCH_3^+$), 319 (82, $C_3F_7Sn(CH_3)_2^+$), 169 (72, $(CH_3)_2SnF^+$), 131 (100, $C_3H_5^+$). Anal. Calc. for $C_8H_{16}F_{14}Sn$: C, 19.74; H, 1.24. Found: C, 19.78; H, 1.33%.

Bis(perfluoropropyl)dimethyltin had been prepared earlier by Clark and Whyman [6b], but no data were given.

3.8. *Bis(perfluoropropyl)divinyltin*

A reaction of 1.7 g (5.1 mmol) of $(CH_2=CH)_2SnBr_2$ and C_3F_7MgBr (from 16.9 mmol each of CH_3MgBr and C_3F_7I) in 100 ml of Et_2O was carried out using the standard procedure. Distillation gave 1.2 g (46%) of $(C_3F_7)_2Sn(CH=CH_2)_2$, b.p. 75°C/30 Torr. ^{19}F NMR ($CDCl_3$): δ_F −121.4 ($\beta - CF_3$), −113.5 ($J_{SnF} = 275.1$ Hz, α-CF_2), −80.3 (CF_3). ^{119}Sn NMR (neat): δ_{Sn} −182 (quin). GC–MS (m/z, relative intensity(%)): 343 (21, $C_3F_7(CH_2=CH)_2Sn^+$), 193 (52, $(CH_2=CH)_2SnF^+$), 139 (100, SnF^+). Anal. Calc. for $C_{10}H_6F_{14}Sn$: C, 23.51; H, 1.18. Found: C, 23.23; H, 1.25%.

3.9. *Perfluoropropyl(diphenyl)tin chloride (attempted synthesis of $(C_3F_7)_2Sn(C_6H_5)_2$)*

The same procedure was used in the reaction of 2.7 g (7.8 mmol) of $(C_6H_5)_2SnCl_2$ with C_3F_7MgCl (from

22.3 mmol each of ^{i}PrMgCl and C_3F_7I) in 120 ml of Et_2O. Distillation gave 1.6 g (43%) of $C_3F_7(C_6H_5)_2SnCl$ as a colorless oil, b.p. 94°C/0.03 Torr. ^{19}F NMR ($CDCl_3$): δ_F -120.4 ($\beta-CF_2$), -114.1 ($J_{SnF} = 311.3$ Hz, α-CF_2), -79.9 (CF_3). ^{119}Sn NMR (neat): δ_{Sn} -85.7 (t). GC–MS (*m/z*, relative intensity(%)): 309 (90, Ph_2SnCl^+), 197 (37, $PhSn^+$), 155 (100, $SnCl^+$). Anal. Calc. for $C_{15}H_{10}F_7ClSn$: C, 37.74; H, 2.11. Found: C, 37.24; H, 2.17%.

3.10. Bromine cleavage of Bis(perfluoropropyl)divinyltin

To a solution of 0.5 g (1.0 mmol) of $(C_3F_7)_2Sn(CH=CH_2)_2$ in 2 ml of CH_2Cl_2 was added one third of a solution of 0.5 g (3.1 mmol) of Br_2 in CH_2Cl_2. The bromine color was not discharged after 3 h at room temperature, but the reaction mixture had become colorless after it had stood overnight. The ^{19}F NMR spectrum showed the presence of $(C_3F_7)_2(CH_2=CH)SnBr$ (δ_F -121.2 ($\beta-CF_2$), -110.6, 111.1 ($J_{SnF} = 515.8$ and 522.7 Hz, respectively, α-CF_2, diastereotopic C_3F_7 groups), -80.4 (CF_3)) and $(C_3F_7)_2SnBr_2$. The rest of the Br_2 solution was added and the mixture was stirred at room temperature for 2 days. On cooling to -20°C a lower liquid layer separated. The latter was maintained at 100 Torr at 30°C to remove residual solvent, leaving 0.5 g (82%) of $(C_3F_7)_2SnBr_2$, which was characterized by ^{19}F NMR and ^{119}Sn NMR spectroscopy: ^{19}F NMR ($CDCl_3$): δ_F -119.4 ($\beta-CF_2$), -107.3 ($J_{SnF} = 526.3$ Hz, α-CF_2), -80.4 (CF_3). ^{119}Sn NMR (neat): δ_{Sn} -240 (quin).

3.11. Chlorination of Bis(perfluoropropyl)dimethyltin

The tin compound (2.3 g, 4.7 mmol) was charged into a 10 ml two-necked, round-bottomed flask equipped with a reflux condenser and a gas inlet tube. The reflux condenser was connected to a trap at -78°C. The $(C_3F_7)_2Sn(CH_3)_2$ was brought to gentle reflux (oil-bath at about 180°C) and then gaseous chlorine was bubbled slowly into the tin compound for 1 h. During this period, at times a spark, accompanied by intense fuming, was observed inside the condenser. The residual reaction mixture (0.9 g) was examined by ^1H NMR spectroscopy. A resonance at δ 3.5 with $^2J_{SnH} = 22$ Hz was observed (compare $(CH_3)_3SnCH_2Cl$: δ 3.03 ($^2J_{SnH} = 19$ Hz [14] and $Sn(CH_2Cl)_4$: δ 3.37 ($^2J_{SnH} = 21.6$ Hz) [15]. GC–MS gave indication of the presence of five products: starting material (57%), $C_3F_7(CH_3)_2SnCl$ (8%), $(C_3F_7)_2(CH_3)SnCH_2Cl$ (14%), C_2Cl_6 (6%) and a compound that was not identified; the percentages given refer to the content of the residual 0.9 g obtained in this experiment. $(C_3F_7)_2(CH_3)SnCH_2Cl$: MS (*m/z*, relative intensity (%)): 3533 (32, $C_3F_7(CH_3)SnCH_2Cl^+$), 203 (53, $CH_3(CH_2Cl)SnF^+$), 131 ($C_3F_5^+$).

3.12. Partial hydrolysis of tetrakis(perfluoropropyl)tin in the presence of pyridine

To a solution of 32 mg (0.04 mmol) of $(C_3F_7)_4Sn$ in 2 ml of hexane was added 6 mg (0.08 mmol) of dry pyridine. The ^{19}F NMR spectrum exhibited a slightly (2 ppm) upfield shifted and broadened signal for the α-CF_2 resonance.

Further addition of pyridine (0.5 g) failed to result in complex formation. Prolonged exposure to moist air, however, caused some C_3F_7–Sn cleavage (formation of C_3F_7H, as evidenced by its ^1F NMR spectrum) and precipitation of $[(C_3F_7)_2Sn]_2O \cdot nC_5H_5N$. EIMS (*m/z*, relative intensity (%)): 763 (40, $(C_3F_7)_3Sn_2O^+$), 627 (8, $(C_3F_7)_3Sn^+$), 477 (22,$(C_3F_7)_2SnF^+$), 273 (5, Sn_2OF^+), 131 (54, $C_3F_5^+$), 79 (100, $C_5H_5N^+$). M.p.: 70–72°C. ^{19}F NMR (THF): δ_F -121.8 ($\beta-CF_2$), -115.6 ($J_{SnF} = 394.8$ Hz, $\alpha-CF_2$), -80.9 (CF_3).

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References

[1] H.D. Kaesz, S.L. Stafford and F.G.A. Stone, *J. Am. Chem. Soc.*, *82* (1960) 6232.

[2] J.M. Holmes, R.D. Peacock and J.C. Tatlow, *Proc. Chem. Soc.*, (1963) 108.

[3] (a) R.A. Jacob and R.J. Lagow, *Chem. Commun.* (1973) 104; (b) R.J. Lagow, L.L. Gerchman, R.A. Jacob and J.A. Morrison, *J. Am. Chem. Soc.*, *97* (1975) 518; (c) E.K.S. Liu and R.J. Lagow, *Inorg. Chem.*, *17* (1978) 618; (d) L.J. Krause and J.A. Morrison, *j. Chem. Soc.*, (1980) 671; (e) L.J. Krause and J.A. Morrison, *J. Am. Chem. Soc.*, *103* (1981) 2995.

[4] (a) H.C. Clark and C.J. Willis, *J. Am. Chem. Soc.*, *82* (1960) 1888; (b) H.D. Kaesz, J.R. Phillips and F.G.A. Stone, *J. Am. Chem. Soc.*, *82* (1960) 6228; (c) L.J. Krause and J.A. Morrison, *Inorg. Chem.*, *19* (1980) 604; (d) R. Eujen and U. Thurmann, *J. Organomet. Chem.*, *433* (1992) 63; (e) R. Eujen, N. Jahn and U. Thurmann, *J. Organomet. Chem.*, *434* (1992) 159; (f) R. Eujen, N. Jahn and U. Thurmann, *J. Organomet. Chem.*, *465* (1994) 153; (g) J.A. Morrison, L.L. Gerchman, R. Eujen and R.J. Lagow, *J. Am. Chem. Soc.*, *100* (1978) 1722; (h) J.A. Morrison, L.L. Gerchman, R. Eujen and R.J. Lagow, *J. Flourine Chem.*, *10* (1977) 333.

[5] (a) D. Seyferth, H. Dertouszos, R. Suzuki and J.Y.-P. Mui, *J. Org. Chem.*, *32* (1967) 2980; (b) W.R. Cullen and W.R. Leeder, *Inorg. Chem.*, *5* (1966) 1004; (c) W.R. Cullen and M.C. Waldman, *Inorg. Nucl. Chem. Lett.* *4* (1968) 205; (d) W.R. Cullen and M.C. Waldman, *Can. J. Chem.*, *47* (1969) 3093; (e) W.R. Cullen and M.C. Waldman, *Inorg. Nucl. Chem. Lett.*, *6* (1969) 205; (f) W.R. Cullen, J.R. Sams and M.C. Waldman, *Inorg. Chem.*, *9* (1970) 1682; (g) W.R. Cullen and M.C. Waldman, *J. Fluorine Chem.*, *1* (1971/2) 151.

[6] (a) F.G.A. Stone and P.M. Treichel, *Chem. Ind. (London)*,

(1960) 837; (b) H.C. Clark and D. Whyman, in *Proceedings of the 2nd International Meeting on Fluorine Chemistry, Estes Park, CO*, 1962, p. 232.

[7] Reviews: (a) P.M. Treichel and F.G.A. Stone, *Adv. Organomet. Chem.*, *1* (1964) 143; (b) *Gmelin Handbook of Inorganic Chemistry*, 8th edn., Supplement Vol. 25, Springer, Berlin, 1975 (there is a Supplement Vol. 1 which brings this volume up to 1981).

[8] P.M. Treichel and F.G.A. Stone, *Adv. Organomet. Chem.*, *1* (1964) 150.

[9] R.N. Haszeldine, *J. Chem. Soc.*, (1952) 3423.

[10] K. Jurkschat, A. Tzschach, J. Meunier-Piret, *J. Organomet. Chem.*, *315* (1986) 45, and references cited therein.

[11] R.D. Chambers, H.C. Clark and C.J. Willis, *Can. J. Chem.*, *39* (1961) 131.

[12] R.K. Ingham, S.D. Rosenberg and H. Gilman, *Chem. Rev.*, *60* (1960) 459.

[13] D. Seyferth, *Chem. Rev.*, *55* (1955) 1155.

[14] D. Seyferth and S.B. Andrews, *J. Organomet. Chem.*, *30* (1971) 151.

[15] R.G. Kostyanovskii and A.K. Prokofiev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1968) 274.