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Vinylboranes as *trans*-Dihydroxyethylene Equivalents for Diels-Alder Reactions

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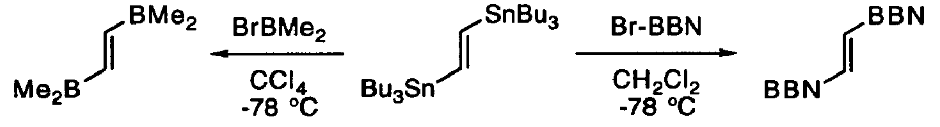
***Abstract*:** Several vinylboranes were explored as *trans*-1,2-dihydroxyethylene equivalents for Diels-Alder reactions. Use of the 1,2-bis(boryl)ethylene **4** allows the direct formation of 1,2-dihydroxycyclohexenes in high yield. The 2-phenyldimethylsilylvinylborane **8** is a good alternative that allows for hydroxyl-group differentiation.

Polyhydroxylated cyclohexanes encompass a number of important groups of natural products, including inositols, quercitols, conduritols, aminocyclitols, and shikimic acid. Diels-Alder strategies for the synthesis of these compounds[1] have been limited by the poor dienophilicity of simple dihydroxyethylene derivatives. For example, vinylidene carbonate has been used in Diels-Alder reactions, but the required reaction conditions are very harsh and the yields are often low.[2] We have recently reported that vinylboranes are highly reactive, regioselective, and endo-stereoselective dienophiles.[3] The facile oxidation of the cyclohexenylborane products into cyclohexenols makes vinylboranes excellent vinyl alcohol equivalents in Diels-Alder reactions. We report here two useful vinylborane-based *trans*-1,2-dihydroxyethylene equivalents for Diels-Alder reactions.

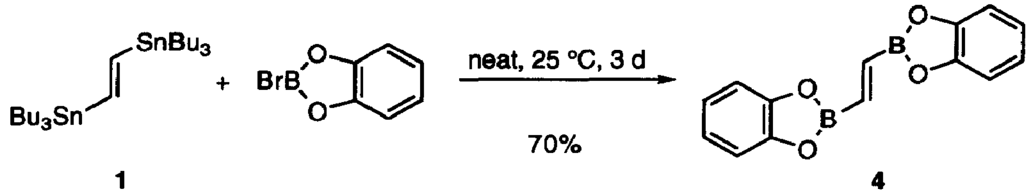
1,2-Diborylethylenes would be logical dihydroxyethylene equivalents. However, the only previous satisfactory synthesis of a diborylethylene required the difficultly accessible B_2Cl_4.[4] We have found that 1,2-diborylethylenes are readily generated from the reaction of *trans*-1,2-bis(tributylstannyl)ethylene[5] (**1**) with haloboranes. The reaction of **1** with two equivalents of bromodimethylborane at -78 °C generates an intermediate in solution with ^1H NMR singlets at δ 7.15 and 0.70 assigned as bis(dimethylboryl)ethylene **2**. A similar reaction with 9-bromo-9-BBN generates **3** with a characteristic singlet at δ 7.54 (C_6D_6). Dienophile **3** is notably less stable than **2** and can be maintained in solution only as its acetonitrile complex.



2 **1** **3**

These bis(dialkylboranes) are reactive dienophiles, but their utility as dihydroxyethylene equivalents is limited by apparent problems with elimination during oxidative workups. Thus, the reaction of **2** with 2-*tert*-butylbutadiene goes to completion within 8.5 h at 25 °C, but oxidative workup with $NaBO_3$[6] afforded only a 44% yield of the dihydroxycyclohexene product. With the required presence of acetonitrile, **3** is less reactive than **2**, but reacts with myrcene in 13 h at 50 °C to afford a 42% yield of the dihydroxycyclohexene product after oxidation. In both cases the Diels-Alder reactions appeared quantitative by NMR but the dihydroxycyclohexene products were accompanied by cyclohexadienes and monohydroxycyclohexenes.[7] A variety of oxidation procedures provided no improvement in yields.

The decreased propensity for elimination in β-alkoxyboronic esters[8] suggested the use of bis boronic esters as dienophiles. We were pleased to find that the *trans*-1,2-bis(catecholboryl)ethylene **4** is an *air stable, crystalline solid*, readily available in 70% yield from the reaction of **1** with bromocatecholborane at 25 °C.

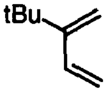
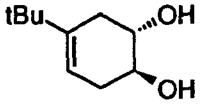
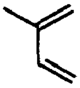
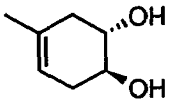
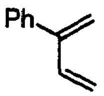
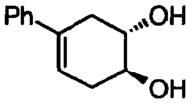
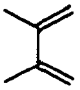
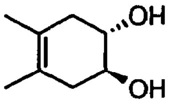
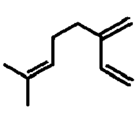
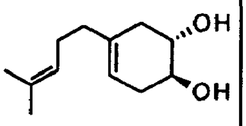
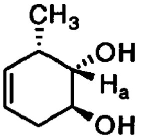
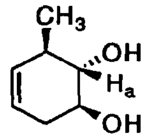
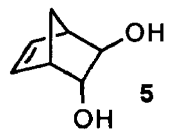


1 **4**

The dienophile **4** is much less reactive than **2** and **3**, but reacts conveniently with simple acyclic dienes at 100 °C. More importantly, the oxidation of the adducts proceeded cleanly to afford the corresponding cyclohexenediols in high yield (Table I).

The *trans* stereochemistry of the cycloadducts was most readily established for the cyclopentadiene product **5**, which cleanly exhibited 7 peaks in the ^{13}C NMR. The major product with piperylene was assigned as **6** based on ^1H decoupling experiments at 400 MHz, in which H_a was a doublet of doublets with $J = 9.6$ and 5.8 Hz, while H_a in **7** was a 9.6 Hz triplet.

Table I. Cyclohexenediols from Reactions of **4**.

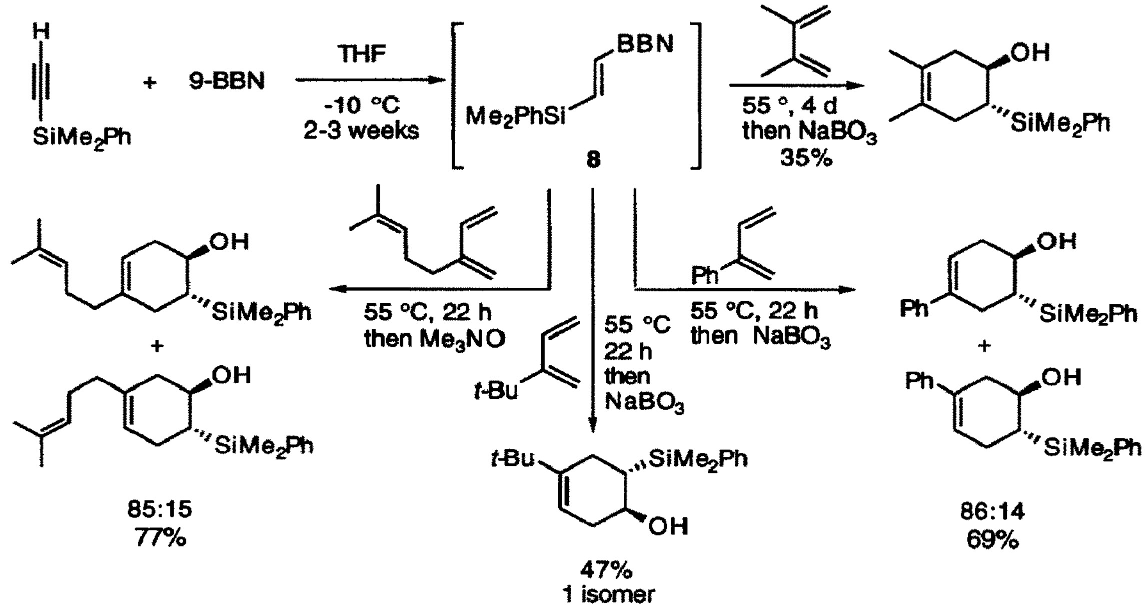
Diene	Rxn conditions and yield[a]	Product	Diene	Rxn conditions and yield	Product(s)
	100 °C, 1 h 70%			Et_3N^b 100 °C, 1 h 71%	
	Xylene, Et_3N^b 100 °C, 24 h 69%			100 °C, 1 h 68%	
	Et_3N^b 100 °C, 5 h 88%		 [c]	Et_3N^b 100 °C, 4 h 50% 2:1 mixture of isomers	 **6** +  **7**
	Et_3N^b 100 °C, 4 h 82%	 **5**			

[a] In a typical procedure, a neat mixture of 0.5 mmol of **4**, 2.5 mmol of myrcene, and 0.2 mmol of Et_3N was heated to 100 °C for 5 h. Oxidation with H_2O_2/NaOH and flash chromatography afforded 88% of the cyclohexenediol. [b] The triethylamine prevents an acid-catalyzed Friedel-Crafts alkylation of the catechol ring by the diene. [c] An excess of a technical mixture of *E* and *Z* isomers and cyclopentene was used.

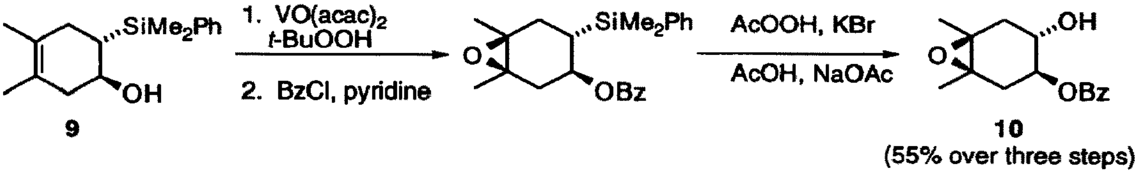
Based on our previous success with 2-trimethylsilylvinylboranes,[3b] and the facility with which a phenyldimethylsilyl group may be converted into a hydroxyl group,[9] 2-phenyldimethylsilylvinyl-9-BBN (**8**) appeared to be a promising dihydroxyethylene equivalent. Attempts to isolate **8** from the hydroboration of phenyldimethylsilylacetylene with 9-BBN failed due to the concomitant formation of an inseparable byproduct.[10] However, the ^{1}H NMR of the hydroboration product mixture indicated that approximately 77% of **8** was formed when the hydroboration was carried out in a dilute THF solution at -10 °C with a 10% excess of phenyldimethylsilylacetylene. Diels-Alder reactions of **8** were carried out by reacting the concentrated hydroboration product mixture directly with dienes (Scheme I).

The reactivity and selectivity of **8** is largely comparable with the trimethylsilyl analog.[3b] However, the oxidation of the Diels-Alder adducts of **8** proved more precarious than had been previously observed.[3b] Basic hydrogen peroxide oxidation often afforded poor yields and apparent elimination products. The yields with $NaBO_3$ and trimethylamine oxide[11] were inconsistent.

Scheme I



Although the use of **8** as a dihydroxyethylene equivalent is indirect, it has the advantage that the latent hydroxyl groups are automatically differentiated, and this differentiation may be used for further stereochemical elaboration. As shown in the example below, the silyl alcohol **9** can be used in a hydroxyl-directed epoxidation, and then oxidized to afford the nicely polyoxygenated **10**. Another advantages of using **8** is that alternative borane conversions of the initial Diels-Alder adduct are possible, which makes **8** more versatile than **4**.



The ready availability of **4** and **8**, the efficiency of their Diels-Alder reactions, and the versatility of their subsequent transformations should make them widely attractive dienophiles. We plan to continue developing diverse dienophiles which exploit the unique properties of vinylboranes in Diels-Alder reactions.

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