by using thianthrene 5,5-dioxide, 5,10-dioxide, and 5,5,10-trioxide concentrations as determined by calibrated integrals obtained from HPLC analysis of the reaction mixtures. For Hammett parameters, relative rates of oxidation (k_X/k_H) were determined by HPLC analysis of the competition reaction mixtures containing either *p*-methyl-, *p*-chloro-, or *p*-fluoro-substituted phenyl sulfoxides and the parent unsubstituted phenyl sulfoxide. Calibrated integrals were used to determine the relative yields of sulfones from which the following k_X/k_H values were calculated, taking the mean of at least three independent measurements: for peroxonium ion **2**, k_X/k_H (substituent) = 2.22 (*p*-Me), 1.00 (*p*-H), 0.74 (*p*-F), 0.49 (*p*-Cl); for peroxonium ion **4**, 1.99 (*p*-Me), 1.00 (*p*-H), 1.05 (*p*-F), 0.07 (*p*-Cl). Assuming a Hammett linear free energy relationship,[23] plots of log (k_X/k_H) versus 2σ gave ρ values of -0.83 ± 0.11 ($R = 0.98$) for peroxonium ion **2** and -1.77 ± 0.58 ($R = 0.91$) for peroxonium ion **4**.

Acknowledgment. We thank the SERC for the award of an Earmarked Studentship.

(23) σ values used in the linear free energy calculation are taken from: Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323.

Notes

Stereochemical Control in the Synthesis of 2,5-Disubstituted Tetrahydrofurans

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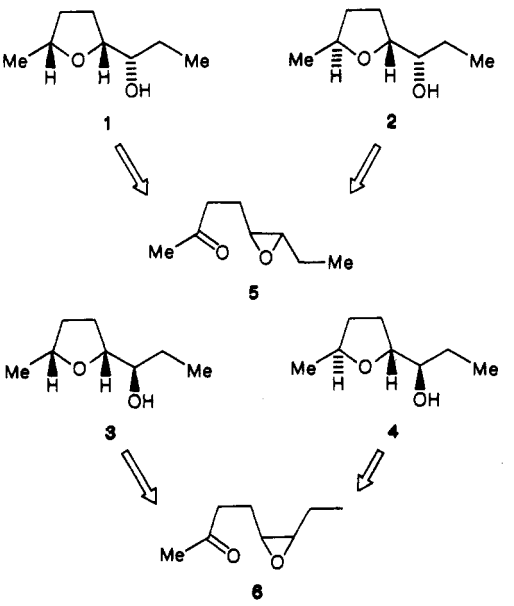
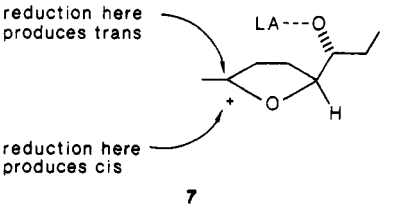
The synthesis of polyether antibiotics and other complex targets containing oxacyclic subunits has led to the development of many procedures for constructing substituted tetrahydrofurans.[1] Despite several notable examples of stereoselection in the synthesis of 2,5-disubstituted tetrahydrofurans, a completely satisfactory general method of stereochemical control has yet to be reported. One noteworthy example was demonstrated by Kishi, where cyclization of a hydroxy epoxide with the relative stereochemistry *predetermined* yielded a *trans*-2,5-tetrahydrofuran.[2] In the process of addressing the general problem of substituted tetrahydrofuran formation, we have found a new method of constructing these ring systems that appears to be particularly promising for the stereoselective formation of the especially troublesome[3] 2,5-trans derivatives such as **2** and **4**.

We originally sought a method that might allow complete stereochemical control (in a *predictable* direction) at each of three centers in the hydroxy tetrahydrofuran diastereomers **1**-**4**.[4] The general plan was to effect an electrophilic epoxide opening with carbonyl participation, followed by either inter- or intramolecular reduction of the resulting carbonium ion. Control of the tetrahydrofuran stereochemistry would thus derive from the choice of reduction mode (inter → cis tetrahydrofuran and intra → trans tetrahydrofuran), while the relative stereochemistry of the resultant alcohol group would simply depend upon



whether the cis or trans epoxide was cyclized (opening of protonated epoxides by internal or external nucleophiles generally proceeds with inversion).[5]



The first obstacle presenting itself in the intermolecular cyclization/reduction was the necessity of finding a source of hydride compatible with the acidic conditions necessary to initiate cyclization. Fortunately, trialkylsilanes survive mild Lewis and protic acid conditions and are known to reduce simple cationic intermediates related to **7** (i.e., reduction of ketals to ethers).[6]

(1) (a) Semple, J. E.; Joullie, M. M. *Heterocycles* **1980**, *14*, 1825. (b) Williams, D. R.; Harigaya, Y.; Moore, J. L.; D'sa, A. *J Am. Chem. Soc.* **1984**, *106*, 2641. (c) Ting, P. C.; Barlett, P. A. *J. Am. Chem. Soc.* **1984**, *106*, 2668 and references therein.

(2) (a) Fukuyama, T.; Vransic, B.; Negri, D. P.; Kishi, Y. *Tetrahedron Lett.* **1978**, 2741. (b) Nakata, T.; Kishi, Y. *Tetrahedron Lett.* **1978**, 2745.

(3) See ref 1c for examples of difficulties in forming 2,5-trans tetrahydrofurans stereoselectively.

(4) This particular set of diastereomers was chosen because all are known compounds, distinguishable by NMR: Porter, N. A.; Zuraw, P. J. *J. Org. Chem.* **1984**, *49*, 1345. We did experience some problems in the workup and isolation because of water solubility and volatility.

(5) See for example: (a) Coxon, J. M.; Hartshorn, M. P.; Swallow, W. H. *Aust. J. Chem.* **1973**, *26*, 2521. (b) Roush, W. R.; Brown, R. J.; DiMare, M. *J. Org. Chem.* **1983**, *48*, 5083.

(6) (a) Lancelin, J.-M.; Zollo, P. H. A.; Sinay, P. *Tetrahedron Lett.* **1983**, *24*, 4833. (b) Doyle, M. P.; DeBruyn, D. J.; Kooistra, D. A. *J. Am. Chem. Soc.* **1972**, *94*, 3659. (c) Kursandov, D. N.; Parnes, Z. N.; Loim, N. M. *Synthesis* **1974**, 633.

0022-3263/88/1953-1082$01.50/0

Table I. Formation of Cis Tetrahydrofurans

starting material	conditions	products	ratio	% yield[a,b]
5	Et_3SiH/TFA	1,2	2:1	68 (58)
5	Ph_3SiH/BF_3–Et_2O	1,2	5:1	51 (43)
5	Ph_3SiH/TIPSOTr	1,2	4:1	50 (43)
6	Ph_3SiH/BF_3–Et_2O	3,4	4:1	30 (27)
6	Et_3SiH/BF_3–Et_2O	3,4	2:1	37 (34)

[a] Purified by flash chromatography on silica gel. [b] Yields in parentheses are based on starting olefin.

Since a stable intermolecular reducing agent was available, the formation of cis tetrahydrofurans was investigated. Addition of 1.1 equiv of BF_3–Et_2O to a solution of triethylsilane (Et_3SiH) and **5** or **6** yielded a 2:1[7] mixture of the cis–trans tetrahydrofurans **1** and **2** (or **3** and **4**), as shown in Table I. This result was not particularly surprising, since 1, 3 induction in five-membered rings often is weak. The ratio could be improved somewhat by increasing the steric bulk of the reducing agent. A variety of other trialkylsilanes were tested to determine the stereoselectivity of intermolecular reduction of intermediate **7**. Dimethylphenylsilane (Me_2PhSiH) gave a 2:1 ratio of the cis–trans tetrahydrofurans **1** and **2** from **5**.[8] Diphenylmethylsilane (Ph_2MeSiH) and *tert*-butyldiphenylsilane (*t*-$BuPh_2SiH$) both gave a 4:1 ratio of the cis–trans tetrahydrofurans tetrahydrofurans **1** and **2** from **5**.[8] The best result obtained for this intermolecular reduction was a 5:1 ratio of the cis–trans tetrahydrofurans **1** and **2** for the reduction of **5** with triphenylsilane (Ph_3SiH). Reduction of ketone **6** behaved in a similar manner, yielding a 4:1 ratio of cis–trans tetrahydrofurans **3** and **4** with Ph_3SiH and a 2:1 ratio of cis–trans tetrahydrofurans **3** and **4** with Et_3SiH.

The effect of the reducing agent's steric bulk is consistent with the proposed mechanism of cyclization followed by reduction; however, the alternative mechanism of ketone reduction followed by ring closure cannot be ruled out completely. An epoxy alcohol mixture obtained by careful $LiAlH_4$ reduction of **5** cyclizes under the proposed intermolecular reduction conditions to give a 2:1 (cis–trans) mixture of tetrahydrofurans.

The intramolecular version of this reduction simply requires the use of a Lewis acid that becomes a hydride donor after epoxide opening. There are a number of examples of intramolecular hydride delivery to other function groups by oxygen–borane reducing agents,[9] serving as precedent for that step. The most obvious choice, BH_3, proved to work well. For instance, the reaction of **5** with borane–dimethyl sulfide complex (Me_2S–BH_3) in dichloromethane at –60 °C yielded the trans tetrahydrofuran **2** as the major product. Interestingly, the cis–trans tetrahydrofuran ratio was dependent upon concentration (see Table II). In order to obtain a cis–trans ratio of 1:15 or better, the reaction medium had to be less than 0.005 M. Increasing the concentration lowered the trans selectivity, presumably due to intermolecular reduction competing with intramolecular reduction. The dependence on concentration suggests that the intramolecular reduction was slow enough to allow intermolecular reduction to compete at higher concentrations.

(7) Diastereomer ratios were determined on samples of crude reaction mixtures, by ^1H NMR[4] and capillary GC analyses. Chromatography did not significantly change the ^1H NMR and GC ratios or the purity of the reaction products.

(8) Data not shown. See: Mulholland, R. L. Ph.D. Thesis, University of California, Irvine, 1985.

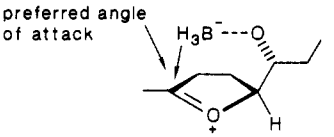
(9) For some recent examples, see: Salmon, R. G.; Sachinvala, N. D.; Raychaudhuri, S. R.; Miller, D. B. *J. Am. Chem.* Soc. **1984**, *106*, 2211 and references therein.

Table II. Formation of Trans Tetrahydrofurans

starting material	conditions	products	ratio	% yield[c]
5	Me_2S–BH_3/0.005 M	1,2	1:24	90[b] (77)
5	Me_2S–BH_3/0.012 M	1,2	1:11	58[a] (49)
5	thexylborane/0.030 M	1,2	1:9	41[a] (35)
5	catechol borane/0.016 M	1,2	1:3	85[a] (72)
6	Me_2S–BH_3/0.005 M	3,4	1:15	67[b] (61)
6	Me_2S–BH_3/0.018 M	3,4	1:8	79[b] (72)

[a] Purified by flash chromatography on silica gel. [b] Crude yield; chromatography did not improve purity. [c] Yields in parentheses are based on starting olefin.

The sluggishness of the intramolecular process could result from unfavorable stereoelectronics. Drieding models of **7** (LA = BH_3) reveal considerable strain upon moving the hydride source to a proper angle of attack. Several other boranes were used in the intramolecular reduction of ketone **5**, but no significant improvement over the ratio of 1:24 cis–trans was noticed (see Table II).



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In conclusion, it is possible to prepare any of the four possible diastereomers **1**–**4** with fair to excellent control of stereochemistry. While the intermolecular reduction suffers because of moderate 1,3 induction, the intramolecular process promises to be a useful method of preparing trans-2,5-disubstituted tetrahydrofuran derivatives. These methods provide useful alternatives to known procedures for constructing substituted tetrahydrofurans which are subunits of polyether antibiotics.

Experimental Section

General Methods. All reactions sensitive to moisture or oxygen were performed according to the methods outlined in Chapter 9 of *Organic Synthesis via Boranes*[10] or modifications thereof. Argon was used as the inert atmosphere and was passed through a 6-in. column of $CaCO_3$ before use. Reagents and solvents were introduced by canula or syringe.

IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer. ^1H NMR spectra were recorded on a Bruker WM250 (250 MHz) spectrometer. Chemical shifts are reported in ppm relative to chloroform (7.27 ppm). ^{13}C NMR spectra were recorded on a bruker WM250 (62.9 MHz) spectrometer. Chemical shifts are reported in ppm relative to the center peak of deuteriochloroform (77.2 ppm). Low-resolution mass spectra were recorded on a Finnigan 4000 spectrometer at 70 eV. Gas chromatography was conducted on a Hewlett-Packard Model 5830A chromatograph equipped with a flame-ionization detector using a 15-m capillary column. TLC was performed on 0.25-mm E. Merck precoated silica gel plates (60F-254).

Standard workup of reactions was as follows: addition of saturated $NaHCO_3$ solution, extraction three times with diethyl ether, drying ($MgSO_4$), and concentration in vacuo.

Preparation of Cis and Trans Keto Epoxides. *rel*-(5*S*,6*S*)-5,6-Epoxy-2-octanone (5). A solution of 9.5 g (0.110 mol) of 1-penten-3-ol, 15.9 (0.221 mol) of 2-methoxypropene, and 6.54 g (0.088 mol) of propanoic acid was refluxed for 12 h.[11] Then, the mixture was distilled to remove MeOH, washed with 3.0 M HCl, extracted three times with diethyl ether, dried ($MgSO_4$), concentrated in vacuo, and distilled (48 mmHg) to yield 7.72 g (56%) of *trans*-5-octen-2-one: ^1H NMR (250 MHz, $CDCl_3$) δ 5.46

(10) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Synthesis via Boranes*; Wiley: New York; 1975.

(11) Daub, G. W.; McCoy, M. A.; Sanchez, M. G.; Carter, J. S. *J. Am. Chem. Soc.* **1983**, *48*, 3876.

(m, 1 H), 5.40 (m, 1 H), 2.50 (t, J = 7.4 Hz, 2 H, H-3), 2.26 (app q, J = 6.7 Hz, 2 H, H-4), 2.14 (s, 3 H, H-1), 1.99 (app quintet, J = 7.1 Hz, 2 H, H-7), 0.95 (t, J = 7.1 Hz, 3 H, H-8); IR 2980, 1720, 1260 cm^{-1}; TLC (5:1 petroleum ether–ether, R_f 0.28).

To a solution of 162 mg (1.29 mmol) of *trans*-5-octen-2-one in 3.0 mL of pentane at 0 °C was added 0.291 g (1.35 mmol) of 85% *m*-chloroperoxybenzoic acid. After the reaction was complete by TLC, the suspension was filtered through Celite (0 °C), washed twice with saturated $NaHCO_3$ solution and concentrated in vacuo to yield 0.158 g (86%) of crude **5**,[12] which was used as is in the formation of tetrahydrofurans. **5**: ^1H NMR (250 MHz, $CDCl_3$) δ 2.70 (m, 2 H, H-5, H-6), 2.59 (t, J = 7.2 Hz, 2 H, H-3), 2.17 (s, 3 H, H-1), 1.97 (m, 1 H), 1.70–1.53 (m, 3 H), 0.98 (t, J = 7.5 Hz, 3 H, H-8); IR 2940, 1700, 1360, 1210, 1060 cm^{-1}; Mass spectrum, m/e (relative intensity) 142 (M^+, 7.03), 127 (M^+ – Me 9.29), 101 ($M^+ - C_3H_5$, 88.00), 83 ($M^+ - C_3H_6O$ – H, 67.87), 71 ($M^+ - C_4H_7O$, 100.00); TLC (2:1 petroleum ether–ether, R_f 0.15).

***rel*-(5*S*,6*R*)-5,6-Epoxy-2-octanone (6).** To a solution of 15.0 mmol of methyllithium in 10 mL of tetrahydrofuran at –78 °C under an argon atmosphere is slowly added 1.08 g (20.0 mmol) of 1-butyne, and then the mixture is stirred for 10 min, warmed to 0 °C, mixed with 10 mL of HMPA and 2.42 g (10.0 mmol) of 2-methyl-2-(2-iodoethyl)-1,3-dioxolane,[13] warmed to room temperature, and quenched after 12 h with H_2O. The reaction mixture was extracted three times with pentane, dried ($MgSO_4$), and concentrated in vacuo to yield 1.56 g (93%) of crude 2-(ethylenedioxy)-5-octynone. Flash chromatography (10:1 petroleum ether–ether, SiO_2) yielded 0.81 g (48%) of a clear colorless oil: ^1H NMR (250 MHz, $CDCl_3$) δ 3.95 (m, 4 H), 2.26 (m, 2 H), 2.14 (m, 2 H), 1.87 (t, J = 7.5 Hz, 2 H, H-3), 1.33 (s, 3 H, H-1), 1.11 (t, J = 7.5 Hz, 3 H, H-8); IR 2980, 2890, 1380, 1120, 1135, 1055, 860 cm^{-1}; TLC (10:1 petroleum ether–ether, R_f 0.21); GC (8.8 min, 100%).

A solution of 1.00 g (5.95 mmol) of 2-(ethylenedioxy)-5-octynone in 2 mL of pyridine and 4 mL of MeOH and 30 mg of $Pd/BaSO_4$ was stirred for 1 h under an atmosphere of H_2, then filtered through Celite, washed with H_2O, extracted with pentane, dried ($MgSO_4$), and concentrated in vacuo. The crude product (1.00 g, 5.88 mmol) was added to 10 mL of acetone and 10 mL of 3.0 M hydrochloric acid, refluxed 3 h, and then quenched following the standard workup procedure to yield 0.735 g (98%) of crude *cis*-5-octen-2-one. Flash chromatography (10:1 petroleum ether–ether, SiO_2) yielded 0.528 g (71%) of a clear colorless oil: ^1H NMR (250 MHz, $CDCl_3$) δ 5.38 (m, 1 H), 5.30 (m, 1 H), 2.48 (t, J = 7.2 Hz, 2 H, H-3), 2.32 (app q, J = 7.2 Hz, 2 H, H-4), 2.15 (s, 3 H, H-1), 2.06 (app quintet, J = 7.4 Hz, 2 H, H-7), 0.96 (t, J = 7.4 Hz, 3 H, H-8); IR 2950, 1715, 1360, 1160 cm^{-1}; mass spectrum, m/e (relative intensity) 126 (M^+, 8.20), 97 (M^+ – Et, 28.02), 84 ($M^+ - C_3H_6$, 14.05), 83 ($M^+ - C_3H_3O$, 23.99), 71 ($M^+ - C_4H_7$, 100.00); TLC (5:1, petroleum ether–ether, R_f 0.35); GC (3.5 min, 100%).

To a solution of 146 mg (1.16 mmol) of *cis*-5-octen-2-one in 5.0 mL of pentane at 0 °C was added 262 mg (1.22 mmol) of 85% *m*-chloroperoxybenzoic acid. After the reaction was complete by TLC, the suspension was filtered through Celite (0 °C), washed twice with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated in vacuo to yield 0.149 g (91%) of crude **6**,[12] which was used as is in the formation of tetrahydrofurans. **6**: ^1H NMR (250 MHz, $CDCl_3$) δ 2.94 (m, 2 H, H-5, H-6), 2.64 (dt, J = 7.5, 3.0 Hz, 2 H, H-3), 2.19 (s, 3 H, H-1), 1.90 (m, 1 H), 1.71–1.48 (m, 3 H), 1.05 (t, J = 7.5 Hz, 3 H, H-8); IR 2960, 1720, 1260 cm^{-1}; mass spectrum, m/e (relative intensity) 143 (M^+ + 1, 100.00), 125 (M^+ + 1 – H_2O, 37.24), 101 (M^+ + 1 – CH_2CO, 9.42), 99 (M^+ + 1 – CH_3COH, 12.36); TLC (2:1 petroleum ether–ether, R_f 0.15); GC (7.5 min, 5%; 7.8 min, 95%).

Synthesis of Hydroxytetrahydrofurans. General Procedures. Method A. *cis*-Hydroxytetrahydrofuran Formation. To a solution of 0.20 mmol of the appropriate epoxy ketone and 1.1 equiv of the selected trialkylsilane in 2.0 mL of dichloromethane at –60 °C was added 1.1 equiv of either trifluoroacetic acid or boron trifluoride etherate (see Table I). The reaction mixture was stirred until the reaction was complete by TLC and quenched by using the standard workup procedure to yield the following tetrahydrofurans.

***rel*-(2*S*,5*S*,α*R*)-α-Ethyl-5-methyltetrahydrofuranmethanol (1).** Method A was performed on 28.8 mg (0.203 mmol) of **5** with 25.9 mg (0.223 mmol) of Et_3SiH and 31.7 mg (0.223 mmol) of trifluoroacetic acid to yield 20.0 mg (68%) of **1** after flash chromatography (1:1 petroleum ether–ether, SiO_2) as a clear colorless oil. **1**: ^1H NMR (250 MHz, $CDCl_3$) δ 4.01 (app hextet, J = 7.1 Hz, 1 H, H-5), 3.85 (dt, J = 7.3, 3.2 Hz, 1 H, H-2), 3.72 (m, H-α), 2.05 (m, 2 H), 1.88 (m, 2 H), 1.63 (br s, OH), 1.47 (m, 2 H), 1.24 (d, J = 6.0 Hz, 3 H, H-6), 0.98 (t, J = 6.9 Hz, 3 H, H-δ), 66% by ^1H NMR. Minor isomer **2**: ^1H NMR δ 4.14, 3.96, 1.23, 33% by ^1H NMR; IR 3550–3300, 2980, 2940, 2880, 1470, 1380, 1000; TLC (2:2:1 hexane–CH_2Cl_2–ethyl acetate, R_f 0.37); GC (5.3 min, 65%, 5.9 min, 35%). The ^{13}C NMR data was the same as reported in ref 4.

Method A was performed on 75.3 mg (0.530 mmol) of **5** with 152 mg (0.583 mmol) of Ph_3SiH and 83 mg (0.583 mmol) of BF_3 Et_2O to yield 39.2 mg (51%) after flash chromatography of **1** (83%) and **2** (17%) by ^1H NMR and GC analyses.

Method A was performed on 41.7 mg (0.294 mmol) of **5** with 84.1 mg (0.323 mmol) of Ph_3SiH and 99.0 mg (0.323 mmol) of TIPSOTr[14] to yield 21.2 mg (50%) after flash chromatography of **1** (80%) and **2** (20%) by ^1H NMR and GC analyses.

***rel*-(2*S*,5*S*,α*S*)-α-Ethyl-5-methyltetrahydrofuranmethanol (3).** Method A was performed on 440 mg (0.310 mmol) of **6** with 84.7 mg (0.325 mmol) of Ph_3SiH and 46.2 mg (0.325 mmol) of BF_3–Et_2O to yield 10.6 mg (30%) of **3** after flash chromatography (1:1 petroleum ether–ether, SiO_2) as a clear colorless oil. **3**: ^1H NMR (250 MHz, $CDCl_3$) δ 4.04 (app hextet, J = 6.2 Hz, 1 H, H-5), 3.76 (app q, J = 6.4 Hz, 1 H, H-2), 3.34 (m, H-α), 2.01 (m, 2 H), 1.75–1.42 (m, 4 H), 1.24 (d, J = 6.2 Hz, 3 H, H-6), 1.01 (t, J = 7.4 Hz, 3 H, H-γ); IR 3600–3400, 2980, 2940, 2880, 1470, 1385, 1090, 970 cm^{-1}; TLC (2:2:1, hexane–CH_2Cl_2–ethyl acetate, R_f 0.30); GC (5.2 min, 80%, 5.7 min, 20%). The ^{13}C NMR data was the same as reported in ref 4.

Method A was performed of 44.0 mg (0.310 mmol) of **6** with 37.8 mg (0.325 mmol) of Et_3SiH and 46.2 mg (0.325 mmol) of BF_3–Et_2O to yield 13.2 mg (37%) after flash chromatography of **3** (66%) and **4** (33%) by ^1H NMR and GC analyses.

Method B. *trans*-Hydroxytetrahydrofuran Formation. A solution of 0.20 mmol of the appropriate epoxy ketone at the noted molarity (see Table II) and 1.0 equiv of a 1.0 M borane reagent in dichloromethane (see Table II) was stirred at –60 °C for 2 h, allowed to warm to room temperature, and then quenched by the standard workup procedure.

***rel*-(2*S*,5*R*,α*R*)-α-Ethyl-5-methyltetrahydrofuranmethanol (2).** Method B was performed on 56.6 mg (0.399 mmol) of **5** with 0.40 mL (0.399 mmol) of Me_2S–BH_3 (1.0 M in dichloromethane) and 80 mL (0.005 M) of dichloromethane to yield 51.4 mg (90%) of crude **2** as a clear colorless oil. **2**: ^1H NMR (250 MHz, $CDCl_3$) δ 4.14 (app dq, J = 10.9, 5.9 Hz, 1 H, H-5), 3.96 (dt, J = 6.7, 3.6 Hz, 1 H, H-2), 3.72 (m, H-β), 2.06 (m, 2 H, H-4), 1.88 (m, 2 H, H-3), 1.64 (br s, OH), 1.43 (m, 2 H, H-α), 1.23 (d, J = 5.9 Hz, 3 H, H-6), 0.99 (t, J = 7.4 Hz, 3 H, H-γ); IR 3500–3300, 2980, 2940, 2880, 1470, 1380, 1090, 1050 cm^{-1}; mass spectrum, m/e (relative intensity) 145 (M^+ + 1, 17.52), 143 (M^+ + 1 – 2 H, 49.38), 127 (M^+ + 1 – H_2O, 41.98), 99 (M^+ + 1 – H_2O – C_2H_4, 100.00); TLC (2:2:1 hexane–CH_2Cl_2–ethyl acetate, R_f 0.30); GC (5.3 min, 4%; 5.9 min, 96%). The ^{13}C NMR data was the same as reported in ref 4.

Method B was performed on 50.1 mg (0.353 mmol) of **5** with 0.37 mL (0.370 mmol) of Me_2S–BH_3 (1.0 M in dichloromethane) and 30.0 mL (0.012 M) of dichloromethane at –78 °C for 4 h to yield 46.1 mg (91%) crude **2**: GC (5.3 min, 8%; 5.9 min, 92%); flash chromatography yielded 29.3 mg (58%) of **2**; GC (5.3 min, 7%; 5.9 min, 93%).

Method B was performed on 298 mg (2.10 mmol) of **5** with 2.20 mmol of thexylborane in 70 mL (0.030 M) of dichloromethane

(12) Compounds **5** and **6** were unstable to flash chromatography, distillation, and sublimation. They also experience the volatility and solubility problems of **1**–**4**. This instability was also noted by Anderson and Veysoglu (Anderson, W. K.; Veysoglu, T. *J. Org. Chem.* **1973**, *38*, 2267), for similar 5,6-epoxy-2-alkanones.

(13) Stowell, J. C.; King, B. T.; Hauck, H. F. *J. Org. Chem.* **1983**, *48*, 5381.

(14) Corey, E. J.; Cho, H.; Rucker, C.; Hua, D. H. *Tetrahedron Lett.* **1981**, *22*, 3455.

at −50 °C to yield 124 mg (41%) of **2** after flash chromatography; GC (5.3 min, 10%; 5.9 mim, 90%).

Method B was performed on 23.2 mg (0.163 mmol) of **5** with 0.17 mL (0.170 mmol) of catechol borane (1.0 M in THF) and 10.0 mL (0.016 M) of dichloromethane at −78 °C to yield 20.0 mg (85%) of **2** after flash chromatography; GC (5,3 min, 29%; 5.9 min, 71%).

***rel*-(2*S*,5*R*,α*S*)-α-Ethyl-5-methyltetrahydrofuranmethanol (4).** Method B was performed on 29.7 mg (0.209 mmol) of **6** with 0.21 mL (0.210 mmol) of Me_2S–BH_3 (1.0 M in dichloromethane) and 42 mL (0.005 M) of dichloromethane to yield 22.9 mg (67%) of crude **4**, and flash chromatography produced 10.5 mg (35%) of **4** as a clear colorless oil. **4**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.07 (app hextet, J = 6.0 Hz, 1 H, H-5), 3.85 (app q, J = 7.0 Hz, 1 H, H-2), 3.32 (m, H-α), 2.03 (m, 2 H), 1.70–1.37 (m, 4 H), 1.23 (d, J = 6.0 Hz, 3 H, H-6), 1.00 (t, J = 7.4 Hz, 3 H, H-γ); IR 3600–3400, 2980, 2940, 2880, 1470, 1380, 990 cm^{-1}; TLC (2:2:1 hexane–CH_2Cl_2–ethyl acetate, R_f 0.32); GC (5.2 min, 6;% 5.7 min, 94%). The ^{13}C NMR data was the same as reported in ref 4.

Method B was performed on 33.2 mg (0.234 mmol) of **6** with 0.23 mL (0.230 mmol) of Me_2S–BH_3 (1.0 M in dichloromethane) and 13.0 mL (0.018 M) of dichloromethane at −50 °C to yield 26.7 mg (79%) of crude **4**; GC (5.2 min, 11%; 5.7 min, 89%).

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Registry No. 1, 89122-04-3; 2, 89194-24-1; 3, 89194-25-2; 4, 89194-26-3; 5, 112087-58-8; 5 (epoxy alcohol-isomer 1), 112087-59-9; 5 (epoxy alcohol-isomer 2), 112243-76-2; 6, 112087-60-2; 1-penten-3-ol, 616-25-1; 2-methoxypropene, 116-11-0; *trans*-5-octen-2-one, 19093-20-0; 1-butyne, 107-00-6; 2-methyl-2-(2-iodoethyl)-1,3-dioxolane, 53750-51-9; 2-(ethylenedioxy)-5-octynone, 104311-67-3; *cis*-5-octen-2-one, 22610-86-2.

Preparation and Crystal Structure of 3-(1-Naphthylmethyl)-3-chlorodiazirine

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Since the discovery of diazirines in 1960, extensive investigations have been conducted covering various aspects of this class of compounds. Advances in this field have been reviewed constantly to reflect the high level of activity in the chemistry of diazirines.[1-4]

Thus far, the C—N and N=N distances in diazirines have been obtained mostly by theoretical calculations based on observed rotational spectra.[3] The rotational spectra of diazirine and several methyl- and halogen-substituted diazirines have been recorded, and the structural parameters have been reported.[5-9] The structure of difluorodiazirine has been determined by electron-diffraction techniques.[10] The only X-ray analysis of a diazirine that has been reported is that of a heterodimetal complex of diazirine.[11,12] No X-ray studies of simple diazirines have been reported, and this is primarily because of the unsuccessful synthesis of a diazirine compound, which is crystalline and stable enough for X-ray analysis. Most diazirines are either gaseous or liquid at room temperature. The present study reports the first single-crystal X-ray diffraction analysis for a free diazirine, 3-(1-naphthylmethyl)-3-chlorodiazirine (1).

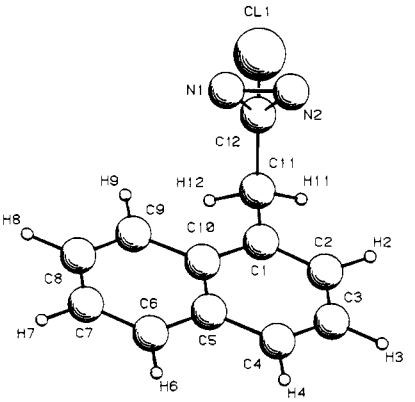

Figure 1. The molecular structure of 1.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for 1 (Estimated Standard Deviations Are in Parentheses)

Distances			
Cl–C(12)	1.716 (8)	N(2)–C(12)	1.467 (11)
N(1)–N(2)	1.244 (10)	C(1)–C(11)	1.509 (11)
N(1)–C(12)	1.463 (10)	C(11)–C(12)	1.522 (12)
Angles			
N(2)–N(1)–C(12)	65.0 (6)	Cl–C(12)–N(2)	115.4 (6)
N(1)–N(2)–C(12)	64.7 (6)	Cl–C(12)–C(11)	115.4 (5)
C(2)–C(1)–C(11)	117.4 (6)	N(1)–C(12)–N(2)	50.3 (5)
C(10)–C(1)–C(11)	122.5 (6)	N(1)–C(12)–C(11)	123.0 (6)
C(1)–C(11)–C(12)	113.9 (7)	N(2)–C(12)–C(11)	121.8 (7)
Cl–C(12)–N(1)	115.5 (6)		

Results and Discussion

Although 1 is a new compound, it can be synthesized according to Graham's[13] method with minor modification. This method involves the conversion of 1-naphthylacetonitrile to the corresponding amidine hydrochloride, followed by oxidation by sodium hypochlorite to the diazirine. The title compound has been subjected to IR, UV, NMR, and MS analyses. Unlike other diazirines, the intensities of both the infrared N=N stretching frequency (1560 cm^{-1}) and the UV absorption band (356 nm) are very weak. In addition, 1 shows a moderately intense molecular ion peak in the mass spectrum, which is not at all a characteristic for diazirines. Most chlorodiazirines lose chlorine readily when subjected to mass spectral analysis and therefore produce no molecular ion peak.

Selected interatomic distances and interbond angles for 1 are listed in Table I. The aromatic rings exhibit no unusual features. Compound 1, shown in Figure 1, is essentially a substituted derivative of methylchlorodiazirine.[6] The structural parameters of the diazirine moiety of 1 are

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