Scope and Mechanism of Stannylalumination of 1-Alkynes

Sunaina Sharma and Allan C. Oehlschlager*

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

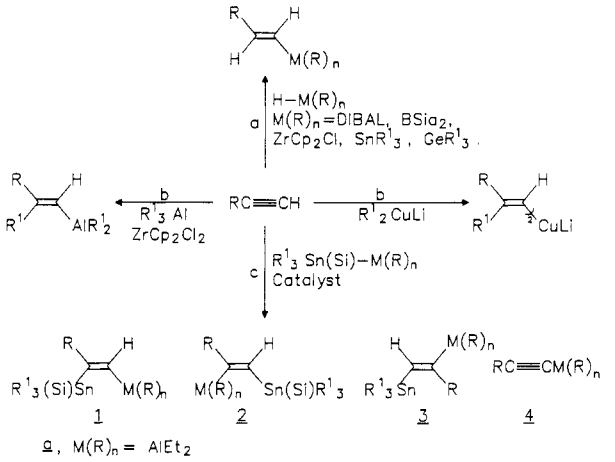
Received April 20, 1989

Terminal acetylenes react with $Bu_3SnAlEt_2$ in the presence of Cu^+ or Pd^0 catalysts to give 1,2-dimetallo-1-alkenes in highly regio- and stereoselective reactions. These intermediates can be selectively functionalized at the vinyl–aluminum bond to provide vinylstannanes, which upon transmetalation and further reaction with electrophiles give stereodefined trisubstituted olefins. In sharp contrast to the normal behavior of alkylaluminum reagents, this process tolerates a number of functional groups including OH, OAc, OTHP, and Br. Mechanistic investigations suggest that the addition of $Bu_3SnAlEt_2$ to 1-alkynes proceeds via stannylcupration followed by capture of the stannylcuprate adduct by electrophilic aluminum.

The types of organometallics used in organic synthesis have expanded in the past decade, from the classical organoalkali and Grignard reagents to include organometallics containing less electropositive metals such as Cu, B, Al, Si, Sn, Zn, and Zr. Organometallics based on these metals are more compatible with polar functional groups yet may be combined with electrophilic centers in highly stereospecific reactions. Vinyl organometallics based on these metals are the synthons of choice for synthesis of regio- and stereodefined olefins. Two popular methods for preparation of vinyl organometallics are hydrometalation (Scheme Ia) and carbometalation (Scheme Ib) of 1-alkynes. The former proceeds well for Al,[1] B,[2] Zr,[3] Sn,[4] and Ge[5] while the latter is a high-yield process for Cu[6] and Al.[7]

In contrast to hydrometalation and carbometalation, metallometalation (the addition of two metals to 1-alkynes, Scheme Ic) are not well-studied reactions. Metallometalations reported to date involve only Si or Sn organometallics in which the accompanying metal (e.g., Li, Mg, Al, Cu, B, or Zn) yields an organometallic more reactive than either Si or Sn. The reactivities of the derived adducts require electrophilic consumption of the more reactive organometallic center prior to isolation. Reaction

Scheme I



of the second vinyl organometallic center with an electrophile commonly involves electrophilic addition[8] in the case of Si or transmetalation[9,10] in the case of Sn. Thus, the utility of metallometalation lies in the simultaneous generation of two stereo- and regiodefined vinyl organometallics of differential reactivity.

Russian workers[11] were the first to report metallometalation of 1-alkynes. They reported that addition of (trialkylstannyl)lithium (or -sodium) to 1-alkynes gave mainly vinyl (*Z*) products (**3** > **1** and **2**) along with the corresponding metalated alkynes **4**. Although use of internal alkynes would seem a logical extension that would avoid formation of **4**, stannyl lithiations of internal alkynes are accompanied by appreciable amounts of products of metalations at propargylic positions.[12]

(1) (a) Okukado, N.; Van Horn, D. E.; Klinia, W. L.; Negishi, E. *Tetrahedron Lett.* **1978**, 1027. (b) Zweifel, G.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 2753. (c) Miller, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1983**, *105*, 1383. (d) Negishi, E. *Aspects of Mechanism and Organometallic Chemistry*; Brewster, J. H., Ed.; Plenum: New York, 1978.

(2) (a) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979**, 3437. (b) Miyaura, N.; Suzuki, A. *J. Chem. Soc., Chem. Commun.* **1979**, 866. (c) Zweifel, G.; Buckland, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 3184. (d) Brown, H. C. *Organic Synthesis via Organoboranes*; Wiley-Interscience: New York, 1975.

(3) (a) Van Horn, D. E.; Negishi, E. *J. Am. Chem. Soc.* **1978**, *100*, 2252. (b) Schwartz, J.; Loots, M. J.; Kosugi, H. *J. Am. Chem. Soc.* **1980**, *102*, 1333. (c) Negishi, E.; Boardman, L. D. *Tetrahedron Lett.* **1982**, 3327. (d) Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254. (e) Negishi, E.; Swanson, D. R.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1987**, 917. (f) Fryzuk, M. D.; Bates, G. S.; Stone, C. *Tetrahedron Lett.* **1986**, 1537.

(4) (a) Collins, P. W.; Jung, C. J.; Gasiecki, A.; Pappo, K. *Tetrahedron Lett.* **1978**, 3187. (b) Leusink, A. J.; Budding, H. A.; Marsman, J. W. *J. Organomet. Chem.* **1967**, *9*, 285. (c) Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1967**, *9*, 295. (d) Leusink, A. J.; Marsman, J. W.; Budding, H. A.; Noltes, J. G.; Kerk, V. D. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 567. (e) Leusink, A. J.; Marsman, J. W.; Budding, H. A. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 689. (f) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547. (g) Nozaki, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3465.

(5) (a) Ichinose, Y.; Oda, H.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3468. (b) Ichinose, Y.; Nozaki, K.; Wakamatsu, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1987**, 3709.

(6) (a) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841. (b) Westmijze, H.; Meijer, J.; Bas, H. J. T.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 299. (c) Lipshutz, B. H. *Synthesis* **1987**, 325. (d) Foulon, J. P.; Bourgain-Commercon, M.; Normant, J. F. *Tetrahedron* **1986**, *42*, 1389. (e) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley-Interscience: New York, 1980.

(7) (a) Negishi, E.; Valente, L. F.; Kobayashi, M. *J. Am. Chem. Soc.* **1980**, *102*, 3298. (b) Negishi, E.; Takahashi, T. *Aldrichimica Acta* **1985**, *18*, 31.

(8) (a) Koening, K. E.; Weber, W. P. *Tetrahedron Lett.* **1973**, 2533. (b) Miller, R. B.; Reichenbach, T. *Tetrahedron Lett.* **1974**, 543. (c) Brook, A. G.; Duff, J. M.; Reynolds, W. F. *J. Organomet. Chem.* **1976**, *121*, 293. (d) Jarvie, A. W. P.; Holt, A.; Thompson, J. *J. Chem. Soc. B* **1976**, 852. (e) Fleming, I.; Pearce, J. *J. Chem. Soc., Chem. Commun.* **1975**, 633. (f) Calas, R.; Pillot, J. P. *Bull. Soc. Chim. Fr.* **1975**, 2143. (g) Koening, K. E.; Weber, W. P. *J. Am. Chem. Soc.* **1973**, *95*, 3416. (h) Chan, T. H.; Lau, P. W, K.; Mychajlowskij, W. *Tetrahedron Lett.* **1977**, 3317. (i) Fleming, I.; Henning, R.; Plaut, H. *J. Chem. Soc., Chem. Commun.* **1984**, 29.

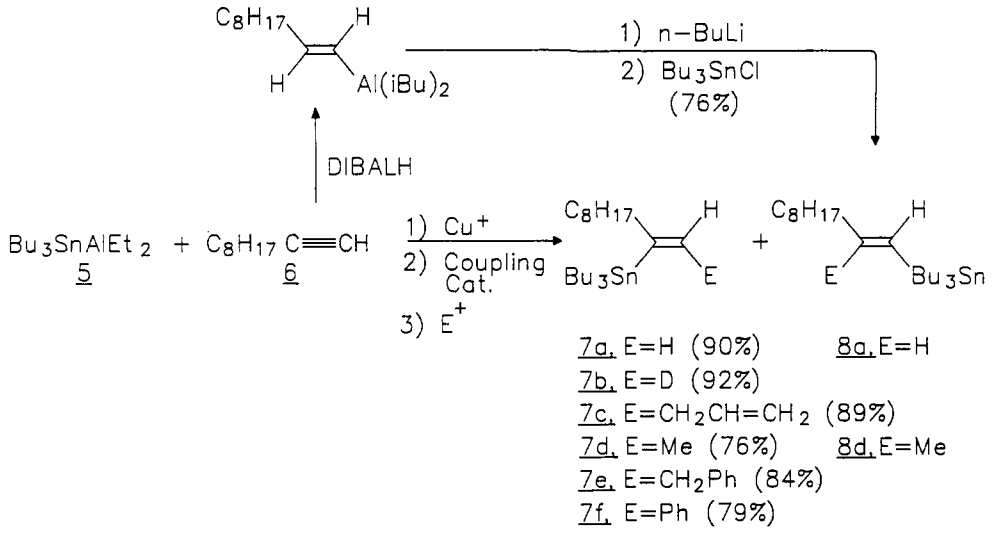
(9) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508, and references therein. (b) Mitchell, T. N.; Amamria, A. *J. Organomet. Chem.* **1981**, *210*, C17. (c) Mitchell, T. N.; Amamria, A. *J. Organomet. Chem.* **1983**, *47*, 252. (d) Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1962**, *84*, 361. (e) Seyferth, D.; Vaughan, L. G. *J. Am. Chem. Soc.* **1964**, *86*, 883. (f) Wulff, W. D.; Peterson, G. A.; Bauta, W. E.; Chan, K. S.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. J. *J. Org. Chem.* **1986**, *51*, 277.

(10) Behling, J. R.; Babiak, K. A.; Ng, J. S.; Campbell, A. L.; Moretti, R.; Koerner, M.; Lipshutz, B. H. *J. Am. Chem. Soc.* **1988**, *110*, 2641.

(11) (a) Zavgorodnii, V. S.; Simin, V. B.; Zubova, T. P.; Petrov, A. A. *Zh. Obshch. Khim.* **1976**, *46*, 197. (b) Zavgorodinii, V. S.; Zubova, T. P.; Simin, V. B.; Petrov, A. A. *Zh. Obshch. Khim.* **1981**, *51*, 2048. (c) Lysenko, Yu. A.; Troshina, E. A.; Pekhtereva, T. M. *Zh. Obshch. Khim.* **1981**, *51*, 2058.

0022-3263/89/1954-5064$01.50/0

Scheme II



The use of weakly electropositive metals is another logical extension to circumvent formation of metalated alkynes. Such reactions have been extended to bimetallic reagents derived from Sn–Al,[13] Sn–Mg,[13] Sn–Zn,[13] Sn–Cu,[14] Sn–Mn,[15] Sn–B,[16] Sn–Si,[17] Sn–Sn,[18] Si–Al,[19] Si–Mg,[19] Si–Zn,[19,20] Si–Si,[21] Si–Mn,[22] and Si–Cu.[23,24] Additions are very slow without added catalysts, and Cu^+ and Pd^0 are emerging as most effective in terms of yields and regiochemical bias.

Table I. Efficiency of Production of R_3SnLi Observed upon Quenching with MeI[a]

entry	reactants and conditions	% yield of R_3SnMe	byproducts (yield)
1	$SnCl_2$, 3BuLi, THF, 0 °C, 15 min	33	Bu_4Sn (45%), Bu_3SnCl (15%)
2	Bu_3SnCl, Li (wire), THF, 0 °C, 24 h	48	Bu_6Sn_2 (30%), Bu_4Sn (30%), Bu_3SnCl (4%)
3	Me_3SnCl, Li (dis), THF, 0 °C, 8 h	70	Me_6Sn_2 (30%)
4	Bu_3SnH, BuLi, THF, 0 °C, 15 min	4	Bu_4Sn
5	Bu_3SnH, LDA, THF, −30 °C, 15 min	90	Bu_6Sn_2 (8%)
6	$Me_3SnSnMe_3$, MeLi, −40 °C, THF, 20 min	80	

[a] See Experimental Section.

Several problems beset Sn- and Si-based metallometalation of 1-alkynes. Reactions utilizing Sn- and Si-based reagents wherein $M(R)_n$ = Al,[13,19] Mg,[13,19] and Zn[13,19,20] are reported to require a 3-fold excess of reagent to achieve high alkyne consumption. The use of excess reagent leads to the formation of byproducts that are not easily separated from the vinylsilane[23,24] or stannane[13c] products unless the alkyne carries a polar functional group. Addition of Sn–Cu reagents to alkynes reportedly requires consumption of one vinyl center by in situ protonolysis. This is presumably to overcome an unfavorable adduct ⇄ alkyne equilibrium.[14b-e]

Regiospecificity is high for some stannylmetalations (Scheme I, 1/2: Sn–Cu[14] (100/0), Sn–Zn[13] (95/5), Sn–Si[17]

(12) (a) Reich, H. J.; Yelm, K. E.; Reich, I. L. *J. Org. Chem.* **1984**, *49*, 3438. (b) Miller, J. A.; Zweifel, G. *Synthesis* **1983**, 128.

(13) (a) Hibino, J.-I.; Matsubara, S.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, 2151. (b) Matsubara, S.; Hibino, J.-I.; Morizawa, Y.; Oshima, K.; Nozaki, H. *J. Organomet. Chem.* **1985**, *285*, 163. (c) Sharma, S.; Oehlschlager, A. C. *Tetrahedron Lett.* **1986**, 6161. (d) Nonaka, T.; Okuda, Y.; Matsubara, S.; Oshima, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1986**, *51*, 4716.

(14) (a) Westmijze, H.; Ruitenberg, K.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1982**, 2797. (b) Piers, E.; Chong, J. M. *J. Chem. Soc., Chem. Commun.* **1984**, 934. (c) Cox, S. D.; Wudl, F. *Organometallics* **1983**, *2*, 184. (d) Piers, E.; Chong, M. J. *Can. J. Chem.* **1988**, *66*, 1425. (e) Piers, E.; Morton, H. E.; Chong, J. M. *Can. J. Chem.* **1987**, *65*, 78. (f) Zweifel, G.; Leong, W. *J. Am. Chem. Soc.* **1987**, *109*, 6409. (g) Piers, E.; Fresen, R. W.; Keay, B. A. *J. Chem. Soc., Chem. Commun.* **1985**, 809. (h) Piers, E.; Chong, J. M. *J. Org. Chem.* **1982**, *47*, 1602. (i) Piers, E.; Morton, H. E. *J. Org. Chem.* **1980**, *45*, 4263. (j) Piers, E.; Chong, J. M.; Keay, B. A. *Tetrahedron Lett.* **1985**, *26*, 6265. (k) Piers, E.; Chong, J. M.; Morton, H. *Tetrahedron Lett.* **1981**, 4905. (l) Taddei, M.; Mann, A. *Tetrahedron Lett.* **1986**, 2913.

(15) (a) Hibino, J.-I.; Nakatsukasa, S.; Fugami, K.; Matsubara, S.; Oshima, K.; Nozaki, H. *J. Am. Chem. Soc.* **1985**, *107*, 6416.

(16) (a) Nozaki, K.; Wakamatsu, K.; Nonaka, T.; Tückmantel, W.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1986**, 2007. (b) Sharma, S.; Oehschlager, A. C. *Tetrahedron Lett.* **1988**, 261. (c) Bihlmayer, C.; Kerschl, S.; Wrackmeyer, B. *Z. Naturforsch.* **1987**, *42b*, 715. (d) Chu, K.-H.; Wang, K. K. *J. Org. Chem.* **1986**, *51*, 767.

(17) (a) Mitchell, T. N.; Killing, H.; Dicke, R.; Wickenkamp, R. *J. Chem. Soc., Chem. Commun.* **1985**, 354. (b) Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561. (c) Chenard, B. L.; Van Zyl, C. M.; Sanderson, D. R. *Tetrahedron Lett.* **1986**, 2801. (d) Chenard, B. L.; Laganis, E. D.; Davidson, F.; RajanBabu, T. V. *J. Org. Chem.* **1985**, *50*, 3666.

(18) (a) Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1983**, *241*, C45. (b) Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1986**, *304*, 257. (c) Mitchell, T. N.; Reimann, W. *J. Organomet. Chem.* **1985**, *281*, 163. (d) Mitchell, T. N.; Amamria, A. *J. Organomet. Chem.* **1983**, *252*, 47. (e) Killing, H.; Mitchell, T. N. *Organometallics* **1984**, *3*, 1318.

(19) (a) Hayami, H.; Sato, M.; Kanemoto, S.; Morizawa, Y.; Oshima, K.; Nozaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 4491. (b) Wakamatsu, K.; Nonaka, T.; Okuda, Y.; Tückmantel, W.; Oshima, K.; Utimoto, K.; Nozaki, H. *Tetrahedron* **1986**, *42*, 4427. (c) Okuda, Y.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, 2483.

(20) Okuda, Y.; Wakamatsu, K.; Tückmantel, W.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1985**, 4629.

(21) (a) Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *J. Organomet. Chem.* **1980**, 186. (b) Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, 149.

(22) (a) Fugami, K.; Oshima, K.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1986**, 2161. (b) Fugami, K.; Nakatsukasa, S.; Oshima, K.; Utimoto, K.; Nozaki, H. *Chem. Lett.* **1986**, 869.

(23) (a: Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc., Perkin Trans 1* **1981**, 2527. (b) Fleming, I.; Percival, A. *J. Chem. Soc., Chem. Commun.* **1978**, 278. (c) Fleming, I.; Roessler, F. *J. Chem. Soc., Perkin Trans 1* **1980**, 260. (d) Fleming, I.; Roessler, F. *J. Chem. Soc. Chem. Commun.* **1980**, 276. (e) Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans 1* **1981**, 2520. (f) Fleming, I.; Marchi, D. *Synthesis* **1981**, *560*. Chen, H.-M.; Oliver, J. P. *J. Organomet. Chem.* **1986**, *316*, 255. (g) Fleming, I.; Taddei, M. *Synthesis* **1985**, 899. (h) Fleming, I.; Taddei, M. *J. Chem. Soc., Chem. Commun.* **1985**, 899. (i) Fleming, I.; Newton, T. W. *J. Chem. Soc., Perkin Trans 1* **1984**, 119. (j) Fleming, I.; Newton, T. W. *J. Chem. Soc., Perkin Trans 1* **1984**, 1805. (k) Fleming, I.; Waterson, D. *J. Chem. Soc., Perkin Trans 1* **1984**, 1809. (l) Chow, H.-F.; Fleming, I. *J. Chem. Soc., Perkin Trans 1* **1984**, 1815.

(24) Sharma, S.; Oehlschlager, A. C. *Tetrahedron Organocopper Symp.* **1989**, *2*, 557.

Table II. Addition of $Bu_3SnAlEt_2$ to 1-Decyne[a]

entry	$Bu_3SnM(R)_n$	$Bu_3SnM(R)_n$: Alkyne	cat. (solvt)	temp, °C	7a[b]	8a[b]	% yield,[b] 7a + 8a (alkyne unreacted)	tin products Bu_4Sn	tin products Bu_6Sn_2
1	$Bu_3SnAlEt_2$[c]	3:1	CuCN (THF)	−30	81	19	85 (15)	52	8
2	$Bu_3SnAlEt_2$[d]	3:1	CuCN (THF)	−30	91	9	quant	6	41
3	$Bu_3SnAlEt_2$[c]	3:1	CuI (THF)	−30	19	81	21 (58)	50	7
4	$Bu_3SnAlEt_2$[d]	3:1	CuI (THF)	−30	10	90	51 (22)	12	23
5	$Bu_3SnAlEt_2$[c]	3:1	$Pd(Ph_3P)_2Cl_2$ (THF)	0	57	43	27 (59)	50	13
6	$Bu_3SnAlEt_2$[d]	3:1	$Pd(Ph_3P)_2Cl_2$ (THF)	0	60	40	48 (17)	12	42
7	$Bu_3SnAlEt_2$[c]	3:1	$Pd(Ph_3P)_4$ (THF)	0	35	65	36 (28)	38	14
8	$Bu_3SnAlEt_2$[d]	3:1	$Pd(Ph_3P)_4$ (THF)	0	15	85	44 (21)	17	33
9	$Bu_3SnAlEt_2$[d]	3:1	$Pd(Ph_3P)_2Cl_2$ (DIBALH, THF)	−30	35	65	59 (11)	15	37
10	$Bu_3SnAlEt_2$[d]	3:1	$CuBr\cdot Me_2S$ (THF)	−30	85	15	32 (28)	12	31
11	$Bu_3SnAlEt_2$[c]	3:1	CuCN (HMPA)	0	6	94	45 (51)	45	1
12	$Bu_3SnAlEt_2$[d]	3:1	CuCN (HMPA)	0	6	94	56 (18)	22	37
13	$Bu_3SnAlEt_2$[d]	2:1	CuCN (THF)	−30	90	10	90 (7)	11	28
14	$Bu_3SnAlEt_2$[d]	2:1 (inv)	CuCN (THF)	−30	76	24	57 (24)	3	52
15	$Bu_3SnAlEt_2$[d]	1:1	CuCN (THF)	−30	92	8	31 (53)	28	8
16	$Bu_3SnAlEt_2$[d]	1:1 (inv)	CuCN (THF)	−30	80	20	11 (82)	0	48
17	$Bu_3SnAlEt_2$[e]	1:1.2	CuCN (THF)	−30	87	13	59 (5)	15	15
18	$Bu_3SnAlEt_2$[e]	1:1.2 (inv)	CuCN (THF)	−30	90	10	21 (43)	17	18
19	$Bu_3SnAlEt_2$[e]	1:1.2	CuCN (THF)	−78	92	8	52 (7)	7	17

[a] See Scheme II for numbering. [b] Yields were calculated by using relative weight response of products vs dodecane internal standard and for **7a** and **8a** are based on alkyne used. [c] Bu_3SnLi prepared from $SnCl_2$ and BuLi. [d] Bu_3SnLi prepared from Bu_3SnH and LDA. [e] Half of the theoretical amount of alkyne was added, followed by CuCN (5 mol %), and then the remaining amount of alkyne.

(90/10)) but low for others (Sn–Al[13] (62/38), Sn–Mg[18] (30/70), and Sn–B[16a] (35/65)). Only for the Sn–Zn, Sn–Cu, and Sn–Si cases is the regiochemical bias synthetically useful. Control of regiochemistry in the addition of Si–$M(R)_n$ and Sn–$M(R)_n$ reagents to 1-alkynes is a goal that has been pursued only for silicon–zinc reagents. Nozaki and co-workers[20] reported that the Cu^+-catalyzed addition of $Ph_3SiZnEt_2Li$ to 1-alkynes gave only regioisomer **2**. A related reagent[20] possessing larger zinc alkyl groups, $PhMe_2SiZn^tBu_2Li$, added to 1-alkynes to give (>99:1) the alternate regioisomer, **1**.[20]

We report conditions for the Cu^+-catalyzed stannylalumination of 1-alkynes that give high yields of adducts while minimizing the formation of Sn-based byproducts. We also report the formation of either regioisomeric adduct as well as selective functionalization of both vinyl metal centers to generate stereo- and regiodefined trisubstituted alkenes. Finally, we report the initial mechanistic studies of these important reactions.

Results and Discussion

Effect of Method of Preparation of (Trialkylstannyl)lithium on the Efficiency of Stannylalumination. Capture of R_3SnLi by methyl iodide provided a facile assay of the efficiency of R_3SnLi preparation (Table I). Reaction of Bu_3SnH[25] with LDA (entry 5)[26] at low temperature and reaction of $Me_3SnSnMe_3$ with MeLi (entry 6)[26] were clearly the most efficient.[27]

Reaction of Bu_3SnLi with Et_2AlCl in THF gave solutions of $Bu_3SnAlEt_2$ (**5**), which in the presence of Cu^+ catalysts reacted with 1-decyne (**6**) to give the vinylstannanes **7a** and **8a** (Scheme II, Table II). The more efficient the reaction yielding Bu_3SnLi, the more efficient the subsequent stannylalumination of 1-decyne (Table II, compare entries 1 and 2, 3 and 4, 5 and 6, 7 and 8). Vinylstannanes **7a** and **8a** were separated by preparative gas chromatography, and their structures deduced by ^1H, ^{13}C, and ^{119}Sn[28] NMR spectroscopies as well as GC/MS. Evidence for the structure and stereochemistry of **7a** and **8a** was provided by the magnitude of the coupling constants ($^3J_{Sn-H} \sim 140$ Hz for **7a** and ~70 Hz for **8a**) between the ^{117}Sn and ^{119}Sn isotopes and ^1H. This value is typical of vinylstannanes having trialkylstannyl groups trans or cis respectively to vinyl hydrogens. Cis addition to the alkyne was confirmed by the disappearance of the high-field[13] vinyl hydrogen signal in the ^1H NMR spectrum of **7b** when the reaction of **5** with **6** was quenched with ^2HCl. Regioisomer **8a** was prepared independently by hydroalumination[1] of **6** with DIBALH, transmetalation (*n*-BuLi), and reaction of the alkenylalanate with Bu_3SnCl (Scheme II). Proton magnetic resonance and mass spectra as well as the gas chromatographic retention time of this sample were indistinguishable from those of **8a** obtained by metallometalation (Scheme II).

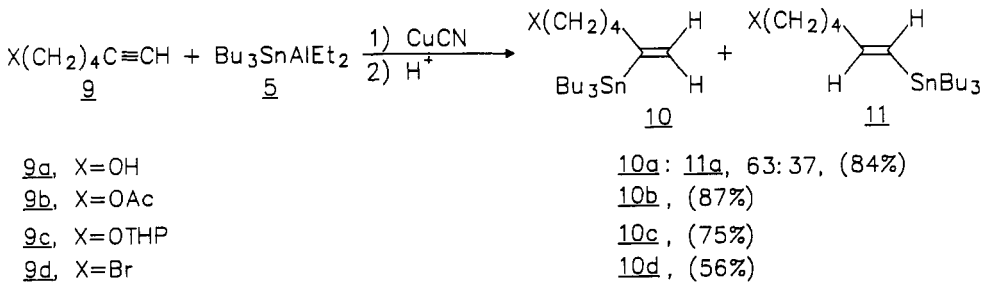
Effect of Catalyst on Stannylalumination. Use of Pd^0, Pd^{2+}, or Cu^+ as catalysts resulted in efficient addition of **5** to **6** (Table II). Addition of **6** to THF solutions of **5** at −30 °C in the presence of Cu^+ salts resulted in high yields of vinylstannanes **7a** and **8a** with a synthetically useful regiochemical bias favoring **7a**. Use of CuCN gave higher yields and higher regiochemical bias than $CuBr\cdot Me_2S$ (Table II, compare entry 2 with 10). Regioisomer **8a** was favored (90:10) when CuI was used as the catalyst (compare entry 2 with 4). Catalysts based on Pd^0 and Pd^{2+} generally gave mixtures of **7a** and **8a** that were rich in **8a** (Table II, entries 5–9). Yields and regiochemical biases were lower for palladium catalysts than for CuCN.

Effect of Mode of Addition of Reagents on Stannylalumination. Addition of **6** to cold THF solutions of **5** followed by Cu^+ and quenching with 1 N HCl yielded vinylstannane products (**7a** > **8a**) of higher regiochemical purity than when the reaction was conducted by adding solutions of **5** to **6** (Table II, compare entry 13 with 14, 15 with 16, and 17 with 18).

When alkyne was added in one portion to the organometallic reagent, it was necessary to use excess reagent to achieve high alkyne consumption (Table II, entries 2, 13, and 15). Excess reagent was eventually converted to hexaalkylditin and tetraalkyltin. Slow addition of alkyne to 1.2 equiv of **5** at −30 °C resulted in high alkyne consumption and minimal formation of hexabutylditin (Table

(25) Kuivila, H. G. *Synthesis* **1970**, 499.
(26) Still, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4836.
(27) The same observation was made by Quintard: Quintard, J.-P.; Dumartin, G.; Guerin, C.; Dubac, J.; Laporterie, A. *J. Organomet. Chem.* **1984**, *266*, 123.
(28) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, and references therein.

Scheme III



9a, X=OH
9b, X=OAc
9c, X=OTHP
9d, X=Br

10a: 11a, 63:37, (84%)
10b, (87%)
10c, (75%)
10d, (56%)

II, entries 17 and 19). Excess 1-alkyne can presumably provide a proton, which can react with the intermediate generated. Normant has recently shown that slow addition of 1-alkynes to organometallics at low temperature improved yields of carbocupration reactions.[29]

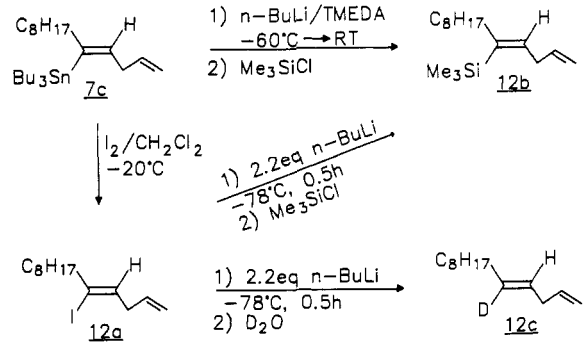
Effect of Solvent on Stannylalumination. Addition of polar aprotic solvents such as DMF or DMSO had no effect on the course of Cu^+-catalyzed stannylalumination, whereas addition of HMPA reversed the regiochemistry of the reaction. The reaction was conducted by adding HMPA to cold THF solutions of Bu_3SnLi followed by addition of Et_2AlCl, **6**, and CuCN. After consumption of **6** ceased the reaction was quenched with 1 N HCl to yield vinylstannane **8a** as the major regioisomer (94:6; Table II, compare entry 1 with 11 and 2 with 12).

Reactions of 1,2-*cis*-Dimetallo-1-alkenes with Electrophiles. The dimetallic adducts generated in the reaction of **5** with **6** underwent either transmetalation with *n*-BuLi or Pd^0-catalyzed cross-coupling reactions exclusively at the vinyl–aluminum bond (Scheme II). For instance, stannylalumination of 1-decyne catalyzed by CuCN, followed by transmetlation of the vinylalane moiety with *n*-BuLi followed by addition of excess of allyl bromide[30] in THF or methyl iodide in HMPA gave good yields of **7c** and mixtures of **7d** and **8d**, respectively. Addition of 3 mol % of $Pd(Ph_3P)_2Cl_2$–DIBALH[31] to the adduct derived from the addition of **6** to **5** under CuCN catalysis followed by addition of allyl bromide, benzyl bromide, or iodobenzene[32] gave excellent yields of **7c**, **7e**, or **7f** in high stereo- and regiochemical purity (Scheme II).

Compatibility of Polar Functional Groups with Stannylalumination. That stannylalumination is compatible with polar functional groups was shown by efficient reaction of **5** with 5-hexyn-1-ol (**9a**), 6-acetoxy-1-hexyne (**9b**), 1-(tetrahydropyranyloxy)-5-hexyne (**9c**), and 1-bromo-5-hexyne (**9d**) in the presence of CuCN to yield after the usual workup vinyl stannanes **10a–d** and **11a** (Scheme III). In case of 1-bromo-5-hexyne, a product arising from intramolecular cyclization was also obtained. The only other tin-containing product in these reactions was hexabutylditin, which was easily separated by silica gel chromatography.

Synthesis of Trisubstituted Alkenes. Vinylstannanes **7c**, **7d**, and **8d** were further reacted with electrophiles under transmetalation conditions to afford olefins **12a–i** (Schemes IV and V). In each case the reactions resulted in cross-coupled products derived from retention of configuration with respect to the vinyl–tin bond. In the case of **7c** (Scheme IV), reaction with I_2 in CH_2Cl_2 smoothly produced the vinyl iodide **12a**, which underwent facile lithiation with excess *n*-BuLi.[33] Addition of Me_3SiCl gave **12b** in good yield, whereas quenching the reaction with ^2H_2O gave an excellent yield of **12c**. Olefin **12b** was also synthesized in moderate yield by treatment of **7c** with *n*-BuLi/TMEDA[17b] followed by trapping of the vinyl anion with Me_3SiCl. The low yield of product in this reaction is attributed to poor transmetalation due to steric congestion of the tributylstannyl group.[4,33b,34]

Scheme IV



Oxidative addition of $(Ph_3P)_4Pd$ to either benzyl bromide or allyl bromide followed by coupling with vinylstannane, **7d** (Scheme V), in refluxing THF gave excellent yields of **12d** and **12e**, respectively.[35] **8d** also underwent facile coupling with (*E*)-1-iodo-hexene (**12f**) under Pd^0 catalysis to yield stereochemically pure 1,3-diene **12g**.[36] Palladium-catalyzed cross coupling of the iodide derived from **8d** with 1-hexynyltributylstannane (**12h**) cleanly gave stereodefined 1,3-enyne **12i**.[37] The rate of coupling reaction was sensitive to the catalyst. Higher ratios of phosphine ligand to palladium slowed the reaction as observed earlier,[37] and hence $(Ph_3P)_2PdCl_2$–DIDALH[31] complex was used as the catalyst for cross-coupling reactions for the synthesis of **12g** and **12i**.

Mechanistic Studies. The formation of hexabutylditin and tetrabutyltin as side products as well as the incomplete consumption of alkyne even with 3 equiv of $Bu_3SnAlEt_2$ suggested that stannylalumination was competing with other processes. The mechanistic possibilities shown in Scheme VIa–h illustrate the wide variety of processes that

(29) Gardette, M.; Alexakis, A.; Normant, J. F. *Tetrahedron* **1985**, *41*, 5887.

(30) (a) Zweifel, G.; Steele, R. B. *J. Am. Chem. Soc.* **1967**, *89*, 2754. (b) Baba, S.; Van Horn, D. E.; Negishi, E. *Tetrahedron Lett.* **1976**, 1927. (c) Eisch, J. J.; Damasevitz, J. E. *J. Org. Chem.* **1976**, *41*, 2214. (d) Uchida, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1976**, *41*, 2215.

(31) Negishi, E.; Takahashi, T.; Akiyoshi, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1338.

(32) (a): Matsushita, H.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 2882. (b) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393. (c) Negishi, E.; Baba, S. *J. Chem. Soc., Chem. Commun.* **1976**, 596. (d) Baba, S.; Negishi, E. *J. Am. Chem.* **1976**, *98*, 6729. (e) Negishi, E.; Valente, L. F.; Kobayshi, M. *J. Am. Chem. Soc.* **1980**, *102*, 3298. (f) Kobayashi, M.; Negishi, E. *J. Org. Chem.* **1980**, *45*, 5223.

(33) (a) Corey, E. J.; Beames, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 7210. (b) Jung, M. E.; Light, L. A. *Tetrahedron Lett.* **1982**, 3851.

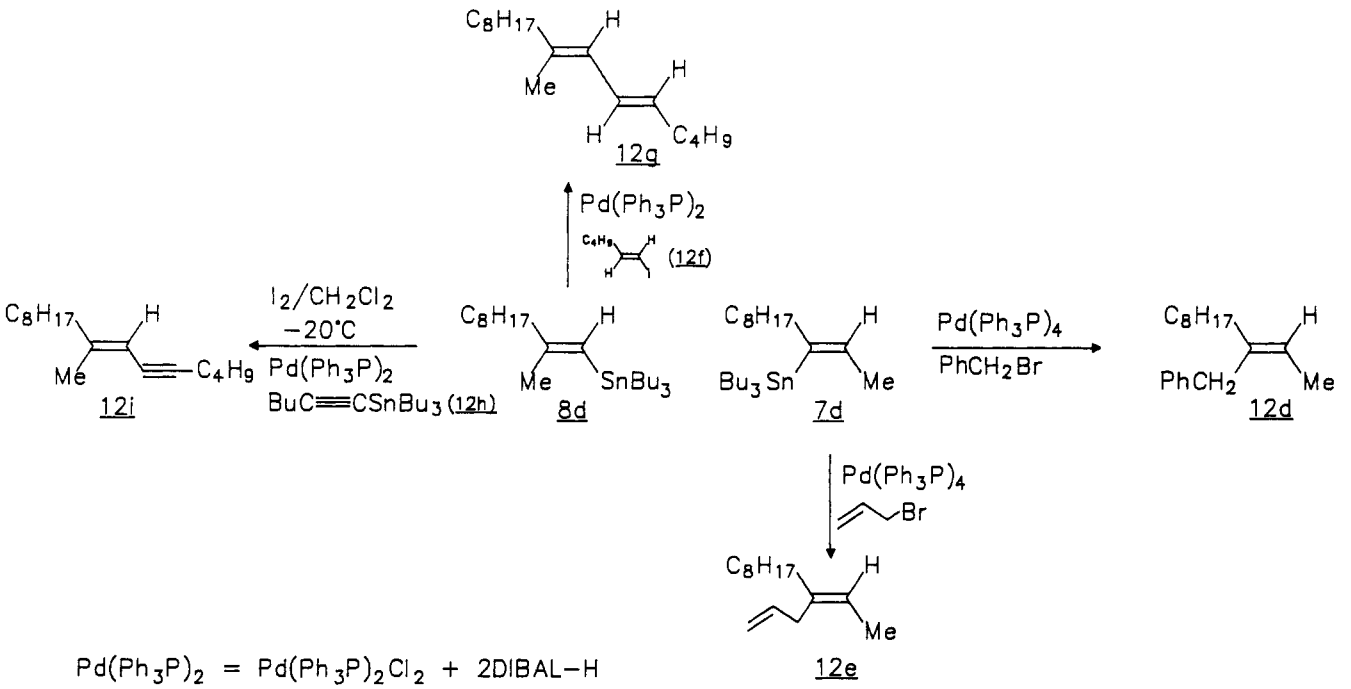
(34) Piers, E.; Skerlj, R. T. *J. Org. Chem.* **1987**, *52*, 4423.

(35) (a) Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4838. (b) Sheffy, F. K.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 7173.

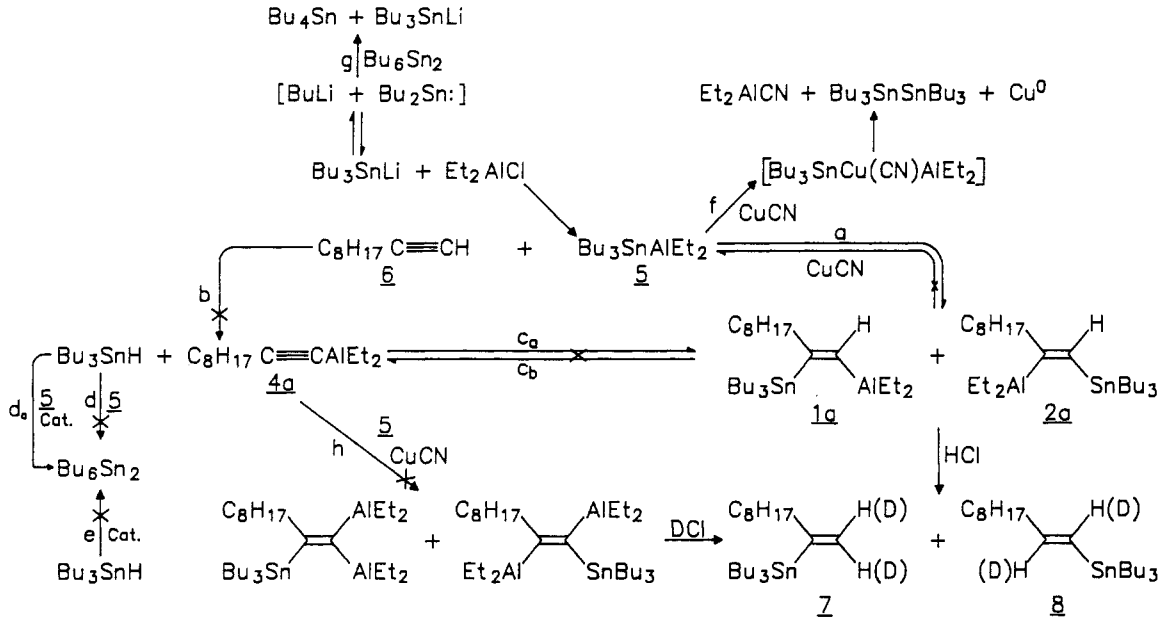
(36) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630.

(37) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138.

Scheme V



Scheme VI



have literature precedent in related systems.

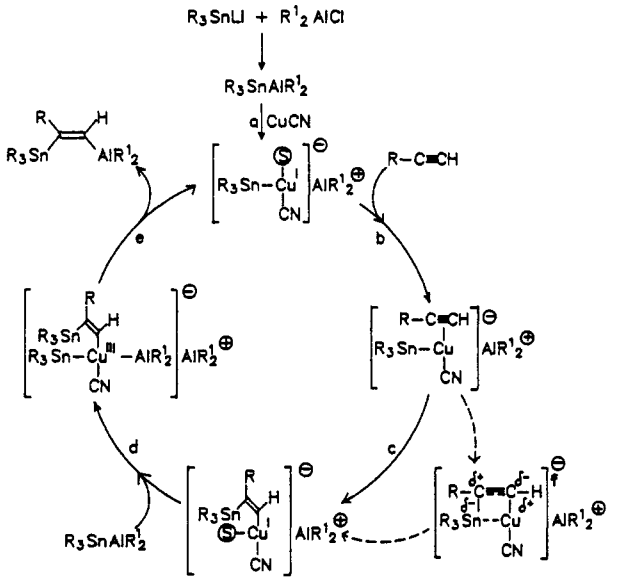
The reversibility of process a was queried by conducting the addition of **5** and **6** using an equimolar ratio of reactants and allowing the reaction to proeed until no further consumption of alkyne was observed. At this point an equivalent amount of [1-^{2}H]-**6** was added and the reaction proceeded for an additional time equivalent to that for the initial reaction. Protolytic workup of the reaction followed by analysis of the vinylstannane adducts by ^{1}H NMR and GC/MS revealed no ^{2}H incorporation in either vinylstannane (**7** and **8**). These results suggest that the addition of **5** to **6** is not reversible under these reaction conditions (i.e., **1a** and **2a** are not converted to **5** and **6**).

Process b was shown to be inoperative by conducting the reaction of **5** with [1-^{2}H]-**6** in the presence of CuCN followed by protolytic workup and examination of the ^{2}H content of unreacted **6**. No diminution of ^{2}H in **6** was observed in this experiment. Thus, $Bu_3SnAlEt_2$ did not remove the C-1 hydrogen from **6** as is found for the reaction of 1-alkynes with alkylcopper reagents.[38] This experiment also suggests that the conversion of **1a** and **2a** to $C_8H_{17}C{\equiv}CAlEt_2$ (**4a**) as shown in process c_b is not occurring. To check the forward process c_a, reaction of Bu_3SnH with **4a** prepared from $C_8H_{17}C{\equiv}CLi$ and $ClAlEt_2$ in the presence of Cu^+ was examined. Recovery of only 1-decyne from this reaction suggests that process c_a is not operative.

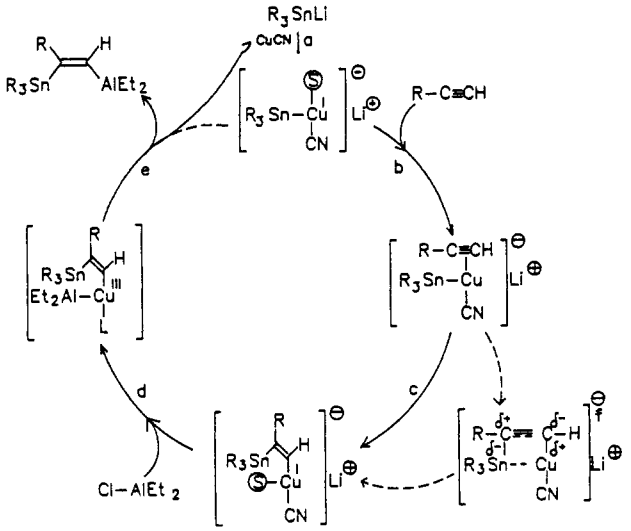
To investigate the operation of process d, $Bu_3SnAlEt_2$ was reacted with Bu_3SnH. Without added catalyst no hexabutylditin was observed over 24 h. Metallometalations are normally complete in 3 h. When either CuCN or CuI were added to THF solutions of $Bu_3SnAlEt_2$ containing Bu_3SnH (process d_a), the only product detected (GC) was

(38) Normant, J. F. *New Appl. Organomet. Chem.* **1976**, *1*, 219.

Scheme VII



Scheme VIII



$Bu_3SnSnBu_3$. No hexabutylditin was obtained when the above catalysts were reacted with Bu_3SnH alone (process e), but reaction of $Bu_3SnAlEt_2$ with CuI and $Pd(Ph_3P)_4$ gave hexabutylditin in 69 and 77% yield, respectively. Thus, hexabutylditin can be formed by reaction of $Bu_3SnAlEt_2$ with catalyst in the absence of alkyne. These results are consistent with formation of hexabutylditin via reductive elimination from a stannylaluminocuprate as shown in process f. The formation of tetrabutyltin from decomposition of alkali-metal stannides in the presence of hexabutylditin (process g) is a known process.[39]

The possible operation of process h was examined by conducting the reaction of **4a** with $Bu_3SnAlEt_2$ in the presence of CuCN. No vinylstannanes were obtained from quenching this reaction after 24 h. An independent check of reaction h involved reaction of **5** (method b, Table II) with **6** in a 1:1 molar ratio followed by quenching with ^2HCl. Incorporation of only one ^2H into each of the vinylstannane products **7** and **8** (^1H NMR) ruled out the operation of this process.

The preparative synthetic procedure that was found to give good yields of products involves addition of the (trialkylstannyl)lithium and diethylaluminum chloride to the reaction solution prior to cuprous ion. Monitoring these solutions by ^{119}Sn and ^{13}C NMR[40] revealed that reaction between trialkylstannyl anion and aluminum cation occurred prior to addition of Cu^+. Although the reagent is formulated as $Bu_3SnAlEt_2$, cuprous ion is undoubtedly an integral part of the reactive species. The mechanism (Scheme VII) we consider to be operative involves oxidative addition (a) of $Bu_3SnAlEt_2$ to Cu^+ to generate a three-coordinate Cu^+ species followed by insertion (b) of the alkyne, a step that does not involve a change in the oxidation state of copper. This is followed by rearrangement (c) to a vinylstannyl cuprate adduct with oxidation of the copper to Cu^{3+} through addition (d) of a second equivalent of $Bu_3SnAlEt_2$. The next logical step is reductive elimination (e) of the (vinylstannyl)aluminum adduct to regenerate the initial Cu^+ complex, thereby making the process catalytic.

Stannylalumination also proceeds well when diethylaluminum chloride is added to the reaction mixture after addition of the trialkylstannate anion, Cu^+ salt, and alkyne (Scheme VIII). In this case we consider the reaction to proceed via initial formation of the lithium (trialkylstannyl)cyanocuprate (a).[40,41] Complexation of this species with alkyne (b) followed by rearrangement (c) to a vinylstannyl cuprate adduct yields a Cu^+ species. Reaction of this complex with diethylaluminum chloride (d) would give a Cu^{3+} species with an expected propensity for reductive elimination (e) to the catalytic Cu^+ species and the (vinylstannyl)aluminum adduct. In this proposal the question of reversibility in the stannylcupration step[14b,d] revolves around the rate of the reverse of step c compared to the rate of step d in Scheme VIII. Under the conditions of reactions as performed for synthetic purposes, d appears to be much faster than the reverse of step c.

Regioselectivity in metallometalations is influenced by the catalyst employed as well as by the metals and steric bulk of the alkyl groups in the bismetalloid. According to Schemes VII and VIII, a change in regiochemistry in the cuprous ion catalyzed stannylmetalations of 1-alkynes is due to a change in the regioselectivity in step c. Under normal circumstances (THF, −50 to −70 °C) the trialkylstannyl group preferentially migrates to the most substituted carbon. This outcome could be due to the polarity shown in Schemes VII and VIII for step c wherein the trialkylstannyl group bears a negative charge relative to the copper. Electron donation to the latter from a counterion or solvent (HMPA) could reverse the polarity in the Sn–Cu bond and reverse the regioselectivity in this step. Thus it is possible to envision a change in regiochemistry for stannylalumination in the presence of HMPA or the presence of functional groups on the 1-alkyne without requiring either stannylcupration or subsequent steps to be reversible.

Recent ^{13}C NMR experiments in this laboratory have shown that in THF lower order silyl and stannyl cuprates exhibit broad signals of low intensity, indicating aggregated species for these reagents. Addition of HMPA to these reagents leads to sharpened signals of increased intensity, suggesting less aggregation in this solvent. These observations raise the possibility that the change in regiochem-

(39) (a) Kobayashi, K.; Kawanisi, M.; Hitomi, T.; Kozima, S. *J. Organomet. Chem.* **1982**, *233*, 299. (b) Kitching, W.; Olszowy, H. A.; Drew, G. M. *Organometallics* **1982**, *1*, 1244.

(40) Sharma, S.; Oehlschlager, A. C. *J. Am. Chem. Soc.* (submitted).

(41) For analogous alkylcuprates see: (a) Hamon, L.; Levisalles, J. *J. Organomet. Chem.* **1983**, *251*, 133. (b) Marino, J. P.; Fernadez de la Pradilla, R.; Laborde, E. *J. Org. Chem.* **1984**, *49*, 5279. (c) Acker, R. D. *Tetrahedron Lett.* **1977**, 3402. (d) Acker, R. D. *Tetrahedron Lett.* **1978**, 2399 (e) Corriu, R. J. P.; Guerin, C.; M'Boula, J. *Tetrahedron Lett.* **1981**, 2985. For analogous silylcuprates see ref 24.

istry of Cu^+ addition of **5** to 1-alkynes upon addition of HMPA is due to a lower steric requirement for the copper center in this solvent compared to THF resulting from a lower aggregation state of the reagent in the former.

Experimental Section

^1H NMR and ^{119}Sn spectra were recorded on a Bruker WM-400 spectrometer in $CDCl_3$ using $CHCl_3$ (δ 7.25) and Me_4Sn (δ 0), respectively, as internal standards. The tin–proton coupling constants (J_{Sn-H}) are given as an average of the ^{117}Sn and ^{119}Sn values. Low-resolution mass spectra were obtained on a Hewlett-Pckard 5985B GC/MS system operating at 70 eV. High-resolution mass spectra were recorded on a Kratos/AEI MS 50 spectrometer. For compounds containing a Bu_3Sn group, molecular mass measurements are based on ^{120}Sn and were based on the (M^+ – Bu) peak. Gas chromatographic analyses utilized a Hewlett-Packard 5880A instrument equipped with a with a flame ionization detector and employing a J/W fused silica DB-1 capillary column (15 m × 0.25 mm), using a linear temperature gradient. The purity of all the title compounds was ≥95% as judged by gas chromatographic analysis using dodecane as an internal standard.

Tetrahydrofuran was freshly distilled over potassium benzophenone–ketyl. Hexamethylphosphorous triamide and diisopropylamine were distilled over calcium hydride and stored over activated 3-A molecular sieves. Unless otherwise stated, chemicals obtained from commercial sources were used without further purification.

All organometallic reactions were conducted in flame-dried glassware under an atmosphere of argon. Usual workup involved quenching of the reaction with 1 N HCl, extraction of the organic layer with Et_2O (2 × 5 mL), back-washing the combined organic extracts with saturated NH_4Cl (2 × 5 mL), and drying of the organic layer over anhydrous $MgSO_4$.

Preparation of Bu_3SnH. Reduction of Bu_3SnCl with $LiAlH_4$[25] gave Bu_3SnH in 82% chemical yield and 97% purity as measured by gas chromatographic analysis after distillation (bp 49 °C (0.05 mmHg)). A modified workup procedure was employed that involved the transfer of the supernatant liquid via a canula, removal of Et_2O, and addition of *n*-hexane. Further removal of solvent and distillation of product under reduced pressure gave oxide-free Bu_3SnH, which could be stored in the freezer without any noticeable decomposition for several months.

Preparation of (Trialkylstannyl)lithium and Quenching with Methyl Iodide (Table I). Entry 1. Bu_3SnLi was prepared according to the procedure of Nozaki.[13] Stannous chloride (0.6 g, 3.16 mmol) was stirred in 5 mL of dry THF at 0 °C, and then *n*-BuLi (3.65 mL, 9.48 mmol) was added dropwise over 30 min. To an aliquot of the deep-red solution was added excess MeI in THF at 0 °C. The reaction was stirred for 15 min and then quenched by addition of NH_4Cl solution, and the separated organic layer analyzed by gas chromatography using dodecane as an internal standard. Bu_3SnMe was formed in 33% yield.

Entry 2. A solution of Bu_3SnCl (4.0 g, 12.5 mmol) in 25 mL of THF was added to a suspension of Li clippings (0.35 g, 50 mmol) in 20 mL of THF at 0 °C according to the procedure of Soloski.[43] The reaction was stirred overnight at this temperature, and the green solution treated with excess MeI. The yield of Bu_3SnMe was 48% as calculated by GC against an internal standard (dodecane).

Entry 3. A Li dispersion (1.4 g, 200 mmol) in *n*-hexane was transferred in a preweighed Schlenk tube under argon. THF (75 mL) was added, followed by Me_3SnCl (10 g, 50 mmol) in 50 mL of THF. The reaction was stirred at 0 °C for 8 h. An aliquot was quenched with excess MeI. The yield of Me_3SnLi was calculated from the amount of Me_4Sn detected by gas chromatographic analysis vs decane as an internal standard.

Entry 4. *n*-BuLi (0.38 mL, 1.0 mmol), was added to a stirred solution of Bu_3SnH (0.291 g, 1.0 mmol) in 5 mL of THF at 0 °C. The reaction was quenched with MeI after 15 min. Gas chromatographic analysis revealed Bu_4Sn as the major product accompanied by only 4% of Bu_3SnMe.

Entry 5. Preparation of Bu_3SnLi by the modified procedure of Still[26] involved addition of BuLi (1.0 mL, 2.5 mmol) to an efficiently stirred solution of diisopropylamine (0.35 mL, 2.5 mmol) in 5 mL of THF at –10 °C. The reaction was stirred for 30 min, and then Bu_3SnH (0.72 g, 3.5 mmol) was added at –30 °C. The reaction turned pale green at this point. The yield of Bu_3SnMe was 90% as determined by gas chromatographic analysis using dodecane as an internal standard.

Entry 6. To an efficiently stirred solution of $Me_3SnSnMe_3$ (1.63 g, 5.0 mmol) in 20 mL of THF was added MeLi (3.6 mL, 5 mmol) while maintaining the temperature below –40 °C. After 20 min the reaction was quenched with excess MeI, and the yield (80%) of Me_4Sn was calculated as before.

Reaction of 1-Decyne (6) with $Bu_3SnAlEt_2$ (5). Representative Procedures for the Preparation of 2-(Tributylstannyl)-1-alkenes 7a, 7b, 8a, and 8b. The following three procedures are representative of the addition of **5** to **6** (Table II).

(a) Using $SnCl_2$ and *n*-BuLi (Method A). *n*-BuLi (11.4 mL, 28.44 mmol) was added dropwise to a solution of stannous chloride (1.8 g, 9.48 mmol) in 15 mL of dry THF at 0 °C. After this stirred for 30 min, diethylaluminum chloride (9.48 mL, 9.48 mmol) was added, and the reaction stirred for a further 0.5 h. 1-Decyne (0.437 g, 3.16 mmol) and catalyst (0.3 mmol) were then added at –30 °C. The reaction was stirred for 3 h, after which it was allowed to warm to 0 °C. The normal workup gave vinylstannanes **7a** and **8a** in the ratios shown in the Table II.

(b) Using Bu_3SnH and LDA (Method B). Bu_3SnH (1.45 g, 5 mmol) was added to 5 mL of THF containing lithium diisopropylamide (prepared by dropwise addition of *n*-BuLi (2 mL, 5 mmol) to an efficiently stirred solution of diisopropylamine (0.70 mL, 5 mmol) in 5 mL of THF at –10 °C) while the temperature was maintained below –30 °C. After stirring for 0.5 h, Et_2AlCl (5 mL, 5 mmol) was added dropwise at –30 °C. The clear solution was further stirred for 0.5 h, and then 1-decyne (0.22 g, 1.6 mmol) in 5 mL of THF was added dropwise followed by the addition of a catalyst (0.16 mmol). The reaction turned orange at this point. After 3 h the reaction was warmed to 0 °C and subjected to the normal workup.

(c) General Procedure for Slow Addition Reactions (Method C). To 3.2 mmol of lithium diisopropylamide in 5 mL of THF was added Bu_3SnH (0.87 g, 3 mmol) in 12 mL THF at –30 °C. After this stirred for 0.5 h, Et_2AlCl (2.8 mL, 2.8 mmol) in hexane was added dropwise. After this stirred for 0.5 h, one-half of the 1-decyne to be reacted (0.32 g, 2.3 mmol) was added in 15 mL of THF. This was followed by addition of CuCN (0.022 g, 0.23 mmol) in 5 mL of THF. The remainder of the alkyne was added over 0.75–1.0 h. The reaction was stirred at –30 °C for 3 h, then warmed to 0 °C, and subjected to the normal workup.

The experimental results of the addition of **5** to **6** are summarized in Table II, and the products gave the following spectral data.

2-(Tributylstannyl)-1-decene (7a): ^1H NMR ($CDCl_3$) δ 0.82 (t, 3 H, CH_3, J = 7.5 Hz), 0.88 (t, 9 H, CH_3, J = 7.0 Hz), 1.2–1.4 (m, 22 H, CH_2), 1.45–1.6 (m, 8 H, CH_2), 2.23 (ddt, 2 H, C=CCH_2, J = 7.56, 1.45, 1.04 Hz), 5.09 (dt, 1 H, C=CH, J = 2.9, 1.04 Hz, $^3J_{Sn-H}$ = 64 Hz), 5.66 (dt, 1 H, C=CH, J = 2.9, 1.45 Hz, $^3J_{Sn-H}$ = 140 Hz); allylic region decoupled δ 2.21 (s), 5.09 (d, 1 H, C=CH, J = 2.9 Hz), 5.66 (d, 1 H, C=CH, J = 2.9 Hz); ^{13}C NMR δ 156.0 (C=CSnBu$_3$), 124.5 (C=CH_2), 41.4, 32.0, 29.7, 29.5, 29.3, 29.1, 27.4, 22.6, 13.6, 9.7; ^{119}Sn NMR δ –45.6; GC/MS, *m/e* (rel intensity) 373 (M^+ – 56, 37.5), 291 (100.0). Anal. Calcd for $C_{18}H_{37}Sn$ 373.1917, found 373.1920; for $C_{14}H_{29}Sn$ 317.1291, found 317.1288.

(*E*)-2-(Tributylstannyl)-1-decene (8a): ^1H NMR ($CDCl_3$) δ 0.8 (t, 3 H, CH_3, J = 5.7 Hz), 0.88 (t, 9 H, CH_3, J = 7.0 Hz), 1.2–1.4 (m, 22 H, CH_2), 1.45–1.6 (m, 8 H, CH_2), 2.2 (dq, 2 H, C=CCH_2, J = 5.5, 2.0 Hz), 5.85 (dt, 1 H, C=CH, J = 18.0, 2.0 Hz, $^2J_{Sn-H}$ = 60 Hz), 5.96 (dt, 1 H, C=CH, J = 18.0, 5.5 Hz, $^3J_{Sn-H}$ = 47 Hz); allylic region decoupled δ 2.2 (s, 2 H), 5.85 (d, 1 H, C=CH, J = 18.0 Hz), 5.96 (d, 1 H, C=CH, J = 18.0 Hz); ^{13}C NMR δ 155.3 (C=CSnBu$_3$), 121.4 (C=CH), 42.2, 31.9, 29.5, 29.3, 28.2, 27.3, 24.4, 22.7, 13.6, 10.0; ^{119}Sn NMR δ –50.1; GC/MS, *m/e* (rel intensity) 373 (M^+ – 56, 31.25), 291 (100.0). Anal. Calcd for $C_{18}H_{37}Sn$ 373.1917, found 373.1916; for $C_{14}H_{29}Sn$ 317.1291, found 317.1290.

(42) Sharma, S.; Oehlschlager, A. C. unpublished results.
(43) Tamborski, C.; Ford, F. E.; Soloski, E. J. *J. Organomet. Chem.* **1963**, *28*, 237.

Independent Preparation of 8a (Scheme II). To 1-decyne (0.138 g, 1.0 mmol) in 5 mL of *n*-hexane DIBALH (1 mL, 1.0 mmol) was added dropwise with stirring. The reaction was refluxed for 2 h, after which time the solvent was removed under vacuum. THF (5 mL) was then added, and the solution was cooled to −78 °C, whereupon *n*-BuLi (0.8 mL, 2.0 mmol) and HMPA (2 mL) were added. The reaction was stirred for 0.5 h, then Bu_3SnCl (0.65 g, 2.0 mmol) was added, and the reaction was further stirred for an hour at −78 °C and 2 h at 0 °C. The normal workup gave 0.32 g (76%) of **8a**. Bu_4Sn was the other product detected.

Preparation of 7b and 8b. The reaction was conducted as described above (method B) but was quenched by stirring with ^{2}HCl for 0.5 h and then processed in the usual fashion.

(*Z*)-1-Deuterio-2-(tributylstannyl)-1-decene (7b): ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 9 H, CH_3, J = 7.0 Hz), 0.9 (t, 3 H, CH_3, J = 7.7 Hz), 1.2–1.4 (m, 22 H, CH_2), 1.45–1.6 (m, 8 H, CH_2), 2.24 (dt, 2 H, C=CCH_2, J = 7.66, 1.5 Hz), 5.66 (t, 1 H, C=CH, J = 1.5 Hz, $^3J_{Sn-H}$ = 140 Hz); GC/MS, m/e (rel intensity) 374 (M^+ − 56, 97). Anal. Calcd for $C_{14}H_{28}SnD$ 318.1354, found 318.1350.

(*E*)-2-Deuterio-1-(tributylstannyl)-1-decene (8b): ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 9 H, CH_3, J = 7.0 Hz), 0.9 (t, 3 H, CH_3, J = 5.7 Hz), 1.2–1.4 (m, 22 H, CH_2), 1.45–1.6 (m, 8 H, CH_2), 2.2 (dt, 2 H, C=CCH_2, J = 5.5, 3.0 Hz), 5.85 (t, 1 H, C=CH, J = 3.0 Hz, $^2J_{Sn-H}$ = 60 Hz); GC/MS, m/e (rel intensity) 374 (M^+ − 56, 100). Anal. Calcd for $C_{14}H_{28}SnD$ 318.1354, found 318.1361.

Bu_4Sn and $Bu_3SnSnBu_3$ were identified by NMR and gas chromatographic comparison with authentic samples.

In the absence of a catalyst but otherwise under the same conditions the reaction did not produce vinylstannanes.

General Procedure for the Preparation of Disubstituted Vinylstannanes, Scheme II. 1-Decyne (0.69 g, 5.0 mmol) in 5 mL of THF was added to a solution of **5** at −30 °C (10 mmol, vide supra) in 20 mL of THF followed by CuCN (0.045 g, 0.5 mmol). The reaction turned orange at this point. After stirring for 3 h at −30 °C, it was allowed to warm to 0 °C (wine red in color), when it was subjected to two separate set of conditions as described below.

(a) Transmetalation Using *n*-BuLi: Preparation of 7c, 7d, and 8d. *n*-BuLi (2.4 mL, 6.0 mmol) was added at −78 °C to 1,2-dimetallo-1-alkene (prepared as described above). After this stirred for 30 min, an excess of allyl bromide (**7c**) and MeI in HMPA (5 mL, **7d** and **8d**) was added. The reaction was left to stir overnight. The usual workup followed by silica gel chromatography (*n*-hexane as eluant) gave the desired products in >98% stereoisomeric purity.

5-(Tributylstannyl)-4(*Z*),1-tridecadiene (7c): 1.6 g (68%); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 12 H, CH_3, J = 7.0 Hz), 1.2–1.4 (m, 22 H, CH_2), 1.45–1.6 (m, 8 H, CH_2), 2.23 (dt, 2 H, C=CCH_2, J = 7.0, 1.5 Hz), 2.73 (ddt, 2 H, C=CCH_2C=C, J = 7.0, 2.0, 1.5 Hz), 4.99 (ddt, 1 H, HC=CH_{cis}, J = 10.0, 2.0, 1.5 Hz), 5.02 (dq, 1 H, HC=CH_{trans}, J = 17.0, 2.0 Hz), 5.8 (ddt, 1 H, HC=CH$_2$, J = 17.0, 10.0, 6.0 Hz), 5.96 (ddt, 1 H, C=CHCH$_2$, J = 7.0, 2.0, 1.5 Hz, $^3J_{Sn-H}$ = 138 Hz); ^{13}C NMR δ 156.0 (C=CSnBu$_3$), 148.0 (C=CH), 139.5 (HC=CH$_2$), 138.0 (C=CH$_2$), 115.0 (C=CCH$_2$-C=C), 41.4, 32.0, 29.6, 29.3, 29.2, 29.1, 27.4, 22.6, 13.6, 9.7; ^{119}Sn NMR δ −52.1; GC/MS, m/e (rel intensity) 413 (M^+ − 56, 100). Anal. Calcd for $C_{21}H_{43}Sn$ 413.1354, found 413.1361.

2-(Tributylstannyl)-1(*Z*)-undecene (7d): 0.5 g (38%); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 12 H, CH_3, J = 7.0 Hz), 1.2–1.4 (m, 22 H, CH_2), 1.45–1.6 (m, 8 H, CH_2), 1.96 (d, 3 H, CH_3, J = 7.0 Hz), 2.23 (dt, 2 H, C=CCH_2, J = 7.0, 1.9 Hz), 6.1 (qt, 1 H, C=CH, J = 7.0, 1.9 Hz, $^3J_{Sn-H}$ = 138 Hz); ^{13}C NMR δ 145.2 (C=CSnBu$_3$), 134.0 (C=CH), 40.8, 30.7, 29.3, 29.2, 27.8, 26.8, 24.2, 15.5, 14.0, 10.2; ^{119}Sn NMR δ −45.0; GC/MS, m/e (rel intensity) 387 (M^+ − 56, 100). Anal. Calcd for $C_{19}H_{39}Sn$ 387.2199, found 387.2139.

1-(Tributylstannyl)-2-methyl-1(*E*)-decene (8d): 0.85 g (38%); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 12 H, CH_3, J = 6.6 Hz), 1.2–1.4 (m, 22 H, CH_2), 1.45–1.6 (m, 8 H, CH_2), 1.78 (s, 3 H, CH_3), 2.23 (dt, 2 H, C=CCH_2, J = 6.7, 2.0 Hz), 5.45 (s, 1 H, $^3J_{Sn-H}$ = 75 Hz); ^{13}C NMR δ 155.3 (C=CSnBu$_3$), 121.3 (C=CH), 42.2, 32.0, 29.5, 29.3, 29.2, 28.2, 27.3, 24.4, 22.7, 19.7, 13.6, 10.0; ^{119}Sn NMR δ −49.0; GC/MS, m/e (rel intensity) 387 (M^+ − 56, 100). Anal. Calcd for $C_{19}H_{39}Sn$ 387.2199, found 387.2169.

(b) Palladium-Catalyzed Cross-Coupling Reactions of 1,2-Dimetallo-1-alkenes. Preparation of 7c, 7e, and 7f. To 0.74 g (1 mmol) of $Pd(PPh_3)_2Cl_2$ in 20 mL of THF were sequentially added DIBALH (2 mL, 2 mmol; 25 °C, 30 min), *cis*-1,2-dimetallovinyl adduct (10 mmol, prepared in a separate flask as described above), and the electrophilic coupling reagent (15.0 mmol). The reactions were stirred at room temperature overnight. The usual workup followed by silica gel chromatography (*n*-hexane as eluant) gave the bifunctionalized vinylstannanes. Cross-coupled products derived from reaction of the vinylstannyl bonds were not detected.

7c: 2.1 g (89%).

1-Phenyl-3-(tributylstannyl)-2(*Z*)-undecene (7e): 2.17 g (84%); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 12 H, CH_3, J = 7.0 Hz), 1.2–1.4 (m, 22 H, CH_2), 1.45–1.6 (m, 8 H, CH_2), 2.25 (dt, 2 H, C=CCH_2, J = 7.0, 2.0 Hz), 3.4 (d, 2 H, C=CCH_2Ph, J = 7.0 Hz), 6.2 (tt, 1 H, C=CCHCH$_2$, J = 7.0 Hz, 2.0, $^3J_{Sn-H}$ = 140 Hz), 7.15–7.4 (m, 5 H, Ph); ^{119}Sn NMR δ −50.1; GC/MS, m/e (rel intensity), 463 (M^+ − 56, 100).

1-Phenyl-2-(tributylstannyl)-1(*Z*)-decene (7f): 2.0 g (79%); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 9 H, CH_3, J = 7.0 Hz), 0.9 (t, 3 H, CH_3, J = 7.0 Hz), 1.2–1.4 (m, 12 H, CH_2), 1.45–1.6 (m, 18 H, CH_2), 2.25 (dt, 2 H, C=CCH_2, J = 7.0, 1.5 Hz), 6.15 (t, 1 H, C=CH, J = 1.5 Hz, $^3J_{Sn-H}$ = 135 Hz), 7.1–7.4 (m, 5 H, Ph); ^{119}Sn NMR δ −47.0; GC/MS, m/e (rel intensity) 449 (M^+ − 56, 100).

Stannylalumination of Functionalized 1-Alkynes, Scheme III. Preparation of 6-Acetoxy-1-hexyne (9b). Pyridine (5.45 g, 0.069 mol), Ac_2O (6.9 g, 0.068 mol), and 5-hexyn-1-ol (6.7 g, 0.069 mol) were stirred together for 3 h at room temperature, after which time the reaction was worked up in the normal manner. Vacuum distillation yielded 9.25 g (97%) of the acetate (bp 61 °C (10 mmHg)). GC analysis revealed a purity of 97%. ^{1}H NMR ($CDCl_3$) δ 1.62 (pentet, 2 H, CH_2, J = 6.6 Hz), 1.77 (pentet, 2 H, CH_2, J = 6.6 Hz), 1.96 (t, 1 H, C≡CH, J = 1.9 Hz), 2.1 (s, 3 H, COCH_3), 2.22 (dt, 2 H, C≡CCH_2, J = 6.6, 1.9 Hz), 4.1 (t, 2 H, OCH_2, J = 6.6 Hz); CI (isobutane) GC/MS, m/e (rel intensity) 141 (M^+ + 1, 100).

Preparation of 6-(Tetrahydropyranyloxy)-1-hexyne (9c). To 5-hexyne-1-ol (5.0 g, 0.50 mol) and freshly distilled dihydropyran (10.5 g, 0.125 mol) were added 4 drops of concentrated HCl, and the mixture was stirred overnight at room temperature. Ether (30 mL) was then added, and the mixture shaken with 10% NaOH solution until it was neutral. The usual workup followed by vacuum distillation yielded 8.4 g (91%) of the protected alcohol (bp 108 °C (17 mmHg)). GC analysis revealed a purity of 98%. ^{1}H NMR ($CDCl_3$) δ 1.2–1.8 (m, 1/ H, CH_2), 1.96 (t, 1 H, C≡CH, J = 1.9 Hz), 2.22 (dt, 2 H, C≡CCH_2, J = 6.6, 1.9 Hz), 3.38 (ddd, 1 H, OCH_2CH$_2$), 3.5 (dt, 1 H, CH_2 on OTHP), 3.75 (ddd, 1 H, OCH_2CH$_2$), 3.85 (dt, 1 H, CH_2 on OTHP), 4.1 (tt, 1 H, OCHO); GC/MS, m/e (rel intensity), 182 (M^+, 100).

Preparation of 1-Bromo-5-hexyne (9d). PBr_3 (4.86 mL, 0.05 mmol) was added dropwise to 5-hexyn-1-ol (13.72 g, 0.14 mol) in 50 mL of anhydrous Et_2O at −5 °C. The reaction was stirred for 2 h and then warmed to room temperature. It was then quenched by pouring onto ice-cold $NaHCO_3$ solution. The usual workup followed by distillation gave 19.8 g (88%) of the bromide (bp 68 °C) (21 mmHg)). GC analysis revealed a purity of 92%. ^{1}H NMR ($CDCl_3$) δ 1.73 (pentet, 2 H, CH_2, J = 6.6 Hz), 1.96 (t, 1 H, C≡CH, J = 1.9 Hz), 2.02 (pentet, 2 H, CH_2, J = 6.6 Hz), 2.30 (dt, 2 H, C≡CCH_2, J = 6.6, 1.9 Hz), 3.5 (t, 2 H, BrCH_2, J = 6.6 Hz); CI (isobutane) GC/MS, m/e (rel intensity) 163 (M^+ + 2, 12.5), 161 (M^+, 14.6).

Preparation of 6-Hydroxy-2-(tributylstannyl)-1-hexene (10a). To an efficiently stirred solution of lithium diisopropylamide (5.8 mmol) in 5 mL of THF was added Bu_3SnH (1.69 g, 5.8 mmol) in 5 mL of THF at −30 °C. After this stirred for 30 min, Et_2AlCl (5.8 mL, 5.8 mmol) was added, and the reaction was further stirred for 30 min. 5-Hexyn-1-ol (**9a**, 0.29 g, 3.0 mmol) in 5 mL of THF was added dropwise followed by CuCN (0.026 g, 0.3 mmol). The reaction turned light orange at this point. The reaction was stirred at −30 °C for 3 h and then overnight. The usual workup, followed by chromatography on silica gel (hexane:ethyl acetate, 96:4, as eluant) gave 0.97 g (84%) of a mixture of **10a** and **11a** (2:1): ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 14 H, CH_3, J = 6.7 Hz), 1.32 (q, 18 H, CH_2, J = 6.7 Hz), 1.47 (m, 12 H, CH_2), 1.55 (m, 3 H, OCH$_2$CH_2), 2.7–3.2 (m, 3 H, C=CH_2), 3.6 (m, 3 H, OCH_2), 5.1 (dt, 1 H, C=CH, J = 4.2, 1.1 Hz, $^3J_{Sn-H}$ = 64 Hz), 5.7 (dt, 1 H, C=CH, J = 4.2, 2.9 Hz, $^3J_{Sn-H}$ = 140 Hz), 5.9 (m, 0.5 H, C=CH); ^{13}C NMR δ 155.2 (C=CSnBu$_3$), 149.2 (C=CSnBu$_3$),

127.7 (C=CH_2), 125.0 (C=CH_2), 62.9 (COH), 62.8 (COH), 40.9, 37.5, 32.4, 32.3, 32.2, 29.3, 29.2, 29.1, 27.5, 27.2, 25.6, 25.1, 13.6, 9.6; GC/MS, *m/e* (rel intensity) for **10a** 333 (M^+ - 56, 100), for **11a** 333 (M^+ - 56, 40). Anal. Calcd for $C_{14}H_{29}OSn$ 333.1241, found 333.1239.

Preparation of 6-Acetoxy-2-(tributylstannyl)-1-hexene (10b). 1-Acetoxy-5-hexyne (**9b**, 0.39 g, 2.8 mmol) in 10 mL THF was added dropwise to an efficiently stirred solution of $Bu_3SnAlEt_2$ (3.0 mmol, vide supra) followed by CuCN (0.012 g, 0.14 mmol). The reaction was stirred at -30 °C for 3 h (bright orange), then warmed to room temperature, and further stirred for 2 h. The usual workup, followed by silica gel chromatography (hexane:ethyl acetate, 95:5, as eluant) gave 1.05 g (87.5%) of **10b** in 99% purity as measured by GC analysis; ^1H NMR ($CDCl_3$) δ 0.88 (t, 9 H, CH_3, J = 6.6 Hz), 1.32 (q, 12 H, CH_2, J = 6.6 Hz), 1.5 (m, 8 H, CH_2), 1.6 (t, 2 H, CH_2O, J = 6.7 Hz), 2.1 (s, 3 H, $COCH_3$), 2.3 (tt, 2 H, C=CCH_2, J = 6.6, 1.9 Hz), 4.1 (t, 2 H, CH_2O, J = 6.6 Hz), 5.1 (dt, 1 H, C=CH, J = 5.0, 1.2 Hz, $^3J_{Sn-H}$ = 63 Hz), 5.7 (dt, 1 H, C=CH, J = 5.0, 2.9 Hz, $^3J_{Sn-H}$ = 138 Hz); ^{13}C NMR δ 154.9 (C=CSnBu_3), 125.2 (C=CH_2), 64.4 (OCH_2), 40.8, 29.1, 28.3, 27.3, 25.9, 20.9, 13.6, 9.6; ^{119}Sn NMR δ -44.7; GC/MS, *m/e* (rel intensity) 375 (M^+ - 56, 61). Anal. Calcd for $C_{16}H_{31}O_2Sn$ 375.1346, found 375.1353.

Preparation of 6-(Tetrahydropyranyloxy)-2-(tributylstannyl)-1-hexene (10c). A solution of $Bu_3SnAlEt_2$ (5.8 mmol) in 10 mL of THF was prepared as described above. 6-(Tetrahydropyranyloxy)-1-hexyne (**9c**, 0.546 g, 3.0 mmol) in 5 mL of THF was added dropwise with stirring, followed by CuCN (0.02 g, 0.3 mmol). The reaction was stirred at -30 °C for 3 h, after which time it turned clear yellow. The reaction was then warmed to room temperature and subjected to the usual workup. This was followed by chromatography on silica gel (hexane:ethyl acetate, 99:1, as eluant) to give 1.05 g (75%) of **10c** in >99% purity; ^1H NMR ($CDCl_3$) δ 0.88 (t, 9 H, CH_3, J = 6.6 Hz), 1.32 (q, 12 H, CH_2, J = 6.6 Hz), 1.5 (m, 8 H, CH_2), 1.6 (t, 2 H, CH_2O, J = 6.7 Hz), 2.3 (tt, 2 H, C=CCH_2, J = 6.6 Hz, 1.9 Hz), 3.38 (ddd, 1 H, OCH_2CH_2), 3.5 (tt, 1 H, CH_2 on OTHP), 3.75 (ddd, 1 H, OCH_2CH_2), 3.85 (tt, 1 H, CH_2 on OTHP), 4.6 (tt, 1 H, OCHO), 5.1 (dt, 1 H, C=CH, J = 3.0, 1.2, $^3J_{Sn-H}$ = 64 Hz), 5.7 (dt, 1 H, C=CH, J = 3.0, 1.2 Hz, $^3J_{Sn-H}$ = 140 Hz); ^{13}C NMR δ 155.4 (C=CSnBu_3), 124.8 (C=CH_2), 98.7 (OCHO), 67.4 (OCH_2), 62.1 (OCH_2), 41.1, 30.8, 29.5, 29.1, 27.3, 26.3, 25.5, 19.6, 13.6, 9.6; GC/MS, *m/e* (rel intensity) 417 (M^+ - 56, 2.3). Anal. Calcd for $C_{19}H_{37}O_2Sn$ 417.1816, found 417.1808.

Preparation of 6-Bromo-2-(tributylstannyl)-1-hexene (10d). 1-Bromo-5-hexyne (**9d**, 0.48 g, 3 mmol) was added to a solution of $Bu_3SnAlEt_2$ (5.8 mmol) in 10 mL of THF followed by CuCN (0.02 g, 0.3 mmol). The reaction was stirred at -30 °C for 3 h and then warmed to room temperature. The usual workup followed by chromatography on silica gel (hexane, as eluant) gave 0.75 g (56%) of **10d** and 30% of the cyclized product presumably arising from the intramolecular cyclization of the trans regioisomer. ^1H NMR ($CDCl_3$) δ 0.88 (t, 9 H, CH_3, J = 6.6 Hz), 1.32 (q, 12 H, CH_2, J = 6.7 Hz), 1.40 (m, 8 H, CH_2), 1.85 (t, 4 H, CH_2, J = 6.7 Hz), 2.3 (tt, 4 H, C=CCH_2, J = 6.6, 1.9 Hz), 3.41 (t, 4 H, CH_2Br, J = 6.6 Hz), 5.1 (dt, 1.5 H, C=CH, J = 3.0, 1.2 Hz, $^3J_{Sn-H}$ = 64 Hz), 5.7 (dt, 1.5 H, C=CH, J = 3.0, 1.9 Hz, $^3J_{Sn-H}$ = 140 Hz). Cyclized product: ^1H NMR ($CDCl_3$) δ 5.9 (br s, 0.5 H, C=CH, $^2J_{Sn-H}$ = 66 Hz); ^{13}C NMR δ 155.4 (C=CSnBu_3), 125.3 (C=CH_2), 40.3 (CH_2Br), 32.4, 30.6, 29.1, 27.4, 27.3, 13.6, 9.6; GC/MS, *m/e* (rel intensity) for **10d** 395 (M^+ - 56, 2), for cyclized product 315 (M^+ - 80, 75). Anal. Calcd for $C_{14}H_{28}BrSn$ 395.0397, found 395.0398.

Preparation of Trisubstituted Alkenes, Schemes IV and V. Preparation of 5-Iodo-4(*Z*),1-tridecadiene (12a). To a solution of **7c** (1.4 g, 3 mmol) in CH_2Cl_2 (10 mL) was added a solution of I_2 in CH_2Cl_2 dropwise at -50 °C until a faint coloration persisted. The reaction was warmed to -20 °C and quenched with saturated NH_4Cl. The vinyl iodide was extracted into pentane, and combined extracts were washed with water and sodium thiosulfate and then dried over potassium carbonate. Silica gel chromatography using hexane as the eluant gave the desired product in 72% (0.65 g) yield; ^1H NMR ($CDCl_3$) δ 0.87 (t, 3 H, CH_3, J = 7.1 Hz), 1.26-1.4 (m, 12 H, CH_2), 2.23 (dt, 2 H, C=CCH_2, J = 7.0, 2.0 Hz);, 2.73 (dt, 2 H, C=CCH_2C=C, J = 6.0, 2.0 Hz), 4.99 (dq, 1 H, C=CH_{cis}, J = 10.0, 2.0 Hz), 5.02 (dq, 1 H, C=CH_{trans}, J = 17.0, 2.0 Hz), 5.8 (ddt, 1 H, CH_2HC=CCH_2, J = 17.0, 10.0, 6.0 Hz), 6.96 (tt, 1 H, C=CH, J = 6.0, 2.0 Hz); GC/MS, *m/e* (rel intensity) 306 (M^+, 40).

Preparation of 12b and 12c from 12a. *n*-BuLi (1.5 mL, 3.6 mmol) was added to **12a** (0.49 g, 1.6 mmol) at -78 °C. After 0.5 h the reaction was quenched with excess Me_3SiCl (**12b**) or ^2H_2O (**12c**) and slowly warmed to room temperature. The usual workup followed by column chromatography using *n*-hexane as eluant gave the desired products in the yields listed below.

5-(Trimethylsilyl)-4(*Z*),1-tridecadiene (12b): 0.3 g (78%); ^1H NMR ($CDCl_3$) δ 0.15 (s, 9 H, CH_3Si), 0.87 (t, 3 H, CH_3, J = 7.1 Hz), 1.26-1.4 (m, 12 H, CH_2), 2.23 (dt, 2 H, C=CCH_2, J = 7.0, 2.0 Hz), 2.73 (dt, 2 H, C=CCH_2HC=C, J = 6.0, 2.0 Hz), 4.99 (dq, 1 H, C=CH_{cis}, J = 10.0, 2.0 Hz), 5.02 (dq, 1 H, C=CH_{trans}, J = 17.0, 2.0 Hz), 5.8 (ddt, 1 H, CH_2HC=CH_2, J = 17.0, 10.0, 6.0 Hz), 5.96 (tt, 1 H, C=CH, J = 6.0, 2.0 Hz); ^{13}C NMR δ 148.5 (C=CSiMe_3), 139.3 (C=CH_2), 137.5 (C=CH), 137.4 (C=$CHCH_2$), 114.8 (C=CHCH_2CH=C), 38.4, 36.2, 32.0, 29.5, 29.4, 29.3, 22.7, 13.6, 0.3; GC/MS, *m/e* (rel intensity), 252 (M^+, 100). Anal. Calcd for $C_{16}H_{32}Si$ 252.2273, found 252.2281.

5-Deuterio-4(*E*),1-tridecadiene (12c): 0.25 g (87%); ^1H NMR ($CDCl_3$) δ 0.87 (t, 3 H, CH_3, J = 7.1 Hz), 1.26-1.4 (m, 12 H, CH_2), 2.20 (dt, 2 H, C=CCH_2, J = 7.0, 2.0 Hz), 2.73 (dt, 2 H, C=CCH_2HC=C, J = 6.0, 2.0 Hz), 5.0 (dq, 1 H, C=CH_{cis}, J = 10.0, 2.0 Hz), 5.02 (dq, 1 H, C=CH_{trans}, J = 17.0, 2.0 Hz), 5.40 (tt, 1 H, C=CH, J = 6.0, 2.0 Hz), 5.8 (ddt, 1 H, CH_2HC=CH_2, J = 17.0, 10.0, 6.0 Hz); ^{13}C NMR δ 137.6 (HC=CH_2), 131.9 (C=CD), 127.5 (C=CH), 114.8 (C=CHCH$_2$CH=C), 36.7, 32.5, 31.9, 29.5, 29.3, 29.2, 22.6, 14.1; GC/MS, *m/e* (rel intensity) 181 (M^+, 52). Anal. Calcd for $C_{13}H_{23}D$ 181.1941, found 181.1933.

12b was also prepared from **7c** via transmetalation with *n*-BuLi. Thus, to a solution of **7c** (1.17 g, 2.5 mmol) in 5 mL of THF was added *n*-BuLi (1.2 mL, 3 mmol) in 5 mL of TMEDA at -60 °C. The reaction was stirred at this temperature for 2 h and then warmed to room temperature. After this stirred for a further 1 h, Me_3SiCl (0.6 mL, 5 mmol) was added slowly at -78 °C. The reaction was warmed to room temperature and worked up as usual. Silica gel chromatography using hexane as the eluant gave **12b** in 63% (0.39 g) yield.

General Procedure for Palladium-Catalyzed Cross-Coupling Reactions. Preparation of 12d and 12e. To a Schlenk tube at room temperature was sequentially added $Pd(Ph_3P)_4$ (5 mol %) in 5 mL of benzene, benzyl bromide (1.0 g, 6 mmol), and vinylstannane **7d** (2.36 g, 5.0 mmol).[35] The reaction was refluxed until palladium metal precipitated (24 h). The reaction was cooled to room temperature and partitioned between Et_2O (20 mL) and saturated KF (20 mL). After 0.5 h of vigorous stirring, Bu_3SnF was removed by filteration, and the organic layer was separated, washed with brine, and dried. The solvent was evaporated, and the crude mixture passed through a silica gel column (hexanes:ethyl acetate, 99:1, as eluant) to give the desired alkene. **12e** was prepared as described for **12d**.

3-Benzyl-2(*Z*)-undecene (12d): ^1H NMR ($CDCl_3$) δ 0.9 (t, 3 H, CH_3, J = 7.0 Hz), 1.2-1.5 (m, 12 H, CH_2), 1.4 (d, 3 H, CH_3, J = 6.6 Hz), 2.1 (dt, 2 H, C=CCH_2, J = 7.0, 1.9 Hz), 3.3 (s, 2 H, C=CCH_2Ph), 5.5 (qt, 1 H, C=CH, J = 6.6, 1.9 Hz), 7.0-7.5 (m, 5 H, Ph); ^{13}C NMR δ 149.6, 136.1, 129.0, 128.2, 126.0, 110.9, 65.8, 43.0, 35.5, 31.9, 29.4, 29.3, 29.2, 22.7, 22.6, 14.0; GC/MS, *m/e* (rel intensity) 244 (M^+, 12.3). Anal. Calcd for $C_{18}H_{28}$ 244.2191, found 244.2187.

3-Propenyl-2(*Z*)-undecene (12e): ^1H NMR ($CDCl_3$) δ 0.9 (t, 3 H, CH_3, J = 7.0 Hz), 1.2-1.5 (m, 12 H, CH_2), 1.6 (d, 3 H, CH_3, J = 7.0 Hz), 1.95 (dt, 2 H, C=CCH_2, J = 7.0, 1.5 Hz), 2.8 (ddd, 2 H, C=CCH_2C=C, J = 7.0, 2.0, 1.5 Hz), 4.99 (ddd, 1 H, C=CH_{cis}, J = 10.0, 2.0, 1.5 Hz), 5.02 (dq, 1 H, C=CH_{trans}, J = 17.0, 2.0 Hz), 5.3 (qt, 1 H, C=CH, J = 7.0, 1.5 Hz), 5.75 (ddt, 1 H, HC=CCH_2, J = 17.0, 10.0, 7.0 Hz); GC/MS, *m/e* (rel intensity) 194 (M^+, 100).

Preparation of (*E*)-1-Iodo-1-hexene (12f). This compound was prepared by the known procedure;[1b] ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H, CH_3, J = 7.0 Hz), 1.26-1.4 (m, 4 H, CH_2), 1.98-2.0 (dt, 2 H, J = 7.0, 1.9 Hz), 5.95 (dt, 1 H, C=CHI, J = 15.0, 1.8 Hz), 6.5 (dt, 1 H, CH=CHI, J = 14.8, 7 Hz); ^{13}C NMR δ 146.6, 73.9, 35.6, 30.5, 21.9, 13.7.

Preparation of 8-Methyl-5(*E*),7(*E*)-hexadecadiene (12c). To a solution of "$Pd(Ph_3P)_2$" (0.05 mmol) in 5 mL of THF, (generated in situ by the reaction of DIBALH (0.1 mL, 0.1 mmol)

and $Pd(Ph_3P)_2Cl_2$ (0.037 g, 0.05 mmol in THF)) were sequentially added **8d** (0.50 g, 1.2 mmol) and **12f** (0.211 g, 1.0 mmol) at room temperature. The homogeneous reaction mixture turned black in 24 h. The reaction mixture was diluted with ether and stirred with saturated KF. After filtration of Bu_3SnF, the reaction was worked up as usual, and the crude product purified by column chromatography (hexane as eluant) to give 0.14 g (88%) of **12g**: ^1H NMR ($CDCl_3$) δ 0.86 (t, 6 H, CH_3, J = 7.0 Hz), 1.02–1.4 (m, 16 H, CH_2), 1.9 (s, 3 H), 2.3 (dt, 2 H, C=CCH_2, J = 7.0, 1.6 Hz), 2.9 (dq, 2 H, C=CCH_2, J = 7.0, 1.6 Hz), 5.5 (ddt, 1 H, HC=C*H*C, J = 18.0, 10.0, 1.6 Hz), 5.8 (dt, 1 H, C=C*H*HC=C, J = 10.0, 1.6 Hz), 6.0 (ddt, 1 H, C*H*=CHC, J = 18.0, 10.0, 7.0 Hz); ^{13}C NMR δ 142.6 (*C*=CHCH=C), 132.7 (C=CHCH=*C*), 129.6 (C=*C*HCH=C), 123.5 (C=CH*C*H=C), 33.2, 32.7, 31.9, 29.9, 29.3, 22.6, 17.6, 14.1; GC/MS, m/e (rel intensity) 280 (M^+, 35.0). The spectral data matched the published results.[36]

Preparation of 1-Hexynyltributylstannane[37] (12h). To a solution of 1-hexyne (0.82 g, 10.0 mmol) in Et_2O (15 mL) was added dropwise *n*-BuLi (3.8 mL, 10.0 mmol) at −30 °C. After 30 min Bu_3SnCl (3.25 g, 10.0 mmol) was added. The reaction was warmed to room temperature and then subjected to the normal workup. Bulb-to-bulb distillation (bath temperature, 65 °C (0.03 mmHg)) gave 3.5 g (95%) of **12h**: ^1H NMR ($CDCl_3$) δ 0.86 (t, 9 H, CH_3, J = 7.0 Hz), 0.89 (t, 3 H, CH_3, J = 7.0 Hz), 1.2–1.4 (m, 12 H, CH_2), 1.4–1.5 (m, 10 H, CH_2), 2.20 (t, 2 H, CH_2, J = 7.0 Hz); ^{119}Sn δ −68.2; GC/MS, m/e (rel intensity) 315 (M^+ − 56, 100).

Preparation of 8-Methyl-7(*E*)-hexadecen-5-yne (12i). To a solution of **8d** (0.211 g, 1.0 mmol, prepared as described earlier) and **12h** (0.44 g, 1.2 mmol) at room temperature was added "$Pd(Ph_3P)_2$" (0.05 mmol) in 5 mL of THF (generated *in situ* by the reaction of 2 equiv of DIBALH and 1 equiv of $Pd(Ph_3P)_2Cl_2$ in THF). The homogeneous reaction mixture turned black within an hour. The black reaction mixture was added to 25 mL of water, and this aqueous mixture was extracted with ether (3 × 25 mL) which was back extracted with brine (1 × 25 mL) and dried over potassium carbonate. The dried extracts were filtered through alumina and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane as eluant) to give 0.155 g (88%) of **12i**: ^1H NMR ($CDCl_3$) δ 0.87 (t, 6 H, CH_3, J = 6.7 Hz), 1.26–1.4 (m, 12 H, CH_2), 1.54–1.64 (m, 4 H, CH_2), 1.9 (s, 3 H, CH_3), 2.1 (dt, 2 H, C≡CCH_2, J = 6.7, 1.8 Hz), 2.23 (dt, 2 H, C=CCH_2, J = 6.7, 1.9 Hz), 5.7 (t, 1 H, C=C*H*C=C, J = 1.9 Hz); ^{13}C NMR δ 142.9 (*C*=CHC≡C), 120.1 (C=*C*H), 110.1, 88.6, 79.3, 39.1, 32.7, 32.5, 31.0, 22.1, 22.0, 19.0, 13.7, 13.5; GC/MS, m/e (rel intensity) 278 (M^+, 23.0).

Reaction of 1-Decynyldiethylaluminum with Tributylstannyl Hydride. To a solution of 1-decynyldiethylaluminum in THF (prepared from 1-decyne (0.138 g, 1.0 mmol) in 5 mL of THF, *n*-BuLi (0.40 mL, 1.04 mmol), and Et_2AlCl (1.0 mL, 1.0 mmol); 0 °C, 0.5 h), Bu_3SnH (0.291 g, 1.0 mmol) was added dropwise, and the reaction stirred overnight at 0 °C. Only 1-decyne and Bu_3SnH were recovered. Vinylstannane products were not detected by gas chromatographic analysis after the normal workup.

Reaction of $Bu_3SnAlEt_2$ and Tributylstannyl Hydride. To a THF solution of $Bu_3SnAlEt_2$ (1.0 mmol) prepared by method b was added Bu_3SnH (0.291 g, 1.0 mmol) at 0 °C, and the reaction was stirred at this temperature. Only Bu_3SnH was obtained upon the usual workup. Formation of hexabutylditin was not observed even after 24 h.

Reaction of $Bu_3SnAlEt_2$ with Tributylstannyl Hydride in the Presence of Catalyst. $Bu_3SnAlEt_2$ (1.0 mmol) was prepared according to method b. Bu_3SnH (0.291 g, 1.0 mmol) and CuCN (0.004 g, 0.05 mmol) in 5 mL of THF were added to this solution at 0 °C. After stirring for 0.5 h, the reaction was quenched with 1 N HCl and subjected to the normal workup. Hexabutylditin (0.04 g, 69%) was obtained as the only product after bulb-to-bulb distillation.

Reaction of Tributylstannyl Hydride with CuCN. No reaction was observed when Bu_3SnH was reacted with CuCN in THF under argon at 0 °C for 12 h.

Reaction of $Bu_3SnAlEt_2$ with CuCN. CuCN (0.004 g, 0.05 mmol) was added to a solution of $Bu_3SnAlEt_2$ (1.0 mmol, method b) in 5 mL of THF. The solution immediately turned brick red. Workup after 30 min yielded 69% of hexabutylditin.

Reaction of 1-Decynyldiethylaluminum with $Bu_3SnAlEt_2$. Decynyldiethylaluminum (vide supra) was transferred via a canula to a THF solution of $Bu_3SnAlEt_2$ (1.0 mmol, vide supra) while the temperature was maintained at 0 °C. The reaction was stirred overnight at 0 °C, after which it was subjected to the normal workup to give 1-decyne.

Acknowledgment. This work was supported through a Natural Sciences and Engineering Research Council of Canada Operating Grant to A.C.O. and an S.F.U. Open Graduate Scholarship to S.S.

Registry No. **4**, 28688-36-0; **5**, 92074-24-3; **6**, 764-93-2; **7a**, 112164-71-3; **7b**, 122593-83-3; **7c**, 122593-85-5; **7d**, 122593-86-6; **7e**, 122593-88-8; **7f**, 122593-89-9; **8a**, 112164-72-4; **8b**, 122593-84-4; **8d**, 122593-87-7; **9a**, 928-90-5; **9b**, 68274-83-9; **9c**, 1720-37-2; **9d**, 66977-99-9; **10a**, 119288-35-6; **10b**, 122593-90-2; **10c**, 119288-42-5; **10d**, 119288-37-8; **11a**, 119288-45-8; **12a**, 122593-91-3; **12b**, 122593-92-4; **12c**, 122593-93-5; **12d**, 122593-94-6; **12e**, 122593-95-7; **12f**, 16644-98-7; **12g**, 122593-96-8; **12h**, 35864-20-1; **12i**, 122593-97-9; Bu_3SnLi, 4226-01-1; Bu_3SnMe, 1528-01-4; Bu_3SnCl, 1461-22-9; Me_3SnCl, 1066-45-1; Me_4Sn, 594-27-4; Bu_3SnH, 688-73-3; Bu_4Sn, 1461-25-2; $Me_3SnSnMe_3$, 661-69-8; CuCN, 544-92-3; $Pd(Ph_3P)_2Cl_2$, 13965-03-2; $Pd(Ph_3P)_4$, 29032-53-9; $CuBr{\cdot}Me_2S$, 54678-23-8; CuI, 7681-65-4; $Pd(Ph_3P)_2$, 31989-57-8; allyl bromide, 106-95-6; benzyl bromide, 100-39-0; iodobenzene, 591-50-4; dihydropyran, 110-87-2; 1-hexyne, 693-02-7; hexabutylditin, 813-19-4.

Scope of Tandem Cycloaddition/Radical Cyclization Methodology

Tirthankar Ghosh and Harold Hart*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Received January 26, 1989

Tandem cycloaddition/radical cyclization is an effective strategy for the rapid assembly of a wide variety of ring systems. To set up the reagents for this sequence, it is necessary to include a potential radical site in one of the two cycloaddition partners, located at an appropriate distance from a new double bond that will be formed in the cycloaddition step. Examples in which the cycloaddition step is [4 + 2] or [3 + 2] and in which the radical cyclization creates 5-, 6-, or 7-membered rings are described. Examples of the tandem methodology carried out in a completely intramolecular mode are also described.

Introduction

The construction of polycyclic systems from acyclic precursors with a minimum number of steps and with regio- and stereochemical control remains a synthetic challenge. Two of the most important ring-forming reactions currently in use for this purpose are cycloadditions

0022-3263/89/1954-5073$01.50/0