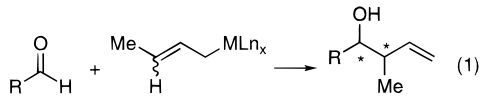
On the Relative Reactivities of Allyl, Crotyl, α-Oxygenated Crotyl, γ-Oxygenated α-Methylallyl, and Allenyl Tri-*n*-butylstannane Reagents in Lewis Acid Promoted Additions to Aldehydes

James A. Marshall,* Jill A. Jablonowski, and Gregory S. Welmaker

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

Received November 10, 1995

The addition of allylmetal reagents to carbonyl compounds, especially aldehydes, has received a great deal of attention as an important C−C bond forming reaction in natural product synthesis.[1] Of the various possible combinations of metals and allylic groups, crotylboron and tin reagents have shown particular promise.[2,3] These reagents are readily prepared, relatively stable, and typically undergo highly diastereoselective addition reactions with the formation of two contiguous stereocenters.

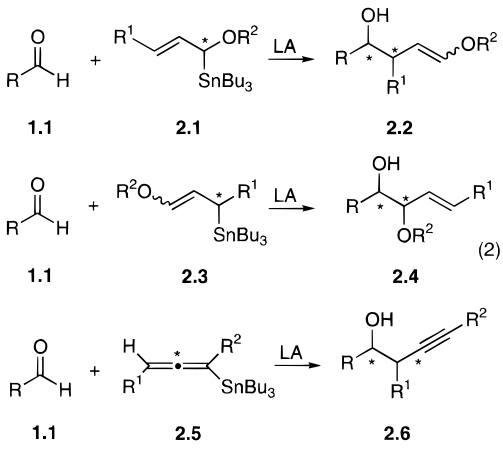


1.1 **1.2** **1.3**

In the case of boron, the use of chiral auxiliaries makes possible the synthesis of highly enantioenriched homoallylic alcohols. This approach is effective because these reactions proceed through cyclic six-center transition states in which the chiral ligands interact with the aldehyde substituent. However, most of the synthetically useful allylic tin additions to aldehydes proceed by an acyclic transition state in which the tin substituent orients *anti* to the forming carbon−carbon bond. Accordingly, chiral ligands on tin would not be expected to interact with the aldehyde substituent. In principle, the use of a chiral Lewis acid could provide a chiral environment at the carbonyl center, thereby leading to enantioface selectivity in the ensuing addition. Several recent studies confirm this expectation.[4]

A second approach to enantioselective additions entails the design of reagents in which the tin substituent resides at a stereogenic allylic center. In view of the well-established stereoelectronic requirements of allyltin S_E2' reactions, this approach should be highly effective for enantio- and diastereoselective synthesis.[3]

For several years we have been pursuing such a strategy first with α- and γ-oxygenated stannanes such as **2.1** and **2.3**[5] and, more recently, with allenic stannanes exemplified by **2.5**.[6]



1.1 **2.1** **2.2**

1.1 **2.3** **2.4**

1.1 **2.5** **2.6**

In the course of this work we noted that a number of reactions reported for allyl- and crotylstannanes, such as transmetalations with metal halides, could not be effected with the oxygenated counterparts. We also sensed that the oxygenated stannanes were less reactive in additions to certain aldehydes. Since these issues directly bear on the potential scope and limitations of the foregoing methodology, we decided to examine competition reactions between various allylic stannanes and representative aldehydes as a means of assessing relative reactivities.[7,8]

The studies were conducted by treating an equimolar solution of crotylstannane (**3.1**) and the competing stannane **3.3** with the aldehyde and 1.2 equiv of $BF_3{\cdot}OEt_2$ in CH_2Cl_2 at low temperature, allowing the reaction to proceed until the aldehyde was no longer present. After quenching, the mixture was analyzed by ^1H NMR and GC to ascertain the identity and ratio of products. In each case the competition was run two or three times to assure reproducibility. Response factors were determined for the GC analyses to ensure accuracy.

With cyclohexanecarboxaldehyde (eq 3) allyltri-*n*-butylstannane (**3.3a**) showed comparable reactivity to the standard, crotylstannane (**3.1**). As suspected, the (*E*)-γ-(silyloxy)stannane **3.3b** was significantly less reactive than stannane **3.1**.[9] Furthermore, the (*Z*)-isomer **3.3c** was even less reactive; only the crotyl adduct **3.2** could be isolated from the competition experiment.[10] The (*Z*)-γ-MOM **3.3d**,[11] the α-OTBS **3.3e**,[12] and the α-OMOM stannane **3.3f**[11] were similarly uncompetitive.

(1) For an overview, see: Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207.

(2) Boron: Roush, W. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 2, Chapter 1.1; pp 1−49.

(3) Tin: ref 2 and Yamamoto, Y.; Sheda, N. *Advances in Detailed Reaction Mechanisms*; JAI Press, 1994; Vol. 3, pp 1−44.

(4) (a) Marshall, J. A.; Tang, Y. *Synlett* **1992**, 653. (b) Keck, G. E.; Krishnamurthy, D.; Grier, M. C. *J. Org. Chem.* **1993**, *58*, 6543 and references cited therein.

(5) Marshall, J. A. *Chemtracts*: *Org. Chem.* **1992**, *5*, 75. Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31.

(6) Marshall, J. A.; Perkins, J. F.; Wolf, M. A. *J. Org. Chem.* **1995**, *60*, 5556.

(7) Kinetics have been reported for reactions of allylic silanes, stannanes, and germanes with carbocations. Hagen, G.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 4954.

(8) These studies were initiated at the University of South Carolina. Preliminary results are reported in the Ph.D. Thesis of G. S. Welmaker, University of South Carolina, 1992.

(9) For leading references to the synthesis of these stannanes, see: Marshall, J. A.; Jablonowski, J. A.; Elliott, L. M. *J. Org. Chem.* **1995**, *60*, 2662.

(10) Keck and co-workers have also noted that *trans*-crotyl tri-*n*-butylstannane is more reactive than the *cis* isomer in additions to various aldehydes. Keck, G. E.; Savin, K. A.; Cressman, E. N. K.; Abbott, D. E. *J. Org. Chem.* **1994**, *59*, 7889.

(11) Marshall, J. A.; Welmaker, G. S.; Gung, B. W. *J. Am. Chem. Soc.* **1991**, *113*, 647.

(12) Marshall, J. A.; Welmaker, G. S. *Tetrahedron Lett* **1991**, *32*, 2101.

(13) Marshall, J. A.; Hinkle, K. W. *J. Org. Chem.* **1995**, *60*, 1920.

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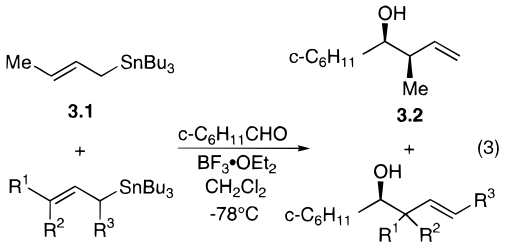
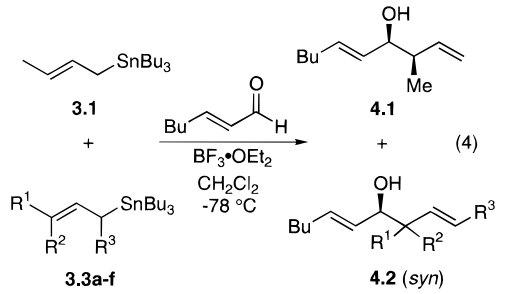


R^1	R^2	R^3	3.3/3.4	3.2:3.4
H	H	H	**a**	46:54
TBSO	H	Me	**b**	91:9
H	OTBS	Me	**c**	>99:1
H	OMOM	Me	**d**	>99:1
Me	H	OTBS	**e**	>99:1[a]
Me	H	OMOM	**f**	>99:1[b]

[a] a 45:55 mixture of (*E*) and (*Z*) isomers **3.4e**
[b] a 69:31 mixture of (*E*) and (*Z*) isomers **3.4f**[13]

When these experiments were performed with (*E*)-2-heptenal, the ratios of crotyl to competitor stannane adducts **4.1**:**4.2** decreased. Also, with this aldehyde allyltributylstannane (**3.3a**) was somewhat less reactive than crotylstannane **3.1**. Interestingly, the (*E*)- and (*Z*)-γ-(silyloxy)stannanes **3.3b** and **3.3c** now showed comparable reactivity to each other, but they were still considerably less reactive than the crotylstannane **3.1**. The γ- and α-OMOM stannanes **3.3d** and **3.3f** were the least competitive of the series. Both the γ-OTBS stannane **3.3c** and the γ-OMOM stannane **3.3d** showed higher reactivity than their α-isomers **3.3e** and **3.3f**. However, in all cases the crotylstannane **3.1** consumed the lion's share of the aldehyde.

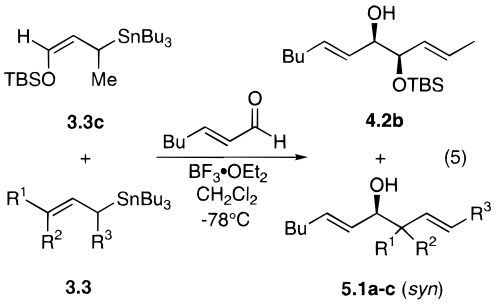


R^1	R^2	R^3	3.3/3.4	4.1:4.2
H	H	H	**a**	76:24
TBSO	H	Me	**b**	90:10
H	OTBS	Me	**c**	88:12
H	OMOM	Me	**d**	97:3
Me	H	OTBS	**e**	94:6[a]
Me	H	OMOM	**f**	98:2[b]

[a] a 79:21 mixture of (*E*) and (*Z*) isomers **4.2e**
[b] a 60:40 mixture of (*Z*) and (*E*) isomers **4.2f**

A competition experiment in which the crotylstannane **3.1** (1 equiv) was allowed to react with 1 equiv each of cyclohexanecarboxaldehyde and (*E*)-2-heptenal yielded a 1:1 mixture of adducts **3.2** and **4.1**. Thus it may be concluded that stannanes **3.3b**−**f** react relatively faster with (*E*)-2-heptenal than with cyclohexanecarboxaldehyde, possibly due in part to steric effects.

As a cross check on the foregoing results, we conducted studies in which the (*Z*)-γ-(silyloxy)allylic stannane **3.3c** was allowed to compete in turn with the α-isomer **3.3e**, the (*Z*)-γ-OMOM **3.3d**, and the α-OMOM analogue **3.3f** (eq 5). The ratios of adducts from the latter two competitions **4.2b**:**5.1b** and **4.2b**:**5.1c** showed good agreement with those predicted from eq 4 (81:19 vs 12:3 and 88:12 vs 12:2), but the ratio of adducts **4.2b**:**5.1a** (49:51) from **3.3c** and the α-isomer **3.3e** was less than would be expected from the results of eq 4 (12:6). Conceivably, selective decomposition of stannane **3.3c** could account for the discrepancy. However, when this reaction was monitored by quenching at various times, the ratios of the two products and the unreacted stannanes were each found to be essentially constant.



3.3	R^1	R^2	R^3	5.1	4.2b:5.1
e	Me	H	OTBS	**a**	49:51
d	H	OMOM	Me	**b**	81:19
f	Me	H	OMOM	**c**	88:12

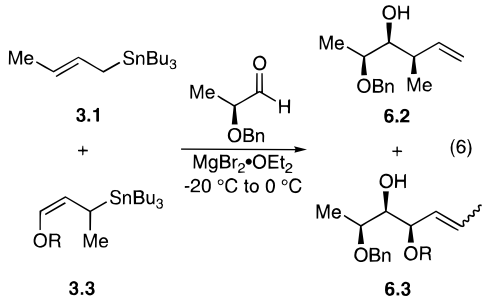
This experiment also showed that as long as unreacted aldehyde was present, no isomerization of the α-OTBS stannane **3.3e** to the γ-isomer **3.3c** occurred. However, upon complete consumption of aldehyde the isomerization was complete within 10−20 min. Thus it would appear that the unreacted aldehyde somehow retards α to γ isomerization. Clearly this phenomenon makes possible the use of α-oxygenated allylic stannanes as S_E2' reagents except with relatively unreactive aldehydes.[5,14]

We also monitored the competition reaction between crotylstannane **3.1** and the (*Z*)-γ-OTBS stannane **3.3c** for 2-heptenal as a function of time (see eq 4). Within 2 min, all of the aldehyde was consumed. Furthermore, during the course of this reaction the intial 85:15 ratio of (*E*)- and (*Z*)-crotyl isomers decreased as the faster reacting (*E*)-isomer was consumed.[10,15] Thus, most of the adduct **4.1** arises from the (*E*)-crotyl isomer over a time period in which negligable decomposition of the competitor stannanes **3.3b**−**f** would be expected to occur. In light of these findings, we believe that the trends reflected in eq 4 are valid, but clearly care must be exercised in their extrapolation.

In the second phase of this study we examined the relative reactivity of crotylstannane **3.1** vs the (*R*)- and (*S*)-γ-OTBS and the (*S*)-OMOM allylic stannanes **3.3c(*R*)**, **3.3c(*S*)**, and **3.3d(*S*)** in $MgBr_2$-promoted additions to (*S*)-2-(benzyloxy)propanal (**6.1**) (eq 6). All of these

(14) *Cf.* Marshall, J. A.; Gung, W. Y. *Tetrahedron* **1989**, *45*, 1043. Marshall, J. A.; Gung, B. W. *Israel J. Chem.* **1991**, *31*, 199. Marshall, J. A.; Yashunsky, D. V. *J. Org. Chem.* **1991**, *56*, 5493.
(15) The crotylstannane used in the study was prepared from (*E*)-crotyl chloride and Bu_3SnLi. Matarasso-Tchiroukhine, E.; Cadiot, P. J. *Organomet. Chem.* **1976**, *121*, 155, 169.

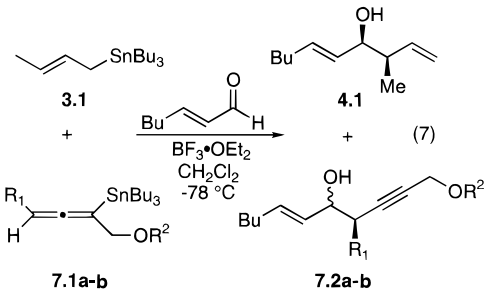
oxygenated stannanes were significantly less reactive than crotyl.[10] As we have previously shown, both the (*R*)- and (*S*)-OTBS stannanes **3.3c(*R*)** and **3.3c(*S*)** give rise to single adducts differing in double bond geometry with the former reacting at the faster rate.[16]



3.3	R	6.3	6.2:6.3
c (*R*)	TBS	**a**	98:2[a]
c (*S*)	TBS	**b**	>99:1[b]
d (*S*)	MOM	**c**	88:12[b]

[a](*Z*) - double bond
[b](*E*) - double bond

In the final phase of this survey we pitted the allenylstannanes **7.1a** and **7.1b**[6] against crotylstannane **3.1**, an 85:15 mixture of (*E*)- and (*Z*)-isomers, in additions to 2-heptenal with BF_3·OEt_2 as the Lewis acid promoter. Both allenyl stannanes were markedly less reactive than crotyl.

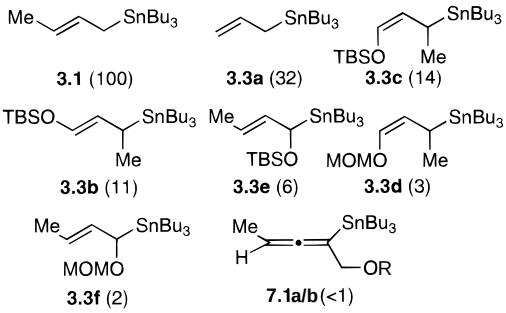


R^1	R^2	7.1/7.2	4.1:7.2
Me	TBS	**a**	99:1[a]
Me	Piv[b]	**b**	99:1[c]

[a] a 65:35 *syn:anti* mixture of **7.2a**
[b] Piv = Me_3CCO
[c] a 68:32 *syn:anti* mixture of **7.2b**

The foregoing studies provide a semiquantitative comparison of reactivities for some of the more synthetically useful stannane reagents (Table 1). In all cases the parent crotyl- and allylstannanes **3.1** and **3.3a** are the most reactive. The relative reactivity is also dependent upon the structure of the aldehyde (compare eq 3 with eq 4). Thus, the α- and γ-OTBS and OMOM allylic stannanes **3.3b**−**f** react faster with (*E*)-2-heptenal than with cyclohexanecarboxaldehyde, but none can effectively compete with crotylstannane **3.1**. We were unable to examine a range of Lewis acids as the oxygenated stannanes are decomposed by the stronger of these and fail to react when weaker Lewis acids are used as promoters.

Table 1. Relative Reactivities of Allylic and Allenic Stannanes with (*E*)-2-Heptenal Promoted by BF_3·OEt_2 in CH_2Cl_2 at −78 °C



As a consequence of these reactivity differences, a number of prototype addition reactions reported for allyl- and crotylstannanes may not be applicable to oxygenated stannanes and allenylstannanes.[4] Included in this category are reactions that require harsh Lewis acid promoters and those that proceed slowly at room temperature.[17] Considering the enormous potential of these latter reagents in asymmetric synthesis, it is of interest to search for more compatible and effective promoters and, ideally, true catalysts that will accommodate the less reactive allenic and oxygenated allylic stannanes.

Experimental Section[18]

General Procedure for BF_3·OEt_2-Promoted Competitive Additions. To a 0.1 M solution of the aldehyde and stannanes (1.0 equiv each) in CH_2Cl_2 cooled to −78 °C was added BF_3·OEt_2 (1.2 equiv). After 1 h, TLC analysis indicated that all of the aldehyde had been consumed and the reaction was quenched with saturated $NaHCO_3$ solution. After warming to rt, the mixture was extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under reduced pressure. The adducts were separated from residual stannane by flash chromatography on silica gel with ethyl acetate in hexane. The ratio of adducts was determined by GC and ^{1}H NMR analysis.

Stannanes and Product Composition as a Function of Reaction Time. Three individual experiments were performed simultaneously according to the foregoing protocol. Each of the three was quenched after varying time intervals from 2 to 30 min. Analysis of the products and unreacted stannane was performed as described. Known mixtures of stannanes and products were analyzed by GC to establish relative response factors. ^{1}H NMR analysis was employed as a cross check on the structures of components and composition of the mixtures.

General Procedure for $MgBr_2$·OEt_2-Promoted Competitive Additions. A 0.1 M solution of the aldehyde and stannanes (1.0 equiv each) in CH_2Cl_2 was cooled to −23 °C, and $MgBr_2$·OEt_2 (1.2 equiv) was added. After 1 h, the mixture was warmed to 0 °C. After an additional 0.5 h, TLC analysis indicated that all of the aldehyde had been consumed and the reaction was quenched with saturated $NaHCO_3$ solution. After warming to rt, the mixture was extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under reduced pressure. The adducts were separated from residual stannane by flash chromatography on silica gel with ethyl acetate in hexane. The ratio of adducts was determined by GC and ^{1}H NMR analysis.

Previously Uncharacterized Stannanes and Adducts: (*rel* 1*R*,2*S*,*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-cyclohexyl-2-methyl-3-penten-1-ol (3.4e). To a stirred solution of stan-

(16) Marshall, J. A.; Jablonowski, J. A.; Luke, G. P. *J. Org. Chem.* **1994**, *59*, 7825.

(17) *Cf.* Hachiya, I.; Kobayashi, S. *J. Org. Chem.* **1993**, *58*, 6958. Bedeschi, P.; Casolari, S.; Costa, A. L.; Tagliavini, E.; Umani-Ronchi, A. *Tetrahedron Lett.* **1995**, *36*, 7897. Aspinall, H. C.; Browning, A. F.; Greeves, N.; Ravenscroft, P. *Tetrahedron Lett.* **1994**, *35*, 4639. Henry, K. J.; Grieco, P. A.; Jagoe, C. T. *Tetrahedron Lett.* **1992**, *33*, 1817.

(18) For typical experimental protocols, see: Marshall, J. A.; Wang, X-j. *J. Org. Chem.* **1991**, *56*, 960. Unless otherwise stated ^{1}H and ^{13}C NMR spectra were determined at 300 and 75 MHz, respectively, on dilute solutions in $CDCl_3$.

nane **3.3e**[12] (128 mg, 0.27 mmol) and cyclohexanecarboxaldehyde (27 mg, 0.24 mmol) in 1.5 mL of CH_2Cl_2 was added $BF_3{\cdot}OEt_2$ (31 μL, 0.30 mmol). After 1.5 h, TLC analysis indicated that all the aldehyde had been consumed and the reaction was quenched with saturated $NaHCO_3$ solution. After warming to rt, the mixture was extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel. Elution with 5% ethyl acetate in hexane provided 71.5 mg (65%) of a 45:55 mixture of (*E*)- and (*Z*)-isomers of adduct **3.4e**. Data for the (*Z*)-isomer: ^{1}H NMR δ 6.16 (dd, J = 5.8, 0.8 Hz, 1H), 4.33 (dd, J = 9.2, 5.8 Hz, 1H), 3.19 (dd, J = 6.0, 6.0 Hz, 1H), 2.86 (dm, J = 6.9 Hz, 1H), 1.90 (m, 1H), 1.83−1.35 (m, 6H), 1.36−1.02 (m, 4H), 0.98 (d, J = 6.9 Hz, 3H), 0.92 (s, 9H), 0.12 (s, 6H) ppm; IR (film) ν 3415 cm^{-1}.

(*rel* 3*S*,4*R*,*E*,*E*)-1-((*tert*-Butyldimethylsilyl)oxy)-3-methyl-1,5-decadien-4-ol (4.2e). The above procedure was employed with stannane **3.3e**[12] (300 mg, 0.63 mmol), (*E*)-2-heptenal (64 mg, 0.56 mmol), and $BF_3{\cdot}OEt_2$ (77 μL, 0.75 mmol). The crude residue was purified by flash chromatography on silica gel. Elution with 5% ethyl acetate in hexane provided 139 mg (83%) of a 79:21 mixture of (*E*)- and (*Z*)-isomers of silyl enol ether **4.2e**. Data for the (*E*)-isomer: ^{1}H NMR δ 6.24 (dd, J = 5.9, 1.0 Hz, 1H), 5.62 (ddd, J = 15.3, 6.7, 6.7 Hz, 1H), 5.43 (ddd, J = 15.4, 6.9, 1.2 Hz, 1H), 4.30 (dd, J = 9.0, 6.0 Hz, 1H), 3.93 (dd, J = 5.5, 5.5 Hz, 1H), 2.85 (m, 1H), 2.01 (m, 2H), 1.47−1.20 (m, 4H), 1.85−0.75 (m, 16H), 0.13 (s, 6H) ppm; ^{13}C NMR δ 132.5, 130.1, 111.5, 76.4, 34.8, 31.8, 31.2, 25.6, 25.5, 21.9, 18.0, 16.4, 13.7, −5.6, −5.7 ppm; IR (film) ν 3450 cm^{-1}. Anal. Calcd for $C_{17}H_{34}O_2Si$: C, 68.39; H, 11.48. Found: C, 68.48; H, 11.43.

(*rel* 3*S*,4*R*,*E*,*E*)-1-(Methoxymethoxy)-3-methyl-1,5-decadien-4-ol (4.2f). The above procedure was employed with stannane **3.3f**[11] (255 mg, 0.63 mmol), (*E*)-2-heptenal (64 mg, 0.56 mmol), and $BF_3{\cdot}OEt_2$ (77 μL, 0.75 mmol). The product was purified by flash chromatography on silica gel. Elution with 20% ethyl acetate in hexane provided 88 mg (69%) of a 60:40 mixture of (*Z*)- and (*E*)-isomers of enol ether **4.2f**. Data for the (*E*)-isomer: ^{1}H NMR δ 6.18 (d, J = 6.4 Hz, 1H), 5.66 (ddd, J = 15.3, 6.7, 2.2 Hz, 1H), 5.35 (ddd, J = 15.4, 5.8, 1.4 Hz, 1H), 4.80 (s, 2H), 3.66 (dd, J = 9.5, 6.5 Hz, 1H), 3.94 (dd, J = 6.0, 6.0 Hz, 1H), 3.40 (s, 3H), 2.90 (m, 1H), 2.02 (m, 2H), 1.40−1.20 (m, 4H), 0.98 (d, J = 7.0 Hz, 3H), 0.90 (d, J = 6.8 Hz, 3H), 0.87 (d, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz) δ 143.0, 133.0, 130.0, 110.2, 96.4, 76.8, 55.8, 35.4, 32.0, 31.4, 22.2, 16.7, 13.9 ppm; IR (film) ν 3450 cm^{-1}.

(*rel* 4*S*,5*R*,*E*)-1-((*tert*-Butyldimethylsilyl)oxy)-4-methyl-6-undecen-2-yn-5-ol (7.2a). The procedure described for **3.4e** was employed with stannane **7.1a**[19] (91 mg, 0.19 mmol), (*E*)-2-heptenal (21 mg, 0.19 mmol), and $BF_3{\cdot}OEt_2$ (22 μL, 0.22 mmol). The product was purified by flash chromatography on silica gel. Elution with 5% ethyl acetate in hexane provided 40 mg (69%) of a 65:35 mixture of *syn* and *anti* isomers of adduct **7.2a**. Data for the *syn* isomer: ^{1}H NMR δ 5.71 (ddd, J = 15.3, 7.2, 6.5 Hz, 1H), 5.45 (ddd, J = 15.3, 7.0, 1.4 Hz, 1H), 4.32 (dd, J = 5.8, 1.9 Hz, 2H), 3.89 (dd, J = 9.9, 6.8 Hz, 1H), 2.54 (dq, J = 9.9, 7.2 Hz, 1H), 2.03 (m, 2H), 1.91−1.48 (m, 3H), 1.47−1.22 (m, 4H), 1.15 (d, J = 7.0 Hz, 3H), 0.12 (s, 6H) ppm; ^{13}C NMR δ 134.3, 19.9, 85.8, 81.7, 75.8, 51.9, 33.7, 31.9, 31.2, 25.8, 22.1, 18.3, 17.0, 13.9, −5.1 ppm; IR (film) ν 3415, 2200 cm^{-1}. Anal. Calcd for $C_{18}H_{34}O_2Si$: C, 69.62; H, 11.04. Found: C, 69.35; H, 11.10.

(*rel* 4*S*,5*R*,*E*)-1-(Pivaloyloxy)-4-methyl-6-undecen-2-yn-5-ol (7.2b). The procedure described for **3.4e** was employed with stannane **7.1b**[18] (89 mg, 0.20 mmol), (*E*)-2-heptenal (21 mg, 0.19 mmol), and $BF_3{\cdot}OEt_2$ (22 μL, 0.22 mmol). The product was purified by flash chromatography on silica gel. Elution with 10% ethyl acetate in hexane provided 28 mg (60%) of a 68:32 mixture of *syn* and *anti* isomers of adduct **7.2b**. Data for the *syn* isomer: ^{1}H NMR δ 5.72 (ddd, J = 15.4, 8.3, 6.2 Hz, 1H), 5.45 (dd, J = 15.7, 7.2 Hz, 1H), 4.66 (s, 2H), 3.89 (dd, J = 6.6, 6.4 Hz, 1H), 2.58 (m, 1H), 2.08 (m, 3H), 1.58−1.22 (m, H), 1.22 (s, 9H), 1.16 (d, J = 7.2, 3H), 0.91 (d, J = 6.9, 3H) ppm; IR (film) ν 3475, 2200 cm^{-1}.

Acknowledgment. We are grateful to the National Science Foundation for support of this study through a research grant (CHE 9220166). We thank Drs. Shiping Xie and Mark Wolf and Ms. Michelle Elliott for providing the various stannanes used in this study.

Supporting Information Available: ^{1}H NMR spectra for previously unknown adducts (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9519975

(19) Marshall, J. A.; Xie, S. *J. Org. Chem.* **1995**, *60*, 7230.