to proceed at 115 °C under 95 psig of CO for 3 h. After this time the reaction mixture was concentrated in vacuo and the residue extracted with hot toluene (3 × 50 mL). The toluene extracts were combined and concentrated to dryness, and the pale yellow solid was dissolved in toluene and filtered through a short silica gel column eluting with toluene. The product was collected, concentrated, and recrystallized from ethanol/water to give 1.98 g product (95%): mp 112–114 °C; IR (KBr) 3330, 1666, 1626, 1536, 1477, 1443, 1325, 1245, 1201, 871, 734 $cm^{-1}$. Anal. Calcd for $C_{13}H_9F_2NO$: C, 66.95; H, 3.89; N, 6.01. Found: C, 67.01; H, 3.88; N, 5.96.

**6-Fluoro-2-phenylbenzoxazole (3b).** Iodobenzene (1.0 mL, 8.94 mmol), **1b** (910 μL, 8.94 mmol), $PdCl_2L_2$ (94 mg, 0.134 mmol), DBU (6.0 mL, 40.0 mmol, 4.2 equiv), and DMF (27 mL) were allowed to react at 155–160 °C and 95 psig of CO for 16 h. The temperature was then raised to 210 °C and allowed to remain there for 3 days. After this time, GC analysis of the reaction mixture indicated that >95% cyclization had taken place. The reaction mixture was filtered, concentrated, dissolved in a toluene/chloroform mixture, and passed through a short column of silica gel (eluting with toluene), and the product fraction was collected and then concentrated again. The product was recrystallized from methanol/water to give 820 mg (43%) of colorless crystals: mp 104.5–105 °C; IR (KBr) 1625, 1557, 1480, 1345, 1290, 1128, 1103, 1050, 1022, 957, 838, 770, 700, 685 $cm^{-1}$. Anal. Calcd for $C_{13}H_8FNO$: C, 73.23; H, 3.78; N, 6.57. Found: C, 73.09; H, 3.98; N, 6.74.

**Acknowledgment.** We thank J. Lugert for GC–MS data and P. Keogh for their interpretation, W. Lenhart and M. Goodberlet for NMR spectra, and D. Margevich for FTIR spectra.

**Supplementary Material Available:** Experimental details and physical and spectral properties of all amides and benzoxazoles synthesized (10 pages). This material is contained in many 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.

## An Improved Method for the Preparation of Pyrrolidines by the Cycloaddition of Nonstabilized 2-Azaallyl Anions with Alkenes

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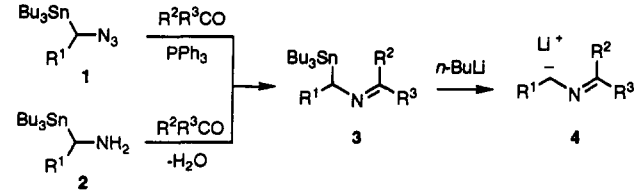
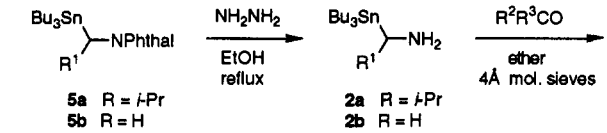
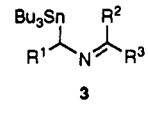
We have previously shown that nonstabilized 2-azaallyl anions **4** may be generated by the transmetalation of (2-azaallyl)stannanes **3**. These anions were found to undergo efficient [π4s + π2s] cycloaddition reactions with certain alkenes to afford pyrrolidines after quenching with an electrophile.[1,2] The imines **3** were prepared in good yield from azides **1** by an aza-Wittig reaction with aldehydes or ketones. However, this method was limited to *N*-(trialkylstannyl)methanimines (**3**, $R^1$ = H), since azides **1** were found to be thermally unstable where $R^1$ = alkyl. This limitation prevented the study of nonstabilized 1,3-disubstituted 2-azaallyl anions. We now wish to report that (2-azaallyl)stannanes **3** may be more conveniently prepared from (1-aminoalkyl)stannanes **2** and that these imines increase the scope of the 2-azaallyl anion route to pyrrolidines.




Initial attempts to prepare (1-aminoalkyl)stannanes **2** by the reduction of azides or nitriles or by reductive amination of stannyl ketones were unsuccessful.[1b] However, Chong recently reported the synthesis of these amines by deprotection of phthalimides **5**, obtained by a Mitsunobu reaction on α-hydroxystannanes.[3] We prepared phthalimides **5a**[3] and **5b**, which were deprotected with hydrazine to afford the amines **2a**[3] and **2b**. Although **5b** could be prepared by the Mitsunobu route, it was more conveniently prepared by N-alkylation of potassium phthalimide. Without purification, the amines **2a** and **2b** were condensed with isobutyraldehyde, acetone, and cyclopentanone in the presence of molecular sieves to give the (2-azaallyl)stannanes **3a–d** in good yield after distillation. The preparation of **3a–3c** illustrates the superiority of this method to the aza-Wittig approach in the preparation of branched (2-azaallyl)stannanes. In addition, although imines such as **3d** may be prepared by the aza-Wittig reaction,[1b] the current method is more convenient.




| | $R^1$ | $R^2$ | $R^3$ | Overall Yield from 5 |
|---|---|---|---|---|
| **3a** | *i*-Pr | H | *i*-Pr | 79% |
| **3b** | *i*-Pr | $CH_3$ | $CH_3$ | 84% |
| **3c** | *i*-Pr | $-(CH_2)_4-$ | | 75% |
| **3d** | H | $-(CH_2)_4-$ | | 86% |

Transmetalation of (2-azaallyl)stannanes **3a** and **3b** in the presence of various anionophiles led to smooth cycloaddition reactions (Table I). To facilitate isolation, the *N*-methylpyrrolidine derivatives were prepared by quenching the *N*-lithiopyrrolidines with iodomethane. Other electrophiles (e.g., $H_2O$ or *p*-TsCl) have been used previously to generate N-unsubstituted or N-protected pyrrolidines.[1b] Imines such as **3d** have been used previously in cycloaddition reactions.[1b]

The ability to generate more highly substituted nonstabilized 2-azaallyl anions provides the first information on the geometry of such anions.[4] Cycloadditions of the anion derived from imine **3a** produce only a cis relationship between the 2- and 5-substituents. This is consistent with a reaction proceeding through the "W"-form of the anion, assuming the "U"-form may be ruled out on steric grounds.

(1) (a) Pearson, W. H.; Szura, D. P.; Harter, W. G. *Tetrahedron Lett.* **1988**, *29*, 761–764. (b) Pearson, W. H.; Szura, D. P.; Postich, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1329–1345.

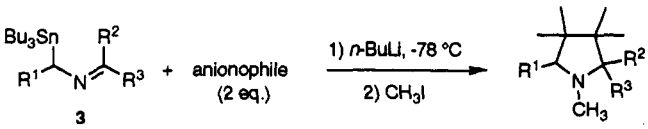
(2) For reviews on 2-azaallyl anion cycloadditions, see: (a) Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 627–639. (b) Pearson, W. H. In *Studies in Natural Products Chemistry*; Atta-ur-Rahman, Ed.; Elsevier: Amsterdam, 1988; Vol. 1, pp 323–358.

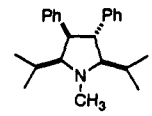
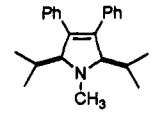
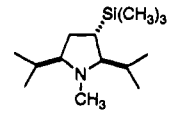
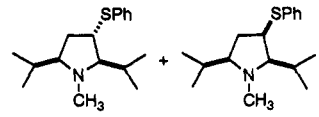
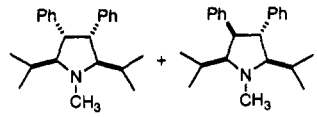
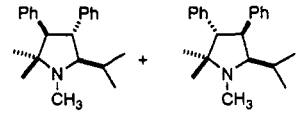
(3) Chong, J. M.; Park, S. B. *J. Org. Chem.* **1992**, *57*, 2220–2222.

(4) Although unstabilized 1,3-disubstituted 2-azaallyl anions have not been generated, 1,3-diaryl-2-azaallyl anions have been studied and are proposed to react in the "W"-form. See ref 2a and: (a) Eidenschink, R.; Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 292. (b) Young, R. N.; Ahmad, M. A. *J. Chem. Soc., Perkin Trans. 2* **1982**, 35. (c) Pearson, W. H.; Walters, M. A.; Oswell, K. D. *J. Am. Chem. Soc.* **1986**, *108*, 2769–2771 and references cited therein. (d) Andrews, P. C.; Mulvey, R. E.; Clegg, W.; Reed, D. *J. Organomet. Chem.* **1990**, *386*, 287–297.

0022-3263/92/1957-6354$03.00/0 

**Table I. Formation of Pyrrolidines by 2-Azaallyl Anion Cycloadditions**




| imine | anionophile | product(s) | % yield (ratio) |
|---|---|---|---|
| 3a | (*E*)-stilbene |  6 | 84 |
| 3a | Ph-C≡C-Ph |  7 | 55 |
| 3a | $TMSCH=CH_2$ |  8 | 77 |
| 3a | $PhSCH=CH_2$ |  9 + 10 | 78 (2.7 : 1) |
| 3a | (*Z*)-stilbene |  11 + 6 | 54 (1.6 : 1) |
| 3b | (*E*)-stilbene |  12 + 13 | 71 (1.4 : 1) |

The formation of **11** and **6** from **3a** and (*Z*)-stilbene is significant, since this is the first example of scrambling of the original alkene stereochemistry during a 2-azaallyl anion cycloaddition. Previous examples showed complete retention of alkene stereochemistry in the cycloaddition reaction.[1,2a,4c] The formation of **6** from (*Z*)-stilbene provides the first evidence that the cycloaddition of these anions may proceed through a stepwise mechanism. Isomerization of (*Z*)-stilbene to (*E*)-stilbene by *n*-BuLi or by the product 1-lithiopyrrolidine prior to the cycloaddition was ruled out by treatment of (*Z*)-stilbene with either *n*-BuLi or the lithium salt of pyrrolidine at −78 °C for 15 min in the absence of the (2-azaallyl)stannane. No isomerization was detected by $^1H$ NMR or GC in either case.

In our earlier work, it was found that unstabilized 2-azaallyl anions generated by tin–lithium exchange had a limited lifetime due to oligomerization, thus necessitating the presence of a reactive anionophile during transmetalation.[1b] The more highly substituted 2-azaallyl anions reported herein were also found to be short-lived. For example, transmetalation of imine **3a** with *n*-BuLi at −78 °C for 5 min followed by addition of (*E*)-stilbene produced none of the cycloadduct **6**, in contrast to an 84% yield of **6** when the anionophile is present during the transmetalation. Less reactive anionophiles (e.g., norbornene) did not undergo cycloaddition.

In conclusion, a more general and convenient preparation of (2-azaallyl)stannanes **3** has been developed, which allows the preparation of more highly substituted pyrrolidines by the 2-azaallyl anion method.

## Experimental Section[5]

***N*-[(Tri-*n*-butylstannyl)methyl]phthalimide (5b). Method A.** *n*-Butyllithium (3.57 mL, 2.08 M solution in hexanes, 7.43 mmol) was added to a solution of diisopropylamine (0.75 g, 7.44 mmol) in THF (14 mL) at −50 °C. Upon warming to 0 °C for 15 min, tri-*n*-butylstannane (2.16 g, 7.44 mmol) was added. After 15 min, paraformaldehyde (0.22 g, 7.44 mmol) was added, and the mixture was stirred at room temperature for 3 h and then quenched at −78 °C with saturated aqueous $NH_4Cl$. After being warmed to room temperature, the mixture was washed with $H_2O$ (2 × 15 mL) and saturated brine (1 × 15 mL) and then dried ($MgSO_4$), filtered, and carefully concentrated in vacuo to give the crude *N*-(hydroxymethyl)phthalimide as a clear, colorless oil: IR (neat) 3381 (mbr), 2958 (s), 2919 (s), 1457 (m), 1069 (m), 980 (m) $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ 4.03 (s, 2 H, and $^2J(^{117/119}Sn^1H)$ = 43.2 Hz), 1.58–1.44 (m, 6 H), 1.39–1.28 (m, 6 H), 1.02–0.87 (m, 15 H). The crude stannane (≤7.44 mmol) was taken up in THF (14 mL), and triphenylphosphine (2.34 g, 8.92 mmol) and phthalimide (1.31 g, 8.92 mmol) were added. The white suspension was cooled to 0 °C and treated with a solution of diethyl azodicarboxylate (1.55 g, 8.92 mmol) in THF (3 mL). After being stirred at room temperature for 1 h, the bright orange mixture was concentrated in vacuo, yielding a thick oil. After trituration with hexane, the solid precipitate was removed by filtration, and the filtrate was concentrated in vacuo. Chromatography (0–4% EtOAc/hexane gradient) afforded 2.50 g (75%) of the title compound as a bright yellow oil.

**Method B.** (Iodomethyl)tri-*n*-butylstannane[7] (2.15 g, 5.00 mmol) was added to a suspension of potassium phthalimide (1.02 g, 5.50 mmol) in DMF (10 mL). After being stirred for 1.5 h at room temperature, the resulting bright yellow suspension was diluted with $Et_2O$ (50 mL), washed with $H_2O$ (5 × 20 mL) and saturated brine (1 × 20 mL), and then dried ($MgSO_4$) and concentrated in vacuo. Chromatography (5–10% EtOAc/hexane gradient) afforded 2.17 g (96%) of the title compound as a bright yellow oil: $R_f$ = 0.30 (10% EtOAc/hexane); IR (neat) 2919 (s), 1771 (m), 1708 (s), 1388 (s), 1054 (s), 961 (s), 882 (s) $cm^{-1}$; $^1H$ NMR (360 MHz) $\delta$ 7.81–7.77 (m, 2 H), 7.69–7.66 (m, 2 H), 3.24 (s, 2 H, $^2J(^{117/119}Sn^1H)$ = 26.5 Hz), 1.54–1.45 (m, 6 H), 1.32–1.22 (m, 6 H), 0.96–0.92 (m, 6 H), 0.85 (t, 9 H, $J$ = 7.3 Hz); $^{13}C$ NMR (90 MHz) $\delta$ 168.7, 133.5, 132.3, 122.7, 28.8, 27.2 (56 Hz), 12.1 (253 Hz), 13.6 (20 Hz), 10.4 (327 Hz); MS *m/z* (rel int) 394 (100, M − $C_4H_9$), 393 (39), 392 (75), 391 (31), 390 (42), 280 (21), 278 (16), 86 (20), 84 (30), 49 (34); HRMS (CI, $NH_3$) calcd for $C_{17}H_{24}NO_2{}^{120}Sn$ (M − $C_4H_9$)$^+$ 394.0829, found 394.0826. Anal. Calcd for $C_{21}H_{33}NO_2Sn$: C, 56.03; H, 7.39; N, 3.11. Found: C, 56.43; H, 7.76; N, 3.04.

**General Procedure for the Preparation of *N*-[(1-Tri-*n*-butylstannyl)alkyl]alkanimines 3.** Chong's method was used for the hydrazinolysis of phthalimides **5**.[3] Hydrazine monohydrate

(5) All ractions were carried out under an atmosphere of dry argon or nitrogen in flame-dried glassware equipped with a tightly fitted rubber septum. Chromatography refers to the method of Still.[6] It was sometimes found that isomeric mixtures of cycloadducts could not be completely separated by flash chromatography in one pass. In these cases, all fractions containing one or more of the isomers were combined to determine the overall yield for the reaction. To obtain analytically pure samples of each isomer for characterization, the mxiture was rechromatographed, and column fractions containing pure isomers were collected. Radial chromatography was performed using a Harrison Research Chromatotron 7924T equipped with a 2-mm silica gel plate using a flow rate of 7 mL/min. For $^1H$ NMR resonances which exhibit satellite peaks due to coupling with $^{117}Sn$ and $^{119}Sn$, the average of the two couplings is reported when measurable. $^1H$ NMR assignments were made on the basis of homonuclear decoupling experiments and stereochemical assignments were made using difference nuclear Overhauser effect (DNOE) experiments, which were performed at ambient temperature on thoroughly degassed samples. Otherwise, stereochemical assignments were made on the basis of comparison with analogous compounds reported in the literature. For $^{13}C$ NMR data, coupling constants in parentheses refer to the average of the couplings to $^{117}Sn$ and $^{119}Sn$, when measurable. Mass spectra were obtained using electron-impact ionization at 70 eV unless otherwise noted.

(6) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 4923.

(7) Seyferth, D.; Andrews, S. B.; Lambert, R. L., Jr. *J. Organomet. Chem.* **1972**, *37*, 69.

(50 equiv) was added to a solution of **5** in absolute ethanol (1 M), and the mixture was heated at reflux for the indicated time. After being cooled to room temperature and concentration in vacuo, the mixture was diluted with $Et_2O$, washed with $H_2O$ and saturated brine, and then dried ($Na_2SO_4$) and concentrated in vacuo to give the crude primary amine **2** which was used immediately without further purification.

A solution of an aldehyde or ketone (1 equiv) in $Et_2O$ (3 M) was added to the crude amine **2** (1 equiv) and 4 Å molecular sieves (0.47 g) in $Et_2O$ (1.7 M) at 23 °C. After the amine had been consumed (GLC), the mixture was filtered through Celite and concentrated in vacuo and then Kugelrohr distilled.

***N*-[1-(Tri-*n*-butylstannyl)-2-methylpropyl]-2-methylpropan-1-imine (3a).** The amine **2a**[3] was prepared from **5a**[3] (1.69 g, 3.43 mmol) and hydrazine monohydrate (8.59 g, 172 mmol) in EtOH (3.4 mL) for 18 h. The crude amine was combined with isobutyraldehyde (0.25 g, 3.43 mmol) for 6 h as described above to produce 1.13 g (79%) of the title compound as a clear, colorless oil after Kugelrohr distillation: bp 125–130 °C (air bath) (0.11 mmHg); IR (neat) 2956 (s), 2929 (s), 1649 (m), 1462 (m), 1378 (m), 1074 (m) $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ 7.28 [d, 1 H, $J$ = 5.5 Hz, $^4J(^{117/119}Sn-^1H)$ = 17.3 Hz], 3.14 [d, 1 H, $J$ = 8.7 Hz, $^2J(^{117/119}Sn-^1H)$ = 35.1 Hz], 2.41 (d hept, 1 H, $J$ = 5.5, 6.8 Hz), 2.18 (d hept, 1 H, $J$ = 8.7, 6.6 Hz), 1.52–1.41 (m, 6 H), 1.35–1.23 (m, 6 H), 1.04 (d, 6 H, $J$ = 6.8 Hz), 0.93–0.81 (m, 21 H); $^{13}C$ NMR (75 MHz) $\delta$ 162.1 (46 Hz), 72.3 (365 Hz), 33.3, 32.1, 28.8 (19 Hz), 27.1, 21.8, 21.5, 19.5 (357 Hz), 19.4, 13.1, 9.3 (307 Hz); MS (CI, $NH_3$) $m/z$ (rel int) 418 (8, M + 1), 185 (26), 175 (31), 141 (23), 140 (100), 136 (71), 128 (98), 126 (15), 105 (59), 88 (22); HRMS (CI, $NH_3$) calcd for $C_{20}H_{44}N^{120}Sn$ (M + H)$^+$ 418.2496, found 418.2493. Anal. Calcd for $C_{20}H_{43}NSn$: C, 57.52; H, 10.39; N, 3.36. Found: C, 57.86; H, 10.76; N, 3.34.

***N*-[1-(Tri-*n*-butylstannyl)-2-methylpropyl]-1-methylethan-1-imine (3b).** The amine **2a**[3] was prepared from **5a**[3] (1.63 g, 3.31 mmol) and hydrazine monohydrate (8.30 g, 166 mmol) in EtOH (3.3 mL) for 18 h. The crude amine was combined with acetone (0.19 g, 3.31 mmol) for 8 h as described above to provide 1.12 g (84%) of the title compound as a clear, colorless oil after Kugelrohr distillation: bp 122–125 °C (air bath) (0.18 mmHg); IR (neat) 2956 (s), 2922 (s), 2856 (s), 1646 (m), 1464 (m), 1377 (m), 1366 (m), 1234 (w), 1071 (w) $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ 3.30 [d, 1 H, $J$ = 10.0 Hz, $^2J(^{117/119}Sn-^1H)$ = 30.0 Hz], 2.24 (d hept, 1 H, $J$ = 10.0, 6.5 Hz), 2.00 [s, 3 H, $^5J(^{117/119}Sn-^1H)$ = 19.0 Hz], 1.74 [s, 3 H, $^5J(^{117/119}Sn-^1H)$ = 5.2 Hz], 1.52–1.41 (m, 6 H), 1.36–1.24 (m, 6 H), 0.91–0.82 (m, 21 H); $^{13}C$ NMR (75 MHz) $\delta$ 157.3, 64.4, 33.1, 29.2, 28.5, 27.5 (55 Hz), 22.4, 22.2, 18.2, 13.4, 9.9 (295 Hz); MS $m/z$ (rel int) 346 (1, M – $C_4H_9$), 179 (8), 177 (7), 121 (5), 113 (8), 112 (100), 55 (17), 49 (10), 42 (8), 41 (6); HRMS (CI, $NH_3$) calcd for $C_{19}H_{42}N^{120}Sn$ (M + H)$^+$ 404.2339, found 404.2333.

***N*-[1-(Tri-*n*-butylstannyl)-2-methylpropyl]cyclopentanimine (3c).** The amine **2a**[3] was prepared from **5a**[3] (0.68 g, 1.39 mmol) and hydrazine monohydrate (2.73 g, 54.5 mmol) in EtOH (1.0 mL) for 18 h. The crude amine was combined with cyclopentanone (0.12 g, 1.39 mmol) for 8 h as described above to produce 0.45 g (75%) of the title compound as a clear, colorless oil after Kugelrohr distillation: bp 123–130 °C (air bath) (0.06 mmHg); IR (neat) 2955 (s), 2927 (s), 1660 (m), 1464 (s), 1377 (m), 1071 (w) $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ 3.13 [d, 1 H, $J$ = 10.1 Hz, $^2J(^{117/119}Sn-^1H)$ = 39.2 Hz], 2.45–2.14 (m, 4 H), 1.93–1.69 (m, 5 H), 1.53–1.41 (m, 6 H), 1.36–1.24 (m, 6 H), 0.95–0.79 (m, 21 H); $^{13}C$ NMR (75 MHz) $\delta$ 170.7, 66.9 (345 Hz), 35.6, 33.0 (103 Hz), 29.1, 27.7, 27.4, 25.0, 24.4, 22.0, 13.4 (297 Hz), 9.9 (298 Hz); MS (Cl, $NH_3$), $m/z$ (rel int) 430 (54, M + 1), 429 (22), 428 (39), 426 (20), 308 (24), 307 (19), 306 (20), 138 (40), 136 (100), 105 (24); HRMS (CI, $NH_3$) calcd for $C_{21}H_{44}N^{120}Sn$ (M + H)$^+$ 430.2496, found 430.2504.

***N*-[(Tri-*n*-butylstannyl)methyl]cyclopentanimine (3d).** The amine **2b** was prepared from **5b** (0.49 g, 1.08 mmol) and hydrazine monohydrate (2.71 g, 54.0 mmol) in EtOH (2.4 mL, 0.5 M) for 10 min. *Extended reaction times were found to be detrimental.* The crude amine was combined with cyclopentanone (0.09 g, 1.08 mmol) for 6 h as described above to produce 0.36 g (86%) of the title compound as a clear, colorless oil after Kugelrohr distillation: bp 120–125 °C (air bath) (0.22 mmHg); IR (neat) 2952 (s), 1663 (s), 1459 (m), 1376 (w), 1068 (w), 1002 (w) $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ 3.44 [s, 2 H, $^2J(^{117/119}Sn-^1H)$ = 46.2 Hz], 2.29 (app t, 2 H, $J$ = 7.0 Hz), 2.08 (app t, 2 H, $J$ = 7.0 Hz), 1.81 (app quint, 2 H, $J$ = 7.0 Hz), 1.71 (app quint, 2 H, $J$ = 7.0 Hz), 1.55–1.44 (m, 6 H), 1.36–1.24 (m, 6 H), 0.91–0.79 (m, 18 H); $^{13}C$ NMR (75 MHz) $\delta$ 172.6 (40 Hz), 41.3 (277 Hz), 35.8, 29.0, 28.1 (20 Hz), 27.2 (52 Hz), 24.9, 24.4, 13.3, 9.6 (305 Hz); MS (CI, $NH_3$) $m/z$ (rel int) 388 (100, M + 1), 387 (50), 386 (77), 384 (50), 308 (9), 306 (7), 279 (11), 98 (21), 96 (45), 84 (6); HRMS (CI, $NH_3$) calcd for $C_{18}H_{38}N^{120}Sn$ (M + H)$^+$ 388.2026, found 388.2021.

**General Procedure for Cycloadditions.** All reactions were caried out on the following scale, unless otherwise noted. A mixture of the imine **3** (0.48 mmol) and an alkene or alkyne (0.96 mmol) in THF (1 mL) was added over a 5-min period to a solution of *n*-butyllithium (0.35 mL of a 2.08 M solution in hexanes, 0.74 mmol) in THF (3.5 mL, 0.2 M) at −78 °C. After 15 min, iodomethane (0.11 g, 0.74 mmol) was added, and the mixture was allowed to warm to room temperature. The solution was diluted with $Et_2O$ (10 mL) and washed with $H_2O$ (2 × 10 mL), saturated aqueous $NaHCO_3$ (10 mL), and saturated brine (1 × 10 mL) and then dried ($MgSO_4$) and concentrated in vacuo. After analysis by $^1H$ NMR to determine the ratio of isomers, chromatography of the residue provided the pure cycloadducts.

**1-Methyl-2$\beta$,5$\beta$-bis(1-methylethyl)-3$\beta$,4$\alpha$-diphenylpyrrolidine (6).** From **3a** and (*E*)-stilbene. $^1H$ NMR analysis (300 MHz) of the crude reaction mixture indicated the presence of a single diastereomer. Chromatography (0–5% EtOAc/hexane gradient) afforded 130 mg (84%) of the title compound as a pale yellow solid: mp 63.5–65 °C; $R_f$ = 0.42 (10% EtOAc/hexane); IR (neat) 3031 (m), 2963 (s), 2872 (s), 1667 (m), 1598 (m), 1451 (s), 1382 (m), 1263 (m), 1029 (m), 699 (s) $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ 7.25–7.04 (m, 10 H), 3.55 (dd, 1 H, $J$ = 10.5, 8.5 Hz), 3.38 (dd, 1 H, $J$ = 10.5, 9.4 Hz), 2.72 (dd, 1 H, $J$ = 8.5, 5.9 Hz), 2.63 (dd, 1 H, $J$ = 9.4, 3.4 Hz), 2.49 (s, 3 H), 1.93 (d hept, 1 H, $J$ = 3.4, 7.0 Hz), 1.56 (d hept, 1 H, $J$ = 5.9, 6.8 Hz), 1.01 (d, 3 H, $J$ = 7.0 Hz), 0.89 (d, 3 H, $J$ = 6.8 Hz), 0.67 (d, 3 H, $J$ = 7.0 Hz), 0.44 (d, 3 H, $J$ = 6.8 Hz); $^{13}C$ NMR (75 MHz) $\delta$ 143.7, 141.0, 129.7, 128.5, 128.3, 127.8, 126.1, 126.0, 79.4, 76.2, 55.5, 51.4, 44.6, 30.6, 30.2, 21.1, 19.7, 19.4, 18.7; MS (CI, $NH_3$) $m/z$ (rel int) 322 (100, M), 320 (8), 318 (8), 308 (12), 306 (19), 278 (20), 108 (5), 101 (7), 91 (7), 77 (7); HRMS (CI, $NH_3$) calcd for $C_{23}H_{32}N$ (M + H)$^+$ 322.2535, found 322.2528. Anal. Calcd for $C_{23}H_{31}N$: C, 85.92; H, 9.72; N, 4.36. Found: C, 85.70; H, 9.60; N, 4.27. Only two of the possible diastereomers of **6** can have four distinct methyl doublets in the $^1H$ NMR spectrum and 19 lines in the $^{13}C$ NMR spectrum; the 2$\beta$,3$\beta$,4$\alpha$,5$\beta$ isomer and the 2$\beta$,3$\beta$,4$\beta$,5$\alpha$ isomer. The 2$\beta$,3$\beta$,4$\beta$,5$\alpha$ diastereomer was ruled out since it would require a reaction between (*Z*)-stilbene and the "sickle"-form of the 2-azaallyl anion.

**1-Methyl-2,5-dihydro-2$\beta$,5$\beta$-bis(1-methylethyl)-3,4-diphenylpyrrole (7).** From **3a** and diphenylactylene. $^1H$ NMR analysis (300 MHz) of the crude reaction mixture indicated the presence of a single diastereomer. Chromatography (0–10% EtOAc/hexane gradient) afforded 85 mg (55%) of the title compound as a white solid: $R_f$ = 0.31 (10% EtOAc/hexane); $^1H$ NMR (300 MHz) $\delta$ 7.17–7.12 (m, 6 H), 7.00–6.97 (m, 4 H), 4.38 (s, 2 H), 2.64 (s, 3 H), 2.05 (hept, 2 H, $J$ = 7.1 Hz), 0.94 (d, 6 H, $J$ =7.1 Hz), 0.56 (d, 6 H, $J$ = 7.1 Hz). Due to the symmetry of this molecule, H-2 and H-5 are equivalent; thus, NOE studies were not possible. Stereochemistry was assigned on the basis of other examples here, which show that the 2-azaallyl anions react solely in the "W"-form. Upon standing, **7** oxidized to 1-methyl-2,5-bis(1-methylethyl)-3,4-diphenylpyrrole: mp 190–191.5 °C; IR (neat) 2961 (s), 1602 (m), 1453 (m), 704 (s) $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ 7.18–7.00 (m, 10 H), 3.70 (s, 3 H), 3.20 (hept, 2 H, $J$ = 7.1 Hz), 1.27 (d, 12 H, $J$ = 7.1 Hz); $^{13}C$ NMR (75 MHz) $\delta$ 137.8, 133.3, 131.5, 127.2, 125.2, 121.2, 32.0, 25.9, 22.4; MS $m/z$ (rel int) 317 (51, M), 303 (26), 302 (100, M – $CH_3$), 244 (8), 144 (8), 128 (9), 115 (7), 43 (10), 42 (15), 41 (9); HRMS calcd for $C_{23}H_{27}N$ (M)$^+$ 317.2144, found 317.2130.

**1-Methyl-2$\beta$,5$\beta$-bis(1-methylethyl)-3$\alpha$-(trimethylsilyl)pyrrolidine (8).** From **3a** and vinyltrimethylsilane. $^1H$ NMR analysis (300 MHz) of the crude reaction mixture indicated the presence of a single diastereomer. Chromatography (0–10% EtOAc/hexane gradient) afforded 90 mg (77%) of the title compound as a clear, colorless oil: $R_f$ = 0.49 (10% EtOAc/hexane); IR (neat) 2956 (s), 2878 (m), 2778 (w), 1461 (w), 1250 (s), 833 (s) $cm^{-1}$; $^1H$ NMR (300 MHz, $C_6D_6$) $\delta$ 2.33 (dd, 1 H, $J$ = 9.5, 3.8 Hz),

2.28 (ddd, 1 H, $J$ = 10.4, 6.0, 4.5 Hz), 2.21 (s, 3 H), 1.84–1.62 (m, 3 H), 1.45 (ddd, 1 H, $J$ = 12.1, 6.0, 2.6 Hz), 0.99–0.98 (m, 1 H), 0.97 (d, 3 H, $J$ = 6.8 Hz), 0.94 (d, 3 H, $J$ = 6.8 Hz), 0.90 (d, 3 H, $J$ = 6.9 Hz), 0.89 (d, 3 H, $J$ = 6.9 Hz); $^{13}$C NMR (75 MHz, $C_6D_6$) δ 74.5, 72.6, 40.0, 33.2, 29.4, 27.4, 24.9, 20.4, 19.5, 18.6, 15.5, −1.8; MS $m/z$ (rel int) 198 (100), 124 (18), 82 (39), 74 (6), 73 (74), 59 (10), 45 (11), 43 (8), 42 (12), 41 (9); HRMS (CI, $NH_3$) calcd for $C_{14}H_{32}NSi$ (M + H)$^+$ 242.2304, found 242.2306. Due to badly overlapping signals, NOE studies were not possible. The stereochemical assignment was based on previous work which detailed the highly stereoselective nature of 2-azaallyl anion cycloadditions with vinyltrimethylsilane.[1b]

**1-Methyl-2β,5β-bis(1-methylethyl)-3α-(phenylthio)-pyrrolidine (9) and 1-Methyl-2β,5β-bis(1-methylethyl)-3β-(phenylthio)pyrrolidine (10).** Formed from **3a** and phenyl vinyl sulfide as a 2.7:1 mixture (300-MHz $^1$H NMR analysis of crude reaction mixture). Chromatography (0–5% EtOAc/hexane gradient) afforded 100 mg (78%) of the title compounds as a clear, pale yellow oil. Radial chromatography (0–100% EtOAc/hexane gradient) allowed the isolation of pure fractions of each isomer for characterization. Data for **9**: $R_f$ = 0.48 (10% EtOAc/hexane); IR (neat) 3074 (w), 2956 (s), 2869 (s), 2781 (m), 1585 (m), 1480 (s), 1466 (s) cm$^{-1}$; $^1$H NMR (300 MHz) δ 7.35–7.15 (m, 5 H), 3.40 (ddd, 1 H, $J$ = 6.9, 4.0, 1.3 Hz), 2.62 (ddd, 1 H, $J$ = 9.4, 4.1, 1.1 Hz), 2.28–2.25 (m, 4 H), 1.91–1.74 (m, 3 H), 1.62 (ddd, 1 H, $J$ = 12.9, 5.5, 1.3 Hz), 0.95 (d, 3 H, $J$ = 6.9 Hz), 0.88 (d, 3 H, $J$ = 6.9 Hz), 0.84 (d, 3 H, $J$ = 6.9 Hz), 0.81 (d, 3 H, $J$ = 6.9 Hz); DNOE ($C_6D_6$), irradiation at 3.43 ppm (H-3β) failed to enhance the signals at 2.70 ppm (H-5α) and 2.38 ppm (H-2α); $^{13}$C NMR (75 MHz) δ 137.2, 130.6, 128.9, 126.3, 78.2, 69.8, 45.4, 40.6, 32.9, 31.2, 28.3, 20.2, 19.5, 17.5, 15.3; MS (CI, $NH_3$) $m/z$ (rel int) 278 (75, M + 1), 234 (4), 180 (3), 170 (4), 168 (19), 166 (14), 137 (8), 136 (100), 124 (4), 94 (4); HRMS (CI, $NH_3$) calcd for $C_{17}H_{28}NS$ (M + H)$^+$ 278.1942, found 278.1929. Data for **10**: $R_f$ = 0.36 (10% EtOAc/hexane); IR (neat) 2959 (s), 1583 (m), 1478 (s), 1382 (m), 737 (s), 689 (m) cm$^{-1}$; $^1$H NMR (300 MHz) δ 7.34–7.13 (m, 5 H), 3.70 (ddd, 1 H, $J$ = 11.1, 6.8, 3.3 Hz), 2.76 (dd, 1 H, $J$ = 8.5, 3.3 Hz), 2.37 (s, 3 H), 2.38–2.26 (m, 1 H), 2.07–1.93 (m, 2 H), 1.85 (d hept, 1 H, $J$ = 1.6, 6.9 Hz), 1.71–1.60 (m, 1 H), 1.00 (d, 6 H, $J$ = 7.1 Hz), 0.89 (d, 3 H, $J$ = 6.9 Hz), 0.88 (d, 3 H, $J$ = 6.9 Hz); DNOE, irradiation at 3.7 ppm (H-3α) produced a 2.6% enhancement of the signal at 2.3 ppm (H-5α) and a 6.7% enhancement of the signal at 2.75 ppm (H-2α). Irradiation of the signal at 2.75 ppm (H-2α) produced a 6.2% enhancement of the signal at 2.3 ppm (H-5α) and an 8.1% enhancement of the signal at 3.7 ppm (H-3α); $^{13}$C NMR (90 MHz) δ 137.9, 129.1, 128.8, 125.6, 73.2, 71.6, 47.9, 44.0, 34.4, 31.2, 30.0, 21.7, 20.7, 18.5, 16.6; MS (CI, $NH_3$) $m/z$ (rel int) 278 (100, M + 1), 274 (14), 234 (64), 168 (25), 166 (13), 165 (15), 150 (29), 142 (26), 124 (23), 82 (29); HRMS (CI, $NH_3$) calcd for $C_{17}H_{28}NS$ (M + H)$^+$ 278.1942, found 278.1923.

**1-Methyl-2β,5β-bis(1-methylethyl)-3α,4α-diphenylpyrrolidine (11) and 1-Methyl-2β,5β-bis(1-methylethyl)-3β,4α-diphenylpyrrolidine (6).** Formed from **3a** and (*Z*)-stilbene as a 1.6:1 mixture (300-MHz $^1$H NMR analysis of crude reaction mixture). Chromatography (0–5% EtOAc/hexane gradient) afforded 80 mg (54%) of a mixture of the title compounds as a clear, colorless oil. Radial chromatography (0–20% EtOAc/hexane gradient) allowed the isolation of pure fractions for characterization. Data for **11**: $R_f$ = 0.46 (10% EtOAc/hexane); IR (neat) 3028 (s), 2953 (br), 1602 (s), 1454 (s), 1170 (m), 1034 (m), 699 (s) cm$^{-1}$; $^1$H NMR (300 MHz) δ 7.02–6.97 (m, 6 H), 6.75–6.72 (m, 4 H), 3.25 (dd, 2 H, $J$ = 4.8, 1.7 Hz), 2.97 (dd, 2 H, $J$ = 4.8, 4.1 Hz), 2.60 (s, 3 H), 1.85 (d hept, $J$ = 4.1, 6.9 Hz), 0.99 (d, 6 H, $J$ = 6.9 Hz), 0.74 (d, 6 H, $J$ = 6.9 Hz). [Due to the symmetry of this molecule, the relative stereochemistry between the two phenyl groups could not be rigorously assigned. However, only the 2β,3β,4β,5β and 2β,3α,4α,5β isomers (assuming the "W"-form of the 2-azaallyl anion) would show only two methyl doublets in the $^1$H NMR spectrum and 10 lines in the $^{13}$C NMR spectrum. Irradiation at 3.25 ppm (H-3β) produced a 4.6% enhancement of the signal at 1.85 ppm (H-2′) yet failed to enhance the signal at 2.97 ppm (H-2α)]; $^{13}$C NMR (75 MHz) δ 142.1, 129.6, 127.5, 125.7, 75.4, 52.3, 41.3, 31.3, 19.3, 18.2; MS $m/z$ (rel int) 279 (22, M − $C_3H_7$), 278 (100), 145 (24), 117 (14), 91 (27), 84 (11), 49 (19), 43 (10), 42 (55), 41 (9); HRMS (CI, $NH_3$) calcd for $C_{23}H_{32}N$ (M + H)$^+$ 322.2535, found 322.2528. See above for spectral data on **6**.

**1-Methyl-5β-(1-methylethyl)-2,2-dimethyl-3β,4α-diphenylpyrrolidine (12) and 1-Methyl-5β-(1-methylethyl)-2,2-dimethyl-3α,4β-diphenylpyrrolidine (13).** Formed from **2b** (0.50 mmol) and *trans*-stilbene (0.99 mmol) as a 1.4:1 mixture (360-MHz $^1$H NMR analysis of crude reaction mixture). Chromatography (5–100% EtOAc/hexane gradient) afforded 100 mg (71%) of a mixture of the title compounds as a pale yellow oil. The mixture was rechromatographed (same solvent system) in order to isolate pure fractions of each isomer for characterization. Data for **12**: $R_f$ = 0.13 (10% EtOAc/hexane); IR (neat) 3061 (w), 3027 (m), 2962 (s), 2779 (m), 1601 (m), 1452 (s) cm$^{-1}$; $^1$H NMR (360 MHz) δ 7.23–7.06 (m, 10 H), 3.31 (dd, 1 H, $J$ = 9.6, 9.6 Hz), 2.91 (dd, 1 H, $J$ = 9.6, 3.2 Hz), 2.89 (d, 1 H, $J$ = 9.6 Hz), 2.31 (s, 3 H), 1.97 (d hept, 1 H, $J$ = 3.2, 7.0 Hz), 1.19 (s, 3 H), 1.02 (d, 3 H, $J$ = 7.0 Hz), 0.71 (s, 3 H), 0.62 (d, 3 H, $J$ = 7.0 Hz); $^{13}$C NMR (90 MHz) δ 143.9, 142.0, 129.2, 128.2, 127.7, 126.1, 125.8, 73.7, 64.8, 63.0, 51.4, 34.1, 29.7, 26.6, 23.4, 19.9, 16.9; MS $m/z$ (rel int) 292 (4, M − $CH_3$), 265 (22), 264 (100, M-$C_3H_7$), 132 (9), 131 (29), 117 (8), 112 (7), 91 (18), 56 (13), 42 (10); HRMS (CI, $NH_3$) calcd for $C_{22}H_{30}N$ (M + H)$^+$ 308.2378, found 308.2368. Stereochemical assignment inferred from the confirmed stereochemistry of **13**, since only two diastereomers are possible (assuming the stereochemical integrity of (*E*)-stilbene). Data for **13**: pale yellow solid, mp 86–88 °C; $R_f$ = 0.23 (10% EtOAc/hexane); IR (neat) 3027 (m), 2962 (s), 1601 (m), 1451 (s), 1363 (m), 1253 (m), 699 (s) cm$^{-1}$; $^1$H NMR (300 MHz) δ 7.23–7.05 (m, 10 H), 4.07 (dd, 1 H, $J$ = 13.3, 9.8 Hz), 3.46 (d, 1 H, $J$ = 13.3 Hz), 2.96 (dd, 1 H, $J$ = 9.8, 3.4 Hz), 2.39 (s, 3 H), 1.46 (d hept, 1 H, $J$ = 3.4, 6.9 Hz), 1.18 (s, 3 H), 0.76 (d, 3 H, $J$ = 6.9 Hz), 0.73 (s, 3 H), 0.72 (d, 3 H, $J$ = 6.9 Hz); $^{13}$C NMR (90 MHz) δ 139.9, 139.3, 129.8, 129.1, 127.8, 127.7, 126.2, 125.7, 71.5, 63.1, 56.8, 48.2, 36.5, 30.5, 27.1, 22.6, 18.1, 16.3; MS $m/z$ (rel int) 292 (2, M − $CH_3$), 265 (21), 264 (100, M − $C_3H_7$), 132 (11), 131 (32), 117 (10), 115 (5), 91 (18), 56 (8), 42 (10); HRMS (CI, $NH_3$) calcd for $C_{22}H_{30}N$ (M + H)$^+$ 308.2378, found 308.2364; DNOE, irradiation at 4.07 ppm (H-4α) produced an 8.5% enhancement of the signal at 2.96 ppm (H-5α), yet failed to produce an enhancement of the signal at 3.46 ppm (H-3β).

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**Supplementary Material Available:** $^1$H NMR and $^{13}$C NMR spectra of the compounds which had no elemental analysis: **3b**, **3c**, **3d**, **7–13**, and 1-methyl-2,5-bis(1-methylethyl)-3,4-diphenylpyrrole, the oxidation product of **7** (21 pages). This material is contained in many 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.

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# A Nonphotochemical Approach for Synthesizing Functionalized Pentacyclo[5.4.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]-undecanes Using Samarium(II) Iodide

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For the last two decades, substituted pentacyclo[5.4.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecanes (PCUD)[1] have been explored extensively as intermediates in the synthesis of polycyclic

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