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DIALKYLBORANE-CATALYZED HYDROBORATION OF ALKYNES WITH 1,3,2-BENZODIOXABOROLE IN TETRAHYDROFURAN

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Abstract: Dialkylborane catalyzed hydroboration of alkynes with an equimolar amount of 1,3,2-benzodioxaborole in tetrahydrofuran efficiently to provide 2-alkenyl-1,3,2-benzodioxaborole under mild reaction conditions.

Hydroboration of alkynes with 1,3,2-benzodioxaborole (catecholborane)[1,2] provides 2-alkenyl-1,3,2-benzodioxaboroles (**1**), useful intermediates.[3] However, the hydroboration of alkynes with this reagent is rather sluggish, especially when a solvent is used, and thus it has to be carried out under rather forced conditions. For example, in the cases of 1-hexyne and 3-hexyne, 90% of the hydroboration was achieved by employing neat catecholborane at 68 °C for 4 h and 8 h respectively.[2] Accordingly, it is desirable to explore a procedure in which the hydroboration is carried out more conveniently and efficiently under mild reaction conditions.

Few metal complex-catalyzed hydroborations of alkyne have been reported.[4] However, they are not so effective as similar hydroborations of alkene.[5] On the other hand, Suseela et al. reported an acceleration of the hydroboration of terminal alkyne with catecholborane by *N*, *N*-diethylaniline–borane complex where the reaction was carried out with a considerably excess amount of 1-alkyne (1.6 times the amount of catecholborane) at 25 °C for 24 h.[6]

We wish to report here a dialkylborane-catalyzed hydroboration of alkyne with catecholborane where **1** are provided in high yields by employing stoichiometric amounts of alkyne and catecholborane under mild reaction conditions, at room temperature in tetrahydrofuran (THF).

In the reaction of 1-hexyne (5 mmol) with catecholborane (5 mmol in 10 ml of THF), carried out without any additives at room temperature for 2 h, 75% of the alkyne was recovered. However, when a similar reaction was carried out in the presence of dicyclohexylborane (0.25 mmol, 5 mol%), 1-hexyne was consumed completely and hexanal was obtained in 96% yield by a controlled oxidation of the reaction mixture with alkaline hydrogen peroxide. On the other hand, the ^{1}H NMR spectral datum[7] of the reaction product, obtained after removal of THF just after the hydroboration, agreed very closely with that of 2-[(*E*)-1-hexenyl]-1,3,2-bezodioxaborole reported previously.[2] These results show that dicyclohexylborane acts as a catalyst providing 2-[(*E*)-1-hexenyl]-1,3,2-benzodioxaborole in a nearly quantitative yield and in a stereospecific manner.

Similar results were obtained when different types of 1-alkynes were employed. Yields of the carbonyl compounds (**2**) formed by the oxidation of **1** are shown in Table. The reaction of 4-octyne, an internal alkyne, gave a poor result even in the reaction for 24 h. However, the

Table. Hydroboration of alkyne with catecholborane in THF in the presence of 5 mol% of dialkylborane, followed by oxidation,[a] iodination,[b] and cross-coupling reaction with iodobenzene.[b]

Alkyne	Catalyst	React. time, h	Residual alkyne, %[c]	Yield, %		
				2[c]	3[d]	4[d]
1-Hexyne	Dicyclohexyl-[e] borane	2	0	96		
"	9-BBN[f]	2	28	61		
1-Octyne	Dicyclohexyl-[e] borane	2	0	96	83	82
3,3-Dimethyl-1-butyne	"	2	0	90		
Phenylethyne	"	2	0	65[g]	82	
4-Octyne	"	24	47	50		
"	9-BBN[f]	24	5	92		83

[a] The hydroboration was carried out by using 5 mmol of catecholborane, 5 mmol of alkyne, 0.25 mmol of dialkylborane, and 10 ml of THF.

[b] The amounts of the reagents and solvent were twice those used in the oxidation.

[c] Determined by GLC and based on alkyne employed.

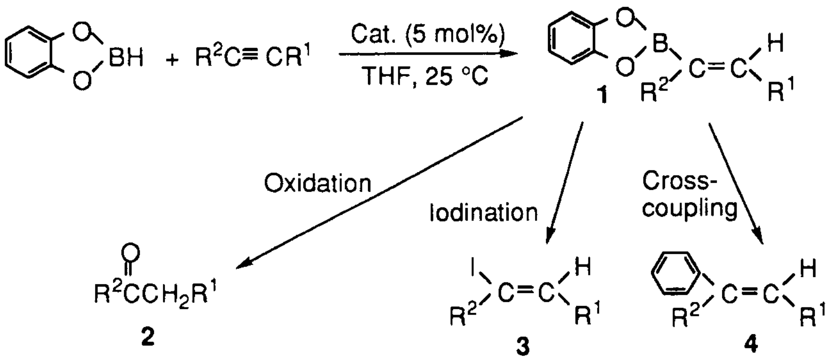
[d] Isolated by column chromatography and based on alkyne employed.

[e] The catalyst was used as a suspension in THF.

[f] The catalyst was used as a THF solution.

[g] The low yield may be attributed to a loss of phenylacetaldehyde by condensation.

presence of 5 mol% of 9-borabicyclo[3.3.1]nonane (9-BBN), instead of dicyclohexylborane, catalyzed the hydroboration satisfactorily to provide 4-octanone in 92% yield by the followed oxidation. Thus, the present reaction seems to be generally applicable to the monohydroboration of a wide variety of alkynes.



Scheme 1

On the other hand, a treatment of 1-alkenylboronic acid, formed by hydrolysis of **1**, with iodine in the presence of aqueous sodium hydroxide[8] provided isomerically pure (*E*)-1-iodo-1-alkenes (**3**) in good yields (Scheme 1, Table). In addition, $Pd(PPh_3)_4$-catalyzed cross-coupling reaction of **1** with iodobenzene[9] provided phenylated (*E*)-alkenes (**4**) in excellent stereochemical purities (>99%) and in good yields (Scheme 1, Table).

These results suggest that **1** obtained by the present reaction can be used as synthetic intermediates as well as those prepared from neat catecholborane.

It has been reported that hydroboration of 1-alkyne with dicyclohexylborane in THF proceeds rapidly at 0 °C,[10] and hydroboration of internal alkynes with 9-BBN in THF proceeds sufficiently at 25 °C.[11] Thus, in the present reaction, dialkylborane added as the catalyst must react with alkyne faster than catecholborane does forming alkenyldialkylborane. Accordingly, the reaction seems to involve a transfer of the alkenyl group from alkenyldialkylborane to catecholborane as a key step.

The present dialkylborane-catalyzed hydroboration seems to be not only useful as a method for providing **1** but also interesting as one of relatively few cases where organoborane is used as a catalyst.

Experimental:

To catecholborane (5 mmol, 0.6g) in THF (10 ml) were added 1-alkyne (5 mmol) and dicyclohexylborane (0.25 mmol), freshly prepared by hydroboration of cyclohexene with BH_3 in THF just before use, successively at room temperature and the mixture was stirred at this temperature.

The controlled oxidation was carried out in the following way. Thus, after the hydroboration, the reaction mixture was treated with 2 mol dm^{-3} aqueous sodium hydroxide (5 mmol, 2.5 ml) and 30% hydrogen peroxide (5 mmol, 0.52 ml) at 0 °C.

The iodination[6] and the cross-coupling[7] reactions were carried out in a similar manner as described in the literatures.

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