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Silylstannylation of ethyl diazoacetate with novel silylstannyl triflates

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Abstract

Reaction of $Ph_2{}^tBuSiSnMe_3$ or $^iPr_3SiSnMe_3$ with triflic acid (CF_3SO_3H; TfOH) at −40 °C yields the first silylstannyl triflates, $Ph_2{}^tBuSiSnMe_2OTf$ and $^iPr_3SiSnMe_2$-OTf. The former triflate is thermally unstable above 0 °C, but the latter has been isolated as a thermally stable crystalline solid. Both triflates can be used for efficient silylstannylation of ethyl diazoacetate.

Silylstannes, first described in 1933 [1], have only recently been put to use in organic synthesis [2–6]. Pd^0-catalyzed cleavage of the silicon–tin bond is generally involved in these applications. The metal–metal bond is also cleaved in reactions of electrophiles such as HCl or ICl with $Me_3SiSnMe_3$ [7].

We describe here the results of a study of the reactions of triflic acid with some hexaorgano-silylstannes in which a tin–carbon bond is cleaved selectively while the Si–Sn and Si–C bonds are left intact.

By analogy with earlier preparations [4,6], silylstannanes **1a**, **1b** were prepared by the reaction (eq. 1):

$$Me_3SnLi + R^1_2R^2SiCl \longrightarrow R^1_2R^2SiSnMe_3 \qquad (1)$$

$$(\mathbf{1a}: R^1 = R^2 = {}^iPr;\quad \mathbf{1b}: R^1 = Ph;\ R^2 = {}^tBu)$$

Compounds **1a**, **1b** react with a stoichiometric amount of triflic acid, even at −40 °C, and one equivalent of methane is evolved. Work-up gives the silylstannyl triflate **2a** in quantitative yield as a crystalline solid which is thermally stable up to its melting point (119–120 °C). On the other hand, the triflate **2b**, bearing a less bulky silyl group, is thermally rather labile, and decomposes both in pure form (at ≥ 0 °C) or in CH_2Cl_2 solution (at room temperature) to form mainly the silyl triflate **4b**, and Me_2Sn which then polymerizes (see Experimental part).

To provide chemical evidence for their identities, **2a**, **2b** were treated with ethyl diazoacetate (EDA) in the presence of NEt^iPr_2. In keeping with the well-established

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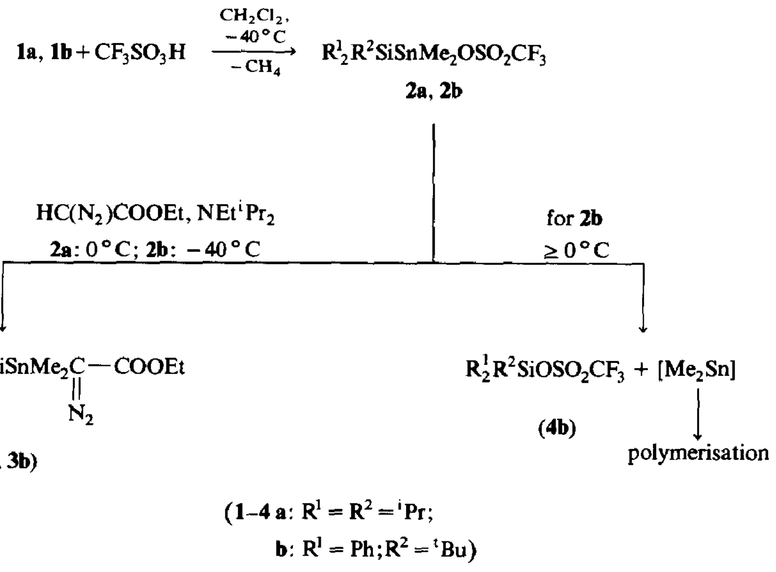

Scheme 1

silylation of EDA by silyl triflates [8–10], the novel diazo(silylstannyl)acetates **3a**, **3b** were obtained in high yield by electrophilic substitution at the diazo carbon atom (Scheme 1).

Stannylation of diazo acetates and diazomethyl ketones is usually carried out with (triorgano)(dialkylamino)stannanes [11] or (trialkyl)(methoxy)stannanes [12]; another method involves the reaction of α-metallated (Hg, Li) diazoacetic esters with bis(triorganostannyl)sulfides [13] or chlorostannanes [14]. It appears that stannyl triflates, although known for some time [15], have never been used for this purpose.

The thermal decomposition of **2b** is not very surprising, since distannanyl halides break down thermally in a similar fashion [$R_3SnSnR_2Hal \rightarrow R_3SnHal + (SnR_2)_n$]; $Me_3SnSnMe_2Br$ decomposes even at −30 °C [16]. In both the distannanyl halide and in the silylstannyl triflate series, the thermal stability is apparently greater the bigger the organic substituents. Thus, we were unable to prepare the silylstannyl triflate **2c** from **1c** and triflic acid (Scheme 2). On mixing the components in CH_2Cl_2 at −78 °C, evolution of one equivalent of a gas was observed, but at room temperature only trimethylsilyl triflate (**4c**) and a yellow inhomogeneous polymer were obtained. Similarly, addition of ethyl diazoacetate and NEt^iPr_2 to the reaction mixture at −78 °C produced only the silylated diazoester **3c** [17*]. It can be concluded, therefore, that **2c** is unstable even at −78 °C.

It should be noted that electrophilic cleavage of the Si–Sn bond of **1c** by triflic acid cannot be responsible for the formation of **4c**, since in this case **4c** and trimethylstannyl triflate would be formed in equal amounts (eq. 2). Furthermore, none of the latter compound (^1H NMR: $\delta = -0.99$ ppm [18]) was detected in the

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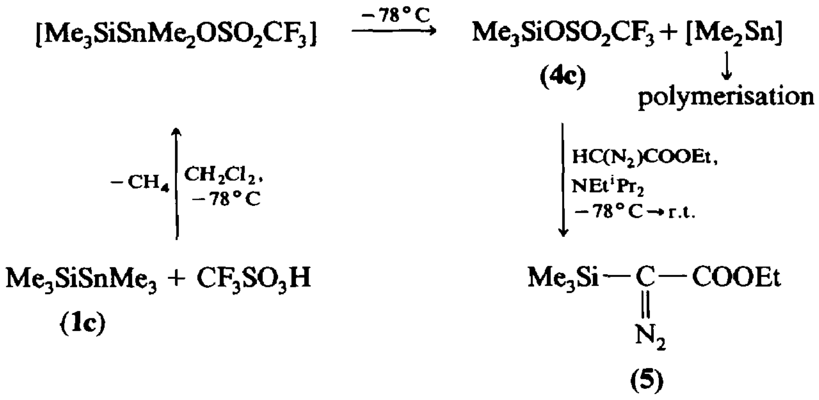
* Reference number with asterisk indicates a note in the list of references.



Scheme 2

reaction mixture, and also the stoichiometry of eq. 2 is not consistent with our observations.

$$1c + 2CF_3SO_3H \not\longrightarrow \underset{(4c)}{Me_3SiOSO_2CF_3} + Me_3SnOSO_2CF_3 + H_2 \tag{2}$$

In summary, we have shown that triflic acid cleaves the Sn–C bond in hexaorganosilylstannanes more readily than the SnSi bond. It is noteworthy that the Si–phenyl bond is also left intact, even though it is known to be particularly reactive towards triflic acid [19,20].

Experimental

All preparations were carried out in dried solvents under argon.

(Triisopropylsilyl)trimethylstannane (1a)

To a solution of trimethylstannyl lithium in THF (60 ml) prepared as described in ref. 6 from chlorotrimethylstannane (5.90 g, 29.6 mmol) and lithium metal (1.96 g, 296 mmol) was added chlorotriisopropylsilane (5.71 g, 29.6 mmol). The mixture was stirred overnight, and the LiCl then filtered off. Evaporation of the solvent followed by sublimation of the residue at 100–110 °C/0.02 Torr gave **1a** (5.60 g, 59%), m.p. 70 °C. IR (KBr): 2820 (vs), 1400 (w, br), 1255 (w), 1070 (s), 1005 (vs), 875 (m), 790 (vs), 655 (w), 635 (w) cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): $\delta = 0.17$ (9 H, ^2J(Sn,H) 44 Hz, $SnMe_2$), 1.15 (d, $CHMe_2$; the $CHMe_2$ signal was largely obscured by this signal). Anal. Found: C, 44.88; H, 9.41. $C_{12}H_{30}SiSn$ (321.1) calcd.: C, 44.4, H, 9.41%.

(t-Butyldiphenylsilyl)trimethylstannane (1b)

(a) To a solution of trimethylstannyl lithium in THF (50 ml) (prepared from chlorotrimethylstannane (3.84 g, 19.3 mmol) and lithium metal (1.35 g, 193 mmol) as described in ref. 6) was added (t-butyldiphenyl)chlorosilane (5.31 g, 19.3 mmol). After 12 h stirring the solvent was removed and pentane (ca. 30 ml) added to the residue. The LiCl that separated was filtered off, the filtrate was evaporated, and the residue distilled at 110 °C/0.01 Torr to yield **1b** (5.68 g, 73%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 90 MHz): $\delta = 0.25$ (9 H, ^2J(Sn,H) 46.6 Hz, $SnMe_2$), 1.20 (s, 9 H, ^{t}Bu), 7.25–7.71 (m, 10 H). ^{13}C NMR ($CDCl_3$, 50.28 MHz): $\delta = -9.2$ ($SnMe_2$), 21.0 (*C*Me_3), 29.1 (C*Me*$_3$), 126.5–138.0 (Ph). Anal. Found: C, 57.00; H, 6.94. $C_{19}H_{28}SiSn$ (403.2) calcd.: C, 56.59; H, 6.99%.

(b) To a solution of trimethylstannyllithium in THF (100 ml), prepared from trimethyltin hydride (9.00 g, 54.6 mmol) and lithium diisopropylamide (5.84 g, 54.6 mmol) as described in ref. 4, was added (t-butyldiphenyl)chlorosilane (15.00 g, 54.6 mmol). Subsequent procedures as described under (a) gave 17.83 g (81%) of **1b**.

Dimethyl(triisopropylsilyl)stannyl trifluoromethanesulfonate (2a)

Trifluoromethanesulfonic acid (0.38 ml, 0.65 g, 4.36 mmol) was added dropwise to a solution of **1a** (1.40 g, 4.36 mmol) in dichloromethane (10 ml) at −40 °C. A white precipitate appeared immediately. After 15 min at room temperature the solvent was removed at 20 °C/0.02 Torr and the solid residue washed with CH_2Cl_2; yield: 1.95 g (99%); m.p. 119–120 °C (dec.). IR (KBr): 1440 (w), 1230 (vs, br), 1170 (vs), 1115 (vs), 1025 (vs), 640 (vs). ^{1}H NMR ($CDCl_3$, 90 MHz): $\delta = 0.97$ (6 H, ^2J(Sn, H) 36 Hz, $SnMe_2$), 1.29 (d, 18 H, CH*Me*$_2$), ca. 1.3–1.7 (m, 3 H, CH). Anal. Found: C, 29.6; H, 5.7. $C_{12}H_{27}F_3O_3SSiSn$ (455.2) calcd.: C, 31.66; H, 5.98%.

(t-Butyldiphenylsilyl)dimethylstannyl trifluoromethanesulfonate (2b)

Trifluoromethanesulfonic acid (1.09 ml, 1.85 g, 12.4 mmol) was added dropwise to a solution of **1b** (5.00 g, 12.4 mmol) in CH_2Cl_2 (20 ml) maintained at −40 °C. After an additional 30 min stirring at −40 °C, the solvent was removed at 0 °C/0.02 Torr. The residual colorless solid gradually deliquesced at 0 °C, and the colorless liquid formed became yellow and then red. From an ethereal solution of this liquid, an air-sensitive orange solid was obtained; its ^{1}H NMR spectrum showed signals only in the SnMe region [21*].

The ^{1}H NMR spectrum ($CDCl_3$) of the colorless solid recorded immediately after its isolation showed the following major signals, attributed to **2b**: $\delta = 0.95$ (6 H, ^2J(Sn,H) 41 Hz, $SnMe_2$), 1.34 (s, 9 H, ^{t}Bu), 7.21–7.65 (m, 10 H, Ph).

When a solution of **2b** in CH_2Cl_2, prepared as described above, was kept at ambient temperature for 12 h and then distilled, t-butyldiphenylsilyl trifluoromethanesulfonate (**4c**) [19] was obtained at 125 °C/0.02 Torr (Kugelrohr apparatus) in ca. 60% yield.

Ethyl α-diazo-α-[(triisopropylsilyl)dimethylstannyl]acetate (3a)

Triflate **2a** (4.55 g, 10 mmol) was added in small portions to a solution of ethyl diazoacetate [22] (1.14 g, 10 mmol) and ethyldiisopropylamine (1.74 ml, 10 mmol) in CH_2Cl_2 (50 ml) kept at 0 °C. After 12 h stirring at room temperature the solvent was removed and pentane (30 ml) is added. The solid was filtered off, and the residue subjected to column chromatography (silica gel; chloroform) to give 3.00 g (71%) of **3a** as a yellow oil, b.p. 155 °C/0.01 Torr. IR (film): 2060 (vs, CN_2), 1665 (vs, CO) cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz); $\delta = 0.40$ (6 H, ^2J(Sn,H) 43 Hz), 1.15 (d, CH*Me*$_2$), 1.27 (t, CH_2*CH*$_3$), C*H*Me_2 obscured by the signals from CH*Me*$_2$ and CH_2*CH*$_3$, 3.98 (q, CH_2). ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = -6.8$ ($SnMe_2$), 13.2 (*C*HMe_2), 14.5 (CH_2*C*H_3), 19.8 (CH*Me*$_2$), 36.5 (CN_2), 60.4 (CH_2), 171.1 (CO).

Anal. Found: C, 43.9; H, 7.7; N, 6.3. $C_{15}H_{32}N_2O_2SiSn$ (419.20) calcd.: C, 42.9; H, 7.69; N, 6.68%.

*Ethyl [(t-butyldiphenylsilyl)dimethylstannyl]-α-diazoacetate (**3b**)*

The solution of **2b** in CH_2Cl_2 (20 ml) prepared as described above was cooled to −40 °C then transferred to a dropping funnel cooled with dry ice/acetone. The solution was added dropwise to a solution of ethyl diazoacetate [22] (1.41 g, 12.4 mmol) and ethyldiisopropylamine (1.60 g, 12.4 mmol) in CH_2Cl_2 (40 ml) kept at −40 °C. After 3 h at this temperature, the mixture was allowed to warm to room temperature, and filtered. The solvent was evaporated to leave analytically pure **3b**, a yellow oil (6.03 g, 97%) which solidified at 5 °C. IR (film): 2078 (vs, CN_2), 1660 (vs, CO) cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz): $\delta = 0.48$ (6 H, ^{2}J(Sn,H) 47 Hz, $SnMe_2$), 1.23 (t, 3 H, CH_2CH_3), 1.25 (s, 9 H, ^{t}Bu), 4.07 (q, 2 H, CH_2), 7.32–7.77 (m, 10 H, Ph). ^{13}C NMR ($CDCl_3$, 50.28 MHz): $\delta = -7.5$ ($SnMe_2$), 14.5 (CH_2CH_3), 23.4 (CMe_3), 28.4 (CMe_3), 37.4 (CN_2) 60.6 (CH_2), 123.5–136.5 (Ph), 171.2 (CO). Anal. Found: C, 52.2; H, 6.04; N, 5.4. $C_{22}H_{30}N_2O_2SiSn$ (501.2) calcd.: C, 52.72; H, 6.03; N, 5.59%.

*Ethyl α-diazo-α-(triisopropylsilyl)acetate (**5**)*

Trifluoromethanesulfonic acid (1.69 g, 10 mmol) was added at −78 °C to a solution of trimethyl(trimethylsilyl)stannane [4] in CH_2Cl_2 (20 ml), whereupon a yellow solid separated. After 30 min the suspension was transferred to a dropping funnel cooled with dry ice/acetone, and then slowly added to a solution of ethyl diazoacetate [22] (1.14 g, 10 mmol) and ethyldiisopropylamine (1.29 g, 10 mmol) in CH_2Cl_2 (40 ml), also kept at −78 °C. After 3 h, the mixture was allowed to warm to room temperature and filtered. The solvent was removed from the filtrate and the residue distilled at 85 °C/0.01 Torr (Kugelrohr apparatus) to give 0.95 g (55%) of **5** as a yellow oil. The compound was identified by comparison of its IR and ^{1}H NMR spectra with those of an authentic sample [10], and gave a correct elemental analysis.

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