dence for a similar initial step in analogous reactions of sodium biphenyl; (d) J. F. Garst, *Acc. Chem. Res.*, **4**, 400 (1971); (e) J. F. Garst in "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, pp 520–529; (e) J. F. Garst, ref 3, Chapter 6.
(3) A. R. Lepley and G. L. Closs, Ed., "Chemically Induced Magnetic Polarization", Wiley, New York, N.Y., 1973.
(4) (a) J. F. Garst, R. H. Cox, J. T. Barbas, R. D. Roberts, J. I. Morris, and R. C. Morrison, *J. Am. Chem. Soc.*, **92**, 5761 (1970); (b) J. F. Garst, F. E. Barton, II, and J. I. Morris, *ibid.*, **93**, 4310 (1971); (c) for a more detailed exposition see ref 2e.
(5) J. F. Garst and J. A. Pacifici, *J. Am. Chem. Soc.*, **97**, 1802 (1975).
(6) W. Adam and J. Arce, *J. Org. Chem.*, **37**, 507 (1972).
(7) J. F. Garst and J. T. Barbas, *J. Am. Chem. Soc.*, **96**, 3239 (1974).
(8) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).
(9) Alkylation products were not isolated and identified, but the peaks attributed to them in the NMR spectra have chemical shifts corresponding to those of dihydronaphthalene, which we have studied in detail.[5] The chemical shifts of the peaks attributed to dihydronaphthalene derivatives are: aromatic protons, δ 6.85; olefinic protons, δ 5.75.
(10) I. M. Mathai, K. Schug, and S. I. Miller, *J. Org. Chem.*, **35**, 1733 (1970).
(11) (a) W. C. Kray, Jr., and C. E. Castro, *J. Am. Chem. Soc.*, **86**, 4603 (1964); (b) D. M. Singleton and J. K. Kochi, *ibid.*, **89**, 6547 (1967); (c) J. K. Kochi and D. M. Singleton, *ibid.*, **90**, 1582 (1968).
(12) R. J. Strunk, P. M. DiGiacomo, K. Aso, and H. G. Kuivila, *J. Am. Chem. Soc.*, **92**, 2849 (1970).
(13) The product of anti elimination from a *meso*-2,3-dihalobutane is *trans*-2-butene and from a *dl*-2,3-dihalobutane it is *cis*-2-butene.
(14) See footnote *c* of Table III for a summary of the conditions under which this statement is true.
(15) P. S. Skell and K. J. Shea in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 26, pp 809–852.
(16) Estimated from the rate constant, $2 \times 10^9\ M^{-1}\ sec^{-1}$, for the reaction of sodium naphthalene with 5-hexenyl radicals.[17]
(17) J. F. Garst and F. E. Barton, II, *J. Am. Chem. Soc.*, **96**, 523 (1974); *Tetrahedron Lett.*, 587 (1969).
(18) J. K. Kochi and J. W. Powers, *J. Am. Chem. Soc.*, **92**, 137 (1970).
(19) J. Casanova and H. R. Rogers, *J. Org. Chem.*, **39**, 2408 (1974).
(20) For reasons detailed elsewhere,[17] we urge abandoning "sodium naphthalenide" for $NaC_{10}H_8$ in favor of "sodium naphthalene".
(21) (a) C. Castro and W. Kray, Jr., *J. Am. Chem. Soc.*, **85**, 2768 (1963); (b) J. K. Kochi and D. Davis, *ibid.*, **86**, 5264 (1964).
(22) L. W. Manapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964).
(23) J. I. Morris, R. C. Morrison, D. W. Smith, and J. F. Garst, *J. Am. Chem. Soc.*, **94**, 2406 (1972).
(24) J. I. Morris, V. L. Benton, and J. F. Garst, 165th National Meeting of the American Chemical Society, Dallas, Texas, April, 1973. This model is an extension of that of R. Kaptein, *J. Am. Chem. Soc.*, **94**, 6269 (1972), to include all radical pair encounters. The first treatment of a diffusional radical pair model for CIDNP was published by F. J. Adrian, *J. Chem. Phys.*, **53**, 3374 (1970).
(25) A uniform density matrix represents equally populated basis states in any complete basis. This is a very close approximation to thermal equilibrium among nuclear spin states.

Hydroboration. XXXIX. 1,3,2-Benzodioxaborole (Catecholborane) as a New Hydroboration Reagent for Alkenes and Alkynes. A General Synthesis of Alkane- and Alkeneboronic Acids and Esters via Hydroboration. Directive Effects in the Hydroboration of Alkenes and Alkynes with Catecholborane

Herbert C. Brown* and S. K. Gupta[1]

Contribution from the Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907. *Received January 20, 1975*

Abstract: Catecholborane (1,3,2-benzodioxaborole), readily available from the reaction of catechol with borane in THF, reacts rapidly with alkenes and alkynes at 100 and 70°, respectively, to give the corresponding alkyl- and alkenylcatecholboranes in high yield. These hydroborations proceed stereospecifically in a cis manner. Greater regioselectivity is realized in comparison with such hydroborations with diborane itself. The alkyl- and alkenylcatecholboranes undergo rapid hydrolysis with water to give the corresponding alkane- and alkeneboronic acids. The alkenylcatecholboranes (2-alkenyl-1,3,2-benzodioxaboroles) undergo ready protonolysis with acetic acid to give the corresponding alkenes in essentially quantitative yield. The alkaline hydrogen peroxide oxidation of alkyl- and alkenylcatecholboranes give the corresponding oxygenated products in high yield.

Alkane- and alkeneboronic acids and esters are becoming of increasing significance as intermediates in organic synthesis. For example, the *B*-alkylcatecholboranes [2-alkyl-1,3,2-benzodioxaboroles (**2**)] are converted by lithium aluminum hydride ($LiAlH_4$) or aluminum hydride (AlH_3) to the corresponding monoalkylboranes (RBH_2) in essentially quantitative yield.[2] The reaction of Grignard reagents with **2** provides a route to mixed trialkylboranes.[3] The reaction of 2-alkenyl-1,3,2-benzodioxaboroles (**3**) with mercuric acetate provides an entry to alkenylmercuric salts;[4] the latter derivatives have been used for the introduction of the prostaglandin side chain.[5] Alkeneboronic acids have been transformed to the corresponding *trans*-1-alkenyl iodides[6] (with retention) and *cis*-1-alkenyl bromides[7] (with inversion). Attention is also called to the fascinating chemistry of alkeneboronic esters, as studied extensively by Matteson and his coworkers.[8]

These developments suggested the desirability of a search for a simple, straightforward synthesis of alkane- and alkeneboronic esters. In the past, the main reliance has been organometallics. Thus, many different organometallic reagents have been reacted with various borate esters to provide simple, functionally unsubstituted alkane- and alkeneboronic esters.[8,9] Unfortunately, the yields are often low, and the procedure cannot tolerate the presence of many functional groups. A potentially more convenient and general approach, that involving the hydroboration of alkenes and alkynes with a disubstituted borane, such as 4,4,6-trimethyl-1,3,2-dioxaborinane, has been studied by Woods and Strong.[10] This reagent, however, proved to be a poor hydroborating agent.[11]

We have discovered that catecholborane (1,3,2-benzodioxaborole), readily available by the reaction of catechol with borane in THF, hydroborates representative alkenes[12]

Table I. The Rate of Hydroboration of 1-Decene with Catecholborane at Various Temperatures[a]

Time, hr	Refluxing THF solution (68°), % hydroboration	Neat reactants, at 68°	% hydroboration at 120°
1	10	30	90
2	20	48	90
4	35	65	90
8	45	90	90

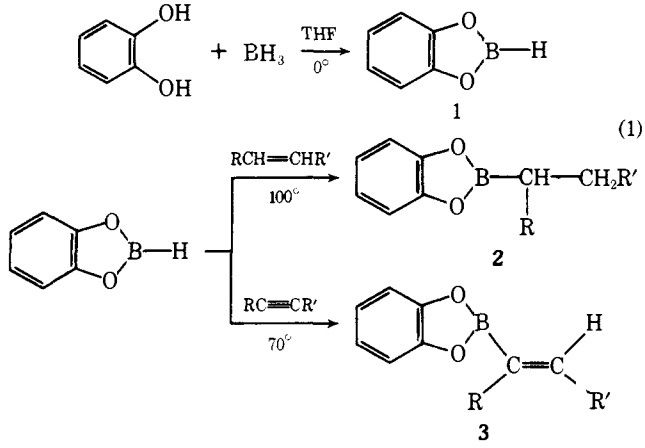
[a] A mixture of 1-decene (10 mmol), catecholborane (10 mmol), and nonane (internal standard, 10 mmol) was stirred under nitrogen. In the cases where a solvent was used, THF (10 ml) was also added. The utilization of 1-decene (GLC analysis) indicated the progress of the reaction.

Table II. The Rate of Hydroboration of 1-Decene and Norbornene with Varying Quantities of Catecholborane at 100°[a]

Time, hr	Hydroboration of 1-decene, %		Hydroboration of norbornene, %	
	Stoichiometric ratio	10% excess[b]	Stoichiometric ratio	10% excess
1	90	93	48	50
2	92	96	81	80
4	91	98	90	96
6	92	98	91	98
8			91	98

[a] A mixture of olefin (10 mmol), catecholborane (10 or 11 mmol), and nonane (10 mmol) was stirred under nitrogen at 100°. [b] Catecholborane.

and alkynes[13] in nearly quantitative yield under relatively mild conditions (eq 1). It became highly desirable to inves-



tigate systematically the synthetic scope of this new hydroboration reagent. The present paper reports our results in this area.

Results and Discussion

The Hydroboration of Alkenes with Catecholborane: Rate and Stoichiometry. The hydroboration of 1-decene with freshly distilled catecholborane was selected as the representative reaction. The hydroboration is very slow at 25°. Fortunately, at higher temperatures, the rate of hydroboration becomes sufficiently rapid to be practical as a synthetic procedure. These data are summarized in Table I.

The data in Table I clearly indicate that hydroboration proceeds at a much more satisfactory rate at higher temperatures. The fact that the hydroboration did not proceed beyond 90% even at 120° suggested the possible loss of hydroborating agent at such temperatures. Therefore, the hydroboration of a straight chain olefin, such as 1-decene, and a cyclic olefin, such as norbornene, was studied using both stoichiometric and 10% excess of catecholborane. For convenience, a 100° (boiling water bath) reaction temperature was selected. The results are given in Table II. The data in Table II clearly show that the hydroboration of olefins proceeds rapidly at 100°, and the yields of the desired alkaneboronic esters are virtually quantitative when a 10% excess of the hydroborating agent is used.

Table III. The Rate of Hydroboration of Cyclohexene with Varying Quantities of Crude Catecholborane at 100°[a]

Time, hr	Quantity of Catecholborane Used		
	10 mmol	11 mmol (10% excess)	12 mmol (20% excess)
1	19	20	20
2	32	31	30
4	52	53	55
6	65	66	70
8	78	80	82
12	80	88	95
24	80	86	94

[a] A mixture of cyclohexene (10 mmol), catecholborane (10–12 mmol), and nonane (10 mmol) was stirred under nitrogen at 100°. The percent yield of the product, 2-cyclohexyl-1,3,2-benzodioxaborole, was determined by GLC analysis.

Table IV. The Synthesis of 2-Alkyl-1,3,2-benzodioxaboroles (*B*-Alkylcatecholboranes) from Olefins via Hydroboration with Catecholborane

Alkyl substituent	Yield, %[a]	Bp, °C (mm)	n^{20}D
1-Decyl	(98)[b]		
1-Pentyl	90	75 (0.5)	1.4805
2,4,4-Trimethyl-1-pentyl	88	78 (0.25)	1.4890
Cyclopentyl	90	72 (0.2)	1.5260
Cyclohexyl	95	80 (0.4)	1.5250
exo-Norbornyl	95 (98)	104 (0.5)	1.5405

[a] By isolation. The yields by GLC are given in parentheses. [b] The product was identified by alkaline hydrogen peroxide oxidation to give 1-decanol.

At this time, we explored the possible use of crude catecholborane, as produced in the reaction of catechol with borane in THF with simple removal of solvent, for the hydroboration of olefins. For this study, we utilized cyclohexene as the representative olefin and treated it with increasing quantities of catecholborane to achieve the hydroboration. These results are summarized in Table III.

These data reveal that crude catecholborane hydroborates olefins satisfactorily at 100°. By using a moderate excess (20%) of the reagent, excellent yields of the desired alkaneboronic esters may be obtained. This procedure is quite satisfactory in cases where the product is oxidized or is transformed into another substance which is readily purified. For cases where the product is utilized to produce other substances not readily purified, as in the synthesis of monoalkylborane,[2] we realized much better results using distilled catecholborane. Consequently, we recommend the purification of catecholborane by distillation prior to its use in the hydroboration reaction for such applications. Once purified, catecholborane may be stored in a cold room for long periods of time (6 months) without any appreciable loss of its active hydride content or detectable change. The results on the hydroborations of representative olefins with catecholborane are given in Table IV.

Directive Effects in the Hydroboration of Alkenes with Catecholborane. The hydroboration of terminal alkenes, such as 1-butene, with diborane in THF proceeds in a highly regioselective manner to place the boron atom preferentially at the terminal position (94%).[14] The hydroboration

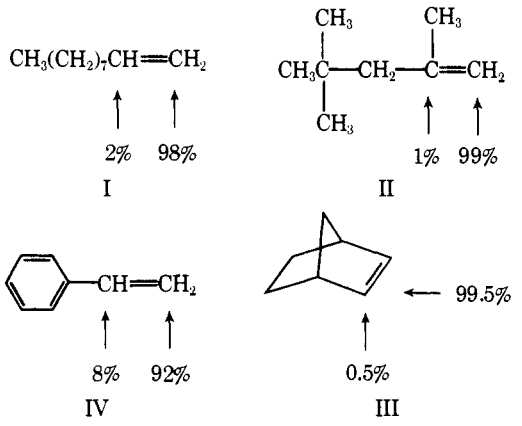
Table V. The Rate of Hydroboration of 1-Hexyne and 3-Hexyne with Catecholborane (1) at Various Temperatures[a]

Reaction time, hr	% product formation at 25°			% product formation at 68°			
	Neat reagents		THF solvent	Neat reagents		THF solvent	
	1-Hexyne	3-Hexyne	1-Hexyne	1-Hexyne	3-Hexyne[b]	1-Hexyne	3-Hexyne
0.5	30	Trace	Trace	66	22 (50)	24	5
1	48	5	5	80	37 (78)	50	10
2	63	15	8	89	62 (85)	60	18
4	72	25	15	90	80 (86)	80	30
6	80	28	27	90	85	90	40
8	80	35	38	90	90	90	50
24	85	60	58	90	90	95	80

[a] A mixture of hexyne (10 mmol), borole 1 (10 mmol), tridecane (5 mmol, internal standard), and/none THF (10 ml) was reacted. The percent yield of desired product is given (by GLC analysis). [b] Reactions performed at 100° are indicated in parentheses.

of terminal alkenes with an alkyl substituent at the 2-position, such as isobutylene, proceeds to give almost exclusively (99%) the terminal hydroboration product.[14] On the other hand, the hydroboration of yet another terminal alkene, styrene, results in only 81% of the boron atom entering the terminal position, reflecting the powerful directive influence of the phenyl substituent.[14] The stereospecific nature of hydroboration is illustrated in the hydroboration of norbornene with diborane, a reaction which proceeds to place the boron atom exclusively (99.5%) at the less hindered exo position.[14] Other substituents also reveal powerful directive influences on the direction of hydroboration.[15,16]

It thus became of interest to investigate such directive effects in the hydroboration of representative alkenes with catecholborane. We selected 1-decene (I), 1-diisobutylene (II), norbornene (III), and styrene (IV) to serve as the test series. After the standard hydroboration with catecholborane (10% excess) at 100°, the product in each case was oxidized with alkaline hydrogen peroxide, and the oxygenated products were identified by GLC analysis. The following results were obtained:



The above results indicate that catecholborane is somewhat more selective than borane in placing the boron atom preferentially at the less hindered carbon atom. Even the directive effect of the phenyl ring in the case of styrene is less pronounced. In the hydroboration of norbornene, however, the product ratio of exo/endo alcohols is the same as that realized in the hydroboration of norbornene with diborane.

The Hydroboration of Alkynes with Catecholborane. Rate and Stoichiometry. Because of the increasing interest in the chemistry of alkeneboronic acids and esters, we undertook study of the rate of monohydroboration of alkynes with catecholborane in the stoichiometric ratio (1:1). 1-Hexyne and 3-hexyne, representative of aliphatic terminal and internal alkynes, were selected for the preliminary study. The hydroborations were performed at various temperatures, either in THF or by using neat reagents in the absence of any solvent. These results are summarized in Table V. The rate data in Table V reveal that, in general, the terminal alkynes undergo hydroboration at a rate faster than the internal alkynes. The hydroboration is sluggish at 25°, especially when a solvent is used. On the other hand, the hydroboration is quite rapid at 100°, even in the case of the internal alkynes and proceeds at a satisfactory rate at 70°. Consequently, we selected 70° as the preferred reaction temperature. The utilization of the neat reagents in the hydroboration offers both the convenience of faster reaction rates and a greater ease in isolating the desired products.

Table VI. The Directive Effects in the Monohydroboration of 1-Alkynes with Catecholborane at 70°

Alkyne	Total yield, %[a] of 3 (R = H)	% composition[b]	
		α product[c]	β product[c]
1-Pentyne	92	93 (93)[d]	7 (7)[d]
1-Hexyne	90	93 (94)	7 (6)
1-Cyclohexylethyne	93	98	2
1-Phenylethyne	85[e]	91	9
3,3-Dimethyl-1-butyne	94	101	0
3-Chloropropyne	85	81 (83)	19 (17)
3-Bromopropyne	88	87	13

[a] By GLC analysis. [b] Of the distilled product. [c] Position of the attachment of boron in $R—C_\beta=CH_\alpha$. [d] Estimated by NMR (by GLC). [e] By isolation of the product.

Directive Effects in the Monohydroboration of Alkynes with Catecholborane. (A) Terminal Alkynes. The hydroboration of representative terminal alkynes with catecholborane was carried out in a 1:1 ratio at 70° in the absence of any solvent. The crude reaction products were examined, in several cases, by GLC analysis for the composition of the isomeric monohydroboration products. Subsequently, the pure products were obtained by distillation, and these were analyzed by NMR and also by GLC, whenever possible. NMR was especially useful in determining the presence of isomeric products in the mixtures since the proton attached to the carbon atom also carrying the boron atom was somewhat shielded, and consequently its signals were not obscured by the aromatic protons of the molecule. The GLC and NMR analyses gave nearly identical values for the isomer composition.

As is evident from the data in Table VI, both the steric and the electronic natures of the substituents play major roles in influencing the direction of addition of the >B-H bond. 1-Pentyne and 1-hexyne gave only 93% of the terminal hydroboration product. Cyclohexylethyne, with the bulkier cyclohexyl substituent, gave predominantly the terminal hydroboration product, 98%. Only the terminal substitution product was obtained in the case of 3,3-dimethyl-1-butyne, corresponding to the greater steric requirements of the *tert*-butyl group.

Table VII. Preparation of Alkeneboronic Esters (2-Alkenyl-1,3,2-benzodioxaboroles) from 1-Alkynes and Catecholborane

Alkyl substituent, R′, in 3 (R = H)	Yield, % GLC/(isol)	Bp, °C (mm)	n^{20}D	Mol formula (mol wt)	Analysis Found	Analysis Calcd
1-Propyl	92 (80)	67 (0.4)	1.5225	$C_{11}H_{13}BO_2$ (188)	C, 69.91 H, 7.14	C, 70.21 H, 6.91
1-Butyl	90 (75)	82 (0.25)	1.5180	$C_{12}H_{15}BO_2$ (202)	C, 71.33 H, 7.73	C, 71.28 H, 7.92
Cyclohexyl	93 (82)	114 (0.2)	1.5430	$C_{14}H_{17}BO_2$ (228)	C, 73.74 H, 7.56	C, 73.67 H, 7.45
Phenyl	(85)	78–78.5[a]		$C_{14}H_{11}BO_2$ (222)	C, 74.93 H, 4.87	C, 75.67 H, 4.98
tert-Butyl	94 (85)	74 (0.3)	1.5145	$C_{12}H_{15}BO_2$ (202)	C, 71.16 H, 7.64	C, 71.28 H, 7.29
Chloromethyl	85 (70)	80 (0.25)	1.5560	$C_9H_8BClO_2$ (194, 196)	C, 55.35 H, 4.17	C, 55.55 H, 4.11
Bromomethyl	88 (70)	88 (0.3)	*b*	$C_9H_8BBrO_2$ (239)	C, 44.48 H, 3.74	C, 45.19 H, 3.34
3-Chloropropyl	(82)	114 (0.6)	1.5434	$C_{11}H_{12}BClO_2$ (222.2)	C, 59.30 H, 5.48	C, 59.45 H, 5.40

[a] Melting point. [b] Light sensitive, highly moisture sensitive, low melting solid.

Phenylethyne, 3-bromopropyne, and 3-chloropropyne, all revealed the considerable electronic effects of these substituent groups in directing the boron atom in significant quantities to the internal position. Phenylethyne, for example, gave a mixture of the isomeric monohydroboration products in 85% isolated yield, of which only 91% was the terminal hydroboration product with the remaining 9% coming from attack of the hydroborating agent at the internal position. From this mixture, the terminal hydroboration product can be readily obtained by hydrolysis of the crude reaction mixture with recrystallization of the mixture of the two phenylethaneboronic acids thus obtained. The pure β-phenylethaneboronic acid thus obtained may be reesterified easily, as with ethylene glycol, to give the corresponding cyclic ester, 2-(β-phenylethenyl)-1,3,2-dioxaborolane, in nearly quantitative yield.

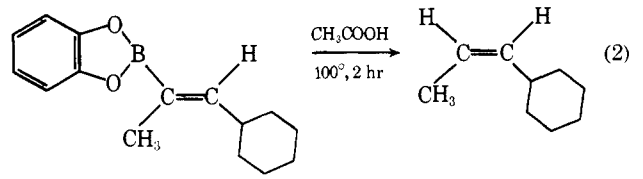
It is evident that catecholborane hydroborates terminal alkynes readily, placing the boron atom in a highly regioselective and stereospecific manner to give the corresponding alkeneboronic esters **3** in high yield. The physical and the analytical data for the representative alkynes transformed with catecholborane to the corresponding **3** are summarized in Tables VII and VIII.

(B) Unsymmetrically Substituted Internal Alkynes. It has been reported that monohydroboration of unsymmetrically disubstituted alkynes with a dialkylborane, such as dicyclohexylborane, proceeds with better steric control, compared with such hydroboration involving borane itself.[17] This prompted us to explore such directive effects in the monohydroboration of several unsymmetrically disubstituted alkynes with catecholborane. The results are given in Table IX.

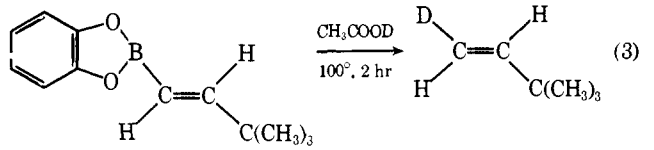
These results reveal that the bulky substituents have a more pronounced directive effect in placing the boron atom preferentially on the carbon atom at the less hindered position of the triple bond. The electronic effect of the phenyl substituent in part overcomes this steric influence, and a considerable quantity (27%) of the product is obtained resulting from the attack on the carbon atom carrying the phenyl ring. The physical and analytical properties of the alkeneboronic esters **3** prepared from representative internal alkynes are given in Table X.

(C) The Stereochemistry of Alkyne Hydroborations. An analysis of the NMR spectra of alkeneboronic esters obtained by the hydroboration of alkynes with catecholborane revealed that the addition of the boron-hydrogen bond to the triple bond occurs in a stereospecific cis manner.[18]

Thus, NMR examination of the compound **3** (R = H), obtained by the hydroboration of a terminal alkyne with catecholborane, reveals the trans relationship of the two vinylic protons. The protonolysis or deuteriolysis of these alkeneboronic esters proceeds readily. Examination of the products by NMR shows again the predicted stereochemistry of the olefinic products (eq 2 and 3).

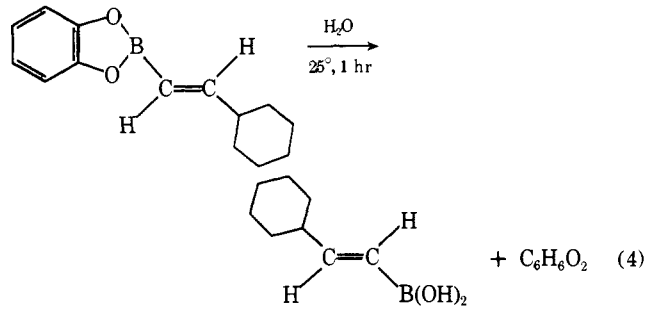


(2)



(3)

Synthetically Useful Reactions of Alkeneboronic Esters. The alkenylcatecholboranes undergo rapid hydrolysis upon stirring with water at 25° (eq 4). The alkeneboronic acids



(4)

thus obtained may be worked up in the air without significant alteration of the boron-carbon bond. The alkeneboronic acids are often crystalline solids of low solubility in water. On the other hand, the catechol by-product is highly soluble in water. Thus simple filtration can provide the alkeneboronic acid in essentially analytical purity from such hydrolyses.

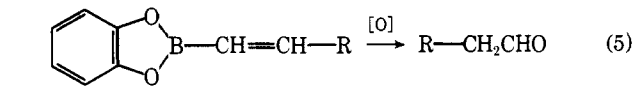
The protonolysis reaction, described in the preceding section, provides a simple means to achieve the stereospecific hydrogenation of the triple bond to the double bond stage.

The oxidation of these alkeneboronic esters with alkaline hydrogen peroxide permits a ready synthesis of the aldehydes and ketones from the corresponding alkynes (eq 5 and 6).

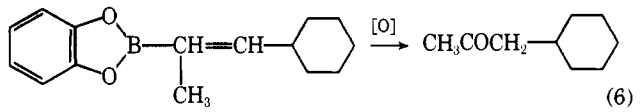
Table VIII. NMR and Mass Spectral Data of Alkeneboronic Esters (2-Alkenyl-1,3,2-benzodioxaboroles) Obtained from 1-Alkynes and Catecholborane

Alkyne	NMR spectral data[a]	Mass spectral data
1-Pentyne	7.08 (m, 5), 5.75 (pair of t, 1, J = 18 and 1.5 Hz), 2.21 (q, 2, J = 6.5 Hz), 1.50 (poor sixtet, 2), and 0.9 (t, 3)	189 (6), 188 (43), 187 (11), 173 (10), 172 (3), 160 (17), 159 (17), 147 (16), 146 (100), 145 (25), 144 (9), 133 (11), 132 (3), 120 (25), 119 (7), 93, 92, 65, 55
1-Hexyne	7.1 (m, 5), 5.76 (pair of t, 1, J = 18 Hz), 2.20 (c, 2), 1.43 (c, 4), and 0.9 (c, 3)	203 (14), 202 (94), 201 (25), 174 (9), 173 (32), 172 (10), 161 (11), 160 (94), 159 (37), 147 (16), 146 (100), 145 (36), 134 (16), 133 (16)
1-Cyclohexyl-ethyne	7.2 (m, 5), 5.71 (pair of d, 1, J = 18 Hz and J = 1.0 Hz), and 2.45–0.71 (c, br, 11)	229 (16), 228 (100), 227 (26), 200 (12), 199 (9), 186 (8), 185 (9), 172 (11), 160 (16), 159 (15), 147 (13), 146 (94), 145 (15), 95
1-Phenyl-ethyne	7.73 (d, 1, J = 18.5 Hz), 7.23 (m, 9), and 6.41 (d, 1, J = 18.5 Hz)	223 (16), 222 (100), 221 (28), 196 (8), 195, 144 (10), 143 (3), 120 (14), 119 (4), 104 (1), 103 (7), 102 (12), 44 (21), 41 (80)
3,3-Dimethyl-1-butyne	7.08 (m, 5), 5.68 (d, 1, J = 18.5 Hz), and 1.06 (s, 9)	203 (14), 202 (100), 201 (26), 186 (56), 185 (15), 158 (66), 157 (18), 69, 67, 65, 63
3-Chloro-propyne	7.08 (m, 5), 5.96 (pair of t, 1, J = 18.0 Hz), and 4.1 (pair of d, 2, J = 6.0 and 1.5 Hz)	196 (25), 195 (15), 194 (21), 193 (21), 160 (5), 159 (17), 156 (38), 155 (5), 154 (100), 153 (31), 133 (7), 67, 65, 64, 63
5-Chloro-1-pentyne	7.1 (m, 5), 5.78 (pair of d, 1, J = 18 and 1.0 Hz), 3.48 (t, 2, J = 6.5 and 6.0 Hz), 2.37 (q, 2, J = 14 and 13 Hz), and 1.95 (q, 2, J = 13 and 14 Hz)	224 (32), 223 (20), 222 (100), 221 (25), 186 (30), 185 (13), 173 (33), 172 (10), 160 (23), 159 (30), 156 (25), 155 (12), 154 (70), 153 (18), 120 (33), 119 (9), 93 (18), 92 (11)
3-Bromo-propyne	7.15 (m, 5), 6.0 (pair of t, 1, J = 18 Hz), and 4.07 (pair of d, 2, J = 6.5 Hz)	Not recorded

[a] All NMR spectra were recorded in $CDCl_3$ solution (about 20% by volume).



(5)



(6)

It should be noted that the presence of the catechol moiety in these compounds does not interfere with the oxidation reaction outlined in eq 5 and 6.

Pyridine reacts rapidly with these alkyl- and alkenylcatecholboranes to give crystalline 1:1 addition compounds. These adducts provide solid, easily identified derivatives of these boronic esters.[19]

Conclusion

Catecholborane is a new useful reagent for many applications involving hydroboration where previously dialkylboranes were required. However, in many instances, catecholborane offers a major advantage. It makes possible the simple, ready removal of the group blocking two positions of the borane moiety. Thus, it offers a direct, simple route to the synthesis of alkane- and alkeneboronic esters and acids. The latter possibility has opened up promising new areas of research in organic synthesis via these organometallic synthons.

Table IX. The Directive Effects in the Monohydroboration of Unsymmetrically Disubstituted Alkynes with Catecholborane at 70°

Alkyne	Total yield, %[a] of 3	% composition[b]	
		α product	β product[c]
3-Hexyne	85	(50)[d]	(50)[d]
2-Hexyne	(93)	60[e]	40
1-Cyclohexylpropyne	86	92	8
1-Phenylpropyne	88	73	27
4,4-Dimethyl-2-pentyne	89	95 (95)	5 (5)

[a] By isolation. The values obtained by GLC are indicated in parentheses. [b] Of distilled product. [c] The position of the attachment of boron in $R—C_\beta=C_\alpha—CH_3$. [d] Theoretical ratio. [e] The reaction product was oxidized, and the oxygenated products were determined by GLC.

Experimental Section

Analyses and Spectra. GLC analyses were carried out on F & M Model 500 instrument using SE-30 (5% on 60–80 mesh firebrick, 0.25 in. × 3 ft columns) for all boron-containing compounds. The oxygenated products, obtained by the oxidation of the corresponding boron compounds, were analyzed on Carbowax 20M columns. Ir (Perkin-Elmer 137), NMR (Varian A-60-A), and mass spectra (Hitachi RMU-6D) were recorded on the instruments mentioned.

Materials. Catechol (resublimed, 99% pure), obtained from Matheson Coleman Bell, was dried at 25° (0.2 mm) for 1 hr prior to use. Borane in THF was prepared and stored as described elsewhere.[20] Alkenes (Phillips, 99% pure) and alkynes (Farchan, Chemical Samples Co.) were commercial samples of highest purity.

Preparation of Catecholborane (1,3,2-Benzodioxaborole). A 2 *M* solution of borane in THF[20] (100 ml, 200 mmol), maintained under nitrogen, was placed in a dry 500-ml flask which was connected to a hood vent through a mercury bubbler. The flask was immersed in an ice bath, and a solution of *o*-dihydroxybenzene (catechol) (22 g, 200 mmol) in THF (50 ml) was added over 30 min to the borane solution with efficient stirring at 0°. After completion of the addition, the reaction mixture was stirred at 25° for an additional 30 min. Distillation under nitrogen provided 19.2 g (80–) of borole **1**: bp 76–77° (100 mm); n^{20}D 1.5070 [lit.[8] bp 88° (156 mm)]; ir (neat) 2680, 1465, 1235, 1130, 740 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 121 (10), 120 (100), 119 (33), 92 (15), 91 (4), 64 (24), 63 (18), 62 (6).

Stability of Catecholborane at Various Temperatures. The stability of catecholborane at various temperatures was examined by following a change in the quantity of this borane with time by GLC analysis. The results are summarized in Table X1.

Behavior of Catecholborane toward Air. The following tests were made in order to ascertain this property.

1. A 1-ml sample of this borane was discharged through air into an evaporating dish using a hypodermic syringe. The sample did not catch fire but slowly evolved a gas (hydrogen). This indicates that the compound is not spontaneously inflammable.

2. A 1-ml sample of this borane was placed in an evaporating dish and allowed to stand exposed to air. Slow evolution of a gas (presumed to be hydrogen) was noted. After 1 hr, a white residue was deposited. The latter did not show the presence of any reactive hydride upon the addition of water.

3. The reaction of this borane with air was determined as follows. Catechol borane (50 mmol) was dissolved in THF (50 ml), and the solution was divided into two parts. One part was placed in a 100-ml flask which was flushed with dry air. The other part was placed in an identical flask and was flushed with dry nitrogen. Both samples were stirred at 25°, and the aliquots were analyzed

Table X. Preparation of Alkenylboronic Esters (2-Alkenyl-1,3,2-Benzodioxaboroles) from Internal Alkynes and Catecholborane

Alkyl substituent, R' in 3 (R = CH_3)	Yield, % (GLC/(isol)	Bp, °C (mm)	n^{20}D	Mol formula (mol wt)	Analysis	
					Found	Calcd
Ethyl[a]	92 (85)	81 (0.2)	1.5160	$C_{12}H_{15}BO_2$ (202)	C, 71.46 H, 8.17	C, 71.28 H, 7.92
Cyclohexyl[b]	95 (86)	124 (0.15)	1.5400	$C_{15}H_{19}BO_2$ (242)	C, 74.20 H, 7.83	C, 74.46 H, 7.85
tert-Butyl[c]	97 (89)	86 (0.5)	1.5180	$C_{13}H_{17}BO_2$ (216)	C, 72.69 H, 8.15	C, 72.22 H, 7.87

[a] R = ethyl. NMR: 7.1 (m, 4), 6.73 (t, 1, J = 7 Hz), 2.28 (m, 4), and 0.98 ppm (m, 6). Mass spectrum: 202 (80), 201 (20), 187 (11), 186 (4), 174 (15), 173 (50), 172 (15), 161 (14), 160 (100), 159 (43), 158 (5), 147 (10), 146 (15), 145 (20), 144 (14), 134 (9), 133 (11), 120 (20), 119 (6), 101, 69, 67, 65, 55, 41. [b] NMR: 7.10 (m, 4), 6.63 (pair of d, 1, J = 9.0 and 1.5 Hz), 2.80–2.2 (br, 1), 1.91 (d, 3, J = 1.5 Hz), and 1.90–0.93 ppm (c, 10). [c] NMR: 7.1 (m, 4), 6.77 (unresolved quartet, 1), 2.02 (d, 3, J = 1.5 Hz), and 1.2 ppm (s, 9).

Table XI. Stability of Catecholborane at Various Temperatures[a]

Time, hr	Refluxing THF solution, % loss with time	Neat reagents, at 68°	% loss at 120°
0.5	0	0	0
1.0	0	0	0
2.0	0	0	0
4	0	2	6
8	10	20	25
24	15	30	40

[a] A mixture of catecholborane (10 mmol), nonane (10 mmol), and/none THF (10 ml) was refluxed under nitrogen. The percent loss in the quantity of boron compound was estimated by GLC analysis.

Table XII. Loss of Hydride from a Solution of Catecholborane in THF in the Presence of Dry Air at 25°

Time, hr	Residual hydride, %		Reaction of borane with air, %
	sample under N_2	sample under air	
1	100	100	0
4	100	97	3
8	100	94	6
12	98	88	10
24	95	80	15

by reacting with water for the residual hydride content. The observed decrease in hydride concentration is summarized in Table XII.

Reaction of Catecholborane with Water or Methanol. Catecholborane (10 mmol) was reacted with water (10 ml) or methanol (10 ml). In both cases, an immediate reaction took place, and hydrogen gas (9.8 mmol) was evolved.

Reaction of Catecholborane with Catechol. Catecholborane (10 mmol) was dissolved in THF (10 ml), and then a solution of catechol (5 mmol) in THF (1 ml) was added to it at 0°. An immediate reaction took place, and hydrogen gas (10 mmol) was evolved in 1 min, giving a clear solution. On evaporation of the solvent, *o*-phenyleneborate (10 mmol) was obtained as a white solid.

Hydroboration of Alkenes with Distilled Catecholborane. For all preparative purposes, distilled samples of catecholborane (98–99% purity minimum) were used. The conversion of norbornene into 2-*exo*-norbornyl-1,3,2-benzodioxaborole is representative of the general reaction. A mixture of norbornene (9.4 g, 100 mmol) and borole **1** (13.2 g, 110 mmol) was stirred under nitrogen at 100°. GLC monitoring of the reaction revealed it to be essentially complete (98% yield) in 4 hr (terminal alkenes required 2 hr). Distillation then provided 20.3 g (95%) of desired product, bp 104° (0.5 mm). In the case of low boiling alkenes, a sealed ampoule was required to reach the 100° reaction temperature. In this way, highly volatile alkenes, such as 1-pentene or cyclopentene, could be readily converted into the corresponding products **2** in 90% yield.

Hydroboration of Cyclohexene with Crude Catecholborane. Catecholborane was prepared by reacting catechol (22 g, 200 mmol) with borane in THF (200 mmol) in the usual manner. After the reaction was over, the solvent was distilled off at 25° (150 mm), and the residue borane was found to contain about 80% of catecholborane (the remainder was presumably the polymeric *o*-phenyleneborate). This crude sample of catecholborane was then reacted with cyclohexene, as described in the text (Table III). The consumption of catecholborane was determined by GLC analysis.

Hydroboration of Alkynes with Catecholborane. The Preparation of 2-Alkenyl-1,3,2-benzodioxaboroles (3). The conversion of 1-cyclohexylpropyne into *cis*-2-(2-cyclohexyl-1-methyl)ethenyl-1,3,2-benzodioxaborole is representative of this transformation. A mixture of 1-cyclohexylpropyne (12.2 g, 100 mmol) and catecholborane (12.0 g, 100 mmol) was stirred under nitrogen at 70°. GLC monitoring of the reaction revealed it to be complete in 4 hr (terminal alkynes require 1 hr, internal alkynes require 2–4 hr heating period). Distillation under nitrogen then provided 20.8 g (86%) of pure product: bp 124° (0.15 mm); n^{20}D 1.5400.

Preparation of β-Phenylethenylboronic Acid and 2-(β-Phenyl)-ethenyl-1,3,2-dioxaborolane. The isomeric mixture of crude β-phenylethenylcatecholborane was obtained by the hydroboration of phenylethyne with catecholborane in the manner described above. The product (11.1 g, 50 mmol) was stirred with water (100 ml) for 1 hr at 80°. Upon cooling, a white crystalline compound separated. A 0.5-g sample of this solid was recrystallized from hexane–THF to give pure β-phenylethenylboronic acid as cubic crystals, mp 163–164°.

Anal. Calcd for $C_8H_9BO_2$: B, 7.43. Found: B, 7.20.

The remaining β-phenylethenylboronic acid was converted to 2-(β-phenyl)ethenyl-1,3,2-dioxaborolane by heating with ethylene glycol (3.1 g, 50 mmol) and toluene (100 ml) with the azeotropic removal of water for 2 hr. Distillation of solvent left a liquid which soon crystallized, giving 7.4 g (85%) of desired alkenylborolane, mp 47–48°. After one recrystallization from hexane, the melting point was 48°: NMR ($CDCl_3$) δ 7.36 (m, 6), 6.20 (d, 1, J = 18.5 Hz), 4.25 (s, 4).

Anal. Calcd for $C_{10}H_{11}BO_2$: C, 68.96; H, 6.32. Found: C, 69.16; H, 6.49.

Reaction of 2-Alkyl- and 2-Alkenyl-1,3,2-benzodioxaboroles with Water. Preparation of Alkyl- and Alkenylboronic Acids. This procedure is illustrated by the following examples. 2-(2-Cyclohexyl)ethenyl-1,3,2-benzodioxaborole (2.3 g, 10 mmol) was stirred with water (10 ml) at 25° for 1 hr. The white crystalline product formed was filtered and recrystallized from hot water, giving 1.5 g (97%) of 2-cyclohexylethenylboronic acid: mp 104–105; NMR (Me_2SO, Me_4Si) δ 7.48 (s, 2), 6.47 (pair of d, 1, J = 18 and 6.0 Hz), 5.30 (pair of d, 1, J = 18 and 1.0 Hz).

Anal. Calcd for $C_8H_{15}BO_2$: C, 62.33; H, 9.73. Found: C, 62.29; H, 10.00.

The hydrolysis of 2-(5-chloro)pentenyl-1,3,2-benzodioxaborole was similarly carried out, giving 5-chloropentenylboronic acid in 95% yield after recrystallization from hot water, mp 94°.

Anal. Calcd for $C_5H_{10}BClO_2$: Cl, 23.85. Found: Cl, 23.98.

The hydrolysis of 2-cyclohexyl-1,3,2-benzodioxaborole to give cyclohexaneboronic acid is illustrative of the method for the synthesis of alkaneboronic acids. The cyclohexylborole (6.06 g, 30 mmol) was stirred with water (50 ml) at 25° for 1 hr. The white crystalline material formed was filtered and recrystallized from hot water, giving 3.4 g (90%) of cyclohexaneboronic acid, mp 112–114° (lit.[21] mp 116–117°).

Reaction of 2-Alkenyl-1,3,2-benzodioxaboroles with Pyridine. The preparation of 2-(4,4-dimethyl-2-pentenyl)-1,3,2-benzodioxaborole–pyridine adduct will illustrate this procedure. The alkenylborole **3** (R^1 = *tert*-butyl, R = methyl) (2.16 g, 10 mmol) was dis-

solved in hexane (20 ml), and pyridine (0.8 g, 10 mmol) was added to it with stirring at 25°. A crystalline precipitate was formed almost immediately. It was filtered after cooling with an ice bath. Recrystallization from hexane gave 2.8 g (94%) of the desired adduct: mp 97–98°; NMR ($CDCl_3$, Me_4Si) δ 7.93 (c, 9), 6.53–6.07 (br, 1), 1.90 (d, 3, J = 1.5 Hz), 1.2 (s, 9).

Anal. Calcd for $C_{18}H_{22}BNO_2$: B, 3.72; N, 4.40. Found: B, 3.71; N, 4.64.

Protonolysis and Deuteriolysis of 2-Alkenyl-1,3,2-benzodioxaboroles. A representative example follows. A 7.2-g sample (30 mmol) of **3** (R′ = cyclohexyl, R = methyl) was stirred with acetic acid under nitrogen at 100° for 2 hr. GLC monitoring of the reaction revealed it to be complete (100%) at this time. The resulting yellow solution was poured over ice water and then extracted with pentane. The organic extract was then washed with ice cold 1 *N* sodium hydroxide solution, dried, and then distilled. *cis*-Propenylcyclohexane, 3.55 g (95%), was thus obtained: bp 150° (750 mm); $n^{20}D$ 1.4535; ir (neat) 1455 cm^{-1}; NMR ($CDCl_3$, Me_4Si) δ 5.25 (pair of d, J = 5.0 and 2.5 Hz), 5.22 (pair of d, J = 9.0 and 11.0 Hz).

The deuteriolysis of 4.04 g (20 mmol) of **3** (R′ = *tert*-butyl, R = H) was similarly carried out using perdeuterioacetic acid (10 ml) at 100° for 2 hr. Distillation then provided 1.5 g (90%) of *trans*-3,3-dimethylbutene-*1*-d_1: bp 58° (750 mm); $n^{20}D$ 1.3730; ir (neat) 990 cm^{-1}.

Alkaline Hydrogen Peroxide Oxidation of 2-Alkyl- and 2-Alkenyl-1,3,2-benzodioxaboroles. Conversion of the Alkenes and Alkynes into the Corresponding Oxygenated (Alcohol, Aldehyde, Ketone) Products. The following is a representative example. A 4.8-g sample of **3** (R′ = cyclohexyl, R = methyl) (20 mmol) was dissolved in THF–ethanol mixture (1:1, 50 ml) and cooled at 0°. The oxidation was done by the dropwise addition of 3 *N* sodium hydroxide (34 ml, 100 mmol) followed by the dropwise addition of 30% hydrogen peroxide (13.5 ml, 40 mmol) at 0°. More than the usual quantity of sodium hydroxide was found to be necessary in these oxidations since it reacts with liberated catechol to form the corresponding phenolate. The temperature was subsequently brought to 25–30°. After 2 hr, the mixture—a pale liquid—was diluted with water and, after saturation with potassium carbonate, was extracted with pentane. The extract was washed with brine and then dried, and the solvent upon evaporation gave cyclohexylacetone in 98% yield (GLC), uncontaminated by other products (GLC, NMR). The oxidation of crude 2-(β-phenyl)ethyl-1,3,2-benzodioxaborole (2.24 g, 10 mmol) with hydrogen peroxide and sodium hydroxide was similarly carried out. After the usual work-up, GLC analysis indicated the formation of the oxygenated products in 85% yield, comprising 2-phenylethanol (92%) and 1-phenylethanol (8%). Other determinations, reported in the text, were carried out in a similar manner.

References and Notes

(1) Postdoctorate research associate on Grant GM-10937 supported by the National Institutes of Health.
(2) H. C. Brown and S. K. Gupta, *J. Am. Chem. Soc.*, **93**, 4062 (1971); E. Negishi and H. C. Brown, *Synthesis*, 197 (1972).
(3) S. Cabiddu, A. Maccioni, and S. Mario, *Gazz. Chim. Ital.*, **102**, 555 (1972).
(4) R. C. Larock, S. K. Gupta, and H. C. Brown, *J. Am. Chem. Soc.*, **94**, 4371 (1972).
(5) R. Pappo and P. W. Collins, *Tetrahedron Lett.*, 2627 (1972).
(6) H. C. Brown, T. Hamaoka, and N. Ravindran, *J. Am. Chem. Soc.*, **95**, 5786 (1973).
(7) H. C. Brown, T. Hamaoka, and N. Ravindran, *J. Am. Chem. Soc.*, **95**, 6456 (1973).
(8) D. S. Matteson, *Acc. Chem. Res.*, **3**, 186 (1970); D. S. Matteson in "Progress in Boron Chemistry", Vol. 3, A. L. McCloskey and R. J. Brotherton, Ed., Pergamon Press, New York, N.Y., 1970, Chapter 2.
(9) G. D. Schaumberg and S. Donovan, *J. Organomet. Chem.*, **20**, 261 (1969); B. M. Mikhailov, Yu N. Bubnov, and S. N. Korobeinikova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2466 (1969); W. G. Woods, I. S. Bengeisdorf, and P. L. Hunter, *J. Org. Chem.*, **31**, 2766 (1966); D. J. Pasto, J. Chow, and S. K. Arora, *Tetrahedron*, **25**, 1557 (1969); D. S. Matteson and J. R. Thomas, *J. Organomet. Chem.*, **24**, 262 (1970).
(10) W. G. Woods and P. L. Strong, *J. Am. Chem. Soc.*, **88**, 4667 (1966); R. H. Fish, *J. Org. Chem.*, **38**, 158 (1973); *J. Am. Chem. Soc.*, **90**, 4435 (1968).
(11) The hydroboration of 1-heptyne, for example, proceeds at 110° for 2 days followed by 1 day at 210° to give, after distillation, a 69% yield of the desired monohydroboration product.[10]
(12) H. C. Brown and S. K. Gupta, *J. Am. Chem. Soc.*, **93**, 1816 (1971).
(13) H. C. Brown and S. K. Gupta, *J. Am. Chem. Soc.*, **94**, 4370 (1972).
(14) H. C. Brown, "Hydroboration", W. A. Benjamin, New York, N.Y., 1962.
(15) H. C. Brown and M. K. Unni, *J. Am. Chem. Soc.*, **90**, 2902 (1968); H. C. Brown and R. M. Gallivan, Jr., *ibid.*, **90**, 2906 (1968); H. C. Brown and R. L. Sharp, *ibid.*, **90**, 2915 (1968).
(16) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972.
(17) G. Zweifel, G. M. Clark, and N. L. Polston, *J. Am. Chem. Soc.*, **93**, 8895 (1971).
(18) The NMR spectrum of 2-(1-hexenyl)-4,4,6-trimethyl1,3,2-dioxaborinane, obtained by the hydroboration of 1-hexyne with 4,4,6-trimethyl-1,3,2-dioxaborinane, was consistent with a cis addition of the B–H bond to the triple bond.[10]
(19) For an intramolecularly amine coordinated 2-alkyl-1,3,2-benzodioxaborole derivative, see: D. S. Matteson and G. D. Schaumberg, *J. Org. Chem.*, **31**, 726 (1966); J. C. Catlin and H. R. Snyder, *ibid.*, **34**, 1660, 1664 (1969).
(20) H. C. Brown, "Organic Syntheses *via* Boranes", Wiley-Interscience, New York, N.Y., 1975.
(21) H. Hartmann and K. H. Birr, *Z. Anorg. Allg. Chem.*, **299**, 174 (1959).