Notes

Synthesis and Properties of Trimethyl(trifluorosilyl)stannane†

John J. D'Errico and Kenneth G. Sharp*
Electronics Research, Dow Corning Corp., Midland, Michigan 48686, U.S.A.

Trimethyltin hydride reacts with SiF_3SiF_3 or SiF_3SiF_2H to give the new compound $SnMe_3(SiF_3)$ in 75—80% yield. No reaction was observed between $SnMe_3H$ and SiF_3SiH_3. Hydrogen–deuterium exchange was observed between tin and silicon during the course of deuterium-labelling experiments. Dimethylstannylene ($SnMe_2$) was implicated as an intermediate by trapping experiments in the thermolysis of $SnMe_3(SiF_3)$.

Alkyltin hydrides have demonstrated selective, stepwise, reducing properties toward a variety of halogenosilanes. Mixed halogeno-silanes and -disilanes such as SiF_2X_2 and SiF_3SiHX_2[1] (X = Br or Cl) are preferentially attacked at the heavier halogen and converted into the corresponding fluorosilanes in nearly quantitative yield. This behaviour is in contrast to conventional reducing agents such as $LiAlH_4$ which reduce Si–X, Si–F, and often Si–Si bonds as well.

This report describes the interaction of alkyltin hydrides with fluorodisilanes in the absence of Si–X (X = Br or Cl) bonds. Except for SiF_3SiH_3, these reactions are characterized by Si–Si bond cleavage and the formation of a new compound containing a Si–Sn bond.

Results and Discussion

Trimethyltin hydride reacts with SiF_3SiF_3 and SiF_3SiF_2H as shown in equation (1). The major product of the reaction,

$$\begin{array}{l} \mathrm{SiF_3SiF_3} \\ \text{or} + \mathrm{SnMe_3H} \xrightarrow[25\,^{\circ}\mathrm{C}]{1.5\,\mathrm{h}} \mathrm{SnMe_3(SiF_3)} + \\ \mathrm{SiF_3SiF_2H} \qquad \mathrm{SnMe_3(SiH_3)} + \mathrm{SiF_xH_{4-x}} \quad (1) \\ \qquad\qquad\qquad\qquad (x = 2\text{—}4) \end{array}$$

$SnMe_3(SiF_3)$, is obtained in 75—80% yield. Although there are several examples of compounds containing Si–Sn bonds,[2] this is the first example of a stable trihalogenosilyl-substituted derivative.

The compound $SnMe_3H$ did not react with SiF_3SiH_3, even after the mixture was warmed to 75—80 °C for 1.5 h.

There are several possible mechanisms for the formation of $SnMe_3(SiF_3)$. One possibility involves the free-radical attack of $Me_3Sn^{\bullet}$ or $H^{\bullet}$ on the Si–Si bond. The reaction between SiF_3SiF_2H and $SnMe_3H$ was repeated in the presence of $CF_2{=}CF_2$, an efficient scavenger of trialkyltin radicals.[3] Neither the rate of the reaction nor the product distribution was affected by $CF_2{=}CF_2$, indicating that a free-radical mechanism is not operative.

Deuterium-labelling experiments were performed [equation (2)] in the hope of elucidating mechanistic pathways. However, the results were compromised by Sn–D/Si–H exchange. Independent experiments demonstrated that Sn–D/Si–H exchange was slow with SiF_3H, but much faster with SiF_3SiH_3; this may reflect the increase in Si–H bond strength observed with increasing fluoro substitution.[4]

$$\begin{array}{l} \mathrm{SiF_3SiF_2H} + \mathrm{SnMe_3D} \longrightarrow \mathrm{SnMe_3(SiF_3)} \\ \qquad + \mathrm{SiF_4} + \mathrm{SiF_3H} + \mathrm{SiF_3D} + \mathrm{SiF_3SiH_xD_{3-x}} \quad (2) \end{array}$$

The formation of SiF_3SiH_3 from the reaction of SiF_3SiF_2H and $SnMe_3H$ may result from Si–F reduction as well as F/H redistribution, since SiF_3SiF_3 was observed as a product in the early stages of the reaction. Intermediate fluorosilylstannanes such as $SnMe_3(SiF_2H)$ were not observed during the reaction.

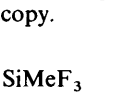
Halogeno-substituted distannanes typically decompose at less than 150 °C.[5,6] In contrast, there was apparent decomposition of $SnMe_3(SiF_3)$ after 40 min at 250 °C. A powder [presumably $(SnMe_2)_x$] formed after 40 min at 330 °C [equation (3)]. The sole volatile product detected was $SiMeF_3$.

$$\mathrm{SnMe_3(SiF_3)} \xrightarrow[40\,\mathrm{min}]{330\,^{\circ}\mathrm{C}} \mathrm{(SnMe_2)_x} + \mathrm{SiMeF_3} \quad (3)$$

Evidence for the intermediacy of dimethylstannylene was obtained when the thermolysis was performed in the presence of MeBr [equation (4)]; $SnBrMe_3$ was isolated and identified by i.r. and mass spectroscopy.

$$\begin{array}{l} \mathrm{SnMe_3(SiF_3)} \xrightarrow{330\,^{\circ}\mathrm{C}} \mathrm{SiMeF_3} \\ \qquad\qquad + \mathrm{SnMe_2} \xrightarrow{\mathrm{MeBr}} \mathrm{SnBrMe_3} \quad (4) \end{array}$$

There was no evidence for the formation of $SiBrF_3$, suggesting that the reaction does not proceed *via* a free-radical mechanism. The methyl-bridged transition state postulated for the decomposition of distannanes[5] and disilanes[7] seems reasonable for the decomposition of $SnMe_3(SiF_3)$ [structure (I)].



(I)

Essentially, no reaction was observed between $SnMe_3(SiF_3)$ and $SnMe_3H$, HCl, or water after several hours at room temperature (a small amount of SiF_4 was observed in the latter case). The compound $SnMe_3(SiF_3)$ did react with ICl to form $SiClF_3$; there was no evidence for the formation of SiF_3I

---

† *Non-S.I. unit employed:* Torr ≈ 133 Pa.

{$SnMe_3I$ was not isolated, [equation (5)]}. Similar results were reported by Shaw and Allred[8] for $SnMe_3(SiMe_3)$.

$$SnMe_3(SiF_3) + ICl \longrightarrow SiClF_3 + SnMe_3I \qquad (5)$$

Several other reactions involving $SnMe_3H$ and various silicon compounds [Si_2Cl_6O, Si_2Me_6, $Si_2Me_6(NH)$] were attempted. In each case, no reaction was observed after warming the mixture to 85 °C for several hours. This lack of reactivity may reflect the decreased acidity of these compounds as compared to fluoro-substituted disilanes.

Conclusions

The reaction of SiF_3SiF_3 or SiF_3SiF_2H with $SnMe_3H$ resulted in the formation of the new compound $SnMe_3(SiF_3)$ in 75—80% yield. No reaction was observed between SiF_3SiH_3 and $SnMe_3H$. The use of a free-radical trapping agent indicated that these reactions did not proceed *via* a free-radical mechanism.

During the course of the deuterium-labelling experiments, H/D exchange was observed between silicon and tin ($SnMe_3D$). The exchange was fastest with SiF_3SiH_3, with little exchange observed for SiF_3H. This behaviour is consistent with increasing Si–H bond strength with increasing fluorine substitution on silicon.

The compound $SnMe_3(SiF_3)$ decomposes at 330 °C to form $(SnMe_2)_x$ and $SiMeF_3$. When the thermolysis was carried out in the presence of MeBr, $SnBrMe_3$ was isolated, thus supplying evidence for the intermediacy of $SnMe_2$.

The Si–Sn bond in $SnMe_3(SiF_3)$ showed surprisingly little reactivity with HCl, water, and $SnMe_3H$; ICl did react with $SnMe_3(SiF_3)$ to form $SiClF_3$ (and presumably $SnMe_3I$).

Experimental

Materials and Manipulations.—The details regarding the preparation of fluorodisilanes[1,7] and organotin hydrides[9] are presented elsewhere. All other materials were obtained from commercial sources. All chemical manipulations were conducted in the absence of air and moisture using a recirculating dry-box (nitrogen atmosphere) and a grease-free glass high-vacuum line (background pressure $<10^{-4}$ Torr). All reactions were performed on a high-vacuum line in the absence of solvent.

Spectral Measurements.—Fluorine-19 n.m.r. spectra were obtained on a Varian XL-200 spectrometer operating at 188 MHz, ^1H n.m.r. spectra at 90 MHz on a Varian EM-390 spectrometer. The progress of the reactions was monitored by i.r. spectroscopy using a Nicolet 5SXB Fourier-transform spectrometer (gas cell, KBr windows, resolution 2 cm^{-1}). Mass spectra were obtained using a Hewlett-Packard 5790A series mass spectrometer.

Preparation of $SnMe_3(SiF_3)$.—(*a*) The compounds Si_2F_6 (or SiF_3SiF_2H) (1.0 mmol) and $SnMe_3H$ (1.0 mmol) were condensed into a trap (100 cm^3) and warmed to room temperature (liquid was present in the trap). After 1.5 h, an i.r. spectrum of the most volatile components indicated the presence of SiF_4, SiF_3H,[10] SiF_3SiH_3,[11] and small amounts of SiF_2H_2 and unreacted $SnMe_3H$. The reaction mixture was passed through a trap cooled to −78 °C, at which temperature monosilanes, SiF_3SiH_3, and $SnMe_3H$ are volatile. The material trapped at −78 °C was then passed through a trap cooled to −46 °C (cyclohexanone). The material trapped at this temperature was shown to be $SnMe_3(SiH_3)$[12] (5% yield). I.r. (cm^{-1}): 2 985w, 2 924w, 2 141s, 953w, 862s, 770m, and 525m. δ_H(solvent C_7D_8, standard $SiMe_4$): 3.38 (3 H, s, SiH_3) and 0.14 (9 H, s, $SnMe_3$).

The material which passed −46 °C is a liquid at room temperature. The spectroscopic data which follow allow characterization of this compound as $SnMe_3(SiF_3)$; yield 0.19 g (77%, based on fluorodisilanes) (Found: C, 14.4; H, 3.7. $C_3H_9F_3SiSn$ requires C, 14.5; H, 3.6%). I.r. (cm^{-1}): 3 057vw, 2 995w, 2 928w, 935vs, 841s, 782m, 532m, and 460s. δ_H (solvent C_7D_8, standard $SiMe_4$): 0.22 [s, J(SnH) = 55.5 Hz, $SnMe_3$]. Note: ^{117}Sn and ^{119}Sn couplings could not be resolved from each other. δ_F(solvent C_7D_8, standard $CFCl_3$): −107.5 [s, $J(^{117}SnF)$ = 201.5, $J(^{119}SnF)$ = 209.7, J(FSi) = 417.5 Hz, SiF_3]. Mass spectral data: m/z 234 ($M - 15^+$, 42.5), 204 (4.5), 164 (46.6), 134 (100.0), 118 (48.0), 85 (12.1), 66 (4.1), and 47 (9.1%).

(*b*) The same results as described in (*a*) were obtained when the reaction between $SnMe_3H$ and SiF_3SiF_2H was conducted in the presence of $CF_2{=}CF_2$ (1:1:3 molar ratio).

(*c*) The reaction between $SnMe_3D$ and SiF_3SiF_2H proceeded in the same fashion as described in (*a*). The silicon by-products consisted of SiF_4, SiF_3D,[13] SiF_3H, and $SiF_3SiH_xD_{3-x}$ (Si–H stretch at 2 185 cm^{-1}, Si–D stretch at 1 590 cm^{-1}). There were also absorptions due to $SnMe_3H$.

Si–H/Sn–D *Exchange.*—(*a*) Equimolar quantities of SiF_3H and $SnMe_3D$ were condensed into a trap and warmed to room temperature for 1.5 h; traces of SiF_3D[13] and $SnMe_3H$ were observed. After 12 h at room temperature there were only slight increases in the amounts of these compounds.

(*b*) Equimolar quantities of SiF_3SiH_3 and $SnMe_3D$ were condensed into a trap and warmed to room temperature. After 15 min, absorptions due to $SnMe_3H$ and $SiF_3SiH_xD_{3-x}$ were apparent. The intensity of these absorptions increased over 48 h. The estimated conversion (by i.r. spectroscopy) of $SnMe_3D$ into $SnMe_3H$ during that period was 20%.

Thermolysis of $SnMe_3(SiF_3)$.—(*a*) The compound $SnMe_3(SiF_3)$ (15 Torr) was condensed into a medium-wall glass tube (100 cm^3), which was flame sealed, and warmed to 250 °C for 40 min. No visual evidence of decomposition was apparent. The tube was then warmed to 330 °C for 40 min. A powder was observed on the walls of the tube. The tube was opened on a vacuum line and the volatile products were collected in a trap. An i.r. spectrum of this material indicated it to be $SiMeF_3$.[14]

(*b*) The compound $SnMe_3(SiF_3)$ and MeBr (1:5 molar ratio) were condensed into a medium-wall glass tube (100 cm^3), which was flame sealed and warmed to 330 °C for 40 min. An i.r. spectrum of the volatile by-products indicated the presence of MeBr and $SiMeF_3$. There was no evidence for the formation of $SiBrF_3$.[10] A liquid remained in the tube; i.r. and mass spectra were consistent with it being $SnBrMe_3$.[15]

Miscellaneous.—The compounds $SnMe_3(SiF_3)$ (0.5 mmol) and ICl (0.5 mmol) were allowed to react at room temperature for 10 min. An i.r. spectrum of the volatile products indicated the presence of $SiClF_3$[10] (0.48 mmol, 96%); there was no evidence for SiF_3I.[10] A solid, presumably $SnMe_3I$, was also present.

References

1 J. J. D'Errico and K. G. Sharp, *Inorg. Chem.*, in the press.
2 M. J. Newlands, in 'Organotin Compounds,' ed. A. K. Sawyer, Marcel Dekker, New York, 1972.
3 H. C. Clark, S. G. Furnival, and J. T. Kwon, *Can. J. Chem.*, 1963, **41**, 2889.
4 R. Walsh, *Acc. Chem. Res.*, 1981, **14**, 246.
5 U. Schroer and W. P. Neumann, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 246.
6 W. P. Neumann and A. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 812.

7 S. K. Bains, P. N. Noble, and R. Walsh, *J. Chem. Soc., Faraday Trans. 2*, 1986, 837.

8 C. F. Shaw and A. L. Allred, *Inorg. Chem.*, 1971, **10**, 1340.

9 M. L. Maddox, N. Flitcroft, and H. D. Kaesz, *J. Organomet. Chem.*, 1965, **4**, 50.

10 M. Bures, C. Cerny, and J. Pavlicek, *Chem. Listy*, 1982, **76**, 375.

11 D. Solan and A. B. Burg, *Inorg. Chem.*, 1972, **11**, 1253.

12 E. Amberger and E. Mulhofer, *J. Organomet. Chem..*, 1968, **12**, 55.

13 H. Burger, S. Biedermann, and A. Ruoff, *Spectrochim. Acta, Part A*, 1971, **27**, 1687.

14 R. L. Collins and J. R. Nielsen, *J. Chem. Phys.*, 1955, **23**, 351.

15 E. J. Kupchik, in 'Organotin Compounds,' ed. A. K. Sawyer, Marcel Dekker, New York, 1971.

Received 14*th November* 1988; *Paper* 8/04515A