Preparation of (Aminomethyl)stannanes by Reduction of α-Amidoorgano Stannanes

Andrew F. Burchat, J. Michael Chong,* and Nathan Nielsen

Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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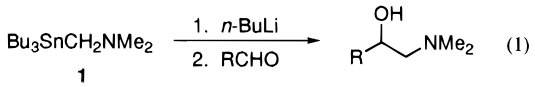
α-Aminoorgano stannanes are becoming increasing popular as reagents in organic synthesis.[1,2] They were first described by Peterson who showed that [(dialkylamino)methyl]stannanes such as **1** may be transformed into organolithium reagents which in turn may used as nucleophiles to prepare *β*-amino alcohols (eq 1).[3] Subsequently, other workers have provided additional examples of this approach to *β*-amino alcohols.[4,5] α-Aminomethyl stannanes have also served as intermediates in syntheses of α-amino ketones,[6] α-amino acids,[7] and cyclic amines.[2,8]



(1)

[(Dialkylamino)methyl]stannanes have been classically prepared by the reaction of amines with halomethylorgano stannanes[2] or by reaction of Bu_3SnM (M = Li, MgCl) with R_2NCH_2SR'[3] or R_2NCH_2OR'.[4] The former method has the disadvantage of low yields, particularly when the amine is hindered,[9] while the latter method employs Galvinoxyl (in the preparation of $Bu_3SnMgCl$) which can give rise to products which are detrimental to transmetalation of the organostannane.[10] More recently, Quintard has introduced a method to (aminoorgano)stannanes via addition of $Bu_3SnMgCl$ to iminium salts,[5] Pearson has reported a route which involves displacement of sulfones with Bu_3SnLi,[11] and both Katrizky[12] and Pearson[13] have shown that benzotriazoles may be useful precursors to aminostannanes. α-Amino stannanes may also be prepared by reduction of α-stannyl imines but this route is limited since these imines are prepared from acylstannanes which are notoriously air-sensitive.[14] We now report that α-aminoorgano stannanes may be prepared in excellent yields by reduction of α-amidoorgano stannanes.

Scheme 1

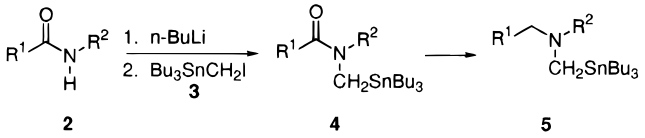
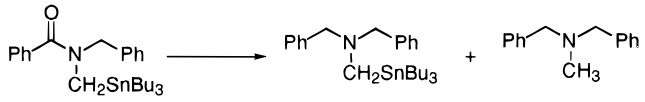


Table 1. Reaction of Amide 4a under Different Conditions



entry	reducing agent	conditions	ratio **5a**:**6**[a]
1	$LiAlH_4$	Et_2O, reflux, 10 min	14:1[b]
2	$LiAlH_4$	Et_2O, reflux, 10 min	9.4:1[c]
3	$LiAlH_4$	Et_2O, 0 °C, 15 min	18:1[b]
4	$LiAlH_4$	Et_2O, 0 °C, 45 min	1:1[c]
5	$LiAlH_4$	THF, reflux, 3 h	1:3.4[d]
6	$LiAl(OEt)_2H_2$	Et_2O, reflux, 1 h	8.8:1[b]
7	DIBAL-H	toluene, rt, 3.5 h	6.6:1[d]
8	DIBAL-H	Et_2O, reflux, 1 h	5.2:1[d]
9	AlH_3	THF, rt, 30 min	>50:1[b]

[a] Determined by ^1H NMR analysis of crude reaction products. [b] Amide **4a** was added to a solution of the reducing agent. [c] Solid $LiAlH_4$ was added to a solution of amide **4a** in Et_2O. [d] A solution of the reducing agent was added to a solution of amide **4a**.

The reduction of amides with hydride reagents is a proven route to amines.[15] Since the alkylation of amide anions is a much cleaner reaction than the alkylation of amines, the short sequence shown in Scheme 1 was an attractive route to α-amino stannanes. Many secondary amides are commercially available or easily prepared while iodide **3** may be obtained in 100 g batches using the method of Seitz.[16] The one missing link was the reduction itself since it was not known how the reduction of the amide would be affected by the presence of the tributylstannyl group.[17]

Results and Discussion

In our initital investigations, *N*-benzylbenzamide was alkylated with iodide **3** to give the expected amide **4a** in good yield. This amide was then treated with hydride reagents; results are summarized in Table 1. Reductions employing $LiAlH_4$ gave the desired amine **5a** in moderate to good yields, but a minor side product was also formed. This material was identified as *N*-methyldibenzylamine (**6**).[18] The presence of this side product along with Bu_3SnH in the crude reduction mixture suggested that attack of a hydride reagent on the tributyltin group was competing with reduction of the carbonyl group.[19] Treat-

(1) For a review of earlier work, see: Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987; pp 172−173.
(2) For a compilation of recent work, see reference 2 in: Coldham, I.; Hufton, R. *Tetrahedron Lett.* **1995**, *36*, 2157−2160.
(3) (a) Peterson, D. J. *J. Organomet. Chem.* **1970**, *21*, P63−P64. (b) Peterson, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 4027−4031. (c) Peterson, D. J.; Ward, J. F. *J. Organomet. Chem.* **1974**, *66*, 209−217.
(4) Quintard, J.-P.; Elissondo, B.; Jousseaume, B. *Synthesis* **1984**, 495−498.
(5) Elissondo, B.; Verlhac, J.-P.; Quintard, J.-P.; Pereyre, M. *J. Organomet. Chem.* **1988**, *339*, 267−275.
(6) Verlhac, J.-B.; Quintard, J.-P. *Tetrahedron Lett.* **1986**, *27*, 2361−2364.
(7) Ekhato, I. V.; Huang, C. C. *J. Labelled Compd. and Radiopharm.* **1994**, *34*, 107−115.
(8) Coldham, I. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1275−1276.
(9) Abel, E. W.; Rowley, R. J. *J. Organomet. Chem.* **1975**, *97*, 159−165.
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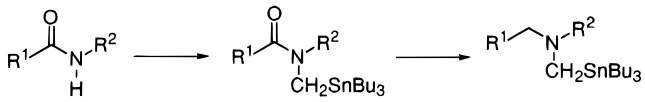
(12) Katritzky, A. R.; Chang, H.-X.; Wu, J. *Synthesis* **1994**, 907−908.
(13) Pearson, W. H.; Stevens, E. P. *Synthesis* **1994**, 904−906.
(14) Ahlbrecht, H.; Baumann, V. *Synthesis* **1994**, 770−772.
(15) (a) Larock, R. C. *Comprehensive Organic Transformations*; VCH: New York, 1991; pp 432−433. (b) March, J. *Advanced Organic Synthesis*, 4th ed.; Wiley: New York, 1992; pp 1212−1213.
(16) Seitz, D. E.; Carroll, J. J.; Cartaya, M. C. P.; Lee, S.-H.; Zapata, A. *Synth. Commun.* **1983**, *13*, 129−134.
(17) BOC-protected aminostannanes have been reduced with DIBAL-H to the corresponding *N*-methyl compounds: (a) Gawley, R. E.; Zhang, Q. *Tetrahedron* **1994**, *50*, 6077−6088. (b) Gawley, R. E.; Zhang, Q. *J. Org. Chem.* **1995**, *60*, 5763−5769.
(18) Gribble, G. W.; Nutaitis, C. F. *Synthesis* **1987**, 709−711.
(19) Formation of Bu_3SnH in reductions of α-epoxy stannanes has previously been observed: Chong. J. M.; Mar, E. K. *J. Org. Chem.* **1992**, *57*, 46−49.

S0022-3263(96)00913-9 CCC: $12.00

Table 2. Preparation of Amines 5 from Secondary Amides



2 **4** **5**

entry	R^1	R^2	yield of **4** (%)[a]	yield of **5** (%)[a] using $LiAlH_4$		yield of **5** (%)[a] using AlH_3
1	Ph	$PhCH_2$	81 (**4a**)	79	**5a**	96
2	Ph	CH_3	69 (**4b**)	84	**5b**	91
3	Ph	Bu	88 (**4c**)	70	**5c**	96
4	Ph	*i*-Pr	67 (**4d**)	73	**5d**	83
5	Ph	c-C_6H_{11}	66 (**4e**)	41	**5e**	86
6	Ph	*p*-$CH_3OC_6H_4CH_2$	65 (**4f**)	88	**5f**	97
7	Ph	*t*-Bu	85 (**4g**)	*b*	**5g**	93
8	*o*-$CH_3C_6H_4$	$PhCH_2$	68 (**4h**)	*b*	**5h**	84
9	*o*-$CH_3OC_6H_4$	$PhCH_2$	92 (**4i**)	*b*	**5i**	87
10	*o*-$CH_3OC_6H_4$	*t*-Bu	73 (**4j**)	81	**5j**	c
11	$CH_2CH_2CH_2$		64 (**4k**)	*b*	**5k**	91
12	CH_3	$PhCH_2$	67 (**4l**)	71	**5l**	84
13	CH_3	*p*-$CH_3OC_6H_4CH_2$	68 (**4m**)	63	**5m**	81
14	H	CH_3	40 (**4n**)	36[d]	**1**	90
15	H	$PhCH_2$	51 (**4o**)	61[d]	**5b**	97

[a] Yield of isolated, purified (SiO_2) product. [b] Reaction not attempted. [c] Low conversion was observed; amide **4j** was recovered in high yield. [d] Yield based on amide **2**; see text.

ment of amine **5a** with $LiAlH_4$ did not produce any **6** but returned only starting material, indicating that the Bu_3-Sn group was being cleaved in amide **4a** but is stable once the amide is reduced.

The amount of amine **6** formed with $LiAlH_4$ was sensitive to the reaction conditions and the order of addition. When a solution of amide **4a** was added to a solution of $LiAlH_4$ in Et_2O (prepared by heating $LiAlH_4$ in Et_2O at gentle reflux for 1 hour) at reflux, the ratio of **5a:6** was 14:1 (entry 1); when solid $LiAlH_4$ was added to a solution of the amide in Et_2O and the reaction mixture was subsequently heated at reflux, the ratio changed to 9.4:1 (entry 2). Much more dramatic was the difference observed in reactions at 0 °C: addition of amide **4a** to an ethereal solution of $LiAlH_4$ at 0 °C gave a ratio (18:1) slightly better than the comparable reaction at reflux temperature (entry 3); however, addition of solid $LiAlH_4$ to a solution of the amide in ether at 0 °C gave a 1:1 mixture of products. Interestingly, amine **6** was the major product when the reaction was carried out in THF (entry 5).

We reasoned that an electrophilic reagent such as DIBAL-H would be less likely to promote this cleavage. To our dismay, DIBAL-H gave more of the undesired side product (entries 7, 8). Fortunately, AlH_3 (generated *in situ* by treatment of $LiAlH_4$ with H_2SO_4,[20] either with or without removal of the Li salts by centrifugation) effected a very clean reduction to give amine **5a** in 96% yield with no detectable amount (by ^1H NMR spectroscopy) of *N*-methylamine **6** (entry 9).

We prepared a series of amides and examined their reactions with $LiAlH_4$ and AlH_3 (Table 2). In general, alkylations of amides **2** ($R^1 \neq H$) with Bu_3SnCH_2I proceeded smoothly to give amides **4** in reasonable yields (64−88%). For a series of *N*-substituted benzamides (entries 1−6), reductions using $LiAlH_4$ yielded amine **5** in acceptable yields with no clear correlations between structure and yields. In each case, a byproduct (presumed to be the corresponding destannylated amine) was formed which was removed by column chromatography. In contrast, reductions with AlH_3 gave very clean products in consistently excellent (83−97%) yields. The only amide which was problematic was *N*-*tert*-butyl-*o*-anisamide (**4j**) (entry 10) which did not react under our standard conditions (THF, rt, 30 min) or even under more vigorous ones (THF, reflux, 12 h). Since the related *N*-*tert*-butylbenzamide (**4g**) (entry 7) and *N*-benzyl-*o*-anisamide (**4i**) (entry 9) were reduced smoothly with AlH_3, it suggests that the *o*-methoxy group or the *N*-*tert*-butyl group alone is not detrimental to the reduction but with both moieties on the same molecule (as in **4j**) reactivity toward AlH_3 is considerably diminished. Fortunately, $LiAlH_4$ reduction of **4j** gave the desired amine **5j** in good yield.

With formamides (**2**, $R^1 = H$), competing *O*-alkylation was a problem; the amides **4n** and **4o** were difficult to separate from Bu_3SnCH_2OH[21] resulting from *O*-alkylation/hydrolysis. In these cases, $LiAlH_4$ reductions were carried out on unpurified alkylation mixtures; the lower yields of amines reflect the poor alkylation step and additional chromatography required to provide pure amines. When pure samples of amides **4n** and **4o** were obtained (by repeated chromatography), alane reduction provided the expected amines in high yields.

In summary, we have found that competing destannylation occurs when α-amidoorganostannanes are treated with $LiAlH_4$. Reductions with alane give consistently high yields of α-aminoorganostannanes. Such reductions, in combination with alkylations of secondary amides with Bu_3SnCH_2I, offer a convenient route to *N*,*N*-disubstituted (aminomethyl)tributylstannanes.

Experimental Section

All reactions were carried out with dry glassware under an atmosphere of argon unless otherwise noted. Tributyltin hydride was prepared according to Szammer and Otvos and was freshly distilled before use.[22] Other reagents were purchased (Aldrich) or prepared by modification of literature methods; most amides were prepared by the addition of an acid chloride to an amine

(20) (a) Yoon, N. M.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 2927−2938. (b) Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1464−1472.

(21) This compound was readily identified by its TLC behavior (R_f = 0.75 using hex: EtOAc, 2:1; stains blue at rt using phosphomolybdic acid visualization) and ^1H NMR signature (δ 3.99, s, J_{Sn-H} = 15 Hz).

(22) Szammer, J.; Otvos, L. *Chem. Ind.* **1988**, 726.

under Schotten−Baumann type conditions (aqueous NaOH). Infrared spectra were recorded as neat liquids between NaCl plates. ^{1}H and ^{13}C NMR spectra were recorded at 250/63 MHz using $CDCl_3$ as solvent; tetramethylsilane (^{1}H, δ 0.0) or $CDCl_3$ (^{13}C, δ 77.0) were used as internal references. ^{1}H NMR data are presented as follows: chemical shift (multiplicity, integration, J in Hz). For ^{13}C NMR signals, coupling constants for satellites due to $^{117/119}$Sn (where discernible) are reported in parentheses in hertz; an asterisk (*) indicates signals that could be unequivocally attributed to the major rotamer. Mass spectra were recorded in CH_3CN/CH_2Cl_2 using electrospray ionization unless otherwise noted; for compounds containing Sn, data are reported for the most abundant isotope, ^{120}Sn. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

General Procedure for the Alkylation of Amides with (Iodomethyl)tributylstannane. To a cold (0 °C), stirred solution of the amide (20 mmol) in THF (40 mL) was added dropwise *n*-BuLi (13.1 mL of a 1.6 M solution in hexanes, 21 mmol). The solution was stirred at 0 °C for 10 min, and then DMF (40 mL) and (iodomethyl)tributylstannane (**3**, 9.48 g, 22 mmol) were added and the mixture was allowed to warm to room temperature. The reaction was stirred overnight and then diluted with hexane and water . The mixture was extracted with hexane, and the organic washings were combined, washed with brine, dried ($MgSO_4$), and evaporated to yield the crude product as an oil. Chromatography of the oil on silica gel with hexanes−EtOAc, 10:1, gave the pure compound.

***N*-Benzyl-*N*-[(tributylstannyl)methyl]benzamide (4a):** oil; IR (neat film) 1617, 729, 700 cm^{-1}; ^{1}H NMR δ 7.5−7.1 (m, 10 H), 4.51 (s, 2 H), 2.93 (s, 2 H, $^2J_{H-Sn}$ = 28 Hz), 1.7−1.2 (m, 12 H), 1.0−0.7 (m, 15 H); ^{13}C NMR δ 170.9, 136.9, 136.3, 129.3, 128.7, 128.4, 127.5, 126.9, 126.8, 56.1, 33.3, 29.0 (19 Hz), 27.4 (56 Hz), 13.7, 10.6 (316, 330 Hz); MS (EI) *m*/*z* 514 (M^+ − H, 1), 458 (100), 105 (69); HRMS (EI) Calcd for $C_{27}H_{41}NOSn$ (M^+ − C_4H_9): 458.1508, found: 458.1512. Anal. Calcd for $C_{27}H_{41}NOSn$: C, 63.05; H, 8.04; N, 2.72. Found: C, 62.97; H, 7.88; N, 2.71.

***N*-Methyl-*N*-[(tributylstannyl)methyl]benzamide (4b):** oil; IR (neat film) 1611 cm^{-1}; ^{1}H NMR δ 7.40 (s, 5 H), 3.08 (s, 2 H, $^2J_{H-Sn}$ = 20 Hz), 3.00 (s, 3 H), 1.7−1.1 (m, 12 H), 1.09−0.6 (m, 15 H); ^{13}C NMR δ 170.0, 136.5, 129.1, 128.2, 127.0, 40.7, 35.5, 29.1 (19 Hz), 27.4 (56 Hz), 13.7, 13.5, 10.4 (314, 327 Hz), 9.6; MS (ES) *m*/*z* 440 (M + 1, 100). Anal. Calcd for $C_{21}H_{37}NOSn$: C, 57.56; H, 8.51; N, 3.20. Found: C, 57.44; H, 8.38; N, 3.13.

***N*-Butyl-*N*-[(tributylstannyl)methyl]benzamide (4c):** oil; IR (neat film) 1613, 1577, 785, 699 cm^{-1}; ^{1}H NMR δ 7.5−7.3 (m, 5 H), 3.35−3.15 (t, 2 H, J = 7 Hz), 2.95 (s, 2 H, $^2J_{H-Sn}$ = 30 Hz), 1.7−1.1 (m, 16 H), 1.1−0.75 (m, 18 H); ^{13}C NMR δ 170.4, 136.8, 128.8, 128.2, 126.5, 52.1, 32.5, 30.5, 29.0 (18 Hz), 27.4 (56 Hz), 19.6, 13.6, 10.6 (331 Hz); MS (ES) *m*/*z* 482 (M + 1, 100). Anal. Calcd for $C_{24}H_{43}NOSn$: C, 60.02; H, 9.02; N, 2.92. Found: C, 60.20; H, 8.88; N, 3.18.

***N*-Isopropyl-*N*-[(tributylstannyl)methyl]benzamide (4d):** oil; IR (neat film) 1608 cm^{-1}; ^{1}H NMR δ 7.5−7.2 (m, 5 H), 4.12−3.92 (m, 1 H), 2.74 (s, 2 H, $^2J_{H-Sn}$ = 32 Hz), 1.7−1.25 (m, 12 H), 1.2−1.1 (d, 6 H, J = 7 Hz), 1.05−0.8 (m, 15 H); ^{13}C NMR: δ 170.0, 137.2, 128.8, 128.4, 126.2, 50.6, 29 (19 Hz), 27.4 (56 Hz), 25.6, 20.4, 13.6, 10.8 (319, 334 Hz); MS (ES) *m*/*z* 468 (M + 1, 100). Anal. Calcd for $C_{23}H_{41}NOSn$: C, 59.25; H, 8.86; N, 3.00. Found: C, 59.03; H, 8.64; N, 2.98.

***N*-Cyclohexyl-*N*-[(tributylstannyl)methyl]benzamide (4e):** oil; IR (neat film) 2911, 1608, 1449, 1371, 1126, 1072, 943, 893, 814, 697 cm^{-1}; ^{1}H NMR δ 7.5−7.2 (m, 5 H), 3.6−3.4 (m, 1 H), 2.8 (s, 2 H), 1.9−0.7 (m, 37 H); ^{13}C NMR δ 170.1, 137.1, 128.8, 128.3, 126.1, 59.2, 30.8, 29.1 (19 Hz), 27.4 (56 Hz), 25.4, 25.1, 13.6, 10.7); MS (ES) *m*/*z* 508 (M + 1, 100). Anal. Calcd for $C_{26}H_{45}NOSn$: C, 61.80; H, 8.78; N, 2.77. Found: C, 62.00; H, 8.70; N, 2.82.

***N*-(4-Methoxybenzyl)-*N*-[(tributylstannyl)methyl]benzamide (4f):** oil; IR (neat film) 1616, 1248 cm^{-1}; ^{1}H NMR δ 7.5−7.25 (m, 5 H), 7.11 (d, 2 H, J = 8.6 Hz), 6.89 (d, 2 H, J = 8.7 Hz), 4.43 (s, 2 H), 3.80 (s, 3 H), 2.93 (s, 2 H, J_{H-Sn} = 28 Hz), 1.72−1.12 (m, 12 H), 1.08−0.73 (m, 15 H); ^{13}C NMR δ 170.7, 159.0, 136.4, 129.3, 128.8, 128.4, 128.2, 126.8, 114.1, 55.5, 55.2, 33.0, 29.0 (19 Hz), 27.4 (57 Hz), 13.7, 10.6 (315, 330 Hz); MS (EI) *m*/*z* 544 (M^+ − H, 1) , 488 (51), 121 (100); HRMS (EI) Calcd for $C_{24}H_{34}NO_2Sn$ (M^+ − C_4H_9): 488.1613, found: 488.1630. Anal. Calcd for $C_{24}H_{43}NO_2Sn$: C, 61.78; H, 7.96; N, 2.57. Found: C, 61.70; H, 7.82; N, 2.58.

***N*-*tert*-Butyl-*N*-[(tributylstannyl)methyl]benzamide (4g):** oil; IR (neat film) 1630, 1582 cm^{-1}; ^{1}H NMR δ 7.35−7.2 (m, 5 H), 3.09 (s, 2 H, $^2J_{H-Sn}$ = 25.1 Hz), 1.6−1.2 (m, 12 H), 1.36 (s, 9 H), 1.05−0.75 (m, 15 H); ^{13}C NMR δ 171.2, 140.7, 128.2, 128.0, 126.2, 57.3, 33.5 (317.2, 332.3 Hz), 29.5, 28.8 (19.1 Hz), 27.2 (55.4 Hz), 13.4, 10.27 (306.5, 320.3 Hz); MS (ES) *m*/*z* 482 (M + 1, 100). Anal. Calcd for $C_{24}H_{43}NOSn$: C, 60.02; H, 9.02; N, 2.92. Found: C, 60.22; H, 8.89; N, 2.94.

***N*-Benzyl-*N*-[(tributylstannyl)methyl]-2-methylbenzamide (4h):** oil; IR (neat film) 1618, 1250, 1075 cm^{-1}; ^{1}H NMR δ 7.4−7.1 (m, 9 H), 4.38 (s, 2 H), 2.88 (s, 2 H), 2.34 (s, 3 H), 1.65−1.15 (m, 12 H), 1.05−0.75 (m, 15 H); ^{13}C NMR δ 170.1, 136.6, 136.4, 134.5, 130.4, 128.6, 128.6, 127.5, 127.3, 126.2, 125.7, 55.7, 31.7, 29.1 (27 Hz), 27.4 (57 Hz), 19.3, 13.7, 10.9 (320 Hz); MS (ES) *m*/*z* 530 (M + 1, 100), 472 (18); HRMS (EI) Calcd for $C_{24}H_{34}NOSn$ (M^+ − C_4H_9): 472.1664, found: 472.1645. Anal. Calcd for $C_{24}H_{43}NOSn$: C, 63.65; H, 8.20; N, 2.65. Found: C, 63.49; H, 7.96; N, 2.61.

***N*-Benzyl-*N*-[(tributylstannyl)methyl]-2-methoxybenzamide (4i):** oil; IR (neat film) 1615, 1247 cm^{-1}; ^{1}H NMR (500 MHz) δ 7.32−7.21 (m, 5 H), 7.17 (d, 2 H, J = 7.0 Hz), 6.93 (t, 1 H, J = 7.5 Hz), 6.86 (d, 1 H, J = 8.7 Hz), 4.36 (ABq, 2 H, $\Delta\nu$ = 15.6 Hz, J_{AB} = 14.1 Hz), 3.78 (s, 3 H), 2.89 (ABq, 2 H, $\Delta\nu$ = 29.9 Hz, J_{AB} = 13.2 Hz), 1.55−1.42 (m, 6 H), 1.31 (sextet, 6 H, J = 7.3 Hz), 0.92 (m, 6 H), 0.88 (t, 9 H, J = 7.3 Hz); ^{13}C NMR δ 168.4, 155.3, 137.1, 130.0, 128.4, 128.2, 127.4, 127.3, 126.3, 120.7, 110.9, 55.6, 55.1, 32.1, 29.0 (19.7 Hz), 27.4 (56.3 Hz), 13.6, 10.6 (315.7, 330.0 Hz); MS (ES) *m*/*z* 546 (M + 1, 100). Anal. Calcd for $C_{28}H_{43}NO_2Sn$: C, 61.78; H, 7.96; N, 2.57. Found: C, 61.93; H, 7.80; N, 2.53.

***N*-*tert*-Butyl-*N*-[(tributylstannyl)methyl]-2-methoxybenzamide (4j):** oil; IR (neat film) 1629, 1585, 871, 753 cm^{-1}; ^{1}H NMR δ 7.35−6.8 (m, 4 H), 3.83 (s, 3 H), 3.06 (s, 2 H, $^2J_{H-Sn}$ = 25 Hz), 1.8−1.1 (m, 12 H), 1.1−0.6 (m, 15 H); ^{13}C NMR δ 167.3, 154.9, 130.5, 129.2, 127.0, 120.3, 110.9, 58.0, 55.2, 32.8, 29.5, 29.0 (18 Hz), 27.4 (56 Hz), 13.6, 10.1 (308, 321 Hz); MS (EI) *m*/*z* 510 (M^+ − H, 1), 135 (100), 91 (94); HRMS (EI) Calcd for $C_{21}H_{36}NO_2Sn$ (M^+ − C_4H_9): 454.1770, found: 454.1768. Anal. Calcd $C_{21}H_{36}NO_2Sn$: C, 58.84; H, 8.89; N, 2.74. Found: C, 58.87; H, 8.67; N, 2.75.

***N*-[(Tributylstannyl)methyl]-2-pyrrolidinone (4k):** oil; IR (neat film) 1671 cm^{-1}; ^{1}H NMR δ 3.36 (t, 2 H, J = 7 Hz), 2.78 (s, 2 H, $^2J_{H-Sn}$ = 29.3 Hz), 2.35 (t, 2 H, J = 8 Hz), 1.97 (quint, 2 H), 1.7−1.2 (m, 12 H), 1.1-0.7 (m, 15 H); ^{13}C NMR δ 173.3, 50.9, 30.0, 28.6 (20 Hz), 27.3 (294, 281 Hz), 26.9 (56 Hz), 16.9, 13.2, 10.4 (318, 334 Hz); MS (ES) *m*/*z* 390 (M + 1, 100). Anal. Calcd for $C_{17}H_{35}NOSn$: C, 52.60; H, 9.09; N, 3.61. Found: C, 52.70; H, 9.19; N, 3.78.

***N*-Benzyl-*N*-[(tributylstannyl)methyl]acetamide (4l):** oil; IR (neat film) 1636, 1437, 1353, 1241 cm^{-1}; ^{1}H NMR δ 7.4−7.1 (m, 5 H), 4.52 (s, 2 H), 3.05 (s, 0.14 H), 2.78 (s, 1.86 H, $^2J_{H-Sn}$ = 30 Hz), 2.14 (s, 3 H), 1.7−1.1 (m, 12 H), 1.05−0.6 (m, 15 H); ^{13}C NMR δ 169.5, 136.8, 128.8*, 128.5, 128.0, 127.6*, 127.3, 126.5*, 55.5*, 51.0, 34.0, 33.7*, 29.0 (19 Hz), 27.4 (56 Hz), 21.9, 21.0*, 13.7, 10.7; MS (ES) *m*/*z* 454 (M + 1, 100). Anal. Calcd for $C_{22}H_{39}NOSn$: C, 58.43; H, 8.69; N, 3.10. Found: C, 58.09; H, 8.86; N, 3.04.

***N*-(4-Methoxybenzyl)-*N*-[(tributylstannyl)methyl]acetamide (4m):** oil; IR (neat film) 1630, 1513 cm^{-1}; ^{1}H NMR δ 7.2−7.0 (AA′ of AA′XX′, 2 H), 6.98−6.8 (XX′ of AA′XX′, 2 H), 4.57 (s, 0.08 H), 4.45 (s, 1.92 H), 3.84 (s, 3 H), 3.05 (s, 0.08 H), 2.57 (s, 1.92 H), 2.24 (s, 0.12 H), 2.16 (s, 2.88 H), 1.7−1.1 (m, 12 H), 1.0−0.5 (m, 15 H); ^{13}C NMR δ 169.4, 159.1, 129.4, 128.7, 127.9, 114.2, 113.9, 55.3*, 54.9, 33.5, 29.1 (19 Hz), 27.4, 21.1, 13.7, 10.7; MS (ES) *m*/*z* 484 (M + 1, 100). Anal. Calcd for $C_{23}H_{41}NO_2Sn$: C, 57.28; H, 8.57; N, 2.90. Found: C, 57.27; H, 8.48; N, 2.91.

***N*-Methyl-*N*-[(tributylstannyl)methyl]formamide (4n):** oil; IR (neat film) 1666 cm^{-1}; ^{1}H NMR δ 8.03 (s, 0.1 H), 7.95 (s, 0.9 H), 3.14 (s, 0.3 H), 3.06 (s, 0.2 H), 2.95 (s, 2.7 H), 2.86 (s, 1.8 H, $^2J_{H-Sn}$ = 30 Hz), 1.7−1.15 (m, 12 H), 1.1−0.7 (m, 15 H); ^{13}C NMR δ 160.9, 37.7, 30.4, 28.8, 27.1 (56 Hz), 13.4, 10.3*, 9.4; MS (ES) *m*/*z* 364 (M + 1, 19). Anal. Calcd for $C_{15}H_{33}NOSn$: C, 49.75; H, 9.19; N, 3.87. Found: C, 49.71; H, 9.30; N, 3.94.

***N*-Benzyl-*N*-[(tributylstannyl)methyl]formamide (4o):** oil; IR (neat film) 1662 cm^{-1}; ^{1}H NMR δ 8.25 (s, 1 H), 7.45−7.15 (m, 5 H), 4.50 (s, 0.2 H), 4.35 (s, 1.8 H), 2.93 (s, 0.2 H), 2.66 (s,

1.8 H, $^2J_{H-Sn}$ = 27.5 Hz), 1.7−1.1 (m, 12 H), 1.05−0.6 (m, 15 H); ^{13}C NMR δ 162.2, 161.5*, 135.9, 128.6*, 128.4, 127.8, 127.3, 54.7*, 49.0, 28.8 (19.8 Hz), 28.2, 27.1 (57 Hz), 13.5, 10.5* (319, 334 Hz), 9.5; MS (ES) *m/z* 440 (M + 1, 13), 382 (100). Anal. Calcd for $C_{21}H_{37}NOSn$: C, 57.56; H, 8.51; N, 3.20. Found: C, 57.66; H, 8.33; N, 3.21.

General Procedure for the Reduction of α-Amidoorgano Stannanes with Lithium Aluminum Hydride. To a cold (0 °C), stirred solution of α-amidoorgano stannane (1 mmol) in Et_2O (15 mL) was added in one portion, solid $LiAlH_4$ (56.9 mg, 1.5 mmol). The reaction mixture was heated to reflux for 30 min, cooled to room temperature, and quenched with $Na_2SO_4 \cdot 10H_2O$.[23] Solids were removed by filtration through Celite, and the solvent was evaporated. The residue was subjected to column chromatography (hexanes−ethyl acetate = 10:1) to afford the pure product.

General Procedure for the Reduction of α-Amidoorgano Stannanes with Alane. To a cold (0 °C), stirred solution of $LiAlH_4$ (1.0 mL of a 1.0 M solution in THF, 1.0 mmol) in 5 mL of THF was added H_2SO_4 (0.5 mL of a 1 M solution in Et_2O, 0.5 mmol). The solution was allowed to warm to room temperature and was stirred for 30 min. The solution was then cooled (0 °C), and the α-amidoorgano stannane (0.5 mmol) was added via syringe (neat). The reaction mixture was allowed to warm to room temperature for 30 min and then quenched with $Na_2SO_4 \cdot 10H_2O$. Subsequent workup and chromatography as described for reductions with $LiAlH_4$ afforded the indicated products.

[(*N*,*N*-Dibenzylamino)methyl]tributylstannane (5a): oil; IR (neat film) 2955, 1602, 1455 cm^{-1}; ^{1}H NMR δ 7.4−7.2 (m, 10 H), 3.46 (s, 4 H), 2.55 (s, 2 H, $^2J_{H-Sn}$ = 23 Hz), 1.6−1.2 (m, 12 H), 1.0−0.7 (m, 15 H); ^{13}C NMR δ 140.0, 128.7, 128.1, 126.8, 62.7 (28 Hz), 42.9, 29.3 (20 Hz), 27.5 (53 Hz), 13.7, 10.1 (287, 300 Hz); MS (EI) *m/z* 500 (M^+ − H, 1.7), 210 (100), 91 (96). Anal. Calcd for $C_{27}H_{43}NSn$: C, 64.82; H, 8.66; N, 2.80. Found: C, 65.00; H, 8.46; N, 2.95.

[(*N*-Benzyl-*N*-methylamino)methyl]tributylstannane (5b): oil; IR (neat film) 2955, 1455 cm^{-1}; ^{1}H NMR δ 7.4−7.2 (m, 5 H), 3.39 (s, 2 H), 2.5 (s, 2 H, $^2J_{H-Sn}$ = 22 Hz), 2.17 (s, 3 H), 1.7−1.2 (m, 12 H), 1.05−0.7 (m, 15 H); ^{13}C NMR δ 139.6, 128.8, 128.1, 126.8, 66.1 (35.5 Hz), 46.4, 46.3, 29.2 (20 Hz), 27.4 (53 Hz), 13.7, 10.0 (288, 302 Hz).

[(*N*-Benzyl-*N*-butylamino)methyl]tributylstannane (5c): oil; IR (neat film) 2956, 1457 cm^{-1}; ^{1}H NMR δ 7.3−7.15 (m, 5 H), 3.42 (s, 2 H), 2.61 (s, 2 H, $^2J_{H-Sn}$ = 18 Hz), 2.28 (t, 2 H, *J* = 7 Hz), 1.7−1.1 (m, 16 H), 1.05−0.7 (m, 18 H); ^{13}C NMR δ 128.7, 128.1, 126.7, 63.7, 58.0, 43.9, 30.5, 29.9, 29.3 (14 Hz), 27.5 (52 Hz), 20.5, 14.1, 13.7, 10.3; MS (ES) *m/z* 468 (M + 1, 100). Anal. Calcd for $C_{24}H_{45}NSn$: C, 61.82; H, 9.73; N, 3.00. Found: C, 61.63; H, 9.63; N, 3.13.

[(*N*-Benzyl-*N*-isopropylamino)methyl]tributylstannane (5d): oil; IR (neat film) 2929, 1455 cm^{-1}; ^{1}H NMR δ 7.4−7.2 (m, 5 H), 3.46 (s, 2 H), 2.76 (septet, 1 H, *J* = 7 Hz), 2.47 (s, 2 H, $^2J_{H-Sn}$ = 25 Hz), 1.6−1.2 (m, 12 H), 1.03 (d, 6 H, *J* = 7 Hz), 1.2−0.7 (m, 15 H); ^{13}C NMR δ 141.3, 128.5, 128.0, 126.4, 57.3, 52.6, 37.6, 29.3, 27.5 (50 Hz), 17.8, 13.7, 9.6 (291, 305 Hz); MS (EI) *m/z* 452 (M^+ − H, 2), 162 (100), 91 (98); HRMS (EI) Calcd for $C_{23}H_{43}NSn$ (M^+): 453.2420, found: 453.2417. Anal. Calcd for $C_{23}H_{43}NSn$: C, 61.08; H, 9.58; N, 3.10. Found: C, 61.20; H, 9.58; N, 3.13.

[(*N*-Benzyl-*N*-cyclohexylamino)methyl]tributylstannane (5e): oil; IR (neat film) 2926, 1653, 1453 cm^{-1}; ^{1}H NMR δ 7.4−7.1 (m, 5 H), 3.52 (s, 2 H), 2.54 (s, 2 H, $^2J_{H-Sn}$ = 23 Hz), 2.40−2.25 (m, 1 H), 1.95−0.6 (m, 37 H); ^{13}C NMR δ 141.5, 128.4, 128.1, 128.0, 126.3, 62.6, 57.6, 38.7, 29.2 (19 Hz), 28.8, 27.5 (52 Hz), 26.5, 26.2, 13.7, 9.7; MS (ES) *m/z* 494 (M + 1, 100), 452 (10). Anal. Calcd for $C_{26}H_{47}NSn$: C, 63.43, H, 9.62; N, 2.84. Found: C, 63.39; H, 9.20; N, 2.88.

[(*N*-Benzyl-*N*-(4-methoxybenzyl)amino)methyl]tributylstannane (5f): oil; IR (neat film) 2955, 1611, 1455 cm^{-1}; ^{1}H NMR δ 7.4−7.15 (m, 7 H), 6.84 (d, 2 H, *J* = 8.7 Hz), 3.77 (s, 3 H), 3.44 (s, 2 H), 3.40 (s, 2 H), 2.54 (s, 2 H, J_{H-Sn} = 25.5 Hz), 1.7−1.17 (m, 12 H), 1.05−0.7 (m, 15 H); ^{13}C NMR δ 158.6, 140.1, 132.0, 129.8, 128.7, 128.1, 126.7, 113.6, 62.4, 61.9, 55.2, 42.79, 29.2 (19 Hz), 27.5 (53 Hz), 13.7, 10.0 (302 Hz); MS (ES) *m/z* 532 (M + 1, 100). Anal. Calcd for $C_{28}H_{43}NOSn$: C, 63.41; H, 8.55; N, 2.64. Found: C, 63.32; H, 8.73; N, 2.67.

[(*N*-Benzyl-*N*-*tert*-butylamino)methyl]tributylstannane (5g): oil; IR (neat film) 1458, 1195 cm^{-1}; ^{1}H NMR δ 7.35−7.15 (m, 5 H), 3.56 (s, 2 H), 2.56 (s, 2 H, $^2J_{H-Sn}$ = 20.3 Hz), 1.5−1.15 (m, 12 H), 1.12 (s, 9 H), 0.84 (t, 9 H, *J* = 7.0 Hz), 0.69 (m, 6 H); ^{13}C NMR δ 142.5, 128.0, 126.3, 56.8, 55.2, 36.6 (355.8, 372.8 Hz), 29.2 (18.7 Hz), 27.4 (52.1 Hz), 26.7, 13.6, 10.0 (277.6, 290.7 Hz); MS (ES) *m/z* 468 (M + 1, 100). Anal. Calcd for $C_{24}H_{45}NSn$: C, 61.82; H, 9.73; N, 3.00. Found: C, 61.45 ; H, 9.87 ; N, 2.84.

[[*N*-Benzyl-*N*-(2-methylbenzyl)amino]methyl]tributylstannane (5h): oil; IR (neat film) 3026, 2910, 1457 cm^{-1}; ^{1}H NMR δ 7.4−7.1 (m, 9 H), 3.46 (s, 2 H), 2.56 (s, 2 H, $^2J_{H-Sn}$ = 20 Hz), 2.30 (s, 3 H), 1.6−1.2 (m, 12 H), 1.1−0.8 (m, 15 H); ^{13}C NMR δ 140.1, 137.7, 137.2, 130.2, 129.6, 128.9, 128.2, 126.9, 126.9, 125.7, 62.9 (20 Hz), 20.9 (54 Hz), 19.5, 13.8, 10.3 (283, 297 Hz); MS (EI) *m/z* 515 (M^+, 4), 224 (90), 105 (100), 91 (25). Anal. Calcd for $C_{28}H_{45}NSn$: C, 65.38; H, 8.82; N, 2.72. Found: C, 65.44; H, 8.69; N, 2.83.

[[*N*-Benzyl-*N*-(2-methoxybenzyl)amino]methyl]tributylstannane (5i): oil; IR (neat film) 1595, 1242 cm^{-1}; ^{1}H NMR δ 7.52 (d, 1 H, *J* = 7.5 Hz), 7.4−7.1 (m, 6 H), 6.93 (t, 1 H, *J* = 7.4 Hz), 6.80 (d, 1 H, *J* = 8.1 Hz), 3.76 (s, 3 H), 3.51 (s, 2 H), 3.50 (s, 2 H), 2.61 (s, 2 H, $^2J_{H-Sn}$ = 19.9 Hz), 1.6−1.2 (m, 12 H), 1.05−0.75 (m, 15 H); ^{13}C NMR δ 157.7, 140.3, 129.8, 128.6, 128.1, 128.0, 127.4, 126.6, 120.4, 110.2, 62.9 (27.7 Hz), 55.8 (27.1 Hz), 55.1, 43.3 (322.4, 337.3 Hz), 29.2 (19.5 Hz), 27.4 (52.6 Hz), 13.6, 10.1 (283.5, 296.5 Hz); MS (ES) *m/z* 532 (M + 1, 100). Anal. Calcd for $C_{28}H_{45}NOSn$: C, 63.29; H, 8.54; N, 2.64. Found: C, 63.47; H, 8.38; N, 2.64.

[[*N*-*tert*-Butyl-*N*-(2-methoxybenzyl)amino]methyl]tributylstannane (5j): oil; IR (neat film) 2957, 2852, 1591 cm^{-1}; ^{1}H NMR δ 7.60 (d, 1 H, *J* = 6.9 Hz), 7.16 (t, 1 H, *J* = 7.5 Hz), 6.92, (t, 1 H, *J* = 7.4 Hz), 6.79 (d, 1 H, *J* = 8.1 Hz), 3.81 (s, 3 H), 3.59 (s, 2 H), 2.62 (s, 2 H, $^2J_{H-Sn}$ = 23 Hz), 1.5−1.1 (m, 12 H), 1.12 (s, 9 H), 1.0−0.5 (m, 15 H); ^{13}C NMR δ 157.0, 130.6, 129.0, 126.8, 120.3, 109.5, 55.6, 55.0, 50.6, 37.0, 29.2 (19 Hz), 27.5 (53 Hz), 26.7, 13.7, 9.9 (279, 293 Hz); MS (ES) *m/z* 498 (M + 1, 100), 454 (78), 332 (82). Anal. Calcd for $C_{25}H_{47}NSn$: C, 60.50; H, 9.54; N, 2.82. Found: C, 60.30; H, 9.39; N, 2.70.

(1-Pyrrolidinylmethyl)tributylstannane (5k): oil; IR (neat film) 2921, 1459, 1377 cm^{-1}; ^{1}H NMR δ 2.59 (s, 2 H, $^2J_{H-Sn}$ = 25.2 Hz), 2.48 (unres t, 4 H), 1.81 (m, 4 H), 1.7−1.2 (m, 12 H), 1.1−0.7 (m, 15 H); ^{13}C NMR δ 58.2 (30 Hz), 42.0, 29.1 (19 Hz), 27.3 (54 Hz), 24.2, 13.6, 9.9 (306 Hz); MS (ES) *m/z* 376 (M + 1, 100). Anal. Calcd for $C_{17}H_{37}NSn$: C, 54.57; H, 9.97; N, 3.74. Found: C, 54.33; H, 9.79; N, 3.56.

[(*N*-Benzyl-*N*-ethylamino)methyl]tributylstannane (5l): oil; IR (neat film) 2933, 1646, 1457 cm^{-1}; ^{1}H NMR δ 7.35−7.2 (m, 5 H), 3.43 (s, 2 H), 2.62 (s, 2 H, $^2J_{H-Sn}$ = 19.6 Hz), 2.34 (q, 2 H, *J* = 7.1 Hz), 1.7−1.2 (m, 12 H), 1.05 (t, 3 H, *J* = 7.1 Hz), 0.95−0.7 (m, 15 H); ^{13}C NMR δ 140.1, 128.7, 128.1, 126.7, 62.6 (28 Hz), 51.1 (28 Hz), 42.5 (337, 358 Hz), 29.3 (20 Hz), 27.5 (53 Hz), 13.7, 12.7, 10.2 (280, 293 Hz); MS (ES) *m/z* 440 (M + 1, 100). Anal. Calcd for $C_{22}H_{41}NSn$: C, 60.29; H, 9.43; N, 3.20. Found: C, 60.44; H, 9.55; N, 3.35.

[[*N*-Ethyl-*N*-(4-methoxybenzyl)amino]methyl]tributylstannane (5m): oil; IR (neat film) 2956, 1607 cm^{-1}; ^{1}H NMR δ 7.3−7.15 (AA′ of AA′XX′, 2 H), 6.95−6.75 (XX′ of AA′XX′, 2 H), 3.78 (s, 3 H), 3.36 (s, 2 H), 2.62 (s, 2 H, $^2J_{H-Sn}$ = 19.4 Hz), 2.32 (q, 2 H, *J* = 7.1 Hz), 1.75−1.2 (m, 12 H), 1.15−1.0 (t, 3 H, *J* = 7.1 Hz), 1.0−0.7 (m, 15 H); ^{13}C NMR δ 158.5, 132.0, 129.8, 113.5, 61.9 (33 Hz), 55.2, 51.6 (35 Hz), 42.4, 29.3 (20 Hz), 27.5 (50 Hz), 13.7, 12.7, 10.3; MS (ES) *m/z* 470 (M + 1, 100). Anal. Calcd for $C_{23}H_{43}NOSn$: C, 58.99; H, 9.26; N, 2.99. Found: C, 58.63; H, 9.36; N, 2.94.

[(*N*,*N*-Dimethylamino)methyl]tributylstannane (1):[2] oil; ^{1}H NMR δ 2.48 (s, 2 H, $^2J_{H-Sn}$ = 22 Hz), 2.21 (s, 6 H), 1.75−1.1 (m, 12 H), 1.08−0.6 (m, 15 H); ^{13}C NMR δ 49.4 (32 Hz), 48.2, 29.7 (20 Hz), 27.3 (54 Hz), 13.5, 9.8 (290, 303 Hz).

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