+ 2 (10), 411 (8.6), 369 (10); HRMS m/z calcd for $C_{28}H_{38}O_3Si$ 426.2588, found 426.2583.

4-[(*tert*-Butyldimethylsilyl)oxy]-2-(4-methyl-2-oxo-3-pentenyl)-2*H*-1-benzopyran (12): yellow oil, 0.56 g (85%); ^1H NMR ($CDCl_3$) δ 0.10 (s, 6 H), 0.88 (s, 9 H), 1.77 (d, J = 1.3 Hz, 3 H), 2.05 (d, J = 1.3 Hz, 3 H), 2.70 (dd, J = 14.7, 6.5 Hz, 1 H), 3.00 (dd, J = 14.7, 7.2 Hz, 1 H), 4.85 (d, J = 4.0 Hz, 1 H), 5.15-5.38 (m, 1 H), 5.94 (dd, J = 2.6, 1.3 Hz, 1 H), 6.50-7.30 (m, 4 H); HRMS m/z calcd for $C_{21}H_{30}O_3Si$ 358.1962, found 358.1942.

Protonolysis of 11c-cis and 11-trans. General Procedure. To a solution of 11c-cis (0.75 g, 1.84 mmol) in 3 mL of CH_2Cl_2 at room temperature was added a 10 mL of dilute HCl (10%). The mixture was stirred at room temperature for ca. 3 h, extracted with CH_2Cl_2, and washed sequentially with water. The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The crude solid was then recrystallized (CH_2Cl_2-hexane) to give 0.51 g (95%) of the corresponding ketone (13a-cis) as a colorless crystalline solid.

1,2,3,4,4a,9a-Hexahydro-1-phenyl-9*H*-xanthene-3,9-dione (13a-cis): colorless crystalline solid, 0.51 g (95%); mp 235-237 °C; ^1H NMR ($CDCl_3$) δ 2.65-3.00 (m, 4 H), 3.13 (dd, J = 10.3, 2.5 Hz, 1 H), 3.45-3.78 (m, 1 H), 4.95-5.08 (m, 1 H), 6.90-7.80 (m, 9 H); HRMS m/z calcd for $C_{19}H_{16}O_3$ 292.1089, found 292.1088. Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.90; H, 5.34.

1,2,3,4,4a,9a-Hexahydro-1-phenyl-9*H*-xanthene-3,9-dione (13b-trans): colorless crystalline solid, 0.25 g (82%); mp 182-184 °C; ^1H NMR ($CDCl_3$) δ 2.52-3.20 (m, 4 H), 3.26-3.65 (m, 2 H), 4.40-4.75 (m, 1 H), 6.90-7.80 (m, 9 H); HRMS m/z calcd for $C_{19}H_{16}O_3$ 292.1100, found 292.1102.

2-[[4-(*tert*-Butyldimethylsilyl)oxy]-2-methyl-(2*H*-1-benzopyran-2-yl)methyl]-4*H*-1-benzopyran-4-one (14). Treatment of 2d derived from 1d (0.21 g, 1.31 mmol) with 2,6-lutidine (0.15 mL, 1.31 mmol) in 4 mL of CH_2Cl_2 at room temperature gave 14 (0.26 g, 91%) as a colorless oil: IR (neat, cm^{-1}) 2900, 1640, 1600, 1570, 1380; ^1H NMR ($CDCl_3$) δ 0.15 (d, J = 1.0 Hz, 6 H), 0.98 (s, 9 H), 1.56 (s, 3 H), 2.95 (d, J = 1.5 Hz, 2 H), 4.83 (s, 1 H), 6.22 (s, 1 H), 6.75-7.11 (m, 7 H), 8.17 (dd, J = 6.4, 2.0 Hz, 1 H); MS m/z 434 (M^+); HRMS m/z calcd for $C_{28}H_{30}O_4Si$ 434.1912, found 434.1902.

Reaction of 2a,b with Isoprene (15a) and 2,3-Dimethylbutadiene (15b) (Table IV). General Procedure. To a solution of 2a derived from 1a (0.66 g, 4.52 mmol) in 10 mL of CH_2Cl_2 was added 2.26 mL (22.6 mmol) of isoprene at room temperature. After 5 h, the reaction mixture was poured into ice-cooled water (50 mL) and extracted with CH_2Cl_2 (30 mL × 3). The combined organic layers were dried ($MgSO_4$), concentrated, and purified with flash chromatography on silica gel (hexane-ethyl acetate = 5:1 as an eluent) to give 0.48 g (50%) of 16a as a yellow oil.

1,4,4a,9a-Tetrahydro-3-methyl-9*H*-xanthen-9-one (16a): yellow oil, 0.48 g (50%); ^1H NMR ($CDCl_3$) δ 1.67 (s, 3 H), 2.10-2.61 (m, 4 H), 2.73 (ddd, J = 8.4, 7.1, 2.7 Hz, 1 H), 4.76 (dt, J = 4.2, 2.7 Hz, 1 H), 5.49-5.58 (m, 1 H), 6.80-7.03 (m, 2 H), 7.42 (ddd, J = 8.5, 7.0, 1.9 Hz, 1 H), 7.84 (dd, J = 8.2, 1.9 Hz, 1 H); MS m/z M^+ 214 (85), M^+ + 1 (43), M^+ - 1 (68), 199 (100); HRMS m/z calcd for $C_{14}H_{14}O_2$ 214.0992, found 214.0981.

1,4,4a,9a-Tetrahydro-2,3-dimethyl-9*H*-xanthen-9-one (16b): yellow oil, 0.35 g (42%); ^1H NMR ($CDCl_3$) δ 1.76 (s, 6 H), 2.10-2.50 (m, 4 H), 2.81 (ddd, J = 9.4, 6.7, 2.8 Hz, 1 H), 4.76 (dt, J = 4.2, 2.8 Hz, 1 H), 6.80-7.03 (m, 2 H), 7.42 (ddd, J = 8.5, 7.0, 1.9 Hz, 1 H), 7.84 (dd, J = 8.5, 1.9 Hz, 1 H); MS m/z M^+ 228 (87.5), M^+ + 1 (44), M^+ - 1 (28), 213 (100), 195 (75); HRMS m/z calcd for $C_{15}H_{16}O_2$ 228.1148, found 228.1146. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.18; H, 7.30.

1,4,4a,9a-Tetrahydro-2,3,9a-trimethyl-9*H*-xanthen-9-one (16c): yellow oil, 0.18 g (25%); ^1H NMR ($CDCl_3$) δ 1.24 (s, 3 H), 1.67 (bs, 6 H), 2.34-2.61 (m, 4 H), 4.40 (t, J = 3.9 Hz, 1 H), 6.88-7.72 (m, 4 H); MS m/z M^+ 242 (77), M^+ + 1 (38), M^+ - 1 (11), 227 (50), 160 (100); HRMS m/z calcd for $C_{16}H_{18}O_2$ 242.1305, found 242.1300. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.41; H, 7.73.

Dehydrogenation of 16a: 3-Methylxanthone (17). To a solution of 16a (0.15 g, 0.70 mmol) in 4 mL of toluene was added p-toluenesulfonic acid (0.03 g) and DDQ (0.32 g, 1.40 mmol), and the mixture was heated at reflux with vigorous stirring for 3 h, cooled to room temperature, filtered, and concentrated. Purification by thin-layer chromatography using 20% ethyl acetate in hexane as eluent gave 0.11 g (75%) of 3-methylxanthone (17) as colorless solid: mp 94-95 °C (97 °C);[23] ^1H NMR ($CDCl_3$) δ 2.54 (s, 3 H), 7.23 (dd, J = 8.1, 1.5 Hz, 1 H), 7.30 (d, J = 1.5 Hz, 1 H), 7.37 (dt, J = 8.2, 1.7 Hz, 1 H), 7.48 (dd, J = 8.2, 1.7 Hz, 1 H), 7.72 (dt, J = 8.2, 1.7 Hz, 1 H), 8.23 (d, J = 8.1 Hz, 1 H), 8.34 (dd, J = 8.2, 1.7 Hz).

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Supplementary Material Available: ^1H NMR spectra for compounds 2a, 4a-c, 6a,c,d,f, 7a,b, 8a,b, 9a-c, 11a,b, 11c-cis, 11c-trans, 11d-h,j, 12, 13a,b, 14, and 16a-c; ^{13}C NMR spectra of compounds 11c-cis and 11c-trans (36 pages). Ordering information is given on any current masthead page.

(23) Goldberg, A. A.; Wragg, A. H. *J. Chem. Soc.* **1958**, 4227.

1,3-Elimination Reactions of (3,4-Epoxybutyl)stannanes. Approach to the Synthesis of Cycloeudesmol

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The reactions that occur when stereochemically defined spirocyclic (3,4-epoxybutyl)stannanes are treated with $C_2H_5AlCl_2$ depend critically on the relative orientation of tin, oxygen, and the three connecting atoms of carbon. A W arrangement of these atoms tends to favor formation of cyclopropanes by a concerted 1,3-elimination with inversion at both carbon centers. If this orientation cannot be achieved, cleavage of the epoxide occurs to give an ionic intermediate that can undergo a subsequent 1,3-elimination or a 1,2-shift of hydride promoted by an antiperiplanar carbon-tin bond.

Loss of X^- from silane 1a or stannane 1b can trigger three characteristic reactions.[2-5] One is a 1,2-shift from the central carbon that leads to demetalation and formation of a derivative of propene (path a); another is a 1,3-

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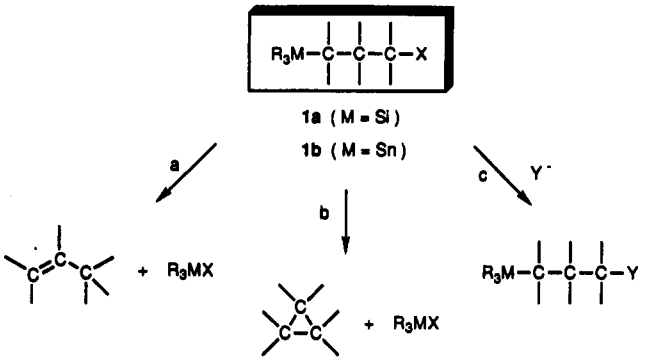
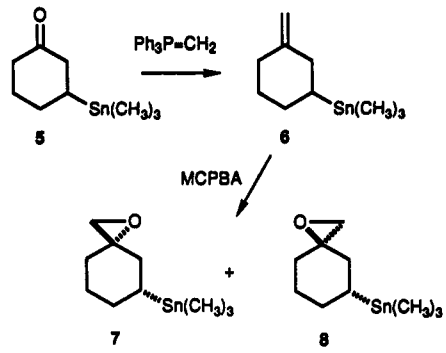
elimination that provides a derivative of cyclopropane (path b); and the third is simple nucleophilic substitution (path c) or 1,2-elimination. The ratio of these products

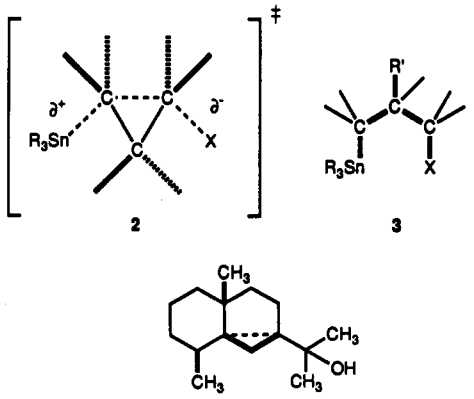


depends critically on several factors, including the nature of M, the degree and type of substitution at the nucleophilic and electrophilic carbons, and the relative orientation of the bonds that must be broken. In general, stannanes are more prone than the corresponding silanes to undergo 1,3-eliminations. Detailed kinetic and stereochemical studies of 1,3-elimination reactions of simple stannanes have provided evidence for a concerted process in which the new C–C bond is formed as the C–Sn and C–X bonds are cleaved.[6-8] In this process, inversion of configuration at both carbon centers is apparently favored.[3c,6,10] The preferred transition state for concerted 1,3-elimination reactions of stannanes therefore appears to have the W orientation of structure **2**. In contrast,

Scheme I



competing 1,2-shifts are promoted by the orientation of structure **3**, in which bonds to R_3Sn, the group R′ that migrates, and X are mutually antiperiplanar.[13] The



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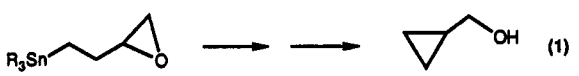
predictable stereospecificity of simple examples of these reactions suggests that more complex variations will be useful in organic synthesis. In this paper, we describe the reactions of monocyclic and bicyclic stannanes designed to test the stereochemical postulates represented by structures **2** and **3**, and we summarize our efforts to use 1,3-eliminations to synthesize cycloeudesmol (**4**), a tricyclic sesquiterpene antibiotic containing a cyclopropane ring.[14]

Simple 1,3-eliminations produce cyclopropanes without functional groups that can be used for subsequent manipulations, so we decided to prepare more versatile (hydroxymethyl)cyclopropanes by 1,3-elimination reactions of (3,4-epoxybutyl)stannanes induced by Brønsted and Lewis acids (eq 1).[15] Spirocyclic derivatives **7** and **8**,[16]



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which allowed us to achieve greater control of the relative orientation of the reactive C–Sn and C–O bonds, were

(1) Fellow of the Natural Sciences and Engineering Research Council of Canada, 1983–1987.

(2) For references to studies of cationic rearrangements in silanes, see: Fleming, I.; Patel, S. K.; Urch, C. J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 115–124.

(3) For references to studies of 1,3-eliminations in stannanes, see: (a) Sato, T. *Synthesis* **1990**, 259–270. Sato, T.; Watanabe, T.; Hayata, T.; Tsukui, T. *Tetrahedron* **1989**, *45*, 6401–6408. (b) Johnson, C. R.; Kadow, J. F. *J. Org. Chem.* **1987**, *52*, 1493–1500. (c) Fleming, I.; Urch, C. J. *J. Organomet. Chem.* **1985**, *285*, 173–191.

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(7) McWilliam, D. C.; Balasubramanian, T. R.; Kuivila, H. G. *J. Am. Chem. Soc.* **1978**, *100*, 6407–6413.

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(9) Negishi, E.-i. *Organometallics in Organic Synthesis*; Wiley-Interscience: New York, 1980; Chapter 6.

(10) The formation of cyclopropanes from stannanes by 1,3-eliminations belongs to a general class of reactions in which cycloalkanes are generated from stannanes by analogous intramolecular 1,*n*-eliminations.[11] Although cyclopropanes are formed with inversion of configuration at the nucleophilic center, larger rings are formed with retention in the cases that have been studied.[12] Just as 1,2-shifts can compete with 1,3-eliminations, 1,(*n* – 1)-shifts can compete with 1,*n*-eliminations when *n* is greater than 3.[11]

(11) For references, see: Sato, T.; Haramura, M.; Taka, N. *Tetrahedron Lett.* **1989**, *30*, 4983–4984. Lee, T. V.; Ellis, K. L. *Ibid.* **1989**, *30*, 3555–3556. Macdonald, T. L.; Delahunty, C. M.; Mead, K.; O'Dell, D. E. *Ibid.* **1989**, *30*, 1473–1476.

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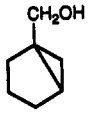
(14) Ando, M.; Sayama, S.; Takase, K. *J. Org. Chem.* **1985**, *50*, 251–264. Ando, M.; Wada, K.; Takase, K. *Tetrahedron Lett.* **1985**, *26*, 235–238. Chen, E. Y. *J. Org. Chem.* **1984**, *49*, 3245–3250. Suzuki, T.; Furusaki, A.; Kikuchi, H.; Kurosawa, E. *Tetrahedron Lett.* **1981**, *22*, 3423–3426.

(15) For previous examples of 1,3-elimination reactions of (3,4-epoxybutyl)stannanes, see: Sato, T.; Watanabe, M.; Murayama, E. *Synth. Commun.* **1987**, *17*, 781–788. Fish, R. H.; Broline, B. M. *J. Organomet. Chem.* **1978**, *159*, 255–278. Peterson, D. J.; Robbins, M. D.; Hansen, J. R. *Ibid.* **1974**, *73*, 237–250. Kuivila, H. G.; Scarpa, N. M. *J. Am. Chem. Soc.* **1970**, *92*, 6990–6991.

(16) We chose to use trimethylstannyl compounds because their ^1H NMR spectra are simpler than those of analogous tributylstannanes and because their 1,3-elimination reactions are much faster than those of analogous triphenylstannanes.[6b]

prepared efficiently by the reactions summarized in Scheme I. Trimethylstannyl ketone **5**, obtained from cyclohexenone by the method of Still,[17] was transformed into olefin **6** by a Wittig reaction. Treatment of compound **6** with *m*-chloroperbenzoic acid (MCPBA) in the presence of $NaHCO_3$[18] then provided an approximately 1:1 mixture of two diastereomeric epoxides assigned structures **7** and **8**.[19] Since the two epoxides could not be separated by flash chromatography,[21] the mixture was used in subsequent 1,3-eliminations. Addition of CF_3COOH or CF_3SO_3H cleanly converted one diastereomer into bicyclo[3.1.0]-hexane-1-methanol (**9**)[22] and left the other diastereomer unchanged.



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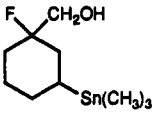
Selective formation of bicyclic alcohol **9** from diastereomer **7** is entirely consistent with the stereochemical postulate represented by structure **2**. The conformation of 1-oxaspiro[2.5]octane with a pseudoaxial oxygen is approximately 0.3 kcal/mol more stable than the pseudoequatorial alternative,[20c,23] and the trimethylstannyl group has an *A* value of 1.1,[24] so a simple calculation that neglects 1,3-diaxial interactions[25] suggests that conformer **7a** of epoxide **7** should be 0.8 kcal/mol more stable than conformer **7b**. Similarly, conformer **8a** of epoxide **8** should be 1.4 kcal/mol more stable than alternative **8b**. Of these

four structures, only conformer **7a** has the W orientation of tin and oxygen presumably required for a concerted 1,3-elimination. As a result, only diastereomer **7** reacts when a mixture of epoxides **7** and **8** is treated with acid, and we suggest that the products are derived from a concerted 1,3-elimination reaction of the protonated form of major conformer **7a**.

Although this simple conformational analysis accounts for our observations, it ignores several potential complications. One is that the products of a concerted rearrangement are derived not from structure **7a** but from a derivative in which the oxygen atom is protonated or bound to a Lewis acid.[26] This should tend to favor conformations with pseudoequatorial oxygens. In addition, the ground states of structures incorporating a W orientation of tin and an activated oxygen may be weakly stabilized by interactions similar to those that strongly stabilize the transition states of concerted 1,3-eliminations.[27] If so, the preference for conformer **7a** and activated derivatives with similar conformations should be reinforced. Finally, conformer **7b** offers the possibility of a through-space, stabilizing 1,3-diaxial interaction of tin and oxygen. We doubt that this effect plays an important role, however, since the pseudoaxial orientation of oxygen increases its distance from tin, and since tin in tetraalkylstannanes is not sufficiently Lewis acidic to form adducts with simple Lewis bases.[28]

Treatment of the mixture of epoxides **7** and **8** with $BF_3{\cdot}O(C_2H_5)_2$, followed by an aqueous workup, provided bicyclic alcohol **9** in 51% yield and also generated minor amounts of a fluorohydrin assigned structure **10**.[29] We



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propose that the major product is derived from a concerted 1,3-elimination reaction of the BF_3 complex of the major conformer **7a** of epoxide **7**, and that the minor product is formed from epoxide **8** by a stepwise process involving an ionic intermediate.[30] Treatment of epoxides **7** and **8** with $SnCl_4$ or $TiCl_4$ generated complex mixtures of products, but the addition of $C_2H_5AlCl_2$ at −78 °C led exclusively to the formation of bicyclic alcohol **9** in 83% yield.[31] The $C_2H_5AlCl_2$ complex of conformer **7a** may undergo a concerted 1,3-elimination that provides the bicyclic skeleton of alcohol **9** directly, whereas the complex of epoxide **8** presumably opens to give an ionic intermediate **11** in which oxygen is bound to the Lewis acid AlL_n.[30] Intermediate **11** can adopt conformation **11a**, which is primed to undergo

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(19) Peracid epoxidation of methylenecyclohexanes normally favors axial attack,[20] but the percentage of equatorial attack increases as the substituent at C_3 becomes more electropositive.[20a]
(20) (a) Cieplak, A. S.; Tait, B. D.; Johnson, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 8447–8462. (b) Vedejs, E.; Dent, W. H., III *Ibid.* **1989**, *111*, 6861–6862. (c) Sevin, A.; Cense, J.-M. *Bull. Soc. Chim. Fr.* **1974**, 963–968. (d) Berti, G. *Top. Stereochem.* **1973**, *7*, 93–251. (e) Carlson, R. G.; Ardon, R. *J. Org. Chem.* **1971**, *36*, 216–217. (f) Carlson, R. G.; Behn, N. S. *Ibid.* **1967**, *32*, 1363–1367. (g) Favre, H.; Gravel, D. *Can. J. Chem.* **1963**, *41*, 1452–1462.
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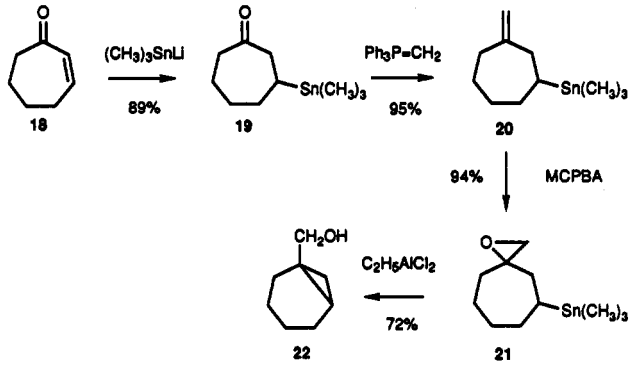
(27) For discussions of 1,3-interactions in the ground states of similar stannanes, see: Wickham, G.; Olszowy, H. A.; Kitching, W. *J. Org. Chem.* **1982**, *47*, 3788–3793. Hudec, J. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1020–1023.
(28) Ochiai, M.; Iwaki, S.; Takaoka, Y.; Nagao, Y. *Organometallics* **1989**, *8*, 1751–1755. Ochiai, M.; Iwaki, S.; Ukita, T.; Matsuura, Y.; Shiro, M.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4606–4610.
(29) For examples of the formation of fluorohydrins from epoxides, see: Fujimoto, Y.; Kanzawa, Y.; Ikuina, Y.; Kakinuma, K.; Ikekawa, N. *J. Chem. Soc., Chem. Commun.* **1989**, 1107–1109. Ayi, A. I.; Remli, M.; Condom, R.; Guedj, R. *J. Fluorine Chem.* **1981**, *17*, 565–580. Berti, G.; Macchia, B.; Macchia, F.; Monti, L. *J. Chem. Soc. C* **1971**, 3371–3375. Coxon, J. M.; Hartshorn, M. P.; Muir, C. N. *Tetrahedron* **1969**, *25*, 3925–3933.
(30) Evidence that Lewis acids can cleave similar epoxides to form ionic intermediates has been presented by: Blackett, B. N.; Coxon, J. M.; Hartshorn, M. P.; Jackson, B. L. J.; Muir, C. N. *Tetrahedron* **1969**, *25*, 1479–1487.
(31) Snider, B. B.; Rodini, D. J.; Karras, M.; Kirk, T. C.; Deutsch, E. A.; Cordova, R.; Price, R. T. *Tetrahedron* **1981**, *37*, 3927–3934.

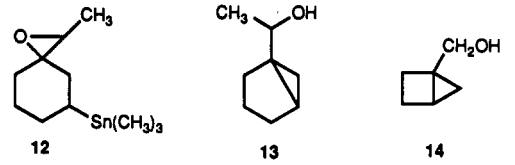
Scheme II



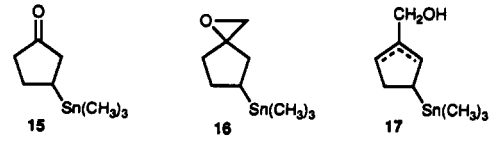
a 1,3-elimination with inversion at the carbon bearing tin, or conformation **11b**, which is better suited to a 1,2-shift

of axial hydride driven by the antiperiplanar carbon–tin bond. Since the equatorial orientation of the trimethylstannyl group and the possibility of stabilizing 1,3-interactions make conformer **11a** significantly more stable than conformer **11b**, we believe that the reaction of epoxide **8** with $C_2H_5AlCl_2$ leads primarily to bicyclic alcohol **9** via intermediate **11a**. The use of $C_2H_5AlCl_2$ to promote 1,3-eliminations is therefore preparatively advantageous; although epoxides **7** and **8** are formed with low diastereoselectivity, *both* are converted cleanly into alcohol **9**.

To test the generality of this procedure, we treated other spirocyclic (3,4-epoxybutyl)stannanes with $C_2H_5AlCl_2$. The reaction of (trimethylstannyl)cyclohexanone **5**[17] with ethylidenetriphenylphosphorane, followed by the addition of buffered MCPBA,[18] provided a mixture of the four diastereomers of epoxide **12** in 95% overall yield. Treatment of the mixture with $C_2H_5AlCl_2$ at −78 °C, followed by an aqueous workup, then produced the diastereomeric alcohols **13** in 98% yield.[32] Not surprisingly, an

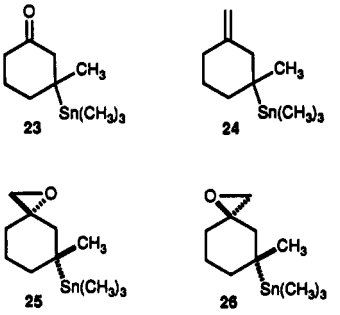


attempt to produce bicyclo[2.1.0]pentane-1-methanol (**14**) by a similar 1,3-elimination was unsuccessful. (Trimethylstannyl)cyclopentanone **15**, prepared in 71% yield from 2-cyclopentenone by the addition of $(CH_3)_3SnLi$, was converted into an inseparable mixture of diastereomeric epoxides **16** by the normal sequence of Wittig methylenation and MCPBA epoxidation. Treatment of compounds



16 with $C_2H_5AlCl_2$ led to a complex mixture of products containing the regioisomeric allylic alcohols represented by structure **17**. Since strain inhibits the formation of bicyclic alcohol **14** by concerted or nonconcerted 1,3-eliminations, epoxides **16** open to give ionic intermediates that are converted into olefins **17** by subsequent deprotonation. In contrast, bicyclo[4.1.0]heptane-1-methanol (**22**)[33] could be prepared in high yield by the sequence of reactions summarized in Scheme II. These syntheses demonstrate that bicyclo[3.1.0] and bicyclo[4.1.0] skeletons can be generated efficiently by 1,3-elimination reactions of spirocyclic epoxy stannanes and that the epoxy stannane precursors can be synthesized in three easy steps from cycloalkenones.

We were therefore encouraged to try to join two fully substituted carbons by similar 1,3-eliminations. Addition of $(CH_3)_3SnLi$ to 3-methyl-2-cyclohexenone efficiently produced ketone **23**,[34] but a subsequent Wittig reaction provided only low yields of olefin **24**.[35] Much better results



could be achieved by using the methylenation reagent devised by Lombardo ($Zn/TiCl_4/CH_2Br_2$),[36] which converted ketone **23** into olefin **24** in 81% yield. MCPBA epoxidation of compound **24** then provided a 1:2 mixture of two diastereomeric epoxides. These compounds could be separated with difficulty by flash chromatography,[21] and their structures were assigned by ^1H NMR spectroscopy. In the major epoxide, a nuclear Overhauser enhancement of 2.8% was measured in the epoxide methylene signal when the $(CH_3)_3Sn$ hydrogens were irradiated, whereas no such enhancement was observed in the minor epoxide. We therefore assign structure **25** to the minor epoxide and structure **26** to the major epoxide.

Minor epoxide **25** should exist as a mixture of conformers **25a** and **25b**. Since the *A* value of CH_3 is 1.7,[37] a simple calculation that neglects 1,3-diaxial interactions[25] predicts that conformer **25b** should be approximately 0.9 kcal/mol more stable. This prediction can be tested by using the

well-established Karplus relationship that governs $^3J(^{119}Sn,^{13}C)$.[38] In conformer **25a**, the spirocyclic carbon, tin, and the two connecting carbons form a dihedral angle of approximately 180°, so $^3J(Sn,C)$ should be about 70 Hz. In conformer **25b**, the same atoms define an angle of 60°,

(32) Steinberg, N. G.; Rasmusson, G. H.; Reynolds, G. F.; Springer, J. P.; Arison, B. H. *J. Org. Chem.* **1979**, *44*, 3416–3420.

(33) Olah, G. A.; Fung, A. P.; Rawdah, T. N.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 4646–4647. Harding, K. E.; Trotter, J. W.; May, L. M. *J. Org. Chem.* **1977**, *42*, 2715–2719.

(34) Piers, E.; Tillyer, R. D. *J. Org. Chem.* **1988**, *53*, 5366–5369. Sato, T.; Watanabe, M.; Watanabe, T.; Onoda, Y.; Murayama, E. *Ibid.* **1988**, *53*, 1894–1899.

(35) Deprotonation by the Wittig reagent may provoke an elimination of $(CH_3)_3Sn^-$.

(36) Lombardo, L. *Tetrahedron Lett.* **1982**, *23*, 4293–4296.

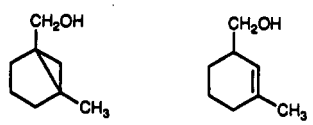
(37) Booth, H.; Everett, J. R. *J. Chem. Soc., Chem. Commun.* **1976**, 278–279. Anet, F. A. L.; Bradley, C. H.; Buchanan, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 258–259.

(38) Mitchell, T. N.; Podesta, J. C.; Ayala, A.; Chopa, A. B. *Magn. Reson. Chem.* **1988**, *26*, 497–500. Olszowy, H. A.; Kitching, W. *Organometallics* **1984**, *3*, 1670–1675. Doddrell, D.; Burfitt, I.; Kitching, W.; Bullpitt, M.; Lee, C.-H.; Mynott, R. J.; Considine, J. L.; Kuivila, H. G.; Sarma, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 1640–1642.

so ^3J(Sn,C) should be close to 10 Hz. Since the observed coupling constant in the ^{13}C NMR spectrum of minor epoxide **25** is 25.8 Hz at 25 °C, we conclude that the ratio of conformers **25a** and **25b** is approximately 1:3.[39] This analysis agrees reasonably well with the prediction based on additive *A* values and demonstrates that any special 1,3-interaction present in conformer **25a** cannot be strongly stabilizing.[27] Similarly, major epoxide **26** should exist as a mixture of conformers **26a** and **26b**, and an analysis of *A* values suggests that structure **26b** should be favored by about 0.3 kcal/mol. Since the observed ^3J(Sn,C) for the spirocyclic carbon is 19.6 Hz, the ratio of conformers **26a** and **26b** must actually be 1:5.

26a **26b**

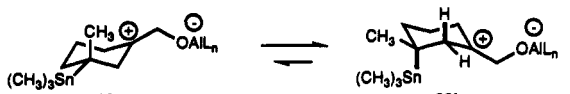
Of the four conformations of epoxides **25** and **26**, only structure **25a** can undergo a concerted 1,3-elimination with inversion at both carbon centers. Although it is the minor conformer of epoxide **25**, substantial amounts are nevertheless present at equilibrium, and adducts of epoxide **25** with Lewis acids are likely to contain even higher proportions of similar conformations in which both tin and oxygen are equatorial. Furthermore, the rate of ring inversion in 1-oxaspiro[2.5]octane is 50 s^{-1} at 186 K,[23a] so interconversion of conformers **25a** and **25b** is at least as fast as 1,3-elimination. The Curtin–Hammett principle therefore suggests that minor epoxide **25** may react exclusively by a concerted 1,3-elimination of an activated adduct of conformer **25a**,[40] which would lead to the formation of 5-methylbicyclo[3.1.0]hexane-1-methanol (**27**).



27 **28**

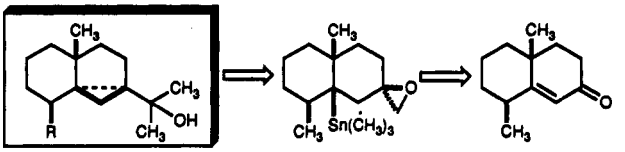
In contrast, activated adducts of major conformer **25b** contain bonds to oxygen, hydrogen, and tin that are mutually antiperiplanar and ideally arranged for a concerted process in which opening of the epoxide promotes a transfer of hydride driven by tin. This alternative reaction would produce 3-methyl-2-cyclohexene-1-methanol (**28**).[41] In fact, treatment of epoxide **25** with $C_2H_5AlCl_2$ at −78 °C produced cyclopropane **27** in 75% yield, and olefin **28** was not detected. This is consistent with earlier observations that 1,3-elimination reactions of stannanes are intrinsically faster than tin-promoted 1,2-shifts of hydride,[3] possibly because hydride shifts require significant cationic character at the electrophilic center.

In contrast, a similar reaction of major epoxide **26** produced an inseparable 1:3 mixture of cyclopropane **27** and olefin **28** in 37% combined yield. Since epoxide **26** cannot undergo a concerted 1,3-elimination with double inversion, it is presumably cleaved to give two conformers **29a** and **29b** of an ionic intermediate that incorporates the Lewis



29a **29b**

Scheme III



4 (R = CH_3) **30** **31**

32 (R = H)

acid AlL_n. Conformer **29a** can then produce cyclopropane **27** by a 1,3-elimination with inversion at the carbon bearing tin, while conformer **29b** is arranged to give olefin **28** by a 1,2-shift of axial hydride driven by an antiperiplanar carbon–tin bond. The reactions of epoxides **25** and **26** therefore show that bicyclic structures can be made by 1,3-elimination reactions of spirocyclic epoxy stannanes even when fully substituted carbon atoms are brought together, but the process is efficient only when it is possible to achieve the W orientation of tin and oxygen required for a concerted elimination with double inversion.

These observations encouraged us to try to use a similar 1,3-elimination as the key step in a synthesis of cycloeudesmol (**4**).[14] The retrosynthetic analysis of Scheme III proposes spirobicyclic epoxy stannane **30** as a stereochemically suitable precursor that can in principle be made from the known octalone **31**[42] by the normal reactions of conjugate addition of $(CH_3)_3Sn^-$, methylenation, and epoxidation. This sequence is attractively short but subjects the 1,3-elimination to a severe test, since fully substituted carbons must be joined to produce a tricyclic structure. We were not confident that this reaction would work, so we chose racemic norcycloeudesmol **32** as a simpler target for preliminary studies, and we synthesized all four diastereomers **33**–**36** of possible epoxy stannane precursors (Scheme IV).

The *cis*-decalone **37** required for the syntheses of epoxides **33** and **34** could be prepared in 69% yield by normal conjugate addition of $[(CH_3)_3Sn]_2CuLi$[43] to the convex face of octalone **38**.[44,45] In contrast, addition of $(CH_3)_3SnLi$ led to the formation of *trans*-decalone **39** in 87% yield, and none of the cis isomer **37** could be detected. We attribute this preference to intramolecular rearrangement of the kinetic product,[46] a 1,2-adduct formed by attack on the α-face of octalone **38**.[47] Indirect evidence supporting the assignments of cis and trans structures to decalones **37** and **39** came from further reactions of the trans isomer. Reduction with $LiAlH_4$, followed by an aqueous workup, provided two diastereomeric alcohols in a 2:1 ratio. Measurement of the half-widths of the carbinolic hydrogens showed that the major diastereomer ($w_{1/2}$ = 8 Hz) should be assigned structure **40** and the minor diastereomer ($w_{1/2}$ = 20 Hz) should be assigned structure **41**.[48]

(39) In principle, other vicinal pairs of tin and carbon atoms can be used for the conformational analysis, but the spirocyclic carbon is particularly easy to identify in the ^{13}C NMR spectrum.

(40) Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83–134.

(41) (a) Stork, G.; Kahne, D. E. *J. Am. Chem. Soc.* **1983**, *105*, 1072–1073. (b) Umehara, T.; Inouye, Y.; Kakisawa, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3492–3494.

(42) (a) Gula, M. J.; Vitale, D. E.; Dostal, J. M.; Trometer, J. D.; Spencer, T. A. *J. Am. Chem. Soc.* **1988**, *110*, 4400–4405. (b) Caine, D.; Boucugnani, A. A.; Pennington, W. R. *J. Org. Chem.* **1976**, *41*, 3632–3634.

(43) Piers, E.; Morton, H. E.; Chong, J. M. *Can. J. Chem.* **1987**, *65*, 78–87.

(44) Moss, R. A.; Smudin, D. J. *J. Org. Chem.* **1976**, *41*, 611–619. Heathcock, C. H.; Ellis, J. E.; McMurry, J. E.; Coppolino, A. *Tetrahedron Lett.* **1971**, 4995–4996.

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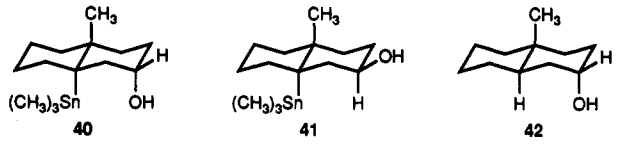
(46) Still, W. C.; Mitra, A. *Tetrahedron Lett.* **1978**, 2659–2662.

(47) (a) D'incan, E.; Loupy, A.; Maia, A.; Seyden-Penne, J.; Viout, P. *Tetrahedron* **1982**, *38*, 2923–2927. (b) Marshall, J. A.; Flynn, K. E. *J. Am. Chem. Soc.* **1982**, *104*, 7430–7435. (c) Dauben, W. G.; Dietsche, T. J. *J. Org. Chem.* **1972**, *37*, 1212–1216.

(48) Di Maio, G.; Li, W.; Migneco, L.; Vecchi, E. *Tetrahedron* **1986**, *42*, 4837–4842.

When the major diastereomer **40** was treated with KH, decalol **42**[47a,49] was formed by destannylation. This unusual reaction presumably requires the rigid juxtaposition of tin and oxygen provided uniquely by diastereomer **40**.[50]

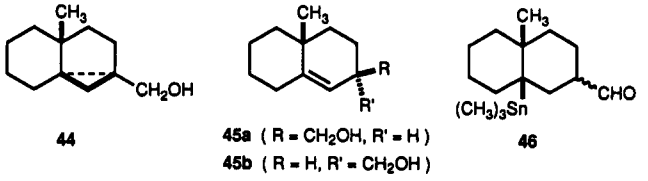


40 **41** **42**

Treatment of *cis*-decalone **37** with the Lombardo reagent and then with buffered MCPBA provided two of the four epoxides required for the synthesis of norcycloeudesmol **32**. The major product, isolated in 48% yield, was tentatively assigned structure **33** resulting from addition to the β-face, while the minor product, isolated in 30% yield, was assigned structure **34**. A similar sequence of reactions converted *trans*-decalone **39** into the single epoxide **35**. Evidence for this configuration was provided by measurement of a nuclear Overhauser enhancement of 2.7% in the epoxide methylene signal when the $(CH_3)_3Sn$ hydrogens were irradiated. As expected, $^3J(^{119}Sn,^{13}C)$ for the spirocyclic carbon was 9.3 Hz, which is very close to the normal value for a dihedral angle of 60°.

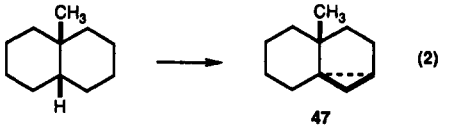
Synthesis of the missing epoxide **36** proved to be unexpectedly difficult. After a number of other approaches had failed, we found that the reactions of Scheme IV provided compound **36** in acceptable yield.[51] Preferred addition of $LiCH_2SCH_3$ to the β-face of *trans*-decalone **39** gave alcohol **43** in 45% yield.[48] Subsequent reactions with CH_3I and $KOBu^t$ converted compound **43** into the required epoxide **36** in 85% overall yield. As expected, no nuclear Overhauser enhancement was observed in the epoxide methylene signal when the $(CH_3)_3Sn$ hydrogens were irradiated.

Epoxides **33** and **34** can adopt conformations **33a**, **33b**, **34a**, and **34b**, whereas epoxides **35** and **36** exist primarily as single conformers **35a** and **36a**. Of these structures, only conformer **33a** can undergo a concerted 1,3-elimination with inversion at both carbon centers. Our previous observations therefore suggested that epoxide **33** would react via conformer **33a** and undergo 1,3-elimination exclusively, even if unsuitable alternative conformer **33b** were predominant. The ratio of conformers **33a** and **33b** could not be determined simply by measuring $^3J(^{119}Sn,^{13}C)$ at 25 °C, since their relatively slow interconversion produced extensive broadening. At −78 °C, however, separate signals for the two conformers appeared in a 1:3 ratio. The minor conformer was assigned structure **33a** because $^3J(Sn,C)$ for the spirocyclic carbon (75 Hz) was close to the value expected for a dihedral angle of 180°. Since large amounts of conformer **33a** are present at equilibrium, and since the interconversion of structures **33a** and **33b** is approximately as fast as 1,3-elimination,[52] we were optimistic that treatment of epoxide **33** with $C_2H_5AlCl_2$ would produce cyclopropane **44** by 1,3-elimination. Unfortunately,

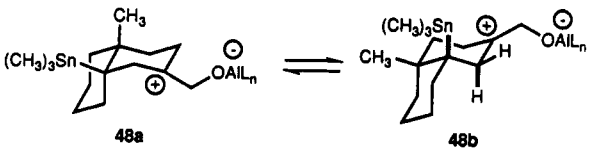


44 **45a** (R = CH_2OH, R' = H) **45b** (R = H, R' = CH_2OH) **46**

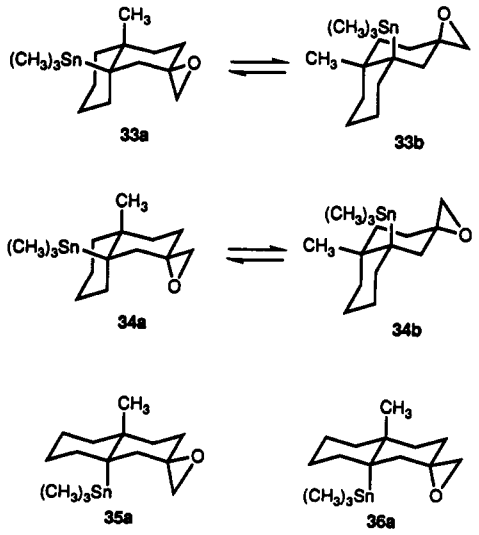
however, only traces of compound **44** could be detected in the crude product by ^1H NMR spectroscopy, which showed characteristic cyclopropane signals at δ −0.02 and 0.58. Instead, the major products proved to be homoallylic alcohol **45a**, formed in 53% yield by a 1,2-shift of hydride, and aldehyde **46**, formed in 30% yield by a conventional rearrangement of the epoxide without participation by tin.[53] Formation of tricycle **44** by a normal concerted 1,3-elimination is presumably opposed by additional strain not present when simple bicyclo[3.1.0]hexanes are formed. Molecular mechanics calculations[54] indicate that generation of bicyclo[3.1.0]hexane by the formal dehydrogenation of cyclohexane is 0.14 kcal/mol less endothermic than formation of tricycle **47** from a *cis*-decalin precursor (eq 2). Since a concerted 1,3-elimination is not feasible, epoxide **33** may cleave to give two conformers **48a** and **48b** of an ionic intermediate that incorporates the Lewis acid AlL_n. Either conformer may provide aldehyde **46**, but only structure **48b** is suitably arranged for a 1,2-shift of axial hydride promoted by an antiperiplanar carbon–tin bond. This would lead predictably to alcohol **45a**, not to epimer **45b**. The absence of significant splitting observed for the vinylic hydrogen in the ^1H NMR spectrum of compound **45a** provided direct evidence that the structural assign-



47 (2)



48a **48b**



33a **33b** **34a** **34b** **35a** **36a**

(49) Grover, S. H.; Stothers, J. B. *Can. J. Chem.* **1974**, *52*, 870–878. Casadevall, A.; Casadevall, É.; Lasperas, M. *Bull. Soc. Chim. Fr.* **1968**, 4506–4515. Baker, R. H.; Minckler, L. S.; Hussey, A. S. *J. Am. Chem. Soc.* **1959**, *81*, 2379–2383.

(50) Newman-Evans, R. H.; Carpenter, B. K. *Tetrahedron Lett.* **1985**, *26*, 1141–1144.

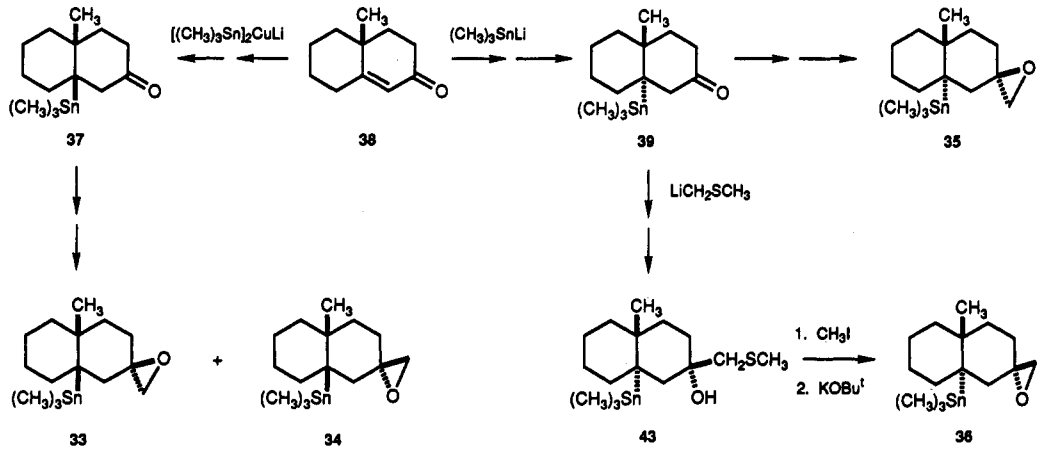
(51) Tanis, S. P.; McMills, M. C.; Herrinton, P. M. *J. Org. Chem.* **1985**, *50*, 5887–5889. Tanis, S. P.; Herrinton, P. M. *Ibid.* **1985**, *50*, 3988–3996.

(52) For kinetic studies of conformational inversion in similar *cis*-decalins, see: Browne, L. M.; Klinck, R. E.; Stothers, J. B. *Can. J. Chem.* **1979**, *57*, 803–806. Brown, L. M.; Klinck, R. E.; Stothers, J. B. *Org. Magn. Reson.* **1979**, *12*, 561–568.

(53) Gorzynski Smith, J. *Synthesis* **1984**, 629–656.

(54) These calculations used the MMX force-field of PCMODEL Version 3.3, available from Serena Software, Bloomington, IN 47701. The MMX enhancement of MM2 is discussed by: Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. In *Advances in Molecular Modeling*; JAI Press: Vol. 2, in press.

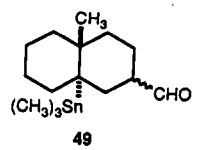
Scheme IV



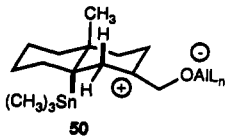
ment was correct.[47b] Alternatively, compound **45a** may be formed from an activated adduct of conformer **33b** by a concerted process in which opening of the epoxide triggers a shift of axial hydride driven by the antiperiplanar carbon–tin bond. In this case, only aldehyde **46** would be derived from ionic intermediates **48a** and **48b**.

The behavior of diastereomeric epoxide **34** was quite different. Analysis of its ^{13}C NMR spectrum at −78 °C showed that conformers **34a** and **34b** were present in a 5:2 ratio. Rearrangement induced by $C_2H_5AlCl_2$ provided a 13% yield of aldehyde **46**, as well as a 68% yield of an inseparable mixture containing approximately equal amounts of alcohol **45a**, alcohol **45b**, and a third compound that was not identified. Normal 1,2-shifts of hydride in ionic intermediates **48a** and **48b** can account for these observations. The products and yields obtained from diastereomeric epoxides **33** and **34** may be distinctly different because conformations **48a** and **48b** of the hypothetical ionic intermediate are generated in different initial ratios, and their subsequent rearrangement may be as fast as equilibration. Moreover, opening of epoxide **34** cannot induce a concerted 1,2-shift of hydride driven by an antiperiplanar carbon–tin bond. In addition, the difference between epoxides **33** and **34** may reflect more subtle variations in the mechanism of ionization that are characteristic of other axially and equatorially substituted cyclohexanes.[55] Epoxide **34** produces none of the cyclopropane **44**, so compound **44** is probably formed directly from diastereomer **33** by a concerted 1,3-elimination, not by a stepwise process involving intermediate **48a**.

Treatment of the second pair of epoxides **35** and **36** with $C_2H_5AlCl_2$ produced homoallylic alcohol **45b** in 75% and 69% yields, respectively, along with small amounts of aldehyde **49**. Since these results are similar, we propose that both epoxides open to give a common ionic intermediate **50**. Structure **50** is primed to undergo a 1,2-shift



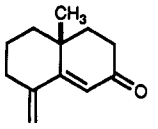
49



50

of axial hydride driven by an antiperiplanar carbon–tin bond, so alcohol **45b** predominates. As expected, splitting of the vinylic hydrogen in the ^1H NMR spectrum of compound **45b** ($^3J(H,H)$ = 2.2 Hz) was larger than in epimer **45a**.[47b] The small amounts of aldehyde **49** presumably come from 1,2-shifts of hydride in intermediate **50** that occur without participation by tin.

Evidence that epoxide **33** had produced small amounts of cyclopropane **44** by a concerted 1,3-elimination offered a slim hope that cycloeudesmol (**4**) itself could be prepared from epoxide **30** as planned (Scheme III). To synthesize compound **30**, we first prepared octalone **31**[42] (Scheme III) in 87% yield by transfer hydrogenation[56] of exocyclic dienone **51**.[57] Unfortunately, attempts to achieve conjugate addition of $[(CH_3)_3Sn]_2CuLi$ to octalone **31** were totally unsuccessful. Similarly, additions of $(CH_3)_3SnLi$ and $[(CH_3)_3Sn]_2CuLi$ to isomeric octalone **52**[58] provided only small amounts of the expected *trans*- and *cis*-decalones. These disappointing results prevented us from attempting to make cycloeudesmol (**4**) by a 1,3-elimination reaction of epoxide **30**.



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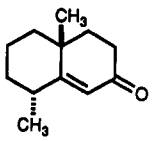

52

In general, however, the observations reported in this paper demonstrate that 1,3-elimination reactions of spirocyclic epoxy stannanes can be used reliably to prepare bicyclo[3.1.0]hexanes. Furthermore, our results support the hypothesis that these eliminations are concerted when inversion can take place at both centers. In other cases, the 1,3-eliminations are stepwise and must compete with 1,2-shifts of hydride driven by tin or normal 1,2-shifts of hydride.

Experimental Section

In all mass spectra, characteristic isotopic distributions were observed for all ions containing tin, but the only peaks reported are those that correspond to ions containing uniquely ^{120}Sn. Gas chromatographic (GC) analyses were done using a 25-m glass capillary column coated with SE-54. Dichloromethane, *N,N,N′,N′*-tetramethylethylenediamine, dimethyl sulfide, and $BF_3{\cdot}O(C_2H_5)_2$ were dried by distillation from CaH_2, and tetrahydrofuran (THF) and ether were dried by distillation from the sodium ketyl of benzophenone. The dimethyl sulfide complex of CuBr

(55) For recent discussions of this problem, see: Coles, C. J.; Maskill, H. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1083–1089. Schneider, H.-J.; Schmidt, G. *Chem. Ber.* **1986**, *119*, 65–73.

(56) Burn, D.; Kirk, D. N.; Petrow, V. *Tetrahedron* **1965**, *21*, 1619–1624.

(57) Danishefsky, S.; Prisbylla, M.; Lipisko, B. *Tetrahedron Lett.* **1980**, *21*, 805–808.

(58) Still, W. C.; VanMiddlesworth, F. L. *J. Org. Chem.* **1977**, *42*, 1258–1259.

was prepared by the standard procedure[59] and recrystallized from dimethyl sulfide/hexane immediately before use. All other reagents were commercial products of the highest purity available. Hexamethyldistannane was supplied by Organometallics, Inc. and a toluene solution of $C_2H_5AlCl_2$ was provided by Aldrich. In general, the purity of title compounds was assayed by ^1H NMR spectroscopy and capillary GC and was judged to be ≥95%.

Trimethyl(3-methylenecyclohexyl)stannane (6). A suspension of methyltriphenylphosphonium bromide (1.28 g, 3.58 mmol) in THF (15 mL) was stirred at 0 °C under dry Ar and treated dropwise with a solution of butyllithium (2.30 mL, 1.43 M in hexane, 3.29 mmol). The resulting mixture was stirred at 0 °C for 20 min and then treated with a solution of ketone **5** (0.584 g, 2.24 mmol)[17] in THF (4 mL). After 35 min, several drops of methanol were added and the reaction mixture was poured into pentane (50 mL). Solids were removed by filtration through silica, and volatiles were removed from the filtrate by evaporation under reduced pressure. Kugelrohr distillation of the residue provided stannane **6** as a colorless liquid (0.513 g, 1.98 mmol, 88%): bp 60 °C (0.15 Torr); IR (liquid film) 1650 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.03 (s, 9 H), 1.3–1.9 (m, 5 H), 2.0–2.4 (m, 4 H), 4.55 (bs, 2 H); MS (CI, isobutane) *m/e* 245, 165, 135, 95.

(3*S,5*R**)- and (3*R**,5*R**)-Trimethyl(1-oxaspiro[2.5]oct-5-yl)stannane (7 and 8).** Saturated aqueous $NaHCO_3$ (2 mL) was added to a solution of stannane **6** (263 mg, 1.02 mmol) in CH_2Cl_2 (6 mL), the mixture was stirred vigorously at 0 °C, and solid *m*-chloroperbenzoic acid (248 mg, 85%, 1.2 mmol) was added.[18] The resulting mixture was stirred at 0 °C for 45 min, treated with 10% aqueous sodium thiosulfate (3 mL), diluted with ether, and washed successively with saturated aqueous $NaHCO_3$ and brine. Volatiles were removed from the organic phase by evaporation under reduced presssure. Flash chromatography (silica, hexane (85%)/ethyl acetate (15%))[21] of the residue provided an inseparable 1:1 mixture of epoxides **7** and **8** as a pale yellow liquid (247 mg, 0.898 mmol, 88%): ^1H NMR (90 MHz, $CDCl_3$) δ 0.02 (s, 9 H, epoxide **8**), 0.03 (s, 9 H, epoxide **7**), 1.1–2.1 (m, 9 H), 2.59 (bs, 2 H, epoxide **7**), 2.61 (bs, 2 H, epoxide **8**); MS (CI, isobutane) *m/e* 261, 165, 111, 95. Anal. Calcd for $C_{10}H_{20}OSn$: C, 43.67; H, 7.35. Found: C, 44.26; H, 7.90.

Reactions of Epoxides 7 and 8 Induced by $BF_3{\cdot}O(C_2H_5)_2$. A solution of a mixture of epoxides **7** and **8** (165 mg, 0.600 mmol) in ether (5 mL) was stirred at 0 °C under dry Ar and treated dropwise with $BF_3{\cdot}O(C_2H_5)_2$ (46 mg, 0.32 mmol). The resulting mixture was stirred at 0 °C for 15 min and then at 25 °C for 15 min. Solids were removed by filtration, the filtrate was washed with 5% aqueous $NaHCO_3$, and volatiles were removed from the organic phase by evaporation under reduced pressure. Flash chromatography (silica, hexane (87%)/ethyl acetate (13%))[21] separated the residue into two major fractions. One was **bicyclo[3.1.0]hexane-1-methanol (9**; 34.1 mg, 0.304 mmol, 51%), which was shown by comparisons of IR and ^1H NMR spectra to be identical with a sample prepared by the method of Closson and Kwiatkowsky.[22] The other product was a fluorohydrin assigned structure **10** (22.4 mg, 0.0759 mmol, 13%): ^1H NMR (90 MHz, $CDCl_3$) δ 0.02 (s, 9 H), 0.80–2.1 (m, 10 H), 3.52 (d, $^3J(^{19}F,^1H)$ = 19.7 Hz, 2 H); MS (CI, isobutane) *m/e* 279, 165, 95.

Reactions of Epoxides 7 and 8 Induced by $C_2H_5AlCl_2$. A solution of a mixture of epoxides **7** and **8** (150 mg, 0.54 mmol) in CH_2Cl_2 (10 mL) was stirred at −78 °C under dry Ar and treated dropwise with a solution of $C_2H_5AlCl_2$ (0.40 mL, 1.8 M in toluene, 0.72 mmol). The mixture was kept at −78 °C for 20 min, treated with saturated aqueous NH_4Cl (1 mL), warmed to 25 °C, diluted with CH_2Cl_2, and washed successively with saturated aqueous $NaHCO_3$, water, and brine. Volatiles were removed from the organic phase by evaporation under reduced pressure, and Kugelrohr distillation of the residue provided a sample of **bicyclo[3.1.0]hexane-1-methanol (9**; 51 mg, 0.45 mmol, 83%) that was shown by comparisons of IR and ^1H NMR spectra to be identical with an authentic sample.[22]

(3-Ethylidenecyclohexyl)trimethylstannane. A suspension of ethyltriphenylphosphonium bromide (870 mg, 2.3 mmol) in THF (10 mL) was stirred at 0 °C under dry Ar and treated dropwise with a solution of butyllithium (1.4 mL, 1.6 M in hexane, 2.2 mmol). The resulting mixture was stirred at 0 °C for 15 min and then treated with a solution of ketone **5** (400 mg, 1.5 mmol)[17] in THF (2 mL). After 30 min, several drops of methanol were added, and the reaction mixture was poured into pentane (50 mL). Solids were removed by filtration through silica, and volatiles were removed from the filtrate by evaporation under reduced pressure. Kugelrohr distillation of the residue provided an approximately 1:1 mixture of the *E* and *Z* isomers of the product as a colorless liquid (440 mg, 1.6 mmol, 100%): bp 60 °C (1.4 Torr); ^1H NMR (90 MHz, $CDCl_3$) δ 0.01 and 0.03 (2 s, 9 H), 1.3–2.7 (m, 9 H), 1.56 (bd, ^3J = 6.5 Hz, 3 H), 5.11 (bq, ^3J = 6.5 Hz, 1 H); MS (CI, isobutane) *m/e* 259, 109.

Trimethyl(2-methyl-1-oxaspiro[2.5]oct-5-yl)stannane (12). A procedure similar to the one used for the epoxidation of stannane **6** provided a mixture of the diastereomers of epoxide **12** in 95% yield after chromatographic purification: ^1H NMR (90 MHz, $CDCl_3$) δ 0.01, 0.02, and 0.04 (3 s, 9 H), 0.80–2.0 (m, 12 H), 2.85 and 3.48 (2 q, ^3J = 7 Hz, ^3J = 6 Hz, 1 H).

Reaction of Epoxides 12 Induced by $C_2H_5AlCl_2$. A procedure similar to the one used for epoxides **7** and **8** converted diastereomers **12** into an approximately 3:2 mixture of the two diastereomers of **α-methylbicyclo[3.1.0]hexane-1-methanol (13)**[32] in 98% yield: ^1H NMR (90 MHz, $CDCl_3$) δ 0.26–0.46 (m, 2 H), 0.70–2.4 (m, 8 H), 1.20 and 1.22 (2 d, 3 H), 3.3–3.8 (m, 1 H); MS (CI, isobutane) *m/e* 109.

3-(Trimethylstannyl)cyclopentanone (15). A solution of hexamethyldistannane (1.9 g, 5.8 mmol) in THF (10 mL) was stirred at −23 °C under dry Ar and treated dropwise with a solution of the complex of methyllithium and LiBr (2.8 mL, 1.89 M in ether, 5.3 mmol). The resulting solution was stirred at 0 °C for 15 min and then was cooled to −78 °C and treated with a solution of freshly distilled 2-cyclopentenone (0.39 g, 4.8 mmol) in THF (2 mL). The resulting solution was stirred at −78 °C for 30 min and at 0 °C for 30 min and then was poured into a 1:1 mixture of hexane and water. The phases were separated, the aqueous phase was extracted with hexane, and volatiles were removed from the combined organic extracts by evaporation under reduced pressure. Flash chromatography (silica, hexane (95%)/ethyl acetate (5%))[21] of the residue provided ketone **15** as a colorless liquid (840 mg, 3.4 mmol, 71%): IR (liquid film) 1740 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.09 (s, 9 H), 1.6–2.3 (m, 7 H); MS (CI, isobutane) *m/e* 165, 83. Anal. Calcd for $C_8H_{16}OSn$: C, 38.91; H, 6.54. Found: C, 38.78; H, 6.76.

Trimethyl(3-methylenecyclopentyl)stannane. The procedure used to make stannane **6** was applied to ketone **15** (403 mg, 1.63 mmol). Flash chromatography (silica, hexane (95%)/ethyl acetate (5%))[21] of the crude product yielded unreacted ketone **15** (140 mg, 0.567 mmol, 35%) as well as trimethyl(3-methylenecyclopentyl)stannane, which was isolated as a colorless liquid (188 mg, 0.764 mmol, 72%): ^1H NMR (90 MHz, $CDCl_3$) δ 0.03 (s, 9 H), 1.3–2.3 (m, 7 H), 4.85 (m, 2 H).

Trimethyl(1-oxaspiro[2.4]hept-5-yl)stannane (16). A procedure similar to the one used for the epoxidation of stannane **6** provided a mixture of the diastereomers of epoxide **16** in 84% yield: ^1H NMR (90 MHz, $CDCl_3$) δ 0.05 and 0.07 (2 s, 9 H), 1.5–2.1 (m, 7 H), 2.86 and 2.90 (2 bs, 2 H).

3-(Trimethylstannyl)cycloheptanone (19). A procedure similar to the one used to synthesize stannane **15** converted 2-cycloheptenone into ketone **19** in 89% yield: IR (liquid film) 1700 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.07 (s, 9 H), 1.3–2.1 (m, 9 H), 2.6–2.9 (m, 2 H); MS (CI, isobutane) *m/e* 261, 165. Anal. Calcd for $C_{10}H_{20}OSn$: C, 43.67; H, 7.35. Found: C, 43.07; H, 7.64.

Trimethyl(3-methylenecycloheptyl)stannane (20). Stannane **20** was prepared from ketone **19** by the method used to make stannane **6**. Flash chromatography (silica, hexane)[21] of the crude product provided stannane **20** as a colorless liquid in 95% yield: IR (liquid film) 1635 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.03 (s, 9 H), 1.3–2.7 (m, 11 H), 4.66 (bs, 2 H); MS (CI, isobutane) *m/e* 259, 165, 109.

Trimethyl(1-oxaspiro[2.6]non-5-yl)stannane (21). A procedure similar to the one used for the epoxidation of stannane **6** provided a mixture of the diastereomers of epoxide **21** in 94% yield: ^1H NMR (90 MHz, $CDCl_3$) δ 0.02 (s, 9 H), 1.3–2.1 (m, 11 H), 2.6 (m, 2 H); MS (CI, isobutane) *m/e* 275, 165, 109.

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Reaction of Epoxide 21 Induced by $C_2H_5AlCl_2$. A procedure similar to the one used for epoxides 7 and 8 converted diastereomers 21 into **bicyclo[4.1.0]heptane-1-methanol (22)**, which was purified by flash chromatography (silica, hexane (75%)/ethyl acetate (25%))[21] and isolated in 72% yield. The product was shown by comparison of ^1H NMR spectra to be identical with an authentic sample.[32]

Trimethyl(1-methyl-3-methylenecyclohexyl)stannane (24). A solution of 3-methyl-3-(trimethylstannyl)cyclohexanone (23; 824 mg, 3.00 mmol)[34] in CH_2Cl_2 (40 mL) was stirred at 25 °C under dry Ar and treated with aliquots of Lombardo reagent[36] until thin-layer chromatography (silica, hexane (95%)/ethyl acetate (5%)) indicated that the reaction was complete. The resulting mixture was poured into equal volumes of ether and half-saturated aqueous $NaHCO_3$, the organic phase was separated and washed successively with 5% aqueous $NaHCO_3$, water, and brine, and volatiles were removed from the organic phase by evaporation under reduced pressure. Flash chromatography (silica, hexane)[21] of the residue provided stannane 24 as a colorless liquid (660 mg, 2.42 mmol, 81%): IR (liquid film) 1650 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.02 (s, 9 H), 1.10 (s, 3 H), 1.3–2.6 (m, 8 H), 4.6 (m, 2 H); MS (CI, isobutane) m/e 259, 165, 109.

(3S*,5R*)- and (3R*,5R*)-Trimethyl(5-methyl-1-oxaspiro[2.5]oct-5-yl)stannane (25 and 26). A procedure similar to the one used for the epoxidation of stannane 6 provided a 1:2 mixture of diastereomeric epoxides 25 and 26. Flash chromatography (silica, hexane (99%)/ethyl acetate (1%))[21] separated the mixture into three fractions. The first contained pure epoxide 25, a colorless liquid isolated in 19% yield; the third contained pure epoxide 26, a colorless solid isolated in 43% yield; and the second contained an additional 21% yield of a mixture of both epoxides. Epoxide 25: ^1H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 9 H), 1.14 (s, 3 H), 1.28–1.88 (m, 8 H), 2.59 (d, ^2J = 4.8 Hz, 1 H), 2.62 (d, ^2J = 4.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −10.51, 22.41, 27.00, 29.68, 32.99, 37.45, 45.15, 54.39, 57.59 ($^3J(^{119}Sn,C)$ = 25.8 Hz); MS (CI, isobutane) m/e 291, 275, 183, 165, 109. Anal. Calcd for $C_{11}H_{22}OSn$: C, 45.71; H, 7.69. Found: C, 45.53; H, 7.53. Epoxide 26: ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 9 H), 1.18 (s, 3 H), 1.40–1.70 (m, 6 H), 1.83–1.92 (m, 2 H), 2.53 (dd, ^2J = 4.8 Hz, ^4J = 1.5 Hz, 1 H), 2.60 (dd, ^2J = 4.8 Hz, ^4J = 1.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −10.41, 23.18, 27.43, 31.32, 33.30, 37.82, 45.73, 54.95, 58.01 ($^3J(^{119}Sn,C)$ = 19.6 Hz); HRMS (EI) calcd for $C_{11}H_{22}OSn$ 290.0686, found 290.0805.

Reaction of Epoxide 25 Induced by $C_2H_5AlCl_2$. A procedure similar to the one used for epoxides 7 and 8 converted epoxide 25 into **5-methylbicyclo[3.1.0]hexane-1-methanol (27)**, which was isolated as a pale yellow liquid in 75% yield: ^1H NMR (90 MHz, $CDCl_3$) δ 0.14 (d, ^2J = 5.0 Hz, 1 H), 0.57 (d, ^2J = 5.0 Hz, 1 H), 1.18 (s, 3 H), 0.7–2.4 (m, 7 H), 3.65 (d, ^3J = 2.4 Hz, 2 H).

Reaction of Epoxide 26 Induced by $C_2H_5AlCl_2$. A similar procedure converted epoxide 26 (100 mg, 0.35 mmol) into an inseparable 1:3 mixture (17 mg, 0.13 mmol, 37%) **5-methylbicyclo[3.1.0]hexane-1-methanol (27)** and **3-methyl-2-cyclohexene-1-methanol (28)**.[40]

***cis*-Octahydro-4a-methyl-8a-(trimethylstannyl)-2(1*H*)-naphthalenone (37).** A solution of hexamethyldistannane (6.28 g, 19.2 mmol) in THF (30 mL) was stirred at −23 °C under dry Ar and treated dropwise with a solution of methyllithium (12.0 mL, 1.55 M in ether, 18.6 mmol). The resulting solution was stirred at −23 °C for 15 min and at 0 °C for 25 min and then was cooled to −78 °C and treated with a freshly recrystallized sample of the dimethyl sulfide complex of CuBr (1.91 g, 9.29 mmol).[59] The solution of cuprate was stirred at −78 °C for 25 min and then was treated dropwise with a solution of octalone 38 (1.32 g, 8.04 mmol)[43] in THF (4 mL). The mixture was stirred at −78 °C for 1 h, at 0 °C for 1 h, and at 25 °C for 13 h, and then 10% aqueous NH_4Cl was added. The resulting mixture was diluted with ether, and the organic phase was washed successively with 10% aqueous NH_4Cl and brine. Volatiles were then removed by evaporation under reduced pressure, and the residue was separated into two fractions by flash chromatography (silica, hexane (96%)/ethyl acetate (4%)).[21] One contained recovered octalone 38 (401 mg, 2.44 mmol, 30%), and the other contained stannane 37, a colorless solid (1.82 g, 5.53 mmol, 69%): IR (liquid film) 1715 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.12 (s, 9 H), 1.25 (s, 3 H), 1.4–2.6 (m, 14 H); MS (CI, isobutane) m/e 315, 165. Anal. Calcd for $C_{14}H_{28}OSn$: C, 51.09; H, 7.98. Found: C, 51.34; H, 8.24.

***trans*-Octahydro-4a-methyl-8a-(trimethylstannyl)-2-(1*H*)-naphthalenone (39).** Octalone 38 (1.59 g, 9.68 mmol)[43] was added to (trimethylstannyl)lithium according to the procedure used for the synthesis of stannane 15. The mixture was stirred at −78 °C for 40 min and then was warmed slowly to 25 °C and stirred for 20 h. The resulting solution was poured into a 1:1 mixture of hexane and water. The phases were separated, the aqueous phase was extracted with hexane, and volatiles were removed from the combined organic phases by evaporation under reduced pressure. Flash chromatography (silica, hexane (95%)/ethyl acetate (5%))[21] of the residue provided stannane 39 as a colorless solid (2.76 g, 8.39 mmol, 87%): mp 128–130 °C; IR (KBr) 1710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 9 H), 1.06 (s, 3 H), 1.24–1.70 (m, 10 H), 2.35–2.46 (m, 4 H); MS (CI, isobutane) m/e 315, 165, 135. Anal. Calcd for $C_{14}H_{26}OSn$: C, 51.09; H, 7.98. Found: C, 51.44; H, 8.11.

Reduction of Stannane 39. A solution of stannane 39 (504 mg, 1.53 mmol) in ether (8 mL) was added dropwise at 0 °C under dry Ar to a stirred suspension of $LiAlH_4$ (152 mg, 4.00 mmol) in ether (12 mL). The mixture was stirred at 0 °C for 15 min, water was added to destroy excess hydride, and enough 10% aqueous H_2SO_4 was added to dissolve the solids. The aqueous phase was extracted with ether, and volatiles were removed from the combined organic phases by evaporation under reduced pressure. Flash chromatography (silica, hexane (90%)/ethyl acetate (10%))[21] separated the residue into two components. The first to be eluted was **(2α,4aβ,8aα)-(±)-decahydro-4a-methyl-8a-(trimethylstannyl)-2-naphthalenol (40)**, which was isolated as a white paste (329 mg, 0.994 mmol, 65%): ^1H NMR (90 MHz, $CDCl_3$) δ 0.13 (s, 9 H), 0.90 (s, 3 H), 1.1–2.1 (m, 15 H), 4.10 (bs, 1 H, $w_{1/2}$ = 8 Hz): HRMS (EI) calcd for $C_{14}H_{28}OSn$ 332.1154, found 332.1115. The second component to be eluted was **(2β,4aβ,8aα)-(±)-decahydro-4a-methyl-8a-(trimethylstannyl)-2-naphthalenol (41)**, which was isolated as a white paste (159 mg, 0.480 mmol, 31%): ^1H NMR (90 MHz, $CDCl_3$) δ 0.17 (s, 9 H), 0.96 (s, 3 H), 1.2–1.9 (m, 15 H), 3.95 (m, 1 H, $w_{1/2}$ = 20 Hz); HRMS (EI) calcd for $C_{14}H_{28}OSn$ 332.1154, found 332.1161.

***cis*-Decahydro-4a-methyl-2-methylene-8a-(trimethylstannyl)naphthalene.** Treatment of stannane 37 with Lombardo reagent[36] under the conditions used to prepare stannane 24 produced the corresponding olefin as a colorless liquid in 95% yield: IR (liquid film) 1650 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.06 (s, 9 H), 1.07 (s, 3 H), 0.99–2.17 (m, 14 H), 4.59 (bd, 2 H); HRMS (EI) calcd for $C_{15}H_{28}Sn$ 328.1205, found 328.1206.

(2β,4aβ,8aβ)- and (2α,4aβ,8aβ)-Octahydro-4a-methyl-8a-(trimethylstannyl)spiro[naphthalene-2(1*H*),2′-oxirane] (33 and 34). A solution of the preceding olefin (130 mg, 0.40 mmol) in CH_2Cl_2 (8 mL) was stirred at 0 °C and treated with solid *m*-chloroperbenzoic acid (110 mg, 85%, 0.54 mmol). The resulting mixture was stirred at 25 °C for 17 h, diluted with CH_2Cl_2, and washed successively with 10% aqueous sodium thiosulfate, saturated aqueous $NaHCO_3$, water, and brine. Volatiles were removed from the organic phase by evaporation under reduced pressure. Flash chromatography (silica, hexane (99%)/ethyl acetate (1%))[21] separated the residue into two components. The first to be eluted was epoxide 33, which was isolated as an oily white solid (64 mg, 0.19 mmol, 48%): ^1H NMR (90 MHz, $CDCl_3$) δ 0.08 (s, 9 H), 1.10 (s, 3 H), 1.2–2.4 (m, 14 H), 2.61 (bs, 2 H); MS (CI, isobutane) m/e 329, 183, 165, 163; HRMS (EI) calcd for $C_{15}H_{28}OSn$ 344.1154, found 344.1164. The second component to be eluted was epoxide 34, which was isolated as a colorless liquid (42 mg, 0.12 mmol, 30%): ^1H NMR (90 MHz, $CDCl_3$) δ 0.08 (s, 9 H), 1.06 (s, 3 H), 1.2–2.4 (m, 14 H), 2.70 (bs, 2 H); MS (CI, isobutane) m/e 329, 165, 163; HRMS (EI) calcd for $C_{15}H_{28}OSn$ 344.1154, found 344.1166.

***trans*-Decahydro-4a-methyl-2-methylene-8a-(trimethylstannyl)naphthalene.** Treatment of stannane 39 with Lombardo reagent[36] under the conditions used to prepare stannane 24 produced the corresponding olefin as a glassy solid in 89% yield: IR (liquid film) 1645 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.11 (s, 9 H), 0.99 (s, 3 H), 1.2–1.7 (m, 10 H), 2.2 (m, 4 H), 4.64 (m, 2 H); MS (CI, isobutane) m/e 313, 163.

(2β,4aβ,8aα)-Octahydro-4a-methyl-8a-(trimethylstannyl)spiro[naphthalene-2(1*H*),2′-oxirane] (35). A pro-

cedure similar to the one used for the epoxidation of stannane **6** provided epoxide **35**, a colorless solid, in 44% yield after chromatographic purification: mp 121–124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 9 H), 1.04 (s, 3 H), 1.23–1.80 (m, 12 H), 2.06 (dd, ^2J = 14.2 Hz, ^4J = 1.7 Hz, 1 H), 2.21–2.31 (m, 1 H), 2.64 (dd, ^2J = 5.1 Hz, ^4J = 1.7 Hz, 1 H), 2.70 (dd, ^2J = 5.1 Hz, ^4J = 1.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −3.97, 15.12, 20.67, 23.06, 28.82, 33.02, 36.71, 39.39, 40.02, 40.65, 49.27, 56.59 (^3J(^{119}Sn,^{13}C) = 9.30 Hz), 60.17; MS (CI, isobutane) *m/e* 345, 329, 179, 165, 163; HRMS (EI) calcd for $C_{15}H_{28}OSn$ 344.1154, found 344.1160. Anal. Calcd for $C_{15}H_{28}OSn$: C, 52.50; H, 8.24. Found: C, 52.88; H, 8.89.

(2*S,4a*R**,8a*S**)-Decahydro-4a-methyl-8a-(trimethylstannyl)-2-[(methylthio)methyl]-2-naphthalenol (43).** A solution of butyllithium (3.2 mL, 0.94 M in hexane, 3.0 mmol) was stirred at 0 °C under dry Ar and treated dropwise with *N,N,N′,N′*-tetramethylethylenediamine (350 mg, 3.0 mmol). The mixture was stirred at 25 °C for 30 min, cooled to 0 °C, and then treated dropwise with dimethyl sulfide (190 mg, 3.1 mmol). The resulting solution was kept at 25 °C for 3.5 h, cooled to −78 °C, and treated dropwise with a solution of stannane **39** (404 mg, 1.23 mmol) in THF (1.5 mL). The resulting solution was kept at −78 °C for 45 min and at 25 °C for 1 h and was then poured into a mixture of ether and 10% aqueous NH_4Cl. The organic phase was separated and washed successively with water and brine. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (99%)/ethyl acetate (1%)).[21] This provided alcohol **43** as a colorless liquid (214 mg, 0.547 mmol, 45%): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.13 (s, 9 H), 0.87 (s, 3 H), 1.2–1.8 (m, 15 H), 2.17 (s, 3 H), 2.58 (m, 2 H).

(2α,4aβ,8aα)-Octahydro-4a-methyl-8a-(trimethylstannyl)spiro[naphthalene-2(1*H*),2′-oxirane] (36). Iodomethane (1.8 g, 13 mmol) was added to a solution of alcohol **43** (200 mg, 0.511 mmol) in acetone (4 mL), and the mixture was stirred at 25 °C for 17 h. Removal of volatiles by evaporation under reduced pressure left a white solid residue of the methylsulfonium iodide derived from alcohol **43**. A suspension of this material in THF (7 mL) was stirred at 25 °C under dry Ar and treated with freshly sublimed $KOBu^t$ (76 mg, 0.68 mmol). The mixture was stirred at 25 °C for 4 h and treated with 5% aqueous $NaHCO_3$. The product was extracted with ether, and the combined extracts were washed successively with saturated aqueous $NaHCO_3$ and brine. Removal of volatiles by evaporation under reduced pressure left a residue that was purified by flash chromatography (silica, hexane (99%)/ethyl acetate (1%)).[21] This provided epoxide **36** as a white solid (149 mg, 0.434 mmol, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.21 (s, 9 H), 0.97 (s, 3 H), 1.13–1.73 (m, 12 H), 2.01 (d, ^2J = 15.1 Hz, 1 H), 2.30 (m, 1 H), 2.51 (d, ^2J = 4.8 Hz, 1 H), 2.53 (d, ^2J = 4.8 Hz, 1 H); MS (CI, isobutane) *m/e* 329, 163; HRMS (EI) calcd for $C_{15}H_{28}OSn$ 344.1154, found 344.1161.

Reaction of Epoxide 33 Induced by $C_2H_5AlCl_2$. Epoxide **33** (120 mg, 0.350 mmol) was treated with $C_2H_5AlCl_2$ under conditions similar to those used for epoxides **7** and **8**, and the crude product was purified by flash chromatography (silica, hexane (90%)/ethyl acetate (10%)).[21] The first fraction to be eluted contained ***cis*-decahydro-4a-methyl-8a-(trimethylstannyl)-2-naphthaldehyde (46)**, which was isolated as a colorless liquid (36.4 mg, 0.106 mmol, 30%): IR (liquid film) 1725 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.10 (s, 9 H), 1.01 (s, 3 H), 1.1–2.3 (m, 15 H), 9.61 (d, ^3J = 1.8 Hz, 1 H); MS (CI, isobutane) *m/e* 345, 329, 165. The second fraction contained ***cis*-2,3,4,4a,5,6,7,8-octahydro-4a-methyl-2-naphthalenemethanol (45a)**, which was isolated as a colorless liquid (33.6 mg, 0.186 mmol, 53%): IR (liquid film) 3340 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (s, 3 H), 1.17–1.80 (m, 11 H), 2.01 (bd, 1 H), 2.20 (m, 2 H), 3.51 (m, 2 H), 5.18 (s, 1 H); MS (CI, isobutane) *m/e* 181, 163; HRMS (EI) calcd for $C_{12}H_{20}O$ 180.1509, found 180.1522. This material contained small amounts of inseparable cyclopropane **44**, which was identified by the following characteristic ^{1}H NMR signals (90 MHz, $CDCl_3$): δ −0.02 (d, ^2J = 5.0 Hz, 1 H), 0.58 (d, ^2J = 5.0 Hz, 1 H), 0.99 (s, 3 H), 3.62 (d, 1 H), 3.72 (d, 1 H).

Reaction of Epoxide 34 Induced by $C_2H_5AlCl_2$. Epoxide **34** (114 mg, 0.332 mmol) was treated with $C_2H_5AlCl_2$ under conditions similar to those used for epoxide **33**. Chromatographic purification of the crude product provided aldehyde **46** (14 mg, 0.042 mmol, 13%) and an inseparable mixture containing alcohols **45a** and **45b** (40.8 mg).

Reaction of Epoxide 35 Induced by $C_2H_5AlCl_2$. Epoxide **35** (112 mg, 0.326 mmol) was treated with $C_2H_5AlCl_2$ under conditions similar to those used for epoxides **7** and **8**. Flash chromatography[21] separated the crude product into two components. The first to be eluted was ***trans*-decahydro-4a-methyl-8a-(trimethylstannyl)-2-naphthaldehyde (49)**, which was isolated as a colorless liquid (8.4 mg, 0.024 mmol, 7%): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.19 (s, 9 H), 0.91 (s, 3 H), 1.2–1.9 (m, 15 H), 9.59 (d, 1 H). The second compound to be eluted was ***trans*-2,3,4,4a,5,6,7,8-octahydro-4a-methyl-2-naphthalenemethanol (45b)**, which was isolated as a colorless liquid (44.1 mg, 0.245 mmol, 75%): IR (liquid film) 3330 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (s, 3 H), 1.18–1.80 (m, 11 H), 1.98 (bd, 1 H), 2.21 (m, 2 H), 3.53 (m, 2 H), 5.21 (d, ^3J = 2.2 Hz, 1 H); HRMS (EI) calcd for $C_{12}H_{20}O$ 180.1509, found 180.1518. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.31; H, 10.97.

Reaction of Epoxide 36 Induced by $C_2H_5AlCl_2$. A procedure similar to the one used for epoxide **35** converted epoxide **36** into alcohol **45b** (69%) and minor amounts of aldehyde **49** (5%).

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Registry No. **4**, 53823-06-6; (±)-**5**, 131905-33-4; (±)-**6**, 131905-34-5; (±)-**7**, 131905-35-6; (±)-**8**, 131905-36-7; (±)-**9**, 131905-37-8; **10**, 131905-38-9; (±)-**12** (isomer 1), 131905-39-0; (±)-**12** (isomer 2), 132015-31-7; (±)-**12** (isomer 3), 132015-32-8; (±)-**12** (isomer 4), 132015-33-9; (±)-**13** (isomer 1), 71183-85-2; (±)-**13** (isomer 4), 71129-81-2; (±)-**15**, 131905-40-3; (±)-*cis*-**16**, 131905-41-4; (±)-*trans*-**16**, 131905-66-3; (±)-**17** (isomer 1), 131905-42-5; (±)-**17** (isomer 2), 131905-67-4; **18**, 1121-66-0; (±)-**19**, 131905-43-6; (±)-**20**, 131905-44-7; (±)-*cis*-**21**, 131905-45-8; (±)-*trans*-**21**, 131905-68-5; (±)-**22**, 131905-46-9; (±)-**23**, 131905-47-0; (±)-**24**, 131905-48-1; (±)-**25**, 131905-49-2; (±)-**26**, 131905-50-5; (±)-**27**, 131905-51-6; (±)-**28**, 98442-48-9; (±)-**31**, 60102-91-2; (±)-**32**, 131905-52-7; (±)-**33**, 131905-53-8; (±)-**34**, 132015-27-1; (±)-**35**, 132015-28-2; (±)-**36**, 132015-29-3; (±)-**37**, 131905-54-9; (±)-**38**, 40573-28-2; (±)-**39**, 131905-55-0; (±)-**40**, 131905-56-1; (±)-**41**, 131905-57-2; (±)-**42**, 111238-76-7; (±)-**43**, 131905-58-3; (±)-**44**, 131905-59-4; (±)-**45a**, 131905-60-7; (±)-**45b**, 131905-71-0; (±)-**46**, 131905-61-8; (±)-**49**, 132015-30-6; (±)-**51**, 131905-62-9; (±)-**52**, 58407-30-0; (*E*)-(±)-(3-ethylidenecyclohexyl)trimethylstannane, 131905-64-1; (*Z*)-(±)-(3-ethylidenecyclohexyl)trimethylstannane, 131905-63-0; 2-cyclopentenone, 930-30-3; (±)-(3-methylenecyclopentyl)trimethylstannane, 131905-65-2; *cis*-(±)-decahydro-4a-methyl-2-methylene-8a-(trimethylstannyl)naphthalene, 131905-69-6; *trans*-(±)-decahydro-4a-methyl-2-methylene-8a-(trimethylstannyl)naphthalene, 131905-70-9.

Supplementary Material Available: NMR spectra of key compounds **6–8**, **15**, **19–21**, **24–26**, **33–37**, **39**, **45a**, and **45b** (17 pages). Ordering information is given on any current masthead page.