in the presence of oxygen from 10 and from its rearranged photoproduct 11.

Quantum Yields of Photorearrangement of Several Pyridazines. By use of merry-go-round quantum yield apparatus and the general procedures described above, quantum yields for decomposition of 1 (Φ_d) and photorearrangement of 1 to 2 (Φ_r) were obtained for 1 (Table VI). By use of the merry-go-round quantum yield apparatus and the general procedures described above, relative quantum yields determined for each of the remaining photorearranging pyridazines were compared with the now established quantum yield for rearrangement of 1 (Table VII).

Photolysis of Other Pyridazines. A degassed solution of pyridazine (1×10^{-3} M) in Freon 113 was prepared. A degassed solution of maleic hydrazide (1×10^{-3} M) was prepared in water since this compound was insoluble in Freon 113, perfluoromethylcyclohexane, and cyclohexane. These solutions were irradiated at 35 °C at 2537 Å. Progress of the photoreaction was followed by UV spectroscopy. The absorption of starting material in all three solutions quickly disappeared, with no hint of pyrazine formation being detectable by UV spectroscopy or by GLC.

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Registry No. 1, 20074-67-3; 2, 13484-50-9; 4, 14161-11-6; 5, 6082-66-2; 6, 873-40-5; 7, 141-30-0; 8, 55271-49-3; 9, 19745-07-4; 10, 34584-69-5; 11, 27023-19-4.

Reaction of Organotin Hydrides with Acetylenic Alcohols

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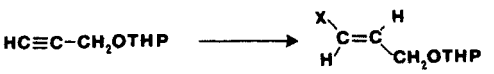
The reaction of di-*n*-butyltin dihydride and tri-*n*-butyltin hydride with mono- and disubstituted acetylenic alcohols has been studied. Di-*n*-butyltin dihydride reacts with certain monosubstituted acetylenic alcohols to give cyclic vinyltin ethers. With disubstituted acetylenic alcohols only divinylstannyl derivatives are obtained. Tri-*n*-butyltin hydride reacts with disubstituted acetylenic alcohols to give (*Z*)-2-(tri-*n*-butylstannyl)-2-alken-1-ols. Metalation and iodination of the resulting vinylstannanes are discussed.

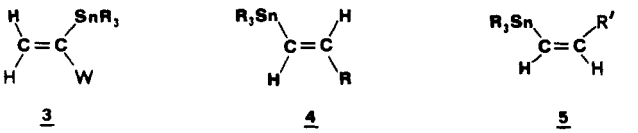
Vinyl organotin reagents have assumed an increasingly important role as intermediates for the synthesis of complex natural products. Corey and co-workers introduced the use of 1 as a convenient source of the protected



1, X = $SnBu_3$
2, X = Li

(*E*)-3-lithiopropenol 2 and its corresponding cuprate.[1] This report was soon followed by other examples of the synthetic utility of vinyltin compounds for the generation of vinylic nucleophiles.[2]

The most convenient method for the preparation of vinyltin compounds is by the addition of trialkyltin hydrides to the corresponding acetylenic compound. The reaction of tributyltin hydride with monosubstituted acetylenes bearing strongly electron-withdrawing substituents (CO_2R, C≡N, etc.) affords mainly, or even exclusively, the α-adduct 3.[3] Monosubstituted acetylenes bearing electron-releasing (alkyl, OR, etc.) or weakly electron-withdrawing substituents (CR_2OH, C_6H_5, etc.) afford mainly the β-*E* (4) and β-*Z* (5) adducts.[2b,d,e,4]



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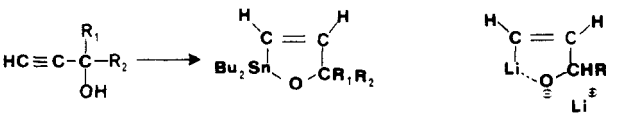
In 1973 Massol and co-workers reported the preparation of a series of cyclic vinyltin ethers (6) by the reaction of



6 a. $R_1 = R_2 = H$
b. $R_1 = H$, $R_2 = CH_3$
c. $R_1 = H$, $R_2 = C_3H_7$
d. $R_1 = R_2 = CH_3$
e. $R_1 = CH_3$, $R_2 = C_2H_5$

7 a. R = CH_3
b. R = C_5H_{11}

propargylic alcohols with dibutyltin dihydride.[5] These cyclic organotin compounds appeared to offer a convenient approach to useful derivatives of (*Z*)-3-lithiopropenols such as 7.[6] Herein we report the results of our study of the hydrostannylation of alkynols with dibutyltin dihydride and tributyltin hydride.

Results and Discussion

Reaction of Dibutyltin Dihydride with Monosubstituted Acetylenic Alcohols. The reaction of dibutyltin

(1) E. J. Corey and R. H. Wollenberg, *J. Org. Chem.*, 40, 2265 (1975).
(2) (a) E. J. Corey and R. H. Wollenberg, *J. Org. Chem.* 40, 3788 (1975); (b) E. J. Corey, P. Ulrich, and J. M. Fitzpatrick, *J. Am. Chem. Soc.*, 98, 222 (1976); (c) R. H. Wollenberg, K. F. Albizati, and R. Peries, *ibid.*, 99, 7365 (1977); (d) P. W. Collins, C. J. Jung, A. Gasiecki, and R. Pappo, *Tetrahedron Lett.*, 3187 (1978); (e) S.-M. L. Chen, R. E. Schaub, and C. V. Grudzinskas, *J. Org. Chem.*, 43, 3450 (1978); (f) M. Gill, H. P. Bainton, and R. W. Richards, *Tetrahedron Lett.*, 1437 (1981).
(3) A. J. Leusink, H. A. Budding, and J. W. Marsman, *J. Organomet. Chem.*, 9, 285 (1967); A. J. Leusink, H. A. Budding, and W. Krenth, *ibid.*, 9, 295 (1967).
(4) A. J. Leusink, J. W. Marsman, and H. A. Budding, *Recl. Trav. Chem. Pays-Bas*, 84, 689 (1965).
(5) M. Massol, J. Satge, and B. Banyssieres, *Synth, Inorg. Met.-Org. Chem.*, 3, 1 (1973).
(6) For potential applications to prostaglandin synthesis see: (a) A. F. Kluge, K. G. Untch, and J. H. Fried, *J. Am. Chem. Soc.*, 94, 9256, (1972); (b) J. G. Miller, W. Kurz, K. G. Untch, and G. Stork, *ibid.*, 96, 6774 (1974).

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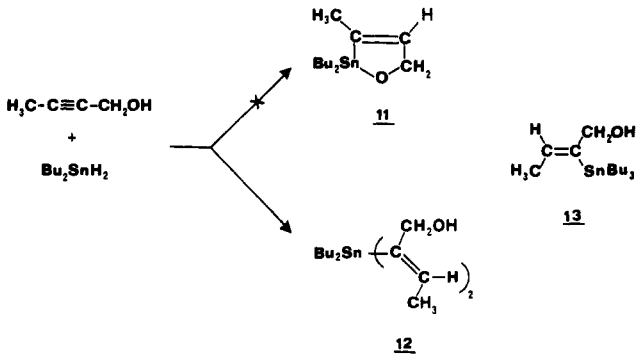
Table I. Addition of Tin Hydrides to Terminal Acetylenic Alcohols

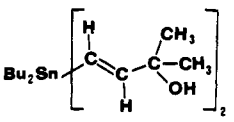
acetylenic alcohols	conditions[a]	hydride	adducts	E/Z ratio[b]	% yield
$HC{\equiv}CCHOHCH_3$	B	Bu_2SnH_2			49
$HC{\equiv}CCHOH(CH_2)_4CH_3$	B	Bu_2SnH_2			61
$HC{\equiv}CCHOH(CH_2)_4CH_3$	A	Bu_2SnH_2			69
$HC{\equiv}CCHOH(CH_2)_4CH_3$	B	Bu_3SnH		3:1	60
$HC{\equiv}CC(CH_3)_2OH$	A	Bu_2SnH_2		7:3	94
$HC{\equiv}CCH_2CH_2OH$	B	Bu_2SnH_2	(*E*)- and (*Z*)-$Bu_2Sn(CH{=}CHCH_2CH_2OH)_2$	1:1	86
$HC{\equiv}CCH_2CHOHCH_3$	B	Bu_2SnH_2	(*E*)- and (*Z*)-$Bu_2Sn(CH{=}CHCH_2CHOHCH_3)_2$	1:1	81
$HC{\equiv}CCH_2C(CH_3)_2OH$	B	Bu_2SnH_2	(*E*)- and (*Z*)-$Bu_2Sn[CH{=}CHCH_2C(CH_3)_2OH]_2$	5:1	69
$HC{\equiv}CCH_2CH_2CH_2OH$	B	Bu_2SnH_2	(*E*)- and (*Z*)-$Bu_2Sn(CH{=}CHCH_2CH_2CH_2OH)_2$	9:1	69
$HC{\equiv}CCH_2C(CH_3)_2CH_2CHCH_3OH$	B	Bu_2SnH_2	(*E*)- and (*Z*)-$Bu_2Sn[CH{=}CHCH_2C(CH_3)_2CH_2CHCH_3OH]_2$	9:1	85

[a] Reaction conditions: A, no radical initiator present; B, AIBN used as radical initiator. [b] Ratio was determined by NMR integration of distilled products.

Scheme I



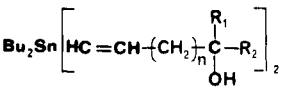
dihydride with 3-butyn-2-ol gave the expected[5] 1,1-di-*n*-butyl-2,3-dihydro-3-methyl-2-oxastannole (**6b**) in 49% yield (Table I). However, the reaction of dibutyltin dihydride with 2-methyl-3-butyn-2-ol produced variable yields of 1,1-di-*n*-butyl-2,3-dihydro-3,3-dimethyl-2-oxastannole (**6d**) and the 1:2 adduct **8**. When the reaction was



8

conducted at 55–65 °C, a 7:3 mixture of **6d** and **8** was produced in a 94% total yield. When the reaction was conducted in the presence of azobis(isobutyronitrile) (AIBN), **8** was the only product of an extremely exothermic reaction.

The reaction of dibutyltin dihydride with homo- and bishomopropargylic alcohols afford only the 1:2 adducts **9** as mixtures of *E* and *Z* isomers (Table I). The cyclic 1:1



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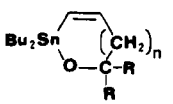

10

adducts **10** were not observed. Coordination of the hydroxyl oxygen to tin favors anti addition (affording the (*Z*)-vinylstannane) when $n = 0$, 1, or 2.[2,7]

When the hydroxyl group and the acetylene were separated by three or more carbons, as in 4-pentyn-1-ol and 4,4-dimethyl-6-heptyn-2-ol, the hydroxyl group had no effect, and as with nonfunctionalized acetylenes, the *E* isomer was the predominant product.

Reaction of Dibutyltin Dihydride with Disubstituted Acetylenic Alcohols. The reaction of organotin hydrides with disubstituted acetylenes has not been extensively studied. With unsymmetrical disubstituted acetylenes, mixtures of the four possible geometric and positional isomers are usually obtained, with the *Z* isomers predominating.[3]

It was anticipated that the reaction of dibutyltin dihydride with 2-butyn-1-ol might furnish the cyclic vinyltin ether **11** (Scheme I) which could function as a useful intermediate in terpene synthesis. However, the product of this reaction is the *Z* 1:2 adduct **12** isolated in 47% yield and >95% isomeric purity (Table II). This relative stereochemistry can be generated more conveniently by

(7) B. R. Laliberte, W. Davidsohn, and M. C. Henry, *J. Organomet. Chem.*, **5**, 526 (1966); M. Massol, J. Barrau, J. Satge, and B. Bougssieres, *ibid.*, **80**, 47 (1974).

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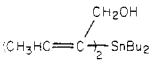
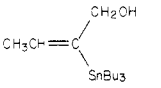
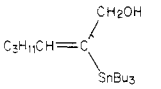
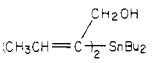
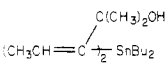
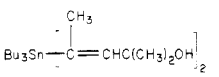
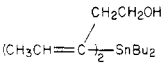
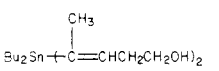
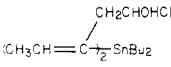
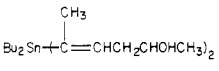
Table II. Addition of Tin Hydrides to Disubstituted Acetylenic Alcohols

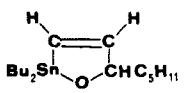
acetylenic alcohol	conditions[a]	hydride	adducts	Z/E ratio[b]	% yield
$CH_3C{\equiv}CCH_2OH$	B	Bu_2SnH_2		95:5	47
$CH_3C{\equiv}CCH_2OH$	B	Bu_2SnH		95:5	74
$C_3H_{11}C{\equiv}CCH_2OH$	B	Bu_2SnH		95:5	87
$CH_3C{\equiv}CCHOHCH_2$	B	Bu_2SnH_2		95:5	75
$CH_3C{\equiv}CCOH(CH_3)_2$	B	Bu_2SnH_2	 	95:5 95:5	86[c]
$CH_3C{\equiv}CCH_2CH_2OH$	B	Bu_2SnH_2	 	Z only 50:50	93[d]
$CH_3C{\equiv}CCH_2CHOHCH_3$	B	Bu_2SnH_2	 	19:1 10:1	93[e]

[a] Reaction conditions: A, no radical initiator present; B, AIBN used as radical initiator. [b] Ratio was determined by NMR integration of distilled products; a 95:5 ratio is minimum purity (only one isomer detected). [c] Ratio of 2-tri-*n*-butylstannyl to 3-tri-*n*-butylstannyl was 5:1. [d] Ratio of 3-tri-*n*-butylstannyl to 4-tri-*n*-butylstannyl was 1:1. [e] Ratio of 4-tri-*n*-butylstannyl to 5-tri-*n*-butylstannyl was 1:1.

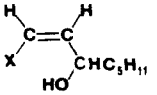
treatment of 2-butyn-1-ol with tributyltin hydride which affords the *Z* adduct **13** in 82% yield and >95% isomeric purity. The geometry assigned to **13** follows from the large (128 Hz) $^3J_{SnH}$ coupling which is indicative of a trans H–C–C–Sn linkage.[9] NOE measurements also support this assignment.

As can be seen from the data in Table II, addition of tin at C-2 of the propargylic system is preferred even when the carbinol carbon is fully substituted. When the hydroxyl group and acetylene are separated by more than one carbon, this type of selectivity is no longer observed, and the organotin radical adds to either acetylenic carbon with equal facility, giving complex mixtures of products.

Reactions of Vinylorganotin Compounds. Treatment of **14** with 1.1 equiv of *n*-butyllithium in tetrahydrofuran at −78 °C followed by the addition of D_2O gave predominantly (*Z*)-1-(tri-*n*-butylstannyl)-1-octen-3-ol resulting from preferential cleavage of the tin–oxygen bond rather than the vinyltin bond.[10] The use of 2.2 equiv of *n*-butyllithium at −20 °C in tetrahydrofuran afforded the lithio dianion **7b** as indicated by the isolation of (*Z*)-1-deuterio-1-octen-3-ol (**15**) in 93% yield on quenching with D_2O.[6a]



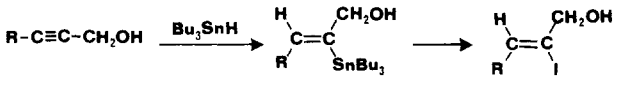
14



15, X = D
16, X = I

Stereospecific cleavage of the vinyl–tin bond with iodine[11] affords a useful approach to a series of functionalized vinyl iodides. Treatment of **14** with 1.1 equiv of iodine in ether gives a nearly quantitative yield of the (*Z*)-vinyl iodide **16** which has proved to be a valuable intermediate in prostaglandin synthesis.[6]

Although the cyclostannylation reaction of dibutyltin dihydride with disubstituted acetylenic alcohols such as **17** fails, the nearly exclusive formation of the *Z* olefin **18**



17a, R = CH_3 **18a**, R = CH_3 **19a**, R = CH_3
b, R = C_5H_{11} **b**, R = C_5H_{11} **b**, R = C_5H_{11}

on treatment with tri-*n*-butyltin hydride is synthetically useful. The hydrostannylation of disubstituted propargyl alcohols followed by treatment with iodine is a mild and convenient alternative to the current methodology[12] for the preparation of vinyl iodides such as **19**.

Experimental Section

Infrared data were obtained on a Beckman IR-18A spectrophotometer or a Perkin-Elmer 298 spectrophotometer. ^1H NMR spectra were taken on a JEOL JNM-MH-100 instrument on solutions in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR spectra were taken at 15.03 MHz on a JEOL FX-60

(9) D. W. Moore and J. A. Happe, *J. Phys. Chem.*, **65**, 224 (1961); S. Cowley and S. S. Danyluk, *ibid.*, **68**, 1240 (1964).
(10) A slow rate of exchange of *cis*-vinylstannanes with *n*-butyllithium has been observed previously: see ref 2d,e.
(11) P. Baekelmans, M. Gielen, P. Malfroid, and J. Nasieski, *Bull. Soc. Chim. Belg.*, **77**, 85 (1968).
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spectrometer. Gas chromatography–mass spectra were obtained by using a Du Pont 491-B mass spectrometer. All alkynols used were commercially available (Aldrich Chemical Co., ICN, or Chemical Procurement Laboratories) except 4,4-dimethyl-6-heptyn-2-ol which was prepared by known procedures.[13] Polymethylhydrosiloxane was obtained from Aldrich Chemical Co.

Dibutyltin Dihydride.[14] Dibutyltin oxide (10 g, 40 mmol) was added to 5.3 g of polymethylhydrosiloxane (88 mmol) in 20 mL of tetrahydrofuran, and the mixture was stirred at reflux under N_2 for 1 h. The THF was evaporated and the residue distilled to give dibutyltin dihydride: 4.8 g (20 mmol, 52%); colorless liquid; bp 49–51 °C (0.6 mm); IR (neat) 2920 (m, CH), 1835 (s, SnH) cm^{-1}; NMR 4.46 (s, 2 H, SnH), 1.70–1.01 (m, 12 H, CH_2), 0.86 (m, 6 H, CH_3) ppm.

Reaction of Dibutyltin Dihydride with 2-Methyl-3-butyn-2-ol in the Absence of Radical Initiators. Procedure A. A mixture of dibutyltin dihydride (2.35 g, 10 mmol) and 2-methyl-3-butyn-2-ol (2.1 g, 25 mmol) was heated under a N_2 atmosphere at 65 °C until TLC (silica gel, CH_2Cl_2) indicated the disappearance of dibutyltin dihydride (ca. 1 h). The resulting pale yellow oil was distilled (bulb-to-bulb) to give a 94% yield of a 7:3 mixture of 1,1-di-*n*-butyl-2,3-dihydro-3,3-dimethyl-2-oxastannole (**6d**) and di-*n*-butylbis[(*E*)-3-hydroxy-3-methyl-1-butenyl]stannane (**8**), respectively. The mixture could be separated by fractional distillation to give **6d** and **8**. For **6d**: 1.98 g (6.2 mmol, 62%); bp 121–127 °C (0.5 mm); IR (neat) 1630 (m, C=C) cm^{-1}; NMR 6.95 (d, J = 10 Hz, 1 H, =CH), 6.20 (d, J = 10 Hz, 1 H, SnCH), 1.70–1.01 (m, 18 H, CH_2 and CH_3), 0.80 (m, 6 H, CH_3) ppm. For **8**: 0.8 g (2.0 mmol, 20%); bp 137–142 °C (0.5 mm); IR (neat) 3350 (s, OH), 1608 (m, C=C) cm^{-1}; NMR 6.11 (m, 4 H, CH=CH), 2.5 (br s, 2 H, OH), 1.60–1.01 (m, 24 H, CH_2 and CH_3), 0.80 (m, 6 H, CH_3) ppm.

1,1-Di-*n*-butyl-2,3-dihydro-3-*n*-pentyl-2-oxastannole (14) was prepared in a similar manner from 1-octyn-3-ol: 68% yield; bp 140–145 °C (0.2 mm); mp 90–92 °C; IR (neat) 1628 (m, C=C) cm^{-1}; NMR 7.10 (d, J = 12 Hz, 1 H, =CH), 6.37 (d, J = 12 Hz, 1 H, SnCH), 4.57 (m, 1 H, OCH), 1.67–0.99 (m, 20 H, CH_2), 0.96–0.75 (m, 9 H, CH_3) ppm.

Anal. Calcd for $C_{16}H_{32}OSn$: C, 53.51; H, 8.98. Found: C, 53.48; H, 9.01.

Reaction of Dibutyltin Dihydride with 2-Methyl-3-butyn-2-ol in the Presence of Azobis(isobutyronitrile). Procedure B. A mixture of dibutyltin dihydride (2.35 g, 10 mmol), 2-methyl-3-butyn-2-ol (2.10 g, 25 mmol), and a catalytic amount of AIBN (20 mg) was heated under a N_2 atmosphere at 65 °C until the very exothermic reaction was initiated. After the exothermic reaction was over, heating was continued at 65 °C for 30 min. The resulting pale yellow oil was distilled at 0.5 mm to give **8** in 61% yield.

The following compounds were prepared in a similar manner.

1,1-Di-*n*-butyl-2,3-dihydro-3 methyl-2-oxastannole (6b) was prepared from 3-butyn-2-ol: 49% yield; bp 120 °C (0.2 mm); mp 106–108 °C; IR (neat) 1630 (m, C=C) cm^{-1}; NMR 6.96 (d, J = 12 Hz, 1 H, =CH), 6.31 (d, J = 12 Hz, 1 H, SnCH), 4.56 (q, J = 7 Hz, 1 H, OCH), 1.60–1.00 (m, 15 H, CH_2 and CH_3), 0.86 (m, 6 H, CH_3) ppm.

1,1-Di-*n*-butyl-2,3-dihydro-3-*n*-pentyl-2-oxastannole (14) was prepared from 1-octyn-3-ol in 51% yield.

Di-*n*-butylbis(4-hydroxy-1-butenyl)stannane was prepared from 3-butyn-1-ol as a 1:1 mixture of *E* and *Z* isomers: 86% yield; bp 107–118 °C (0.12 mm); IR (neat) 3290 (m, OH), 1600 (m, C=C) cm^{-1}; NMR for *Z* isomer 6.48 (m, 2 H, =CH), 6.04 (d, J = 12 Hz, 2 H, SnCH), 3.65 (m, 4 H, OCH_2), 2.61 (s, 2 H, OH) 2.32 (m, 4 H, CH_2), 1.64–1.00 (m, 12 H, CH_2), 0.84 (m, 6 H, CH_3); NMR for *E* isomer, 5.96 (m, 4 H, CH=CH), 3.62 (m, 4 H, OCH_2), 2.61 (s, 2 H, OH), 2.37 (m, 4 H, CH_2), 1.64–1.00 (m, 12 H, CH_2), 0.84 (m, 6 H, CH_3) ppm.

Di-*n*-butylbis(4-hydroxy-1-pentenyl)stannane was prepared from 4-pentyn-2-ol as a 1:1 mixture of *E* and *Z* isomers: 81% yield; bp 95–115 °C (0.1 mm); IR (neat) 3330 (m, OH), 1600 (m, C=C) cm^{-1}; NMR, for *Z* isomer (dt, J_1 = 13 Hz, J_2 = 5 Hz, 2 H, =CH), 6.00 (d, J = 13 Hz, 2 H, SnCH), 4.20–3.94 (m, 2 H, OCH), 2.62 (s, 2 H, OH), 2.28–2.04 (m, 4 H, CH_2), 1.72–1.00 (m, 18 H, CH_2 and CH_3), 0.86 (m, 6 H, CH_3); NMR for *E* isomer 6.03 (m, 4 H, HC=CH), 3.84 (m, 2 H, OCH), 2.62 (s, 2 H, OH), 2.30 (m, 4 H, CH_2), 1.72–1.01 (m, 18 H, CH_2), 0.86 (m, 6 H, CH_3) ppm.

Di-*n*-butylbis(4-hydroxy-4-methyl-1-pentenyl)stannane was prepared from 2-methyl-4-pentyn-2-ol as a 5:1 mixture of *E* and *Z* isomers, respectively: 69% yield; bp 128–132 °C (0.05 mm). For the *Z* isomer: IR (neat) 3340 (m, OH), 1600 (m, C=C) cm^{-1}; NMR 6.78 (dt, J_1 = 14 Hz, J_2 = 5 Hz, 2 H, =CH), 6.14 (d, J = 14 Hz, 2 H, SnCH), 2.72 (s, 2 H, OH), 2.18 (d, J = 5 Hz, 4 H, CH_2), 1.72–1.01 (m, 24 H, CH_2 and CH_3), 0.86 (m, 6 H, CH_3). For the *E* isomer: NMR 6.00 (m, 4 H, HC=CH), 2.72 (s, 2 H, OH), 2.10 (d, J = 5 Hz, 4 H, CH_2), 1.72–1.01 (m, 24 H, CH_2), 0.86 (m, 6 H, CH_3).

Di-*n*-butylbis[(*E*)-5-hydroxy-1-pentenyl]stannane was prepared from 4-pentyn-1-ol: 60% yield; bp 78–82 °C (0.02 mm); IR (neat) 3290 (m, OH), 1605 (m, C=C) cm^{-1}; NMR 5.96 (m, 4 H, HC=CH), 3.60 (m, 4 H, OCH_2), 2.16 (m, 6 H, =C—CH_2 and OH), 1.72–1.01 (m, 16 H, CH_2), 0.86 (m, 6 H, CH_3) ppm.

Anal. Calcd for $C_{18}H_{36}O_2Sn$: C, 53.62; H, 9.00. Found: C, 53.55; H, 8.85.

Di-*n*-butylbis[(*E*)-4,4-dimethyl-6-hydroxy-1-heptenyl]stannane was prepared from 4,4-dimethyl-6-heptyn-2-ol: 82% yield; bp 86–94 °C (0.02 mm); IR (neat) 3330 (m, OH), 1600 (m, C=C) cm^{-1}; NMR 6.00 (m, 4 H, CH=CH), 3.96 (m, 2 H, OCH), 2144 (s, 2 H, OH), 2.12 (d, J = 5 Hz, 4 H, C=C—CH_2, 1.72–1.06 (m, 16 H, CH_2), 1.18 (d, J = 5 Hz, 6 H, $OCCH_3$), 1.06–0.80 (m, 18 H, CH_3) ppm.

Anal. Calcd for $C_{26}H_{52}O_2Sn$: C, 60.59; H, 10.17. Found: C, 60.37; H, 10.01.

Di-*n*-butylbis[(*Z*)-1-(hydroxymethyl)-1-propenyl]stannane (12) was prepared from 2-butyn-1-ol: 47% yield; bp 102–105 °C (0.015 mm); IR (neat) 3360 (m, OH), 1660 (m, C=C) cm^{-1}; NMR 6.32 (m, 2 H, =CH), 4.18 (s, 4 H, CH_2), 2.48 (s, 2 H, OH), 1.74 (d, J = 7 Hz, 6 H, CH_3), 1.78–1.10 (m, 12 H, CH_2), 0.86 (m, 6 H, CH_3) ppm.

Anal. Calcd for $C_{16}H_{32}O_2Sn$: C, 51.23; H, 8.60. Found: C, 51.03; H, 8.47.

Di-*n*-butylbis[(*Z*)-1-(1-hydroxyethyl)-1-propenyl]stannane was prepared from 3-pentyn-2-ol: 75% yield; bp 110–120 °C (0.05 mm); IR (neat) 3330 (m, OH), 1618 (m, C=C) cm^{-1}; NMR 6.24 (m, 2 H, =CH), 4.36 (m, 2 H, OCH), 3.70 (br s, 2 H, OH), 1.72 (d, J = 7 Hz, 6 H, $=CCH_3$), 1.70–1.01 (m, 18 H, CH_2 and CH_3), 0.88 (m, 6 H, CH_3) ppm.

Anal. Calcd for $C_{18}H_{36}O_2Sn$: C, 53.62; H, 9.00. Found: C, 53.48; H, 9.20.

Di-*n*-butylbis[(*Z*)-1-(1-methyl-1-hydroxyethyl)-1-propenyl]stannane and di-*n*-butylbis[(*Z*)-1,3-dimethyl-3-hydroxy-1-butenyl]stannane were prepared as a 5:1 mixture, respectively, in 85% yield from 2-methyl-3-pentyn-2-ol. For di-*n*-butylbis[(*Z*)-1-(1-methyl-1-hydroxymethyl)-1-propenyl]-stannane: bp 75–79 °C (0.1 mm); IR (neat) 3350 (s, OH), 1620 (m, C=C) cm^{-1}; NMR 6.02 (q, J = 6 Hz, 2 H, =CH), 4.24 (br s, 2 H, OH), 1.70 (d, J = 6 Hz, 6 H, $=CCH_3$), 1.72–1.01 (m, 24 H, CH_2 and $OC(CH_3)_2$), 0.86 (m, 6 H, CH_3) ppm. The vinyl hydrogen for the minor product appears as a singlet at 6.40 ppm.

Di-*n*-butylbis[(*Z*)-2-(hydroxyethyl)-1-propenyl]stannane, di-*n*-butylbis[(*Z*)-1-methyl-4-hydroxy-1-butenyl]stannane, and di-*n*-dibutylbis[(*E*)-1-methyl-4-hydroxy-1-butenyl]-stannane were prepared as a 2:1:1 mixture, respectively, in 90% yield from 3-pentyn-1-ol: bp 93–101 °C (0.02 mm); IR (neat) 3370 (m, OH), 1620 (w, C=C) cm^{-1}; NMR of the major product 6.18 (q, J = 7 Hz, 2 H, =CH), 3.32 (m, 6 H, CH_2OH), 2.42 (m, 4 H, CH_2), 1.68 (d, J = 7 Hz, 6 H, CH_3), 1.72–1.01 (m, 12 H, CH_2), 0.86 (m, 6 H, CH_3); NMR of the minor products, *Z* isomer 6.04 (m, 2 H, =CH), 3.80 (m, 6 H, CH_2OH), 2.19 (m, 4 H, CH_2), 1.91 (s, 6 H, CH_3); *E* isomer 6.52 (m, 2 H, =CH), 3.80 (m, 6 H, CH_2OH), 2.19 (m, 4 H, CH_2), 1.91 (s, 6 H, CH_3) ppm.

Di-*n*-butylbis[(*Z*)-2-(hydroxypropyl)-1-propenyl]stannane and di-*n*-butylbis[(*Z*)-methyl-4-hydroxy-1-pentenyl]stannane were prepared as a 1:1 mixture from 4-hexyn-2-ol: 87% yield; bp 82–91 °C (0.02 mm); IR (neat) 3360 (m, OH), 1620 (m, C=C) cm^{-1}: NMR for di-*n*-butylbis[(*Z*)-2-(hydroxy-

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(14) K. Hayashi, J. Iyoda, and I. Shiihara, *J. Organomet. Chem.*, **10**, 81 (1967).

propyl)-1-propenyl]stannane 6.11 (q, J = 6 Hz, 2 H, =CH), 3.75 (m, 2 H, OCH), 3.27 (s, 2 H, OH), 2.14 (m, 4 H, CH_2), 1.72 (d, J = 6 Hz, 6 H, $=CCH_3$), 1.71–1.02 (m, 18 H, CH and $OCCH_3$), 0.86 (m, 6 H, CH_3) ppm; NMR for di-*n*-butylbis[(*Z*)-1-methyl-4-hydroxy-1-pentenyl]stannane 6.42 (m, 2 H, =CH), 3.75 (m, 2 H, OCH), 3.27 (s, 2 H, OH), 2.33 (m, 4 H, CH_2), 1.9 (s, 6 H, $=CCH_3$), 1.72–1.02 (m, 18 H, CH_2 and $OCCH_3$), 0.86 (m, 6 H, CH_3) ppm.

Reaction of Tributyltin Hydride with 2-Butyn-1-ol. A mixture of tributyltin hydride[14] (1.7 g, 5.8 mmol), 2-butyn-1-ol (1.1 g, 16 mmol), and azobis(isobutyronitrile) (27 mg) was heated at 85 °C under a N_2 atmosphere for 2 h. The reaction mixture was distilled to give (*Z*)-2-(tri-*n*-butylstannyl)-2-buten-1-ol (**13**): 1.6 g (4.3 mmol, 74%); bp 107–109 °C (0.2 mm); IR (neat) 3320 (m, OH), 1630 (w, C=C) cm^{-1}; NMR 6.28 (q, J = 7 Hz, 1 H, =CH), 4.08 (s, 2 H, OCH_2), 2.98 (s, 1 H, OH), 1.71 (d, J = 7 Hz, 3 H, $=CCH_3$), 1.60–1.08 (m, 18 H, CH_2), 0.86 (m, 9 H, CH_3) ppm. At 200 MHz the $^3J_{SnH}$ coupling constant was found to be 128 Hz.[9]

Anal. Calcd for $C_{16}H_{34}OSn$: C, 53.21; H, 9.49. Found: C, 53.03; H, 9.27.

The following compounds were prepared in a similar manner.

(*E*)- and (*Z*)-4-(Tri-*n*-butylstannyl)-2-methyl-3-buten-2-ol was prepared from 2-methyl-3-butyn-2-ol as a 1:4 mixture, respectively: 83% yield; bp 90–94 °C (0.1 mm); IR (neat) 3330 (w, OH), 1620 (m, C=C) cm^{-1}; ^1H NMR (200 MHz) 6.57 (d, J = 13.1 Hz, =CH of *Z* isomer), 6.12 (s, 2 H, HC=CH of *E* isomer), 5.80 (d, J = 13.1 Hz, =CHSn of *Z* isomer), 1.73–1.15 (m, 25 H), 1.00–0.80 (m, 9 H, CH_3) ppm. For the *Z* isomer $^2J_{^{117}SnH}$ (gem) = 66.3 Hz, $^2J_{^{119}SnH}$ (gem) = 69.3 Hz, $^3J_{^{117}SnH}$ (trans) = 138 Hz, and $^3J_{^{119}SnH}$ (trans) = 145.2 Hz.

(*Z*)-2-(Tri-*n*-butylstannyl)-2-octen-1-ol was prepared from 3-octyn-1-ol: 87% yield; bp 112–115 °C (0.02 mm); IR (neat) 3340 (m, OH), 1620 (w, C=C) cm^{-1}; NMR 6.40 (t, J = 7 Hz, 1 H, =CH), 4.12 (br s, 3 H, CH_2OH), 2.36–0.80 (m, 38 H) ppm. At 200 MHz the $^3J_{SnH}$ coupling constant was found to be 131 Hz.[9]

Anal. Calcd for $C_{20}H_{42}OSn$: C, 57.57; H, 10.15. Found: C, 57.42; H, 9.92.

(*E*)- and (*Z*)-1-(Tri-*n*-butylstannyl)-1-octen-3-ol was prepared as a 3:1 mixture, respectively, from 1-octyn-3-ol: 62% yield; bp 142–148 °C (0.2 mm); IR (neat) 3320 (m, OH), 1605 (m, C=C); NMR 6.78–5.72 (m, 2 H, cis and trans =CH), 4.27–3.90 (m, 1 H, OCH), 2.30 (br s, 1 H, OH), 1.80–0.79 (m, 38 H). Confirmation of the stereochemical chemical assignment was confirmed by conversion to the vinyl iodide.

(*Z*)-2-Iodo-2-buten-1-ol (19a). To a cooled (4 °C) solution of **12** (3.8 g, 1.2 mmol) in 20 mL of CCl_4 was added 0.76 g (3.0 mmol) of iodine. The solution was stirred for 10 min at 4 °C, decolorized by the addition of excess 10% aqueous sodium bisulfite, and extracted twice with 25 mL of ether. The ether solution was dried (Na_2SO_4) and concentrated, and the residue was purified by filtration through a short column of silica gel to give **19a**: 0.58 g (2.9 mmol, 98%); IR (neat) 3330 (m, OH), 1650 (w, C=C) cm^{-1}; ^1H NMR 5.98 (q, J = 7 Hz, 1 H, =CH), 4.21 (s, 2 H, CH_2), 2.92 (br s, 1 H, OH), 1.70 (d, J = 7 Hz, 3 H, CH_3); ^{13}C NMR 131.0 (C-2), 109.6 (C-3), 71.4 (C-1), 21.4 (C-4) ppm.

Anal. Calcd for C_4H_7IO: C, 24.26; H, 3.56. Found: C, 24.38; H, 3.81.

Treatment of **13** with excess iodine in a similar fashion afforded **19a** in 96% yield.

(*Z*)-1-Iodo-1-octen-3-ol (16) was prepared in a similar manner from **14**: 94% yield; IR (neat) 3340 (m, OH), 1620 (m, C=C) cm^{-1}; ^1H NMR 6.39–6.13 (m, 2 H, HC=CH), 4.45–4.20 (m, 1 H, OCH), 2.66 (br s, 1 H, OH), 1.70–1.08 (m, 8 H, CH_2), 0.85 (t, J = 7 Hz, CH_3) ppm; ^{13}C NMR 143.7 (C-2), 82.0 (C-1), 74.4 (C-3), 35.9, 31.8, 24.7, 22.6, 14.1 (C-8) ppm.

Treatment of the 3:1 mixture of (*Z*)- and (*E*)-1-(tri-*n*-butylstannyl)-1-octen-3-ol with iodine afforded a 3:1 mixture of (*Z*)- and (*E*)-1-iodo-1-octen-3-ol: 92% yield; ^1H NMR of the *E* isomer 6.64 (dd, J_1 = 14 Hz J_2 = 7 Hz, 1 H, =CH), 6.35 (d, J = 14 Hz, 1 H, =CHI), 4.06 (m, 1 H, OCH), 3.12 (br s, 1 H, OH), 1.67–1.03 (m, 8 H, CH_2), 0.85 (t, J = 7 Hz, CH_3) ppm; ^{13}C NMR 148.8 (C-2), 77.0 (C-1), 74.5 (C-3), 36.5, 31.7, 24.9, 22.6, 14.1 (C-8) ppm.

(*Z*)-2-Iodo-2-octen-1-ol was prepared in a similar manner from (*Z*)-2-(tri-*n*-butylstannyl)-2-octen-1-ol: 93% yield; IR (neat) 3330 (m, OH), 1640 (m, C=C) cm^{-1}; ^1H NMR 6.08 (t, J = 7 Hz, =CH), 4.31 (s, 2 H, OCH_2), 2.90 (br s, 1 H, OH), 2.37–2.08 (m, 2 H, $=CH_2$), 1.72–1.24 (m, 6 H, CH_2), 0.91 (t, J = 7 Hz, 3 H, CH_3) ppm; ^{13}C NMR 135.9 (C-3), 108.0 (C-2), 71.4 (C-1), 35.6, 31.4, 27.9, 22.5, 14.0 (C-8) ppm.

Anal. Calcd for $C_8H_{15}IO$: C, 37.81; H, 5.95. Found: C, 37.68; H, 6.01.

(*Z*)-1-Deuterio-1-octen-3-ol (15). A solution of 2.51 g (7.0 mmol) of **14** in 50 mL of dry THF was cooled to −78 °C, and 9 mL (14.4 mmol) of 1.6 M *n*-BuLi was added. The solution was stirred 5 min at −78 °C and 30 min at −20 °C, and then 500 μL of D_2O was added. The solvent was evaporated, and the reaction mixture was purified by filtration through a short column of silica gel. Petroleum ether rapidly eluted the tetra-*n*-butyltin byproduct, and elution with petroleum ether–ethyl acetate (2:1) afforded **15**: 0.84 g (6.5 mmol, 93%); IR (neat) 3350 (OH), 3050, 3010 (w, =CH), 2245 (=CD) cm^{-1}; ^1H NMR 5.97 (1 H, =CH), 5.14 (dd, J_1 = 10.8 Hz, J_2 = 1.3 Hz, 1 H, =CHD), 3.13 (apparent q, J = 6 Hz, 1 H, OCH), 2.79 (br s, 1 H, OH), 1.77–1.08 (m, 8 H, CH_2), 0.83 (t, J = 7 Hz, CH_3) ppm; ^{13}C NMR 141.4 (C-2), 115.8, 114.2, 112.6 (C-1), 73.3 (C-3), 37.1, 31.9, 25.1, 22.7, 14.1 (C-8) ppm.

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Registry No. 6b, 41234-98-4; **6d**, 41235-00-1; (*E*)-**8**, 79970-50-6; (*Z*)-**8**, 79970-51-7; (*E*)-**12**, 79970-52-8; (*Z*)-**12**, 79970-53-9; (*E*)-**13**, 79970-54-0; (*Z*)-**13**, 79970-55-1; **14**, 79970-56-2; (*Z*)-**15**, 80008-81-7; (*Z*)-**16**, 39764-90-4; **17a**, 764-01-2; **17b**, 20739-58-6; (*Z*)-**18b**, 79970-57-3; (*Z*)-**19a**, 79970-58-4; (*Z*)-**19b**, 79970-59-5; dibutyltin dihydride, 1002-53-5; dubutyltin oxide, 818-08-6; 2-methyl-3-butyn-2-ol, 115-19-5; 1-octyn-3-ol, 818-72-4; 3-butyn-2-ol, 2028-63-9; 3-butyn-1-ol, 927-74-2; dibutylbis[(*E*)-4-hydroxy-1-butenyl]stannane, 79970-60-8; dibutylbis[(*Z*)-4-hydroxy-1-butenyl]stannane, 79970-61-9; 4-pentyn-2-ol, 2117-11-5; dibutylbis[4-hydroxy-1-pentenyl]stannane, 79970-62-0; 2-methyl-4-pentyn-2-ol, 590-37-4; dibutylbis[(*E*)-4-hydroxy-4-methyl-1-pentenyl]stannane, 79970-63-1; dibutylbis[(*Z*)-4-hydroxy-4-methyl-1-pentenyl]stannane, 79970-64-2; 4-pentyn-1-ol, 5390-04-5; dibutylbis[(*E*)-5-hydroxy-1-pentenyl]stannane, 79970-65-3; dibutylbis[(*Z*)-5-hydroxy-1-pentenyl]stannane, 79970-66-4; 4,4-dimethyl-6-heptyn-2-ol, 79970-67-5; dibutylbis[4,4-dimethyl-6-hydroxy-1-heptenyl]stannane, 79970-68-6; 3-pentyn-2-ol, 27301-54-8; dibutylbis[1-(1-hydroxyethyl)-1-propenyl]stannane, 79970-69-7; 2-methyl-3-pentyn-2-ol, 590-38-5; dibutylbis[(*E*)-1-(1-methyl-1-hydroxyethyl)-1-propenyl]stannane, 79970-70-0; dibutylbis[(*Z*)-1-(1-methyl-1-hydroxyethyl)-1-propenyl]stannane, 79970-71-1; dibutylbis[(*E*)-1,3-dimethyl-3-hydroxy-1-butenyl]stannane, 79970-72-2; dibutylbis[(*Z*)-1,3-dimethyl-3-hydroxy-1-butenyl]stannane, 79982-93-7; 3-pentyn-1-ol, 10229-10-4; dibutylbis[(*Z*)-2-(hydroxyethyl)-1-propenyl]stannane, 79970-73-3; dibutylbis[(*E*)-1-methyl-4-hydroxy-1-butenyl]stannane, 79970-74-4; dibutylbis[(*Z*)-1-methyl-4-hydroxy-1-butenyl]stannane, 79970-75-5; 4-hexyn-2-ol, 19780-83-7; dibutylbis[2-(hydroxypropyl)-1-propenyl]stannane, 79970-76-6; dibutylbis[1-methyl-4-hydroxy-1-pentenyl]stannane, 79970-77-7; tributyltin hydride, 688-73-3; (*E*)-4-(tributylstannyl)-2-methyl-3-buten-2-ol, 79970-78-8; (*Z*)-4-(tributylstannyl)-2-methyl-3-buten-2-ol, 79970-79-9; (*E*)-2-(tributylstannyl)-2-octen-1-ol, 79970-80-2; (*E*)-1-(tributylstannyl)-1-octen-3-ol, 79970-81-3; (*Z*)-1-(tributylstannyl)-1-octen-3-ol, 79970-81-3; (*E*)-1-iodo-1-octen-3-ol, 39178-65-9.