and refluxed until an aliquot of the resulting clear red solution showed no precipitate when drowned in water. About 650 mL of solvent was then distilled, and the remaining deep red liquid was drowned with 500 mL of water. The red solution was neutralized with 66 g (1.1 mol) of acetic acid and extracted with 1 L of hot heptane and then 300 mL of cold heptane. The aqueous layer was made alkaline with 32 g of 50% aqueous NaOH, saturated with sodium chloride, and extracted with three 200-mL portions of 1,2-dichloroethane. Removal of the dichloroethane in vacuo gave 75 g (94%) of medium-red oil which was identical with the bis[[(2-hydroxyethyl)thio]methyl] ether made from bis(chloromethyl) ether.

Bis[(*n*-butylthio)methyl] Ether. A solution of 12 g (0.13 mol) of butanethiol and 4.6 g (0.02 mol) of bis(phenoxymethyl) ether in 50 mL of DMF was treated with 2.9 g (0.13 mol) of sodium hydride and refluxed for 5 h at 150 °C. The resulting solution was drowned in water and taken up in 200 mL of ether. After the solution was washed with 20% aqueous NaOH and water, the solvent was removed, giving 5.4 g of an oily product shown by VPC to contain 70% bis[(*n*-butylthio)methyl] ether (85% yield) and 30% butyl sulfide and disulfide. Analysis by NMR was consistent with that of authentic product prepared from butyl mercaptan and bis(bromomethyl) ether.

Registry No. 1, 4082-91-1; 2, 88-06-2; 3, 60093-93-8; 4, 3807-05-4; 5, 60-24-2; bis[[(2-hydroxyethyl)thio]methyl] ether, 36727-72-7; butanethiol, 109-79-5; bis[(*n*-butylthio)methyl] ether, 62609-74-9; bis[(4-chlorophenoxy)methyl] ether, 60093-88-1; bis[(2-chlorophenoxy)methyl] ether, 60093-87-0; bis[(2,4-dichlorophenoxy)methyl] ether, 60093-89-2; bis[(2,3,4,5,6-pentafluorophenoxy)methyl] ether, 80484-50-0; bis[(2,4,6-tribromophenoxy)methyl] ether, 61454-70-4; bis[(4-methylphenoxy)methyl] ether, 42818-09-7; bis[(2-methylphenoxy)methyl] ether, 42818-07-5; bis[(4-methoxyphenoxy)methyl] ether, 63195-89-1; phenol, 108-95-2; 4-chlorophenol, 106-48-9; 2-chlorophenol, 95-57-8; 2,4-dichlorophenol, 120-83-2; 2,3,4,5,6-pentafluorophenol, 771-61-9; 2,4,6-tribromophenol, 118-79-6; 4-methylphenol, 106-44-5; 2-methylphenol, 95-48-7; 2,6-dimethylphenol, 25134-01-4; 2-*tert*-butylphenol, 88-18-6; 4-methoxyphenol, 150-76-5; 2-methoxyphenol, 90-05-1; 4-nitrophenol, 100-02-7.

Preparation and Characterization of 2-Silanorbornanes

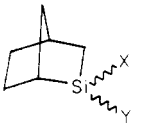
Sheldon E. Cremer* and Craig Blankenship

Chemistry Department, Marquette University, Milwaukee, Wisconsin 53233

Received October 15, 1981

Four members of the new class of 2-silabicyclo[2.2.1]heptanes, or 2-silanorbornanes, were prepared: 2-silanorbornane (1), 2,2-dichloro-2-silanorbornane (2), 2-chloro-2-methyl-2-silanorbornane (3), and 2-methyl-2-silanorbornane (4); the ring-closure reaction involved a platinum-catalyzed, intramolecular hydrosilation. The silanes were characterized by carbon and hydrogen elemental analyses and by ^{1}H, ^{13}C, and ^{29}Si NMR, IR, and mass spectrometry. Isomer assignments for 3 and 4 were made on the basis of the NMR data. In the mass spectra, each compound gave an abundant molecular ion and a major mode of fragmentation peculiar to this bicyclic system. Some initial stereochemical studies of the reactions of 3 and 4 were performed, including fluoride-induced equilibration of the isomers of 4.

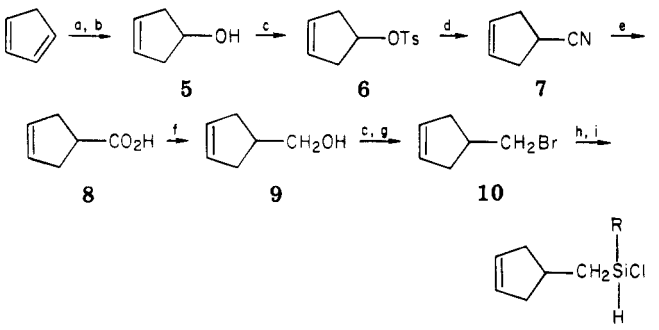
Studies of various bicyclo[2.2.1]heptanes (norbornanes) have provided great insight into the understanding of reaction mechanisms, spectral properties, and structure of organic molecules. As part of a program to prepare new organosilicons for study, we report the first unambiguous synthesis and characterization of 2-silabicyclo[2.2.1]heptane (1), or 2-silanorbornane, and some of its derivatives



1, X = Y = H
2, X = Y = Cl
3, X = Me; Y = Cl
4, X = Me; Y = H

(2-4). The synthetic route developed allows for the placement of different substituents at silicon, which makes systematic studies of this class of compounds possible. The only previous report of any compounds of this type describes the formation of the isomers of 3-neopentyl-2,2-dimethyl-2-silabicyclo[2.2.1]hept-5-ene in 30% yield from the cycloaddition reaction of cyclopentadiene with a silaethylene intermediate.[1] Some 1- and 7-silanorbornanes have been prepared, and a few of their chemical and physical properties have been studied.[2-5] Although 1 and its derivatives are interesting in their own right, another purpose for their preparation was for comparison with the chemistry of the homologous 3-silabicyclo[3.2.1]octanes, which we and others have prepared and studied.[6-8]

Scheme I[a]

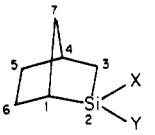


[a] (a) 40% Peracetic acid; (b) LAH, ether; (c) *p*-toluenesulfonyl chloride, pyridine; (d) NaCN, HMPA; (e) NaOH, H_2O, EtOH, Δ; (f) LAH, THF, Δ; (g) LiBr, acetone, Δ; (h) Mg, THF; (i) $HSiCl_3$ or $MeSiHCl_2$.

(1) Jones, P. R.; Lim, T. F. O.; Pierce, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 4970.
(2) Benkeser, R. A.; Mozdzen, E. C.; Muench, W. C.; Roche, R. T.; Siklosi, M. P. *J. Org. Chem.* **1979**, *44*, 1370.
(3) (a) Sommer, L. H.; Bennett, O. F. *J. Am. Chem. Soc.* **1957**, *79*, 1008. (b) Sommer, L. H.; Bennett, O. F.; Campbell, P. G.; Weyenberg, D. R. *Ibid.* **1957**, *79*, 3295. Homer, G. D.; Sommer, L. H. *Ibid.* **1973**, *95*, 7700.
(4) Hilderbrandt, R. L.; Homer, G. D.; Boudjouk, P. *J. Am. Chem. Soc.* **1976**, *98*, 7476.
(5) (a) Nagai, Y.; Inaba, H.; Matsumoto, H.; Watanabe, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3224. (b) Ikeura, T.; Tanaka, K.; Hirota, E.; Inaba, S.; Nagai, Y. *Ibid.* **1977**, *50*, 1309.

0022-3263/82/1947-1626$01.25/0

Table I. NMR Data for 2-Silanorbornanes and Carbon Analogues



compd	chemical shift, δ							
	C-1	C-3	C-4	C-5	C-6	C-7	Me	^{29}Si, [a] δ
1 (X = Y = H)	20.1	13.2	35.7	30.7	25.5	38.5		−25.1
4a (X = Me; Y = H)	22.2	18.3	35.8	30.7	25.1	37.5	−4.4	−2.0
4b (X = H; Y = Me)	21.9	17.3	36.7	31.1	23.2	39.0	−7.3	−5.6
3a (X = Me; Y = Cl)	24.5	23.0	36.4	30.2	26.0	37.5	1.0	
3b (X = Cl; Y = Me)	23.5	22.0	36.0	30.0	25.6	37.3	−1.8	
2 (X = Y = Cl)	28.2	22.2	36.4	29.6	27.3	36.6		
norbornane [b]	36.8	30.1	36.8	30.1	30.1	38.7		
endo-2-methylnorbornane [b]	42.2	38.9	38.2	30.6	22.4	40.7	17.4	
exo-2-methylnorbornane [b]	43.6	40.2	37.5	29.0	30.3	35.0	22.3	

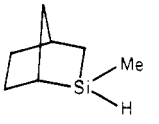
[a] ^{29}Si NMR data were obtained in C_6D_6 with Me_4Si as an internal reference on a Bruker WM 250 spectrometer. [b] See ref 16. The original data was recalculated to correspond to TMS as a reference.

Results and Discussion

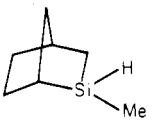
Synthesis. The important ring-closure reaction involved a platinum-catalyzed, intramolecular hydrosilation of the type previously demonstrated by Benkeser and co-workers in a synthesis of some 7-silanorbornanes.[2] In order to prepare silanes suitable for this reaction, we synthesized 4-(bromomethyl)cyclopentene (**10**) by the route shown in Scheme I, which was based on one previously described by Johnson and co-workers.[9] The large-scale preparation of 4-hydroxycyclopentene (**5**) was most easily accomplished by the two-step epoxidation–reduction sequence developed by Crandall and co-workers.[10] This was more suitable than hydroboration of cyclopentadiene with diborane[9,11] or diisopinocamphenylborane;[12] the latter reaction gave varying yields and required sizeable amounts of silver nitrate for purification. Cyclopentadiene was also treated with 9-borabicyclononane (9-BBN) in THF to produce **5** in 55% yield, but this was contaminated with dicyclopentadiene, which could not be easily separated. The *p*-toluenesulfonate **6** was treated with sodium cyanide in hexamethylphosphoramide (HMPA) at room temperature to give **7** in high yield. Previously this cyanation was performed in hot dimethyl sulfoxide to give **7** in fair yields;[9] but HMPA has been shown to be a more effective solvent for such simple cyanations.[13] Cyanide **7** was conveniently isolated by distillation under reduced pressure directly from the reaction mixture and was immediately hydrolyzed to give carboxylic acid **8** in up to 85% overall yield from **6**. Acid **8** was then converted to **10** as shown.

Addition of the Grignard reagent of **10** to a tenfold excess of either trichlorosilane or dichloromethylsilane gave the ring precursors **11** or **12**, respectively, in 70–80% yield. These silanes were treated with catalytic amounts of chloroplatinic acid–isopropyl alcohol solution[14] and heated to 70–80 °C. Normally, but not always, a 2–5-min induction period occurred followed by vigorous bubbling and a color change; continued heating followed by distillation gave **2** or **3** in 65–80% yield. The reaction was monitored by following the disappearance of the vinyl peak in the ^{1}H NMR spectra. The reaction of **11** required 4 h for completion, whereas **12** required 12–14 h. For the latter case, the two geometric isomers, **3a** (*exo*-2-methyl) and **3b** (*endo*-2-methyl), were always produced in a 3:2 ratio, respectively, as determined by ^{1}H NMR analysis. Chlorosilanorbornanes **2** and **3** were reduced with lithium aluminum hydride (LAH) to give **1** and **4** quantitatively.

NMR Spectral Data. The 60-MHz ^{1}H NMR spectra of **1**–**4** revealed several distinguishing features. The hydrogen at C-4 (see Table I for numbering) gave a broad absorption at 2.5 ppm characteristic of such bridgehead hydrogens,[15] while the remaining ring hydrogens absorbed from 0.5 to 2.0 ppm. The methyl absorptions of **3** and **4** occurred at ca. 0.4 and 0.0 ppm, respectively. The chemical shifts for the silyl hydrogens of **1** and **4** appeared at 3.6–4.0 ppm as broad absorptions. Initial attempts to resolve the endo–exo hydrogens by double irradiation experiments have not yet been successful. However, a 400-MHz spectrum of **4a** and **4b** (4:1, respectively) did show a difference in shift for the two hydrogens. On the basis of the fact that an *endo*-hydrogen absorbs upfield from an *exo*-hydrogen in several substituted norbornanes,[15] the absorption at 3.77 ppm was assigned to the *endo*-hydrogen of **4a**, and the absorption at 3.92 ppm was assigned to the *exo*-hydrogen of **4b**. This preliminary isomer assignment was supported by the ^{13}C and ^{29}Si NMR data discussed later.



4a



4b

(6) Cremer, S. E.; Blankenship, C. *Tetrahedron Lett.* **1980**, 3979.
(7) Shen, Q.; Hilderbrandt, R. L.; Blankenship, C.; Cremer, S. E. *J. Organomet. Chem.* **1981**, *214*, 155.
(8) (a) Carleer, R.; Hosten, N.; Anteunis, M. J. O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 709. (b) Carleer, R.; Anteunis, M. J. O. *Org. Magn. Reson.* **1979**, *12*, 673.
(9) Johnson, C. R.; Keiser, J. E.; Sharp, J. C. *J. Org. Chem.* **1969**, *34*, 860.
(10) Crandall, J. K.; Banks, D. B.; Colyer, R. A.; Watkins, R. J.; Arrington, J. P. *J. Org. Chem.* **1968**, *33*, 423.
(11) Allred, E. L.; Sonnenberg, J.; Winstein, S. *J. Org. Chem.* **1960**, *25*, 26.
(12) Hess, H. M.; Brown, H. C. *J. Org. Chem.* **1967**, *32*, 4138.
(13) Shaw, J. E.; Hsia, D. Y.; Parries, G. S.; Sawyer, T. K. *J. Org. Chem.* **1978**, *43*, 1017.
(14) Benkeser, R. A.; Kang, J. *J. Organomet. Chem.* **1980**, *185*, C9. The nature of the catalyst is very important. As mentioned in ref 2, the catalyst solution should be properly aged for consistent results. Also, metal syringes should *not* be used for transfer of the catalyst solution. After two uses, a metal coating appeared in the barrel of a Hamilton microliter syringe, even with immediate washing after use. If this syringe was used again, little or no reaction occurred. The syringe could not be cleaned, even with treatment with concentrated acid.
(15) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry"; Pergamon Press: Oxford, England, 1969; pp 230–231.

Table II. Mass Spectral Data for 2-Silanorbornanes[a]

1	4	3	2
112 (M, 36)	126 (M, 38)	160 (M, 39)	180 (M, 19)
111 (M - 1, 13)	125 (M - 1, 3)		
97 (M - 15, 36)	111 (M - 15, 20)	145 (M - 15, 8)	165 (M - 15, 13)
84 (M - 28, 99)	98 (M - 28, 43)	132 (M - 28, 19)	152 (M - 28, 23)
83 (M - 29, 47)	97 (M - 29, 28)		
		124 (M - 36, 5)	144 (M - 36, 12)
71 (M - 41, 100)	85 (M - 41, 100)	119 (M - 41, 100)	139 (M - 41, 38)
70 (M - 42, 22)	84 (M - 42, 15)	118 (M - 42, 25)	138 (M - 42, 22)
69 (M - 43, 8)	83 (M - 43, 25)	117 (M - 43, 25)	
		93 (M - 67, 25)	116 (M - 64, 20)
		92 (M - 68, 21)	
81 (M - 31, 41)	81 (M - 45, 27)	81 (M - 79, 74)	82 (M - 98, 33)
	80 (M - 46, 15)	80 (M - 80, 45)	81 (M - 99, 34)
67 (M - 45, 48)	67 (M - 59, 30)	67 (M - 93, 87)	67 (M - 113, 100)
66 (M - 46, 16)	66 (M - 60, 25)	66 (M - 94, 38)	
		65 (M - 95, 35)	65 (M - 115, 23)
	59 (M - 67, 15)	63 (M - 97, 64)	63 (M - 117, 41)
	45 (M - 81, 25)		
43 (M - 69, 28)	43 (M - 83, 70)	43 (M - 117, 28)	
	41 (M - 85, 21)	41 (M - 119, 36)	41 (M - 139, 56)
39 (M - 73, 25)	39 (M - 87, 15)	39 (M - 121, 46)	39 (M - 141, 64)

[a] Data given as m/e of fragment (molecular ion minus amu's lost, relative intensity).

The ^{13}C and ^{29}Si NMR data are shown in Table I. Peak assignments were made by selective hydrogen decoupling experiments, off-resonance hydrogen decoupling experiments, and comparison with the data of the hydrocarbon analogues.[16] Individual assignments are discussed separately for convenience.

C-4 and C-1. Bridgehead carbon C-4 was easily distinguished by selective hydrogen decoupling experiments, since, as noted above, the attached hydrogen gave a distinct absorption in the ^1H NMR spectra. The other bridgehead carbon, C-1, appeared as a doublet in the off-resonance experiments; since it is α to silicon, it was shifted upfield and exhibited more variation in shift with differing substitution at silicon.

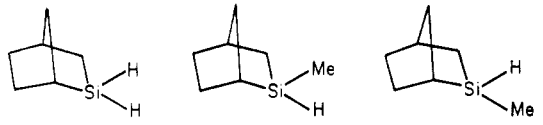
C-3. This α-methylene was assigned by virtue of its upfield chemical shift; in addition, it showed the greatest variation in shift with differing substitution at silicon.

C-5. This carbon is furthest removed from silicon and should be least affected by its presence; the assigned chemical shifts were nearly identical with those observed in the norbornyl analogues.

C-7 and C-6. These carbons were initially assigned from their relative chemical shifts in accordance with the norbornyl analogues. The bridging carbon, C-7, was expected to absorb downfield, and the resonances which occurred in the range 36.8–38.5 ppm were very similar to those in the analogous hydrocarbons. The remaining absorption in this region of the spectra was assigned to C-6. This was the only β-carbon whose chemical shift was significantly affected by silicon incorporation and appeared 3–5-ppm upfield from that observed in the norbornyl analogues.[17]

Further evidence which distinguished C-6 from C-7 was derived from the relative chemical shifts in **4a** and **4b**; the 4:1 isomeric ratio used in the analyses enabled the distinction of the individual carbons ascribed to each isomer. Due to steric interactions,[18,19] the absorption for C-6 in **4b** was upfield from that in **4a**, and the absorption for C-7 was upfield in **4a** compared to that in **4b**, a feature observed in the norbornyl analogues.[16] C-6 and C-7 showed the greatest difference in shift between the two isomers, further differentiating them from the other ring carbons. On the basis of these same steric interactions, the absorption for the *endo*-methyl in **4b** was upfield relative to that of the *exo*-methyl in **4a**, which is consistent with the data for the norbornyl analogues[16] and also with the assignment of isomers made from ^1H NMR data.

The ^{29}Si NMR data for **1** and the isomers of **4** (Table I) are best compared with the data obtained for the homologous 3-silabicyclo[3.2.1]octanes shown below. First,



$\delta(^{29}Si)$ −43.0 $\delta(^{29}Si)$ −20.76 $\delta(^{29}Si)$ −20.74

replacement of a hydrogen with an alkyl group caused a substantial downfield shift in the ^{29}Si absorption in both classes, which is observed for organosilicons in general;[20] second, the increase in ring strain at silicon in **1** and **4** resulted in a shift to lower field, also previously observed.[21] The ^{29}Si absorption in **4b** was upfield from that in **4a**, which was expected on the basis of steric interactions. The chemical shifts of ^{29}Si nuclei have been shown to be sensitive to steric effects in the same manner as ^{13}C nuclei,[22] and the observed results support the isomer assignment made above.

Mass Spectral Data. The partial GC/MS data (70 eV; peaks at $m/e \geq 35$ recorded) for **1–4** are shown in Table II. Each silane gave a relatively abundantly molecular ion (M). The fragment at M - 41 was the base peak for three of the four silanobornanes and corresponded to loss of allyl radical, $C_3H_5\cdot$; the formula for the resulting silicon- or chlorosilicon-containing fragment was supported by the observed isotopic abundances. A mechanism which ac-

(16) Grutzner, J. B.; Jautelat, M.; Dence, J. B.; Smith, R. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7107.

(17) The exception is *endo*-2-methylnorbornane, in which the severe steric interaction between the methyl group and C-6 causes a large upfield shift for the latter carbon.

(18) Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic *Resonance* Spectroscopy", 2nd ed.; Wiley: New York, 1980; pp 33, 55–56.

(19) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972.

(20) Harris, R. K.; Kennedy, J. D.; McFarlane, W. "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978.

(21) Filleux-Blanchard, M. L.; An, N. D.; Manuel, G. *Org. Magn. Reson.* **1978**, *11*, 150.

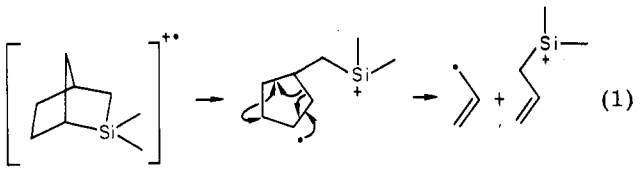
(22) Engelhardt, G.; Schraml, J. *Org. Magn. Reson.* **1977**, *9*, 239.

Table III. Stereochemistry of Reactions of Methylsilanorbornanes 3 and 4 [a]

expt	isomer ratios of starting matl	reagents	isomer ratios of products
1	80% 4a/20% 4b	Ph_3CCl, benzene	60% 3a/40% 3b
2	80% 4a/20% 4b	benzoyl peroxide catalyst, CCl_4, Δ	77% 3a/23% 3b
3	60% 3a/40% 3b	LAH, ether	80% 4a/20% 4b
4	77% 3a/23% 3b	LAH, ether	67% 4a/33% 4b
5	80% 4a/20% 4b	CsF, DMF, 2 h	55% 4a/45% 4b
6	80% 4a/20% 4b	CsF, CD_3CN, 7 days	54% 4a/46% 4b

[a] 3a, *endo*-2-chloro-*exo*-2-methyl-2-silanorbornane; 3b, *exo*-2-chloro-*endo*-2-methyl-2-silanorbornane; 4a, *exo*-2-methyl-2-silanorbornane; 4b, *endo*-2-methyl-2-silanorbornane.

counts for the formation of the M − 41 peaks is shown in eq 1. The initial cleavage of the parent ion to give a



(1)

siliconium ion and an alkyl radical is a common precept in mass spectrometry of organosilicons,[23] and loss of the most substituted radical would be favored. Most cyclic organosilicons,[24] including silacyclobutanes,[25,26] silacyclopentanes,[26,27] and silacyclohexanes,[26] give base peaks corresponding to loss of 28 amu resulting from loss of ethylene. In addition, the base peaks in the spectra of 1-chloro-1-silanorbornane and 1-silanorbornane also result from loss of 28 amu.[5a] For substituted 1,2,5-trimethyl-1-silacyclopentanes, which contain secondary carbons attached to silicon, as do 1–4, loss of neutral three-carbon fragments predominate.[28] It is noted, of course, that the parent silane 1 gave substantial amounts of *both* M − 28 and M − 41 fragments.

A trend which emerges from Table II is the general decrease in the relative abundance of charged fragments containing silicon on going from 1 to 4 to 3 to 2, toward increasing chlorine substitution. The key silicon-containing fragments occurred at M − 15, M − 28, and M − 41, resulting from loss of methyl radical, ethylene, and allyl radical, respectively. The key hydrocarbon fragments occurred at *m/e* 67, 41, and 39. There is no possible formulation containing silicon for the fragment at *m/e* 39, whose formula would be $C_3H_3^+$, and the peak at *m/e* 41 is most likely $C_3H_5^+$ as opposed to $SiCH^+$. The fragment at *m/e* 67, corresponding to $C_5H_7^+$, was the base peak for 2; the formula in this case was clearly supported by the isotopic abundances. Evidently, from this observed trend, the presence of chlorine on silicon decreases its inherent capacity for holding a positive charge, and a different mode of fragmentation results.

Reactions of 3 and 4. Studies of the stereochemistry of the reactions of methylsilanes 3 and 4 have been initiated and are presented in Table III. The relative amount of each isomer was measured by integration of the methyl absorptions in the ^1H NMR spectra. The isomers of 3 and 4 were not separable by GC using a variety of columns, so pure isomers for study have not been obtained at this time.

Two chlorination reactions of 4 were studied in an attempt to obtain a mixture of 3 enriched in one isomer: hydrogen–halogen exchange with chlorotriphenylmethane in benzene[29] (expt 1) and free-radical chlorination in refluxing carbon tetrachloride[30] (expt 2). ^1H NMR studies for the former reaction showed that it was not stereospecific; the same isomer mixture of 3 was obtained from the ring closure of 12. This reaction was previously shown to be stereospecific for acyclic silanes[31] under the reaction conditions used here, but later studies[32] indicated that the stereochemistry was very sensitive to reaction conditions. In addition, this reaction was shown to be nonstereospecific for 1,2,5-trimethyl-1-silacyclopentane.[28a] The second reaction was very stereospecific, which is well documented for acyclic[33,34] and cyclic organosilanes,[28,35–37] and goes with retention of configuration. The high stereospecificity and known stereochemistry allowed for the assignment of isomers for 3, and the correlation of the relative ^1H and ^{13}C chemical shifts of the methyl groups in 3a and 3b with those for 4a and 4b was consistent with the overall reaction stereochemistry. A major problem in making 3 enriched in one isomer on a preparative scale was its tendency to undergo isomerization upon distillation to give an approximate 3:2 ratio of isomers. This isomerization was also observed in studies with 3-chloro-3-methyl-3-silabicyclo-[3.2.1]octane and was mentioned in studies of chlorosilacyclobutanes.[35]

The LAH reduction of 3 was rapid at 0 °C and gave quantitative yields of 4. Experiment 3 was run several times under varying conditions, ranging from short reaction times at 0 °C to prolonged periods at reflux, and the same isomer ratio for 4 was always obtained. LAH reductions of chlorosilanes have been shown to be highly stereospecific with inversion of stereochemistry about silicon in acyclic[38] and unstrained cyclic silanes;[36,37] in strained substrates a high percentage of retention was observed.[39,40] It is difficult to rationalize the result of expt 3 with any predominantly stereospecific reaction mechanism. In an attempt to gather more information, we ran one reaction (expt 4) using the crude product enriched in one isomer, obtained from a previous chlorination reaction, but the result was

(23) Litzow, M. R.; Spalding, T. R. "Mass Spectrometry of Inorganic and Organometallic Compounds"; Elsevier: Amsterdam, 1973; p 207.
(24) Orlov, V. Y. *Russ. Chem. Rev. (Engl. Transl.)* **1973**, *42*, 529.
(25) Laane, J. *J. Am. Chem. Soc.* **1967**, *89*, 1144.
(26) Chernyak, N. Y.; Khmel'nitskii, R. A.; D'yakova, E. V.; Vdovin, V. M.; Ark'hipova, T. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1966**, *36* 99.
(27) Duffield, A. M.; Budzikiewicz, H.; Djerassi, C. *J. Am. Chem. Soc.* **1965**, *87*, 2920.
(28) (a) Franke, F.; Wells, P. R. *J. Org. Chem.* **1979**, *44*, 4055. (b) Wells, P. R.; Franke, F. *Ibid.* **1979**, *44*, 244.
(29) Corey, J. Y.; West, R. *J. Am. Chem. Soc.* **1963**, *85*, 2430.
(30) Nagai, Y.; Yamazaki, K.; Shiojima, I.; Kobori, N.; Hayashi, M. *J. Organomet. Chem.* **1967**, *9*, P21.
(31) Austin, J. D.; Eaborn, C. *J. Chem. Soc.* **1964**, 2279.
(32) Sommer, L. H.; Bauman, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 7076.
(33) Sakurai, H.; Murakami, H.; Kumada, M. *J. Am. Chem. Soc.* **1969**, *91*, 519.
(34) Sommer, L. H.; Ulland, L. A. *J. Org. Chem.* **1972**, *37*, 3878.
(35) McKinnie, B. G.; Bhacca, N. S.; Cartledge, F. K.; Fayssoux, J. *J. Org. Chem.* **1976**, *41*, 1534.
(36) Cartledge, F. K.; Wolcott, J. M.; Dubac, J.; Mazerolles, P.; Fagoaga, P. *Tetrahedron Lett.* **1975**, 3593.
(37) Sakurai, H.; Murakami, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3185.
(38) Sommer, L. H. "Stereochemistry, Mechanism, and Silicon"; McGraw-Hill: New York, 1965.
(39) Roark, D. N.; Sommer, L. H. *J. Am. Chem. Soc.* **1973**, *95*, 969.
(40) McKinnie, B. G.; Bhacca, N. S.; Cartledge, F. K.; Fayssoux, J. *J. Am. Chem. Soc.* **1974**, *96*, 2637.

Table IV. ^{13}C NMR Chemical Shifts for the Synthetic Precursors to 2-Silanorbornanes

compd	chemical shift, δ: vinylic carbons	allylic carbons	methine carbon	other
5	127.9	42.5	71.2	
6	127.4	39.7	81.7	144.2, 134.0, 129.4, 127.3 (aromatic); 21.5 (CH_3)
7	128.4	37.6	25.6	122.8 (CN)
8	128.5	41.4	36.2	182.2 (C=O)
9	129.5	35.6	39.4	67.2 (CH_2OH)
10	128.9	38.9	39.7	39.2 (CH_2Br)
11	129.4	41.0	32.3	27.9 (CH_2Si)
12	129.3	41.0,[a] 41.3	32.9	24.7 (CH_2Si), −0.2 (CH_3)

[a] Diastereotopic carbons.

not helpful. Neither of the final ratios for 4 were equilibrium values as shown by equilibration studies discussed below. The apparent nonstereospecific nature for this reduction was not observed in studies of the reduction of 3-chloro-3-methyl-3-silabicyclo[3.2.1]octane, which gave predominant inversion of stereochemistry at silicon.

The isomers of 4 were treated with CsF in polar, aprotic solvents (expts 5 and 6) in order to determine the equilibrium preference for the methyl group. We have previously shown that this medium catalyzes the equilibration of the isomers of 3-methyl-3-silabicyclo[3.2.1]octane (MSBO),[6] and this has been generalized to include the facile racemization of optically active (α-naphthyl)phenylmethylsilane.[41] We have not been able to approach the "equilibrium" for 4 from a mixture enriched in **4b**, so we hesitate to conclude that this is empirically established. However, molecular mechanics calculations for 4 indicate that there is very little energy difference between the isomers; **4a** is slightly more stable by 0.2 kcal/mol,[42] which agrees with our experimental result. The change in the isomer ratio of 4 was clearly evident in the ^1H NMR spectra. Most notably, reaction of 4 was much more rapid than those for the MSBO isomers. For instance, in dimethylformamide (DMF), the change in the isomer ratio for 4 was apparent after 30 min at room temperature, and equilibration was complete after 2 h; for MSBO, heating to 80 °C up to 14 h was necessary to effect equilibration. In acetonitrile, a slow equilibration of the isomers of 4 occurred at room temperature over a period of 7 days without significant decomposition; for MSBO, heating for prolonged periods (10 days) was necessary, and decomposition was often observed. In DMF, prolonged contact with CsF over 10 h led to complete decomposition of 4. The product of this reaction was collected by preparative GLC, but the NMR spectra were very complex and showed several upfield methyl absorptions. Both ^1H NMR and IR spectral analyses did not show any Si–H bond present, and the IR spectrum showed an absorption indicative of a Si–O–Si linkage. Similar decomposition of silicon hydrides with CsF/DMF was observed in other equilibration studies, and an analogous reaction of triphenylsilane was performed and analyzed to give the results shown in eq 2.[43] The product of the decomposition of 4 is probably

$$Ph_3SiH + DMF \xrightarrow{CsF} Ph_3SiOSiPh_3 + (Me_2N)_2CH_2 \quad (2)$$

the dimeric siloxane, and the various possible isomers would give the complex NMR spectrum observed.

Experimental Section

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. ^1H NMR spectra (60 MHz) were recorded on a Varian A-60A spectrometer in CCl_4; Me_4Si was used as internal reference, or, in the case of methylsilanes, $CHCl_3$ (7.25 ppm) was used. ^{13}C NMR spectra (15 MHz) were recorded on a JEOL FX-60Q spectrometer in $CDCl_3$ by using 10-mm tubes with Me_4Si as an internal reference. ^{29}Si NMR data were obtained from a Bruker WM-250 spectrometer. GC/MS data were obtained from a Finnigan Model 4000 spectrometer at 70 eV. IR spectra were recorded on a Beckman Model 4260 spectrometer in CCl_4 solution by using cells of 0.1-mm pathlength. Preparative GC was performed on a Hewlett-Packard Model F&M 700, and analytical GC (flame ionization) was done on a Hewlett-Packard Model 5710A with a Model 3380A integrator. Capillary melting points were determined by using a Thomas Hoover Uni-melt and are uncorrected. Boiling points are uncorrected.

"Distilled" solvents were fractionally distilled under nitrogen. Anhydrous ether was used directly or for reactions involving organosilicons was distilled from sodium/benzophenone directly before use. THF was distilled from sodium/potassium/benzophenone directly before use. Benzene was distilled from sodium/benzophenone and stored over molecular sieves. Acetonitrile was stirred over calcium hydride, filtered, distilled from phosphorus pentoxide, and stored over molecular sieves. DMF was shaken with KOH, distilled from calcium hydride under reduced pressure, and stored over molecular sieves. Reagent grade HMPA (Aldrich), acetone, dichloromethane, and carbon tetrachloride were used directly. CsF (Cerac) was dried in vacuo at 180 °C and weighed in a glovebag under nitrogen. Trichlorosilane and dichloromethylsilane were distilled from calcium hydride directly before use. Chloroplatinic acid catalyst[14] was prepared by adding chloroplatinic acid (Matheson Coleman and Bell) to reagent grade 2-propanol to give an initial 0.4 M solution.

^{13}C NMR Data. The ^{13}C NMR data for compounds **5–12** are summarized in Table IV.

4-Hydroxycyclopentene (5) was prepared from cyclopentadiene by using the procedure of Crandall.[10] Oxidation with 40% peracetic acid gave 3,4-epoxycyclopentene: 43%; bp 39–40 °C (47 mm) [lit.[10] bp 39–41 °C (46 mm)]; IR ($CHCl_3$) 2950, 1700, 1240 cm^{-1}; ^1H NMR δ 6.2 (m, 2 H), 4.0 (m, 2 H), 2.6 (m, 2 H); ^{13}C NMR δ 137.6, 131.2, 58.9, 56.5, 35.5. Subsequent LAH reduction gave **5**: 77%; bp 67–69 °C (38 mm) [lit.[10] bp 71–73 °C (46 mm)]; IR ($CHCl_3$) 3300 (br), 2900, 1640, 1065, 960, 845 cm^{-1}; ^1H NMR δ 5.7 (s, 2 H), 3.5 (varies with solvent, s, 1 H), 4.4 (septet, 1 H), 1.9–2.6 (m, 4 H).

Preparation of 5 from Cyclopentadiene and 9-BBN. A solution of 9-BBN (Aldrich; 100 mL of a 0.5 M solution in THF, 0.05 mol) and cyclopentadiene (33 g, 0.5 mol) was stirred at reflux for 1 h. Unreacted borane was decomposed by the addition of 2 mL of water. After the mixture was cooled to 0 °C, 17 mL of 3 N NaOH was added followed by the dropwise addition of 17 mL of 30% hydrogen peroxide; the temperature was maintained at 10–20 °C during addition of the peroxide. The mixture was then stirred for 1 h at room temperature and 30 min at reflux, followed by concentration on a rotary evaporator. The residue

(41) Cremer, S. E.; Blankenship, C., results presented at the 15th Organosilicon Symposium, Duke University, Durham, NC, Mar 27–28, 1981; Abstracts, p 28.

(42) Cartledge, F. K., personal communication. For comments on the validity of comparing such calculations with experimental results, see ref 7. The energy difference between the isomers of 2-methylnorbornane at 300 °C was 0.9 kcal/mol in favor of the *exo*-methyl isomer. Ouellette, R. J.; Rawn, J. D.; Jreissaty, S. N. *J. Am. Chem. Soc.* **1971**, *93*, 7117.

(43) This and other reactions of triphenylsilane with various amides in the presence of CsF is under investigation.

was taken up in 100 mL of ether, washed with saturated salt solution, dried (Na_2SO_4), and concentrated by distillation. Fractional distillation (7-cm Vigreux column) gave 4.1 g of a clear liquid, bp 60–65 °C (29 mm). ^1H NMR analysis revealed a 3:2 mixture of **5** and dicyclopentadiene, representing a 55% yield of **5**. A similar reaction in which 9-BBN was stirred with cyclopentadiene at room temperature for 14 h and worked up as above gave **5** in 22% yield.

4-(*p*-Toluenesulfonoxy)cyclopentene (6) was prepared according to a published procedure:[9] 95% yield; mp 48–52 °C [lit.[9] mp 48–52 °C (crude), lit.[11] mp 53.4–54.2 °C]. This product was used without further purification.

4-Cyanocyclopentene (7). To a mechanically stirred suspension of sodium cyanide (12.3 g, 0.25 mol) in 220 mL of HMPA was added **6** (40.5 g, 0.17 mol) in one portion. There was immediate formation of a brown-black reaction mixture, which was stirred for 72 h at room temperature, poured into 250 mL of water, and extracted with four 200-mL portions ether. The combined extracts were washed three times with water, dried (Na_2SO_4), and concentrated by distillation. the residue was distilled to give **7**: 11.7 g (74%); bp 50–53 °C (5.6 mm) [lit.[9] bp 48–51 °C (7 mm)]; ^1H NMR δ 5.7 (s, 2 H), 2.4–3.1 (m, 5 H). An alternative isolation procedure consisted of distilling **7** in ≥90% yield directly from the reaction mixture under reduced pressure. ^1H NMR analysis showed small amounts of HMPA to be the only contaminant. This product was normally used directly.

3-Cyclopentene-1-carboxylic acid (8) was prepared from **7** according to published procedure:[9] 80–85% yield; bp 60–62 °C (0.3 mm) [lit.[9] bp 46–48 °C (0.3 mm)]; ^1H NMR δ 12.3 (s, 1 H), 5.7 (s, 2 H), 2.5–3.3 (m, 5 H).

4-(Hydroxymethyl)cyclopentene (9) was prepared from **8** according to published procedure:[9] 85% yield; bp 64–65 °C (11 mm) [lit.[9] bp 82–85 °C (30 mm)]; ^1H NMR δ 5.6 (s, 2 H), 3.4 (br d, 2 H), 3.2 (underwent exchange upon addition of D_2O, 1 H), 1.9–2.7 (m, 5 H). The tosylate of **9** was prepared according to published procedure:[44] 90% yield; mp 29–30 °C (clear melt) (lit.[44] mp 30–31.5 °C).

4-(Bromomethyl)cyclopentene (10). A magnetically stirred solution of lithium bromide (8.7 g, 0.1 mol) and the tosylate of **9** (8.3 g, 33 mmol) in 80 mL acetone was heated at reflux for 4 h. Lithium tosylate was removed by suction filtration, and the filtrate was concentrated first by distillation at atmospheric pressure and then at reduced pressure (≥60 mm). The residue was taken up in ether and washed twice with water. The dried (Na_2SO_4) organic fraction was concentrated by distillation, and the residue was distilled to give 4.3 g (81%) of a clear, colorless liquid: bp 46–47 °C (8.6 mm); ^1H NMR δ 5.6 (s, 2 H), 3.3 (br d, 2 H), 2.0–2.8 (5 H). An analytical sample was collected by GC using a 6 ft × 0.25 in. column packed with 10% SE-30 on Chromosorb W (column temperature 90 °C, 75 mL/min flow rate).

Anal. Calcd for C_6H_9Br: C, 44.75; H, 5.63. Found: C, 44.96; H, 5.57.

Chloro[(3-cyclopentenyl)methyl]methylsilane (12). To a magnetically stirred mixture of Mg turnings (0.7 g, 0.029 mol) and 1 mL of THF was added 4 or 5 drops ethylene bromide. After the mixture was stirred for 20 min, ca. 1 mL of a solution of **10** (3.5 g, 22 mmol) in 1 mL of THF was added to initiate Grignard reagent formation. After initiation, 10 mL of additional THF was added to the reaction flask, and the remaining bromide solution was diluted with 3 mL of THF. This bromide/THF solution was added dropwise over 20 min, allowing the reaction to reflux from the exotherm. The reaction mixture was then stirred for 30 min at room temperature and 2 h at reflux. The resulting Grignard reagent was transferred via syringe to the addition funnel of another reaction apparatus and was added dropwise over 15 min to a magnetically stirred solution of dichloromethylsilane (25 g, 0.22 mol) in 20 mL of THF at 0 °C. After the mixture was warmed to room temperature and stirred for 2 h, most of the excess dichloromethylsilane and THF were removed by distillation. Ether (50 mL) was added to the blackish residue, and this was stirred overnight. The white solid was removed by pressure filtration through a sintered-glass funnel, and most of the solvents were removed by distillation. Distillation of the residue gave 2.7 g (77%) of **12** as a clear, colorless liquid which fumes in air: bp 48–50 °C (5.6 mm); ^1H NMR δ 5.6 (s, 2 H), 4.8 (m, 1 H), 1.8–2.8 (m, 5 H), 1.1 (m, 2 H), 0.5 (d, 3 H). This product was used shortly after preparation as it discolored with time.

Dichloro[(3-cyclopentenyl)methyl]silane (11) was prepared from **10** and Cl_3SiH in the same manner as **12** above to give a 70–80% yield of a clear colorless liquid which fumes in air: bp 52–54 °C (6.6 mm); ^1H NMR δ 5.6 (s, 2 H), 5.5 (t, 1 H), 1.8–2.9 (m, 5 H), 1.4 (m, 2 H).

Ring Closure of 12 To Give 2-Chloro-2-methyl-2-silanorbornane (3). To the neat silane **12** (2.5 g, 16 mmol) in a round-bottomed flask was added 15 μL of chloroplatinic acid catalyst solution. The reaction mixture was heated to 60 °C. There was a 5-min induction period followed by vigorous bubbling and a color change from clear to clear brown (sometimes a greenish color was observed). The mixture was heated at 70 °C for 14 h; the reaction progress was followed by removal of ca. 10-mg aliquots and analysis by ^1H NMR spectroscopy. After the reaction the mixture was bulb-to-bulb distilled into a dry ice cooled receiver by slowly reducing the pressure to 0.1 mm and then heating the flask to 60 °C, which gave 2.1 g (84%) of **3a/3b** (3:2) as a clear, colorless liquid: ^1H NMR δ 2.5 (br m, 1 H), 0.5–2.1 (m, 9 H), 0.42 (s, *endo*-methyl) and 0.36 (s, *exo*-methyl) (3 H total); IR 2945 (s), 2870 (m), 1255 (s), 1090 (m), 1050 (m), 935 (m) cm^{-1}. Analytical samples were collected by GC using a 6 ft × 0.25 in. column packed with 5% QF-1 on Chromosorb W (column temperature 90 °C, 55 mL/min flow rate).

Anal. Calcd for $C_7H_{13}SiCl$: C, 52.31; H, 8.15. Found: C, 51.94; H, 8.12.

2,2-Dichloro-2-silanorbornane (2) was prepared according to the procedure described for **3** above. The reaction was complete after 4 h as determined by ^1H NMR analysis. Bulb-to-bulb vacuum distillation gave **2** as a clear, colorless liquid: 70% yield; ^1H NMR δ 2.6 (m, 1 H), 0.6–2.1 (m, 9 H); IR 2940 (s), 2870 (m), 1185 (m), 1085 (m), 1040 (s), 930 (s), 880 (m) cm^{-1}. Analytical samples were collected by using the 5% QF-1 column and conditions described for **3** above.

Anal. Calcd for $C_6H_{10}SiCl_2$: C, 39.79; H, 5.56. Found: C, 39.81; H, 5.56.

2-Methyl-2-silanorbornane (4). The isomer mixture **3a/3b** (3:2; 2.4 g, 15 mmol) in 8 mL ether was added dropwise to LAH (0.73 g, 19 mmol) in 90 mL of ether at 0 °C over a period of 5 min. The reaction mixture was stirred at 0–10 °C for 30 min and then slowly poured onto 200 mL of 10% H_2SO_4 plus ice overlaid with 100 mL of pentane. The organic layer was separated and washed with 100 mL of 10% H_2SO_4, 100 mL of water, 100 mL of 5% sodium bicarbonate, and 100 mL of water. The dried (Na_2SO_4) organic layer was concentrated by distillation. The residue was vacuum distilled bulb-to-bulb into a dry ice cooled receiver by slowly reducing the pressure to 1.0 mm and keeping the distillation pot at room temperature to give 1.9 g (100%) of a clear, colorless liquid: ^1H NMR δ 3.8 (m, 1 H), 2.5 (m, 1 H), 0.7–2.0 (m, 7 H), 0.6 (m, 2 H), 0.22 (d, J = 3.6 Hz, *endo*-methyl) and 0.13 (d, J = 3.5 Hz, *exo*-methyl) (total, 3 H); IR 2935 (s), 2870 (s), 2115 (s), 1455 (m), 1185 (m), 1040 (m), 935 (s), 900 (s), 890 (s), 855 (m), 840 (s) cm^{-1}. Careful integration of the methyl absorptions showed an 80:20 ratio of isomers **4a/4b**. Analytical samples were collected by GC using a 12 ft × 0.25 in. column packed with 10% Carbowax 20M on Chromosorb W (column temperature 75° C, 30 mL/min flow rate).

Anal. Calcd for $C_7H_{14}Si$: C, 66.58; H, 11.18. Found: C, 66.58; H, 11.18.

2-Silanorbornane (1) was prepared from **2** according to the procedure described for **4** above. Bulb-to-bulb distillation gave a very volatile, white, waxy solid: 100% yield; mp 65–66 °C; ^1H NMR δ 3.7 (m, 2 H), 2.6 (m, 1 H), 0.5–2.0 (m, 9 H); IR 2945 (s), 2870 (m), 2130 (s), 1050 (m), 955 (s), 940 (m), 895 (m), 840 (s) cm^{-1}. Analytical samples were collected by GC on the Carbowax 20M column described above (column temperature 80 °C, 60 mL/min flow rate).

Anal. Calcd for $C_6H_{12}Si$: C, 64.20; H, 10.78. Found: C, 64.04; H, 10.65.

Reaction of 4 with Chlorotriphenylmethane. To a ^1H NMR tube were added **4a/4b** (4:1; 22 mg, 0.18 mmol), trityl chloride (70 mg, 0.25 mmol), and 0.5 mL of benzene. The reaction occurred at room temperature over 24 h to give the isomers of **3** in a 3:2

(44) Wilt, J. W.; Massie, S. N.; Dabek, R. B. *J. Org. Chem.* **1970**, *35*, 2803.

Table V

expt	wt of 4 used,g (mmol)	wt of CsF used, g (mmol)	solvent (amount, mL)	time	final *exo*-4/*endo*-4 ratio
1	0.10 (0.79)	0.07 (0.49)	DMF (0.5)	2 h	56:44
2	0.10 (0.79)	0.08 (0.56)	DMF (0.5)	2 h	55:45
3	0.02 (0.16)	0.01 (0.07)	CD_3CN (0.4)	7 days	54:46
4 (control)	0.10 (0.79)	none	DMF (0.5)	7 days	80:20

ratio of **3a/3b**. A similar reaction using half the concentration of reagents proceeded at a slower rate with the same overall result.

Free-Radical Chlorination of 4. NMR Tube Reaction. A solution of **4a/4b** (41 mg, 0.33 mmol) and benzoyl peroxide (5.7 mg, 0.024 mmol) in 0.4 mL of carbon tetrachloride was heated at 82 °C for 22 h; ^1H NMR analysis showed that most of the reaction had occurred after 12 h. The isomer ratio of starting material was 81:19 **4a/4b**; the isomer ratio of the product was 77:23 **3a/3b**. No other product was observed.

Preparative Scale Reaction. A solution of **4a/4b** (1.3 g, 10 mmol) in 30 mL of carbon tetrachloride was stirred at reflux temperature for 2.5 days; benzoyl peroxide (80 mg, 0.33 mmol) was added in two 30-mg and one 20-mg increments to effect complete reaction. The isomer ratio for **3** at the end of reaction was 77:23 **3a/3b**. Most of the solvent was removed by bulb-to-bulb distillation at reduced pressure; the distillation pot was maintained at 0 °C, and the receiver was cooled in dry ice; the minimum pressure was 44 mm. The residue (ca. 4 g) consisted of **3a** and **3b** in the same ratio determined above plus carbon tetrachloride and traces of aromatic material; no other silicon-containing product was observed by ^1H NMR or GC analysis. Two 0.4-mL aliquots from this residue were placed in NMR tubes; one was kept at room temperature. To the other was added an equal volume of ether. No isomerization nor decomposition was observed for either sample over 4 days at room temperature.

LAH Reduction of the Crude Product from the Free-Radical Chlorination Reaction. To LAH (2.6 g, 68 mmol) in 125 mL of ether at −25 °C was added crude **3** (77:23 **3a/3b**, from the previous experiment) in 40 mL ether over a period of 20 min. This mixture was stirred for 1.5 h while being allowed to warm to 5 °C and then was stirred for 30 min. The reaction mixture was slowly poured onto 400 mL of 10% H_2SO_4 and ice overlaid with 100 mL of pentane, worked up, and distilled as previously described to give 0.80 g of a clear, colorless liquid. ^1H NMR, ^{13}C NMR, and GC analyses showed this to be **4a/4b** (67:33).

Equilibration Studies of 4 with CsF. Three equilibration experiments were performed in NMR tubes by using the quantity of materials shown in Table V; **4** was purified by preparative GC, and the starting isomer ratio was 80:20 **4a/4b** in each case. All reactions were run at room temperature. Prolonged reaction times (>5 h) for expts 1 and 2 indicated decomposition of starting **4**. Experiment 3 was observed for 3 days after equilibrium had been attained; there was no change in the isomer ratio. Subsequently it was analyzed by GC and then transferred to a ^{13}C NMR tube, rinsing with $CDCl_3$. The ^{13}C NMR spectrum only showed major peaks due to the isomers of **4**.

Acknowledgment. We thank Cerac, Inc., of Milwaukee, WI, for the gift of CsF. C.B. thanks the Society of Sigma Xi for partial support of this research. We also acknowledge partial support of this project from NATO grant No. RG206.80 and to our collaborator, Dr. J. P. Albrand, for the ^{29}Si NMR data. We thank the NSF for Grant TFI 8020268 used to purchase a Varian EM 360 L 60-MHz NMR spectrometer.

Registry No. **1**, 37871-86-6; **2**, 80864-28-4; **3a**, 80864-29-5; **3b**, 80864-30-8; **4a**, 80864-31-9; **4b**, 80864-32-0; **5**, 14320-38-8; **6**, 36367-85-8; **7**, 4492-41-5; **8**, 7686-77-3; **9**, 25125-21-7; **9** tosylate, 25125-22-8; **10**, 80864-33-1; **11**, 80864-34-2; **12**, 80864-35-3; 9-BBN, 25301-61-5; cyclopentadiene, 542-92-7.

α Vinylation of Ketones. A General Method Using (Phenylseleno)acetaldehyde

Derrick L. J. Clive,* Charles G. Russell,† and Suresh Chander Suri

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received July 21, 1981

(Phenylseleno)acetaldehyde can be used as a synthetic equivalent of the vinyl carbonium ion, $CH_2{=}CH^+$. A number of ketone enolates, usually as zinc salts, were condensed with (phenylseleno)acetaldehyde to give β-hydroxy selenides (average yield 78% for 10 examples). Treatment of these substances with methanesulfonyl chloride and triethylamine afforded the corresponding α-vinyl ketones (average yield 72% for 10 examples). This methodology provides access to compounds that are correctly constituted to undergo Cope and oxy-Cope rearrangements. The sequences **1a** → **1e** and **8a** → **8d** are illustrative. Introduction of α-isopropenyl groups is also feasible by using (phenylseleno)acetone in the initial condensation step.

We report here details of our experiments on the use of (phenylseleno)acetaldehyde as a synthetic equivalent of the vinyl carbonium ion, $CH_2{=}CH^+$.[1] The use of this selenium reagent to convert ketones into β,γ-unsaturated ketones (Scheme I, X = PhSe) represents a new route, discovered independently in two laboratories,[1] to substances that are properly constituted to undergo Cope,[2] oxy-Cope,[3] and Cope–Claisen[4] rearrangements (Scheme II).[5]

Such electrocyclic processes are, of course, permanently established as synthetic methods of considerable impor-

† Natural Sciences and Engineering Research Council of Canada Postgraduate Scholar.

(1) (a) Clive, D. L. J.; Russell, C. G. *J. Chem. Soc., Chem. Commun.* **1981**, 434. (b) Kowalski, C. J.; Dung, J.-S. *J. Am. Chem. Soc.* **1980**, *102*, 7950.

(2) (a) Rhoads, S. J.; Raulins, N. R. In "Organic Reactions"; Dauben, W. G., Ed.; Wiley: New York, 1975; Vol. 22, Chapter 1. (b) Evans, D. A.; Baillargeon, D. J.; Nelson, J. V. *J. Am. Chem. Soc.* **1978**, *100*, 2242 and references therein.

(3) (a) Berson, J. A.; Gajewski, J. J. *J. Am. Chem. Soc.* **1964**, *86*, 5019. (b) Evans, D. A.; Golob, A. M. *Ibid.* **1975**, *97*, 4765. (c) Still, W. C. *Ibid.* **1977**, *99*, 4186.

(4) (a) Ziegler, F. E.; Piwinski, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 880. (b) *Ibid.* **1979**, *101*, 1612.

0022-3263/82/1947-1632$01.25/0