The Hydroboration of Silylacetylenes. The "Silyl-Markovnikov" Hydroboration Route to Pure (Z)-1-(2-Borylvinyl)silanes and β-Keto Silanes

John A. Soderquist,* Juan C. Colberg,[1] and Luis Del Valle[2]

Contribution from the Department of Chemistry, University of Puerto Rico, Rio Piedras PR 00931, Puerto Rico. *Received October 24, 1988*

Abstract: The regiochemistry and stoichiometry of the hydroboration of simple 1-silylacetylenes with 9-borabicyclo[3.3.1]nonane (9-BBN) was examined in detail. (Trimethylsilyl)acetylene (**1c**) results in only β-mono- and dihydroboration products, behavior common to nonsilylated terminal acetylenes. It is less reactive than its alkyl counterparts toward 9-BBN. It was also demonstrated that (1-trimethylsilyl)alkynes form (α-borylvinyl)silanes, similar to 1-alkynes, but they are much less reactive. Clean monohydroboration of these silylacetylenes is achieved only with a bulky (e.g. *t*-Bu) group at the C-2 position. However, compared to 1-alkynes, their dihydroboration products differ markedly, with the former giving 1,2-diboryl compounds, while the latter results in 1,1-diboryl adducts. (Triethyl- and *tert*-butyldimethylsilyl)propynes exhibit similar reactivity to that of the analogous trimethylsilyl derivative. The triisopropylsilyl group was found to not only completely suppress dihydroboration but also gave exclusively (Z)-(β-borylvinyl)silane adducts (**9β**). Oxidation of **9β** produces the corresponding β-keto silanes (**12**) in excellent yields (i.e. 83-90%). The bulky (triethyl- and *tert*-butyldimethylsilyl)propyne hydroboration products were found to be thermally unstable with the initially formed (α-borylvinyl)silanes isomerizing to α/β mixtures through their 1,2-diboryl diadducts (**10**). Heating **10** produces (3,3-diborylpropyl)silanes (**14**). Oxidation of the triethylsilyl compound **14b** affords the corresponding γ-silylpropanol (**15b**). The complete characterization of the intermediate organoboranes by 75-MHz ^{13}C NMR was achieved. A detailed discussion of the phenomena involved is presented. The observed results are attributed primarily to the additional steric effects imposed on an unsaturated system by a trialkylsilyl group when compared to a hydrogen atom at that position.

The hydroboration of 1-(trimethylsilyl)acetylenes, while providing valuable access to many α-functionalized organosilanes,[3] has received only limited attention with respect to the details of the hydroboration process. It is well-known that (α-borylvinyl)silanes are products from the monohydroboration of these commpounds, and these intermediates provide the basis for the reported chemistry.[3,4] While the silyl group is thought to have a role,[4] this selectivity is not unlike that exhibited by terminal acetylenes, lacking in this silyl substitution.[5] Hence, we undertook this study to better understand the actual part played by silyl groups, both in governing the regiochemistry of the additions and in the stoichiometry of the reaction.

Many of the studies to date involving the hydroboration of silylacetylenes have utilized dicyclohexylborane as the reagent of choice, because it gives largely monohydroboration products (i.e. >90%).[6] Any dihydroboration products have, until recently, received little attention because of their very minor presence in these mixtures. With 9-borabicyclo[3.3.1]nonane (9-BBN), we were recently able to obtain NMR evidence which indicated that the diadducts from silylacetylenes have a 1,2-diboryl configuration.[3m] Because 9-BBN is a stable, monofunctional reagent[5,7] which is easy to handle and produces stable, distillable products, it has real advantages over other hydroborating agents. These factors, as well as its predictable ^{13}C NMR spectral properties,[8] appeared to make it the reagent of choice to study systems for which detailed spectroscopic information is sought.

The hydroboration of vinylsilanes[3h,o,9] and related systems[3m] had demonstrated to us that the steric effects of the TMS and other silyl groups could be utilized to control both the extent of reaction with polyfunctional hydroborating agents as well as the regiochemistry of the process. A thorough understanding of each aspect of the reactions resulted, only after the successful identification and characterization of all of the organoborane intermediates by ^{13}C NMR. A detailed understanding of comparable processes for silylacetylene substrates is further complicated by the possibility of dihydroboration. Also, the instability of the oxidation products which can be obtained from the organoborane intermediates[3f,10] adds to the difficulties in reaching an accurate, quantitative picture of the products formed. However, we felt that their 9-BBN adducts could be rigorously analyzed by high-field ^{13}C NMR to provide the necessary insight to understand the major factors which are of importance in this reaction.

In the present study, the products formed from the hydroboration of representative silylacetylenes with 9-BBN will be determined. Further, the silyl substitution will be used to redirect the regiochemistry of the process at either the mono- or the dihydroboration stage, to give internally placed new boron adducts of synthetic importance.

Results and Discussion

(Trimethylsilyl)acetylene (1c) and Terminal Acetylenes. The hydroboration of terminal acetylenes has been extensively studied, giving terminally placed boron adducts with 9-BBN in both the mono- and dihydroboration steps.[5] The amounts of these products traditionally are determined by the GC analysis of their protonolysis and oxidation products.[5] Owing to the volatility and/or

(1) Graduate student supported by the NIH-MBRS Program.

(2) Postdoctoral Research Associate supported by the NSF EPSCoR Program.

(3) (a) Cudlin, J.; Schraml, J.; Chavalosky, V. *Coll. Czech. Chem. Commun.* **1964**, *29*, 1476. (b) Miller, R. B.; Reichenbach, T. *Tetrahedron Lett.* **1974**, 543. (c) Hudrlik, P. F.; Peterson, D.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2263. (d) Uchida, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1976**, *41*, 2941; *Tetrahedron* **1977**, *33*, 2987. (e) Hassner, A.; Soderquist, J. A. *J. Organomet. Chem.* **1977**, *131*, C1. (f) Zweifel, G.; Backland, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 3184. (g) Soderquist, J. A.; Thompson, K. L. *J. Organomet. Chem.* **1978**, *159*, 237. (h) Soderquist, J. A.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 3571. (i) Miller, J. A.; Zweifel, G. *Synthesis* **1981**, 288. (j) Miller, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1981**, *103*, 6217. (k) Hosmane, N. S.; Sirokadam, N. N.; Walkinshaw, M. D.; Ebsworth, E. A. V. *J. Organomet. Chem.* **1984**, *270*, 1. (l) Hosmane, N. S.; Sirokadam, N. N.; Mollenhauer, M. N. *J. Organomet. Chem.* **1985**, *279*, 359. (m) Soderquist, J. A.; Najafi, M. R. *J. Org. Chem.* **1986**, *51*, 1330. (n) Zweifel, G.; Najafi, M. R.; Rajagopalan, S. *Tetrahedron Lett.* **1988**, *29*, 1895. (o) Soderquist, J. A.; Hwang-Lee, S.-J. *Tetrahedron* **1988**, *44*, 4033.

(4) In one case, α/β mixtures were obtained from a special silylated enynyl ether. An α-directive effect of the TMS group is used to explain the normal regiochemistry observed in these systems.[3n]

(5) (a) Zaidlewicz, M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 7, pp 143, 161. (b) Brown, H. C.; Scouten, C. G.; Liotta, R. *J. Am. Chem. Soc.* **1979**, *101*, 96. (c) For comparable studies on the hydroboration of 1-haloalkynes, see: Nelson, D. J.; Blue, C. D.; Brown, H. C. *J. Am. Chem. Soc.* **1982**, *104*, 4913 and Blue, C. D.; Nelson, D. J. *J. Org. Chem.* **1983**, *48*, 4538.

(6) Unpublished studies with B. Santiago and J. C. Colberg.

(7) Soderquist, J. A.; Brown, H. C. *J. Org. Chem.* **1981**, *46*, 4599.

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

(9) Hassner, A.; Soderquist, J. A. *J. Organomet. Chem.* **1977**, *131*, C1.

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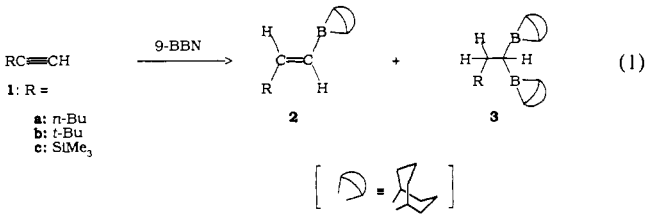
Table I. Hydroboration of Terminal Alkynes with 9-BBN under Neat Conditions[a]

compd	R′	% yield 2α/2β	2	3[b]	temp (time, h)
1a	*n*-Bu	0/100[c]	32	34	25 (5)
1b	*t*-Bu	0/100[c]	79	10	25 (7)
1c	Me_3Si	0/100[c]	9	47	25 (8)

[a] The reactions were monitored by ^{11}B NMR and further analyzed by ^{13}C NMR.[11c] The amount of each product was estimated by the peak heights for selected absorbances and checked against either known mixtures or other absorbances for internal consistency to ±3%. [b] Prepared from the neat reaction of 2 equiv of 9-BBN and **1** maintained for the following times at the cited temperatures: **3a**, 0.5 h, 120 °C; **3b**, 0.5 h, 200 °C; **3c**, 24 h, 25 °C. [c] No spectral evidence for an isomeric product could be found.

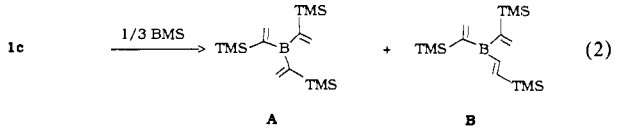
reactivity of such products derived from **1c**, these methods did not seem appropriate for this system.[3f,10] Our previous studies on silicon systems had revealed that the trimethylsilyl group gave sufficiently reproducible correlations between mole fractions of components and ^{13}C NMR peak heights so as to make this a very useful technique to estimate the amounts of each product component formed from such systems.[3h] For the purposes of our present study, we found that, in the case of well-resolved peaks of the same multiplicity in similar groups or ring systems, this technique gave results which, for related compounds of equal concentrations, gave the same peak heights safely within a ±5% range.[11] Thus, NMR provides a clear picture of the organoborane intermediates formed in the hydroboration processes and allows a reasonable estimate of their amounts under various conditions.



(1)

It was considered important to compare the behavior of **1c** to that of other standard terminal acetylenes so that the influence of the TMS group could be better understood. The hydroborations of 1-hexyne (**1a**) and 3,3-dimethyl-1-butyne (**1b**) with 9-BBN have been studied in dilute THF solution with a 100% excess of alkyne, giving 94% and 96% monohydroboration, respectively. 1-Decyne, like **1a**, results in 94% monohydroboration under these conditions, a value which drops to 44% with a 1:1 stoichiometry.[5b] We examined the hydroboration of these alkynes with 9-BBN under essentially neat conditions with a 1:1 alkyne/9-BBN stoichiometry because these conditions provided better line shapes for the carbons α to boron and no interference from solvent absorbances. The process also minimized the possibility of material loss or oxidation by avoiding the need for the removal of reaction solvents. Our measured value of 32% monohydroboration for **1a** (cf. Table I) with near equal amounts of unreacted **1a** and the dihydroboration product **3a**, provides an excellent material balance and gave excellent agreement with the measured GC ratio of **1a** and the 1-hexene derived from the protonolysis of **2a** (i.e. ±3%). The hydroboration of **1b** affords a much higher proportion of vinylborane product **2b**, in agreement with the known influence of steric effects on these processes.[5b]

(Trimethylsilyl)acetylene (**1c**) gives the same type of terminal adducts with 9-BBN as is observed for the other 1-alkynes, differing only in the extent of mono- and dihydroboration which occurs. We also carried out the hydroboration of **1c** with borane–dimethyl sulfide complex (BMS) and obtained two products in a 60:40 ratio. The first was the reported tris(α-silylvinyl)borane (A)[31] and the second we found to be consistent with the ααβ configuration (B). While additional minor products were also



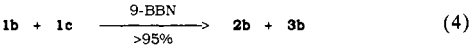
(2)

observed with this reagent, it is clear that the placement of the boron α to silicon is the preferred process with this reagent (i.e. 87:13). In the case of 9-BBN, apparently the steric repulsions between the substituted boron atom and the α-TMS group are sufficiently large so as to prevent this site from competing with the alternative, unencumbered β position.

In all three cases, the *gem*-diboryl adducts (**3**) are formed cleanly from **1** and 9-BBN with a 1:2 stoichiometry. Thus, for the first time, β-boryl products can be prepared from the hydroboration of silylacetylenes. With this data, we can also fully characterize the organoborane products by ^{13}C NMR.[11c]

(3)

The effect of alkyl vs silyl substitution on the relative reactivity of the alkyne was examined. A 1:1:1 mixture of **1b**, **1c**, and 9-BBN gives >95% hydroboration of **1b** to provide **2b** and **3b** in a 88:12 ratio. From **1c** (<5% reaction), **2c** and **3c** are formed in a ca.

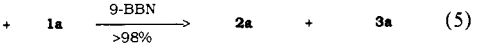


(4)

4:1 ratio. Clearly, the t-Bu group is more effective in activating the triple bond toward placement of the boron at the β position than is a TMS group.

Among the dialkylboranes, 9-BBN is unique, in that it hydroborates alkenes faster than it does the corresponding alkynes.[5a] Relative to other dialkylboranes, it is also more sensitive to electronic factors, showing, in the absence of steric repulsions at the carbon center where the boron is to be placed, a positive correlation between group donor properties and competitive reaction rates.[5a,c] Our data suggests that, in contrast to normal alkynes, the TMS group provides an electronically based preference for α boron placement, a phenomenon consistently observed in the ionic additions to unsaturated organosilanes.[12] However, this effect is less important in the hydroboration reaction because of the limited ionic nature of the process. Steric effects can easily overcome the weak electronic effects of the TMS group so that β boron placement becomes the dominate process. A comparison of vinyltrimethylsilane to **1c** reveals that BMS results in 60% vs 87% α boron placement for these derivatives, respectively.[3h,9] These observations suggest that electronic factors are of more relative importance for silylalkynes than they are for vinylsilanes in the hydroboration reaction, a conclusion which is consistent with observations which can be noted for alkyl substituents.[5a]

Effect of Silylation on the Reactivity of 1-Alkynes toward 9-BBN. It was also considered important to establish how the presence of a TMS group would affect the reactivity of a terminal alkyne. Thus, **1a**, 1-(trimethylsilyl)-1-hexyne (**4**), and 9-BBN were allowed to react at 25 °C for 5 h in a 1:1:1 mol ratio with the result that reaction of **1a** constituted >98% of the process producing **2a** and **3a** in essentially equal amounts with a corre-



(5)

(10) Hudrlik, P. F.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 6251.

(11) (a) For a general discussion of the factors which are important for this technique to have analytical value, see: Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981. (b) For the ^{13}C NMR of TMS derivatives, see: Levy, G. C.; White, D. M.; Cargioli, J. D. *J. Magn. Reson.* **1972**, *8*, 280. (c) Complete, assigned ^{13}C NMR spectra are available in the supplementary material.

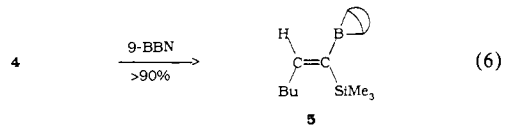
(12) (a) Fleming, I. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon: Oxford, 1979, Vol. 3, p 647. (b) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (c) Weber, W. P. *Silicon Reagents in Organic Synthesis*; Springer-Verlag: Berlin, 1983. (d) Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 2, p 1. (e) Davies, A. G.; Smith, P. J. *Ibid.* 1982; Vol. 2, p 519. (f) Soderquist, J. A.; Anderson, C. L. *Tetrahedron Lett.* **1988**, *29*, 2777.

Table II. Influence of the Silyl Substitution on the Boron Placement in Differing Alkynylsilanes (**8**) with 9-BBN[a]

			% yield			
series	R_3	R′	**9**α/**9**β	**9**	**10** (solvent)	temp (time, h)
a	Me_3	Me	100/0[b]	54	23 ($CDCl_3$)[c]	25 (48)
b	Et_3	Me	97/3	70	15 (neat)	25 (36)
c	(*t*-Bu)Me_2	Me	95/5	71	14 (neat)	25 (48)
d	(*i*-Pr)$_3$	Me	0/100[b]	100	0 (neat)	85 (1)
e	(*i*-Pr)$_3$	*n*-Pr	0/100[b]	100	0 (neat)	85 (3)

[a] The reactions were monitored by ^{11}B NMR and further analyzed by ^{13}C NMR.[11c] The amount of each product was estimated by NMR as described in the Experimental Section.[3h,m] [b] Only one isomer detectable. [c] 0.5 M reagents. Similar results are observed in THF.[3m]

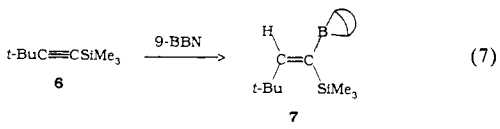
sponding quantity of unreacted **1a**. The silylacetylene **4** was essentially unchanged with only a trace amount of product **5** detectable. To establish the identity of **5**, **4** (10% excess) was allowed to react with 9-BBN to give the expected vinylborane **5** in ca. 90% yield. From these results, we conclude that a TMS



(6)

group does not result in any net activation of any position in an alkyne relative to an alkyl group. Rather, the boron in 9-BBN is slowed by the steric bulk of an α-TMS group from adding to that position.

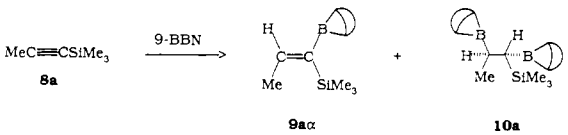
Earlier we had shown that relatively hindered vinylborane adducts such as **2b** have less tendency to undergo competive hydroboration with their alkyne progenitors than do less hindered products such as **2a**. In the above case, the TMS group had essentially prevented the hydroboration of **4** in the presence of **1a** with 1 equiv of 9-BBN. We carried out the hydroboration of **6** with 1 equiv of 9-BBN which gave only **7** in 3.5 h at 60 °C.



(7)

Therefore, we conclude that for 1-alkynes the 1-trimethylsilyl substitution blocks the placement of a second boron on that carbon. With a large alkyl group on the β-carbon, to also effectively block this position, clean monohydroboration can be achieved with 9-BBN under stoichiometric conditions.

Previously, we had briefly examined the behavior of 1-(trimethylsilyl)propyne finding that it gave both mono- and dihydroboration products (i.e. **9a** and **10a**).[3m] While low-field ^{13}C and ^1H NMR were in agreement with the 1,2-diboryl structure, we had been unable to fully assign all of the signals nor rule out the minor presence of other isomeric compounds with the available instrumentation. We repeated these studies to rigorously analyze this process, and this data is summarized in Table II.[11c] The 1:1 stoichiometry for **8a** and 9-BBN gives 54% of the (α-borylvinyl)silane **9a** and 23% of the 1,2-diboryl adduct **10a** with no



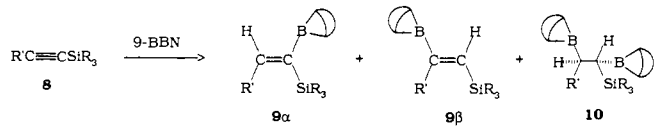
(8)

evidence for other positional isomers in the mixtures. Thus, adding an TMS substituent to the 1-position of a terminal alkyne results in the regiochemistry of the initial process still being dominated by the alkyl group's β-directive effect. Little difference exists between the behavior of these alkynes in this step with both giving the corresponding 1-vinylborane products. However, they differ markedly in the configuration of their dihydroboration products (i.e. 1,1- vs 1,2-diboryl). Thus, for alkyl-substituted silylacetylenes, the TMS group alters the regiochemistry of the process at the vinylborane stage. The dominant stereoelectronic β-directive effect of the alkyl group is overcome in the case of **9a**α which contains both the boryl and silyl substitutions at that carbon center. Steric repulsions between these two large groups and the substituted boron atom in 9-BBN force the boron to the 2-position. Unlike, a *tert*-butyl group which effectively also blocks that position, the methyl group in **9a** is small enough to allow the boron to add α to it to result in the observed 1,2-diboryl regiochemistry of **10a**.[13]

(2-Borylvinyl)silanes from Silylacetylenes. To redirect the regiochemical course of the initial hydroboration of **8** with larger silyl groups to give (β-borylvinyl)silane adducts (i.e. **9**β) is clearly a more difficult task. Only the steric repulsions between the single group and the boron reagent can be operative in this case. This process would provide a simple route to stereodefined, internal vinylboranes which are also vinylsilanes, and both of these are versatile functional groups.[12,14] Moreover, since silyl groups are commonly replaced stereoselectively with a hydrogen atom, this process would, in effect, be equivalent to the unknown, Markovnikov hydroboration of a terminal alkyne. To this end, we carried out a systematic study of the effect of increasing the size of the silyl group on the stoichiometry and regiochemistry of selected silylated acetylenes. These results are presented in Table II.

These data reveal that groups smaller than triisopropylsilyl (TIPS) give initially the α adducts (**9**α), in high regioisomeric purity. These products can compete with **8** for 9-BBN to undergo further hydroboration, resulting in minor amounts of 1,2-diboryl products (**10**). However, the TIPS substitution not only provides the *Z*-β product cleanly, but also completely suppresses the formation of **10**! Therefore, the 1,2,2-substitution pattern, with large groups on both positions of the double bond, unlike the 1,1,2 pattern in the **9**α adducts which had the large groups in a geminal arrangement, prevents the dihydroboration of **8** with 9-BBN under these conditions.

We felt that the redirection of the regiochemical course of the hydroboration of **8** should occur at the expense of the alkyne's reactivity. To test this hypothesis, we carried out a competitive experiment between equal amounts of **8a** and **8d** and 9-BBN under the above conditions employed for **8a**. The products **9d**β, **9a**α, and **10a** were observed by ^{11}B NMR at 78, 81, and 86 ppm,



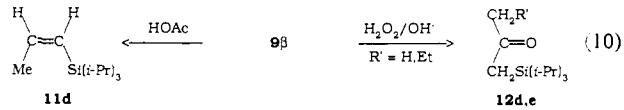
(9)

respectively, with only partial resolution. Fortunately, all five components exhibited separate ^{13}C NMR signals[11c] for all but the ring absorbances, which allowed us to estimate[3h] yields of 19%, 47%, and 15% for these three products, respectively. Consistent with this, both **8a** (40%) and **8d** (80%) remained unreacted. Integration of the ^1H NMR vinylic resonances for **9a**α (6.52 ppm) and **9d**β (6.18 ppm), revealed these products to be in a ca. 3:1 ratio. We interpret this result as a further indication that the acetylene's alkyl group exerts the principal directive effect for the hydroboration process by activating the carbon β to it, toward boron placement. However, when this normal regiochemistry is blocked by the steric bulk of the triisopropylsilyl group, the boron is forced to accept the internal position of the alkyne as a kinetically less preferred process.

(13) The hydroboration of *cis*-1-propenyltrimethylsilane gives an α/β mixture so that both the silicon and boron substitution are essential to give the 1,2-diboryl configuration found in **10a**.[3h]

(14) Negishi, E. In *Comprehensive Organometallic Chemistry*: Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 7, p 303.

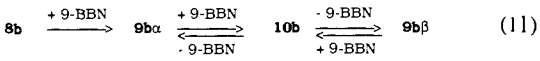
With these novel β-silylated vinylboranes in hand, we carried out the protonolysis of **9dβ** with acetic acid to give the expected *cis*-vinylsilane product **11d** cleanly. The oxidative behavior of **9β**



11d **12d,e** (10)

proved to be far more interesting. Our previous failures to oxidatively obtain β-keto silanes (e.g. **12**), from suitable organoboranes precursors, had confirmed their known sensitivity to bases and nucleophiles.[15] Surprisingly, we found that both **9dβ** and **9eβ** were smoothly converted to **12** with *alkaline hydrogen peroxide* in excellent yields, a truly noteworthy example of the stability imparted to this functionality by the triisopropyl substitution on silicon.[16]

Thermal Isomerizations of Silylated Organoboranes. The hydroborations of the (triethylsilyl- (**8b**) and *tert*-butyldimethylsilyl)-

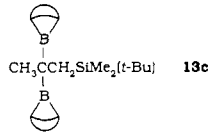


(11)

(**8c**) acetylenes closely resemble the behavior of the trimethylsilyl analogue **8a**. However, the product mixtures derived from these bulkier compounds were more noticeably thermally unstable. For example, whereas the lower boiling **9aα** (bp 82 °C (0.6 Torr)),[3m] could be distilled from its reaction mixture as an essentially pure isomer,[17] the corresponding triethyl derivative **9b** was isolated by distillation (46% yield, bp 116 °C (0.05 Torr)) as a 56:44 α/β mixture. Our explanation for this phenomenon is outlined above.

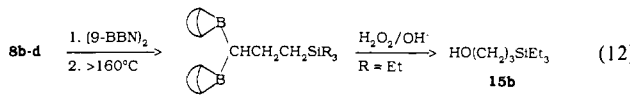
This interpretation is based upon the following experimental results: (1) Redistillation of **9b** neither significantly altered the isomeric ratio (even with ca. 5 mol % of added 9-BBN) nor gave noticeable decomposition. (2) Heating the reaction mixture for 2.5 h at 110 °C changes the ratio of **9bα** to **9bβ** from 94:6 to ca. 50:50. The diminution in the amounts of **8b** and **10b** (15% → 7%) is insufficient to account for the observed increase in **9bβ** with heating. (3) With added styrene (1 equiv/B), this heating process gives *B*-(2-phenylethyl)-9-BBN and a stable α/β ratio for **9b** of 71:29. This suggests that this olefin intercepts the 9-BBN which results from the decomposition of **10b**. Taken together, our data indicate that 9-BBN hydroborates **8b** to give **9bα** which can compete with **8b** for 9-BBN to form **10b**. If these reaction mixtures are heated, **10b** can undergo dehydroboration to form either **9bα** or **9bβ** and 9-BBN. It is through the reversible formation of the intermediate, **10b**, with its two possible dehydroboration pathways, rather than through the dehydroboration of **9b**, that the equilibration of the isomeric vinylboranes occurs.

Heating neat 1:1 mixtures of 9-BBN and **8c** for 17 h at 56 °C gives a ca. 70:30 mixture of **9cα** and **9cβ** (56% total yield), **10c** (16%), and **8c** (22%), as estimated from the ^{13}C NMR analysis of the reaction mixture. We also were able to identify a 2,2-diboryl isomer (**13c**, 6%) which increases to ca. 10% with heating for 1 h at 90 °C.[11e]



13c

Intrigued by the thermal behavior of these mixtures, the hydroboration of **8a** was examined with 2 equiv of 9-BBN under neat conditions (4.5 h, 110 °C), which leads to the clean formation of the 1,2-diboryl adduct **10a**. Further heating of this product (3 h, 170 °C) results in decomposition and a complex mixture. By contrast, after the conversion of **8b** to **10b** (48 h, 110 °C), this triethylsilyl compound is smoothly isomerized to the 3,3-diboryl product (1 h, 165 °C) **14b**, a material which can be easily isolated in excellent yield (84%, bp 162–5 °C (0.2 Torr)). **14b** was also observed in the 1:1 reaction residue after the distillative removal of the vinylboranes (i.e. **9b**). In an related attempt to prepare the corresponding 1,2-diboryl-*tert*-butyldimethylsilyl adduct (i.e. **10c**), we observed, by the analysis of the ^{13}C NMR spectra, the smooth diminution of **10c** prior to the complete consumption of 9-BBN. Also, the minor amount of **13c** disappears only with the complete formation of **14c** (17 h, 120 °C). For **8**, only **9dβ** is observed prior to its conversion to **14d** (2 h, 200 °C). Whereas, normally, diboryl compounds isomerize to mixtures of 1,1- and 1,*n*-diboryl products,[5a] we find this "tandem walk" of the two boryl groups away from bulky silyl groups a fascinating process which, at least for our examples, makes these thermal processes synthetically useful.[18] Oxidation of **14b** gives the expected alcohol, 3-(triethylsilyl)-1-propanol (**15b**), as the only silylated product detectable by ^{13}C NMR, confirming the thermal formation of the *gem*-diboryl compound, **14b**.[5b]



(12)

Conclusions

The role of the trimethylsilyl group in the hydroboration of silylacetylenes with 9-BBN has been found to be based largely upon its size rather than on any electronic factors which enter into more ionic reactions. Thus, (trimethylsilyl)acetylene (**1c**) behaves as a terminal alkyne without the normal β-activating role played by the alkyl groups in terminal acetylenes. For TMS derivatives of terminal acetylenes, the monohydroboration products are the (α-borylvinyl)silanes (i.e. **5**, **7**, and **9**) with the same regiochemistry as is exhibited without the silicon. However, the silyl group now makes the α-carbon of this product disubstituted so that a second boron atom is now forced to form a 1,2-diboryl adduct rather than the normal 1,1-diboryl configuration observed from the dihydroboration of 1-alkynes. With large (e.g. *t*-Bu) groups at the 2-position, clean monohydroboration of TMS alkynes is achieved with 9-BBN under stoichiometric conditions. The triisopropylsilyl group is sufficiently large so as to give clean (β-borylvinyl)silanes (**9β**) from the hydroboration of silylacetylenes with 9-BBN. These compounds are smoothly oxidized to β-keto silanes (**12**). Dihydroboration of (triethyl-, *tert*-butyldimethyl-, or triisopropylsilyl)propyne provides, after thermal treatment, an efficient route to novel (3,3-diborylpropyl)silanes (**14**).

With these new developments, it is now possible to convert silylacetylenes to either (α- or β-borylvinyl)silanes. Additionally, with the proper choice of substituents, interesting 1,2-, 2,2-, or 3,3-diboryl adducts can be efficiently prepared to provide new boron-functionalized organosilanes as intermediates for organic synthesis.

Experimental Section

General Methods. All experiments were carried out in predried (12 h, 110 °C) glassware under a nitrogen atmosphere. Standard handling techniques for air-sensitive compounds were employed throughout this study.[19] THF was distilled from sodium/benzophenone prior to use. Other reagents were obtained from commerical sources or prepared as reported.[3m,7] NMR data were recorded with either a GE QE-300 or a GN-300 NMR spectrometer. MS data was obtained with a HP-5995 mass spectrometer. Analyses of products were performed with Perkin-

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(16) (a) Cunico, R. F.; Bedell, L. *J. Org. Chem.* **1980**, *45*, 4797. (b) Muchowski, J. M.; Naef, R.; Maddox, M. L. *Tetrahedron Lett.* **1985**, *26*, 5375. (c) Corey, E. J.; Rucker, Ch. *Tetrahedron Lett.* **1984**, *25*, 4345.

(17) We have observed that if excessive heating is used during the distillative isolation of **9aα**,[3m] variable amounts of the β isomer can be observed in the product, presumably from the decomposition of **10a**.

(18) Numerous examples of 1,1-diboryl products from the thermal isomerizations of precursors to boracycles are known.[5a] However, these are always found together with α,ω-diboryl coproducts. Thus, the trialkylsilyl group evidently drives the equilibrium away from this alternative configuration to give only **14**.

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

Elmer models Sigma 1B and 8320 gas chromatographic systems equipped with 6 ft × $^1/_8$ in. 20% SE-30 on DCDMS-treated Chrom W and 30 m × 0.23 mm. i.d. 20% SE-30 vitreous silica open tubular columns, respectively. Columns were silylated (MSTFA, Pierce) prior to analytical runs for organoboranes and were used with a low injection-port temperature (120 °C). IR data were obtained with a Nicolet 6000 series FT-IR spectrophotometer.

General Procedure for the Hydroboration of Alkynes for ^{13}C NMR Analysis.[11c] Into a dry 5-mm NMR tube were placed 9-BBN crystals (ca. 1 mmol). The system was sealed from the atmosphere with a rubber septum and thoroughly flushed with dry nitrogen. The alkyne (1 or 0.5 equiv as required) or alkynes (for competitive experiments) were added via a syringe. The reaction was allowed to react at the cited temperatures and prior to analysis either $CDCl_3$ or C_6D_6 (ca. 0.2 mL) was added via a syringe (cf. Tables I and II and the text). For **5**, 1.0 mmol each of 9-BBn and **4** in C_6D_6 (0.2 mL) were allowed to react for 18 h at 25 °C to give **5** (ca. 90%) and **4** (ca. 5%) with additional signals that suggested a diboryl adduct analogous to **10a**. This process was not investigated in further detail. A similar process gave, from **6**, clean formation of **7** in 3.5 h at 60 °C. The thermal experiments for the α/β interconversions of the vinylboranes **9b** are described in the text.

Representative Comparison of the ^{13}C NMR vs GC Analysis. For **1a**, the 1:1 stoichiometry (5 h, room temperature, neat) resulted in peak heights for the C-6 Me groups in **1a**, **2a**, and **3a** which gave estimates of 33%, 33%, and 34% of these compounds at δ 13.8, 14.2, and 14.4 ppm, respectively. Protonolysis with HOAc ($^1/_3$ equiv) at 0 °C converted **2a** to 1-hexene and the GC revealed **1a** and this product were in a 53:47 ratio (correction factors for 1-hexyne and 1-hexene were found to be identical within experimental error). The comparison of the peak heights for the 9-BBN ring (C-3,7) absorbances gave a ratio of **2a** to **3a** of 48:52. For volatile alkynes such as **1c** or **8a**, w found this NMR technique to give better material balances than those that were obtained from GC techniques which employ a standard workup procedure. The ^{13}C NMR assignments for the products described in the text are included in the supplementary material.

Quantitative Treatment of the NMR Data. The amount of unreacted **8** was calculated with ^{13}C NMR as follows: After the hydroboration of **8**, the ratio of a selected peak to the average value for the $CDCl_3$ was determined. A known amount of **8** was added and a new spectrum was recorded under identical conditions and the ratio was redetermined. Multiplication of the first divided by the sum of the ratios, times the additional millimole of **8** added, gave the original unreacted quantity of **8**. From the alkylsilyl peaks for **8** vs **9**, we estimated the amount of **9** formed in each case which gave excellent material balances. For example, for the a series, the calculated value of 54% for **2a**α is identical with our previous GC yield for this material.[3m] With a measured value of 23% each for unreacted **8** and **10**, a quantitative material balance is achieved. For the TMS group and other similar absorbances within a given series, as we previously demonstrated,[3h] the peak characteristics and relaxation times are sufficiently similar, under our conditions (31° pulse, 6-s delay), for such compounds, that their heights reflect the molar quantities for each species in a diagnostically useful manner.

Hydroboration of 1c with BMS. The procedure of Hosmane[31] was adapted to our methodology as follows: To BMS (0.17 mL, 1.7 mmol) in C_6D_6 (ca. 0.5 mL) frozen at −78 °C was added **1c** (0.49 g, 5.0 mmol). The mixture was allowed to warm to 25 °C over 0.5 h and the reaction was allowed to continue at that temperature for 2 h. ^{11}B NMR analysis gave two partially resolved peaks in a ca. 60:40 area ratio at 70 and 63 ppm, attributable to partially complexed forms of A and B, respectively.[8] In addition to residual signals from **1c**. ^{13}C NMR signals were observed for these two products: A, δ 0.55 (TMS), 134.8 (CH_2), 162 (C(B)TMS) ppm; B, δ −1.64–0.04 (1:2 ratio, TMS), 135.3 (CH_2); 150 (br s, C(B)H), 154 (br s, C(B)TMS), 161.0 (CHTMS) ppm.

1-(Triisopropylsilyl)propyne (8d). Into a 1-L reaction assembly, equipped with a dry-ice condenser, which contained Mg gravel (6.0 g, 350 mmol), was added EtBr (38.2 g, 350 mmol, distilled from CaH_2) in THF (400 mL) dropwise to maintain reflux temperature. After heating at reflux for an additional 1 h, the mixture was allowed to reach 25 °C, and a cold (−78 °C) solution of propyne (14 g, 350 mmol) in THF (100 mL) was added. After the gas evolution had ceased, chlorotriisopropylsilane (48 g, 250 mmol) was added. The dry ice condenser was replaced with a water condenser, and the mixture was heated at reflux for 24 h. The mixture was quenched with NH_4Cl (saturated) solution, and the aqueous phase was washed with pentane (2 × 100 mL), concentrated, and distilled at 58 Torr to give 46.1 g (94%, >99% GC purity) of **8d** (bp 130 °C). ^1H NMR ($CDCl_3$) δ 1.07 (s, 21 H), 1.88 (s, 3 H) ppm; IR (TF) 2180 (C≡C), 880 (TIPS) cm^{-1}; MS *m/z* 196 (M^+, 6), 153 (76), 125 (38), 111 (36), 97 (83), 83 (100), 67 (38). Prepared (>99% GC purity) in like manner from the appropriate 1-alkyne were **4** (68%),[20a] **6** (70%),[20b] **8a** (74%),[20a] **8b** (72%),[20c] **8c** (65%),[20d] and **8e** (72%, bp 96 °C (0.02 Torr)). ^1H NMR ($CDCl_3$) δ 1.04 (m, 24 H), 1.53 (sextet, 2 H, *J* = 6.9 Hz), 2.20 (t, 2 H, *J* = 6.6 Hz) ppm; IR (TF) 2180 (C≡C), 880 (TIPS) cm^{-1}; MS *m/z* 224 (M^+, 5), 181 (81), 153 (33), 139 (35), 125 (72), 111 (100), 69 (25), 59 (29). Anal. Calcd for $C_{12}H_{24}Si$: C, 73.38; H, 12.32. Found: C, 73.38; H, 12.30.

***cis*-1-(Triisopropylsilyl)propene (11d).** To 9-BBN (1.95 g, 16.0 mmol) was added **8d** (3.14, 16.0 mmol), and the mixture was stirred at 85–90 °C for 1 h. After cooling to room temperature, dry pentane (16 mL) was added via a syringe and the solution was further cooled to 0 °C. HOAc (0.96 g, 16 mmol) was added dropwise to the stirred mixture which results in the formation of a white precipitate of (presumably) *B*-acetoxy-9-BBN. The clear supernatant was decanted via a double-ended needle and the solid was washed with dry pentane (2 × 10 mL), being certain to avoid the exposure of these solutions to the atmosphere. The solvents were removed in vacuo and distillation gave 2.4 g (75%) of **11d** (bp 120 °C (2.5 Torr): ^1H NMR ($CDCl_3$) δ 1.05–1.21 (m, 21 H, 1.79 (dd, 3 H, *J* = 6.9 Hz, *J* = 1 Hz), 5.42 (dd, 1 H, *J* = 14.3, *J* = 1 Hz), 6.55 (sextet, 1 H, J = 7 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 12.4 (Si*C*HMe$_2$), 19.0 (SiCH*Me*$_2$), 20.3 (Me), 124.9 (Si*C*H=CHMe), 144.5 (SiCH=*C*HMe) ppm; IR (TF) 1609 (c=C); 890 (TIPS) cm^{-1}; MS *m/z* 155 (100, M − (*i*-Pr)), 113 (96, (*i*-Pr)$_2$SiH)), 85 (90). Anal. Calcd for $C_{12}H_{26}Si$: C, 72.63; H, 13.21. Found: C, 72.52; H, 13.15.

1-(Triisopropylsilyl)-2-propanone (12d). To solid 9-BBN (1.95 g, 16.0 mmol) under a nitrogen atmosphere was added **8d** (3.14 g, 16.0 mmol) and the stirred mixture was heated for 1 h at 85 °C. ^{11}b NMR revealed the complete disappearance of 9-BBN (δ 28 ppm) with the appearance of a single peak at δ 79 ppm ($CDCl_3$) for **9d**. ^1H NMR δ 1.08–1.35 (m, 21 H), 1.6–2.0 (m, 14 H), 2.05 (s, 3 H), 6.53 (br s, 1 H) ppm. Oxidation of **9d** (16 mmol) in THF (32 mL) was accomplished by the addition of 3N NaOH (5.3 mL) followed by 30% H_2O_2 (5.3 mL) dropwise, while cooling the mixture with an ice bath. After 1 h at reflux, the aqueous layer was saturated with K_2CO_3 and the separated oragnic phase, together with a C_5H_{12} wash of the aqueous phase, was dried over Na_2SO_4 and concentrated. The residue was loaded onto neutral Al_2O_3 (ca. 100 g), and treated first with pentane and eluted with 50:50 C_5H_{12}/ether, concentrated, and distilled to afford 3.07 g (90%, 98% GC purity) of **12d** (bp 80–2 °C (0.03 Torr)): ^1H NMR δ 0.9 (br s, 21 H), 2.01 (s, 3 H), 2.08 (s, 2 H) ppm; ^{13}C NMR ($CDCl_3$) δ 11.3 (Si*C*HMe$_2$), 18.1 (SiCH*Me*$_2$), 30.6 (*C*H$_2$), 32.0 (*Me*), 207.1 (C=O) ppm; IR (TF) 1690 cm^{-1}; MS *m/z* 171 (M − (*i*-Pr), 100), 143 (42; 115 (56);, 101 (52), 75 (54), 61 (49). Anal. Calcd for $C_{12}H_{26}OSi$: C, 67.21; H, 12.22. Found: C, 67.23; H, 12.20.

1-(Triisopropylsilyl)-2-pentanone (12e). As for **12d**, 9-BBN (0.98 g, 8.0 mmol) and **8e** (1.80 g, 8.0 mmol) heated for 3 h at 85 °C gave **9e**β: ^{11}B NMR δ 80 ppm; ^1H NMR δ 0.95 (t, 3 H, *J* = 7.4 Hz), 1.05–1.25 (m, 21 H); 1.25–1.45 (m, 4 H), 1.7–2.0 (m, 14 H), 2.42 (ct, 2 H, *J* = 8.3 Hz); 6.35 (br s, 1 H) ppm. Oxidation as for **12d** gave 1.61 g (83%; GC purity, 96%) of **12e** (bp 110 °C (1 Torr)): ^1H NMR δ 0.87 (t, 3 H, *J* = 7.3 Hz), 1.02 (m, 21 H); 1.54 (sextet, 2 H, *J* = 7.3 Hz), 2.14 (s, 2 H), 2.37 (t, 2 H, *J* = 7.3 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 11.3 (SiCHMe$_2$), 13.5 (*Me*), 17.4 (*C*H$_2$), 18.3 (SiCH*Me*$_2$), 29.3 (*C*H$_2$Si), 46.8 (EtCH$_2$CO), 209.3 (C=O) ppm; IR (TF) 1690 cm^{-1}; MS *m/z* 199 (M − (*i*-Pr), 100), 171 (37), 75 (86), 61 (62), 59 (47). Anal. Calcd for $C_{14}H_{30}OSi$: C, 69.34; H, 12.47. Found: C, 69.62; H, 12.47.

Thermal Isomerization of (1,2- to 3,3-Diborylpropyl)silanes (14). To 9-BBN (3.66 g, 30.0 mmol) was added **8b** (2.31 g, 15.0 mmol) and the mixture was heated for 48 h at 110 °C giving **10b** cleanly by ^{13}C NMR (cf. Table 4). ^{11}B NMR δ 84 ppm. Slow distillation (1 h) of this material gave 5.0 g (84%) of **14b** (bp 165 °C (0.3 Torr): ^{11}B NMR ($CDCl_3$) 86 ppm; ^1H NMR ($CDCl_3$) δ 0.70 (q, 6 H), *J* = 8.0 Hz), 1.4–2.2 (m, 32 H), 2.9 (t, 1 H, *J* = 6.0 Hz) ppm. Oxidation of **14b**[3b] gives a mixture of *cis*-1,5-cyclooctanediol and **15b**, cleanly, by GC analysis.[4h] A small sample of **15b**[20e] was isolated (53% (5-mmol scale)): bp 72 °C (0.2 torr); ^1H NMR ($CDCl_3$) δ 0.53 (ct, 2 H, *J* = 9.1 Hz), 0.54 (q, 6 H, *J* = 7.8 Hz), 0.95 (t, 9 H, *J* = 7.8 Hz), 1.54 (m, 2 H), 1.76 (br s, 1 H); 3.60 (t, 2 H, *J* = 6.4 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 3.2 (SiCH$_2$Me), 6.9 (SiCH$_2$CH$_2$), 7.1 (SiCH$_2$CH$_3$), 26.9 (C-2), 65.4 (C-H$_2$OH) ppm (cf. ref 4 h); IR (neat) 3350 (OH) cm^{-1}. For **14c,d**, the isomerizations were carried out under the conditions described in the text, giving ^{11}B NMR signals at δ 84 and 85 ppm, respectively.

Acknowledgment. We are indebted to the NIH-RCMI Program (Grant No. RR03641) for the funds to purchase the GE 300-MHz

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NMR spectrometers (QE-300 and GN-300) which made this study possible. The support of the University-Industry Program of Puerto Rico as well as the NSF-EPSCoR and NIH-MBRS Programs (Grant No. RR08102) is gratefully acknowledged.

Supplementary Material Available: Tables III and IV listing complete, assigned ^{13}C NMR spectra for compounds **1-10**, **13c**, and **14** (2 pages). Ordering information is given on any current masthead page.

Oxygenation of Substituted Vinylcyclopropanes: Preparative and Mechanistic Studies

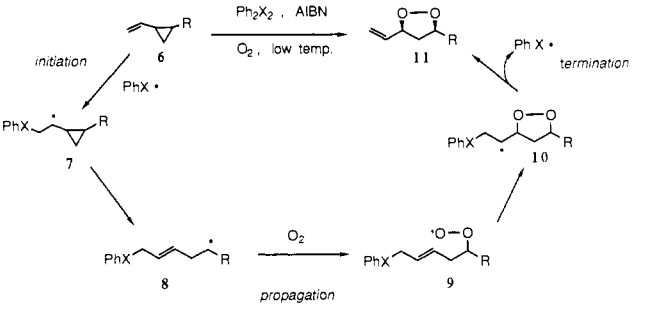
Ken S. Feldman* and Robert E. Simpson

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received November 17, 1988*

Abstract: 1-Vinylcyclopropanes bearing phenyl, vinyl, or ester substituents at C(2) of the cyclopropyl ring or alkyl groups at C(1) of the vinyl moiety were subjected to phenylthio or phenylseleno radical catalyzed oxygenation to furnish the corresponding substituted 1,2-dioxolane products. A self-consistent hypothesis was developed which describes the gross features of this multistep transformation. The mechanistic basis for stereochemical issues, including 1,2 relative asymmetric induction upon oxygen addition and stereochemistry upon cyclization of a putative 5-hexenylperoxy radical, were probed through substituent effects and deuterium-labeling studies. Reduction of the 1,2-dioxolane products afforded functionalized 1,3-diol derivatives.

Regio- and stereoselectivity in the preparation of 1,2- or 1,3-diol subunits has enabled the efficient construction of many polyoxygenated natural products. High levels of selectivity in the synthesis of diol subunits has been achieved, inter alia, through transition-metal-mediated epoxidation[1a] or osmylation[1b] technology or chelation-controlled nucleophilic addition to α-alkoxy aldehydes.[1c] Methods for the elaboration of the 1,3-diol subunit rely on either carbon-carbon bond formation,[2] carbon-hydrogen bond formation,[3] or carbon-oxygen bond formation[4] as key steps. Implementation of carbon-carbon bond forming methodology, usually in the guise of aldol (or aldol-like) condensations, has led to remarkable advances in relative and absolute control of product stereochemistry.[3a-f] Stereochemical control in carbon-oxygen bond forming strategies often depends upon hydroxyl-assisted addition of an oxygen atom equivalent to the olefinic component of homoallylic alcohols.[4b,d,f,h] In contrast, formal addition of dioxygen or a dioxygen equivalent to a hydrocarbon precursor has scarcely been investigated as a means to synthesize 1,3-diols or derivatives. However, a few reports of multistep electrophilic addition of hydrogen peroxide to cyclopropanes[5] or of direct addition of molecular oxygen across the carbon-carbon bond of uniquely activated cyclopropanes[6] (for example, imbedded in the semibulvalene framework[7]) suggested that this strategy may be a valuable complement to the more established approaches mentioned above.

Scheme I



We felt that the advantages associated with *direct oxygenation* of cyclopropane rings to form 1,3-diol derivatives in the form of dioxolane rings, including efficiency in C-O bond construction and the potential for regio- and stereochemical control (vide infra), provided strong impetus for the development of this process as a general synthetic method. Furthermore, many polyoxygenated target molecules contain repetitive 1,3-diol subunits (i.e., polyene and macrolide antibiotics), and so extension of monocyclopropane oxidation to encompass polycyclopropane precursors, thus affording poly-1,3-diol derivatives, would greatly increase the scope of this chemistry.

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