Stereoselective Synthesis of Substituted Cyclohexenols from a Furan-Derived Sultone *via* Tandem Elimination/1,6-Addition

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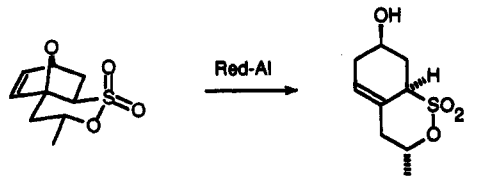
Tandem reactions are powerful tools for organic synthesis.[1] During our studies on intramolecular Diels–Alder cycloadditions of vinyl sulfonates and the synthetic elaboration of the resultant sultones,[2,3] we noted the formation of bicyclic compound **2** upon reaction of the furan-derived sultone **1** with 1 equiv of sodium bis(2-methoxyethoxy)aluminum dihydride (Red-Al).[2d] Since this conversion is likely to proceed *via* elimination followed by an alkoxide-directed remote conjugate addition of hydride, we investigated the reaction of organolithium reagents with **1** in order to achieve a tandem elimination/1,6-addition leading to alkylated products.



1 **2**

Indeed, when sultone **1** was treated with 2 equiv of an alkyllithium species in THF, the desired alkylation was accomplished (Scheme 1). In line with our previous findings,[2d] the first equivalent of R^1Li deprotonates **1** with concomitant ring opening to lithium alkoxide **3** at −78 °C. This electron-deficient diene in turn serves as an extended conjugate acceptor toward the second equivalent of R^1Li. As expected, using only 1 equiv of R^1Li, the dienol corresponding to **3** was isolated after aqueous workup. The facility of the 1,6-addition[4,5] step **3** → **4** depends on the nature of R^1. Whereas *n*-butyllithium rapidly added to **3** at −78 °C already, a comparably fast reaction of methyllithium was only observed after raising the temperature to 0 °C. Since only an addition adjacent and *cis* to the hydroxyl group was noted, the alkyllithium reagent probably coordinates to the alkoxide moiety of **3** prior to C–C coupling.[6] Protonation of the resultant allyl anions **4** led to mixtures of isomeric sultones **5**–**7** with relative proportions varying from run to run, but always yielding **5** as the major product. The reaction pathway depicted in Scheme 1 is further supported by the observation that treatment of sultone **1** with LDA (1 equiv, THF, −78 °C; cf. ref 2d) followed by MeLi (1 equiv, THF, −78 to 0 °C) again gave rise to **5a**–**7a** (43%) after protonation. Gratifyingly, a subsequent equilibration of the mixtures **5a**–**7a** and **5b**–**7b** using catalytic amounts of potassium *tert*-butoxide resulted in complete conversion of isomers **6a**/**7a** and **6b**/**7b** to **5a** and **5b**, respectively.[7] Trapping of allyl anions **4** with methyl iodide instead of aqueous workup allowed for the formation of a second C–C bond in a one-pot procedure. In contrast to protonation of **4**, methylation of these intermediates occurred in a completely regio- and stereoselective fashion to yield only **5c** and **5d**. The relative configuration of sultones **5a**,**b**,**d** follows from diagnostic $^1H-^1H$ coupling constants and NOE difference data, while **5c**[8] was characterized by X-ray diffraction analysis.

Reductive desulfurization[2d] of sultones **5** led with high efficiency to substituted cyclohexenols possessing a defined stereochemical relationship between acyclic and cyclic stereogenic moieties (Scheme 2). Due to protonation at either monosubstituted terminus of the intermediate allyl anions, mixtures of isomers **8** and **9** were obtained from sultones **5a** and **5b**. The position of the trisubstituted double bond in cyclohexenols **8a**,**b** and **9a**,**b** was determined by NMR experiments performed on the pure isomers, easily separated by flash chromatography. Moreover, the structure of **8b**[8] was confirmed by X-ray diffraction analysis, which also secured the *cis* relation of *n*-Bu und OH in an unambiguous manner. Since the corresponding reductive fission of the allylic C–S bond in sultone **5** with $R^1 = H$ and $R^2 = H$ yielded approximately equal amounts of the two product isomers,[2d] the alkyl substituent R^1 is responsible for the predominant formation of **8a** and **8b**, respectively. This regioselectivity reflects a lower free energy of activation for protonation to the less strained cyclohexene isomer featuring the larger dihedral angle $R^1–C–C–O$.[9] Sultones **5c** and **5d** exclusively provided the tetrasubstituted olefins **8** *via* protonation of the intermediate allyl anions at the less substituted terminus.

Applications of this methodology to the control of side-chain chirality in the context of natural products synthesis will be reported in due course.

† X-ray diffraction analyses.

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(8) The authors have deposited atomic coordinates for structures **5c** and **8b** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

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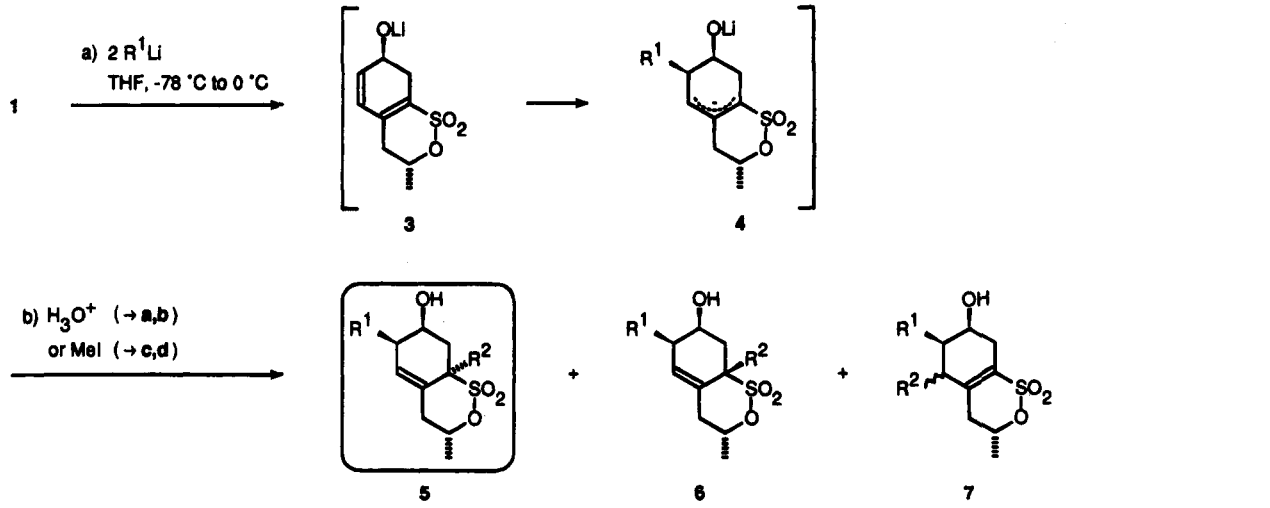
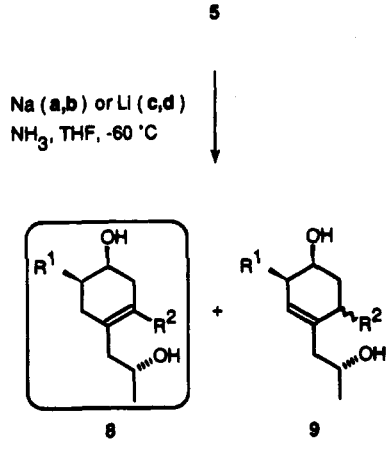
Scheme 1[a,b]



[a] Diastereomeric ratios determined by capillary GC analysis of the crude products. [b] Isolated yields after flash chromatography.

Scheme 2[a,b]



[a] Diastereomeric ratios determined by capillary GC analysis of the crude products. [b] Isolated yields after flash chromatography.

Experimental Section

For general experimental information, see ref 10.

General Procedure for Tandem Elimination/1,6-Addition. An alkyllithium reagent (2 equiv, 1.6 M in *n*-hexane) was added dropwise at −78 °C to a solution of sultone **1** in THF. After further stirring [MeLi (**a,c**): 15 min at −78 °C, then 1 h at 0 °C; *n*-BuLi (**b,d**): 1 h at −78 °C], the reaction mixture was treated at −78 °C with saturated aqueous NH_4Cl (**a,b**) or MeI (**c,d**; after addition, stirring was continued for 30 min at −78 °C followed by addition of saturated aqueous NH_4Cl at −78 °C). The mixture was warmed to rt, adjusted to pH 7 with 2 N HCl, and extracted with ethyl acetate (3×). The combined organic layers were dried over $MgSO_4$, the solvent was evaporated *in vacuo*, and a mixture of sultones **5**–**7** (**a,b**) or pure **5** (**c,d**) was isolated by flash chromatography using ethyl acetate/petroleum ether eluents.

5a/6a/7a: 300 mg (1.39 mmol) of **1** in 10 mL of THF; 1.74 mL (2.78 mmol) of MeLi; 15 mL of saturated aqueous NH_4Cl; ethyl acetate/petroleum ether 3:2; yield 174 mg (54%).

5b/6b/7b: 360 mg (1.67 mmol) of **1** in 12 mL of THF; 2.08 mL (3.33 mmol) of *n*-BuLi; 15 mL of saturated aqueous NH_4Cl; ethyl acetate/petroleum ether 4:5; yield 231 mg (51%).

5c: 1.30 g (6.01 mmol) of **1** in 48 mL of THF; 7.50 mL (12.0 mmol) of MeLi; 1.13 mL (18.2 mmol) of MeI; 50 mL of saturated aqueous NH_4Cl; ethyl acetate/petroleum ether 3:2; yield 633 mg (43%).

5d: 600 mg (2.78 mmol) of **1** in 30 mL of THF; 3.47 mL (5.55 mmol) of *n*-BuLi; 0.52 mL (8.4 mmol) of MeI; 30 mL of saturated aqueous NH_4Cl; ethyl acetate/petroleum ether 4:5; yield 341 mg (43%).

(1*R,3*S**,4*R**,2′*R**)-3-Hydroxy-1,4-dimethyl-6-propyl-5-cyclohexene-1,2′-sultone (5c)**: R_f 0.39 (ethyl acetate/petroleum ether 3:2); mp 96–98 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05 (d, 3 H, J = 7.2 Hz), 1.39 (d, 3 H, J = 6.2 Hz), 1.63 (s, 3 H), 1.84 (dd, 1 H, J = 3.3, 13.8 Hz), 2.22 (dd, 1 H, J = 2.4, 14.6 Hz), 2.37 (m, 1 H), 2.53 (dd, 1 H, J = 9.5, 13.8 Hz, overlapping with m, 1 H), 2.76 (m, 1 H), 3.91 (m, 1 H), 4.67 (ddq, 1 H, J_d = 2.4, 12.4 Hz, J_q = 6.2 Hz), 5.65 (dd, 1 H, J = 1.9, 4.8 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.2 (q), 20.7 (q), 23.5 (q), 33.6 (t), 35.0 (d), 37.6 (t), 62.1 (s), 66.0 (d), 81.9 (d), 130.1 (s), 133.8 (d); MS (GC/MS, 70 eV) m/z (rel intensity) 246 (14) [M^+], 228 (6) [$M^+ - H_2O$], 164 (28) [$M^+ - H_2O - SO_2$], 138 (100) [$M^+ - CH_3CHOSO_2$]; IR (KBr) 3324 (br), 1349, 1180 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_4S$: C, 53.64; H, 7.37. Found: C, 53.57; H, 7.40.

(1*R,3*S**,4*R**,2′*R**)-4-Butyl-3-hydroxy-1-methyl-6-propyl-5-cyclohexene-1,2′-sultone (5d)**: R_f 0.44 (ethyl acetate/petroleum ether 4:5); oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 7.0 Hz), 1.33 (m, 5 H), 1.39 (d, 3 H, J = 6.4 Hz), 1.62 (s, 3 H), 1.63–1.72 (m, 1 H), 1.84 (dd, 1 H, J = 3.6, 14.5 Hz), 2.13 (m, 1 H), 2.23 (dd, 1 H, J = 2.6, 14.8 Hz), 2.57 (m, 1 H), 2.63 (dd, 1 H, J = 7.4, 14.5 Hz), 3.03 (m, 1 H), 3.92 (m, 1 H), 4.69 (ddq, 1 H, J_d = 2.6, 12.4 Hz, J_q = 6.4 Hz), 5.69 (dd, 1 H, J = 1.9, 3.8 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.0 (q), 20.7 (q), 22.8 (t), 24.3 (q), 29.4 (t), 29.8 (t), 35.3 (t), 37.9 (t), 40.2 (d), 61.6 (s), 65.4 (d), 82.3

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(d), 130.4 (s), 132.8 (d); MS (GC/MS, 70 eV) m/z (rel intensity) 270 (20) [$M^+ - H_2O$], 206 (36) [$M^+ - H_2O - SO_2$], 180 (100) [$M^+ - CH_3CHOSO_2$]; IR (film) 3544–3407, 1350, 1180 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_4S$: C, 58.30; H, 8.39. Found: C, 57.92; H, 8.70.

General Procedure for Sultone Equilibration. The mixture of isomeric sultones **5–7** obtained above was dissolved in toluene and a catalytic amount of potassium *tert*-butoxide was added. After the mixture was stirred at rt for 24 h, ether and water were added. The aqueous layer was extracted with ethyl acetate (3×), and the combined organic layers were washed with brine and dried over $MgSO_4$. After removal of the solvent *in vacuo*, flash chromatography using ethyl acetate/petroleum ether eluents provided the pure sultones **5a,b**.

5a: 500 mg (2.15 mmol) of **5a/6a/7a** in 40 mL of toluene; 40 mg (0.36 mmol) of *t*-BuOK; ethyl acetate/petroleum ether 3:2; yield 386 mg (77%).

5b: 221 mg (0.806 mmol) of **5b/6b/7b** in 10 mL of toluene; 20 mg (0.18 mmol) of *t*-BuOK; ethyl acetate/petroleum ether 4:5; yield 201 mg (91%).

(1*R,3*S**,4*R**,2′*R**)-3-Hydroxy-4-methyl-6-propyl-5-cyclohexene-1,2′-sultone (5a)**: R_f 0.32 (ethyl acetate/petroleum ether 3:2); mp 88–90 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (d, 3 H, J = 7.0 Hz), 1.43 (d, 3 H, J = 6.2 Hz), 2.23 (dddd, 1 H, J = 0.6, 3.6, 8.1, 14.4 Hz), 2.37–2.42 (m, 3 H), 2.49 (ddd, 1 H, J = 5.7, 7.7, 14.4 Hz), 3.81 (m, 1 H), 3.92 (ddd, 1 H, J = 3.6, 3.9, 7.7 Hz), 4.74 (ddq, 1 H, J_d = 4.2, 9.7 Hz, J_q = 6.2 Hz), 5.73 (m, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.7 (q), 20.6 (q), 25.8 (t), 34.6 (d), 40.6 (t), 58.3 (d), 66.3 (d), 81.9 (d), 125.4 (s), 133.8 (d); MS (GC/MS, 70 eV) m/z (rel intensity) 232 (1) [M^+], 214 (0.3) [$M^+ - H_2O$], 150 (10) [$M^+ - H_2O - SO_2$], 124 (100) [$M^+ - CH_3CHOSO_2$]; IR ($CHCl_3$) 3420–3450, 1355, 1169 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_4S$: C, 51.71; H, 6.94. Found: C, 51.75; H, 6.99.

(1*R,3*S**,4*R**,2′*R**)-4-Butyl-3-hydroxy-6-propyl-5-cyclohexene-1,2′-sultone (5b)**: R_f 0.39 (ethyl acetate/petroleum ether 4:5); mp 56–60 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 3 H, J = 7.0 Hz), 1.38 (m, 5 H), 1.44 (d, 3 H, J = 6.2 Hz), 1.56–1.75 (m, 1 H), 2.10–2.18 (m, 1 H), 2.20 (ddd, 1 H, J = 3.3, 8.6, 15.0 Hz), 2.38–2.45 (m, 2 H), 2.58 (ddd, 1 H, J = 3.8, 6.1, 15.0 Hz), 2.76 (m, 1 H), 3.82 (m, 1 H), 3.97 (m, 1 H), 4.75 (ddq, 1 H, J_d = 4.2, 9.7 Hz, J_q = 6.2 Hz), 5.74 (m, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.0 (q), 20.7 (q), 22.8 (t), 27.0 (t), 29.3 (t), 30.2 (t), 40.0 (d), 41.2 (t), 58.1 (d), 65.1 (d), 82.2 (d), 125.6 (s), 132.8 (d); MS (GC/MS, 70 eV) m/z (rel intensity) 274 (8) [M^+], 256 (4) [$M^+ - H_2O$], 192 (25) [$M^+ - H_2O - SO_2$], 166 (100) [$M^+ - CH_3CHOSO_2$]; IR (KBr) 3526 (br), 1355, 1170 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_4S$: C, 56.91; H, 8.08. Found: C, 56.50; H, 8.37.

General Procedure for Reductive Desulfurization of Sultones 5. To a solution of a sultone **5** in THF and liquid ammonia (predistilled from sodium) were added small pieces of sodium (**a**,**b**) or lithium (**c**,**d**) at −60° C until a blue color persisted. Stirring was continued for a further 30 min at the same temperature, excess metal was destroyed by addition of EtOH, and saturated aqueous NH_4Cl was added. The cooling bath was removed and after evaporation of ammonia overnight, ethyl acetate was added. The aqueous layer was extracted with additional portions of ethyl acetate (4×), the combined organic layers were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Flash chromatography using ethyl acetate as eluent yielded separated diols **8** and **9** (**a**,**b**) or only **8** (**c**,**d**).

8a/9a: 378 mg (1.63 mmol) of **5a** in 30 mL of THF and 30 mL of NH_3; combined yield 262 mg (95%); the ratio **8a**:**9a** was determined by capillary GC of the crude product after silylation with *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA).

8b/9b: 124 mg (0.452 mmol) of **5b** in 10 mL of THF and 10 mL of NH_3; combined yield 92 mg (96%); the ratio **8b**:**9b** was determined by capillary GC of the crude product after silylation with MSTFA.

8c: 200 mg (0.812 mmol) of **5c** in 25 mL of THF and 25 mL of NH_3; yield 142 mg (95%).

8d: 180 mg (0.624 mmol) of **5d** in 20 mL of THF and 20 mL of NH_3; yield 138 mg (98%).

(1*S,6*R**,2′*R**)-4-(2′-Hydroxypropyl)-6-methyl-3-cyclohexen-1-ol (8a)**: R_f 0.17 (ethyl acetate); mp 87–90 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (d, 3 H, J = 6.5 Hz), 1.28 (d, 3 H, J = 6.2 Hz), 1.77–1.97 (m, 3 H), 2.00–2.20 (m, 3 H), 2.28–2.40 (m, 1 H), 3.85 (m, 1 H), 3.90 (m, 1 H, including J_q = 6.2 Hz), 5.35 (m, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 16.9 (q), 23.1 (q), 32.3 (t), 32.8 (d), 33.6 (t), 48.3 (t), 64.8 (d), 69.0 (d), 120.4 (d), 134.2 (s); MS (GC/MS, 70 eV) m/z (rel intensity) 152 (3) [$M^+ - H_2O$], 134 (5) [$M^+ - 2H_2O$], 126 (11) [$M^+ - CH_3CHO$], 93 (100), 45 (23) [CH_3CHOH^+]; IR (film) 3316 (br), 3232 (br) cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.64; H, 10.66.

(1*S,2*R**,2′*R**)-4-(2′-Hydroxypropyl)-2-methyl-3-cyclohexen-1-ol (9a)**. R_f 0.24 (ethyl acetate); mp 74–75 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (d, 3 H, J = 7.3 Hz), 1.19 (d, 3 H, J = 6.1 Hz), 1.67 (m, 2 H), 1.88 (m, 1 H), 2.01–2.12 (m, 3 H), 2.39 (m, 1 H), 3.82–3.96 (m, 2 H), 5.28 (m, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 15.8 (q), 23.0 (q), 25.1 (t), 28.2 (t), 35.0 (d), 47.5 (t), 65.3 (d), 68.8 (d), 127.9 (d), 134.2 (s); MS (GC/MS, 70 eV) m/z (rel intensity) 152 (3) [$M^+ - H_2O$], 126 (7) [$M^+ - CH_3CHO$], 93 (100), 45 (61) [CH_3CHOH^+]; IR (film) 3321 (br) cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.51; H, 10.88.

(1*S,6*R**,2′*R**)-6-Butyl-4-(2′-hydroxypropyl)-3-cyclohexen-1-ol (8b)**: R_f 0.18 (ethyl acetate); mp 86–88 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, 3 H, J = 6.9 Hz), 1.17 (d, 3 H, J = 6.2 Hz), 1.22–1.48 (m, 6 H), 1.59 (m, 1 H), 1.78–1.97 (m, 2 H), 2.00–2.09 (m, 2 H), 2.14 (m, 1 H), 2.30 (m, 1 H), 2.61 (m, 1 H), 3.89 (m, 2 H), 5.34 (m, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.1 (q), 22.9 (t), 23.2 (q), 29.3 (t), 30.2 (t), 31.7 (t), 34.1 (t), 37.9 (d), 48.5 (t), 64.6 (d), 67.4 (d), 120.5 (d), 134.3 (s); MS (GC/MS, 70 eV; after silylation with MSTFA) m/z (rel intensity) 341 (0.4) [$M^+ - CH_3$], 266 (3) [$M^+ - HOSiMe_3$], 117 (100) [$CH_3CHOSiMe_3^+$], 75 (8) [$C_2H_7OSi^+$], 73 (35) [$(CH_3)_3Si^+$]; IR (KBr) 3417 (br), 3266 (br) cm^{-1}. Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.28; H, 11.50.

(1*S,2*R**,2′*R**)-2-Butyl-4-(2′-hydroxypropyl)-3-cyclohexen-1-ol (9b)**: R_f 0.32 (ethyl acetate); mp 83–85 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 3 H, J = 7.0 Hz), 1.18 (d, 3 H, J = 6.2 Hz), 1.35 (m, 4 H), 1.46–1.71 (m, 3 H), 1.86–2.21 (m, 6 H), 3.89 (m, 1 H, including J_q = 6.2 Hz), 3.98 (m, 1 H), 5.29 (m, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.0 (q), 22.9 (t), 22.9 (q), 24.4 (t), 28.9 (t), 29.3 (t), 30.8 (t), 40.3 (d), 47.5 (t), 65.3 (d), 67.2 (d), 126.4 (d), 134.5 (s); MS (GC/MS, 70 eV; after silylation with MSTFA) m/z (rel intensity) 341 (0.6) [$M^+ - CH_3$], 299 (0.5) [$M^+ - C_4H_9$], 266 (6) [$M^+ - HOSiMe_3$], 117 (100) [$CH_3CHOSiMe_3^+$], 75 (20) [$C_2H_7OSi^+$], 73 (78) [$(CH_3)_3Si^+$]; IR (film) 3356 (br) cm^{-1}. Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.77; H, 11.39.

(1*S,6*R**,2′*R**)-4-(2′-Hydroxypropyl)-3,6-dimethyl-3-cyclohexen-1-ol (8c)**: R_f 0.20 (ethyl acetate); mp 108–111 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (d, 3 H, J = 6.7 Hz), 1.16 (d, 3 H, J = 6.2 Hz), 1.63 (s, 3 H), 1.68–2.08 (m, 5 H), 2.22–2.34 (m, 1 H), 2.38 (dd, 1 H, J = 9.0, 13.4 Hz), 3.78 (m, 1 H), 3.89 (m, 1 H, including J_q = 6.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 16.7 (q), 19.3 (q), 23.2 (q), 33.0 (d), 33.7 (t), 40.1 (t), 43.3 (t), 66.0 (d), 69.7 (d), 125.6 (s), 125.9 (s); MS (GC/MS, 70 eV; after silylation with MSTFA) m/z (rel intensity) 313 (1) [$M^+ - CH_3$], 238 (5) [$M^+ - HOSiMe_3$], 117 (100) [$CH_3CHOSiMe_3^+$], 73 (10) [$(CH_3)_3Si^+$]; IR (KBr) 3337 (br), 3249 (br) cm^{-1}. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.51; H, 11.05.

(1*S,6*R**,2′*R**)-6-Butyl-4-(2′-hydroxypropyl)-3-methyl-3-cyclohexen-1-ol (8d)**: R_f 0.22 (ethyl acetate); mp 83–85 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, 3 H, J = 6.6 Hz), 1.17 (d, 3 H, J = 6.0 Hz), 1.22–1.42 (m, 6 H), 1.54 (m, 1 H), 1.63 (s, 3 H), 1.78–2.09 (m, 4 H), 2.29 (m, 1 H), 2.39 (dd, 1 H, J = 9.3, 13.6 Hz), 2.72 (m, 1 H), 3.84–3.95 (m, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.1 (q), 19.3 (q), 22.9 (t), 23.3 (q), 29.3 (t), 31.5 (t), 31.6 (t), 38.2 (d), 40.6 (t), 43.6 (t), 65.7 (d), 68.1 (d), 125.5 (s), 126.1 (s); MS (GC/MS, 70 eV; after silylation with MSTFA) m/z (rel intensity) 280 (5) [$M^+ - HOSiMe_3$], 117 (100) [$CH_3CHOSiMe_3^+$], 75 (23) [$C_2H_7OSi^+$], 73 (54) [$(CH_3)_3Si^+$]; IR (KBr) 3309 (br), 3238 (br) cm^{-1}. Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58. Found: C, 74.16; H, 11.53.

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Supplementary Material Available: Crystallographic experimental procedures and structure plots for **5c** and **8b** (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.