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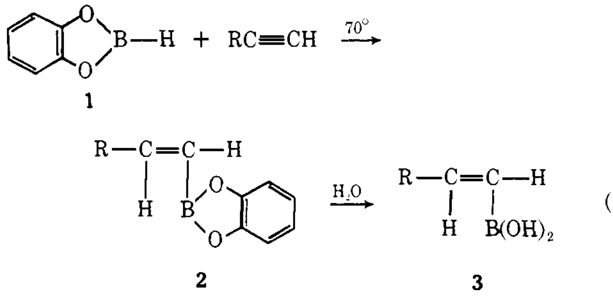
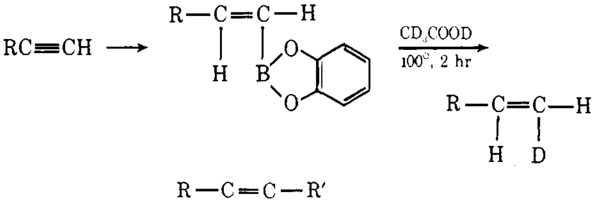
Catecholborane (1,3,2-Benzodioxaborole) as a New, General Monohydroboration Reagent for Alkynes. A Convenient Synthesis of Alkeneboronic Esters and Acids from Alkynes *via* Hydroboration

Sir:

1,3,2-Benzodioxaborole (1), now conveniently available[1] through the reaction of catechol with borane in tetrahydrofuran (THF), reacts rapidly at 70° with alkynes to give stereospecific and regioselective monohydroboration products, the 2-alkenyl-1,3,2-benzodioxaboroles (2), in nearly quantitative yields. The esters 2 are readily hydrolyzed to the corresponding alkeneboronic acids (3) (eq 1). The ready protonolysis or deuterolysis of 2-alkenyl-1,3,2-benzodioxaboroles provides a new procedure for the conversion of the alkynes into the corresponding cis olefins *via* hydroboration (eq 2 and 3). Finally, oxidation of these derivatives 2 provides the corresponding aldehydes or ketones (eq 4 and 5).



(1)



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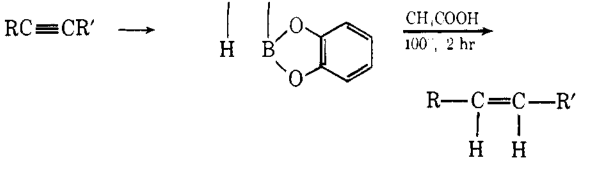

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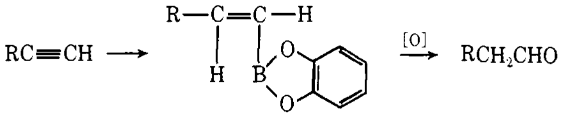

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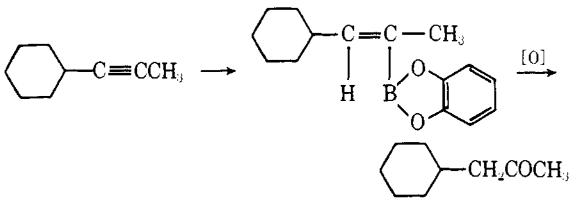
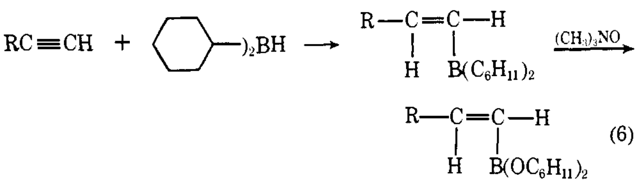


(5)

This novel development, therefore, provides a facile, clean, and highly convenient synthesis of the alkeneboronic esters and acids, cis olefins, and aldehydes and ketones from the corresponding alkynes *via* hydroboration.[2]

Recent investigations have led to the discovery of several new reactions which reveal the increasing importance of alkenylboranes[3] and alkeneboronic esters and acids[4] in organic synthesis. The alkenylboranes are available *via* the treatment of alkynes with borane[2] and its alkyl derivatives.[3] A convenient, general procedure for the synthesis of alkeneboronic acids and esters, however, is presently not available. Organometallic reagents, for example, have been treated with organic borates to give simple, functionally unsubstituted alkeneboronic acids and esters.[4,5] A two-step procedure involving the hydroboration of alkynes with dicyclohexylborane followed by the selective oxidation of the resulting alkenyldialkylborane has been developed by Zweifel, *et al.*[6] (eq 6). The hydroboration of alkynes with a dialkoxyborane, such as 4,4,6-trimethyl-1,3,2-dioxaborinane,[7] or with an alkylazaborane, such as 1-alkyl-1,2-azaborolidine,[8] has also been studied recently. These reagents, however, are poor hydroboration reagents[9] and the reactions are slow even at elevated temperatures.



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(7) W. G. Woods and P. L. Strong, *J. Amer. Chem. Soc.*, **88**, 4667 (1966), and references cited therein; see also, R. H. Fish, *ibid.*, **90**, 4435 (1968).

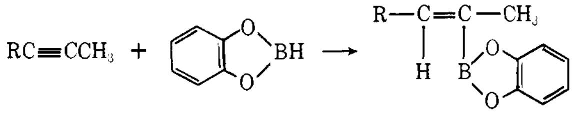
(8) V. A. Dorokhov, O. G. Boldyreva, and B. M. Mikhailov, *Zh. Obshch. Khim.*, 40, 1528 (1970).

(9) The hydroboration of 1-heptyne with 4,4,6-trimethyl-1,3,2-dioxaborinane, for example, proceeded at 110° for 2 days followed by 1 day at 210° to give, after distillation, 69% yield of the desired product.[7] The hydroboration of alkynes with 1-alkyl-1,2-azaborolidines proceeded at 130–150° to give the desired alkenylborolidines in unspecified yields.[8]

Fortunately, our recent work in this area has revealed that 1,3,2-benzodioxaborole (**1**) hydroborates olefins rapidly at 100° to give the corresponding alkaneboronic esters, 2-alkyl-1,3,2-benzodioxaboroles, in almost quantitative yields.[1] This prompted us to investigate the selective monohydroboration of alkynes with this new reagent in the hope of obtaining the corresponding cyclic esters of alkeneboronic acids, 2-alkenyl-1,3,2-benzodioxaboroles (**2**). Indeed, this reaction proceeds in a highly satisfactory manner, without observable dihydroboration, and the desired products **2** are readily isolated by distillation and can be stored under nitrogen for prolonged periods without polymerization or disproportionation.

In addition to the reactions of alkenylboroles **2**, pyridine forms stable 1:1 addition compounds with **2**. These products serve as easily identified solid derivatives of the alkenylboroles **2**.

The hydroboration of alkynes with catecholborane proceeds in a stereospecific cis manner[10] with the boron being attached regioselectively at the less hindered carbon atom of the triple bond. The reaction of the reagent with 4,4-dimethyl-2-pentyne, for example, proceeded almost exclusively (95%) to place the boron atom at the less hindered position (R = *tert*-butyl, eq 7). The reaction is slightly less selective in the case of 1-cyclohexylpropyne, where a 92:8 distribution of the two isomers is observed (R = cyclohexyl, 92%, eq 7). Even in the case of 1-phenylpropyne, the boron atom goes preferentially to the less hindered position, in spite of the strong directive influence of the phenyl group in simple alkenes[2] (R = phenyl, 73%, eq 7).



(7)

Results on the conversion of several representative alkynes into the corresponding alkeneboronic esters and acids *via* the present method are summarized in Table I.[11]

The conversion of 1-cyclohexylpropyne into the corresponding derivative of **2** is illustrative of this new, simple hydroboration procedure. A mixture of 1-cyclohexylpropyne (12.2 g, 100 mmol) and catecholborane (12.0 g, 100 mmol) was stirred at 70° under nitrogen for 4 hr (terminal alkynes require 1 hr, internal alkynes require 2–4 hr). Distillation yielded 20.8 g (86%) of pure *cis*-2-(2-cyclohexyl-1-methyl)ethenyl-1,3,2-benzodioxaborole: bp 124° (0.15 mm); n^{20}D 1.5400.[11]

To achieve the protonolysis of this derivative, 7.2 g (30 mmol) was stirred under nitrogen with acetic acid (15 ml) at 100° for 2 hr. The resulting yellow solution was poured over ice water and extracted with pentane. The pentane extract was washed with ice-cold 1 *N* sodium hydroxide and then with brine, and dried over magnesium sulfate. Evaporation of the solvent gave 3.55 g (95%) of *cis*-propenylcyclohexane: bp 150° (750 mm); n^{20}D 1.4535.[11]

Table I. The Synthesis of Alkeneboronic Esters **2** and Acids **3** from Alkynes *via* the Hydroboration with Catecholborane

Alkyne hydroborated	Yield, %[a]	Bp, °C (mm)	n^{20}D
1-Pentyne	92 (80)	67 (0.4)	1.5225
1-Hexyne	90 (75)	82 (0.25)	1.5180
Cyclohexylethyne	93 (82)	114 (0.2)	1.5430
Phenylethyne	(85)	78–78.5[b]	
3,3-Dimethyl-1-butyne	94 (85)	74 (0.3)	1.5145
3-Chloro-1-propyne	85 (70)	80 (0.25)	1.5560
5-Chloro-1-pentyne	(82)	114 (0.6)	1.5435
3-Hexyne	92 (85)	81 (0.2)	1.5160
1-Cyclohexylpropyne	95 (86)	124 (0.15)	1.5400
4,4-Dimethyl-2-pentyne	97 (89)	86 (0.5)	1.5180
trans-2-Phenyletheneboronic acid	(80)	163–164[b]	
trans-5-Chloro-1-penteneboronic acid	(95)	94[b]	
trans-2-Cyclohexyletheneboronic acid	(97)	104–105[b]	

[a] By glpc analysis. The yields by isolation are given in parentheses. [b] Melting point of the compound.

Oxidation of 4.8 g (20 mmol) of *cis*-2-(2-cyclohexyl-1-methyl)ethenyl-1,3,2-benzodioxaborole with alkaline hydrogen peroxide was carried out in a THF–ethanol solution at 25–30° for 2 hr. The reaction mixture was extracted with pentane, and the pentane extract was washed with ice-cold 1 *N* sodium hydroxide and then with brine, and then dried over magnesium sulfate. The removal of the solvent gave cyclohexylacetone in 98% yield (glpc), essentially free of other products.

The following synthesis of 2-cyclohexyletheneboronic acid from the corresponding cyclohexyletheneboronic ester is representative. A mixture of **2** (R = cyclohexyl, 2.3 g, 10 mmol) and water (10 ml) was stirred rapidly at 25° for 1 hr. The white crystalline product thus formed was filtered and recrystallized from hot water to give 1.5 g (97%) of the desired acid: mp 104–105°.[11]

The reaction of 2-alkenyl-1,3,2-benzodioxaboroles with pyridine is illustrated by the following example. The alkenylborole **2** from 4,4-dimethyl-2-pentyne (2.16 g, 10 mmol) was dissolved in hexane (20 ml) and pyridine (0.8 g, 10 mmol) was added to it with stirring at 25° under nitrogen. A crystalline precipitate was formed almost immediately. After cooling with ice, it was filtered and recrystallized from hexane to give 2.8 g (94%) of the adduct: mp 97–98°.[11]

It is evident that this development of catecholborane as a selective, rapidly reacting, monofunctional hydroboration reagent for alkynes should have wide application and make the highly useful vinylboronic acid far more readily available.

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[10] This was confirmed by the trans relationship of the two vinylic protons in **2**, as indicated by pmr spectroscopy,[3,7] and also by the deuterolysis experiments.

[11] All the compounds gave concordant ir and nmr spectra. New compounds, in addition, gave satisfactory (within 0.3%) carbon–hydrogen analyses and mass spectra.

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Reaction of 2-Alkenyl-1,3,2-benzodioxaboroles with Mercuric Acetate. A Convenient Stereospecific Procedure for the Conversion of Alkynes into Alkenylmercuric Salts

Sir:

2-Alkenyl-1,3,2-benzodioxaboroles (**2**), readily available *via* hydroboration of alkynes with 1,3,2-benzodioxa-