Thermolysis of [α-(Silyloxy)propargyl]stannanes into [γ-(Silyloxy)allenyl]stannanes

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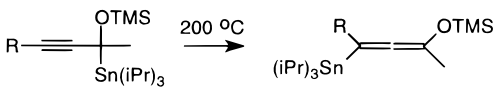
Received August 4, 1997

The electrophilic addition of aldehydes to allenylstannanes has become an increasingly useful entry to homopropargyl alcohols.[1] Although (γ-alkoxyallenyl)stannanes thus suggest themselves as precursors to alkynediol derivatives, only limited reports of their preparation[2] and use in this regard[3] are extant. The analogous (γ-siloxyallenyl)stannanes may be expected to serve in a similar capacity, but to our knowledge their use is currently unknown.

We recently reported that (α-siloxypropargyl)stannanes (**1a**−**e**) were available by alkynylation−silylation of acetyltriisopropylstannane[4] (**1f**, this work). It has long been known that propargylstannanes may be isomerized to allenylstannanes under thermal,[5,6] acidic,[5,7] or nucleophilic[5,8] conditions, although the position of equilibrium may be influenced by steric factors. Since propargyl ethers can also be equilibrated to favor the formation of allenyl ethers,[9] it seemed possible that a synthetically useful isomerization of **1** into the corresponding allenes



1 **2**

1, 2 a, R = TMS **d**, R = $PhCH_2$
b, R = nBu **e**, R = $Me_2C(OTMS)$
c, R = tBu **f**, R = $(EtO)_2CH$

2 could be effected. In the event, it was found that short-term (10−30 min) thermolysis of **1** at ca. 200 °C sufficed for this conversion, with the results obtained outlined in Table 1. A minor competing reaction which became noticeable at the longer reaction times was a degradation to form, in part, 1-(triisopropylstannyl)-1-[(trimethylsilyl)oxy]ethene.[10] All acetylenes underwent essentially complete conversion (^{1}H NMR analysis[11]) under the listed conditions except for **1b,c**, which still survived to the extent of 5−10% after 30 min. Although further heating of these compounds to complete disappearance of **1** was not carried out, a sample of **2b** heated at 210 °C for 30 min showed no detectable amount of **1b**, indicating that equilibrium lay far in the direction of the allene.

Table 1. Thermolysis of **1**[a] into **2**

2	time (min)	temp (°C)	yield (%)[b]	purity (%)[c]
a	10	200	97	88
b	30	210	82	85[d]
c	30	210	92	88[d]
d	20	200	65	90
e	20	200	84	98
f	15	200	83	98

[a] Contained 5−10% of $RC{\equiv}CSn(^iPr)_3$ and/or $CH_2{=}C(OTMS)Sn(^iPr)_3$; see ref 4. [b] Isolated yield from Kugelrohr distillation. [c] By ^{1}H NMR analysis. [d] Contained 5−10% unreacted **1**.

The assignment of the allenic structure to **2** followed from their IR and ^{13}C NMR spectra,[12] the latter showing the characteristic low field (ca. 200 ppm) absorption of the central carbon atom. Confirmatory of overall assignments were some clearly seen tin satellites associated with the terminal allenyl carbons and the isopropylstannyl group. Thus, for example, **2f** displayed $^1J(^{119}Sn,C{=}) = 292$ Hz, $^1J(^{117}Sn,C{=}) = 279$ Hz (both centered at δ 109.1), $^3J(Sn,C{=}) = 41$ Hz[13] (centered at δ 119.6) and $^1J(^{119}Sn,C) = 342$ Hz, $^1J(^{117}Sn,C) = 327$ Hz (both centered at δ 16.6) in the ^{13}C NMR spectrum. These values are consistent with known data for allenylstannanes[14] and for isopropyltin compounds,[15] respectively. The ^{1}H NMR spectra of all **2** displayed tin satellites centered at the (allenyl)methyl group absorption, which for **2f** was at δ 1.85 with $^5J(Sn,H) = 16.6$ Hz.[13]

Several experiments were carried out to ascertain that the rearrangement of **1** to **2** was not a free radical process possibly initiated by thermally induced stannyl radical formation.[16] Thus, a sample of **1b** in excess bromobenzene was heated in a sealed tube at 210 °C for 20 min. Complete conversion to **2b** was observed, with no indication of bromotriisopropylstannane formation[17] (or any other product). Similarly, a sample of **1c** and excess 1,2-dibromoethane was heated in a sealed tube at 200 °C for 30 min to afford only **2c**, with no bromotriisopropylstannane or ethylene in evidence.[18] The intermediacy of stannyl radicals is thus contraindicated. Extant studies by LeQuan and Guillerm led to the conclusion that (only) terminally unsubstituted propargylstannanes thermally

(1) (a) Marshall, J. A.; Yu, R. H.; Perkins, J. F. *J. Org. Chem.* **1995,** *60*, 5550. (b) Marshall, J. A. *Chemtracts-Org. Chem.* **1992**, 75.

(2) (a) Anies, C.; Lallemand, J. Y.; Pancrazi, A. *Tetrahedron Lett.* **1996,** *37*, 5519. (b) Merlic, C. A.; Albaneze, J. *Tetrahedron Lett.* **1995,** *36*, 1011. (c) Takeda, T.; Oshima, H.; Inoue, M.; Togo, A. *Chem. Lett.* **1987**, 1345.

(3) Kadota presents an intramolecular example: Kadota, I.; Hatakeyama, D.; Seki, K.; Yamamoto, Y. *Tetrahedron Lett.* **1996,** *37*, 3059.

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(5) Guillerm, G.; Meganem, F.; LeQuan, M. *J. Organomet. Chem.* **1974**, *67*, 43.

(6) LeQuan, M.; Guillerm, G.; Alain, J. *C. R. Acad. Sci., Paris, Ser. C* **1969**, *268*, 1542.

(7) LeQuan, M.; Guillerm, G. *C. R. Acad. Sci., Paris, Ser. C.* **1969**, *268*, 1001.

(8) LeQuan, M.; Guillerm, G. *C. R. Acad. Sci., Paris, Ser. C.* **1969**, *268*, 858.

(9) Landor, S. R., Ed. *The Chemistry of the Allenes*; Academic Press: London, 1982; Vol. 1, Chapter 2.

(10) Samples of **1** free of the ethene prior to thermolysis were seen to produce crude **2** containing the ethene. Also see the Experimental Section (**2e**) for a quantitative determination.

(11) Conversions could be most conveniently followed by comparing the homopropargyl methyl ^{1}H NMR absorption of **1** to the slightly more downfield allenylmethyl absorption of **2**.

(12) Landor, S. R., Ed. *The Chemistry of the Allenes*; Academic Press: London, 1982; Vol. 3, Chapter 10.

(13) The ^{119}Sn and ^{117}Sn sattelites were unresolved.

(14) (a) Doddrell, D.; Bullpitt, M. L.; Moore, C. J.; Fong, C. W.; Kitching, W.; Adcock, W.; Gupta, B. D. *Tetrahedron Lett.* **1973**, 665. (b) Wrackmeyer, B. *J. Magn. Reson.* **1980**, *39*, 359. (c) Liepins, E.; Birgele, I.; Lukevics, E.; Bogoradovsky, E. T.; Zavgorodny, V. S. *J. Organomet. Chem.* **1991**, *402*, 43.

(15) Mitchell, T. N.; Walter, G. *J. Organomet. Chem.* **1976**, *121*, 177.

(16) Under free radical conditions, propargyltriphenylstannane has been shown to both isomerize to allenyltriphenylstannane and to undergo S_H2' reactions with alkyl halides: Baldwin, J. E.; Adlington, R. M.; Basak, A. *J. Chem. Soc., Chem. Commun.* **1984**, 1284.

(17) Stannyl radicals are known to abstract bromine from bromobenzene: Menapace, L. W.; Kuivila, H. J. *J. Am. Chem. Soc.* **1964**, *86*, 3047.

(18) 1,2-Dibromoalkanes afford alkenes via the intermediacy of stannyl radicals using either tri-*n*-butyltin hydride (Strunk, R. J.; DiGiacomo, P. M.; Aso, K.; Kuivila, H. G. *J. Am. Chem. Soc.* **1970**, *92*, 2849) or hexa-*n*-butylditin (Kuivila, H. G.; Pian, C. H. C. *Tetrahedron Lett.* **1973**, 2561).

S0022-3263(97)01440-0 CCC: $14.00

rearranged in a bimolecular process which nevertheless exhibited apparent first-order kinetics.[5,6] In addition, electron-donor solvents were found to accelerate the conversion, perhaps via a solvent−substrate complex entailing a pentacoordinate tin intermediate.[5,8] Consistent with these and our results with terminally substituted propargylstannanes **1** would be the possibility that the thermal rearrangement proceeds by way of a 1,3-sigmatropic rearrangement within a pentacoordinate tin complex of **1** with itself (acetylenic $\pi \rightarrow$ Sn).[19] The driving force for the rearrangement of **1** (over terminally unsubstituted propargylstannanes) may arise from the stability of allenyl ethers[9] and the relief of crowding at the quaternary propargyl terminus.

Experimental Section

General. Starting acetylenes (**1**) were prepared as reported;[4] characterization data for these materials are given there and below. ^{1}H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra of **2** were obtained in $CDCl_3$ and 1:3 v/v C_6D_6−CCl_4, respectively (the latter was used to avoid C_6D_6 saturation with dilute samples; some samples of **2** in $CDCl_3$ were not completely stable over the ca. 18 h accumulation period). IR spectra were obtained on neat films. Kugelrohr oven temperatures are listed in lieu of boiling points ("Kd" = Kugelrohr distillation). GLPC of **1** was often accompanied by partial isomerization to **2**. Employing injection port and TC detector temperatures below 200 °C minimized or eliminated the rearrangement. Except where noted, analytical data were obtained on GLPC-collected samples.

1-(Trimethylsilyl)-3-(triisopropylstannyl)-3-[(trimethylsilyl)oxy]-1-butyne (1a).[4] Anal. Calcd for $C_{19}H_{42}OSi_2Sn$: C, 49.46; H, 9.18. Found: C, 49.43; H, 9.10.

2-(Triisopropylstannyl)-2-[(trimethylsilyl)oxy]-3-octyne (1b). Kd 125 °C (0.1 mmHg). IR: 2200 (vw) cm^{-1}; ^{1}H NMR: δ 0.15 (s, 9H), 0.88 (m, 3H), 1.1−1.7 (m, 25H), 1.67 (s, 3H), 2.22 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 2.4, 13.6, 16.4, 19,0, 22.1, 22.3, 31.0, 31.4, 66.9, 86.9, 88.2. Anal. Calcd for $C_{20}H_{42}$-OSiSn: C, 53.94; H, 9.51. Found: C, 53.69; H, 9.77.

5,5-Dimethyl-2-(triisopropylstannyl)-2-[(trimethylsilyl)-oxy]-3-hexyne (1c). Kd 120 °C (0.1 mmHg). IR: 2220 (vw) cm^{-1}; ^{1}H NMR: δ 0.14 (s, 9H), 1.17 (s, 9H), 1.2−1.7 (m, 21H), 1.65 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 2.5, 16.3, 22.3, 27.7, 31.1, 31.5, 66.6, 85.6, 95.9. Anal. Calcd for $C_{20}H_{42}OSiSn$: C, 53.94; H, 9.51. Found: C, 54.14; H, 9.44.

1-Phenyl-4-(triisopropylstannyl)-4-[(trimethylsilyl)oxy]-2-pentyne (1d). Kd 160 °C (0.05 mmHg). IR: 2200 (vw) cm^{-1}; ^{1}H NMR: δ 0.14 (s, 9H), 1.1−1.7 (m, 21H), 1.73 (s, 3H), 3.65 (s, 2H), 7.2−7.4 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 2.3, 16.4, 22.2, 25.7, 31.1 66.8, 85.6, 89.2, 126.3, 128.0, 128.3, 137.3. Anal. Calcd for $C_{23}H_{40}OSiSn$: C, 57.63; H, 8.41. Found: C, 57.72; H, 8.57.

5-Methyl-2-(triisopropylstannyl)-2,5-bis[(trimethylsilyl)-oxy]-3-hexyne (1e). Kd 145 °C (0.06 mmHg). IR: 2200 (vw) cm^{-1}; ^{1}H NMR: δ 0.16 (s, 9H), 0.17 (s, 9H), 1.1−1.7 (m, 21H), 1.47 (s, 6H), 1.72 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 2.1, 2.4, 16.5, 22.3, 30.5, 33.0, 66.5, 67.0, 89.1, 92.7. Anal. Calcd for $C_{22}H_{48}O_2Si_2Sn$: C, 50.86; H, 9.31. Found: C, 50.67; H, 9.44.

1,1-Diethoxy-4-(triisopropylstannyl)-4-[(trimethylsilyl)-oxy]-2-pentyne (1f). A solution of 0.26 g (2.0 mmol) of 3,3-diethoxy-1-propyne in 7 mL of ethyl ether was treated at −78 °C with 0.80 mL of 2.5 N (0.20 mmol) *n*-butyllithium in hexane (the metalated acetylene is unstable at 0 °C).[4] After 10 min, 0.60 g (0.21 mmol) of acetyltriisopropylstannane was added dropwise by syringe. After an additional 15 min at −78 °C, 0.40 mL (2.7 mmol) of (trimethylsilyl)imidazole was added and the mixture allowed to warm to 25 °C over 45 min. A pentane−$NaHCO_3$ workup was followed by drying ($MgSO_4$) and Kugelrohr distillation to give, after a 0.14 g forerun (Kd 100 °C/0.05 mmHg), 0.57 g (58%) of **1f** (Kd 135−140 °C/0.05 mmHg). IR: 2220 (w) cm^{-1}. ^{1}H NMR: δ 0.17 (s, 9H), 1.21 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H), 1.3−1.7 (m, 21H), 1.75 (s, 3H), 3.5−3.85 (m, 4H), 5.33 (s, 1H). ^{13}C NMR (1:3 v/v C_6D_6−CCl_4): δ 2.7, 15.4, 16.9, 22.6, 30.9, 60.4, 60.5, 66.3, 84.8, 91.5, 92.1. Anal. Calcd for $C_{21}H_{44}O_3SiSn$: C, 51.33; H, 9.03. Found: C, 51.37; H, 9.12.

The following were isolated from the forerun.

1-(Triisopropylstannyl)-1-[(trimethylsilyl)oxy]ethene. IR: 1570 cm^{-1}. ^{1}H NMR: δ 0.18 (s, 9H), 1.1−1.6 (m, 21H), 4.23 (d, J = 0.6 Hz), 1H), 4.94 (d, J = 0.6 Hz, 1H). Anal. Calcd for $C_{14}H_{32}OSiSn$: C, 46.55; H, 8.93. Found: C, 46.55; H, 9.01.

3,3-Diethoxy-1-(triisopropylstannyl)propyne. ^{1}H NMR: δ 1.1−1.7 (m, 21 H), 1.24 (t, J = 7.2 Hz, 6H), 3.53−3.86 (ABX_3 pattern, 4H), 5.28 (s, 1H). Anal. Calcd for $C_{16}H_{32}O_2Sn$: C, 51.23; H, 8.60. Found: C, 51.04; H, 8.75].

Typical Procedure for the Formation of 2. 5-Methyl-4-(triisopropylstannyl)-2,5-bis[(trimethylsilyl)oxy]-2,3-hexadiene (2e). A fused three-bulb Kugelrohr insert was charged with 0.44 g of **1e** containing as impurity 5% (0.02 g) of 1-(triisopropylstannyl)-1-[(trimethylsilyl)oxy]ethene. The insert was placed into the Kugelrohr oven at a 45° angle for reflux and heated under rotation at 200 °C for 20 min under Ar. After cooling, interior surfaces were washed down with hexane into the terminal bulb and evaporated. The residue was Kugelrohr distilled to give fractions at 105 °C (0.05 mmHg) (0.073 g) and 145 °C (0.05 mmHg) (0.37 g) (84% of analytically pure **2e**) uncontaminated by the ethene (^{1}H NMR analysis). (The forerun contained 50% (0.04 g) of the ethene.) IR: 1930 (w) cm^{-1}. ^{1}H NMR: δ 0.12 (s, 9H), 0.16 (s, 9H), 1.37 (s, 3H), 1.38 (s, 3H), 1.1−1.6 (m, 21H), 1.82 (s, 3H). ^{13}C NMR: δ 1.0, 2.6, 17.4, 22.4, 22.7, 31.4, 32.3, 77.9, 120.1, 121.9, 195.5. Anal. Calcd for $C_{22}H_{48}O_2$-Si_2Sn: C, 50.86; H, 9.31. Found: C, 51.03; H, 9.16.

1-(Triisopropylstannyl)-1-(trimethylsilyl)-3-[(trimethylsilyl)oxy]-1,2-butadiene (2a). Kd 125 °C (0.1 mmHg). IR: 1920 (vw) cm^{-1}. ^{1}H NMR: δ 0.10 (s, 9H), 0.15 (s, 9H), 1.1−1.6 (m, 21H), 1.81 (s, 3H). ^{13}C NMR: δ 0.6, 1.0, 16.9, 21.2, 22.5, 102.2, 115.0, 213.3. Anal. Calcd for $C_{19}H_{42}OSi_2Sn$: C, 49.46; H, 9.18. Found: C, 49.50; H, 9.36.

4-(Triisopropylstannyl)-2-[(trimethylsilyl)oxy]-2,3-octadiene (2b). Kd 130 °C (0.08 mmHg). IR: 1925(w) cm^{-1}. ^{1}H NMR: δ 0.15 (s, 9H), 0.88 (t, 3H), 1.1−1.6 (m, 25H), 1.81 (s, 3H), 2.15 (m, 2H). ^{13}C NMR: δ 0.8, 14.4, 16.1, 22.4, 22.5, 22.9, 32.0, 36.6, 107.5, 118.9, 200.0. Anal. Calcd for $C_{20}H_{42}OSiSn$: C, 53.94; H, 9.51. Found: C, 53.86; H, 9.56.

5,5-Dimethyl-4-(triisopropylstannyl)-2-[(trimethylsilyl)-oxy]-2,3-hexadiene (2c). Kd 120 °C (0.1 mmHg). IR: 1930 (w) cm^{-1}. ^{1}H NMR: δ 0.16 (s, 9H), 1.05 (s, 9H), 1.1−1.6 (m, 21H), 1.81 (s, 3H). ^{13}C NMR: δ 1.1, 17.2, 22.5, 31.5, 37.0, 119.3, 119.6, 196.5 (quaternary *tert*-butyl carbon unseen). Anal. Calcd for $C_{20}H_{42}OSiSn$: C, 53.94; H, 9.51. Found: C, 53.90; H, 9.74.

1-Phenyl-2-(triisopropylstannyl)-4-[(trimethylsilyl)oxy]-2,3-pentadiene (2d). Kd 160 °C (0.05 mmHg). IR: 1930 (vw) cm^{-1}. ^{1}H NMR: δ 0.09 (s, 9H), 1.05−1.6 (m, 21H), 1.83 (s, 3H), 3.3 (AB pattern, J = 18 Hz, 2H), 7.2−7.3 (m, 5H). ^{13}C NMR: δ 0.6, 16.2, 21.9, 22.4, 43.5, 106.5, 118.9, 126.5, 128.4, 129.4, 140.4, 202.0. Anal. Calcd for $C_{23}H_{40}OSiSn$: C, 57.63; H, 8.41. Found: C, 57.60; H, 8.54.

1,1-Diethoxy-2-(triisopropylstannyl)-4-[(trimethylsilyl)-oxy]-2,3-pentadiene (2f). Kd 140 °C (0.05 mmHg). IR: 1940 (vw) cm^{-1}. ^{1}H NMR: δ 0.18 (s, 9H), 1.19 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.2 Hz, 3H), 1.1−1.7 (m, 21H), 1.85 (s, 3H), 3.6 (m, 4H), 4.88 (s, 1H). ^{13}C NMR: δ 0.6, 15.5, 15.6, 16.6, 21.7, 22.4, 60.7, 62.6, 104.7, 109.1, 119.6, 202.0. Anal. Calcd for $C_{21}H_{44}O_3$-SiSn: C, 51.33; H, 9.03. Found: C, 51.49; H, 9.11.

Rearrangement of 1b in Bromobenzene. A mixture of 29 mg (0.052 mmol) of **1b** (glpc-collected; contained 20% of **2b**) and 20 μL (0.19 mmol) of bromobenzene was sealed in a melting point tube and held at 210 °C for 20 min. Glpc and ^{1}H NMR analysis of this sample showed only the presence of **2b** and bromobenzene.

Rearrangement of 1c in 1,2-Dibromoethane. A 1:1 (v/v) mixture of GLPC-collected **1c** (**2c** content < 5%) and 1,2-dibromoethane was sealed in a melting point tube and held at 200 °C for 30 min. GLPC and ^{1}H NMR analysis of this sample showed only the presence of **2c** and 1,2-dibromoethane.

JO971440K

(19) This would correspond to the molecularity associated with "A + A → A + B".