Stereoselective Access to Hydroxy Oxetanes and Tetrahydrooxepines through Isomerization of Oxiranyl Ethers

Alessandro Mordini,* Simona Bindi, Antonella Capperucci, Daniele Nistri, Gianna Reginato, and Michela Valacchi

Centro CNR Composti Eterociclici, Dipartimento di Chimica Organica "U. Schiff", via G. Capponi 9, I-50121 Firenze, Italy

mordini@chimorg.unifi.it

Received April 18, 2000

We have shown in the past few years[1−3] that allyl, benzyl, and propargyl 2,3-epoxy ethers (**1a**, **1b**, and **1c**, respectively, Scheme 1) can be regio- and stereoselectively converted into 2-vinyl-, 2-phenyl-, or 2-alkynyl-3-(α-hydroxyalkyl)oxetanes (**2a**, **2b**, and **2c**, respectively) by treatment with the Schlosser's base[4] (butyllithium/potassium *tert*-butoxide) or other superbasic mixtures[5,6] such as lithium diisopropylamide/potassium *tert*-butoxide (LIDAKOR[7]).

The formation of oxetanes (a) is favored over the alternative five-membered ring cyclization (b) for the benzyl and propargyl oxiranyl ethers **1b** and **1c** and over the 5- (b), 6- (c) and 7-membered (d) ring formation for the allyl oxiranyl ethers **1a** (Scheme 2).[8]

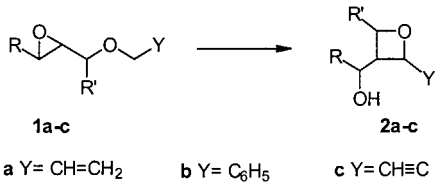
Monosubstituted oxiranes derived from allyl vinyl carbinols (**1**, R = H, R′ = alkyl) are a more intriguing case because the absence of any substituent on one ring carbon may favor to a certain extent the formation of a 5-membered ring (b) with benzyl- or propargyl-substituted substrates (**1b** and **1c**, R = H, R′ = alkyl) and a 5- (b) or 7-membered ring (d) with allyl derivatives (**1a**, R = H, R′ = alkyl).

Previous reports on this matter[9,10] have shown indeed that allyl glycidyl ether **3** is converted into a mixture of *trans*-3-(hydroxymethyl)-2-vinyloxetane **4** and 3-hydroxytetrahydrooxepine **5** upon treatment with *sec*-butyllithium in THF/HMPT at −70 °C (Scheme 3).[9] When alkyl substituents are present on different positions of the allyl glycidyl ether, similar reaction conditions[10] afford usually the tetrahydrooxepine derivative as the major product albeit in less than 50% yield.

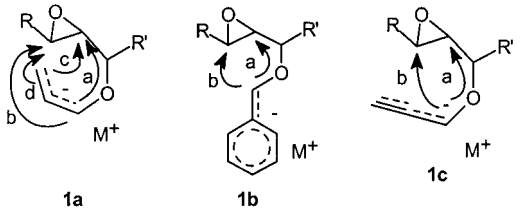
Owing to our previous experience, we have decided to investigate the mixed metal base promoted isomerization of terminal oxiranyl ethers of type **6**, readily prepared via epoxidation of the corresponding allylic alcohols (Scheme 4, Table 1).

Compounds **6g**−**j** have been clearly converted into 2-phenyl- and 2-alkynyl-substituted oxetanes **7g**−**j** in good yields by treatment with the superbase LIDAKOR. The relative stereochemistry of substituents in positions 3 and 4 of the oxetane ring is due to the configuration of the starting epoxy ether, while the *cis* or *trans* relationship between substituents in position 2 and 3 arises during the cyclization step. The selectivity is the one expected according to our previous findings,[3] the *trans*-isomers being always preferred. Compounds **7h** and **7j** are particularly interesting in view of an application to the synthesis of the oxetane containing nucleoside oxetanocin, which has received a great deal of attention in recent years[11−17] due to its potent activity as an antiviral, antibiotic, and antitumor[16] agent.

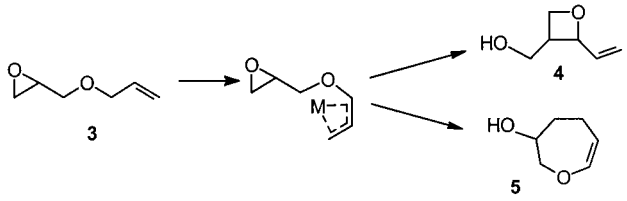
Scheme 1



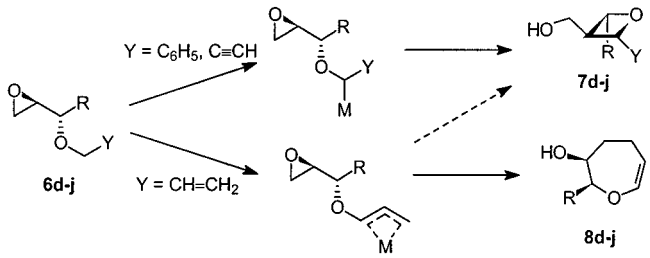
Scheme 2



Scheme 3



Scheme 4



(1) Mordini, A.; Valacchi, M.; Nardi, C.; Bindi, S.; Poli, G.; Reginato, G. *J. Org. Chem.* **1997**, *62*, 8557.
(2) Mordini, A.; Bindi, S.; Pecchi, S.; Capperucci, A.; Degl'Innocenti, A.; Reginato, G. *J. Org. Chem.* **1996**, *61*, 4466.
(3) Mordini, A.; Bindi, S.; Pecchi, S.; Degl'Innocenti, A.; Reginato, G.; Serci, A. *J. Org. Chem.* **1996**, *61*, 4374.
(4) Schlosser, M. *J. Organomet. Chem.* **1967**, *8*, 9.
(5) Mordini, A. In *Advances in Carbanion Chemistry*; Snieckus, V., Ed.; JAI Press: Greenwich CT, 1992; Vol. 1, p 1.
(6) Mordini, A. In *Comprehensive Organometallic Chemistry II*; M. A. v., Ed.; Pergamon Press: Oxford, 1995; Vol. 11, p 93.
(7) Margot, C.; Schlosser, M. *Tetrahedron Lett.* **1985**, *26*, 1035.
(8) Still, W. C. *Tetrahedron Lett.* **1976**, *25*, 2115.
(9) Ichikawa, Y.; Niitsuma, S.; Kuniki, K.; Takita, T. *J. Chem. Soc., Chem. Commun.* **1988**, 625.
(10) Bird, C. W.; Hormozi, N. *Tetrahedron Lett.* **1990**, *31*, 3501.
(11) Hambalek, R.; Just, G. *Tetrahedron Lett.* **1990**, *31*, 5445.
(12) Niitsuma, S.; Ichikawa, Y.; Kato, K.; Takita, T. *Tetrahedron Lett.* **1987**, *28*, 4713.
(13) Niitsuma, S.; Ichikawa, Y.; Kato, K.; Takita, T. *Tetrahedron Lett.* **1987**, *28*, 3967.
(14) Nishiyama, S.; Yamamura, S.; Kato, K.; Takita, T. *Tetrahedron Lett.* **1988**, *29*, 4743.
(15) Nishiyama, S.; Yamamura, S.; Kato, K.; Takita, T. *Tetrahedron Lett.* **1988**, *29*, 4739.

10.1021/jo0005924 CCC: $20.00
Published on Web 04/11/2001

Table 1. Regio- and Stereoselective Outcome in the Cyclization of Epoxy Ethers 6

	R	Y	**7** (*cis*:*trans*): **8** (*cis*:*trans*)	yield[a] (%)
6d	H	CH_2=CH	2:98 (98:2)	90 (45)
6e	C_5H_{11}	CH_2=CH	2:98 (98:2)	94 (65)
6f	CH_2OSiMe_2tBu	CH_2=CH	2:98 (98:2)	68 (53)
6g	C_5H_{11}	C_6H_5	98 (5:95):2	70 (53)
6h	CH_2OSiMe_2tBu	C_6H_5	98 (2:98):2	89 (55)
6i	C_5H_{11}	CH≡C	98 (20:80):2	95 (55)
6j	CH_2OSiMe_2tBu	CH≡C	98 (15:85):2	83 (50)

[a] Calculated by ^{1}H NMR analysis; the yields of isolated products are given in parentheses.

Allyl oxiranyl ethers **6d**−**f** have shown a remarkably selective behavior in their treatment with the Schlosser's base. Only the cyclization to 7-membered rings is followed, leading to the *cis*-tetrahydrooxepines **8d**−**f** in reasonable yields. It is worth noting that previous similar experiments[9,10] conducted with organolithium reagents have led to mixtures of 7- and 4-membered-ring products. It is reasonable to assume that the preference for oxepine formation found in this case is ascribed to the higher preference of the allylpotassium species compared with the lithium analogues, to react at their terminal position.[18]

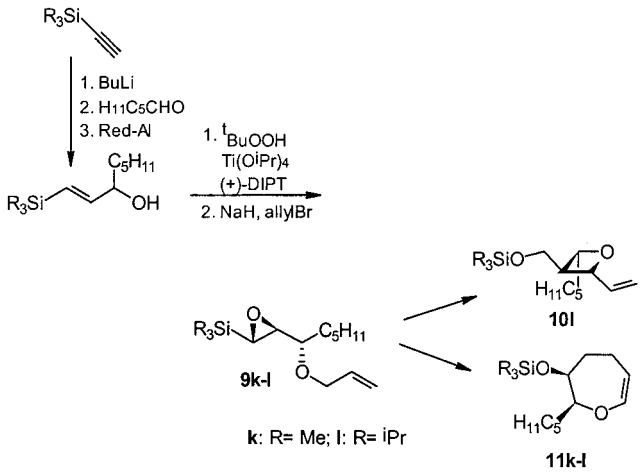
The tetrahydrooxepines **8d**−**f** are all obtained as pure *cis* isomers which are the ones expected for a carbanionic attack on an *erythro* oxirane, without any loss of stereochemical integrity. Interestingly, the oxepines are not configurationally stable and undergo an isomerization to a 50:50 *cis*:*trans* mixture in $CDCl_3$.

To assess the steric and/or electronic influence of a trialkylsilyl group on the cyclization process, we have decided to investigate the isomerization of trialkysilyl substituted oxiranes **9k**,**l**, which are readily prepared from the commercially available trialkylsilyl acetylene via lithiation and reaction with hexanal followed by reduction of the triple bond, Sharpless epoxidation,[19] and allylation of the epoxy alcohol (Scheme 5).

The trimethylsilyl-substituted compound **9k** gives, upon treatment with Schlosser's base, the tetrahydrooxepine **11k** as the only product while the more hindered triisopropyl derivative **9l** leads to a mixture of 4-membered and 7-membered ring products in a 72:28 ratio. Thus, the trialkylsilyl substituent exerts both steric and electronic effects on the mode of cyclization (alkyl-substituted oxiranes give only oxetanes in the same reaction conditions).

In conclusion, we have demonstrated that the superbase-promoted isomerization of oxiranyl ethers is a useful process selectively leading to trisubstituted oxetanes[20,21] or to disubstituted tetrahydrooxepines,[22] both classes of compounds being of high synthetic potential.

Scheme 5



Experimental Section

General Procedures. Air- and moisture-sensitive compounds were stored in Schlenk tubes or in Schlenk burets. They were protected by and handled under an atmosphere of 99.99% pure nitrogen. Ethereal extracts were dried with sodium sulfate. The temperature of dry ice−ethanol baths is consistently indicated as −78 °C, that of ice baths as 0 °C, and "room temperature" as 25 °C. Purifications by flash column chromatography[23] were performed using glass columns (10−50 mm wide); silica gel 230−400 mesh was chosen as stationary phase (15 cm high), with an elution rate of 5 cm/min. Nuclear magnetic resonance spectra of hydrogen nuclei were recorded at 200 or 500 MHz. Chemical shifts were determined relative to the residual solvent peak ($CHCl_3$: 7.26 ppm). Coupling constants (*J*) are measured in Hz. Coupling patterns are described by abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), dd (doublet of a doublet), m (multiplet), bs (broad singlet). Nuclear magnetic resonance spectra of carbon-13 nuclei were recorded at 50.3 or 75.5 MHz. Chemical shifts were determined relative to the residual solvent peak ($CHCl_3$: 77.0 ppm). Mass spectra were obtained at a 70 eV ionization potential.

Materials. Starting materials were commercially available unless otherwise stated. All commercial reagents were used without further purification except diisopropylamine, which was distilled over calcium hydride. Anhydrous tetrahydrofuran was distilled from sodium diphenylketyl. Dimethylformamide was distilled over calcium hydride and then stored over 4 Å molecular sieves. Methylene chloride was dried over calcium chloride and stored over 4 Å molecular sieves. Petroleum ether, unless specified, was the 40−70 °C boiling fraction.

1. Preparation of Oxiranyl Ethers 6e,g,i. 1-Octen-3-ol (1.92 g, 15 mmol) and vanadyl acetylacetonate (0.07 g, 0.25 mmol) were dissolved in CH_2Cl_2 (45 mL) under N_2 and cooled to 0 °C. Then *t*-BuOOH (5.4 mL of 5.5 M solution in decane, dried over molecular sieves, 30 mmol) was slowly added. The mixture was stirred at room temperature for 16 h, washed with saturated aqueous $Na_2S_2O_3$ and brine, and dried. After evaporation of the solvent, the residue was purified by column chromatography (petroleum ether/ethyl acetate, 2:1), affording 1.41 g (65%) of a 80:20 mixture of *erythro*- and *threo*-1,2-epoxyoctan-3-ol.[24] *Erythro*: ^{1}H NMR ($CDCl_3$, 200 MHz) (erythro): δ 3.9−3.8 (1H, m); 3.02 (1H, ddd, J = 5.8, 3.8, 2.8 Hz); 2.81 (1H, dd, J = 4.8, 2.8 Hz); 2.73 (1H, dd, J = 4.8, 3.8 Hz); 2.0−1.7 (1H, bs); 1.6−1.2 (8H, m); 0.89 (3H, t, J = 6.6 Hz). The epoxy alcohol (1.41 g, 9.7 mmol) was dissolved in DMF (10 mL), and after cooling to −5 °C, a suspension of NaH (0.40 g, 10 mmol) in DMF (10 mL) was added during 30 min. After an additional 30 min, a solution of the suitable halide (10 mmol; e: CH_2=$CHCH_2Br$, g: $C_6H_5CH_2Br$, i: CH≡CCH_2Br) in DMF (10 mL) was added, and the mixture warmed to 25 °C, and then stirred for 15 h, before

(16) Norbeck, D. W.; Kramer, J. B. *J. Am. Chem. Soc.* **1988**, *110*, 7217.
(17) Wilson, F. X.; Fleet, G. W. J.; Vogt, K.; Wang, Y.; Witty, D. R.; Choi, S.; Storer, R.; Myers, P. L.; Wallis, C. J. *Tetrahedron Lett.* **1990**, *31*, 6931.
(18) Schlosser, M.; Desponds, O.; Lehmann, R.; Moret, E.; Rauchschwalbe, G. *Tetrahedron* **1993**, *49*, 10175.
(19) Okamoto, S.; Shimazaki, T.; Kobayashi, Y.; Sato, F. *Tetrahedron Lett.* **1987**, *28*, 2033.
(20) Linderman, R. J. In *Comprehensive Heterocyclic Chemistry II*; Padwa, A., Ed.; Pergamon: Oxford, 1996; Vol. 1B, pp 755−771.
(21) Linderman, R. J. In *Comprehensive Heterocyclic Chemistry II*; Padwa, A., Ed.; Pergamon: Oxford, 1996; Vol. 1B, pp 721−753.
(22) Hoberg, J. O. *Tetrahedron* **1988**, *54*, 12631.
(23) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(24) Kitano, Y.; Matsumoto, T.; Sato, F. *Tetrahedron* **1988**, *44*, 4073.

it was treated with H_2O (7 mL) and extracted with ether. The organic phase was washed with H_2O and saturated NaCl and dried. After evaporation of the solvent, the oxiranyl ethers (**6e**,**g**,**i**) were purified by chromatography; only the *erythro* isomer was fully characterized and further used.

3-(2-Propenoxy)-1,2-epoxyoctane 6e. Purification: eluent petroleum ether/ethyl acetate 15:1; yield 56%; *erythro*:*threo* 78:22. ^{1}H NMR ($CDCl_3$, 200 MHz): *erythro*: 5.90 (1H, ddt, J = 17.2, 10.2, 5.6 Hz); 5.25 (1H, app dq, J = 17.2, 1.8 Hz); 5.16 (1H, dq, J = 10.2, 1.8 Hz); 4.04 (2H, AB system); 3.2−3.1 (1H, m); 2.89 (1H, ddd, J = 5.4, 4.0, 2.6 Hz); 2.79 (1H, dd, J = 5.4, 4.0 Hz); 2.72 (1H, dd, J = 5.4, 2.6 Hz); 1.6−1.2 (8H, m); 0.89 (3H, t, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ: 135.1; 116.8; 78.1; 71.2; 53.4; 45.6; 32.8; 31.8; 24.8; 22.5; 14.0. MS (*m*/*z*): 183 (0.01, $M^+ - 1$); 141 (37, $M^+ - C_3H_7$); 99 (57); 81 (49); 71 (82); 69 (28); 68 (21); 67 (33); 57 (71); 55 (100). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.42; H, 10.77.

3-Benzyloxy-1,2-epoxyoctane 6g.[25] Purification: eluent petroleum ether/ ethyl acetate 15:1; yield 55%; *erythro*:*threo* 80:20. ^{1}H NMR ($CDCl_3$, 200 MHz): *erythro*: 7.4−7.2 (5H, m); 4.58 (2H, AB system); 3.3−3.2 (1H, m); 2.93 (1H, ddd, J = 5.6, 3.8, 2.6); 2.78 (1H, dd, J = 5.4, 3.8); 2.72 (1H, dd, J = 5.4, 2.6); 1.7−1.2 (8H, m); 0.89 (3H, t, J = 7.0). ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ: 138.6; 128.4; 127.7; 127.6; 78.1; 72.3; 53.6; 45.6; 32.8; 31.8; 24.8; 22.5; 14.0. MS (*m*/*z*): 234 (0.75, M^+); 127 (2.2, $M^+ - OCH_2C_6H_5$); 107 (61); 91 (100, $C_7H_7^+$); 65 (26); 43 (25); 41 (27).

3-(2-Propynoxy)-1,2-epoxyoctane 6i.[26] Purification: eluent petroleum ether/ ethyl acetate 10:1; yield: 54%. *erythro*:*threo* 80:20. ^{1}H NMR ($CDCl_3$, 200 MHz) (*erythro*): 4.22 (2H, AB of ABX); 3.4−3.3 (1H, m); 2.90 (1H, ddd, J = 5.0, 3.2, 2.6); 2.8−2.7 (2H, m); 2.41 (1H, app t, J = 2.6); 1.6−1.2 (8H, m); 0.89 (3H, t, J = 6.6). ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ: 80.0; 77.4; 74.2; 57.3; 53.1; 45.4; 32.6; 31.8; 24.6; 22.5; 14.0. MS (*m*/*z*): 139 (100, $M^+ - C_3H_7$); 111 (69, $M^+ - C_5H_{11}$); 99 (40); 83 (38); 82 (28); 81 (58); 71 (72); 69 (43); 68 (32); 67 (56); 57 (44); 56 (34); 55 (100); 54 (68), 53 (98).

2. Preparation of Oxiranyl Ethers 6f,h,j. 3-Butene-1,2-diol.[27] A mixture of 2-butene-1,4-diol (25 g, 0.28 mol), water (10 mL), concentrated sulfuric acid (0.14 mL), and mercuric sulfate (0.10 g) was heated under reflux. After 1.5 h, the reaction mixture was cooled to 0 °C, neutralized with 10% sodium hydroxide to pH 7, and then distilled. The first fraction, distilled between 50 and 55 °C/15 mmHg, contained water, the second fraction collected between 110 and 115 °C/15 mmHg, contained 3-buten-1,2-diol (13 g, 52%) as a colorless liquid, and the third fraction, collected between 125 and 130 °C/15 mmHg, had traces of unreacted starting material. 3-Butene-1,2-diol. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 5.86 (1H, ddd, J = 17.6, 10.6, 5.8); 5.37 (1H, app dt, J = 17.6, 1.4); 5.24 (1H, app dt, J = 10.6, 1.6); 4.3−4.2 (1H, m); 3.69 (1H, dd, J = 11.4, 3.6); 3.51 (1H, dd, J = 11.4, 7.2), 2.13 (2H, s).

1-[(*tert*-Butyldimethylsilyl)oxy]-3-buten-2-ol.[28] The 3-butene-1,2-diol (2.64 g, 30 mmol) was dissolved in THF (48 mL), and after the solution was cooled to −78 °C, BuLi (18.7 mL of 1.6 M solution in hexane, 30 mmol) was slowly added. After an additional 15 min, *tert*-butyldimethylsilyl chloride (4.53 g, 30 mmol) was added, and the mixture was warmed to 25 °C and then stirred for 15 h. After evaporation of the solvent, the residue was purified by chromatography, eluent petroleum ether/ethyl acetate 7:1 affording 3.84 g (63%) of monoprotected diol. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 5.81 (1H, ddd, J = 17.6, 10.6, 5.8); 5.34 (1H, app dt, J = 17.4, 1.4); 5.19 (1H, app dt, J = 10.6, 1.4); 4.2−4.1 (1H, m); 3.66 (1H, dd, J = 10.0, 3.6); 3.44 (1H, dd, J = 10.0, 7.8); 2.3−2.1 (1H, bs); 0.90 (9H, s); 0.08 (6H, s).

***anti*-(2*S*,3*R*)-1-[(*tert*-butyldimethylsilyl)oxy]-3,4-epoxy-2-butanol.**[29] Ti(*i*-OPr)$_4$ (5.40 g, 19 mmol), CH_2Cl_2 (65 mL), and L-(+)-diisopropyltartrate (5.34 g, 23 mmol) were mixed under N_2 and cooled to −23 °C. 1-[(*tert*-Butyldimethylsilyl)oxy]-3-buten-2-ol (3.84 g, 19 mmol) was then added and the mixture maintained at −23 °C for 30 min before *t*-BuOOH (2.72 mL of a 5.5 M solution in decane, dried over molecular sieves, 15 mmol) was slowly added. After 3 days, the cold reaction mixture was poured into a precooled (−20 °C) solution consisting of 130 mL of reagent-grade acetone containing 5.5 mL of water. The resulting mixture was stirred and allowed to warm to 25 °C. Stirring was continued until the formation of an opaque solution that was filtered. After evaporation of the solvent, the residue was diluted with 130 mL of ether, and then, after cooling to 0 °C, 52 mL of 1 N sodium hydroxide solution was added. This two-phase mixture was stirred at 0 °C for 0.5 h, and then the ether phase was washed with brine and dried (Na_2SO_4). After evaporation of the solvent, 2.52 g of a 60:40 mixture of (2*R*)-1-[(*tert*-butyldimethylsilyl)oxy]-3-buten-2-ol and *anti*-(2*S*,3*R*)-1-[(*tert*-butyldimethylsilyl)oxy]-3,4-epoxy-2-butanol was obtained, and the compounds were separated by chromatography (petroleum ether/ethyl acetate 4:1) to afford 1.14 g of pure *R*-allylic alcohol and 0.70 g (42%) of pure epoxy alcohol. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 3.76 (2H, AB system); 3.55 (1H, app q, J = 5.0 Hz); 3.04 (1H, ddd, J = 5.4, 4.0, 2.6 Hz); 2.81 (1H, dd, J = 5.2, 4.0 Hz); 2.76 (1H, dd, J = 5.2, 2.6 Hz); 2.44 (1H, bs); 0.91 (9H, s); 0.09 (6H, s).

Preparation of Oxiranyl Ethers. General Procedure. Method A. NaH (0.08 g, 3.2 mmol) suspended in THF (5 mL) was added to a precooled (−5 °C) solution of *anti*-(2*S*,3*R*)-1-[(*tert*-butyldimethylsilyl)oxy]-3,4-epoxy-2-butanol (0.70 g, 3.2 mmol) in THF (5 mL). After 30 min at −5 °C, cat. Bu_4NI and then the suitable halide (3.2 mmol) were added, and the mixture was stirred for 3 h at 25 °C before it was treated with water−ice and extracted with ether. The organic phase was washed with brine and dried.

Method B. A suspension of epoxide (0.70 g, 3.2 mmol), benzyltriethylammonium chloride (0.51 g, 2.24 mmol), and the suitable halide (7.0 mmol) in benzene (7 mL) and 70% aq NaOH (7 mL) was stirred vigorously at 25 °C for 14 h. The mixture was extracted with ether, and the organic phase was washed with water and brine and dried.

anti*-(2*S*,3*R*)-2-(2-Propenoxy)-1-[(*tert*-butyldimethylsilyl)oxy]-3,4-epoxybutane 6f.** Compound **6f** was prepared according to procedure A, giving 0.69 g of crude which was then purified by column chromatography (petroleum ether/ethyl acetate 7:1), affording 0.58 g of **6f** (70%) as an *anti*:*syn* (70:30) mixture. ***Anti: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 5.90 (1H, ddt, J = 17.2, 10.2, 5.6 Hz); 5.58 (1H, app dq, J = 17.2, 1.8 Hz); 5.37 (1H, app dq, J = 10.2, 1.8 Hz); 4.10 (2H, AB system); 3.75 (2H, app d, J = 5.6 Hz); 3.35 (1H, m); 3.1−3.0 (1H, m); 2.77 (2H, app d, J = 3.4 Hz); 0.90 (9H, s); 0.07 (6H, s). Anal. Calcd for $C_{13}H_{26}O_3Si$: C, 60.42; H, 10.14. Found: C, 60.32; H, 10.27. ***Syn:*** ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 6.0−5.8 (1H, m); 5.4−5.1 (2H, m); 4.02 (2H, AB system); 3.9−3.7 (1H, m); 3.52 (1H,app s); 3.49 (1H, AB system); 3.1−3.0 (1H, m); 2.7−2.6 (2H, m); 0.87 (9H, s); 0.07 (6H, s). Only the *anti* isomer was further used.

anti*-(2*S*,3*R*)-2-Benzyloxy-1-[(*tert*-butyldimethylsilyl)oxy]-3,4-epoxybutane 6h.** Compound **6h** was prepared according to procedure A, giving 0.80 g of crude which was then purified by column chromatography (petroleum ether/ethyl acetate 10:1), affording 0.59 g of **6h** (60%) as an *anti*:*syn* (71:29) mixture. ***Anti: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.4−7.2 (5H, m); 4.65 (2H, AB system); 3.78 (2H, app d, J = 5.0 Hz); 3.41 (1H, app q, J = 4.9 Hz); 3.08 (1H, ddd, J = 6.6, 3.6, 2.4 Hz); 2.8−2.7 (2H, m); 0.90 (9H, s); 0.06 (6H, s). Anal. Calcd for $C_{17}H_{28}O_3Si$: C, 66.19; H, 9.15. Found: C, 66.32; H, 9.27. ***Syn:*** ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.4−7.2 (5H, m); 4.57 (2H, AB system); 3.9−3.8 (1H, m); 3.54 (2H, app d, J = 5.0 Hz); 3.1−3.0 (1H, m); 2.8−2.7 (2H, m); 0.87 (9H, m); 0.05 (6H, m).

Only the *anti* isomer was further used.

anti*-(2*S*,3*R*)-2-(2-Propynoxy)-1-[(*tert*-butyldimethylsilyl)oxy]-3,4-epoxybutane 6j.** Compound **6j** was prepared according to procedure B, giving 0.17 g of crude which was then purified by column chromatography (petroleum ether/ethyl acetate 7:1), affording 0.15 g of **6j** (70%) as an *anti*:*syn* (71:29) mixture. ***Anti: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 4.29 (2H, d, J = 2.2 Hz); 3.8−3.7 (2H, m); 3.52 (1H, m); 3.05 (1H, ddd, J = 6.6, 5.2, 3.4 Hz); 2.80 (1H, app d, J = 2.8 Hz); 2.71 (1H, app d, J =

(25) Sato, F.; Kobayashi, Y.; Takahashi, O.; Osamu, C.; Tsunehisa, T.; Takeda, Y.; Kusakabe, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1636.
(26) Maiti, G.; Roy, S. C. *J. Chem. Soc., Perkin Trans. 1* **1996**, 403.
(27) Rama Rao, A. V.; Gurjar, M. K.; Bose, D. S.; Devi, R. R. *J. Org. Chem.* **1991**, *56*, 1320.
(28) Crilley, M. M. L.; Golding, B. T.; Pierpoint, C. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2061.
(29) Gurjar, M. K.; Devi, N. R. *Tetrahedron: Asymmetry* **1994**, *5*, 755.

3.4 Hz); 2.41 (1H, app t, J = 2.2 Hz); 0.90 (9H, s); 0.08 (6H, s). Anal. Calcd for $C_{13}H_{24}O_3Si$: C, 60.89; H, 9.43. Found: C, 60.72; H, 9.37. ***Syn:*** ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 4.19 (2H, d, J = 2.6 Hz); 3.8−3.7 (1H, m); 3.6−3.5 (2H, m); 3.1−3.0 (1H, m); 2.8−2.7 (2H, m); 2.43 (1H, app t, J = 2.6 Hz); 0.88 (9H, s); 0.05 (6H, s). Only the *anti* isomer was further used.

3. Isomerization of Oxiranes. Reaction with LIDAKOR or LICKOR. Hexane was stripped off from a solution of BuLi (0.74 mL of a 1.5 M solution, 1.10 mmol for LIDAKOR; 0.37 mL of a 1.5 M solution, 0.55 mmol for LICKOR), and precooled THF (1.0 mL) was added at −78 °C under N_2, followed by diisopropylamine (112 mg, 1.10 mmol for LIDAKOR) and potassium *tert*-butoxide (124 mg, 1.10 mmol for LIDAKOR; 62 mg, 0.55 mmol for LICKOR). The mixture was stirred at −78 °C for 45 min, after which time the oxirane (0.50 mmol) was added and allowed to react for 15 h at −50 °C; the reaction was then quenched with H_2O (2.0 mL) and extracted twice with Et_2O, after warming to 25 °C. The organic layers were combined, washed with brine, and dried. After evaporation of the solvent the residue was purified.

3-Hydroxy-2,3,4,5-tetrahydroxepine 8d.[9] The procedure with LICKOR was used on epoxide **6d**, obtaining 51 mg (90%) of a crude product which was then purified by column chromatography (petroleum ether/ethyl acetate 3:2), giving 26 mg (45%) of **8d**. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 6.30 (1H, dt, J 6.2, 2.1); 4.79 (1 H, app. q, J = 6.4); 4.02 (1H, dd, J = 11.7, 2.5); 3.9−3.8 (1H, m); 3.87 (1H, dd, J = 11.7, 4.2); 2.6−2.4 (1H, m); 2.3−2.1 (1H, m); 2.0−1.8 (2H, m); 1.8 (1H, m).

***cis*-2-Pentyl-3-hydroxy-2,3,4,5-tetrahydroxepine 8e.** The procedure with LICKOR was used on epoxide **8e**, obtaining 87 mg (94%) of a crude product which was then purified by column chromatography (petroleum ether/ethyl acetate 5:1), giving 60 mg (65%) of *cis*-**8e**. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 6.30 (1H, ddd, J = 6.4, 2.2, 0.8 Hz); 4.75 (1H, app tdd, J = 7.0, 3.2, 0.8 Hz); 3.9−3.8 (1H, m); 3.72 (1H, app td, J = 8.4, 2.6); 2.5−2.3 (1H, m); 2.3−2.0 (1H, m); 2.0−1.8 (1H, m); 1.8−1.2 (10H, m); 0.89 (3H, t, J = 6.2 Hz). ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ: 148.0; 110.0; 85.5; 73.6; 33.9; 33.0; 31.7; 25.5; 22.6; 20.1; 14.0. MS (m/z %): 184 (14, M^+); 166 (6, $M^+ - H_2O$); 113 (19, $M^+ - C_5H_{11}$), 109 (21); 99 (25); 95 (45); 85 (25); 84 (71); 83 (73); 82 (33); 81 (78); 79 (21); 71 (69); 70 (56); 69 (38); 68 (30); 67 (46); 59 (20); 58 (46); 57 (100); 56 (25); 55 (80). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.52; H, 10.87.

***cis*-2-(*tert*-Butyldimethylsilyl)oxymethyl-3-hydroxy-2,3,4,5-tetrahydroxepine 8f.** The procedure with LICKOR was used on epoxide **6f**, obtaining 88 mg (68%) of a 98:2 mixture of *cis*-**8f** and *trans*-**8f,** which was then purified by Florisil (petroleum ether/ethyl acetate 7:1), giving 68 mg (53%) of *cis*-**8f**. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 6.34 (1H, ddd, J = 6.4, 1.8, 1.0 Hz); 4.78 (1H, app tdd, J = 6.6, 3.2, 1.04 Hz); 4.0−3.4 (4H, m); 2.6−2.3 (1H, m); 2.2−2.0 (1H, m); 2.0−1.8 (1H, m); 1.8−1.6 (1H, m); 1.0 (1H, m); 0.88 (9H, s); 0.058 (3H, s); 0.054 (3H, s). ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ: 147.8; 110.5; 86.5; 70.5; 63.7; 34.4; 25.7; 20.0; 17.8; −4.3; −4.9. MS (m/z): 201 (3, $M^+ - C_4H_9$); 145 (13, $CH_2OSi[(CH_3)_2C(CH_3)_3]$); 101 (13, $OSiC(CH_3)_3$); 81 (25); 75 (100); 73 (22); 57 (30). Anal. Calcd for $C_{13}H_{26}O_3Si$: C, 60.42; H, 10.14. Found: C, 60.42; H, 10.37.

(2,3-*trans*-3,4-*trans*)-2-Phenyl-3-(1-hydroxymethyl)-4-pentyloxetane (*trans,trans*-7g). The procedure with LIDAKOR was used on epoxide **6g**, obtaining 82 mg (70%) of a 5:95 mixture of *cis*,*trans*-**7g** and *trans*,*trans*-**7g** which was then purified by column cromatography (petroleum ether/ethyl acetate 3:1), giving 62 mg (53%) of *trans*,*trans*-**7g**. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.5−7.2 (5H, m); 5.44 (1H, d, J = 7.0 Hz); 4.56 (1H, app q, J = 6.8 Hz); 3.84 (2H, d, J = 6.2 Hz); 2.61 (1H, app quint, J = 6.6 Hz); 2.3−2.0 (1H, bs); 2.0−1.6 (2H, m); 1.5−1.2 (6H, m); 0.89 (3H, t, J = 6.2 Hz). ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ: 142.8; 128.4; 127.6; 125.3; 81.2; 80.8; 62.8; 52.0; 37.2; 31.6; 23.8; 22.5; 13.9. MS (m/z): 233 (0.4, $M^+ - 1$); 128 (7, $M^+ - C_7H_6O$); 117 (38); 107 (81); 81 (36); 79 (63); 77 (37); 68 (31); 67 (35); 57 (100); 55 (40); 54 (34). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 77.01; H, 9.12.

(2,3-*trans*-3,4-*trans*)-2-Phenyl-3-(1-hydroxymethyl)-4-(*tert*-butyldimethylsilyloxymethyl)oxetane (*trans,trans*-7h).[30] The procedure with LIDAKOR was used on epoxide **6h**, obtaining 137 mg (89%) of *trans*,*trans*-**7h** which was then purified by column cromatography (petroleum ether/ethyl acetate 3:1), giving 84 mg (55%) of pure *trans*,*trans*-**7h**. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.5−7.2 (5H, m); 5.46 (1H, d, J = 7.0); 4.7−4.6 (1H, m); 3.9−3.8 (4H, m); 2.97 (1H, quint, J = 7.0); 1.8−1.7 (1H, bs); 0.90 (9H, s); 0.09 (6H, s).^{13}C NMR ($CDCl_3$, 75.45 MHz) δ: 142.2; 128.4; 127.9; 125.6; 81.5; 80.6; 65.6; 62.6; 48.7; 25.9; 18.3; −5.5. MS (m/z): 283 (2); 145 (18); 129 (12); 117 (100). Anal. Calcd for $C_{17}H_{28}O_3Si$: C, 66.19; H, 9.15. Found: C, 65.84; H, 8.99.

(2,3-*trans*-3,4-*trans*)-2-Ethynyl-3-(hydroxymethyl)-4-pentyloxetane (*trans,trans*-7i). The procedure with 2 equiv of LIDAKOR was used on epoxide **6i**, obtaining 87 mg (95%) of a 20:80 mixture of *cis*,*trans*-**7i** and *trans*,*trans*-**7i,** which was then purified by column chromatography (petroleum ether/ethyl acetate 3:1), giving 50 mg (55%) of pure *trans*,*trans*-**7i**. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 5.00 (1H, dd, J = 6.6, 1.8 Hz); 4.47 (1H, app q, J = 6.4 Hz); 3.83 (2H, d, J = 5.8 Hz); 2.9−2.7 (1H, m); 2.73 (1H, d, J = 1.8 Hz); 2.0−1.2 (9H, m); 0.89 (3H, t, J = 6.2 Hz).^{13}C NMR ($CDCl_3$, 75.45 MHz) δ: 83.1; 82.0; 76.3; 67.6; 62.0; 50.0; 37.2; 31.5; 23.6; 22.5; 14.0. MS (m/z): 182 (0.2, M^+); 151 (4, $M^+ - CH_2OH$); 95 (20); 83 (45); 82 (71); 81 (83); 72 (22); 71 (38); 68 (36); 67 (31); 65 (20); 57 (44); 55 (100); 54 (92); 53 (91). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.11; H, 9.76.

(2,3-*trans*-3,4-*trans*)-2-Ethynyl-3-(hydroxymethyl)-4-(*tert*-butyldimethylsilyloxymethyl)oxetane (*trans,trans*-7j). The procedure with 2 equiv of LIDAKOR was used on epoxide **6j**, obtaining 106 mg (83%) of a 15:85 mixture of *cis*,*trans*-**7j** and **7j** which was then purified by column cromatography (petroleum ether/ethyl acetate 3:1), giving 64 mg (50%) of pure *trans*,*trans*-**7j**. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 5.03 (1H, dd, J = 7.0, 2.2 Hz); 4.6−4.4 (1H, m); 3.83 (2H, d, J = 6.2 Hz); 3.79 (2H, d, J = 5.0); 3.07 (1H, app quint, J = 6.2 Hz); 2.72 (1H, d, J = 2.2 Hz); 2.0−1.7 (1H, bs); 0.91 (9H, s); 0.10 (3H, s); 0.08 (3H, s). Anal. Calcd for $C_{13}H_{24}O_3Si$: C, 60.89; H, 9.43. Found: C, 61.05; H, 9.60.

(2,3-*trans*-3,4-*trans*)-2-Ethynyl-3-(hydroxymethyl)-4-hydroxymethyl-oxetane. ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ: 81.6; 77.3; 68.0; 64.0; 61.4; 44.8; 40.3.

Preparation of Silyl Oxiranyl Ethers. 1-Trialkylsilyloct-1-yn-3-ol.[24] Trialkylsilyl acetylene (10 mmol) was added dropwise to a 1.5 M solution of BuLi in hexane (10 mmol) at 0 °C. The resulting solution was stirred for 1 h at 25 °C. Then hexanal (1.00 g, 10 mmol) was added dropwise at −30 °C. The mixture was warmed to 25 °C and stirred for 1.5 h, then was poured into ice-cooled saturated NH_4Cl and extracted with hexane, and the combined organic layers were dried (Na_2SO_4) to afford the crude (1.59 g, 80% for alkyl = CH_3 and 1.98 g, 70% for alkyl = $[(CH_3)_2CH]_3$).

1-Trialkylsilyloct-1-en-3-ol.[24] 1-Trialkylsilyloct-1-yn-3-ol (7 mmol) in THF (6.6 mL) was added to $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ (3.5 mL of 3.4 M solution in toluene, 12 mmol) in Et_2O (11 mL) at 0 °C. The mixture was then warmed to 25 °C and stirred for 16 h. After cooling to 0 °C, water (8 mL) and 3 N HCl (8 mL) were slowly added. The organic solution was separated and the aqueous solution extracted with hexanes−Et_2O 1:1. The combined organic layers were washed with aqueous $NaHCO_3$ and brine and dried.

1-Trimethylsilyloct-1-en-3-ol.[31] After the solvent was evaporated, 1.15 g (82%) of crude was obtained and purified by column chromatography (eluent petroleum ether/ethyl acetate 7:1), affording 0.63 g (45%) of product. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 6.04 (1H, dd, J = 18.6, 5.0 Hz); 5.83 (1H, dd, J = 18.6, 1.0 Hz); 4.2−4.0 (1H, m); 1.5−1.2 (8H, m); 0.88 (3H, t, J = 6.6 Hz); 0.06 (9H, s).

1-Triisopropylsilyloct-1-en-3-ol. After the solvent was evaporated, 1.73 g (87%) of crude was obtained and purified by column chromatography (eluent petroleum ether/ ethyl acetate 8:1), affording 0.80 g (40%) of product. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 6.10 (1H, dd, J = 19.2, 5.4 Hz); 5.71 (1H, dd, J = 19.2, 1.6 Hz); 4.2−4.0 (1H, m); 1.5−1.2 (8H, m); 1.05 (18H, m); 1.1−1.0 (3H, m,); 0.88 (3H, t, J = 6.2 Hz).

(*E*)-1-Trialkylsilyl-1,2-epoxy-3-octanol. L-(+)-Diisopropyltartrate (0.84 g, 3.6 mmol) was added to Ti(*i*-OPr)$_4$ (0.85 g, 3 mmol), in CH_2Cl_2 (26 mL), at −20 °C. After 10 min, 1-trialkyl-

(30) Jung, M. E.; Nichols, C. J. *Tetrahedron Lett.* **1996**, *37*, 7667.
(31) Falck-Pedersen, M. L.; Benneche, T.; Undheim, K. *Acta Chem. Scand.* **1989**, *43*, 251.

silyloct-1-en-3-ol (3 mmol) was added, and the resulting solution was stirred for an additional 10 min. *t*-BuOOH (0.82 mL of a 5.5 M solution in decane, dried over molecular sieves, 4.5 mmol) was slowly added. After 12 h, Me_2S (0.66 mL, 9 mmol) was slowly added, and the mixture was stirred for 30 min at −20 °C. Then 10% citric acid (2 mL), Et_2O (26 mL), NaF (2.1 g), and Celite (1.2 g) were added sequentially. The resulting mixture was stirred for 30 min at 25 °C, filtered through a pad of Celite, and washed with Et_2O.

(*E*)-(1*S*,2*S*,3*S*)-1-Trimethylsilyl-1,2-epoxy-3-octanol.[19] After the solvent was evaporated, the residue was purified by column chromatography with triethylamine deactivated silica gel (eluent: petroleum ether/ethyl acetate 7:1) to afford 0.30 g of pure epoxide. ^{1}H NMR ($CDCl_3$, 200 MHz): 3.9−3.8 (1H, m); 2.87 (1H, app t, J = 3.6 Hz); 2.36 (1H, d, J = 3.6 Hz); 1.82 (1H, app d, J = 1.8 Hz); 1.6−1.2 (8H, m); 0.89 (3H, t, J = 6.6 Hz); 0.07 (9H, s).

(*E*)-(1*S*,2*S*,3*S*)-1-Triisopropylsilyl-1,2-epoxy-3-octanol.[24] After the solvent was evaporated, we obtained 0.79 g of crude which we used directly in the following reaction. ^{1}H NMR ($CDCl_3$, 200 MHz): 3.9−3.8 (1H, m); 3.04 (1H, app t, J = 3.6 Hz); 2.47 (1H, d, J = 3.6 Hz); 1.6−1.2 (12H, m); 1.25 (18H, d, J = 5.0 Hz), 0.89 (3H, t, J = 6.6 Hz).

(*E*)-(1*S*,2*S*,3*S*)-1-Trialkylsilyl-3-(2-propenoxy)-1,2-epoxyoctane. The epoxy alcohol (1.4 mmol) was dissolved in DMF (1.6 mL) and, after cooling to −5 °C, a suspension of NaH (0.06 g, 1.46 mmol) in DMF (1.6 mL) was added during 30 min. After an additional 30 min, a solution of CH_2=$CHCH_2Br$ (0.25 g, 2.1 mmol) in DMF (1.6 mL) was added. The mixture warmed to 25 °C and then stirred for 5 h before it was treated with H_2O (1.6 mL) and extracted with ether. The organic phase was washed with H_2O and saturated NaCl and dried.

(*E*)-(1*S*,2*S*,3*S*)-1-Trimethylsilyl-3-(2-propenoxy)-1,2-epoxyoctane. After evaporation of the solvent, the residue was purified by column chromatography (eluent: petroleum ether/dichloromethane 3:1) to afford 0.26 g (71%) of **9k**. ^{1}H NMR ($CDCl_3$, 200 MHz): 5.89 (1H, ddt, J = 17.2, 10.2, 5.6 Hz); 5.25 (1H, dq, J = 17.2, 1.6 Hz); 5.15 (1H, dq, J = 10.2, 1.6 Hz); 4.03 (2H, AB system); 3.2−3.0 (1H, m); 2.71 (1H, dd, J = 5.8, 3.4 Hz); 2.25 (1H, app d, J = 3.4); 1.7−1.2 (8H, m); 0.89 (3H, t, J = 6.6 Hz); 0.08 (9H, s). ^{13}C NMR ($CDCl_3$, 75.45 MHz): 135.1; 116.6; 79.8; 70.9; 57.0; 50.4; 33.4; 31.8; 24.8; 22.5; 14.0; −3.80. MS (*m*/*z*): 199 (1, M^+-C_4H_7); 155 (14); 143 (35); 129 (70); 115 (37); 99 (36); 85 (29); 81 (23); 75 (90); 74 (23); 73 (100, $(CH_3)_3Si$)); 71 (29); 59 (69); 55 (44). Anal. Calcd for $C_{14}H_{28}O_2Si$: C, 65.57; H, 11.00. Found: C, 65.41; H, 10.86.

(*E*)-(1*S*,2*S*,3*S*)-1-Triisopropylsilyl-3-(2-propenoxy)-1,2-epoxyoctane. After evaporation of the solvent, the residue was purified by column chromatography (eluent: petroleum ether/dichloromethane 3:1) to afford 0.31 g (65%) of **9l**. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 5.90 (1H, ddt, J = 17.2, 10.2, 5.6 Hz); 5.24 (1H, dq, J = 17.2, 1.4 Hz); 5.15 (1H, dq, J = 10.2, 1.4 Hz); 4.05 (2H, AB system); 3.2−3.0 (1H, m); 2.89 (1H, dd, J = 5.4, 3.2 Hz); 2.37 (1H, d, J = 3.2 Hz); 1.7−1.2 (11H, m); 1.10 (18H, s); 0.89 (3H, t, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 75.45 MHz): 135.1; 116.8; 80.1; 71.3; 57.0; 48.0; 33.3; 31.9; 25.0; 22.5; 18.5; 14.0; 10.4. MS (*m*/*z*): 297 (1, M^+ − $(CH_3)_3CH$); 255 (11); 131 (22); 129 (80); 127 (25); 115 (57); 113 (20); 103 (51); 101 (100); 99 (75); 87 (55); 85 (41); 75 (76); 73 (50); 71 (46); 61 (58); 59 (91); 55 (27). Anal. Calcd for $C_{20}H_{40}O_2Si$: C, 70.52; H, 11.84. Found: C, 70.41; H, 11.96.

***cis*-(2*S*,3*R*)-2-Pentyl-3-(trimethylsilyloxy)-2,3,4,5-tetrahydroxepine 11k.** The general procedure with LICKOR was used obtaining 124 mg (97%) of a crude product which was then purified by column chromatography (petroleum ether/ethyl acetate 7:1), giving 92 mg (72%) of **11k**. ^{1}H NMR ($CDCl_3$, 200 MHz): 6.22 (1H, dt, J = 6.2, 2.2 Hz); 4.76 (1H, app td, J = 6.2, 4.0 Hz); 3.8−3.6 (2H, m); 2.7−2.5 (1H, m); 2.0−1.6 (2H, m); 1.6−1.0 (9H, m); 0.89 (3H, t, J = 6.6 Hz); 0.06 (9H, s).^{13}C NMR ($CDCl_3$, 75.45 MHz): 148.1; 109.6; 85.8; 75.5; 38.1; 35.9; 33.4; 31.8; 25.4; 22.6; 14.0; −1.27. Anal. Calcd for $C_{14}H_{28}O_2Si$: C, 65.57; H, 11.00. Found: C, 65.61; H, 11.16.

***cis*-(2*S*,3*R*)-2-Pentyl-3-(triisopropylsilyloxy)-2,3,4,5-tetrahydroxepine 11l and (2,3-*trans*-3,4-*trans*)-2-Vinyl-3-[(1-hydroxy-1-triisopropylsilyl)methyl]-4-pentyloxetane 10l.** The general procedure with LICKOR was used obtaining 155 mg (91%) of a crude product as a mixture **11l**:**10l** 28:72 which was then purified by column chromatography (petroleum ether/ethyl acetate 8:1), giving 32 mg of (**11l**) and 98 mg of (**10l**) (total yield 76%).

11l. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 6.27 (1H, app d, J = 6.4 Hz); 4.91 (1H, app q, J = 5.8 Hz); 3.80 (1H, app q, J = 6.6 Hz); 3.58 (1H, ddd, J = 8.6, 7.6, 2.8 Hz); 2.5−2.3 (1H, m); 2.2−2.0 (1H, m); 1.8−1.2 (10H, m); 1.2−1.0 (21H, m); 0.89 (3H, t, J = 6.6 Hz). MS (*m*/*z*): 297 (43); 197 (13); 159 (23); 157 (41); 131 (46); 129 (23); 115 (49); 103 (58); 101 (20); 87 (40); 81 (25); 75 (60); 73 (55); 71 (25); 68 (23); 67 (49); 61 (32); 59 (100).

10l. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 5.96 (1H, ddd, J = 16.8, 10.2, 6.6 Hz); 5.22 (1H, app dt, J = 10.2, 1.4 Hz); 5.11 (1H, app dt, J = 10.2, 1.4 Hz); 4.51 (1H, app t, J = 6.8 Hz); 4.02 (1H, app t, J = 7.2 Hz); 3.6−3.4 (1H, m); 1.6−1.2 (10H, m); 1.2−1.0 (21H, s); 0.88 (3H, t, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$, 75.45 MHz): 140.1; 115.1; 83.8; 80.3; 79.7; 37.9; 33.1; 32.0; 25.8; 22.5; 18.9; 14.0; 11.5. MS (*m*/*z*): 297 (6, M^+ − $(CH_3)_2CH$); 197 (20); 131 (83); 115 (29); 103 (100); 89 (22); 87 (33); 83 (25); 75 (97); 73 (47); 71 (23); 61 (58); 59 (74); 55 (24). Anal. Calcd for $C_{20}H_{40}O_2Si$: C, 70.52; H, 11.84. Found: C, 70.61; H, 11.90.

JO0005924