termined by direct methods. Refinement of 105 parameters (1019 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.182. We believe this relatively high value is at least partly attributable to the high degree of disorder in these crystals.

Compound $2{\cdot}CH_3OH$ crystallized from $CH_3OH/CHCl_3$ as colorless parallelepipeds in the rhombohedral system $R\bar{3}$. Unit cell dimensions are as follows: a = 17.090 (2) Å, γ = 49.33 (1)°, V = 2637 Å^3 (rhombohedral cell), a = 14.262 (2) Å, c = 44.914 (6) Å, V = 7912 Å^3 (hexagonal cell), Z = 6 ($^1/_3$ molecule in the asymmetric unit). The crystal was examined on a Syntex $P\bar{1}$ diffractometer, CuKα radiation, at 25 °C. The structure was determined by direct methods. Refinement of 118 parameters (1233 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.124.

Complete crystallographic details are provided in the supplementary material.

Registry No. 1, 137334-67-9; $1{\cdot}N_2$, 137334-76-0; $1{\cdot}O_2$, 137334-77-1; $1{\cdot}H_2O$, 137334-78-2; $1{\cdot}CO_2$, 137362-96-0; 1·MeOH, 137334-79-3; 2, 137334-68-0; $2{\cdot}N_2$, 137334-80-6; $2{\cdot}O_2$, 137334-81-7; 2·MeCN, 137334-82-8; 2·EtOH, 137334-83-9; 3, 51760-22-6; 4, 137334-69-1; 5, 137334-70-4; 6, 137432-38-3; 7, 137334-71-5; 8, 137334-72-6; 9, 137334-73-7; 10, 137334-74-8; 11, 137334-75-9; $TsNH_2$, 70-55-3; BCl_3, 10294-34-5; sodium anthracenide, 12261-48-2; *N*-formylmorpholine, 4394-85-8.

Supplementary Material Available: Figures A, B, and C as ^{1}H NMR spectra; listings of crystallographic experimental conditions, Figures 1s, 2s, and 3s, of the three host molecules characterized by X-ray diffraction studies, positional and thermal parameters, and interatomic distances and angles for $1{\cdot}2CH_3CN$, $2{\cdot}CH_3OH$, and $2{\cdot}CH_2Cl_2$ (33 pages). Ordering information is given on any current masthead page.

Ring-Opening Reactions of α-Stannyl Epoxides with Metal Hydrides and Organocuprates

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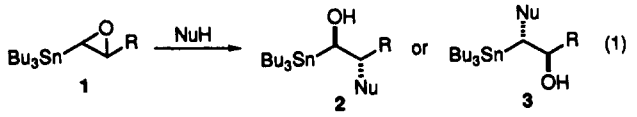
α-Epoxyorganostannanes are attacked by metal hydride reagents (DIBAL-H, $LiAlH_4$, REDAL) and Me_2CuLi at the carbon atom proximal to the tin atom and directly at the tin atom. For example, tributyl(epoxyethyl)stannane (5) reacts with DIBAL-H to give a mixture of 2-(tributylstannyl)ethanol (7) and tributyltin hydride. Reaction of 5 with Me_2CuLi affords predominantly 2-(tributylstannyl)propan-1-ol (8) and some Bu_3SnMe. Similarly, 3-(tributylstannyl)oxiranemethanol (10) reacts with REDAL and Me_2CuLi to provide products of nucleophilic attack at C-3. Cleavage occurs with inversion of stereochemistry. Tributyl(3,4-epoxybutyl)stannane (21) reacts with $LiAlH_4$ to give secondary alcohol 22 as the sole product.

While the nucleophilic opening of α-epoxyorganosilanes has been reasonably well-documented,[1] the literature contains no detailed reports of such reactions with the corresponding stannanes. In fact, α-epoxyorganostannanes do not seem to have been the subject of much attention.[2] In connection with our work with α-alkoxyorganostannanes,[3] it was of interest to study the regioselectivity of the nucleophilic ring opening of α-epoxyorganostannanes. In particular, we wished to ascertain whether ring opening of 1 would afford α-hydroxystannanes 2 (which could be converted into synthetically useful α-alkoxyorganostannanes) or β-hydroxystannanes 3 (eq 1). Our findings in this area are reported below.

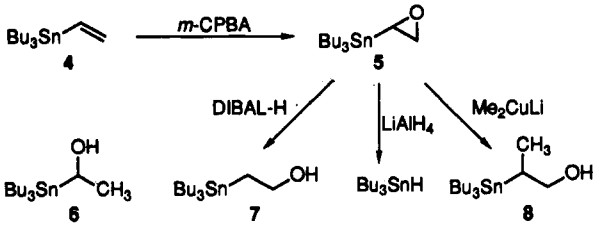


Results and Discussion

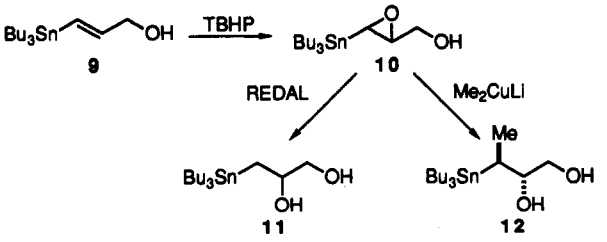
The epoxide derived from tributylvinylstannane (4) has been prepared previously in low yield (12%) by treatment of 4 with *m*-CPBA in benzene.[4] A simple change in solvent dramatically improved the yield of 5: When vinylstannane 4 was allowed to react with *m*-CPBA in $CHCl_3$, epoxide 5 was isolated in reasonable yield (67%) after column chromatography.

There appear to be no reports of studies on nucleophilic openings of 5.[5] When 5 was treated with DIBAL-H at low

Scheme I



Scheme II



(1) (a) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: New York, 1988; Chapter 4. (b) Eisch, J. J.; Trainor, J. T. *J. Org. Chem.* **1963**, *28*, 487. (c) Eisch, J. J.; Trainor, J. T. *J. Org. Chem.* **1963**, *28*, 2870. (d) Hudrlik, P. F.; Peterson, D.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2263. (e) Schaumann, E.; Kirsching, A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 419. (f) Jankowski, P.; Marczak, S.; Masnyk, M.; Wicha, J. *J. Chem. Soc., Chem. Commun.* **1991**, 297.

(2) (a) Kitano, Y.; Matsumoto, T.; Okamoto, S.; Shimazaki, T.; Kobayashi, Y.; Sato, F. *Chem. Lett.* **1987**, 1523. (b) Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1988**, *341*, 293. (c) Lohse, P.; Loner, H.; Acklin, P.; Sternfeld, F.; Pfaltz, A. *Tetrahedron Lett.* **1991**, *32*, 615.

(3) Chan, P. C.-M.; Chong, J. M. *Tetrahedron Lett.* **1990**, *31*, 1985 and references cited therein.

(4) Ayrey, G.; Parsonage, J. R.; Poller, R. C. *J. Organomet. Chem.* **1973**, *56*, 193.

(5) Reaction of 4 with a magnesio cuprate was reported in footnote 11 of: Matsubara, S.; Mitani, M.; Utimoto, K. *Tetrahedron Lett.* **1987**, *28*, 5857.

0022-3263/92/1957-0046$03.00/0

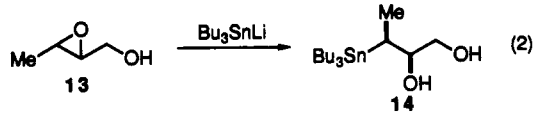
temperature (Et_2O, −78 °C), a single alcohol was produced (32% yield) along with substantial amounts of tributyltin hydride (52% yield) (Scheme I). The ^1H NMR spectrum of the alcohol showed unequivocally that it was 2-(tributylstannyl)ethanol (7) and not the regioisomeric 1-(tributylstannyl)ethanol (6). Specifically, an AA'XX' pattern (with the AA' portion at δ 3.81) was observed for the isolated alcohol while alcohol 6 would be expected to display a quartet (δ 4.1, 1 H). With other reducing agents ($LiAlH_4$, REDAL) the major product was Bu_3SnH. In no cases was the alcohol 6 observed. Similarly, reaction of 5 with Me_2CuLi (Et_2O, −20 °C) afforded 8 as the only alcohol (59% isolated yield) along with a small amount of Bu_3SnMe (7% isolated yield).

We also prepared the 3-tributylstannyl alcohol 10 by epoxidation (*tert*-butyl hydroperoxide, V^{5+}) of the allylic alcohol 9. Previous work with 3-alkyl-2,3-epoxy alcohols had shown that they may be regioselectively opened at C-2 with REDAL[6] or cuprate reagents[7] to afford 1,3-diols. With epoxide 10 (Scheme II), only the product of C-3 opening was observed with both REDAL (53% isolated yield of 11 along with 28% yield of Bu_3SnH) and Me_2CuLi (61% isolated yield of 12 along with 21% yield of Bu_3SnMe).

The above results indicate that the tributylstannyl group exerts a considerable influence on the reactions of α-epoxyorganostannanes with nucleophiles: there is a strong tendency for nucleophilic attack at the carbon α to the tin atom. Previous work with α-epoxysilanes[1b,c] had shown that these compounds react with hydride reagents and cuprates predominantly at the α-carbon. Varying amounts of silicon hydrides were also detected. Thus, the stannyl analogues appear to exhibit very similar behavior. In the silicon cases, these results were explained by inductive stabilization (of the transition state during nucleophilic opening) by silicon and by the participation of silicon d orbitals. Similar phenomena may be operating in the reactions of epoxystannanes.

The exclusive formation of Bu_3SnH from the reaction of $LiAlH_4$ with epoxide 4 contrasts with the results of similar reactions performed with epoxysilanes, in which, in addition to reaction at the α-carbon, only small amounts of silicon hydrides were observed.[1c] This behavior may be attributable to the weaker and more polar Sn–C bond versus the Si–C bond (mean bond dissociation energy of 50–52 kcal/mol for Sn–CH_3 versus 70 kcal/mol for Si–CH_3).[8]

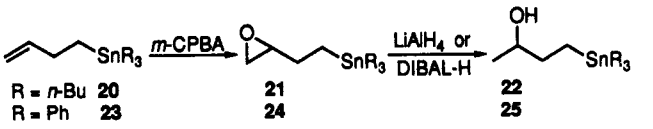
As a single diastereomer (diol 12) was isolated from the reaction of epoxide 10 with Me_2CuLi, it was of interest to establish the relative configurations of the diol and thus demonstrate whether reaction at the α-carbon occurred with inversion. Thus, epoxide 13 was treated with tributyltinlithium, a reagent expected to open the epoxide with inversion of stereochemistry (eq 2).[9,10] The 1,2-diol



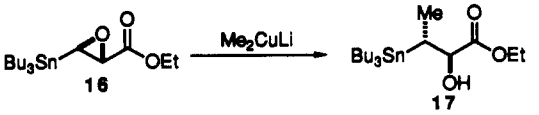
13 14 (2)

14 isolated from this reaction (along with the regioisomeric 1,3-diol) had spectroscopic properties that were clearly different from that of diol 12. Since compound 14 must possess the relative stereochemistry shown, diol 12 must be the diastereomer shown in Scheme II, and hence opening of epoxide 10 with Me_2CuLi must have occurred with inversion of configuration.

Scheme III

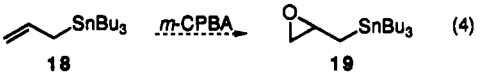


As an additional test of the activating ability of a tributylstannyl group, we examined the nucleophilic opening of glycidic ester 16, readily prepared by epoxidation of ethyl (*E*)-3-(tributylstannyl)-2-propenoate (15). It has been well-documented that 3-substituted glycidic esters typically react with organocuprates exclusively at C-2 (presumably due to the α-activating ability of the ester group) to afford β-hydroxy esters.[11] In stark contrast to these other reactions, only a single regioisomer was isolated upon reaction of epoxide 16 with Me_2CuLi (eq 3): α-hydroxy ester 17. Thus, it seems that the tributylstannyl group completely overrides the normally very powerful effect of the carbethoxy group in this reaction. As with the other α-epoxyorganostannanes examined, the regiochemistry is completely dictated by the tributylstannyl group such that the β-hydroxystannane is the exclusive product of epoxide opening.



16 17 (3)

Attempts to examine the reaction of nucleophiles with β-stannyl epoxides such as tributyl(2,3-epoxypropyl)stannane (19) were thwarted by our inability to prepare such compounds. Treatment of allyltributylstannane (18) with *m*-CPBA did not provide epoxide 19 (eq 4).[12] The elusive



18 19 (4)

stannane 19 also could not be isolated from reactions of epibromohydrin with tributylstannylcopper reagents.[13] A literature search (CAS substructure) revealed that there are no known examples of β-trialkylstannyl epoxides, suggesting that such compounds may not be readily isolated.

A γ-tributylstannyl epoxide tributyl(3,4-epoxybutyl)-stannane (21) has been reported to react with $LiAlH_4$ to afford quantitatively tributyl(4-hydroxybutyl)stannane while treatment of the corresponding triphenylstannane 24 with $LiAlH_4$ afforded only recovered starting material.[4] Neither of these results is expected or readily explained. In fact, we found that reaction of 21 with $LiAlH_4$ (Et_2O, 0 °C) does provide a single alcohol (86%), but that alcohol is the (expected) 3-hydroxybutylstannane 22 (Scheme III). There was no evidence for tributyl(4-hydroxybutyl)stannane.[14] The identity of alcohol 22 was unequivocally

(6) Viti, S. M. *Tetrahedron Lett.* **1982**, *23*, 4541.
(7) (a) Nagaoka, H.; Kishi, Y. *Tetrahedron* **1981**, *37*, 3873. (b) Chong, J. M.; Cyr, D. R.; Mar, E. K. *Tetrahedron Lett.* **1987**, *28*, 5009.
(8) Omae, I. *Organotin Chemistry*; Elsevier: New York, 1989; p 19.
(9) San Filippo, J. Jr.; Silbermann, J. *J. Am. Chem. Soc.* **1981**, *103*, 5588.
(10) Davis, D. D.; Gray, C. E. *J. Org. Chem.* **1970**, 35, 1303.
(11) (a) Johnson, C. R.; Herr, R. W.; Wieland, D. M. *J. Org. Chem.* **1973**, *38*, 4263. (b) Mulzer, J.; Lammer, O. *Chem. Ber.* **1986**, *119*, 2178. (c) Chong, J. M. *Tetrahedron* **1989**, *45*, 623.
(12) It has previously been reported that no epoxy derivative could be isolated from the reaction of allyltributylstannane with perbenzoic acid; the principal product was tributylstannyl benzoate.[4]
(13) Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H.; Reuter, D. C. *Tetrahedron Lett.* **1989**, *30*, 2065.
(14) The ^1H NMR evidence previously reported[4] for this compound consisted of a single resonance at δ 3.63 attributed to the hydroxyl proton.

established by IR, ^1H and ^{13}C NMR spectroscopy, and mass spectrometry. ^1H NMR spectroscopy was especially useful in determining the regiochemistry of the reduction: the signal for a single carbinol proton was observed at δ 3.65 along with a methyl doublet at δ 1.18. The corresponding primary alcohol would not be expected to exhibit such signals.

Reaction of the triphenylstannane **24** with $LiAlH_4$ also did not proceed as previously reported but rather afforded a mixture of the expected (3-hydroxybutyl)stannane **25** (46%) along with the unexpected butenylstannane **23** (13%). It is not clear how this deoxygenation occurs. However, reduction of **24** with DIBAL-H (Et_2O, 0 °C) afforded cleanly alcohol **25** (75%). Thus, epoxides **21** and **24** are reduced at the less hindered primary position as observed for simple (alkyl) epoxides; the tin moiety does not play a major role in controlling the regiochemistry of reduction as it does with α-epoxystannanes.

Experimental Section

General Methods. Common reagents and solvents were purified by procedures noted previously, and spectral data were recorded using common analytical instruments.[3] For ^{13}C NMR data, coupling constants in parentheses refer to the average of the couplings to ^{117}Sn and ^{119}Sn.

Tributyl(epoxyethyl)stannane (5). To a solution of tributylvinylstannane (**4**, 2.27 g, 7.17 mmol) in 15 mL of $CHCl_3$ at rt was added 1.86 g (8.64 mmol) of 80% *m*-CPBA. After 90 min, the reaction mixture was filtered through a cotton plug, and the precipitate (*m*-chlorobenzoic acid) was washed with petroleum ether. The filtrate was concentrated in vacuo, and the residual material was chromatographed on silica gel (80 g, hexane–ether (50:1)) to afford 1.60 g (67%) of **5** as a colorless oil: IR (neat) 3023, 2917, 1462, 1279, 1231, 1072, 868 cm^{-1}; ^1H NMR (250 MHz, C_6D_6) δ 2.77 (1 H, dd, J = 5.4, 5.9 Hz), 2.59 (1 H, dd, J = 4.1, 5.4 Hz), 2.46 (1 H, dd, J = 4.1, 5.9 Hz), 1.7–1.2 (12 H, m), 0.91 (15 H, t, J = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 44.85 (380 Hz), 44.40 (4 Hz), 28.89 (21 Hz), 27.17 (52 Hz), 13.50, 8.47 (330 Hz); MS m/e 291 ($M^+ - C_2H_3O$, 26) 277 (24), 235 (34), 178 (29), 177 (100), 121 (43). Anal. Calcd for $C_{14}H_{30}OSn$: C, 50.48; H, 9.08. Found: C, 50.61; H, 9.21.

Reaction of Epoxide 5 with DIBAL-H: 2-(Tributylstannyl)ethanol (7). To a solution of epoxide **5** (204 mg, 0.61 mmol) in 5 mL of Et_2O at −78 °C was added a solution of diisobutylaluminum hydride (DIBAL-H, 1.0 M in hexane, 0.62 mL). The reaction mixture was stirred at −78 °C for 90 min, then was allowed to warm to rt. After a further 1 h, the reaction was quenched with H_2O and diluted with ether. The organic layer was washed with 0.1 N HCl, dried, and concentrated to afford a yellow oil. This oil was chromatographed on silica gel (2 g). Initial elution with petroleum ether–ether (20:1) provided 104 mg (58%) of Bu_3SnH. Further elution with petroleum ether–ether (4:1) provided 66 mg (32%) of alcohol **7**[15] as a colorless oil: IR (neat) 3310 (br), 2955, 2924, 1461, 1375, 1072, 1034 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 3.81 (2 H, AA′ of an AA′XX′ system), 1.7–1.1 (14 H, m), 1.0–0.8 (15 H, m); ^{13}C NMR (63 MHz, $CDCl_3$) δ 62.10, 29.19 (20 Hz), 27.32 (59 Hz), 14.31 (254 Hz), 13.66, 8.94 (319 Hz); MS m/e 291 ($M^+ - C_3H_7O_2$, 93), 253 (85), 235 (19), 177 (100), 137 (29), 121 (42). Anal. Calcd for $C_{14}H_{32}OSn$: C, 50.19; H 9.62. Found: C, 49.93; H, 9.79.

Reaction of Epoxide 5 with Me_2CuLi: 2-(Tributylstannyl)-1-propanol (8). To a cold (−20 °C), stirred solution of 0.47 mmol of Me_2CuLi (prepared from 96.7 mg of $CuBr{\cdot}SMe_2$ and 0.62 mL of a 1.4 M solution of MeLi in ether) in ether was added 106.9 mg (0.32 mmol) of epoxide **5**. The reaction mixture was stirred at −20 °C for 1 h, quenched with basic saturated NH_4Cl, and allowed to warm to room temperature. The ether layer was washed with basic saturated NH_4Cl, dried ($MgSO_4$), and concentrated to afford a colorless oil. Chromatographic separation of this oil on silica gel (6 g) using petroleum ether–ether (10:1) as eluent provided, in order of elution, 6.8 mg (7%) of Bu_3SnMe, 22.3 mg (21%) of starting material **5**, and 66.4 mg (59%) of alcohol **8**. This latter material exhibited: IR (neat) 3329 (br), 2955, 2923, 1461, 1072, 993, 865 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 3.78 (2 H, AB of an ABX system, J_{AB} = 10.5 Hz, J_{AX} = 5.2 Hz, J_{BX} = 9.1 Hz, $\Delta\delta$ = 18.1 Hz), 1.7–1.2 (13 H, m), 1.24 (3 H, d, J = 7.2 Hz), 1.0–0.8 (15 H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 68.20, 29.28 (20 Hz), 27.49 (54 Hz), 23.86 (301 Hz), 15.08 (15 Hz), 13.65, 8.29 (304 Hz). MS m/e 291 ($M^+ - C_3H_7O$, 12), 251 (100), 177 (41), 137 (35), 121 (19). Anal. Calcd for $C_{15}H_{34}OSn$: C, 51.61; H 9.82. Found: C, 51.78; H, 9.91.

***trans*-3-(Tributylstannyl)oxiranemethanol (10).** To a cold (0 °C), stirred solution of allylic alcohol **9**[16] (974 mg, 2.81 mmol) in 25 mL of CH_2Cl_2 was added 50 mg of $V(O)(acac)_2$ followed by *tert*-butyl hydroperoxide (1.10 mL of a 5.6 M solution in isooctane). The deep red solution was allowed to warm to rt. At 1 h intervals, an additional 5 mg of $V(O)(acac)_2$ was added. After a total of 3 h, the reaction was quenched with H_2O and diluted with ether. The organic layer was washed with H_2O (3 × 25 mL), dried ($MgSO_4$), and concentrated. Chromatography of the residual oil on silica gel (60 g) using petroleum ether–ether (2:1) as eluent provided 844 mg (83%) of epoxide **10** as a colorless oil. This material could be stored in a freezer for months without decomposition, but degraded within a few days at rt: IR (neat) 3415 (br), 2925, 1461, 1051, 862 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 3.98 (1 H, dd, J = 2.3, 12.4 Hz), 3.51 (1 H, dd, J = 6.2, 12.4 Hz), 3.08 (1 H, ddd, J = 2.3, 3.9, 6.2 Hz), 2.69 (1 H, d, J = 3.9 Hz, J_{Sn-H} = 92 Hz), 1.6–1.2 (12 H, m), 1.0–0.8 (15 H, m); ^{13}C NMR (63 MHz, $CDCl_3$) δ 64.31, 56.03, 49.16 (356 Hz), 28.91 (21 Hz), 27.18 (53 Hz), 13.54, 8.76 (332 Hz); MS m/e 291 ($M^+ - C_3H_5O_2$, 85), 251 (20), 235 (38), 177 (100), 137 (27), 121 (33). Anal. Calcd for $C_{15}H_{32}O_2Sn$: C, 49.62; H, 8.88. Found: C, 49.77; H, 8.92.

Reaction of Epoxide 10 with REDAL: 3-(Tributylstannyl)-1,2-propanediol (11). To a solution of the epoxy alcohol **10** (150.8 mg, 0.415 mmol) in 5 mL of dry CH_2Cl_2 at −78 °C was added REDAL (0.25 mL of a 3.6 M solution in toluene, 0.90 mmol). The reaction mixture was stirred at −78 °C for 2 h then at 0 °C for 30 min. A saturated solution of potassium sodium tartrate (Rochelle's salt) was added to quench the reaction, and the reaction mixture was allowed to warm to rt. Dilution with ether followed by washing of the organic layer with H_2O and brine, drying ($MgSO_4$), and concentration afforded a colorless oil. Chromatography of this oil on silica gel (10 g) using petroleum ether–ether (1:1) as eluent provided 33.8 mg (28%) of Bu_3SnH and 81.3 mg (53%) of diol **11**: IR (neat) 3371 (br), 2921, 1461, 1070, 863 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 3.93 (1 H, m), 3.61 (1 H, dd, J = 3.0, 10.8 Hz), 3.31 (1 H, dd, J = 8.1, 10.8 Hz), 1.6–1.2 (12 H, m), 1.0–0.8 (17 H, m); ^{13}C NMR (63 Mz, $CDCl_3$) δ 71.77 (14 Hz), 69.41 (36 Hz), 29.18 (20 Hz), 27.34 (54 Hz), 14.30, 13.63, 9.67 (321 Hz); MS m/e 291 ($M^+ - C_3H_7O_2$, 93), 253 (85), 235 (19), 177 (100), 121 (42). Anal. Calcd for $C_{15}H_{34}O_2Sn$: C, 49.34; H, 9.39; Found: C, 49.40; H 9.17.

Reaction of Epoxide 10 with Me_2CuLi: (2*R,3*R**)-3-(Tributylstannyl)-1,2-butanediol (12).** To a solution of 0.83 mmol of Me_2CuLi (prepared from 170 mg of $CuBr{\cdot}SMe_2$ and 1.10 mL of a 1.5 M solution of MeLi in ether) in 5 mL of ether at −78 °C was added 133.4 mg (0.37 mmol) of epoxy alcohol **10**. The reaction mixture was stirred at −78 °C for 30 min and at 0 °C for 1 h. Standard aqueous workup with basic aqueous NH_4Cl and ether afforded a colorless oil which consisted of two components. Chromatography on silica gel (10 g) using petroleum ether–ether (2:1) as eluent separated the mixture into 23.1 mg (21%) of Bu_3SnMe and 84.6 mg (61%) of diol **12**: IR (neat) 3378 (br), 2923, 1459, 1069, 1002, 860 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 3.72 (2 H, m), 3.41 (1 H, dd J = 8.2, 10.8 Hz), 1.6–1.3 (13 H, m), 1.20 (3 H, d, J = 7.5 Hz), 1.0–0.8 (15 H, m); ^{13}C NMR (63 MHz, $CDCl_3$) δ 77.40 (19 Hz), 66.58 (34 Hz), 29.30 (20 Hz), 27.53 (56 Hz), 24.47 (317 Hz), 15.02 (16 Hz), 13.64, 9.38 (308 Hz); MS m/e 305 (99), 251 (63), 235 (58), 177 (100), 137 (43), 121 (40). Anal. Calcd for $C_{16}H_{36}O_2Sn$: C, 50.69; H, 9.57. Found: C, 50.50; H, 9.44.

Reaction of Epoxide 13 with Bu_3SnLi: (2*R,3*S**)-3-(Tributylstannyl)-1,2-butanediol (14).** To a solution of Bu_3SnLi[17] (2.48 mmol) in 10 mL of THF at −78 °C was added

(15) Lahournère, J.-C.; Valade, J. *J. Organomet. Chem.* **1971**, *33*, C4.

(16) (a) Jung, M. E.; Light, L. A. *Tetrahedron Lett.* **1982**, *23*, 3851. (b) Musachio, J. L.; Lever, J. R. *Tetrahedron Lett.* **1989**, *30*, 3613.

(17) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481.

epoxide **13**[18] (108 mg, 1.22 mmol), and the reaction mixture was allowed to warm to rt overnight. Standard aqueous workup afforded a mixture of diols; the less polar 1,2-diol **14** (56 mg, 12%) was separated from the 1,3-diol (265 mg, 57%) by flash chromatography on silica gel (20 g) using petroleum ether–ether (1:1) as eluent. Diol **14** exhibited: IR (neat) 3371 (br), 1461, 1375, 1057, 1000, 874 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.83 (1 H, ddd, J = 8.5, 7.2, 3.1 Hz), 3.64 (1 H, dd, J = 10.8, 3.1 Hz), 3.41 (1 H, dd, J = 10.8, 8.5 Hz), 1.60–1.25 (13 H, m), 1.22 (3 H, d, J = 7.2 Hz), 1.00–0.80 (15 H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 76.60, 66.97 (25 Hz), 29.23 (20 Hz), 27.49 (55 Hz), 23.47, 13.75, 13.64, 8.98 (306 Hz); MS m/e 305 (100), 251 (69), 177 (52), 137 (18). Anal. Calcd for $C_{16}H_{36}O_2Sn$: C, 50.69; H, 9.57. Found: C, 50.45; H, 9.40.

Ethyl *trans*-3-(Tributylstannyl)-2,3-epoxypropanoate (16). A mixture of ethyl (*E*)-3-(tributylstannyl)propenoate (**15**)[19] (974 mg, 2.50 mmol) and *m*-CPBA (1.08 g of 80% pure material, 6.26 mmol) in 20 mL of CH_2Cl_2 was stirred at rt for 48 h. The reaction mixture was diluted with ether and washed with saturated $NaHCO_3$. The organic layer was dried ($MgSO_4$) and concentrated to afford a colorless oil. Chromatography of this oil on silica gel (35 g) using petroleum ether–ether (20:1) as eluent provided 284 mg (29%) of starting ester **15** followed by 532 mg (53%) of epoxy ester **16** as a colorless oil: IR (neat) 1748, 1727, 1282, 1224, 1191, 1067, 1029 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.24 (2 H, AB of an ABX_3 system, J_{AB} = 10.8 Hz, J_{AX} = J_{AB} = 7.1 Hz, Δδ = 5.0 Hz), 3.29 (1 H, d, J = 3.5 Hz, J_{Sn-H} = 12 Hz), 2.87 (1 H, d, J = 3.5 Hz, J_{Sn-H} = 92 Hz), 1.6–1.3 (12 H, m), 1.30 (3 H, t, J = 7.1 Hz), 1.0–0.9 (6 H, m), 0.90 (9 H, t, J = 7.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.18, 61.21, 52.65 (313 Hz), 50.76, 28.79 (21 Hz), 27.16 (54 Hz), 14.08, 13.54, 9.02 (334 Hz); MS m/e 349 ($M^+ - C_4H_9$, 91), 235 (70), 179 (100), 121 (16). Anal. Calcd for $C_{17}H_{34}O_3Sn$: C, 50.49; H, 8.46. Found: C, 50.23; H, 8.21.

Reaction of Epoxy Ester 16 with Me_2CuLi: Ethyl (2*R,3*R**)-2-Hydroxy-3-(tributylstannyl)butanoate (17).** To a solution of 0.88 mmol of Me_2CuLi (prepared from 181.6 mg of CuBr·SMe_2 and 1.26 mL of 1.4 M MeLi in ether) in 5 mL of ether at −20 °C was added epoxy ester **16** as a solution in 2 mL of ether. The reaction mixture was stirred at −20 °C for 30 min and was then quenched with basic aqueous NH_4Cl. Standard aqueous workup as described above for compound **8** provided 154 mg (83%) of α-hydroxy ester **17** as a colorless oil: IR (neat) 3495 (br), 2954, 2923, 1724, 1460, 1373, 1210, 1026 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.21 (2 H, AB of ABX_3, J_{AB} = 10.8 Hz, J_{AX} = J_{BX} = 7.1 Hz), 4.18 (1 H, d, J = 5.8 Hz), 1.71 (1 H, dq, J = 5.8, 7.7 Hz), 1.6–1.2 (12 H, m), 1.29 (3 H, t, J = 7.1 Hz), 1.21 (3 H, d, J = 7.7 Hz), 1.0–0.8 (15 H, m); ^{13}C NMR (63 MHz, $CDCl_3$) δ 175.35 (23 Hz), 75.55 (13 Hz), 61.50, 29.18 (20 Hz), 27.49 (56 Hz), 26.27 (301 Hz), 14.96 (13 Hz), 14.21, 13.64, 9.20 (312 Hz); MS m/e 365 ($M^+ - C_4H_9$, 28), 249 (100), 193 (80), 137 (44). Anal. Calcd for $C_{18}H_{38}O_3Sn$: C, 51.33, H, 9.09. Found: C, 51.40; H, 8.96.

Tributyl(3,4-epoxybutyl)stannane (21). To a solution of 3-butenyltributylstannane (**20**)[4] (0.785 g, 2.27 mmol) in 35 mL of $CHCl_3$ was added *m*-CPBA (1.0 g of 80% pure material, 4.6 mmol). The reaction was stirred at rt for 4 h. The solvent was removed in vacuo, and the residue was taken up in ether (80 mL). The organic layer was washed with saturated $NaHCO_3$, dried ($MgSO_4$), and concentrated. Chromatography of the residual material on silica gel (25 g) using petroleum ether–ether (50:1) as eluent provided 448 mg (55%) of the desired epoxide **21** as a colorless oil: IR (neat) 2923, 1461, 1375, 1071, 838 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.87 (1 H, ddt, J = 2.8, 4.0, 5.4 Hz), 2.74 (1 H, dd, J = 4.0, 5.0 Hz), 2.47 (1 H, dd, J = 2.8, 5.0 Hz), 1.8–1.2 (14 H, m), 1.0–0.8 (17 H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 54.76 (65 Hz), 47.03, 29.69 (16 Hz), 29.15 (20 Hz), 27.32 (53 Hz), 13.62, 8.76 (314 Hz), 3.53 (295 Hz); MS m/e 305 ($M^+ - C_4H_9$, 21), 291 (37), 275 (20), 235 (18), 191 (19), 177 (100), 161 (15), 121 (24). Anal. Calcd for $C_{16}H_{34}OSn$: C, 53.21; H, 9.49. Found: C, 53.27; H, 9.32.

(3,4-Epoxybutyl)triphenylstannane (24). To a solution of 3-butenyltriphenylstannane (**23**)[4] (508 mg, 1.25 mmol) in 10 mL of $CHCl_3$ was added *m*-CPBA (375 mg of 80% pure material, 1.74 mmol). The reaction mixture was stirred at rt for 15 h. The solvent was removed in vacuo, and the residue was diluted with ether (70 mL). The organic layer was washed with saturated $NaHCO_3$, dried ($MgSO_4$), and concentrated to afford a white solid. Chromatography of this material on silica gel (25 g) using petroleum ether–ether (4:1) as eluent afforded 397 mg (75%) of epoxide **24** as a white solid: mp 95–96 °C; IR ($CHCl_3$) 3064, 3001, 1479, 1428, 1220, 1208, 1075 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.6–7.4 (6 H, m), 7.3–7.2 (9 H, m), 2.90 (1 H, ddt, J = 2.7, 4.0, 5.3 Hz), 2.62 (1 H, dd, J = 4.0, 5.0 Hz), 2.40 (1 H, dd, J = 2.7, 5.0 Hz), 2.0–1.4 (4 H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.41 (477 Hz), 136.89 (35 Hz), 128.85, 128.44 (48 Hz), 54.21 (73 Hz), 46.79, 28.94 (19 Hz), 14.33 (380 Hz); MS m/e 351 ($M^+ - C_4H_7O$, 100), 274 (23), 197 (48), 120 (25). Anal. Calcd for $C_{22}H_{22}OSn$: C, 62.75; H, 5.27. Found: C, 62.51; H, 5.21.

Reaction of Epoxide 21 with $LiAlH_4$: Tributyl(3-hydroxybutyl)stannane (22). To 35 mg (0.92 mmol) of $LiAlH_4$ in 5 mL of Et_2O at 0 °C was added 104 mg (0.29 mmol) of epoxide **21**. The reaction mixture was stirred at 0 °C for 10 min and at rt for 30 min. It was then cooled to 0 °C, quenched with H_2O, and diluted with ether. The organic layer was washed with 1 N HCl, dried ($MgSO_4$), and concentrated to afford a colorless oil. Chromatography of this oil on silica gel (2 g) using petroleum ether–ether (20:1) as eluent provided 90.0 mg (86%) of tributyl(3-hydroxybutyl)stannane (**22**): IR (neat) 3342 (br), 2926, 1457, 1374, 1069, 875 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 3.65 (1 H, m), 1.7–1.2 (14 H, m), 1.18 (3 H, d, J = 6.1 Hz), 1.0–0.7 (17 H, m); ^{13}C NMR (63 MHz, $CDCl_3$) δ 71.04 (60 Hz), 36.38 (18 Hz), 29.22 (20 Hz), 27.35 (52 Hz), 22.63, 13.62, 8.82 (309 Hz), 4.09 (291 Hz); MS m/e 307 ($M^+ - C_4H_9$, 100), 291 (10), 247 (31), 193 (13), 177 (40), 137 (27), 121 (15). Anal. Calcd for $C_{16}H_{36}OSn$: C, 52.92; H, 9.99. Found: C, 52.80; H, 9.85.

(3-Hydroxybutyl)triphenylstannane (25). A. Reaction of Epoxide 24 with $LiAlH_4$. The reaction of epoxide **24** with $LiAlH_4$ was carried out as described above for epoxide **21**. From 176.2 mg (0.416 mmol) of **24** and 40.7 mg (1.07 mmol) there was obtained 22.7 mg (13%) of 3-butenyltriphenylstannane (**23**) and 82 mg (46%) of the expected alcohol **25**.

B. Reaction of Epoxide 24 with DIBAL-H. To a solution of epoxide **24** (108 mg, 0.256 mmol) in 5 mL of Et_2O at −78 °C was added DIBAL-H (0.42 mL of a 1.0 M solution in hexane). The reaction mixture was stirred at −78 °C for 30 min and at 0 °C for 1 h. The reaction was quenched with a saturated solution of Rochelle's salt; the mixture was allowed to warm to rt and was stirred at rt for 30 min. The inorganic salts were washed with ether, and the combined organic layer was dried ($MgSO_4$) and concentrated. Chromatography of the residual material on silica gel (10 g) using petroleum ether–ether (4:1) as eluent afforded 80.7 mg (75%) of (3-hydroxybutyl)triphenylstannane (**25**) as a white solid: mp 69–71 °C; IR ($CHCl_3$) 3609, 3063, 3004, 1427, 1209, 1074, 700, 668 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.7–7.4 (6 H, m), 7.4–7.3 (9 H, m), 3.70 (1 H, sextet, J = 6 Hz), 1.9–1.4 (4 H, m), 1.14 (3 H, d, J = 6.2 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 139.05, 136.96 (36 Hz), 128.77, 128.43 (49 Hz), 70.45 (62 Hz), 35.48 (22 Hz), 22.92, 6.61; MS m/e 351 ($M^+ - C_4H_9O$, 93), 347 ($M^+ - C_6H_5$, 100), 197 (60), 120 (41). Anal. Calcd for $C_{22}H_{24}OSn$: C, 62.45; H, 5.72. Found: C, 62.50; H, 5.66.

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(18) Davies, A. G.; Tse, M.-W. *J. Organomet. Chem.* **1978**, *155*, 25.
(19) Piers, E.; Chong, J. M.; Morton, H. E. *Tetrahedron Lett.* **1981**, *22*, 4905.