Efficient Synthesis of 1-(Trialkylstannyl)- and 1-(Triarylstannyl)bicyclo[1.1.1]pentanes

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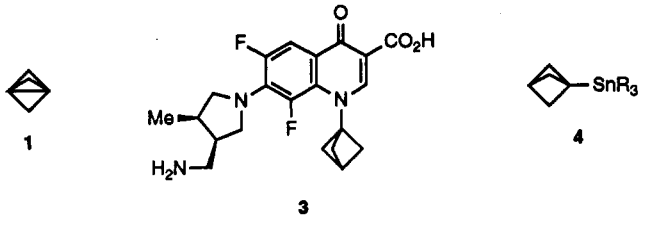
The ready availability of [1.1.1]propellane (1) from 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (2) on a preparative scale[1] has led to increased interest in its reactivity profile.[2] Of particular interest to us was the utilization of 1 to access bridgehead-substituted bicyclo[1.1.1]pentanes that could be further elaborated into novel quinolone antibacterial agents, a goal that was ultimately realized.[3] The salient structural feature of these quinolones, exemplified by U-87947 (3), is their appended bicyclo[1.1.1]-pent-1-yl subunit at N-1. U-87947 exhibits potent activity against aerobic Gram-positive and Gram-negative bacteria and also anaerobic organisms.[4]

One aspect of our research efforts in this area focused on the preparation of 1-(trialkylstannyl)- and 1-(triarylstannyl)bicyclo[1.1.1]pentanes (4).[5] We reasoned that the bridgehead C–Sn bond of 4 would be amenable to further synthetic modification, perhaps allowing access to 1-substituted bicyclo[1.1.1]pentanes suitable for further elaboration to quinolones such as 3. In contemplating synthetic routes to the stannanes 4, we were cognizant of an earlier preparation of 1-(tributylstannyl)bicyclo[1.1.1]pentane (**4b**) by Wiberg and Waddell which involved the reaction of 1-bicyclo[1.1.1]pentyllithium, prepared by reductive lithiation of 1-bicyclo[1.1.1]pentyl phenyl sulfide (5), with tributyltin chloride.[6] The primary limitation of this method is the phenyllithium contaminant generated during formation of the 1-bicyclo[1.1.1]pentyllithium.



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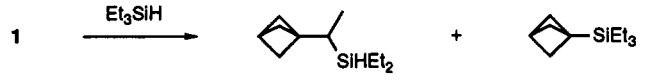
We speculated that a shorter route to 4, involving the addition of a trialkyl- or triaryltin hydride to [1.1.1]-propellane (1), might be feasible. During the course of our investigations (*vide infra*), a preparation of 1-(tributylstannyl)bicyclo[1.1.1]pentane (**4b**) from 1 and tributyltin hydride was described by Zefirov and co-workers.[7] However, their reported yield of 28% for this transformation would not be satisfactory for any potential applications of **4b** to the synthesis of antibacterial agents such as 3. The development of a high-yield process for the direct conversion of 1 to stannanes 4 remained a viable goal.

In one respect the literature offered little hope, a priori, that a high yield hydrostannation could be achieved, since it was previously reported that hydrosilylation of 1 with triethylsilane afforded a 3:1 mixture of the bicyclo[1.1.1]-pentanes 6 and 7.[2]



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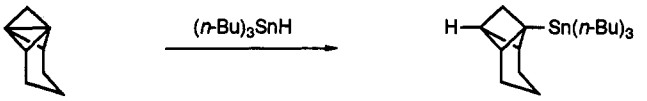
A more encouraging result was described by Belzner and Szeimies wherein tributyltin hydride was successfully added to the central bond of tetracyclo[5.1.0.0^{1,6}.0^{2,7}]octane (8) to furnish the stannane 9 in 72% isolated yield.[8] However, the applicability of this approach to the structurally simpler stannane 4 is further complicated by the propensity of [1.1.1]propellane (1) to undergo anion- and radical-induced polymerization to give [*n*]staffanes.[9] The result reported by Zefirov and co-workers (*vide supra*) also suggests that the addition of tin hydrides to 1 is not a straightforward process.[7] In this paper we report our initial investigations into the preparation of stannanes of structure 4.



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Results and Discussion

We initially prepared propellane 1 from the crystalline dibromocyclopropane 2,[1,9] employing methyllithium as the base in a manner essentially identical to that described by Szeimies[1] and Michl[10] (see Scheme I). Subsequent vacuum transfer of the volatiles to a second chilled flask provided a salt-free solution of crude 1, which was treated with tributyltin hydride (1.5 equiv based on 2), catalytic *tert*-butyl peroxide and light to give a crude product. An examination of the ^{1}H-NMR spectrum of this material revealed that only one bicyclo[1.1.1]pentane-containing material was present. Chromatographic purification over silica gel, eluting with hexane, afforded the targeted adduct **4b**, but in only 15% yield. That **4b** was obtained was clearly evidenced by the characteristic bicyclo[1.1.1]-pentane ^{1}H-NMR fingerprint of two "singlets" at δ 2.88 (1H, methine proton) and 1.97 (6H, methylene protons). A closer examination revealed the previously reported coupling of the bridgehead proton to each of the three magnetic isotopes of tin [J(^{119}Sn^{1}H) = 179.2 Hz, J(^{117}Sn^{1}H) = 171.2 Hz, J(^{115}Sn^{1}H) = 156.2 Hz].[6]

(1) Semmler, K.; Szeimies, G.; Belzner, J. *J. Am. Chem. Soc.* **1985**, *107*, 6410.
(2) Wiberg, K. B.; Waddell, S. T. *J. Am. Chem. Soc.* **1990**, *112*, 2194.
(3) Barbachyn, M. R. Patent Publication No. WO-9006307, filed 1989. Barbachyn, M. R.; Hutchinson, D. K.; Reid, R. J.; Toops, D. S. *Abstracts of Papers*, 31st Interscience Conference on Antimicrobial Agents and Chemotherapy, Chicago, IL, Oct 1991; American Society of Microbiology: Washington, DC, 1991; Abstract No. 1456.
(4) Barbachyn, M. R.; Hutchinson, D. K.; Toops, D. S.; Reid, R. J.; Zurenko, G. E.; Yagi, B. H.; Schaadt, R. D.; Allison, J. W. *Bioorg. Med. Chem. Lett.* **1993**, *3*, 671.
(5) A preliminary account of this chemistry has been presented: Toops, D. S.; Barbachyn, M. R. *Abstracts of Papers*, 203rd National Meeting of the American Chemical Society, San Francisco, CA, April, 1992; American Chemical Society: Washington, DC, 1992; ORGN 50.
(6) Wiberg, K. B.; Waddell, S. T. *Tetrahedron Lett.* **1988**, *29*, 289.
(7) Zefirov, N. S.; Surmina, L. S.; Sadovaya, N. K.; Blokhin, A. V.; Tyurekhodzhaeva, M. A.; Bubnov, Y. N.; Lavrinovich, L. I.; Ignatenko, A. V.; Grishin, Y. K.; Zelenkina, O. A.; Kolotyrkina, N. G.; Kudrevich, S. V.; Kozmin, A. S. *Zh. Org. Khim.* **1990**, *26*, 2317.
(8) Belzner, J.; Szeimies, G. *Tetrahedron Lett.* **1987**, *28*, 3099.
(9) Kaszynski, P.; Friedli, A. C.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 601.
(10) Kaszynski, P.; Michl, J. *J. Org. Chem.* **1988**, *53*, 4593.

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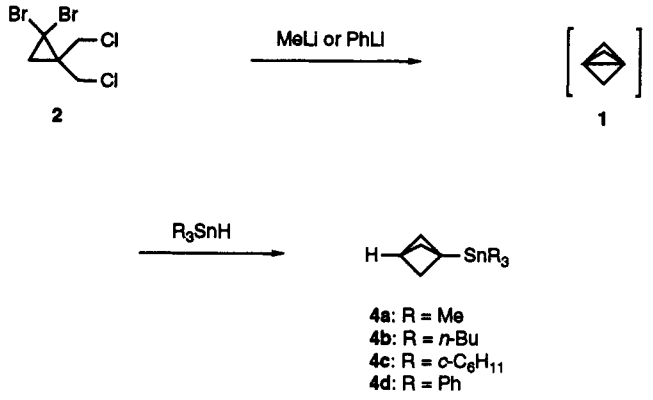
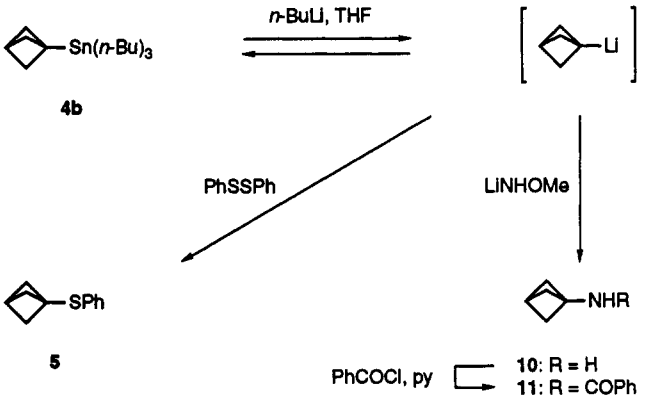
Scheme I



We suspected that the methyl bromide generated during the formation of 1 was competing with 1 for the nascent tributyltin radical. To circumvent this perceived problem we switched the base to phenyllithium, reasoning that the higher boiling bromobenzene generated during the formation of 1 would remain behind when the volatiles were vacuum transferred. In early runs the stoichiometry was also altered so that tributyltin hydride was the limiting reagent (5 equiv of 2 and 1 equiv of tributyltin hydride). In a gratifying result, a 93% isolated yield of **4b** was realized after silica gel chromatography. In an essentially identical manner, the tricyclohexyl derivative **4c** and triphenyl congener **4d** were prepared in 63% and 68% yield, respectively. While these results represented a major advance over previous syntheses of 4, this protocol was still deemed inefficient in terms of the excess **2** employed, along with the attendant excess of phenyllithium used to generate the intermediate propellane 1. Subsequently, we found that the stoichiometry could be further altered (1.3 equiv of **2** and 1 equiv of trialkyl- or triaryltin hydride), allowing for a more economical reaction with minimal impact on the isolated yields of 4 (*vide infra*). We also determined that the recently described reversed-phase (C-18) flash chromatography procedure of Farina was the method of choice for purification of these very hydrophobic compounds.[11] Using the latter experimental and purification protocols (see general procedure) led to 56–68% yields of **4b-d** in analytically pure form. Compound **4b** was isolated as a colorless oil, while **4c** and **4d** were white solids with mp 132–133 and 126–127 °C, respectively. Crude **4a**, obtained in 59% yield and reasonably clean by ^{1}H-NMR and MS analysis, was not stable under the C-18 chromatography conditions, apparently suffering destannylation.[12]

The long-range bridgehead–bridgehead coupling constants of these stannanes merit further comment. The four-bond ^{1}H to ^{119}Sn coupling constants for **4a-d** are 195.9, 179.2, 166.5, and 225.9 Hz, respectively. The value for **4d** is the largest yet reported for this type of long-range coupling constant. Barfield and Della have shown that nonbonded interactions are the dominant factor in determining the magnitude of such coupling constants in bicyclic systems.[13] Their results also suggest an exponential increase in the ^{119,117,115}Sn^{1}H coupling constants will be observed as the bridgehead carbons become closer

Scheme II



together. MNDO- and MM2-based modeling studies of 4 conducted to probe this notion indeed revealed a slight decrease in the predicted bridgehead separation in the order **4c > 4b > 4a > 4d**.[14] While these results are in accord with the observed coupling constants in a relative sense, a more satisfactory explanation remains to be elucidated.

The 1-(trialkylstannyl)- and 1-(triarylstannyl)bicyclo[1.1.1]pentanes 4 are amenable to further modification.[5] Herein we comment on our preliminary investigations into the transmetallation of stannanes 4 (see Scheme II). A successful transmetallation of 4 with an appropriate alkyllithium would allow rapid access, via the intermediacy of 1-bicyclo[1.1.1]pentyllithium,[6] to bridgehead-functionalized bicyclo[1.1.1]pentanes. Our hope was that the unique electronic characteristics of the bridgehead carbon atom of 4, with its pronounced s character,[15] would impart a reactivity similar to that observed for aromatic trialkylstannanes. Due to stability issues (*vide supra*), compound **4a** has not been examined to date in this transmetalation reaction. However, treatment of **4b** with *n*-butyllithium under equilibrating conditions (THF, −10 °C, 24 h), followed by a phenyl disulfide quench, afforded a 40% isolated yield of the known 1-bicyclo[1.1.1]pentyl phenyl sulfide (**5**),[1,2] along with butyl phenyl sulfide and some recovered **4b**. Alternative conditions generally provided reduced yields of the desired sulfide. Stannanes **4c** and **4d** were completely inert under these reaction conditions, apparently due to steric congestion about the tin atom. Direct amination of the 1-bicyclo[1.1.1]pentyllithium-containing equilibrium mixture derived from **4b**, employing the amination protocol devised by Beak,[16] was also examined. A measure of success was achieved in that the targeted 1-bicyclo[1.1.1]pentylamine (**10**)[17] was obtained, albeit in low yield, and characterized as its benzamide derivative **11** (24% isolated yield). Compounds **5** and **10** are pivotal intermediates for the synthesis of potent quinolone antibacterial agents such as U-87947 (**3**).[4] Further investigations to elucidate the utility of stannanes

(11) Farina, V. *J. Org. Chem.* **1991**, *56*, 4985.
(12) ^{1}H-NMR analysis of chromatographed **4a** revealed partial destannylation and the generation of uncharacterized product(s). For another example of destannylation, involving unsaturated stannanes, see: Behling, J. R.; Ng, J. S.; Babiak, K. A.; Campbell, A. L.; Elsworth, E.; Lipshutz, B. H. *Tetrahedron Lett.* **1989**, *30*, 27.
(13) Barfield, M.; Della, E. W.; Pigou, P. E.; Walter, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 3549. Barfield, M.; Della, E. W.; Pigou, P. E. *Ibid.* **1984**, *106*, 5051.
(14) The magnitude of the bridgehead–bridgehead separation varied only ca. 0.02 Å for **4a-d**. MNDO(RHF)-based geometry optimizations were conducted with the MOPAC program. Due to the lack of MM2 parameters for Sn, MM2 modeling of **4a-d** was done with the Sn atom replaced with Si.
(15) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001.
(16) Beak, P.; Basha, A.; Kokko, B.; Loo, D. *J. Am. Chem. Soc.* **1986**, *108*, 6016 and references cited therein.
(17) Wiberg, K. B.; Williams, V. Z., Jr. *J. Org. Chem.* **1970**, *35*, 369.

4 in preparing other bridgehead-substituted bicyclo[1.1.1]-pentanes are in progress and will be reported in due course.[5]

Experimental Section

Melting points were determined on a capillary apparatus and are uncorrected. ^{1}H-NMR spectra were recorded at 300 MHz in $CDCl_3$ with chloroform or TMS as internal standards. Coupling constants (J) are reported in Hz. Electron impact (EI) mass spectra were obtained with an ionization voltage of 70 eV. Data are reported in the form m/e (relative intensity). All moisture-sensitive reactions were conducted under a nitrogen atmosphere in oven- or flame-dried glassware. Unless specified, all commercially available solvents and reagents were used without further purification. THF was distilled under nitrogen from sodium benzophenone ketyl prior to use. Brine refers to a saturated aqueous sodium chloride solution. Solvent removal was accomplished by a rotary evaporator operating at house vacuum (40–50 Torr). Crude products were purified by column chromatography over silica gel (EM Science, 230–400 mesh ASTM) or preparative C-18 (Waters, 55–105 μm). Alternatively, smaller scale purifications were accomplished by preparative TLC (Analtech silica gel GF plates, 20 × 20 cm, 1000 μm) or radial chromatography (Harrison Research Chromatotron equipped with Analtech silica gel GF radial plate, 1000 μm). Silica gel (Analtech silica gel GF, 1 × 3 in., 250-μm thickness) or C-18 reversed-phase (Whatman $MKC_{18}F$, 1 × 3 in., 200-μm thickness) plates were utilized for TLC analyses.

General Procedure for the Preparation of 1-(Trialkylstannyl)- and 1-(Triarylstannyl)bicyclo[1.1.1]pentanes 4. A mixture of **2**[1,9] (2.50 g, 8.42 mmol) and anhydrous diethyl ether (20 mL) was placed in a flask equipped with a magnetic stirrer, septum, and a side arm connected to a second flask outfitted with magnetic stirrer, septum, and dry ice condenser. The solution was cooled to −60 °C with a dry ice/chloroform bath and treated with phenyllithium (10.3 mL or 18.50 mmol of a 1.8 M solution in cyclohexane/diethyl ether, Aldrich) via cannula over 7 min. When the addition was completed, the mixture was stirred at −55 °C for 20 min and then allowed to warm to ambient temperature over 15 min. At this point, the volatiles were vacuum transferred under house vacuum (40–50 Torr) to the second flask which was cooled with a dry ice/acetone bath. When the transfer was completed, the flask was flushed with nitrogen and then the trialkyl- or triaryltin hydride (6.31 mmol) was introduced via syringe. Catalytic *tert*-butyl peroxide (0.080 g, 100 μL, 0.54 mmol) was added to the solution, the cooling bath removed, and the mixture irradiated with a sun lamp (General Electric Model No. RSM, 275W) for 30 min. After being stirred overnight at ambient temperature, the reaction mixture was concentrated by rotary evaporation to an oil and chromatographed over bulk C-18,[11] eluting with 20% CH_2Cl_2 in CH_3CN. Appropriate fractions, based on silica gel or reversed-phase C-18 TLC analysis (visualized by staining with iodine or alternatively, in the case of **4d**, illumination with short-wave UV light), were combined and concentrated by rotary evaporation and judicial high vacuum to provide, in the case of **4b-d**, analytically pure products. Compound **4a**, obtained in reasonable purity in crude form, proved to be unstable under these chromatogrpahic conditions, and in fact slowly decomposed upon standing in the cold. All reported yields for **4a-d** are based on the limiting trialkyl- or triaryltin hydride reagent.

1-(Trimethylstannyl)bicyclo[1.1.1]pentane (4a). Crude **4a** was obtained in 59% yield as a hazy, colorless oil: ^{1}H NMR δ 2.86 [s, 1H, with tin magnetic isotope satellites, $J(^{119}Sn^1H)$, $(^{117}Sn^1H)$ = 195.9, 187.2], 1.93 (s, 6H), 0.00 [s, 9H, with tin magnetic isotope satellites, $J(^{119}Sn^1H)$, $(^{117}Sn^1H)$ = 53.2, 51.0]; MS(EI) 232 (M^+, 0.2), 217 (25), 187 (24), 165 ($M^+ - 67$, 100), 135 (51); HRMS (EI) calcd for $C_8H_{16}Sn$ 232.0271, found 232.0274.

1-(Tri-*n*-butylstannyl)bicyclo[1.1.1]pentane (4b). Stannane **4b** was obtained in 60% isolated yield after reversed-phase chromatography as a colorless oil: ^{1}H NMR δ 2.88 [s, 1H, with tin magnetic isotope satellites, $J(^{119}Sn^1H)$, $(^{117}Sn^1H)$, $(^{115}Sn^1H)$ = 179.2, 171.2, 156.2], 1.97 (s, 6H), 1.54-1.42 (m, 6H), 1.27 (apparent sextet, 6H), 0.89 (t, J = 7.2, 9H), 0.79 [t, J = 7.9, 6H, with tin magnetic isotope satellites, $J(^{119}Sn^1H)$, $(^{117}Sn^1H)$ = 50.5, 48.4]; IR (neat) 2956, 2922, 2903, 2868, 2857, 1465, 1457, 1376, 1212, 1072, 689, 661 cm^{-1}; MS (FAB) 359, 357, 355 ($M + H^+$). Anal. Calcd for $C_{17}H_{34}Sn$: C, 57.17; H, 9.59. Found: C, 56.89; H, 9.79.

1-(Tricyclohexylstannyl)bicyclo[1.1.1]pentane (4c). Stannane **4c** was isolated in 56% yield after chromatography over bulk C-18 as a white solid: mp 132–133 °C; ^{1}H NMR δ 2.89 [s, 1H, with tin magnetic isotope satellites, $J(^{119}Sn^1H)$, $(^{117}Sn^1H)$, $(^{115}Sn^1H)$ = 166.5, 159.0, 146.3], 2.06 (s, 6H), 1.93–1.15 (m, 33H); IR (mull) 1445, 1210, 1168, 990, 880, 840, 656 cm^{-1}; MS (EI) 436 (M^+, 3), 369 ($M^+ - 67$, 36), 353 (92), 287 (35), 271 (66), 203 (100), 121 (56), 83 (59), 81 (68); HRMS (EI) calcd for $C_{23}H_{40}Sn$ 436.2149, found 436.2150. Anal. Calcd for $C_{23}H_{40}Sn$: C, 63.46; H, 9.26. Found: C, 63.60; H, 9.17.

1-(Triphenylstannyl)bicyclo[1.1.1]pentane (4d). Stannane **4d** was obtained in 56–68% isolated yield after reversed-phase chromatographic purification as a white solid: mp 126–127 °C; ^{1}H NMR δ 7.60–7.41 (m, 6H, with tin magnetic isotope satellites), 7.40–7.32 (m, 9H), 2.97 [s, 1H, with tin magnetic isotope satellites, $J(^{119}Sn^1H)$, $(^{117}Sn^1H)$, $(^{115}Sn^1H)$ = 225.9, 216.1, 198.5], 2.27 (apparent t, J = 2.0, 6H); IR (mull) 3061, 1479, 1428, 1213, 1075, 997, 730, 699 cm^{-1}; MS (EI) 351 ($M^+ - 67$, 100), 197 (31), 120 (19). Anal. Calcd for $C_{23}H_{22}Sn$: C, 66.23; H, 5.32. Found: C, 66.18; H, 5.48.

Preparation of 4b-d Employing an Excess of [1.1.1]-Propellane (1). A solution of **2**[1,9] (5.00 g, 16.85 mmol) and anhydrous diethyl ether (40 mL) was placed in a flask equipped with a magnetic stirrer, septum, and a side arm connected to a second flask outfitted with magnetic stirrer, septum, and dry ice condenser. The solution was cooled to −60 °C with a dry ice/chloroform bath and treated with phenyllithium (21.0 mL or 37.10 mmol of a 1.8 M solution in cyclohexane/diethyl ether, Aldrich) via cannula over 15 min. When the addition was completed, the mixture was stirred at −60 °C for 1.25 h and then allowed to warm to ambient temperature. At this point, the volatiles were vacuum transferred under house vacuum (40–50 Torr) to the second flask which was cooled with a dry ice/acetone bath. When the transfer was completed, the flask was flushed with nitrogen, and then the tributyltin hydride (0.981 g or 906 μL, 3.37 mmol) was introduced via syringe. *tert*-Butyl peroxide (0.398 g, 500 μL, 2.72 mmol) was added to the solution, the cooling bath removed, and the mixture irradiated with a sun lamp (General Electric Model No. RSM, 275W) for 1 h. After being stirred overnight at ambient temperature, the reaction mixture was concentrated in vacuo and the crude oil chromatographed over silica gel, eluting with hexane, to give, after concentration of appropriate fractions, 1.120 g (93% based on the tributyltin hydride) of **4b** as a colorless oil identical in all respects to material prepared as described in the general procedure. In an essentially identical manner, **4c** and **4d** were prepared in 63% and 68% yield, respectively.

1-Bicyclo[1.1.1]pentyl Phenyl Sulfide (5). A solution of **4b** (0.140 g, 0.59 mmol) in THF (2 mL) was cooled to −78 °C and treated with *n*-butyllithium (0.419 mL or 0.65 mmol of a 1.55 M solution in hexane, Aldrich). When the addition was completed, the mixture was warmed to 0 °C for 18 h (in a subsequent run, 3.5 h was sufficient). Phenyl disulfide (0.129 g, 0.59 mmol) was then added and the reaction stirred overnight with gradual warming to room temperature. The mixture was diluted with Et_2O and washed with 1 N NaOH, H_2O, and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo to a crude oil. Radial chromatography over silica gel, eluting with hexane, afforded 0.041 g (40%) of **5** as a colorless liquid identical in all respects to an authentic sample.[1,2] In addition, 0.047 mg of butyl phenyl sulfide and 0.015 g of recovered **4b** were obtained.

***N*-(1-Bicyclo[1.1.1]pentyl)benzamide (11).** A solution of stannane **4b** (0.167 g, 0.40 mmol) in THF (5 mL) was cooled to −78 °C and treated with *n*-butyllithium (0.300 mL or 0.48 mmol of a 1.6 M solution in hexanes, Aldrich) via syringe. After 15 min the mixture was warmed to −10 °C for 6 h. In a second flask was placed a solution of methyllithium/lithium bromide complex (0.533 mL or 0.80 mmol of a 1.5 M solution in Et_2O, Aldrich). This solution was cooled to −78 °C and treated dropwise with a solution of methoxylamine (0.038 g, 0.80 mmol) in dry hexane (0.85 mL). When the addition was completed, the equilibrium mixture of 1-bicyclo[1.1.1]pentyllithium prepared earlier was then added via cannula. The resultant mixture was then warmed

to −15 °C for 2 h and then quenched with H_2O (0.050 mL). A solution of pyridine (1 mL) and Et_2O (0.60 mL) was added, followed by benzoyl chloride (0.112 g or 0.093 mL, 0.80 mmol). The reaction mixture was stirred overnight with gradual dissipation of the cooling bath. An extractive workup was done with CH_2Cl_2 (30 mL). The combined organic extracts were washed with 0.5 N HCl (20 mL), saturated aqueous $NaHCO_3$ (20 mL), H_2O (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated by rotary evaporation to give a crude oil. Chromatography over silica gel, eluting with hexane/EtOAc (4:1), afforded 0.018 g (24%) of **11**, identical in all respects to a sample of **11** prepared by benzoylation of an authentic sample of **10**,[4,17] as a white solid: mp 158–159 °C; ^1H NMR δ 7.74 (apparent d, J = 8.1, 2H), 7.51–7.38 (m, 3H), 6.52 (br s, 1H), 2.51 (s, 1H), 2.20 (s, 6H); IR (mull) 3228, 3002, 1638, 1581, 1533, 1491, 1481, 1319, 1299, 1284, 1201, 1151, 692 cm^{-1}; MS (EI) 187 (M^+, 0.6), 105 (100), 77 (43). Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.70; H, 7.11; N, 7.27.

Acknowledgment. We are grateful to the Physical and Analytical Chemistry Department of The Upjohn Company for elemental analyses and IR and mass spectral data. We also thank Randy M. Jensen for help in determining the $^{119,117,115}Sn^1H$ coupling constants of **4**. James R. Blinn's assistance with the MNDO calculations is appreciated. Philip G. Brewer, Thomas A. Runge, Joseph M. Timko, and Terri J. Veldman are especially acknowledged for generous supplies of compound **2**.

Supplementary Material Available: ^1H NMR spectra for compounds **4a-d** and **11** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.