added to a solution of NaN_3 (15 mmol) in 40% aqueous methanol (5 g), and the resulting mixture was allowed to stand for ca. 20 min. The solvent was removed by vigorous shaking under reduced pressure (~20 mmHg) at ambient temperature to 90 °C. The half-dried NaN_3/XAD-4 reagent was further dried at 90 °C for 4 h under vacuum (~0.05 mmHg).

In all reactions, alkylsilyl chloride and a solvent were directly added to the flask in which the NaN_3/XAD-4 was made and dried.

Reaction of Me_3SiCl with NaN_3/XAD-4 in Various Solvents. A mixture of NaN_3 (15 mmol)/XAD-4 (3.75 g), Me_3SiCl (7.5 mmol), and a solvent (20 mL) was stirred for the indicated time and at the indicated temperature. After the mixture had been cooled to room temperature, it was analyzed by GLC with toluene as an internal standard (Silicon OV-17, 10%, 3 m × 3 mm, 40 or 50 °C).

Me_3SiN_3: A mixture of Me_3SiCl (1.62 g, 15 mmol), NaN_3 (2.00 g, 30 mmol)/XAD-4 (8.6 g), and decalin (40 ml) was stirred at 60 °C for 6 h. GLC showed that the conversion of Me_3SiCl was ~100%. The reaction mixture was distilled directly by using a Vigreux column (10 cm), giving 1.41 g (82% yield, 98% purity) of Me_3SiN_3, bp 92–97 °C (760 mmHg) [lit.[3c] bp 95–97 °C (760 mmHg)]. IR (CCl_4): 2140 cm^{-1}.

Diphenylmethylsilyl Azide (Ph_2MeSiN_3): A mixture of diphenylmethylsilyl chloride ($Ph_2MeSiCl$) (3.50 g, 15 mmol), NaN_3 (2.00 g, 30 mmol)/XAD-4 (8.6 g), and CH_2Cl_2 (40 mL) was stirred for 5 h at 40 °C. GLC showed the complete conversion of $Ph_2MeSiCl$ (Silicone SE-30, 10%, 1 m × 3 mm, 190 °C). The solid material was filtered and washed with CH_2Cl_2 (60 mL). After removal of the solvent, the residue was distilled under vacuum, giving 3.18 g (89%) of Ph_2MeSiN_3, bp 96–98 °C (0.2 mmHg) [lit.[6] bp 114 °C (1 mmHg)]. IR (CCl_4): 2143 cm^{-1}.

Dimethylsilyl Diazide ($Me_2Si(N_3)_2$): A mixture of dimethylsilyl dichloride (Me_2SiCl_2) (0.97 g, 7.5 mmol), NaN_3 (2.00 g, 30 mmol)/XAD-4 (8.6 g), and CH_2Cl_2 (40 ml) was stirred for 6 h at 40 °C. The same treatment used with Ph_2MeSiN_3 was performed. After removal of the solvent at room temperature and 160–200 mmHg, the residue was distilled with use of a Vigreux column (15 cm) under reduced pressure, giving 0.86 g (80% yield, 98% purity) of $Me_2Si(N_3)_2$, bp 73–76 °C (60 mmHg) [lit.[3c] bp 144–145 °C (760 mmHg)]. IR (CCl_4): 2163 and 2142 cm^{-1}.

***tert*-Butyldimethylsilyl Azide (*t*-$BuMe_2SiN_3$):** A mixture of *tert*-butyldimethylsilyl chloride (*t*-$BuMe_2SiCl$) (1.96 g, 12 mmol), NaN_3 (2.00 g, 30 mmol)/XAD-4 (8.6 g), and CH_2Cl_2 (40 mL) was stirred at 40 °C for 6 h. GLC showed the complete conversion of the silyl chloride. The same treatment used with Ph_2MeSiN_3 was performed. After removal of the solvent at room temperature and 160–200 mmHg, the residue was distilled under reduced pressure, giving 1.60 g (85%) of *t*-$BuMe_2SiN_3$, bp 90–91 °C (110 mmHg) [lit.[8] bp 78 °C (67 mmHg)]. IR (CCl_4): 2140 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.220 (s, 6 H), 0.950 (s, 9 H). MS (*m/z*): 157 (M^+), 142, 128, 100.

***P,P,P*-Triphenyl-*N*-(*tert*-butyldimethylsilyl)phosphinimine (*t*-$BuMe_2SiN{=}PPh_3$).** A mixture of *t*-$BuMe_2SiN_3$ (0.63 g, 4 mmol), triphenylphosphine (PPh_3) (0.94 g, 3.6 mmol), and toluene (4 ml) was refluxed for 16 h. GLC showed the complete conversion of PPh_3. The insoluble material was filtered off, and the solvent was removed under reduced pressure to give residual solid (1.38 g, 98% yield), recrystallization of which from toluene gave 1.20 g (85%) of *t*-$BuMe_2SiN{=}PPh_3$, mp 81.0–82.5 °C. IR (CCl_4): 1434, 1244 (N=P), 1108 cm^{-1}. ^1H NMR ($CDCl_3$): δ −0.171 (s, 6 H), 0.811 (s, 9 H), 7.427–7.809 (m, 15 H). Anal. Calcd for $C_{24}H_{30}NPSi$: C, 73.62; H, 7.72; N, 3.58. Found: C, 73.75; H, 7.55; N, 3.56. MS (*m/z*): 376 ($M^+ - CH_3$), 334, 277.

Diphenylvinylsilyl Azide ($Ph_2(CH_2{=}CH)SiN_3$). A mixture of diphenylvinylsilyl chloride ($Ph_2(CH_2{=}CH)SiCl$) (3.67 g, 15 mmol), NaN_3 (2.00 g, 30 mmol)/XAD-4 (8.6 g), and CH_2Cl_2 (40 mL) was stirred for 7 h at 40 °C. GLC showed the complete conversion of the silyl chloride and the sole product (Silicone SE-30, 10%, 1 m × 3 mm, 190 → 280 °C). Removal of the solvent gave 3.69 g of the residue, which was distilled under vacuum to give only 0.98 g (28% yield) of $Ph_2(CH_2{=}CH)SiN_3$, because of the decomposition of the silyl azide during distillation. Bp 120–125 °C (0.7 mmHg). IR (CCl_4): 2140 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.717–6.579 (m, 3 H), 7.353–7.740 (m, 10 H). MS (*m/z*): 251 (M^+), 224, 209, 183.

***P,P,P*-Triphenyl-*N*-(diphenylvinylsilyl)phosphinimine ($Ph_2(CH_2{=}CH)SiN{=}PPh_3$).** A mixture of $Ph_2(CH_2{=}CH)SiCl$ (1.84 g, 7.5 mmol), NaN_3 (1.00 g, 15 mmol)/XAD-4 (4.3 g), and CH_2Cl_2 (20 mL) was stirred at 40 °C for 7 h. GLC showed the complete conversion of the silyl chloride. After the same treatment used with Ph_2MeSiN_3 was performed, removal of the solvent gave 1.86 g (~100% yield) of the crude $Ph_2(CH_2{=}CH)SiN_3$, which was heated with PPh_3 (1.95 g, 7.5 mmol) under reflux in benzene (20 mL) for 16 h. The insoluble material was filtered off, and the solvent was removed to give the solid residue, which was washed with benzene–hexane and dried under reduced pressure, giving 3.14 g (90% overall yield). This product was recrystallized from benzene to give pure $Ph_2(CH_2{=}CH)SiN{=}PPh_3$, mp 144–145 °C. IR ($CCl_4$): 1436, 1256 (N=P), 1110 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.815–5.991 (m, 3 H), 7.22–7.848 (m, 25 H). MS (*m/z*): 485 (M^+), 458, 408, 381, 334.

Diphenylsilyl Azide (Ph_2HSiN_3). A mixture of diphenylsilyl chloride (Ph_2HSiCl) (1.64 g, 7.5 mmol), NaN_3 (1.00 g, 15 mmol)/XAD-4 (4.3 g), and CH_2Cl_2 (20 ml) was stirred at 40 °C for 5 h. GLC showed the complete conversion of the silyl chloride (Silicone SE-30, 10%, 1 m × 3 mm, 180 °C). After the same treatment used with Ph_2MeSiN_3, removal of the solvent gave 1.66 g of the crude product, distillation of which gave 1.43 g (84% yield) of Ph_2HSiN_3, bp 106–109 °C (0.4 mmHg) [lit.[6] bp 139 °C (2 mmHg)]. IR (CCl_4): 2145 cm^{-1}.

Reaction of Ph_2HSiCl with NaN_3/XAD-4 in Acetonitrile. A mixture of Ph_2HSiCl (2.19 g, 10 mmol), NaN_3 (1.00 g, 15 mmol)/XAD-4 (4.3 g), acetonitrile (20 mL), and pentadecane as an internal standard was stirred at 40 °C. The reaction mixture was analyzed by GLC at various intervals (Silicone SE-30, 10%, 1 m × 3 mm, 180 °C).

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Phenyl Sulfone-Directed Diastereoselective Cyclization of an Epoxy Allylsilane System

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In order to prepare a trimethylsilyl-substituted cyclization substrate for a planned biomimetic-type total synthesis of the secotrinervitane diterpenes,[1] we required a new 2-[(trimethylsilyl)methyl]allyl anion synthon[2] which would allow *two* sequential alkylations to be performed. An intramolecular epoxy allylsilane cyclization was envisioned to complete the carbon skeleton. Epoxy allylsilane cyclizations were introduced by Fleming,[3] and their utility has been extended by the Weiler,[4a] Procter,[4b] and Chan[4c]

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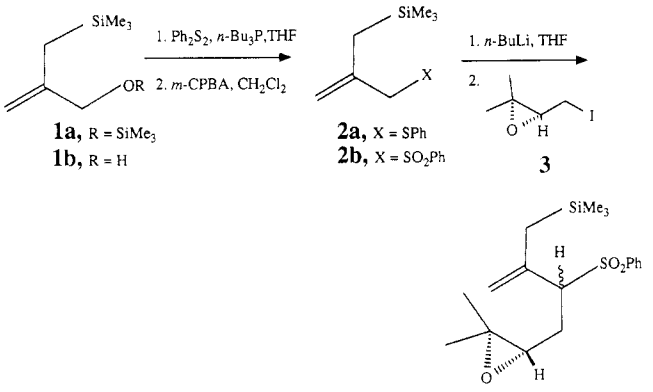
Table I. Lewis Acid Induced Cyclization of Epoxy Allylsilane 4

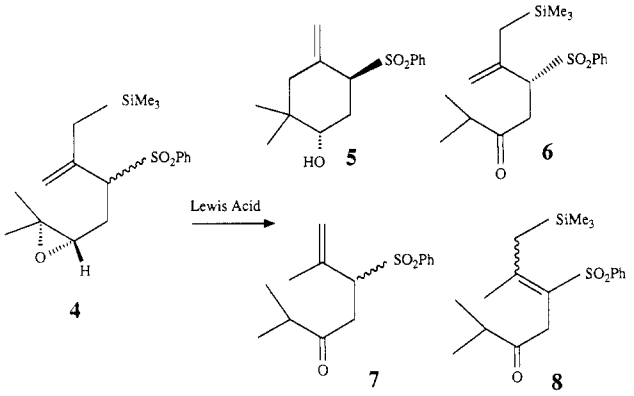
entry[a]	Lewis acid	(equiv)	T, °C	solvent	t, h	yield,[b] %	C:M[c]
1	$SnCl_4$	(1.1)	−78	CH_2Cl_2	1	**5**, 6.7	
2	$SnCl_4$	(5)	−25	CH_2Cl_2	6	**5**, 8.2 **7**, 79	0.1
3	$EtAlCl_2$	(2)	−78 to 20	CH_2Cl_2	10	**8**, 13	0
4	$BF_3{\cdot}Me_2S$	(5)	−25	CH_2Cl_2	0.5	**5**, 8.9 **7**, 64	0.14
5	$BF_3{\cdot}Et_2O$	(3)	−25	CH_2Cl_2	0.5	**5**, 29 **6**, 59	0.49
6	$BF_3{\cdot}Et_2O$	(5)	−25	CH_2Cl_2	10	**5**, 28 **6**, 37	0.78
7	$BF_3{\cdot}Et_2O$	(10)	−25	CH_2Cl_2	0.5	**5**, 19 **6**, 25	0.76
8	$BF_3{\cdot}Et_2O$	(5)	−25	Et_2O	20	**5**, 17 **6**, 43 **8**, 22	0.26
9	$BF_3{\cdot}Et_2O$	(5)	0	CH_2Cl_2	0.5	**5**, 7.5 **6**, 28 **7**, 48	0.1
10	$BF_3{\cdot}Et_2O$	(5)	−78	CH_2Cl_2	0.5	**5**, 28 **6**, 28	1.0
11	$BF_3{\cdot}Et_2O$	(5)	−98	CH_2Cl_2	0.5	**5**, 30 **6**, 32	0.94

[a] Reactions were run on 0.1-mmol scale, except for entries 1 and 3 (0.2 mmol), entry 5 (0.17 mmol), and entry 9 (0.06 mmol). [b] Isolated, chromatographed yields. [c] C:M = (cyclization):(hydride migration).

Scheme I. Preparation of [2-[(Phenylsulfonyl)methyl]allyl]trimethylsilane and Alkylation To Give Model Cyclization Substrate



Scheme II. Products of Cyclization and Hydride Migration Fates for Epoxy Allylsilane in the Presence of Lewis Acids



groups, among others. We describe herein the preparation of [2-[(phenylsulfonyl)methyl]allyl]silane **2b**, alkylation of its corresponding anion with an enantiomerically enriched epoxy iodide, and Lewis acid induced cyclization of a sulfone-containing epoxy allylsilane.

Synthesis and alkylation of the new synthon is illustrated in Scheme I. The dianion of 2-methyl-2-propen-1-ol was prepared with *n*-BuLi in TMEDA–ether–THF (1:3:2) at room temperature and then treated with excess chlorotrimethylsilane to furnish TMS ether **1a**, which gave [2-(hydroxymethyl)allyl]trimethylsilane after hydrolysis.[5] The sulfide **2a** was then prepared by the action of diphenyl disulfide and tri-*n*-butylphosphine in THF at room temperature,[6] and oxidation with *m*CBPA at 0 °C provided the sulfone[7] **2b** in 85% yield from the allylic alcohol **1b**. The allylic sulfone anion was generated selectively with *n*-BuLi in THF at −78 °C and alkylated with epoxy iodide **3** at −78 °C to 0 °C for 1.5 h. The epoxy allylsilane cyclization substrate **4** was obtained in quantitative yield as a 1:1 mixture of two diastereoisomers as determined by proton NMR and capillary GC.

The cyclization reaction was examined with several Lewis acids under a variety of solvent and temperature regimes (Table I). Scheme II shows the cyclization, hydride migration, and protodesilylation products, which have been chemically characterized from the cyclization product mixtures. Stannic chloride gave low yields of cyclized materials at low temperatures and a preponderance of migration products[4d] at higher temperatures. Aluminum- and titanium-based Lewis acids also showed little promise for this cyclization, with chlorohydrin formation,[4b,4c] desilylation, migration, and olefin isomerization competing with cyclization to give complex mixtures. Boron trifluoride etherate appeared to be the most promising agent for cyclization;[4c] in contrast, the dimethyl

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(7) The sulfone was first prepared in a somewhat lower yield procedure from alcohol **1b** by treatment of the alkoxide with phenylsulfenyl chloride, warming to induce rearrangement of the sulfenate to the phenyl sulfoxide, and selective oxidation to sulfone **2b** with 1 equiv of *m*CPBA.

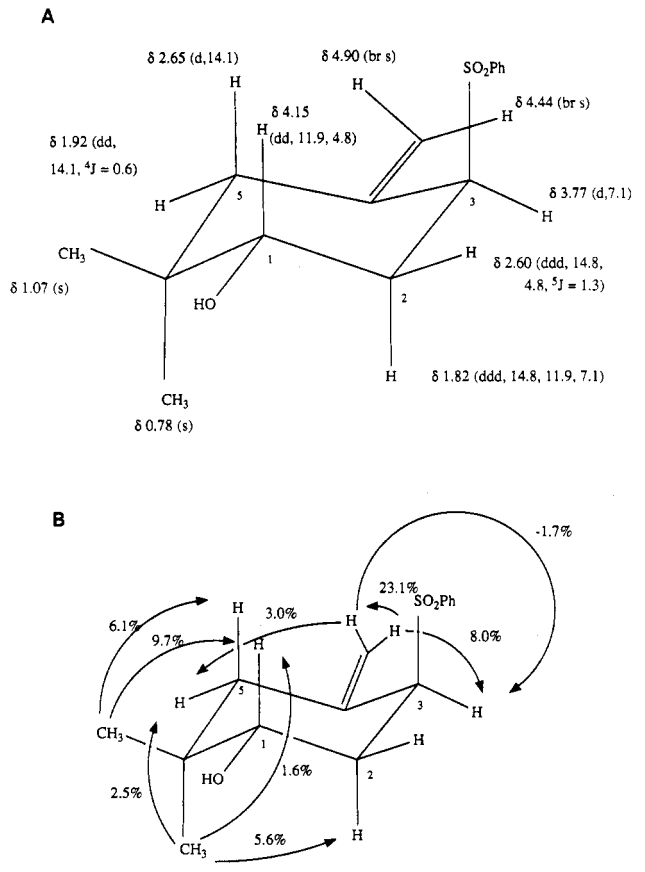

Figure 1. Conformation of cyclization product, indicating NMR assignments.

sulfide complex showed reduced effectiveness in inducing cyclization. Temperature, solvent, and the amount of $BF_3{\cdot}Et_2O$ were varied to obtain an optimal cyclization to hydride migration (C:M) ratio of 1.0 by using 5 equiv of this Lewis acid in methylene chloride at −78 °C. We reasoned that an excess of Lewis acid was required due to complexation with the sulfone oxygens, and that the use of ether as a solvent instead of dichloromethane lowered yields by competing with the epoxide for complexation.

Examination of the NMR of the cyclized product revealed that a *single* homochiral diastereomer had been produced from the 1:1 mixture of diastereomeric starting epoxy sulfones. Apparently, *only one diastereomer of the cyclization substrate could cyclize, while the other suffered preferential hydride migration* as the epoxide opened due to an inappropriate alignment of the allyltrimethylsilyl π electron system. This phenomenon had been reported very recently in an enantiospecific synthesis of a taxol building block.[8] The conformation for the cyclization product **5** can be deduced by analysis of the proton–proton J couplings (Figure 1a) and NOE enhancements (Figure 1b) in the 300-MHz NMR spectrum. Particularly noteworthy are the long-range couplings of ring methylene protons to the *exo*-methylene vinyl protons. The resonance at δ 4.90 (assigned by NOE with H-5e) showed a four-bond J coupling of 0.6 Hz to H-5e, while the resonance at δ 4.44 (NOE to H-3e) showed a five-bond staggered arrangement J coupling of 1.3 Hz to H-2e.

If cyclization of such olefins proceeds via a transition state with a chairlike conformation, then the chairlike conformations of the two diastereomers shows that the 3*R*,5*S* diastereomer **4b** would be expected to experience greater steric compression in attaining the necessary geometry than would the 3*S*,5*S* diastereomer **4a** (Scheme III). Apparently, in order to maximize the overlap between the σ orbital of the C–Si bond and the π orbital of the double bond, the C–$SiMe_3$ bond has to be perpendicular to the plane of the double bond during cyclization.[8] This orientation of the C–$SiMe_3$ bond is restricted by the bulky quasi-equatorial phenylsulfonyl group in the 3*R*,5*S* diastereomer **4b**.

Experimental Section

General Methods. All glassware, syringes, and needles were oven-dried at 110 °C, assembled while hot, and cooled under a flow of dry nitrogen. All reactions were conducted under a slight positive pressure of dry nitrogen. Dry methylene chloride was distilled from phosphorus pentoxide. Anhydrous tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl. Pyridine was dried over potassium hydroxide. TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) was partially dried over 4-Å molecular sieves and distilled from *n*-butyllithium. Acetone was dried over anhydrous potassium carbonate and distilled. NMR spectra were obtained on a QE-300 spectrometer, with chloroform-*d* as the solvent. Flash column chromatography was performed on Universal Adsorbents Silica 32–63 μm with ethyl acetate/hexane (v/v) mixtures under nitrogen.

[2-[(Phenylthio)methyl]allyl]trimethylsilane (2a). To a stirred, cooled (0 °C) solution of 3.93 g (27.2 mmol) of alcohol **1b** (prepared as described by Trost et al.[5]) and 5.90 g (27.0 mmol) of diphenyl disulfide in 34 mL of THF was added 8.9 mL (35.7 mmol) of tri-*n*-butylphosphine. After 18 h at room temperature, the solution was diluted with 400 mL of ether, washed (twice, 10% NaOH; twice, H_2O), dried ($MgSO_4$), and then concentrated in vacuo to give a foul-smelling pale yellow oil. The crude product was purified by column chromatography on silica gel to afford 6.04 g of sulfide **2a** (94%): ^1H NMR δ 0.03 (s, 9 H), 1.71 (s, 2 H), 3.48 (s, 2 H) 4.63 (br, 1 H), 4.78 (br, 1 H), 7.12–7.37 (m, 5 H); ^{13}C NMR δ −1.4, 25.0, 42.4, 111.2, 126.0, 128.6, 129.8, 136.5, 142.2; MS (70 eV), *m*/*z* (relative intensity) 236 (4.5), 131 (18), 130 (13), 73 (100); FT-IR (neat) 3077, 1630, 1249 cm^{-1}.

[2-[(Phenylsulfonyl)methyl]allyl]trimethylsilane (2b). To a cooled (0 °C) solution of sulfide **2a** (6.03 g, 25.5 mmol) in 100 mL of dry methylene chloride, was added a solution of 10.88 g (54 mmol) of *m*CPBA in 80 mL of dry methylene chloride in small portions over 20 min. The reaction was stirred 1.5 h at 0 °C. After dilution with 100 mL of ether, the white precipitate was filtered off, and the reaction solution was diluted further with 300 mL of ether, washed (3 × saturated $NaHCO_3$, brine), dried ($MgSO_4$), and concentrated. The crude product (a white solid) was purified by flash chromatography to give 6.10 g (89%) of pure sulfone **2b**: ^1H NMR δ 0.02 (s, 9 H), 1.71 (s, 2 H), 3.71 (s, 2 H), 4.55 (br, 1 H), 4.79 (br, 1 H), 7.50–7.69 (m, 3 H), 7.85–7.90 (m, 2 H); ^{13}C NMR δ −1.7, 26.3, 64.6, 117.4, 128.4, 128.8, 133.5, 135.0, 138.0; MS (70 eV), *m*/*z* (relative intensity) 268 (0.1), 135 (24), 131 (24), 91 (15), 73 (100); FT-IR (neat) 3077, 1627, 1139, 854 cm^{-1}. Anal. Calcd for $C_{13}H_{20}SSiO_2$: C, 58.17; H, 7.51; S, 11.94; Si, 10.46. Found: C, 58.06; H, 7.30; S, 11.48; Si, 10.63.

(2*R*)-3,3-Dimethyl-2-(iodomethyl)oxirane (3). Asymmetric epoxidation[9] of 3-methyl-2-buten-1-ol (Aldrich) with L(+)-dimethyl tartrate as the chiral catalyst afforded the desired (2*S*)-epoxy alcohol in 62% after column chromatography. Proton NMR analysis of the MTPA ester confirmed an enantiomeric excess greater than 95%. The tosylate was prepared in 81% yield by using 2 equiv of pyridine in chloroform at 0 °C following Kabalka's method.[10] The tosylate (2.55 g, 9.96 mmol) was treated with 3.0 g (20.0 mmol) of sodium iodide in acetone (30 mL) to give 89% (1.89 g) of the epoxy iodide **3**: ^1H NMR δ 1.30 (s, 3 H), 1.36 (s, 3 H), 3.00 (dd, 1 H, J = 9.5, 7.8 Hz), 3.11 (dd, 1 H, J = 5.2, 7.8 Hz), 3.33 (dd, 1 H, J = 9.5, 5.3 Hz); FT-IR (neat) 1289, 1179, 977,

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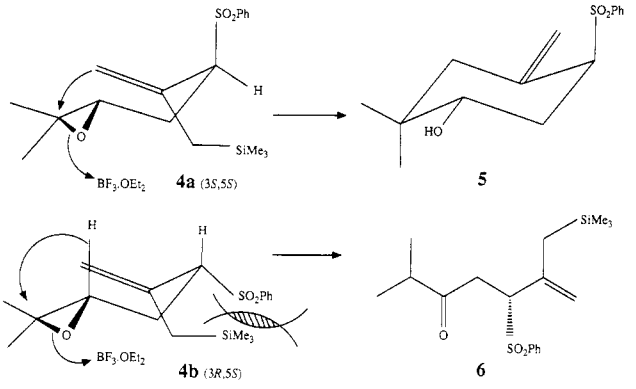
Scheme III. Cyclization and Hydride Migration Can Arise from Different Diastereomers of the Cyclization Substrate



813 cm^{-1}; MS (70 eV), m/z (relative intensity) 212 (1, M^+), 85 (M^+ - I, 100).

(5*S*)-6-Methyl-3-(phenylsulfonyl)-5,6-epoxy-2-[(trimethylsilyl)methyl]-1-heptene (4). Sulfone **2b** (0.998 g, 3.33 mmol) was dissolved in 20 mL of THF and cooled to −78 °C. *n*-Butyllithium (1.6 mL, 4 mmol, 2.5 M in hexane) was added dropwise over 2 min. After the mixture was stirred at −78 °C for 0.5 h, the iodide **3** (0.980 g, 5 mmol, dissolved in 10 mL of THF) was then added dropwise over 5 min. The reaction was warmed up to 0 °C and stirred for 1.5 h. The reaction was quenched with 10% aqueous NH_4Cl (5 mL) and extracted with ether, and the product was isolated as usual. The crude product was purified by column chromatography to give 1.996 g of alkylated product **4** in essentially quantitative yield: ^1H NMR δ 0.012, and 0.043 (s, s, 9 H), 1.21 and 1.23 (s, s, 3 H), 1.26 and 1.28 (s, s, 3 H), 1.56–1.70 (m, 2 H), 2.00–2.4 (m, 2 H), 2.70–2.74 and 2.84–2.94 (m, m, 1 H), 3.60–3.74 (m, 1 H), 4.82 and 4.89 (s, s, 1 H), 4.95 and 5.05 (s, s, 1 H), 7.50–7.90 (m, 5 H); FT-IR (neat) 3066, 1630, 1251, 1245, 849 cm^{-1}; HRMS (70 eV), m/z 337.1301 (M^+ - CH_3 0.9%, calcd for $C_{17}H_{25}SSiO_3$ 337.1293), 211.1516 (M^+ - SO_2Ph, 5.6%, calcd for $C_{12}H_{23}SiO$ 211.1518). Calcd for $C_{18}H_{28}SSiO_3$: C, 61.32; H, 8.00; S, 9.09; Si, 7.97. Found: C, 60.82; H, 8.11; S, 9.80; Si, 6.93.

MPLC was performed with 40% ethyl ether in hexane and 37–63-μm silica gel. This led to an enriched fraction of the first-eluting 3*R*,5*S* stereoisomer **4b** (**4b**:**4a** $\approx$ 85:15), the diastereomer that we predicted could not cyclize. Accordingly, attempted cyclization under optimized conditions (see below) led to an 83% combined yield of isolated ketones **6** and **7**. Apparently, the long contact time during MPLC separation caused decomposition of the cyclizing stereoisomer **4a**, which could not be obtained in homogeneous form.

From the mixed isomers and the enriched **4b**, unambiguous ^1H NMR assignments could be made for each stereoisomer **4a** and **4b**. For 3*S*,5*S* isomer **4a**: δ 0.012 (s, 9 H), 1.24 (s, 3 H), 1.28 (s, 3 H), 1.56 and 1.58 (br s, br s, RCH_2SiMe$_3$), 2.3–2.4 (m, H-4), 2.87 (dd (apparent t), J = 6.0, 6.0 Hz, H-5), 3.62 (dd, J = 6.3, 8.0 Hz, H-3), 4.82 and 4.95 (br s, br s, H-7); 7.5–7.9 (m, 5 H). For 3*R*,5*S* isomer **4b**: δ 0.043 (s, 9 H), 1.21 (s, 3 H), 1.26 (s, 3 H), 1.66 and 1.70 (br s, br s, RCH_2SiMe$_3$), 2.00 (ddd, J = 3.9, 8.1, 14.2 Hz, H-4a), 2.16 (ddd, J = 3.8, 11.3, 14.2 Hz, H-4b), 2.72 (dd, J = 3.8, 8.1 Hz, H-5), 3.71 (dd, J = 3.9, 11.3 Hz, H-3); 4.88 and 5.05 (br s, br s, H-7), 7.5–7.9 (m, 5 H).

General Procedure for Cyclization of 4 with Lewis Acids. Epoxy sulfone **4** (0.04–0.2 mmol) was dissolved in 5 mL of solvent (methylene chloride, ether, or nitromethane) and cooled to the indicated temperature. Then, 0.33–10 equiv of the indicated Lewis acid was added, and the reaction mixture was stirred for the indicated time. The reaction was quenched with 5 mL of 10% aqueous NH_4Cl solution and extracted with ethyl ether (3 × 10 mL), and the combined extracts were washed (brine), dried ($MgSO_4$), and concentrated on a rotary evaporator. The resulting crude product was purified by flash chromatography on silica gel (10 mm × 100 mm with ethyl acetate/hexane, v/v).

Cyclization with 3 equiv of BF_3·Et_2O. Preparation of (1*S*,3*S*)-6,6-Dimethyl-4-methylene-3-(phenylsulfonyl)-cyclohexan-1-ol (5) and 2-Methyl-5-(phenylsulfonyl)-6-[(trimethylsilyl)methyl]-6-hepten-3-one (6). A methylene chloride solution of substrate **4** (0.060 g, 0.17 mmol) was treated with boron trifluoride etherate (0.065 mL, 0.51 mmol) at −25 °C for 0.5 h, giving cyclized product **5** (colorless crystal) and ketone **6** (colorless oil) in yields of 29% (13.7 mg) and 59% (35.2 mg), respectively: ^1H NMR, see Figure 1a for **5**; ^{13}C NMR δ 17.4, 27.8, 28.7, 36.3, 44.3, 68.9, 72.1, 120.2, 121.1, 128.8, 129.0, 133.6, 137.0; FT-IR (KBr) 3532, 3068, 1644, 1301, 1140, 1062, 925 cm^{-1}; HRMS (70 eV), m/z 280.1136 (M^+, 0.4%, calcd for $C_{15}H_{20}SO_3$ 280.1133), 139.1123 (M^+ - SO_2Ph, 46.6% calcd for $C_9H_{15}O$ 139.1123). Anal. Calcd for $C_{15}H_{20}SO_3$: C, 64.26; H, 7.19; S, 11.43. Found: C, 64.47; H, 7.28; S, 11.09.

For ketone **6**: ^1H NMR δ 0.03 (s, 9 H), 1.06 (d, 6 H, J = 6.9 Hz), 1.54 (d, 2 H, J = 6.0 Hz), 2.59 (septet, 1 H, J = 6.9 Hz), 2.87 (dd, 1 H, J = 18, 7.2 Hz), 3.27 (dd, 1 H, J = 18, 5.7 Hz), 4.26 (dd, 1 H, J = 7.2, 5.7 Hz), 4.81 (s, 1 H), 4.91 (s, 1 H), 7.50–7.88 (m, 5 H); ^{13}C NMR δ −1.4, 17.9, 27.2, 39.1, 41.2, 66.6, 115.9, 128.8, 129.2, 133.7, 137.3, 139.9, 208.9; FT-IR (neat) 3064, 1717, 1630, 1248, 1146, 855 cm^{-1}; HRMS (70 eV), m/z 337.1288 (M^+ - CH_3, 2.1%, calcd for $C_{17}H_{25}SSiO_3$ 337.1293), 211.1516 (M^+ - SO_2Ph, 85.6%; calcd for $C_{12}H_{23}SiO$ 211.1518). Anal. Calcd for $C_{18}H_{28}SSiO_3$: C, 61.32; H, 8.00; S, 9.09; Si, 7.97. Found: C, 61.50; H, 8.00; S, 8.82.

Cyclization with 5 equiv of BF_3·Et_2O. Preparation of 2,6-Dimethyl-5-(phenylsulfonyl)-7-(trimethylsilyl)-5-hepten-3-one (8). A solution of substrate **4** (0.0337 g, 0.096 mmol) in ether was treated with BF_3·Et_2O (0.060 mL, 0.048 mmol) for 20 h at −25 °C, giving 4.6 mg (17%) of cyclic product **5**, 14.5 mg (43%) of ketone **6**, and 7.4 mg (22%) of ketone **8**: ^1H NMR (**8**) δ 0.03 (s, 9 H), 1.17 (d, 6 H, J = 7.5 Hz), 1.67 (s, 2 H), 1.95 (s, 3 H), 2.79 (septet, 1 H, J = 7.5 Hz), 3.75 (s, 2 H), 7.46–8.00 (m, 5 H); FT-IR (neat) 3064, 1716, 1610, 1140, 1083, 848 cm^{-1}; HRMS (70 eV), m/z 337.1296 (M^+ - CH_3, 1.9%, calcd for $C_{17}H_{25}SSiO_3$ 337.1293), 211.1516 (M^+ - SO_2Ph, 34.1%, calcd for $C_{12}H_{23}SiO$ 211.1518). Anal. Calcd for $C_{18}H_{28}SSiO_3$: C, 61.32; H, 8.00; S, 9.09; Si, 7.97. Found: C, 61.56; H, 7.98; S, 8.98.

Cyclization with Boron Trifluoride in CH_2Cl_2 at 0 °C. Preparation of 2,6-Dimethyl-5-(phenylsulfonyl)-6-hepten-3-one (7). Treatment of substrate **4** (0.020 g, 0.057 mmol) with boron trifluoride (0.040 mL, 0.33 mmol) in methylene chloride at 0 °C for 0.5 h, according to the general procedure, gave 1.2 mg (7.5%) of cyclic product **5**, 5.5 mg (28%) of **6**, and 7.6 mg (48%) of desilylated sulfone **7**: ^1H NMR (**7**) δ 1.08 and 1.10 (d, d, 6 H, both J = 6.9 Hz), 1.69 (s, 3 H), 2.61 (septet, 1 H, J = 6.9 Hz), 3.11 (dd, 1 H, H-4a, J_{gem} = 17.7, J_{vic} = 9.8 Hz), 3.27 (dd, 1 H, H-b, J_{gem} = 17.7 Hz, J_{vic} = 3.9), 4.19 (dd, 1 H, J = 9.8, 4.1 Hz) 4.82 (s, 1 H), 5.03 (s, 1 H), 7.51–7.90 (m, 5 H), 7.80–7.90 (m, 2 H); FT-IR (neat) 3065, 1714, 1643, 1146, 1026, 720 cm^{-1}; MS (70 eV), m/z 139 (16%, M^+ - SO_2Ph). Anal. Calcd for $C_{15}H_{20}O_3$: C, 64.26; H, 7.19; S, 11.43. Found: C, 64.48; H, 7.52; S, 11.94.

Cyclization with BF_3·Me_2S (5 equiv) in Methylene Chloride. Substrate **4** (0.0310 g, 0.088 mmol) was treated with 0.036 mL (0.5 mmol) of BF_3·Me_2S in 5 mL of methylene chloride at −25 °C for 0.5 h. After chromatography, 2.5 mg (10%) of cyclic product **5** and 18 mg (73%) of ketone **7** were obtained as the products.

Attempted Cyclization with $EtAlCl_2$. Substrate **4** (0.0693 g, 0.20 mmol) was treated with $EtAlCl_2$ (0.40 mL, 0.40 mmol, 1 M in hexane) in methylene chloride (5 mL) between −78 °C and room temperature for 10 h, giving 7.1 mg (10%) of ketone **8** as the sole isolable product from a complex mixture.

Cyclization with Stannic Chloride. A solution of 70.5 mg (0.21 mmol) of epoxide **4** in 5 mL of methylene chloride was treated with $SnCl_4$ (0.22 mL, 0.22 mmol, 1.0 M in methylene chloride) at −78 °C for 1 h, according to the general procedure. With this experiment, 3.8 mg (6.5%) of cyclized product **5** was obtained as the only isolable product. In a second trial, a solution of 35.6 mg of epoxide **4** in 5 mL of methylene chloride was treated with $SnCl_4$ (0.50 mL, 0.50 mmol, 1.0 M in methylene chloride) at −25 °C for 6 h. With 5 equiv, the products isolated were the cyclic alcohol **5** (2.3 mg, 8.2%) and the ketone **8** (22.1 mg, 62%).

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