give 16 mg of **2**. A GC-MS of the filtrate showed benzene and the excess 1,4-cyclohexadiene.

NMR Measurements. All spectra were obtained on a 10-mm broad-band probe of either a Varian XL-200 or XL-300 NMR spectrometer operating at 50.3 or 75.4 MHz, respectively, for carbon-13. Typical parameters included a 15000- or 20000-Hz spectral width, 45° flip angle, acquisition times between 0.5 and 0.8 s, delay time between 0.5 and 1 s, and 16 or 32K data points. The solvents used for all ^{13}C samples were $CDCl_3$ or $CDCl_2CDCl_2$ with Me_4Si added as an internal standard. In all cases, broad-band proton decoupling was used. In several cases, the "APT" (attached proton test) experiment[16] was employed to determine substitution on carbon. With use of $\tau - 6$ ms, methylene and quarternary carbons gave positive peaks while methine and methyl carbons gave negative peaks. Off-resonance decoupling was also used where necessary to identify the different types of carbon atoms.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to The Camille and Henry Dreyfus Foundation for support of this work. We thank Professor Thomas Hoye for obtaining and interpreting of the ^{1}H NMR spectrum of compound **14b**, Mr. Peter Waalwyck for the synthesis of compounds **21** and **22**, and Miss Bernadine Kenesky for the preparation of compound **3**. We thank Mr. Jim Spriggle for obtaining the mass spectral data on most of the compounds described herein and Dr. William J. A. VandenHeuvel for determining the ^{18}O content of compounds **2** and **3** and the ^{18}O-labeled *p*-nitrobenzoyl chloride.

Registry No. **1**, 35758-77-1; **2**, 90368-42-6; **2**-^{18}*O*, 90368-59-5; **3**, 90388-37-7; **3**-^{18}*O*, 90368-61-9; **4**, 90368-43-7; **5**, 90368-44-8; **7**, 90368-45-9; **8**, 90368-46-0; **9**, 90388-38-8; **10**, 90368-47-1; **11**, 90368-48-2; **12**, 90368-49-3; **13**, 90368-50-6; **14a**, 90368-51-7; **14b**, 90368-52-8; **14c**, 90368-53-9; **14d**, 90368-54-0; **14e**, 90368-55-1; **20**, 4476-14-6; **21**, 90368-56-2; **22**, 90368-57-3; **23**, 90368-58-4; $H_2{}^{18}O$, 14314-42-2; 2,4,6-trichloronitrobenzene, 18708-70-8; 4-nitrobenzoyl-*carbonyl*-^{18}*O* chloride, 42969-58-4; *p*-nitrobenzoyl chloride, 122-04-3; 4-nitrobenzoic-*carboxy*-^{18}*O* acid, 90368-60-8; ethyl vinyl ether, 109-92-2; dihydrofuran, 1191-99-7; furan, 110-00-9; *N*-morpholino-1-cyclohexene, 670-80-4; styrene, 100-42-5; *p*-methylstyrene, 622-97-9; *p*-chlorostyrene, 1073-67-2; *p*-methoxystyrene, 637-69-4; *m*-chlorostyrene, 2039-85-2; 2,3-benzofuran, 271-89-6; acenaphthylene, 208-96-8; 1-(diethylamino)propyne, 4231-35-0; 2,3-dimethyl-1,3-butadiene, 513-81-5.

---

[16] Patt, S. L.; Shoolery, J. N. *J. Magn. Reson.* **1982**, *46*, 535.

1,1-Dimethyl-1-silacyclohexan-4-one and Its Germanium Analogue via Boracyclic Intermediates

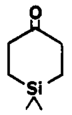
John A. Soderquist,* Fuu-Yau Shiau,[1a] and Russell A. Lemesh[1b]

Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931

Received August 31, 1983

The hydroboration of divinyldimethylsilane (**3**) was examined by using representative hydroborating agents with the finding that 9-borabicyclo[3.3.1]nonane (9-BBN) gives a single 1,5-diboryl adduct. An exchange reaction of this adduct with borane-methyl sulfide complex (BMS) gives, after methanolysis, the corresponding *B*-methoxy-4-silaborinane product (**10**) isomerically pure in 80% isolated yield. Several reactions of this silaboracycle are investigated including its conversion to 1,1-dimethyl-1-silacyclohexan-4-one (**1**) in 67% isolated yield. A related method is reported for the preparation of the corresponding germanium compound (**22**). Spectroscopic data for these heterocyclic derivatives are presented.

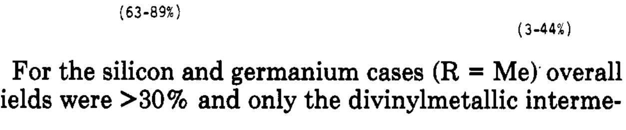
In 1958, Benkeser and Bennett[2] reported the preparation of 1,1-dimethyl-1-silacyclohexan-4-one (**1**), the first compound to contain a silicon atom within a cycloalkanone ring system.



1

Their approach, which utilized a pyrolysis procedure to effect the ring closure to give **1**, requires the isolation of four reaction intermediates and gives a 9-10% overall yield. Weber and co-workers[3a] increased the overall yield of **1** to 24% using a Dieckmann cyclization with a similar number of isolated intermediates. A related approach was used by Rice and co-workers[3b] to prepare **1** and the corresponding germanium derivative.[3c] Larger, as well as other, metallacycloalkanone ring systems have also been described.[3d-k,4-7]

Recently, we have reported the preparation of substituted 4-metallacyclohexanones (**2**) using a cyclic hydroboration approach.[8]



For the silicon and germanium cases (R = Me) overall yields were >30% and only the divinylmetallic interme-

---

[1] (a) Taken, in part, from the M. S. Theses of F.-Y.S., University of San Francisco, 1983. (b) ARCS scholar, University of San Francisco.

[2] Benkeser, R. A.; Bennett, E. W. *J. Am. Chem. Soc.* **1958**, *80*, 5414.

[3] (a) Weber, W. P.; Felix, R. A.; Willard, A. K.; Boettger, H. G. *J. Org. Chem.* **1971**, *36*, 4060. (b) Rice, L. M.; Sheth, B. S.; Wheeler, J. W. *J. Heterocycl. Chem.* **1973**, *10*, 737. (c) Rice, L. M.; Wheeler, J. W.; Geschickter, C. F. *Ibid.* **1974**, *11*, 1041. (d) Benkeser, R. A.; Cunico, R. F. *J. Org. Chem.* **1967**, *32*, 395. (e) Mazerolles, P.; Faucher, A. *Bull. Soc. Chem. Fr.* **1967**, 2134. (f) Mazerolles, P.; Faucher, A.; Laporterie, A. *Ibid.* **1969**, 887. (g) Weber, W. P.; Laine, R. *Tetrahedron Lett.* **1970**, 4169. (h) Weber, W. P.; Felix, R. A. *J. Org. Chem.* **1972**, *37*, 2323. (i) Koch, T. H.; Soderquist, J. A.; Kinstle, T. H. *J. Am. Chem. Soc.* **1974**, *96*, 5576. (j) Barton, T. J.; Banosiak, D. S. *J. Organomet. Chem.* **1978**, *157*, 255. (k) Coleman, B.; Jones, M., Jr. *Ibid.* **1979**, *168*, 393.

[4] Wittenberg, D.; Talukdar, P. B.; Gilman, H. *J. Am. Chem. Soc.* **1960**, *82*, 3608.

[5] Chernyshev, E. A.; Komalenkova, N. G.; Shamshin, L. N.; Bockarev, V. N. *Zh. Obsch. Khim.* **1972**, *42*, 1373.

[6] (a) Brook, A. G.; Pierce, J. B. *J. Am. Chem. Soc.* **1965**, *87*, 2566. (b) Brook, A. G.; Kucera, H. W.; MacRae, D. M. *Can. J. Chem.* **1970**, *48*, 818. (c) Brook, A. G.; Kucera, H. W. *J. Organomet. Chem.* **1975**, *87*, 263.

[7] Brook, A. G.; MacRae, D. M.; Bassindale, A. R. *J. Organomet. Chem.* **1975**, *86*, 185.

[8] Soderquist, J. A.; Hassner, A. *J. Org. Chem.* **1983**, *48*, 1801.

0022-3263/84/1949-2565$01.50/0

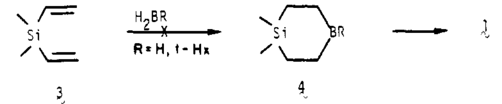
Table I. The Hydroboration/Oxidation of 3 Using Various Hydroborating Reagents

hydroborating reagents[a]	diol products			yield[b]
	5	6	7	
$BH_3 \cdot SMe_2$	38	56	6	100
t-$HxBH_2$	17	68	15	82
$(c\text{-}Hx)_2BH$	0	5	95	100
9-BBN	0	0	100	100

[a] 1:1 mol ratios of the hydroborating reagent to 3 were used for the first two entries while 2:1 ratios were used for the last two entries (t-Hx = thexyl = 2,3-dimethyl-2-butyl, c-Hx = cyclohexyl). [b] The reported yield was determined by gas chromatographic analysis using n-$C_{14}H_{30}$ as an internal standard. The diol mixtures were treated with MSTFA (Pierce) and analysis using a 6 ft × 1/8 in. 20% SE-30 on DCDMS treated Chromosorb W Column. Yields are ± 5%.

diate required isolation. This methodology was also successfully applied to the synthesis of larger ring systems.

However, this approach could not be successfully applied to the preparation of 1 or the corresponding germanium

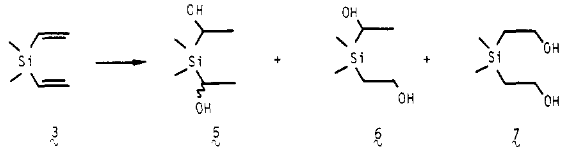


analogue owing to the failure of the cyclic hydroboration step to give sufficient borinane product to make the conversion to 1 feasible.

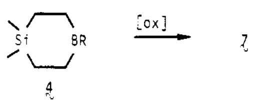
Since 1 represents a β-silyl ketone[9] as well as a useful functionalized silicon heterocycle,[2,3] we undertook a study of alternative routes to 4 from 3 which would make the boracyclic approach to 1 an efficient process.

Results and Discussion

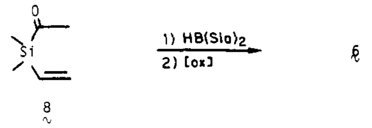
The hydroboration/oxidation of divinyldimethylsilane (3) was carried out using various hydroborating reagents



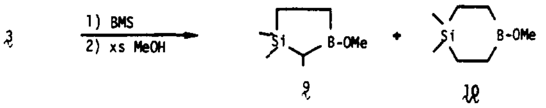
to determine the regiochemistry of the addition process (cf. Table I). Since the oxidation of 4 would give 7 as the



only silicon-containing diol product, neither BMS nor thexylborane gives major amounts of this heterocycle. For analysis purposes, 7 (95% isomeric purity) was prepared in 57% isolated yield from 3 using dicyclohexylborane. The 1,4-diol (6) was prepared from acetyldimethylvinylsilane (8) using disiamylborane in 82% isolated yield (96% isomeric purity).



To understand better the nature of the organoboranes formed in the hydroboration process, the hydroboration of 3 with BMS (1:1 mol ratio) was carried out and, after methanolysis, a 7:1 ratio of silaborolane (9) and silaborinane (10) products were isolated in 47% yield. Oxidation of this mixture gives the silicon diols 6 and 7 in a ratio consistent with the observed ratio of 9 and 10.



The nonvolatile residue obtained from the hydroboration/methanolysis procedure was found by ^{11}B NMR to be mixture of organoboranes with the major component being a trialkylborane species (see Experimental Section). Oxidation of this residue gives 5:6:7 in a 56:34:10 ratio together with significant amounts of other unidentified volatile products evident by the GC analysis of the oxidized mixture.

Summing the amount of 7 derived from the oxidation of the 9/10 mixture and from the nonvolatile residue gives more 7 than is formed from the hydroboration/oxidation of 3 using BMS (cf. Table I).

This suggested that heating the hydroboration mixtures formed from 3 and BMS may give more silaborinane

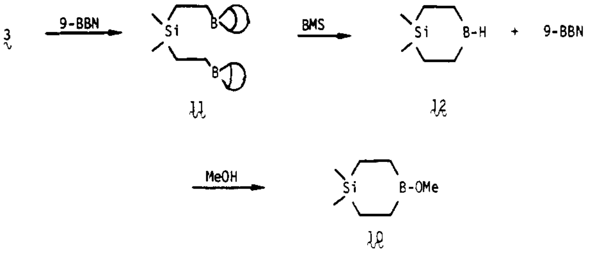
$$3 + \text{BMS} \rightarrow \xrightarrow{175\ ^\circ\text{C}} \xrightarrow{\text{BH}_3\cdot\text{THF}} \xrightarrow{[\text{ox}]} 5 + 6 + 7$$

(3/2 mol ratio of 3 and BMS)

product than was initially formed in the hydroboration step. The hydroboration/thermal treatment used by Brown and Negishi to prepare the analogous carbocyclic borinane system[10] was examined for 3.

The products 5, 6, and 7 were obtained in a 26:42:32 ratio in an overall yield by GC of 50%. Unfortunately, increasing the time of the thermal treatment or the reaction temperature did not result in a higher yield of 7.

Unlike other hydroborating reagents, 9-BBN adds cleanly to 3 giving a single product (11). From earlier



studies on the hydroboration of vinyltrimethylsilane, it has been found that 9-(β-(trimethylsilyl)ethyl)-9-BBN undergoes smooth exchange reaction with borane to give 9-BBN and bis(β-(trimethylsilyl)ethyl)borane.[11] Hydroboration of the appropriate dienyl compounds followed by exchange with borane has been used to prepare the borepane[12] and borinane[13] ring systems. Applying these conditions to 11 gives, after methanolysis, an 80% isolated yield of the desired isomerically and chemically pure silaborinane (10).

From the 12:9-BBN mixture, 65% of the 9-BBN was removed by its selective crystallization from monoglyme. A 31% yield of pure *B*-methoxy-9-BBN was also obtained after fractional distillative isolation of 10.

---

(9) Fleming, I. "Comprehensive Organic Chemistry"; Barton, D., Ollis, W. D., Jones, D. N., Eds.; Pergamon Press: Oxford, 1975; Vol. 3, p 659–660.

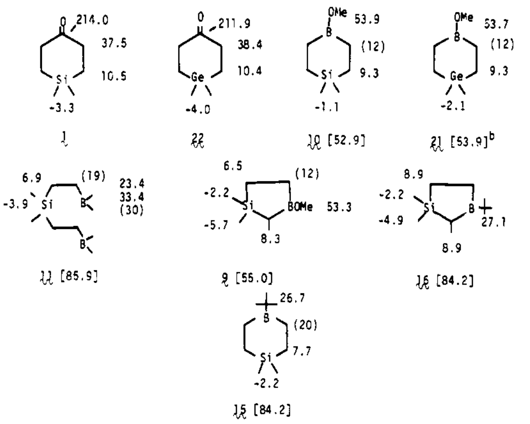
(10) Brown, H. C.; Negishi, E.-I. *J. Organomet. Chem.* **1971**, *26*, C67.

(11) Soderquist, J. A.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 3571.

(12) Negishi, E.-I.; Burke, P. L.; Brown, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 7431.

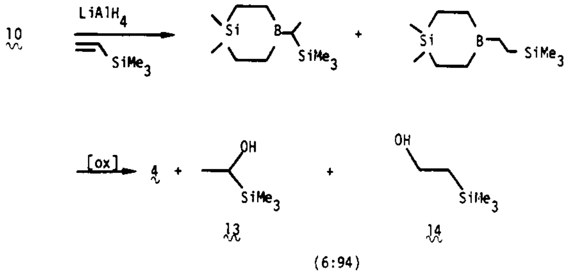
(13) (a) Brown, H. C.; Pai, G. G. *Heterocycles* **1982**, *17*, 77. (b) Brown, H. C.; Pai, G. G. *J. Organomet. Chem.* **1983**, *250*, 13.

Table II. ^{13}C and ^{11}B NMR Data for Heterocyclic Compounds[a]

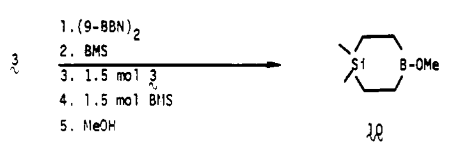


[a] Recorded in C_6D_6 solution except compounds 1 and 11 ($CDCl_3$) relative to Me_4Si (0.0 ppm). ^{11}B NMR signal given in brackets ($BF_3{\cdot}OEt_2$ 0.0 ppm). Peaks in parentheses are broad signals owing to a directly bound boron atom. [b] Assigned in a 1:1 mixture of 21 and *B*-MeO-9BBN.

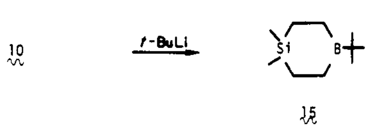
From the above sequence, it is clear that if **12** also hydroborates **3** giving 1,5-diboryl adducts as was the case for 9-BBN, the relative amount of 9-BBN needed to produce **10** could be significantly reduced. To determine the selectivity of **12** in the hydroboration of vinylsilanes, the reduction of **10** to **12** with lithium aluminum hydride in the presence of vinyltrimethylsilane was carried out. After oxidation, 1- and 2-trimethylsilylethanol (**13** and **14**) were formed in a 6:94 ratio indicating that **12**, like other dialkylboranes, is a very regioselective hydroborating reagent for vinylsilanes.[14]

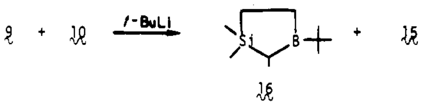


The above result prompted us to add **3** to the **12**:9-BBN mixture to obtain additional adducts which were exchanged with more BMS to scale up the **3** → **12** conversion by a factor of 2.5 without requiring use of additional 9-BBN. This methodology gives **10** in 66% overall yield in 91% isomeric purity (9% of **9**).

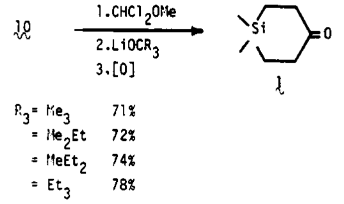


We also converted pure **10** to the corresponding *B*-*tert*-butyl derivative (**15**) in 70% yield using the Kramer, Brown method.[15] Oxidation of **15** gives only **7** (93%) and *tert*-butyl alcohol (94%), with no evidence for isomeric alcohols being formed. Spectroscopic data for **15** were also consistent with the assigned structure[16] (see Table II and Experimental Section). Similarly the 7:1 mixture of borolane (**9**) and borinane (**10**) products obtained from the hydroboration/methanolysis of **3** gives, with *tert*-butyllithium, the corresponding *tert*-butyl boracycles in 60% yield.



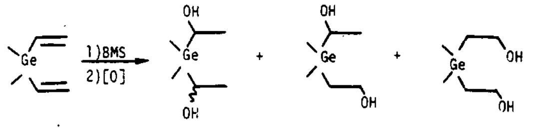


The conversion of **10** to 1,1-dimethyl-1-silacyclohexan-4-one (**1**) was examined using Brown's DCME reaction.[16]



Using a **10**/$CHCl_2OMe$/$LiOCR_3$ ratio of 1:1:2 the yield of **1** increases with the increasing steric bulk of the base (see above). The yield of **1** also increases with the amount of base used (i.e., molar equivalents of $LiOCEt_3$ = 2 (78%), 3 (87%), 4 (98%)). These findings are consistent with those reported by Brown with respect to the DCME reaction.[17] The silicon-containing byproduct in these reactions was **7** in all of the above studies. For experimental convenience and reagent economy, the preparation was carried out using 2 mol equiv of the triethylcarboxide base isolating pure **1** in 67% yield and recovering triethylcarbinol in 76% yield. Thus, the conversion of **3** to **1** is accomplished in a two-step process in 54% overall yield making this approach to such ketones a very synthetically efficient procedure.

For the analogous germanium system, the hydroboration/oxidation of divinyldimethylgermane (**17**) using $BH_3{\cdot}THF$ gives the 2,4-, 1,4- and 1,5-germanium diols in a 27:59:14 ratio in 93% GC yield. Isolation of these products in 81% yield was accomplished using BMS as the hydroborating reagent which gave a similar product distribution (27:61:12). Disiamylborane gives a 1:4 mixture of **19** and **20** in 60% isolated yield (10 mmol scale). The synthesis of the corresponding germanium ketone (**22**) was accomplished using a similar approach to that used to prepare **1** with an overall yield of 17%.



Since it was not possible to separate the **21**–(*B*-methoxy-9-BBN) mixtures conveniently by distillation owing to their similar boiling points, **21** was converted to **22** by limiting the amount of dichloromethyl methyl ether used to correspond to the quantity of **21** present in this mixture.

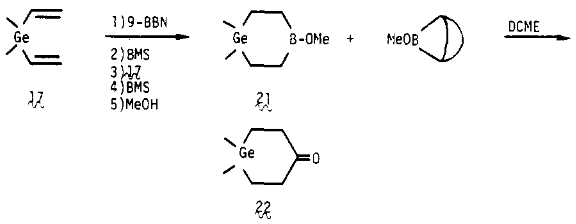
---

[14] Soderquist, J. A.; Hassner, A. *J. Org. Chem.* **1978**, *150*, C12.

[15] Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73*, 1.

[16] Structure **15** was proposed to result from the cyclic hydroboration of **3** with *tert*-butylborane–trimethylamine complex (Hawthorne, M. F. *J. Am. Chem. Soc.* **1961**, *83*, 2541) based upon 40-MHz NMR data. However, after a discussion with Professor Hawthorne, it was mutually concluded that the organoborane(s) obtained from this process probably contain major amounts of the silaborolane **16**.

[17] (a) Brown, H. C.; Carlson, B. A. *J. Am. Chem. Soc.* **1973**, *95*, 6876. (b) Carlson, B. A.; Brown, H. C. *J. Organomet. Chem.* **1974**, *67*, C39.



Under these conditions the GC yield of **22** was 60%.

Conclusion

A vastly improved route to 1,1-dimethyl-1-silacyclohexan-4-one (**1**) and its germanium counterpart, **22**, have been described. The preparation of several new silicon-containing boracycles have been reported and characterized. With this new route to **1** available, the chemistry of this interesting heterocycle can be explored in greater detail more conveniently than was previously possible.

Experimental Section

General Methods. All experiments were carried out in predried (4 h at 110 °C) glassware under a nitrogen atmosphere. Standard handling techniques for air-sensitive compounds were employed throughout this study.[18]

THF was distilled from sodium/benzophenone prior to use. Alkanes were purified using reported methods.[18] Other reagents were either prepared as previously described[8] or obtained from commercial sources.

NMR data were recorded at UCSF using either a Varian XL-100 or FT-80A spectrometer. High-resolution mass spectral (HRMS) and mass spectral (MS) data were obtained at UC Berkeley using either a Dupont CEC-110 or KRATOS MS 50 and KRATO MS 12 mass spectrometers. Analysis of organoboranes and alcohols were performed using a Perkin-Elmer Model Sigma 1B gas chromatographic system equipped with either 6 ft × 1/8 in. 20% SE-30 on DCDMS-treated Chrom W or 30 m × 0.23 mm I.D. 20% SE-30 vitreous silica open tubular column. Columns were silylated (MSTFA, Pierce) prior to analytical runs and for organoboranes, a low injection port temperature (120 °C) was used routinely.

The hydroboration/oxidation procedures used in the present study were carried out as previously described.[8]

3,3-Dimethyl-3-silapentane-1,4-diol (6). To a cold (0 °C) solution of BH_3·THF (29.8 mL, 1.83 M, 54.5 mmol) was added 2-methyl-2-butene (7.65 g, 109 mmol) dropwise. After 2 h, acetyldimethylvinylsilane (2.86 g, 22.3 mmol) was added dropwise. After 1 h, H_2O (18.5 mL) and 3 N NaOH (18.5 mL) were added followed by the dropwise addition of 30% H_2O_2 (18.5 mL). The mixture was stirred at reflux temperature for 1 h, treated with NaCl to saturate the aqueous phase, and the organic layer was dried (K_2CO_3), concentrated to remove the solvents and 3-methyl-2-butanol, and distilled at 0.3 torr to give 2.7 g (82%) of **6** (bp 78–81 °C) which contained ca. 4% of **5**: NMR ($CDCl_3$) δ 0.00 (s, 6 H), 0.92, 0.94 (2 t, 2 H, J = 6.6 Hz), 1.22 (d, 3 H, J = 7.5 Hz), 3.41 (q, 1 H, J = 7.4 Hz), 3.73 (t, 2 H, J = 6.8 Hz), 3.85 (s, 1 H).

3,3-Dimethyl-3-silapentane-1,5-diol (7). To a cold (0 °C) solution of BH_3·THF complex (115 mL, 1.83 M, 210 mmol) was added cyclohexene (34.5 g, 420 mmol) dropwise. After two additional hours at 0 °C, **3** (11.2 g, 100 mmol) was added dropwise. The mixture was allowed to slowly warm to room temperature and, after 12 h, was oxidized using the successive addition of H_2O (70 mL) and 3 N NaOH (70 mL) followed by the dropwise addition of H_2O_2 (106 mL, 6.6 M). After 4 h at reflux temperature, the mixture was treated with NH_4Cl (saturated) and the organic layer was dried (K_2CO_3), concentrated, and distilled at 0.7 torr to give a forerun of cyclohexanol (31 °C) and 8.4 g (57%) of **7** (bp 110 °C) which contained ca. 5% **6**: NMR ($CDCl_3$) δ 0.01 (s, 6 H), 0.94 (t, 4 H, J = 7.8 Hz), 2.69 (br s, 2 H), 3.71 (t, 4 H, J = 7.8 Hz).

3-Methoxy-1,1,2-trimethyl-1-sila-3-boracyclopentane (9) and 4-Methoxy-1,1-dimethyl-1-sila-4-boracyclohexane (10). To a stirred solution of BMS (20.0 mL, 10.0 M, 200 mmol) in THF was added **3** (22.4 g, 200 mmol) dropwise. After 1 h at room temperature, the mixture was heated at reflux temperature for 2 h, cooled to room temperature, and treated with anhydrous methanol (7.5 g, 220 mmol) (H_2 evolution). The mixture was held at reflux for 3 h, concentrated under reduced pressure, and distilled at 11 torr to give 14.7 g (bp 48–54 °C) of a 7:1 (GC) mixture of **9** and **10** (47%). Analysis of the residue by ^{11}B NMR revealed a major peak at 83.1 ppm with shoulders at ca. 54 and 31 ppm. Oxidation of this material (100% excess of $NaOH/H_2O_2$) gives **5**:**6**:**7** in the ratio 56:34:10. Spectroscopic analysis of **9** from the distilled mixture: ^{11}B NMR (C_6D_6) δ 54.6; ^1H NMR ($CDCl_3$) δ 0.01 (s, 3 H), 0.21 (s, 3 H), 0.5–1.0 (m, 5 H), 1.18 (d, 3 H, J = 7.2 Hz), 3.47 (s, 3 H). A singlet at 0.08 ppm, attributable to **10**, was also observed in this mixture. Oxidation of the **9**/**10** mixture on a 10-mmol reaction scale (100% excess $NaOH/H_2O_2$) gives a 6:1 mixture of **6** and **7** in 83% yield. HRMS calcd for $C_7H_{17}OBSi$, 156.1145; found, 156.1134; MS, m/z 156 (11), 142 (32), 141 (27), 114 (98), 113 (67), 99 (100), 98 (21), 97 (29), 86 (38), 85 (44).

Thermal Isomerization of 3:2 Mixtures of 20 and BH_3·THF. To a cold (0 °C) solution of BH_3·THF (11.5 mL, 1.83 M, 21 mmol) was added **3** (3.36 g, 30 mmol) dropwise. After 2 h at 0 °C, the solvents were removed in vacuo and the residue was heated at 175 °C for 3 h. After cooling to room temperature, BH_3·THF (5.46 mL, 1.83 M, 10 mmol) was added and the mixture was stirred for 16 h at 25 °C and oxidized by the successive addition of 11.0 mL each of H_2O, 3 N NaOH, and 30% H_2O_2 (exothermic). The mixture was treated with tetradecane (GC standard) and K_2CO_3. Analysis gave **5**, **6**, and **7** in a 26:42:32 ratio (52% total yield). Attempts to improve the yield of **7** by either increasing the isomerization temperature and/or reaction time were unsuccessful in our hands.

4-Methoxy-1,1-dimethyl-1-sila-4-boracyclohexane (10). To a mixture of 9-BBN (61 g, 0.50 mol) in purified hexanes (600 mL) was added **3** (28 g, 0.25 mol). After heating at reflux temperature for 2 h, the solution of **11** was cooled to room temperature and treated with BMS (25 mL, 10.0 M, 0.25 mol). After 2 h at reflux temperature, the solvents were removed in vacuo, and the residual solid was dissolved in hot monoglyme (ca. 500 mL). After slow cooling to −20 °C, the supernatant liquid was decanted from the crystalline 9-BBN (40 g, 65%). Methanol (20 g, 0.63 mol) was added dropwise to the stirred supernatant solution (H_2 evolution) and, after 2 h at room temperature, the solvents were distilled off at atmospheric pressure using a spinning band distillation assembly. At 11 torr, 31.2 g (80%) of **10** was collected (bp 58–62 °C, 99% pure by GC analysis). Pure *B*-methoxy-9-BBN (bp 81–83 °C) was also collected (23.5 g, 31%). For **10**: NMR (C_6D_6) δ 0.09 (s, 6 H), 0.71 (m, 4 H), 1.08 (m, 4 H), 3.42 (s, 3 H); HRMS calcd for $C_7H_{17}OBSi$, 156.1142; found, 156.1144; MS, m/z 156 (43), 155 (26), 142 (29), 141 (38), 128 (22), 127 (46), 114 (100), 113 (81), 100 (25), 99 (75), 98 (26), 97 (53), 86 (45), 85 (54). Oxidation of **10** gives **7** as the only silicon diol product in quantitative yield.

Hydroboration of Vinyltrimethylsilane with 12. To vinyltrimethylsilane (1.0 g, 10 mmol) in THF (5.0 mL) and $LiAlH_4$ solution in THF (2.1 mL, 1.58 M, 3.3 mmol) at 25 °C was added **10** (1.56 g, 10 mmol) over ca. 10 min. After ca. 3 h, the mixture was hydrolyzed using H_2SO_4 (0.7 g) and H_2O (0.5 mL). After the addition of hexanes (2.5 mL), the mixture was treated with 6 N NaOH (11.2 mL) followed by 4 mL each of H_2O, 3 N NaOH, and 30% H_2O_2. After heating at reflux for 2 h, the aqueous phase was saturated with K_2CO_3, tetradecane was added, and GC analysis gave 1- and 2-trimethylsilylethanol (93%) in a 6:94 ratio and **7** (100%).

10 from the Double Exchange Process. Solid 9-BBN (24.4 g, 200 mmol) in purified hexanes (200 mL) was treated with **3** (11.2 g, 100 mmol). After 2 h at reflux temperature, the mixture was allowed to cool to 25 °C and BMS (10 mL, 10.0 M, 100 mmol) was added. The mixture was heated at reflux for 2 h and subsequently cooled to 0 °C and **3** (16.8 g, 150 mmol) was added. After 2 h at reflux temperature, the mixture was recooled to room temperature, treated with methanol dropwise, and distillation at 14 torr gave 25.8 g (66%) of **10** (bp 65–66 °C) and 20.4 g (67%) of *B*-methoxy-9-BBN (bp 84–86 °C). Analysis of **10** by GC showed that the product contained ca. 9% of **9** and, after oxidation, **6**

---

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

and 7 were found to be in a 9:91 ratio (99% total yield). We repeated this procedure several times and obtained a **9**:**10** ratio as high as 3:97.

4-*tert*-Butyl-1,1-dimethyl-1-sila-4-boracyclohexane (15). To a cold (−78 °C) solution of **10** (7.8 g, 50 mmol) in hexanes (20 mL) was added *tert*-butyllithium solution (28 mL, 1.8 M, 50 mmol) dropwise. After warming to room temperature, the mixture was stirred for 2 h and the lithium methoxide was separated by centrifugation. The solvents were removed by distillation and 6.3 g (70%) of **15** was collected (bp 37–38 °C (0.3 torr)): NMR (C_6D_6) δ 0.14 (s, 6 H), 0.71 (ct, 4 H, J = 7 Hz), 1.01 (s, 9 H), 1.41 (ct, 4 H, J = 7 Hz); HRMS calcd for $C_{10}H_{23}BSi$, 182.1662; found, 182.1669; MS, m/z 182 (5), 125 (30), 97 (18), 86 (29), 59 (62), 57 (89), 56 (74), 55 (21), 43 (100). Oxidation of **31** gives (using n-$C_{14}H_{30}$ as an internal standard) 7 (93%) with no **5** or **6** impurities detectable and *tert*-butyl alcohol (94%).

3-*tert*-Butyl-1,1,2-trimethyl-1-sila-3-boracyclopentane (16) and 15. Dropwise addition of *tert*-butyllithium solution (28 mL, 1.8 M, 50 mmol) to a cold (−78 °C) solution of the **9**/**10** mixture (7.8 g, 50 mmol) in pentane (20 mL) gave a mixture which, after it had reached 25 °C, was stirred for 2 h, centrifuged, together with the pentane washings (2 × 10 mL) of the LiOMe precipitate, and distilled to give 5.5 g (60%) of a 7:1 mixture of **16** and **15** (99% purity by GC analysis). Oxidation of this sample gives **6** and **7** in a 4.5:1 ratio (100% total yield). For **16**: NMR (C_6D_6) δ 0.07 (s, 3 H), 0.18 (s, 3 H), 0.8 (m, 3 H), 1.10 (s, 9 H), 1.23 (d, 3 H, J = 7.2 Hz), 1.47 (m, 2 H). (Singlets for **15** were observed at δ 0.14 and 1.01 in a 2:3 ratio). Integration of the 3 Si–Me signals gives **16**:**15** in a ratio of ca. 4. HRMS calcd for $C_{10}H_{23}BSi$, 182.1662; found, 182.1665; MS, m/z 182 (16), 126 (25), 125 (80), 124 (18), 97 (63), 85 (23), 73 (36), 69 (18), 59 (87), 58 (16), 56 (32), 55 (16), 43 (28), 42 (17), 41 (100).

1,1-Dimethyl-1-silacyclohexan-4-one (1). To a stirred, cold (0 °C) solution of **10** (25 g, 0.16 mol) and dichloromethyl methyl ether (18.5 g, 0.16 mol) in THF (980 mL) was added lithium triethylcarboxide solution (196 mL, 1.63 M, 0.32 mol) dropwise. After ca. 10 min the mixture was allowed to warm to room temperature (LiCl precipitate forms). After 30 min, 95% ethanol (128 mL), water (34 mL), and sodium hydroxide pellets (19.5 g) were added followed by 30% hydrogen peroxide (53 mL) dropwise. After heating at reflux temperature for 1.5 h, the mixture was treated with saturated brine (320 mL) and the organic layer was dried (K_2CO_3), concentrated in vacuo, and distilled at 14 torr to give 28 g (76%) of triethylcarbinol (bp 51 °C) and 9.51 g (67%) of pure (99%) **1** [bp 80–82 °C [lit.[2] 73–74 °C (11 torr)]]. The spectroscopic data obtained for this product were identical with that previously reported.[2] On a 10-mmol scale, the reaction was repeated several times using the various bases and conditions reported in the text giving the varying yields of **1** using an internal GC standard. All bases were prepared from n-butyllithium and the corresponding alcohol.

1,1-Dimethyl-1-germacyclohexan-4-one (22). To a mixture of 9-BBN (12.2 g, 0.1 mol) in purified hexanes (100 mL) was added **17** (7.83 g, 0.05 mol). After heating at reflux temperature for 2 h, the solution was cooled to room temperature and treated with BMS (5 mL, 10.0 M, 0.05 mol). After 2 h at reflux temperature, the mixture was cooled to 0 °C and **17** (11.75 g, 0.075 mol) was added. After 2 h at reflux temperature, the mixture was recooled to room temperature, BMS (7.5 mL, 10.0 M, 0.075 mol) was added, and the mixture was again heated for 2 h at reflux temperature. Methanol (11.2 g 0.35 mol) was added dropwise and after 3 h at room temperature the solvent was removed. The mixture (34.6 g, 0.196 mol) and dichloromethyl methyl ether (8.6 g, 0.075 mol) in THF (100 mL) was cooled to 0 °C. Lithium triethylcarboxide solution (284 mL, 1.385 M, 0.393 mol) was added dropwise. After ca. 10 min, the mixture was allowed to warm to room temperature (LiCl precipitate forms). After 30 min, 95% ethanol (158 mL), water (41 mL), and sodium hydroxide pellets (24 g) were added followed by 30% hydrogen peroxide (61 mL) dropwise. After heating at reflux temperature for 2 h, the mixture was treated with saturated brine (400 mL) and the organic layer was dried (K_2CO_3), concentrated, and distilled at 7 torr to give 38.6 g (78%) of triethylcarbinol (bp 40 °C) and 3.6 g (26%) of pure (97%) **22** [bp 89–93 °C [lit.[3c] 86–90 °C (7 torr)]].

3,3-Dimethyl-3-germapentane-1,5-diol (20) and 3,3-Dimethyl-3-germapentane-1,4-diol (19). To a stirred solution of BMS (1 mL, 10 M, 10 mmol) and THF (10 mL) at room temperature, 2-methyl-2-butene (1.4 g, 20 mmol) was added dropwise. After stirring for 2 h, **17** (0.78 g, 5 mmol) was added dropwise. After 1 h the mixture was concentrated in vacuo, and THF (10 mL) was added followed by water (4 mL), 3 N sodium hydroxide (4 mL), and 30% hydrogen peroxide (4 mL) dropwise. The mixture was heated at reflux temperature for 1 h and, after the usual workup, distilled at 4 torr to give 0.57 g (60%) of **19** and **20** (bp 131–133 °C) in a 1:4 ratio. For **20**: NMR ($CDCl_3/C_6D_6$) 0.20 (s, 6 H), 1.09 (5, 4 H, J = 7.3 Hz), 2.4 (br s, 2 H), 3.75 (t, 4 H, J = 7.3 Hz).

3,3-Dimethyl-3-germapentane-2,4-diol (18), 3,3-Dimethyl-3-germapentane-1,4-diol (19), and 3,3-Dimethyl-3-germapentane-1,5-diol (20). To a stirred solution of BMS (1 mL, 10 M, 10 mmol) and THF (5 mL) was added **34** (1.56 g 10 mmol) dropwise. After 2 h, water (4 mL) and 3 N sodium hydroxide (4 mL) were added dropwise. The mixture was heated at reflux temperature for 1 h, concentrated, and distilled at 0.35 torr to give 1.52 g of **18**, **19**, and **20**, (81%) (bp 93–95 °C) in a 27:61:12 ratio by GC analysis of the silylated diols. The NMR spectrum of the mixture revealed the presence of minor amounts of dimethyl sulfone (2.97 ppm) and dimethyl sulfoxide (2.60 ppm). In addition to complex triplets and dimethylsilyl signals attributable to **20**, **18** (meso/dl), and **19** gave doublets (J = 7.3 Hz) at 1.35 and 1.38 ppm. Through the successive addition of Eu(fod)$_3$ reagent signals attributable to diols **18**, **19**, and **20** were found which qualitatively agreed with reported observations made for the related silicon diols.[8]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society and to a William and Flora Hewlett Grant of Research Corporation for their sponsorship of this work. We express our thanks to M. Ramin Najafi for his help with the NMR spectra presented in this study. We also thank Professor H. C. Brown and Professor M. F. Hawthorne for their helpful suggestions regarding this work. We also express our thanks to Deans D. A. Harnett and G. L. Stevens for their support of this study at the University of San Francisco.

Registry No. **1**, 18276-42-1; **3**, 10519-87-6; **5**, 89555-69-1; **6**, 85337-65-1; **7**, 85337-82-2; **8**, 89555-78-2; **9**, 89555-70-4; **10**, 89555-71-5; **11**, 89555-72-6; **12**, 89555-73-7; **13**, 13246-39-4; **14**, 2916-68-9; **15**, 18162-76-0; **16**, 89555-74-8; **17**, 35935-16-1; **18**, 89555-75-9; **19**, 89555-76-0; **20**, 89555-77-1; **22**, 55454-73-4; $LiOCEt_3$, 32777-93-8; 9-BBN, 280-64-8; *B*-MeO-9-BBN, 38050-71-4; 2-methyl-2-butene, 513-35-9; cyclohexanol, 108-93-0; vinyltrimethylsilane, 754-05-2; triethylcarbinol, 597-49-9.