Direct Synthesis of Metallacycloalkanones via the Cyclic Hydroboration of Dialkenyl Derivatives of Silicon, Germanium, and Tin

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The hydroboration of a number of representative dialkenylsilanes was examined to determine the regiochemistry of the addition process. For compounds containing a vinylsilane moiety, the relative amount of products containing the boron atom in a β position with respect to silicon was invariably greater on using thexylborane as opposed to borane–methyl sulfide complex (BMS). Compounds which contain an allylsilane group undergo hydroboration to give exclusively a terminally placed boron adduct for that portion of the molecule. Diisopropenyl and bis(α-styryl) derivatives of silicon, germanium, and tin were directly converted to the corresponding novel metallacyclohexanones by using Pelter's cyanoborate procedure. In several cases, the DCME reaction could also be used to prepare these metallacyclohexanones. The cyanoborate methodology was used to prepare silacyclohept-4-one and silacyclooctan-5-one systems in an improved manner. Novel disilacycloalkanones and germacyclooctanone systems were also prepared. All metallacycloalkanones were isolated isomerically pure from the simple sequence. Spectroscopic data for reaction intermediates and products are also reported and discussed.

The cyclic hydroboration of dienes provides a simple entry to boracyclic compounds[1] which are readily converted to cyclic ketones by several methods.[1b,2,3]
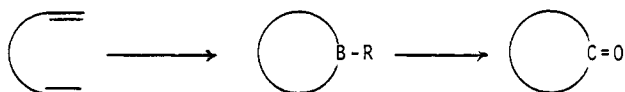
For some time we have had an interest in the chemistry of cycloalkanones which contain silicon and other metalloidal atoms within the ring system[4] (see structure below).
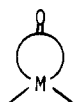
However, available routes to such systems are quite long and routinely give low overall yields.[4a,5] Our recent work on the hydroboration of alkenylsilanes[6] suggested that metallacycloalkanones might be more conveniently prepared by using an organoborane approach.

Results and Discussion

We examined the regiochemistry of the hydroboration process for several representative dialkenylsilanes to determine the feasibility of this approach for the preparation

Table I. Distribution of Regioisomeric Diols from the Hydroboration/Oxidation of Representative Divinylsilanes[a]

dialkenyl-silane	diol products	H₃B·SMe₂	H₂BHxᵗ	HBHx₂ᶜ
1	2,4 (2)	38	17	
	1,4 (3)	56	68	5
	1,5 (4)	6	15	95
9a	2,4			
	1,4 (10)	30		
	1,5 (11)	70	100	
20	2,6 (21)	56	17	2
	1,6 (22)	44	83	98
29	2,5	*b*		
	1,5 (30)	72	43	
	1,6 (31)	28	57	
34	1,6			
	1,7 (35)	100	100	

a All alcohol distributions were determined from isolated mixtures. Analyses were performed on silylated (MSTFA, Pierce) mixtures by using either and Hewlett-Packard Model 5750 or a Perkin-Elmer Model Sigma 1b instrument employing a 6 ft × 1/8 in. 10% SE-30 on DCDMS-treated Chromosorb W column. (Hxᵗ = CMe₂CHMe₂; Hxᶜ = c-C₆H₁₁). *b* While a minor amount (3–4%) of this isomer as well as similar amounts of oxidation (SiOSi) products were suggested by VPC, no confirming evidence was obtained

of the desired boracyclic intermediates. Oxidation of the boron intermediates gave the diol products presented in Table I.

For divinyldimethylsilane (1), the hydroboration/oxidation using BMS gives a quantitative yield of four isomeric diols.
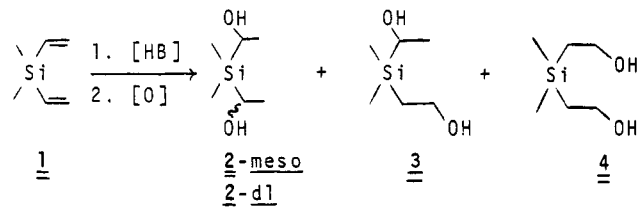
GC analysis of the silylated diol mixture revealed retention times in the order **2 < 3 < 4**. This ordering is representative for all of the diol mixtures given in Table I in that for all of the systems examined the more internally placed alcohols elute prior to their terminal counterparts.

(1) (a) Brown, H. C.; Midland, M. M.; Levy, A. B.; Kramer, G. W. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975. (b) Brown, H. C. *Acc. Chem. Res.* **1969**, *2*, 65. (c) Negishi, E.; Kulkarni, S. U.; Brown, H. C. *Heterocycles* **1976**, *5*, 883. (d) Brown, H. C.; Negishi, E. *Tetrahedron* **1977**, *33*, 2331.

(2) (a) Brown, H. C.; Carlson, B. A. *J. Org. Chem.* **1973**, *38*, 2422. (b) Carlson, B. A.; Brown, H. C. *J. Am. Chem. Soc.* **1973**, *95*, 6876. (c) Carlson, B. A.; Brown, H. C. *Synthesis* **1973**, 776. (d) Carlson, B. A.; Brown, H. C. *Org. Synth.* **1978**, *58*, 25.

(3) (a) Pelter, A.; Hutchings, M. G.; Smith, K. *Chem. Commun.* **1971**, 1048. (b) Pelter, A.; Smith, K.; Hutchings, M. G.; Rowe, K. *J. Chem. Soc., Perkin Trans. 1* **1975**, 129. (c) Zweifel, G; Pearson, N. R. *J. Am. Chem. Soc.* **1980**, *102*, 5919.

(4) (a) Koch, T. H.; Soderquist, J. A.; Kinstle, T. H. *J. Am. Chem. Soc.* **1974**, *96*, 5576. (b) Soderquist, J. A.; Hassner, A. *J. Org. Chem.* **1980**, *45*, 541. (c) Soderquist, J. A. "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Las Vegas 1982; American Chemical Society: Washington, DC, 1982; ORGN 161.

(5) (a) Benkeser, R. A.; Bennett, E. W. *J. Am. Chem. Soc.* **1958**, *80*, 5414. (b) Benkeser, R. A.; Cunico, R. F. *J. Org. Chem.* **1967**, *32*, 395. (c) Weber, W. P.; Felix, R. A.; Willard, A. K.; Boettger, H. G. *J. Org. Chem.* **1971**, *36*, 4060. (d) Rice, L. M.; Sheth, B. S.; Wheeler, J. W. *J. Heterocycl. Chem.* **1973**, *10*, 737. (e) Rice, L. M.; Wheeler, J. W.; Geschicker, C. F. *Ibid.* **1974**, *11*, 1041. (f) Mazerolles, P.; Faucher, A. *Bull. Soc. Chim. Fr.* **1967**, 2134. (g) Mazerolles, P.; Faucher, A.; Laporterie, A. *Ibid.* **1969**, 887.

(6) (a) Soderquist, J. A.; Hassner, A. *J. Organomet. Chem.* **1978**, *156*, C1. (b) Soderquist, J. A.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 3571 and references cited therein.

Table II. Influence of Europium Shift Reagent on the ^{1}H NMR Spectral Data of Silicon Diol Mixtures^a

major components of mixture (origin) ⟶ Eu(fod)$_3$ ⟶ δ (lines) ⟶ 2nd Eu(fod)$_3$ ⟶

2 + 3 (1-BMS) ⟶ 1.01(1), 1.04(1); OH 2.30(2), 5.90(4), Si, OH 6.40(3)*, 2.70(3), 2.75(3) [3^b] ⟶ 2.47(1), 4.03(1); OH 3.66(2), 9.40(4), Si, OH [2-meso^c] ; 3.03(1) OH 3.72(2), 9.95(4), Si [2-dl^c]

10 + 11 (9a-BMS) ⟶ 2.95(1), 3.28(1); 4.37(1) OH 4.88(1), Si OH 6.93(m), 4.27(2) [10^d]

11 (9a·H$_2$BHx^t) ⟶ 3.32(1), 3.60(1); OH OH Si 10.1(m) 15.95(m), 16.15(m) 6.98(2) [11-meso^e] + 3.52(1) OH OH Si 10.1(m) 14.00(m) 6.15(2) [11-dl^f]

21 + 22 (20 ~ BMS) ⟶ 0.50(1), 0.53(1); OH 1.84(2), 4.66(4), Si OH 5.27(3), 2.73(m) 1.70(m) [21^g] + 0.62(1) OH 5.90(3)*, 2.54(3)*, Si OH 5.50(3), 1.68(m) 2.90(m) [22^h]

30 + 31 (29-BMS) ⟶ 1.77(1), 1.81(1), 1.92(1), 2.00(1); OH 3.28(2), 8.54(4), Si OH 9.3(m), 4.73(3)* [30^i] + 1.56(1) Si OH Si OH 5.33(3)*, 9.83(3)* [31]

^{a} All spectra were recorded by using a Varian EM360 NMR spectrometer in CDCl$_3$ solvent. Chemical shifts are given by using Me$_4$Si (δ 0.00) as an internal standard. The asterisk notation is used for absorbances which appear as a complex triplet (A$_2$X$_2$). Absorbances due to OH groups were too broad and downfield to be assigned at the resolution shifts cited. The quantities of Eu(fod)$_3$ added are arbitrary. ^{b} J_{Me-H} = 7.5 Hz; $J_{H_4-H_5}$ = 6.8 Hz. ^{c} J_{Me-H} = 7.5 Hz. ^{d} The chemical shifts of protons on C-4 and C-5 could not be clearly resolved free of overlapping absorbances due to 11. ^{e} J_{Me-H} = 7.5 Hz. ^{f} J_{Me-H} = 7.7 Hz. ^{g} J_{Me-H} = 7.6 Hz; $J_{H_5-H_6}$ = 6.4 Hz. ^{h} $J_{H_5-H_6}$ = 6.4 Hz. ^{i} J_{Me-H} = 7.3 Hz.

The meso/*dl* ratio of the 2,4-diol **2** was found to be ca. 1 as determined by ^{1}H NMR by using europium shift reagent on the isolated diol mixtures. Selected integrated peak areas of mixtures containing the shift reagent were completely consistent with the product ratios as determined by GC integration (Table II). The ^{13}C NMR spectra (Table III) of the isolated diol mixtures gave peak height data which were also consistent with the product ratios given in Table I.

Thexylborane,[7] a reagent widely used for the cyclic hydroboration of dienes, showed an increase in the amount of the terminal diol (**4**) relative to BMS. However, the hydroboration failed to reach completion, giving an overall GC yield of diol products of only 82%. Dicyclohexylborane gave a quantitative yield of diols, with **4** being formed in 95% regioisomeric purity. Unfortunately, this mono-

Table III. Carbon-13 NMR Data of Alcohols Derived from the Hydroboration/Oxidation of Dialkenylsilanes^a

(meso)-6.9, -10.6 (dl) -8.1; HO, Si 18.7, 60.0, OH 60.9 [2]

HO 60.5, -4.9, -6.2; Si 18.4, OH 19.3 59.0 [3]

-3.0; Si OH OH 59.0, 20.3 [4]

12.3, -5.7, -8.9; 22.1 65.3, Si OH 63.1 27.2 27.3 HO [10]

(meso) -5.9, -6.5, -6.5; 12.0 65.3, Si OH 22.9, 22.6 (meso) (dl) [11]

HO 19.5, -6.2, -5.6; 60.9 65.1, Si OH 8.8 26.8 [21]

20.2 59.1, -3.4; Si OH 64.9 OH 11.0 26.7 [22]

138.9 131.7, -3.5; Si 65.7, OH 11.1 27.2 [25]

133.5, 127.7, 128.8, 139.1, -3.1; Si 65.3 OH 11.4 27.1 [24]

HO 20.2, -6.8, -5.7, -3.3, -3.6; Si 61.3 Si OH 20.2 59.4 [30]

-3.9; Si Si OH OH 20.2 59.8 [31]

-3.6; Si OH OH 65.2 10.7 26.9 [35]

^{a} Recorded in CDCl$_3$ by using a Varian CFT-20 spectrometer. Chemical shifts are given relative to Me$_4$Si (δ 0.00).

functional hydroborating reagent does not lead to the desired borinane product **5**,[8] an intermediate which could be converted to a silacyclohexanone **6**.

1 ⟶ Si B-R [5] ⟶ ⟶ Si =O [6] ; [O] ⟶ 4
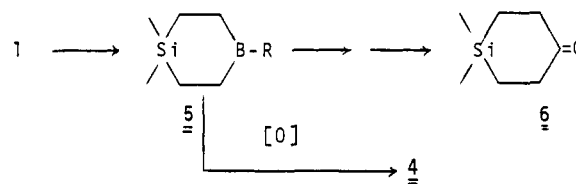
Further, owing to the extreme susceptibility of β-oxosilanes to nucleophilic attack,[9] any silacyclopentanone

(7) (a) Brown, H. C.; Negishi, E. *J. Am. Chem. Soc.* **1972**, *94*, 3567. (b) Negishi, E.; Brown, H. C. *Synthesis* **1974**, 77.

(8) One silaborinane system has been reported: Hawthorne, M. F. *J. Am. Chem. Soc.* **1961**, *83*, 2541.

(9) Fleming, I. "Comprehensive Organic Chemistry"; Barton, D.; Ollis, W. D.; Jones, D. N., Eds.; Pergamon Press: Oxford, 1975; Vol. 3, p 654 and references therein.

product **8** formed from a borolane **7** intermediate would not be expected to survive the reaction conditions under which it was generated.
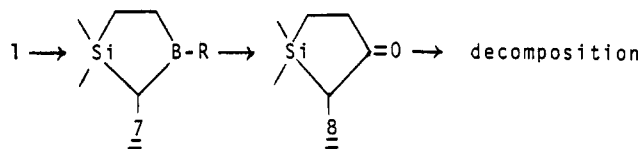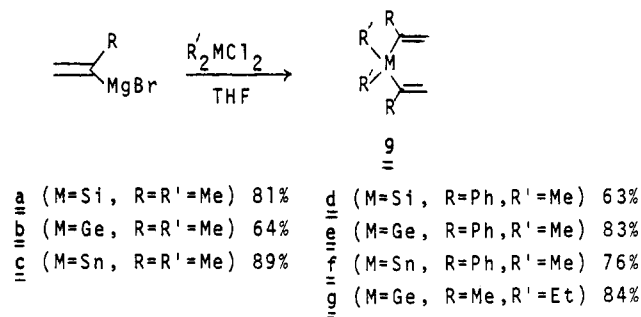

Attempted conversion of the 1/thexylborane reaction products to ketonic products by using Pelter's cyanoborate process[3] gives only a very complex product mixture from which we were unable to isolate either **6** or **8**.

For **1**, both the lack of a β–directive effect by the silicon group[6] as well as cyclic hydroboration effects[1] evidently tend to lower the yield of borinane products such as **5** and favor the formation of internally placed boron adducts which give **3** and **4** upon oxidation.

Findings of Negishi and Brown[10] that a borinane product could be efficiently prepared from 2,4-dimethyl-1,4-pentadiene together with our results for the isopropenyl- vs. vinylsilane systems[6] led us to investigate the hydroboration of similarly substituted divinylsilanes.

To this end, we prepared several novel substituted divinyl derivatives of silicon, germanium, and tin in good yield using a Grignard procedure.

a (M=Si, R=R'=Me) 81% **d** (M=Si, R=Ph,R'=Me) 63%
b (M=Ge, R=R'=Me) 64% **e** (M=Ge, R=Ph,R'=Me) 83%
c (M=Sn, R=R'=Me) 89% **f** (M=Sn, R=Ph,R'=Me) 76%
                            g (M=Ge, R=Me,R'=Et) 84%

It is important to note that the preparation of the styryl derivatives is not trivial, and at least one unsuccessful attempt to prepare **9d** has been reported.[11]

As had been observed for the carbodiene system,[10] the substitution on **9a** markedly increases the amount of the terminal diol product (**11**) observed when compared to the amount of **4** obtained from **1** (see Table I).
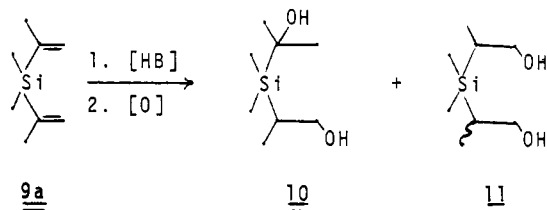
With thexylborane the hydroboration/oxidation of **9a** gives the terminal diol product **11** exclusively.

We chose to isolate the boron products formed from the hydroboration of **9a** using both BMS and thexylborane. Both ^{1}H and ^{13}C NMR data were in accord with the borinane structures illustrated above (cf. Table V and the Experimental Section). Additionally, ^{11}B NMR revealed a single resonance for **12** at 55.4 ppm and for **13a** at 88
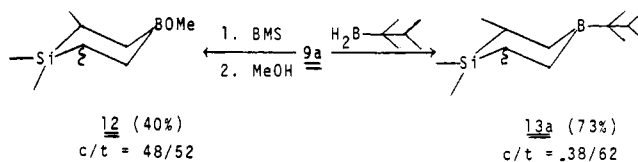

ppm, consistent with dialkylborinate and trialkylborane species, respectively. Oxidation of both **12** and **13a** gives the silicon diol **11** exclusively, indicating the absence of any borolane impurity in these compounds.

To establish that these cis/trans mixtures did not represent thermodynamic mixtures, we heated **13** at 180 °C for 3 h.
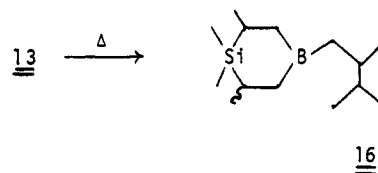
With dehydroboration/hydroboration evident by the isomerization of the thexyl moiety,[13] the cis/trans ratio changed to 1. Thus, it appears likely that the high proportion of *trans*-borinanes in these mixtures represents a kinetic rather than a thermodynamic mixture.

The high-boiling residue left after the distillative isolation of **12** was found to exhibit major ^{11}B NMR peaks at 55 and 88 ppm, indicating the presence of dialkylborinate and trialkylborane species, respectively.[6b] However, the lack of ^{13}C NMR signals in the 50–60-ppm region suggests that the former species was probably due to a diboroxane product rather than a borinate ester such as **12** (cf. Table IV). The downfield boron resonance suggested that trialkylboranes such as **14** were also formed in this process. By analogy to carbodiene systems, such 3:2 adducts[12] would be expected to undergo an exchange process[13] with BMS to give borinane products (**15**) from the cyclization of the central portion of the molecule.

+ "other products"
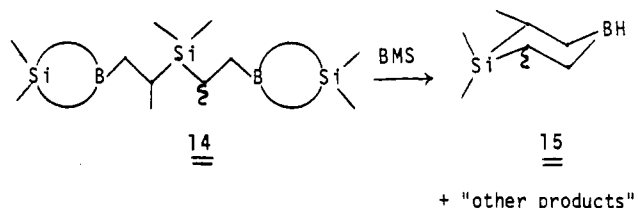
The hydroboration of **9a** with BMS was carried out at 25 °C with the finding that, after oxidation, a 30:70 mixture of **10** and **11**, respectively, was formed. Examination of **11** revealed that it consisted of a 45:55 mixture of meso and *dl* diols. However, if the hydroboration mixture was subsequently heated at reflux temperature for 1 h prior to oxidation, the 30:70 mixture remained constant while the meso/*dl* ratio for **11** changed to 55:45. Longer heating times did not alter this result. Since B-[(Me₃Si)-CH₂CH₂]-9-BBN had been shown to undergo exchange reactions under these conditions[6b] and since this primary-alkyl organoborane would appear to be a reasonable model for either half of **14**, we interpreted the change in meso/*dl* alcohol distribution on heating as arising from cyclization processes such as **14** → **15**.

Any 1,4-diboryl adducts derived from **9a** and giving **10** upon oxidation would contain an (α-silylalkyl)borane portion which is known to resist exchange with borane.[6b] Further, bis[borolane] is known to rapidly isomerize, giving

(10) Negishi, E.; Brown, H. C. *J. Am. Chem. Soc.* **1973**, *95*, 6757.
(11) Petrov, A. D.; Mironov, V. F.; Glukhovtsen, V. G. *Zh. Obshch. Khim.* **1957**, *27*, 1535. *J. Gen. Chem. USSR (Engl. Transl.)* **1957**, *27*, 1609.
(12) Negishi, E.; Burke, P. L.; Brown, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 7431.

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

Table IV. Carbon-13 Assignments for Selected Metallaboracycles[a,b]

^{a} Recorded in CDCl$_3$ solution on a Varian FT-80A spectrometer. Chemical shifts are reported relative to Me$_4$Si (δ 0.00). ^{b} Broad absorbances were observed for carbons bonded directly to boron: 12, 24 ppm; 13, 31 ppm; 36, 26.6 ppm.

1,6-diboracyclodecane which slowly gives B-methoxy-borolane upon methanolysis.[14] Since 14 could contain silaborolane rings,[12] we repeated the preparation of 12 using an excess of methanol and heated the mixture for 2 h at reflux temperature. Additional ^{13}C peaks attributable to a methoxyborolane coproduct (14%) were observed in 12. The high-boiling afterrun exhibited a small ^{11}B signal at 26 ppm attributable to a dialkylborane which must be particularly resistant to methanolysis like the 1,6-diboracyclodecane system.[15]

Thus, while the distribution of products may vary considerably with silicon systems as compared to the analogous carbon systems, once formed, like boron species appear to behave similarly regardless of whether a silicon or carbon atom is present in these species.

We chose to examine both the DCME reaction[2] and the cyanoborate process[3] to obtain the desired metallacyclohexanone products (see below).

Comparable isolated yields of 17 (40% and 38%, respectively) were obtained in these one-pot reaction sequences. While the DCME approach gave 17 as a 55:45
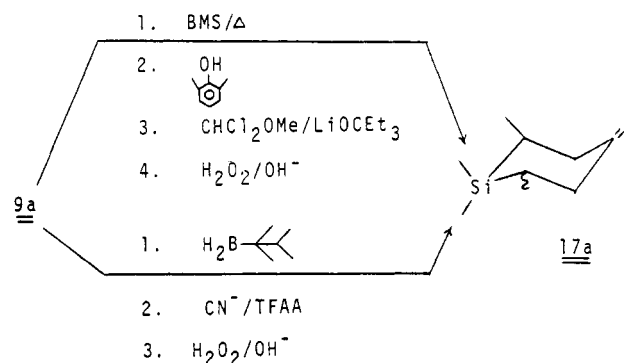

cis/trans mixture, which corresponds to the meso/dl mixture of 11 obtained upon the oxidation of such mixtures, the cyanoborate process gave 17 as a 59:41 mixture where the isolated borane, 13, had a cis/trans ratio of 38:62. Since it was difficult to imagine a loss of the stereochemistry during this reaction, this process was examined in greater detail.

The addition of cyanide ion to 13 was followed by ^{11}B NMR which smoothly gives rise to the cyanoborate, 18,
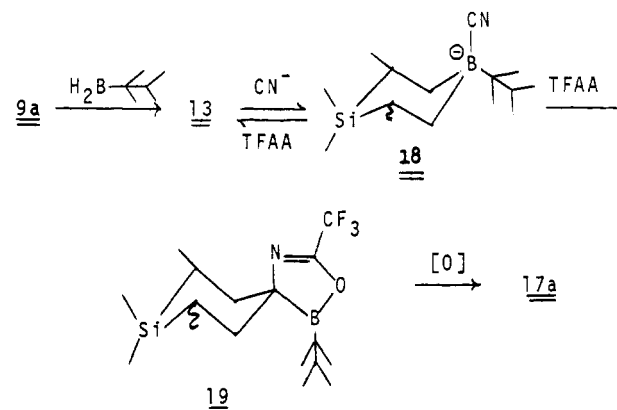
at −19 ppm in 1 h at room temperature. Acetylation of 18 at −78 °C with trifluoroacetic anhydride, gives, after reaching room temperature, three signals at 89, 57, and 5 ppm in an area ratio of 38:3:59, respectively. While the latter two signals were consistent with 19 and a ligand-complex form of 19,[6b,16] the former signal at 89 ppm was most consistent with a decyanidation process giving back 13. We isolated the high-boiling product of the cyanoborate process and found it to be 11 in a 28:72 ratio of meso/dl diols. This data is consistent with the conclusion that two processes are operative upon acetylation of 18. The first is the expected rearrangement process which leads through 19 to the desired ketone, 17, a process favored by the cis-borinane. The second is a decyanidation process leading back to 13, a process favored by the presumably more crowded trans-borinane which is forced to have one of the ring methyl groups in an axial conformation in 18. Extension of this approach to other α-substituted divinyl systems provides convenient routes to other novel silicon, germanium, and tin heterocyclic ketones (17 Table V).
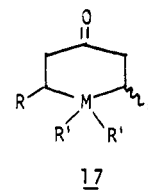
(14) Brown, H. C.; Negishi, E. *J. Am. Chem. Soc.* 1971, *93*, 6682.
(15) Kulkarni, S. U.; Brown, H. C. *Inorg. Synth.* 1979, *19*, 239.

(16) Brown, H. C.; Soderquist, J. A. *J. Org. Chem.* 1980, *45*, 846.

The ^{13}C NMR of these metallacyclohexanones provided very useful diagnostic information on the composition of the mixtures owing to the nonequivalence of the methyl groups on the metalloid in the cis isomers and, conversely, their equivalence in the trans isomers (Table VI).

While the ^{1}H NMR of ketone mixtures such as **17a** gave only a 2:1 area ratio of peaks in the 1–2-ppm region compared to the upfield methyl groups on silicon, treatment of such mixtures with europium shift reagent gave a remarkably well-resolved spectrum.
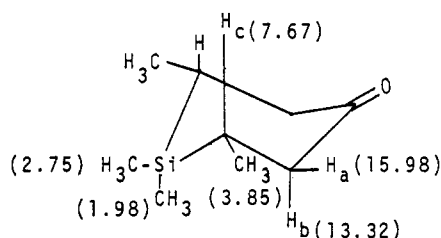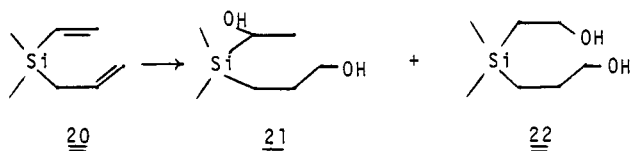

cis-**17a**

$J_{CH_3-H_c} = 7.8$ Hz

$J_{ab} = 13.8$ Hz

$J_{ac} = 5$ Hz

$J_{bc} = 13.8$ Hz
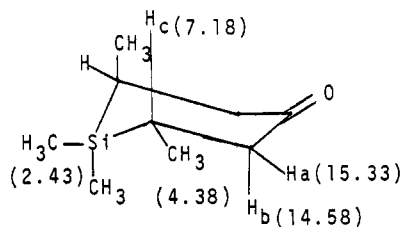
trans-**17a**

$J_{CH_3-H_c} = 7.8$ Hz

$J_{ab} = 15.5$ Hz

$J_{ac} = 5$ Hz

$J_{bc} = 11$ Hz

From the J_{ac} and J_{bc} values, using Lambert's relationships,[17] internal dihedral angles for these compounds of 61° and 58° can be estimated. Similar calculations for other systems (see Table VII) result in an apparent flattening of the ring in the series Si, Ge, Sn. This seems likely to be due to the increasing length of the metalloidal–carbon bonds in these series of compounds.

In order to examine the application of this approach to the preparation of the silacycloheptanone system, we prepared allylvinyldimethylsilane (**20**) in high yield (81%) using a Grignard procedure. Hydroboration/oxidation of **20** gives regioisomeric diols resulting from the two possible positions of boron placement on only the vinyl moiety (see Table I).
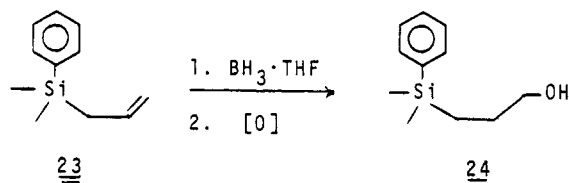

20   **21**   **22**

(17) Lambert, J. B. *Acc. Chem. Res.* **1971**, *4*, 87.

As a spectroscopic model, the hydroboration/oxidation of allylphenyldimethylsilane (**23**) was also examined and gave only the expected terminal alcohol (**24**) even on using

23   **24**

BH$_3$·THF as the hydroborating reagent.[18] These hydroboration studies indicated that thexylborane gives significantly more of the 1,6-boron-placed adducts from **20** than does BMS. We also found that BMS gives only a maximum of ca. 40% of dialkylborane products, intermediates which could be converted to cyclic ketones by using the DCME procedure (see Experimental Section).

From these results as well as from other reported findings, it is clear that the silylmethyl group exerts an extraordinary directive effect in the hydroboration reaction compared to that of simple alkyl groups.[6b] To examine this phenomenon in somewhat greater detail, we chose to examine the hydroboration of **20** with only 1 equiv of

25
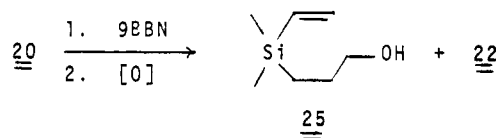
9-BBN, a reagent known to hydroborate both vinylsilanes and allylic silanes regiospecifically to give only terminally placed boron adducts.[6b]

By GC analysis **25** was the exclusive monool product obtained in 69% yield with unreacted **20** (15%) and the terminal diol **22** (15%) comprising the remainder of the quantitative material balance.

(18) For other examples of the hydroboration of arylallylsilanes see: (a) Felix, R. A.; Weber, W. P. *J. Org. Chem.* **1972**, *37*, 2323. (b) Barcza, S.; Hoffman, C. W. *Tetrahedron* **1975**, *31*, 2263.

Table VI. Carbon-13 Assignments for Metallacycloalkanones[a]

17a-cis

17a-trans

17b-cis

17b-trans

17c-cis

17c-trans

17d-cis[b]

17e-cis[b]

17f-cis[b]

17g-trans

6

28

32

37

39

[a] Recorded in CDCl₃ solution on a Varian FT-80A spectrometer, except for 32 which was recorded in C₆D₆ on a Varian XL-100 spectrometer. Chemical Shifts are in parts per million relative to Me₄Si (δ 0.00). [b] The phenyl absorbances are given in the order ipso, ortho, meta, and para, respectively.

Table VII. Calculated Torsional Dihedral Angles for Cis-1,1,2,6-Tetrasubstituted Metallacyclohexan-4-ones[a]

| compd	J(cis), Hz	J(trans), Hz	R	Ψ, deg
17a	5.0	13.8	2.8	61.5
17b	4.6	11.2	2.4	59.5
17c	5.0	10.0	2.0	57
17d	5.0	13.5	2.7	61
17e	5.0	12.5	2.5	60
17f	5.0	11.0	2.2	58
17g	5.0	11.0	2.2	58

[a] Calculated as described in ref 17. [b] Geminal couplings of 13.8, 12.8, 14.0, 13.5, 13.7, 13.0, and 13.5 Hz, respectively, were also measured for these compounds.

Clearly the hydroboration of **20** with thexylborane is a more complicated process that that with 9-BBN. Thexylborane is a monoalkylborane which can hydroborate two carbon–carbon double bonds in sequential processes and gives minor amounts of internally placed boron adducts with vinylsilanes.[6a] Also, polymeric organoborane products could also be formed by a noncyclic hydroboration process.[1] However, we felt that if thexylborane selectively hydroborates the allylic double bond in **20** first, the resulting dialkylborane (**26**) would be ideally arranged to
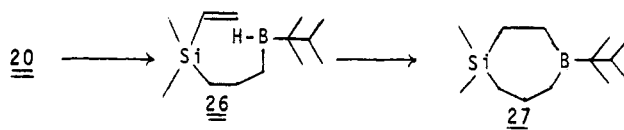

close to the borepane system since this terminal boron placement is the preferred mode of addition of dialkylboranes to vinylsilanes.[6]

We carried out the cyclic hydroboration of **20** with thexylborane and, without isolation of the intermediate organoborane products, prepared the desired silacycloheptanone (**28**) isomerically pure in 27% yield, a significantly better result than has been reported previously.[5b,c]
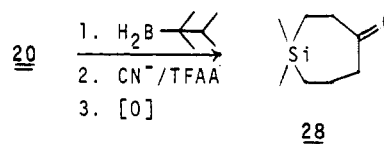

The hydroboration of the 1,2-divinyldisilane system (**29**) gives significant amounts (57%) of the desired 1,6-diol product **31** on using thexylborane as the hydroborating reagent (see Table I).
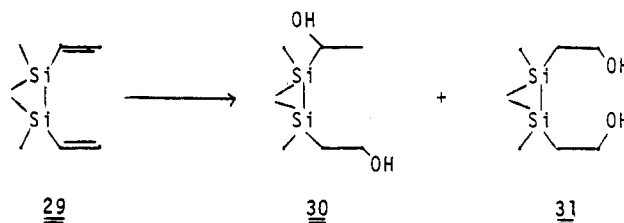
The larger fraction of the terminal diol **31** obtained from **29** compared to the amount of terminal diol **4** obtained from **1** under similar conditions is consistent with Kumada's findings[19] that the hydroborations of vinyldisilanes give more β boron placement than do those of vinylsilanes.

Direct conversion of the hydroboration mixture to the novel 1,2-disilacycloheptan-5-one (**32**) in 16% isolated yield was accomplished by using the cyanoborate approach. However, it was necessary to use stoichiometric amounts of hydrogen peroxide to prevent the further oxidation of **32** to give the 1,3-disila-2-oxacyclooctan-6-one **33**.
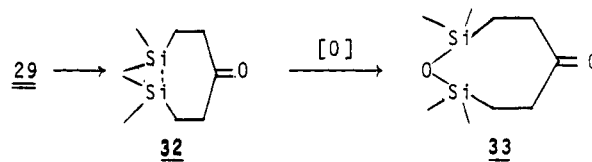
As has been observed in other disilacyclic systems,[20] we found that **32** was slowly oxidized in air to give **33**.

As expected from earlier studies by Weber and co-workers,[5c] the hydroboration/oxidation of diallyldimethylsilane (**34**) gives only the terminal diol **35**.

However, BMS gives only an insoluble polymeric organoborane product. This polymerization process is largely

(19) Kumada, M.; Imaki, N.; Yamamoto, K. *J. Organomet. Chem.* **1966**, *6*, 490.

(20) Kumada, M.; Tamao, K. *Adv. Organomet. Chem.* **1968**, *6*, 19 and references cited therein.

Table VIII. NMR[a] Parameters for α-Substituted Divinylmetalloids 9

compd	chemical shift[b,c]				coupling constant, Hz		
	a	b	c	d	$J_{cd}{}^d$	J_{bd}	J_{bc}
9a	0.08 (1)	1.73 (3)	5.20 (m)	5.54 (6)	3.4	1.8	1.4
9b	0.30 (1)	1.85 (3)	5.10 (6)	5.49 (6)	2.8	1.6	1.2
9c[e]	0.23 (1)	2.01 (3)	5.11 (6)	5.66 (m)	2.6	1.6	1.2
9d	0.36 (1)	7.22 (m)	5.70 (2)	5.97 (2)	3.0		
9e	0.47 (1)	7.17 (m)	5.65 (2)	5.91 (2)	2.4		
9f[f]	0.40 (1)	7.29 (m)	5.56 (2)	6.15 (2)	2.2		
9g	1.00 (m)	1.87 (3)	5.11 (m)	5.66 (6)	3.0	1.6	1.4

[a] Recorded on Varian EM360 equipped with a lock/decoupler. [b] Recorded in parts per million relative to Me₄Si by using either benzene (δ 7.23) or acetone (δ 2.09) as an internal standard approximately 10% solutions in CCl₄. [c] The designation in parentheses is the number of lines observed, m indicating multiplet where no clear description is possible. [d] Verified by decoupling. [e] Additional coupling was observed for the tin isotopes (¹¹⁷Sn, ¹¹⁹Sn; I = 1/2). The CH₃–Sn coupling was found to be 56 and 52 Hz for isotopes ¹¹⁹Sn and ¹¹⁷Sn, respectively (Sn-a). The coupling for the allylic methyl protons (Sn-b) was found to be 48 Hz (average of Sn isotopes). This coupling (cis) with the c protons was 72 Hz (average) and for the d protons (trans) was 144 Hz. [f] J_{Sn-a} = 56 (¹¹⁹Sn) and 54 Hz (¹¹⁷Sn); J_{Sn-c} = 76 Hz (cis) and J_{Sn-d} = 160 Hz (trans).
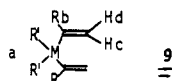
overcome by using thexylborane as the hydroborating reagent which gives a 48% isolated yield of the desired eight-membered ring system 36.

Using the cyanoborate procedure we were able to isolate the isomerically pure silacyclooctan-5-one 37 directly from 34 in 26% yield.
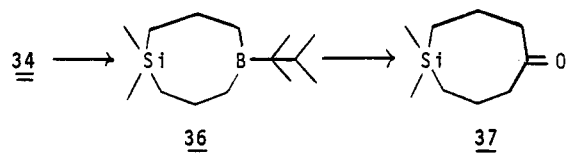
This procedure was also extended to the corresponding germanium ketone (39) which was prepared from diallyldimethylgermane (40) in 23% yield.

Conclusions

In this study we examined the hydroboration of a number of dialkenylsilanes, finding that the vinylsilane portion of these compounds, if present, invariably gives mixtures of regioisomeric boron adducts. This effect could be largely overcome by the introduction of substituents at the α position of vinylsilane moiety. The hydroborations of allylsilane groupings were regiospecific in all of the cases examined, placing the boron at the terminal position of the carbon–carbon double bond. Thexylborane was found to give significant amounts of boracyclic products in the hydroboration of these dialkenylsilanes in all but the divinylsilane case. A one-pot hydroboration/cyanoborate process gave moderate yields of metallacycloalkanones, thus providing a significantly improved route to several such compounds over those previously reported. A number of new heterocyclic ketones including the first stannacyclohexanones as well as the first disilacycloheptanone were reported.

Experimental Section

General Methods. All experiments were carried out in predried (4 h at 110 °C) glassware under either a nitrogen or an argon atmosphere. Standard handling techniques for air-sensitive compounds were employed throughout this study.[1a]

THF was distilled from lithium aluminum hydride prior to use. Alkenyl bromides, dichloromethyl methyl ether, and dichlorodimethylsilane were obtained from Aldrich and distilled from calcium hydride prior to use. Other standard reagents were used as obtained from commercial sources: germanium compounds (Laramie, Alfa, Eagle-Picher), tin compounds (Alfa), magnesium (Alfa), other reagents (Aldrich). Some starting materials were

prepared as previously described.[21]

NMR data were obtained by using Varian EM-360, CFT-20, and FT-80A instruments. Mass spectral data were obtained by using a Du Pont Model 21-491B double-focusing mass spectrometer, and, unless otherwise noted, masses are reported only for the ⁷⁴Ge and ¹²⁰Sn isotopes. Infrared data were obtained by using a Perkin-Elmer Model 457 spectrophotometer (TF = thin film). Elemental analyses were performed by Atlantic Microlabs.

Preparative gas chromatography was performed by using a Varian 90-P3 instrument with a 9 ft × ³/₈ in. column packed with 5% QF-1 on Chromosorb W. Analytical GC was performed by using the instruments cited in Table I. Diols were silylated by using MSTFA (Pierce) prior to analysis. Separation of the isomeric metallacyclohexanones (e.g., cis-17a/trans-17a) was accomplished with the Sigma 1b instrument by using a 25 m × 0.23 mm i.d. Carbowax 20M vitreous silica open tubular column.

α-Bromostyrene was prepared by the addition of bromine (266 g, 1.66 mol) in CCl₄ (1.5 L) dropwise to styrene (173 g, 1.66 mol) in CCl₄ (200 mL) at 0 °C followed by solvent removal, dissolution of the styrene dibromide in Me₂SO (2 L), and the dropwise addition of 50% NaOH solution (431 g). After 8 h and 25 °C, water (1.5 L) was added, and the mixture was extracted with pentane (5 × 400 mL). The dried (MgSO₄) pentane solution was concentrated and distilled to give 250 g (83%) of product: bp 95 °C (19 torr) [lit.[22] bp 67–70 °C (4 torr)]; NMR (CCl₄) δ 5.79 (d, 1 H, J = 2 Hz), 6.13 (d, 1 H, J = 2 Hz), 7.42 (m, 5 H); MS, m/z (relative intensity) 184 (53), 182 (56), 103 (100).

Dimethyldiisopropenylsilane (9a). To a stirred mixture of Mg turnings (10.0 g, 0.41 mol) and dry THF (125 mL) was added 2-bromopropene (50.0 g, 0.41 mol) dropwise to maintain reflux temperature. After an additional 30 min at reflux, the dichlorodimethylsilane (20.7 g, 0.16 mol) was added dropwise, and the stirred mixture was allowed to solidify. After 8 h at room temperature the mixture was warmed briefly to fluidize the magnesium salts, and the mixture was poured onto an ice- (ca. 200 g) saturated NH₄Cl solution (100 mL). The organic layer was dried (MgSO₄) and distilled to give 18.3 g (81%) of 9a: bp 126–128 °C (740 torr); IR (TF) 1610, 925 cm⁻¹ (C=CH₂); MS, m/z (relative intensity) 140 (29), 125 (100). Anal. Calcd. for C₈H₁₆Si: C, 68.48; H, 11.51. Found: C, 68.52; H, 11.51 (see Table VIII).

Dimethyldiisopropenylgermane (9b). This compound was prepared on a 115-mmol (Ge) scale as for 9a in 64% yield: bp 140–142 °C (740 torr). Anal. Calcd for C₈H₁₆Ge: C, 52.00; H, 8.73. Found: C, 52.00; H, 8.77. IR (TF) 1615, 920 cm⁻¹ (C=CH₂); MS, m/z (relative intensity) 186 (9), 171 (100).

Dimethyldiisopropenyltin (9c). This compound was prepared on a 50-mmol (Sn) scale as for 9a in 89% yield: bp 156–158 °C (740 torr); IR (TF) 1605, 920 cm⁻¹ (C=CH₂); MS, m/z (relative

(21) Soderquist, J. A.; Hassner, A. *J. Organomet. Chem.* 1978, 156, 227.
(22) Beets, M.; Drukker, E. A. *Recl. Trav. Chim. Pays-Bas* 1953, 72, 247.

intensity) 217 (100), no M⁺· observed. Anal. Calcd for C₈H₁₆Sn: C, 41.61; H, 6.98. Found: C, 41.73; H, 7.00.

Dimethylbis(α-styryl)silane (9d). This compound was prepared as for **9a** by substituting α-bromostyrene for 2-bromopropene on a 120-mmol (Si) scale: 63% yield, bp 109–110 °C (0.15 torr); IR (TF) 1600, 940 cm⁻¹ (C═CH₂); MS, *m/z* (relative intensity) 264 (8); 135 (100). Anal. Calcd for C₁₈H₂₀Si: C, 81.75% H, 7.62. Found: C, 81.80; H, 7.62.

Dimethylbis(α-styryl)germane (9e). This compound was prepared as for **9d** on a 100-mmol (Ge) scale: 83% yield; bp 117–118 °C (0.07 torr); IR (TF) 1602, 930 cm⁻¹ (C═CH₂); MS, *m/z* (relative intensity) 310 (72), 103 (100; peak does not contain Ge). Anal. Calcd for C₁₈H₂₀Ge: C, 69.97; H, 6.53. Found: C, 69.74; H, 6.52.

Dimethylbis(α-styryl)tin (9f). This compound was prepared as for **9d** on a 100-mmol (Sn) scale: 76% yield; bp 123–125 °C (0.07 torr); IR (TF) 1598, 930 cm⁻¹ (C═CH₂); MS, *m/z* (relative intensity) 356 (4), 103 (100; peak does not contain Sn). Anal. Calcd for C₁₈H₂₀Sn: C, 60.89; H, 5.68. Found: C, 60.98; H, 5.72.

Diethyldiisopropenylgermane (9g). This compound was prepared as for **9a** from dichlorodiethylgermane (75 mmol); 84% yield; bp 77 °C (16 torr); IR (TF) 1610, 920 cm⁻¹ (C═CH₂); MS, *m/z* (relative intensity) 214 (6), 185 (100). Anal. Calcd for C₁₀H₂₀Ge: C, 56.43; H, 9.47. Found: C, 56.48; H, 9.49.

General Procedure for the Hydroboration of Dialkenyl-silanes. BMS Reactions. On a 5–25-mmol scale, the appropriate dialkenylsilane was added dropwise by using a syringe to an equimolar amount of BMS (1.0 M in THF) at 25 °C. After the addition was completed, the mixtures were normally heated for 1 h at reflux temperature, except as noted in the text. After returning to room temperature, the mixtures were either meth-anolyzed or oxidized.

Methanolysis was accomplished by treating the borane mixture with 1.1–1.2 equiv of methanol followed by heating at reflux temperature for 1 h and then by concentration of the mixture under a stream of nitrogen or in vacuo. For **9a**, distillation at 11 torr gave 38% of **12**, bp 84–86 °C. A repeat of this procedure with 2 molar equiv of MeOH followed by 2 h at reflux temperature gave a similar yield of **12**: ¹H NMR (C₆D₆) δ 0.20, 0.25, 0.28 (6 H), 1.27 (m, 12 H), 3.75 (s, 3 H). In addition to the ¹³C signals cited in Table IV for **12**, smaller signals attributable to a silaborane were also observed: δ –8.2, –6.9 (SiMe), 15.0, 17.5, 17.9 (Me at C-5, C-4, C-4). Oxidation of this sample gave **10** and **11** in a ca. 14:86 ratio in agreement with selected ¹³C peak height compar-isons. This material exhibited a ¹¹B resonance at 55.4 ppm. A higher boiling material (bp ca. 100–200 °C) exhibited resonances at 26.1, 54.9, and 87.5 ppm. No significant ¹³C resonances were observed in the 40–70-ppm region for this material, but rather only multiple absorbances in the 10–20-ppm region as well as broad (B–C) absorbances in the 20–30-ppm region and major Me–Si resonances at –5.0, –6.6, and –11.2 ppm. Methanolysis, using the former procedure, of the 1:1 mixture obtained from BMS and **20** gave a residue with ¹H NMR peaks at 3.63 and 3.48 ppm (OMe) as well as in the 0.5–2.0 ppm region and the –0.2 to +0.2 ppm region (Me–Si). Comparison of the peak areas of the first and last absorbances gave a OMe/Me–Si ratio of ca. 1:5 instead of the expected 1:2 ratio for a cyclic methyl borinate, suggesting that the maximum amount of such products was ~40%. Since only the 1,6 boron relationship would be expected to give a single absorbance for the two methyl groups on silicon because the 2,6 relationship would create an asymmetric center at C-2, we ex-amined the Si–Me region in detail, finding one central peak (0.06 ppm) with two sets of equal-intensity, bracketing, two-line signals. Comparison of the central peak with the other four gives an area ratio of ca. 1, agreeing with the diol distribution. Also, comparison of the 0.5–2.0-ppm region with the Me–Si region gives the expected 5:3 area ratio. For **34**, methanolysis gives only polymeric material (R₃B) and (presumably) methyl borate. The ¹H NMR spectrum of this material reveals no methoxy signals.

Oxidation of the borane mixtures was accomplished by the addition of 3 N NaOH (B/OH⁻ ratio of 1) followed by the dropwise addition of 30% H₂O₂ (equal volume to the amount of 3 N NaOH solution added) and then by 1 h at reflux temperature. The aqueous layer was saturated with K₂CO₃, and the organic material was dried (K₂CO₃) and distilled. The diols were isolated: from **1**, 86% (bp 86–88 °C (0.2 torr)); from **9a**, 86–94% (bp 101–107

°C (0.3 torr)); from **20**, 82% (bp ca. 120–135 °C (0.5 torr)); from **29**, 68% (bp 98–99 °C (0.15 torr)); from **34**, 85–90% (bp 134 °C (1.5 torr)).[5c]

Thexylborane Reactions. To a solution of thexylborane (1.0 M) in THF[1a] maintained at 0 °C was added the appropriate dialkenylsilane dropwise. After the addition was completed, the mixture was treated for 1 h at reflux temperature. An oxidation and workup as for the BMS reactions gave 2,3-dimethyl-2-butanol as identified by the GC comparison of the material with an au-thentic sample. Distillation gave the diol mixtures given in Table I. **11:** 80%; bp 116 °C (1 torr); ¹H NMR (CDCl₃) δ 0.30 (br s, 6 H), 1.1 (m, 8 H), 2.7 (br s, 2 H), 3.7 (m, 4 H) (cf. Table II). Concentration of the mixtures prior to oxidation under a stream of nitrogen gave the organoboranes. **13a:** bp 70–78 °C (0.20 torr); 73%; ¹H NMR (CCl₄) δ 0 (3 peaks, 6 H), 0.7–1.2 (m, 21 H), 1.5–2.1 (m, 4 H); cis/trans ratio of 38/62; ¹¹B NMR 88 ppm. **13b** and **13c** were not distilled and exhibited ¹H NMR absorbances es-sentially identical to with those of **13a**. However, from the methyl–metalloid signals, cis/trans ratios of 53:47 and 52:48 were determined. The ¹³C NMR spectra (Table IV) of these materials supported this relative isomer distribution. ¹¹B NMR gave ab-sorbances at 88 and 90 ppm, respectively, for these compounds. **36:** bp 97 °C (0.20 torr); 48%; ¹H NMR (CCl₄) δ 0.03 (s, 6 H), 0.8 (m, 16 H), 1.4 (m, 5 H), 1.9 (m, 5 H); ¹¹B NMR 90 ppm. Oxidation of a small sample (ca. 2 mmol) of **13a** gave 2,3-di-methyl-2-butanol and **11** as the only products by GC. However, thermal treatment of this compound on a 5-mmol scale at 180 °C (oil bath) for 3 h, followed by the normal oxidation procedure, gave 2,3-dimethyl-1-butanol as identified by comparison with an authentic sample and **11**, which was found by using Eu(fod)₃ reagent to be an essentially 50:50 mixture of *meso-* and *dl-11* by NMR analysis.

Dicyclohexylborane Reactions. The dicyclohexylborane was prepared in THF by using reported procedures,[1a] and the di-alkenylsilane (50 mol % of the boron reagent) was added at 0 °C. After 1 h, oxidation as above gave cyclohexanol (bp 31 °C (0.7 torr)) and the diol **4**: 60%; bp 110 °C (0.7 torr); ¹H NMR (CDCl₃) δ 0.01 (s, 6 H), 0.94 (ct, 4 H), 2.69 (br s, 2 H), 3.71 (ct, 4 H). **22:** 74%; bp 143 °C (33 torr); ¹H NMR (CDCl₃) δ 0.03 (s, 6 H), 0.4–1.8 (m, 6 H), 2.6 (br s, 2 H), 3.4–3.9 (m, 4 H). For **1**, an internal standard (C₁₄H₃₀) was used to determine the overall efficiencies cited in the text for each reagent.[1a]

1,1,2,6-Tetramethyl-1-silacyclohexan-4-one (17a). Method A. Thexylborane[1] (40 mmol) in THF (30 mL) and **9a** (5.6 g, 40 mmol) in THF (30 mL) were simultaneously added by using a dual syringe pump to a flask containing THF (50 mL) held at reflux temperature over ca. 30 min. After an additional 30 min, the mixture was allowed to cool to room temperature, KCN (2.8 g, 43 mmol) was added all at once, and the mixture was stirred for 1 H. The solution was cooled to –78 °C by using a dry ice/acetone bath, and trifluoroacetic anhydride (6.7 mL) was added by using a syringe. The mixture was allowed to slowly warm to room temperature, and stirring was continued for 8 h. The solution was treated with 3 N NaOH (28 mL) followed by 30% H₂O₂ (18 mL) dropwise. The mixture was stirred at reflux tem-perature for 1 h and treated with saturated salt solution (90 mL). The separated organic layer was dried (MgSO₄), concentrated at reduced pressure, and distilled to give 1.7 g (25%) of **17a**, bp 111–113 °C (16 torr).

Method B. Quantities identical with those for method A were used. To a thexylborane solution in THF was added **9a** dropwise at room temperature. After the addition was completed, the stirred mixture was heated at reflux temperature for 3 h. **17a** (2.6 g, 38%) was obtained. Distillation of the residue gave **11** (bp 130 °C (1 torr)) in ca. 40% yield.

Method C. A 500-mL round-bottomed flask was charged with BMS (10 mL, 100 mmol) and THF (100 mL). **9a** (14.0 g, 100 mmol) was added dropwise while the stirred mixture was cooled by using an ice bath. The mixture was heated at reflux tem-perature for 1 h after the addition was complete. 2,6-Di-methylphenol (12.2 g, 100 mmol) in THF (10 mL) was added dropwise by using a syringe, resulting in rapid hydrogen gas evolution. After 2 h the cooled (0 °C) mixture was treated with dichloromethyl methyl ether (10 mL, 110 mmol) followed by lithium triethylcarboxide solution (125 mL 1.6 M, 200 mmol) over 30 min. After 30 min at 25 °C, ethanol (80 mL), water (20 mL),

NaOH pellets (12.0 g, 300 mmol) were added successively followed by the dropwise addition of 30% H_2O_2 (30 mL). After an additional hour at reflux temperature, the mixture was extracted with saturated salt solution (50 mL) and concentrated under reduced pressure. The residue was treated with pentane (100 mL) and 5 N NaOH solution (50 mL). After additional extractions with 5 N NaOH (2 × 30 mL) and saturated salt solution (50 mL), the pentane solution was dried (K_2CO_3), concentrated, and distilled to give 6.9 g (40%) of **17a**: IR (TF) 1710 cm^{-1} (C=O); MS, m/z (relative intensity) 170 (11), 155 (100). Anal. Calcd for $C_9H_{18}OSi$: C, 63.47; H, 10.65. Found: C, 63.31; H, 10.72.

1,1,2,6-Tetramethyl-1-germacyclohexan-4-one (17b). This compound was prepared from **9b** as for **17a** on a 16-mmol scale in 44% yield (method B) and on a 50-mmol scale in 37% yield (method C): bp 119–122 °C (23 torr); IR (TF) 1708 cm^{-1} (C=O); MS, m/z (relative intensity) 216 (26), 201 (100). Anal. Calcd for $C_9H_{18}OGe$: C, 50.32; H, 8.40. Found: C, 50.06; H, 8.40.

1,1,2,6-Tetramethyl-1-stannacyclohexan-4-one (17c). This compound was prepared from **9c** as for **17a** on a 30-mmol scale: 26% yield (method B); bp 72–73 °C (0.2 torr). Method C gave a dark mixture during the hydroboration step, and no **17c** could be obtained by using the DCME approach. **17c:** IR (TF) 1698 cm^{-1} (C=O); MS, (relative intensity) 262 (29), 135 (100). Anal. Calcd for $C_9H_{18}OSn$: C, 41.43; H, 6.95. Found: C, 41.68; H, 7.04.

cis-**1,1-Dimethyl-2,6-diphenyl-1-silacyclohexan-4-one (17d).** This compound was prepared from **9d** as for **17a** on a 67.5-mmol scale in 18% yield (method A) and on a 42-mmol scale in 10% yield (method B). The residue after solvent removal was eluted through an alumina column (100 g, 30 cm), after removal of a styrene-containing forerun with pentane, by using a 65:35:1 mixture of hexanes, ether, and methanol. Recrystallization from ether–cyclohexane gives **17d**, mp 155–156 °C. No *trans*-**17d** could be observed by NMR in the crude material. **17d:** IR (CCl$_4$) 1715 cm^{-1} (C=O); MS, m/z (relative intensity) 294 (29), 190 (100). Anal. Calcd for $C_{19}H_{22}OSi$: C, 77.50; H, 7.53. Found: C, 77.46; H, 7.56.

cis-**1,1-Dimethyl-2,6-diphenyl-1-germacyclohexan-4-one (17e).** This compound was prepared from **9c** as for **17d** (method B) on a 42-mmol scale: 24% yield; mp 135–137 °C; IR (CCl$_4$) 1715 cm^{-1} (C=O); MS, m/z (relative intensity) 340 (100). Anal. Calcd for $C_{19}H_{22}OGe$: C, 67.32; H, 6.54. Found: C, 67.25; H, 6.54.

cis-**1,1-Dimethyl-2,6-diphenyl-1-stannacyclohexan-4-one (17f).** This compound was prepared from **9f** as for **17d** (method B) on a 42-mmol scale: 3% yield; mp 97–98 °C; IR (CCl$_4$) 1713 cm^{-1} (C=O); MS, m/z 386 (12), 105 (100) (not Sn containing). Anal. Calcd for $C_{19}H_{22}OSn$: C, 59.26; H, 5.76. Found: C, 59.45; H, 5.81. The major product (ca. 90%) was styrene.

cis-**1,1-Diethyl-2,6-dimethyl-1-germacyclohexan-4-one (17g).** This compound was prepared from **9a** as for **17a** (method A) on a 47-mmol scale: 44% yield; bp 72–74 °C (0.15 torr); IR (TF) 1702 cm^{-1} (C=O); MS, m/z (relative intensity) 244 (88), 229 (100). Anal. Calcd for $C_{11}H_{22}OGe$: C, 54.50; H, 9.13. Found: C, 54.47; H, 9.17.

Allylvinyldimethylsilane (20). To a mixture of Mg turnings (2.43 g, 0.10 mol) in THF (50 mL) was added a mixture of chlorodimethylvinylsilane[23] (12.1 g, 100 mmol) and allyl bromide (12.1 g, 100 mmol) dropwise at a rate sufficient to maintain the reflux temperature. After an additional 15 min at reflux temperature, the mixture was poured onto ice (ca. 100 g) and saturated NH$_4$Cl solution (100 mL). The organic material was dried (MgSO$_4$) and distilled to give 10.7 g (81%) of **20**: bp 108–109 °C (740 torr);[24] ^{1}H NMR (CCl$_4$) δ 0.15 (s, 6 H), 1.60 (m, 2 H), 4.67 (m, 1 H), 5.37–6.45 (m, 4 H); IR (TF) 1600, 1635 cm^{-1} (C=C); MS, m/z (relative intensity) 126 (100). Anal. Calcd for $C_7H_{14}Si$: C, 66.58; 11.18. Found: C, 66.70; H, 11.20.

Allyldimethylphenylsilane (23). Allyl bromide (12.1 g, 0.100 mol) was added dropwise to a stirred mixture of Mg turnings (2.67 g, 0.110 mol), chlorodimethylphenylsilane (17.0 g, 0.100 mol), and THF (100 mL) at a rate sufficient to maintain gentle reflux. After being stirred at 25 °C for 12 h, the mixture was poured onto ice, and the organic layer was extracted with saturated NaCl solution

(50 mL), dried (MgSO$_4$), and distilled to give 16.4 g (93%) of **23**: bp 96–97 °C (14 torr);[25] ^{1}H NMR (CCl$_4$) δ 0.27 (s, 6 H), 1.73 (m, 2 H), 4.70 (m, 1 H), 4.90 (m, 1 H), 5.78 (m, 1 H), 7.33 (m, 5 H); IR (TF) 1632 cm^{-1} (C=C); MS, m/z (relative intensity) 176 (10), 135 (100).

3-(Dimethylphenylsilyl)propanol (24). To stirred BH$_3$·THF (30 mL, 2.5 M, 75 mmol) and THF (100 mL) at 0 °C was added **23** (30 g, 0.17 mol) dropwise. After 2 h, H$_2$O (25 mL) was carefully added (H$_2$ evolution) followed by 3 N NaOH (25 mL) and then by 30% H$_2O_2$ (25 mL) dropwise. After the mixture was heated at reflux temperature for several hours, the layers were separated by using saturated salt solution, and the organic layer was dried over anhydrous Na$_2$SO$_4$. Distillation gave 31.7 g (96%) of **24**: bp 90 °C (0.2 torr); ^{1}H NMR (CDCl$_3$) δ 0.23 (s, 6 H), 0.65 (m, 2 H), 1.55 (m, 3 H), 3.48 (t, 2 H, J = 6.5 Hz), 7.30 (m, 5 H), with D$_2$O added δ 1.55 (m, 2 H); IR (TF) 3450 cm^{-1} (OH); MS, m/z (relative intensity) 179 (18, m – CH$_3^+$), 137 (100). Anal. Calcd for $C_{11}H_{18}OSi$: C, 67.98; H, 9.34. Found: C, 67.93; H, 9.36.

3,3-Dimethyl-3-silahex-1-en-6-ol (25). To 9-BBN dimer (0.82 g, 3.5 mmol) in THF (5 mL) was added **20** (0.88 g, 7.0 mmol), and the mixture was heated at reflux temperature for 1 h. After oxidation with 3 N NaOH (2.3 mL) and 30% H$_2O_2$ (2.2 mL, dropwise), a saturated salt solution (3 mL) was added, the dried (K$_2$CO$_3$) organic material was concentrated, and 0.5 g (50%) of **25** was isolated by molecular distillation at 25 torr: ^{1}H NMR (CCl$_4$) δ 0.16 (s, 6 H), 0.60 (m, 2 H), 1.5 (m, 2 H), 2.86 (s, 1 H), 3.52 (t, 2 H, J = 6.5 Hz), 5.95 (m, 3 H); IR (TF) 3350 (OH), 1595 cm^{-1} (SiCH=CH$_2$); MS, m/z (relative intensity) 129 (8, M – CH$_3^+$), 87 (100). In a similar experiment the products were not isolated; however, by use of an internal standard (C$_{14}$H$_{30}$), yields were obtained for **25** (69%), **22** (15%), *cis*-1,5-cyclooctanediol (100%), and unreacted **20** (15%) by using corrected area ratios.[1a]

1,1-Dimethyl-1-silacycloheptan-4-one (28). This compound was prepared from **20** as for **17a** (method A) on a 33-mmol scale. Distillation gives a fraction (bp 100–150 °C (25 torr)) which was eluted through an alumina column (100 g; 30 cm) with ether. Redistillation of the material gave 1.4 g (27%) of **28**: bp 115 °C (25 torr);[5b,c] IR (TF) 1705 cm^{-1} (C=O); $_1$H NMR (CCl$_4$) δ 0.07 (s, 6 H), 0.82 (m, 4 H), 1.86 (m, 2 H), 2.41 (m, 4 H); MS, m/z (relative intensity) 156 (6), 128 (100). Anal. Calcd for $C_8H_{16}OSi$: C, 61.48; H, 10.32. Found: C, 61.69; H, 10.38.

1,1,2,2-Tetramethyl-1,2-disilacycloheptan-5-one (32). This compound was prepared from **29** on a 25-mmol scale as for **17a** (method A) except that the quantity of 30% H$_2O_2$ (5.0 mL, 50 mmol) was stoichiometric, and only 15 min of subsequent heating at reflux temperature was used. The residue, after the workup, which distilled at 40–75 °C (0.30 torr) was eluted through alumina as for **28**. Distillation gave 0.70 g (16%) of **32**, bp 59 °C (0.30 torr). This solid (mp ca. 40 °C) was further purified by preparative GC which raised the melting point to 56–58 °C: IR (CCl$_4$) 1700 cm^{-1} (C=O); MS, m/z (relative intensity) 185 (8), 157 (100) (no M$^+$· observed); ^{1}H NMR (CCl$_4$) δ 0.00 (s, 12 H), 1.21 (m, 4 H), 2.76 (m, 4 H). Anal. Calcd for $C_9H_{20}OSi_2$: C, 59.93; H, 10.06. Found: C, 59.88; H, 10.09.

1,1,3,3-Tetramethyl-1,3-disila-2-oxacyclooctan-6-one (33). This compound was prepared from **29** on a 20-mmol scale as for **17a** (Method A). Distillation of the residue gives **33**: 1.1 g (20%); bp 108 °C (45 torr); IR (TF) 1702 (C=O), 1065 cm^{-1} (Si–O–Si); MS, m/z (relative intensity) 216 (4), 133 (100); ^{1}H NMR (CCl$_4$) δ 0.12 (s, 6 H), 0.95 (m, 4 H), 2.47 (m, 4 H). Anal. Calcd for $C_9H_{20}O_2Si_2$: C, 49.95; H, 9.31. Found: C, 50.06; H, 9.34. A sample of **32** (40 mg, 0.2 mmol) was heated at reflux temperature in THF (2 mL) with 4 N NaOH (0.5 mL) and 30% H$_2O_2$ (0.1 mL) for 1 h. An oil was obtained containing Si–OH groups (IR 3600–3200, 1065 cm^{-1}) which formed **33** on being dried over molecular sieves (3 Å).

1,1-Dimethyl-1-silacyclooctan-5-one (37). This compound was prepared from **34** on a 50-mmol scale as for **17a** (method A). Distillation gives 2.2 g (26%) of **37**: bp 65 °C (1.5 torr);[5b,c] IR (TF) 1705 cm^{-1} (C=O); MS, m/z (relative intensity) 170 (2), 142 (100); ^{1}H NMR (CCl$_4$) δ 0.03 (s, 6 H), 0.82 (m, 4 H), 1.98 (m, 4 H), 2.36 (m, 4 H). Anal. Calcd for $C_9H_{18}OSi$: C, 63.46; H, 10.65. Found: C, 63.27; H, 10.61.

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Diallyldimethylgermane (38). To a stirred mixture of Mg turnings (107 g, 4.4 mol) and THF (2.5 L) was added a solution of methyl iodide (312 g, 2.2 mol), allyl bromide (266 g, 2.2 mol), and germanium tetrachloride (215 g, 1.0 mol) at a rate which was sufficient to maintain reflux temperature. After the addition was complete, the mixture was heated at reflux temperature for an additional 2 h and poured onto ice, and the organic layer was dried (MgSO₄) and distilled at 740 torr to give three fractions:[26] allyltrimethylgermane [bp 100–102 °C; 10.5 g (7%)], **38** [bp 147–148 °C; 37.4 g (20%)], and triallylmethylgermane [bp 188 °C; 18.3g (9%)]. For **38**: ¹H NMR (CCl₄) δ 0.17 (s, 6 H); 1.73 (d, 4 H, J = 8 Hz), 4.87 (m, 4 H), 5.84 (m, 2 H); MS, m/z (relative intensity) 186 (4), 171 (7), 145 (100), 105 (23), 89 (20).

1,1-Dimethyl-1-germacyclooctan-5-one (39). This compound was prepared from **38** on a 12-mmol scale as in for **17a** (method A). Distillation gives 0.6 g (23%) of **39**: bp 70 °C (1.5 torr); IR (TF) 1705 cm⁻¹ (C=O); MS, m/z (relative intensity) 216 (6), 188 (100); ¹H NMR (CCl₄) δ 0.05 (s, 6 H), 0.85 (m, 4 H), 1.98 (m, 4 H), 2.33 (m, 4 H). Anal. Calcd for C₉H₁₈OGe: C, 50.32; H, 8.45. Found: C, 50.40; H, 8.48.

Registry No. meso-2, 85337-66-2; dl-2, 85337-67-3; 3, 85337-65-1; 4, 85337-82-2; 9a, 76240-84-1; 9b, 85337-43-5; 9c, 68561-25-1; 9d, 72761-80-9; 9e, 85337-44-6; 9f, 85337-45-7; 9g, 85337-46-8; 10, 85337-47-9; meso-11, 85337-48-0; dl-11, 85337-68-4; cis-12, 85337-49-1; trans-12, 85337-50-4; cis-13a, 85337-51-5; trans-13a, 85337-52-6; cis-13b, 85337-69-5; trans-13b, 85337-70-8; cis-13c, 85337-71-9; trans-13c, 85337-72-0; 15, 85337-54-8; 16, 85337-53-7; cis-17a, 85337-55-9; trans-17a, 85337-56-0; cis-17b, 85337-73-1; trans-17b, 85337-74-2; cis-17c, 85337-75-3; trans-17c, 85337-76-4; cis-17d, 85337-77-5; cis-17e, 85337-78-6; cis-17f, 85337-79-7; cis-17g, 85337-80-0; 20, 22146-25-4; 21, 85337-57-1; 22, 85337-58-2; 23, 18001-18-8; 24, 68469-62-5; 25, 85337-59-3; 26, 85337-60-6; 27, 85337-61-7; 28, 10325-26-5; 29, 1450-29-9; 30, 85337-62-8; 31, 85337-63-9; 32, 85337-81-1; 33, 85337-64-0; 34, 1113-12-8; 35, 10325-32-3; 36, 85354-83-2; 37, 10325-31-2; 38, 1793-69-7; 39, 85354-84-3; α-bromostyrene, 98-81-7; styrene, 100-42-5; 2-bromopropene, 557-93-7; dichlorodimethylsilane, 75-78-5; dichlorodimethylgermane, 1529-48-2; dichlorodimethylstannane, 753-73-1; dichlorodiethylgermane, 13314-52-8; chlorodimethylvinylsilane, 1719-58-0; allyl bromide, 106-95-6; chlorodimethylphenylsilane, 768-33-2.

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Diels–Alder Reactions of Cycloalkenones. 2. Preparation and Structure of Cyclohexadienone Adducts[1]

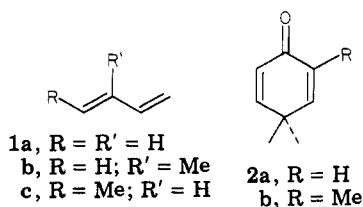Francesco Fringuelli,*[2a] Lucio Minuti,[2a] Ferdinando Pizzo,[2a] Aldo Taticchi,*[2a] Timothy D. J. Halls,[2b] and Ernest Wenkert*[2b,3]

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Uncatalyzed and aluminum chloride induced Diels–Alder reactions of 4,4-dimethyl-2,5-cyclohexadienone and 2,4,4-trimethyl-2,5-cyclohexadienone with 1,3-butadiene, isoprene, and (E)-piperylene are described. Structure analysis of the 1:1 adducts by standard means and ¹³C NMR spectroscopy is presented.

In continuation of a broad study of the Diels–Alder reaction of cycloalkenones, especially under Lewis acid catalysis,[1] the reactions of 2,5-cyclohexadienones were investigated. These more highly functionalized dienophiles were expected to be more reactive than their 2-cyclohexenone equivalents and perhaps to reveal altered regio- and/or stereochemistry.

Three dienes, 1,3-butadiene (1a), isoprene (1b), and (E)-piperylene (1c), and two dienophiles, 4,4-dimethyl-2,5-cyclohexadienone (2a) and 2,4,4-trimethyl-2,5-cyclohexadienone (2b) were chosen for the investigation, and experiments on uncatalyzed, thermal reactions (at 160 °C for 70 h) and reactions under aluminum chloride catalysis (at 40 °C for less than 1 day, except for one case) were carried out under conditions of predominant 1:1 adduct formation. The structures of the products were determined by ¹³C NMR spectroscopy.

As Table I, presenting the six sets of results, indicates, the acid-induced reactions, in contrast to their uncatalyzed counterparts, are high yielding.[4] The acid-catalyzed reactions of the unsymmetrical dienone 2b yield ca. 4:1 mixtures of adducts favoring the products of reaction on the unsubstituted double bond of the dienone.[6] This regiochemical preference is in consonance with previous

1a, R = R' = H
  b, R = H; R' = Me
  c, R = Me; R' = H

2a, R = H
  b, R = Me

(1) For previous papers see: Fringuelli, F.; Pizzo, F.; Taticchi, A.; Wenkert, E. Synth. Commun. 1979, 9, 391. Fringuelli, F.; Pizzo, F.; Taticchi, A.; Halls, T. D. J.; Wenkert, E. J. Org. Chem. 1982, 47, 5056.
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(4) For a recent report on the uncatalyzed addition of (E)-piperylene to 4,4-dimethyl-2,5-cyclohexadienone in high yield, presumably under different conditions, see ref 5.
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(6) Contrastingly, cyclohexadienones 2 (R = CHO or CO₂Me) show preference for diene addition on their substituted double bond.[5,7]
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