Organoboranes. 56. Systematic Study of the Reactions of 1-Alkenylboronic Esters with Representative Organolithium and Grignard Reagents To Provide an Efficient, Selective Synthesis of Organyl-1-alkenylborinic Esters

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Received October 13, 1992

A selective reaction of the "ate" complexes formed with 1-alkenylboronic esters and organolithium or Grignard reagents, by treatment with either Brønsted or Lewis acids at −78 °C to give the corresponding organylalkenylborinic esters, is explored in this study. This systematic, detailed study reveals that the nature of the alkoxy group on boron, the nature and the amount of the alkyllithium or Grignard reagent used, the solvent, the reaction temperature, and the nature and amount of the acid used all play significant roles in influencing both the yield and the selectivity achieved for the formation of the desired organylalkenylborinates. Optimized procedures for the syntheses of representative organylalkenylborinic esters in high yield are summarized.

Considerable interest has been paid in the past decade to the chemistry and synthetic utility of borinic and boronic acids and esters.[2] Borinic esters are useful intermediates in many carbon–carbon bond-forming reactions, such as 1,2-migration,[2c] the synthesis of cyclic and acyclic ketones,[3,4] α-chiral acyclic ketones,[5] α-chiral alkynyl ketones,[6] and optically active amines,[7] and the stereospecific synthesis of cis and trans disubstituted and structurally defined trisubstituted alkenes.[8,9] No loss of alkyl groups is noted in the 1,2-migration reaction. This synthesis is especially valuable in view of the complete retention of both the stereochemistry and the configuration of the migrating carbon group.

Many methods have been developed for the preparation of dialkylborinic acids and esters which include the reactions of trialkylboranes with carboxylic acids[10] or with aldehydes,[11] their thermal redistribution with trialkoxyboranes[12a] or with boron trichloride, followed by hydrolysis or alcoholysis,[12b–d] and the stepwise hydridation–hydroboration of alkyldihaloboranes.[13] However, relatively little is known about the related synthesis of alkylalkenylborinates, or, more broadly, organylalkenylborinates. Hydroboration of alkynes with alkylbromoboranes to the corresponding alkylalkenylbromoboranes, followed by esterification with methanol, provides alkylalkenylborinates.[14] Optically active alkylalkenylborinates can also be obtained by the hydroboration of alkynes with isopinocampheylalkylborane, IpcR*BH, followed by removal of the Ipc group by treatment with acetaldehyde.[15]

We have developed a simple methodology for the synthesis of dialkylborinic esters[16a] and organyl-1-alkynylborinic esters[16b] which involves the stepwise addition of a suitable organolithium reagent (alkyl- or 1-alkynyllithium) to an alkylboronic ester to give the corresponding "ate" complex (eq 1), followed by treatment with hydrogen chloride in diethyl ether (eq 2).

$$R'B(OR)_2 + R''Li \xrightarrow[-78\ °C]{\text{Ether}} [R'R''B(OR)_2]Li \quad (1)$$

$$[R'R''B(OR)_2]Li \xrightarrow[-78\ °C\ \text{to}\ 25\ °C]{\text{HCl/Ether}} R'R''BOR + ROH + LiCl\downarrow \quad (2)$$

Organylalkenylborinic esters are used both as potential intermediates in organic synthesis[15,16c,d] and for the

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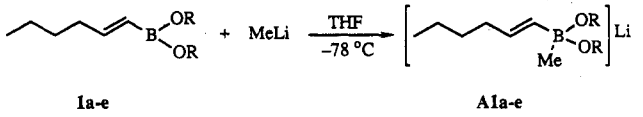
synthesis of other organoboranes.[14] However, there is no simple and efficient method presently available for the synthesis of these useful esters. Accordingly, we decided to undertake a detailed study of the synthesis of organylalkenylborinic esters in the hope of arriving at procedures which would permit their synthesis in high yields.

In our earlier communication,[16c] we reported the application of this methodology for selected systems. Further research in this area suggested that the reactions of alkenylboronic esters with alkyllithium, unlike those of the corresponding alkylboronic esters, are quite complex, providing a mixture of products under similar experimental conditions. In the hope of understanding the precise nature of the reactions which lead to these byproducts, establishing conditions which would minimize their formation, a systematic study was undertaken. This has now been achieved.

Results and Discussion

In the present study, the reaction of representative cyclic and acyclic esters of 1-hexenylboronic acid with methyllithium was selected as a model test reaction. This test reaction was carried out under conditions similar to those used earlier to convert the alkylboronic esters into the dialkylborinic esters.[16-18]

There are two important steps involved in this reaction. The first one (eq 3) is the well-known formation of "ate" complexes.[8b] 1-Hexenylboronic esters **1a–e** react readily

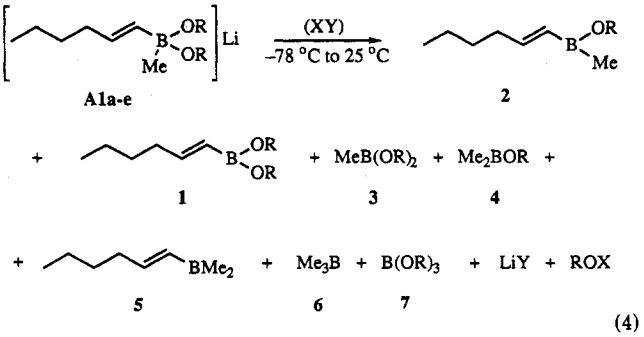


1a-e **A1a-e**

R = Me (**1a**), *i*-Pr (**1b**), -$(CH_2)_3$- (**1c**), -$(CH_2)_2$- (**1d**), -Me_2C-CMe_2- (**1e**)

(3)

with an equivalent amount of methyllithium in diethyl ether or THF at −78 °C to form the corresponding "ate" complexes **A1a–e** quantitatively. The second step (eq 4) is the decomposition of the "ate" complex **A1a–e** by selected acids into a variety of organoboranes **2–7**. The selectivity to a desired product depends critically upon various factors, such as the alkoxy group on boron, the reaction temperature, the solvent, and the nature of the acidic agent.



A1a-e **2** **1** **3** **4** **5** **6** **7**

(4)

These products, **2–7**, have been identified and estimated in the present study from the chemical shifts and the intensity of the corresponding peaks in the ^{11}B NMR spectrum. The results for the reaction of various esters of 1-hexenylboronic acid with methyllithium are summarized in Table I.

Table I. Effect of the Alkoxy Group on Boron on the Product Distribution in the Reaction of Various 1-Hexenylboronic Esters with MeLi at Different Temperatures[a]

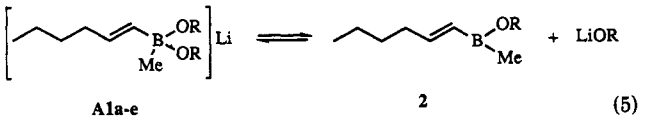
		yield,[d,e] %				
substrate[b]	temp,[c] °C	**2**	**1**	**3**	**4**	**7**
1a	−78[f]	7	48	1	10	14
	25[g]	5	45	4	20	15
1b	−78	77	23			
	25	77	16	7		
1c	−78	78	8	3	7	4
	25	63	5	25	2	4
1d	−78	66	21	1	10	2
	25[h]	44	19	19	14	1
1e	−78	24	1	76		
	25	29	1	68	1	1

[a] Reactions were carried out in THF using CH_3SO_3H as the acidic agent. [b] Refer to eq 3 in the text for individual substrates (1-hexenylboronic esters). [c] Temperature at which the acid was added. [d] Yields are based on ^{11}B NMR. [e] Refer to eq 4 in the text for individual products. [f] About 12% of **5** and 8% of **6** were also obtained. [g] About 8% of **5** and 7% of **6** were also obtained. [h] About 3% of **5** was also obtained.

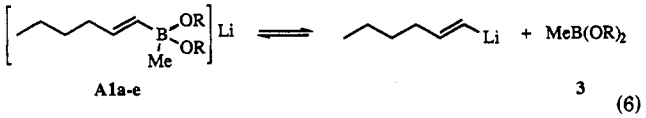
From the results in Table I, it is evident that a broad mixture of products is formed with the methyl ester (**1a**) and the cyclic esters (**1c–e**) examined. However, in the case of the isopropyl ester (**1b**) of 1-hexenylboronic acid, the reaction at −78 °C gives the desired alkylalkenylborinic ester selectively in 77% yield. The corresponding 1,3-propanediol ester (**1c**) also gives the desired alkenylborinic ester in 78% yield, but the reaction is not selective, forming other side products, such as dialkylborinate, alkylboronate, and borate, which can increase the difficulties involved in isolating the pure product.

The formation of each product in the above reaction can be tentatively rationalized by the following reaction pathways. The possible evidence for the proposed reaction routes is given in the text where the individual reaction or compound is discussed on the basis of ^{11}B NMR, other supplementary reactions, or the literature.

Methyl-1-hexenylborinate (2) and Methylboronate (3). The addition of methyllithium to 1-hexenylboronic esters **1a–e** at −78 °C forms the corresponding "ate" complexes **A1a–e**, methyl-1-hexenyldialkoxyborates (^{11}B NMR δ 7 ppm) (eq 3). This complex **A1** is in equilibrium with the desired borinic ester **2** and lithium alkoxide (eq 5). The formation of **3** suggests that there may be a small amount of **A1** in equilibrium with 1-hexenyllithium and methylboronate **3** (eq 6).



A1a-e **2** (5)



A1a-e **3** (6)

Depending upon the reaction conditions, the "ate" complex **A1**, on treatment with an acid, undergoes either an alkoxy oxygen–boron bond cleavage to give the desired borinic ester **2** (^{11}B NMR δ 47 ppm) or an alkenyl carbon–boron bond cleavage to give the methylboronate **3** (^{11}B NMR δ 31 ppm).

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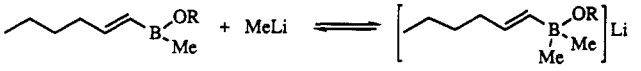
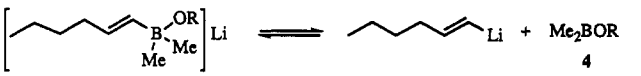
Dimethylborinate (4) and Dimethyl-1-hexenylborane (5). The desired borinic ester **2** is also susceptible to further reaction with another 1 equiv of methyllithium, if available, to give an "ate" complex, dimethyl-1-hexenylalkoxyborane **A2** (^{11}B NMR δ −18 ppm) (eq 7). This

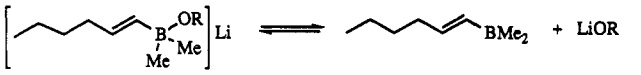


2 A2 (7)

"ate" complex **A2** may now be in equilibrium either with 1-hexenyllithium and dimethylborinate **4** (eq 8) or with dimethyl-1-hexenylborane **5** and lithium alkoxide (eq 9).



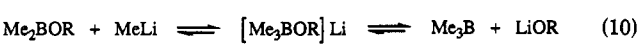
A2 4 (8)



A2 5 (9)

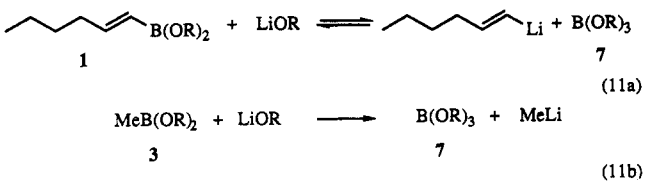
Here again, it is obvious that the formation of dimethylborinate **4** (^{11}B NMR δ 53 ppm), involves an alkenyl carbon–boron bond cleavage. The selective formation of **4** or **5** depends upon the reaction conditions.

Trimethylborane (6). Dimethylborinate **4** may also react with excess methyllithium present in the reaction mixture to give the corresponding "ate" complex **A4**, which may dissociate to trimethylborane (**6**; ^{11}B NMR δ 83 ppm) and lithium alkoxide (eq 10).



4 A4 6 (10)

Borate (7). The starting material, 1-hexenylboronate **1**, may also react with the lithium alkoxide, the side product obtained in the first reaction (eq 5), to give the borate **7** (^{11}B NMR δ 18 ppm) (eq 11a). However, one cannot rule out the possible direct formation of **7** from the reaction of the methylboronate with lithium alkoxide (eq 11b).



1 7 (11a)

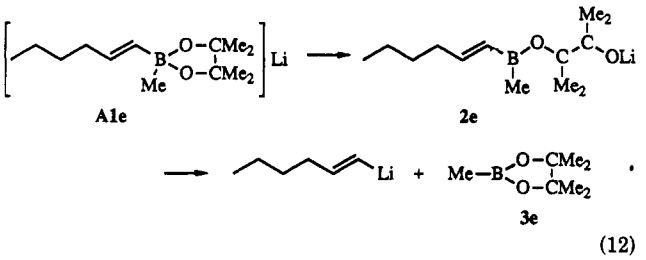
3 7 (11b)

It appears that both the favorable formation of the initial "ate" complex **A1** and the absence of any uncatalyzed self-decomposition are responsible for the acid-catalyzed selective reaction to give either **2**, the desired product, or **3**, the methylboronate. The primary objective of the present study, however, focuses on the selective formation of the desired product **2** by optimizing conditions, such as the effect of the alkoxy group on boron, the solvent, the temperature, the nature and the amount of the alkyllithium, and the acidic agent.

Effect of Alkoxy Group. From the results in Table I, it is quite clear that the choice of the alkoxy group on boron strongly influences the reaction selectivity. In the case of acyclic alkoxy boronic esters, the reaction of 1-hexenyldimethoxyborane (**1a**) with methyllithium is less selective and gives a greater mixture of products compared to that realized with 1-hexenyldiisopropoxyborane (**1b**). A similar result has also been observed for the methyl and isopropyl esters of the alkylboronic acids.[16a] The steric requirements of the alkoxy group probably play a significant role in this selectivity.

In the case of the cyclic esters of alkylboronic acids, such as 1,3-propanediol and pinacol esters, the dialkylborinic ester was obtained essentially as the only product.[16a] However, in the present study, under similar conditions, the corresponding alkenylboronic esters give a mixture of products, in contrast to the behavior of the alkylboronic esters.

In the case of cyclic esters, such as the 1,3-propanediol, the 1,2-ethanediol, and the pinacol esters of 1-hexenylboronic acid, in addition to cleavage of the oxygen–boron bond, yielding the desired borinic ester, **2**, cleavage of the alkenyl carbon–boron bond also occurs, giving various other products, such as the methylboronate **3** (eq 6), the dimethylborinate **4** (eq 8), and the borate **7** (eq 11). The enhanced labile nature of the 1-alkenyl– and aryl–boron bonds in the "ate" complexes has also been observed previously.[19] The labile nature of the 1-alkenyl group is expected to be greater for the cyclic esters than for the corresponding acyclic esters. Consequently, undesired alkylboronate and dialkylborinate are formed in the case of the cyclic esters. In the case of the pinacol ester, the methylboronate **3e** is formed as the major product. Even if there is a formation of the expected borinic ester **2e**, the alkoxide part of the cleaved ester may attack boron intramolecularly, eliminating the alkenyl part to give the more stable product **3e** (eq 12).



A1e 2e 3e (12)

A careful GC analysis of the products obtained from the reaction of the pinacol ester of 1-decenylboronic acid with *n*-butyllithium showed a quantitative formation of 1-decene, which may result from the dissociation of the "ate" complex into 1-decenyllithium.

From the above studies, it can be concluded that, of the esters examined, the isopropyl esters of alkenylboronic acids are preferred substrates for the preparation of the organylalkenylborinic esters.

Effect of Solvent and Temperature. After a favorable alkoxy group, isopropoxyl, was selected to achieve the desired synthesis, 1-hexenyldiisopropoxyborane was used as a model substrate for further study to understand the effects of solvent and temperature on the selectivity and yield.

The solvent often plays an important role in the rate and the selectivity of reactions in boron chemistry. For example, the selectivity in the reaction of trimethoxyborane[18] with methyllithium varies significantly with the solvent, giving a more favorable selectivity in ether or THF than in pentane. In contrast, a similar reaction of

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triisopropoxyborane with methyllithium is essentially solvent-independent, and the yields of the boronic esters are essentially the same in pentane, ether, and THF. This shows that the selectivity varies with both substrate and solvent. In the preparation of dialkylborinic esters, however, ether has been used irrespective of the nature of the substrate[16a,20] and no detailed study on the solvent effect has been carried out.

As mentioned earlier, the preparation of alkylalkenylborinic esters involves two important steps. The first is the formation of the "ate" complex. Alkenylboronic esters are known to form clean "ate" complexes with alkyllithium or Grignard reagents in ether.[8b,9c] However, the second step, the transformation of the "ate" complex by acid, is the crucial one which determines the overall product selectivity. This, in turn, depends upon various factors, such as solvent, temperature, and the acidic agent. Hence, a systematic study has been carried out using both polar and nonpolar solvents. The "ate" complex formation is very clean in polar solvents, such as ether and THF, as compared to that with nonpolar hexane. The reaction temperature also influences the reaction selectivity.

The reaction of 1-hexenyldiisopropoxyborane with methyllithium gives poor selectivity in hexane even at −78 °C. With higher alkyllithiums, such as *n*-butyllithium and *sec*-butyllithium, a nonhomogeneous gummy mass was obtained in the first step itself and the reaction could not be continued due to difficulties in stirring.

Even though "ate" complex formation is complete at −78 °C in both ether and THF, the "ate" complex is not stable at relatively higher temperature in ether. When the "ate" complex formed in ether is allowed to warm up slowly to room temperature, it decomposes to give a mixture of products. The ^{11}B NMR spectrum shows the formation of the desired borinic ester **2** (δ 47 ppm) in addition to other products, such as methylboronate **3** (δ 31 ppm), dimethylborinate **4** (δ 53 ppm), and borate **7** (δ 18 ppm). These side products may be formed from the alkenyl carbon–boron bond cleavage of the corresponding "ate" complexes (eqs 6, 8, and 11a). This shows that the alkenyl carbon–boron bond cleavage occurs at higher temperature. A similar observation has also been reported for the synthesis of (*E*)-1-substituted-1-hexenylboronic esters from 1-bromo-1-hexenylboronic esters and *n*-butyllithium.[21]

Surprisingly, the "ate" complex **A1** is quite stable in THF even at room temperature and the dissociation reaction observed in ether is not observed when the solution is brought to room temperature. It appears that both the formation and the stability of the "ate" complex depend on solvent and temperature. The results of the acid-catalyzed reactions of the 1-hexenylboronic ester with methyllithium in various solvents at different temperatures are given in Table II.

From the results in Table II, it is clear that the solvent influences the selectivity for the reaction of 1-hexenylboronic ester with methyllithium. The nonpolar solvent hexane is less selective as compared to polar solvents. The transformation of the "ate" complex by acid achieves a better selectivity in both ether and THF at the lower temperature (−78 °C). Thus, the second step depends on both solvent and temperature. The addition of acid in ether at relatively higher temperature, such as 0 or 25 °C, reduces both the selectivity and the yield of the desired borinic ester **2** with increased formation of side products. However, even though the addition of acid at 0 °C or at 25 °C gives the desired borinic ester in essentially the same yield in THF as that obtained at −78 °C, the formation of undesired side products occurs at the higher temperature. Hence, it is imperative to do the addition of the acid at −78 °C.

Table II. Effect of Solvent and Temperature on the Product Distribution in the Reaction of 1-Hexenyldiisopropoxyborane with MeLi[a]

		yield,[c,d] %				
solvent	temp,[b] °C	**2**	**1**	**3**	**4**	**7**
hexane	−78	43	35	9	20	5
	0[e]	25	24	15	12	2
	25[f]	21	29	19	9	2
ether	−78	73	25		2	
	0	65	19	10	6	
	25	64	22	12	2	
THF	−78	77	23			
	0	78	12	9		
	25	77	16	7		

[a] Reactions were carried out using CH_3SO_3H as the acidic agent. [b] Temperature at which the acid was added. [c] Yields are based on ^{11}B NMR. [d] Refer to eq 4 in the text for individual products. [e] About 10% of **5** and 12% of **6** were also obtained. [f] About 9% of **5** and 11% of **6** were also obtained.

Even though the initial experiments, as discussed above, suggest that THF is a better solvent than diethyl ether, further reactions have been carried out in both ether and THF to explore the possibility that the reaction selectivity with different acids and substrates might vary with solvent.

Effect of the Acidic Agent. In the conversion of alkylboronic esters to dialkylborinic esters, good selectivity has been achieved using anhydrous hydrogen chloride,[16a] acetyl chloride,[20] or trimethylsilyl chloride.[4] However, in our present study, a poor selectivity was realized with these acids under similar experimental conditions. In order to achieve a good yield and favorable selectivity, reactions were carried out with different acids, with both the nature and the amount being varied. To our surprise, it is observed in the case of alkylalkenylborinic esters that both the nature and the amount of acid play an important role in influencing both the yield and the selectivity.

Various Brønsted acids, such as hydrogen chloride and methanesulfonic acid, and Lewis acids, such as acetyl chloride, mono-, di-, and trichloroacetyl chloride, and trimethylsilyl chloride, have been used. The standard reaction, that of 1-hexenyldiisopropoxyborane and methyllithium, was carried out in both ether and THF at −78 °C. After the addition of the acid at −78 °C, the reaction mixture was slowly warmed up to room temperature and then maintained at room temperature until the transformation of the "ate" complex was complete. Different acids require different experimental conditions to get the desired borinic ester in good yield and selectivity. The results are summarized in Table III and IV.

Hydrogen Chloride. In the preparation of the dialkylborinic esters,[16a,20] it was sufficient to use 1.0 equiv of acid for the conversion of the "ate" complex to get the desired product selectively in good yield. However, in the case of alkenylborinic esters it was observed that both the nature and the amount of acid play an important role in influencing the product selectivity and yield.

(20) Brown, H. C.; Srebnik, M.; Cole, T. E. *Organometallics* **1986**, *5*, 2300.

(21) Brown, H. C.; Imai, T.; Bhat, N. G. *J. Org. Chem.* **1986**, *51*, 5277.

Table III. Effect of Various Brønsted Acids on the Product Distribution in the Reaction of 1-Hexenyldiisopropoxyborane with MeLi[a,b]

solvent	amt of MeLi, equiv[c]	amt of acid, equiv[c]	yield,[d,e] % 2	1	3	4
		HCl/Ether				
ether	1.0	1.0[f]		16	81	3
THF	1.0	1.0[f,g]	5	8	70	2
ether	1.0	1.3	73	27		
	1.0	1.5	77	9	1	13
	1.0	2.0	77	7	2	14
THF	1.0	1.3	81	8	4	5
	1.0	1.5	82	7	4	5
	1.0	2.0	82	7	4	5
	1.2	1.5	77	7	2	14
	1.2	1.8	77	9	1	13
		CH_3SO_3H				
ether	1.0	1.0	80	8	8	4
	1.0	1.3	80	5	2	13
	1.0	2.0	81	4	1	14
THF	1.0	1.0	77	23		
	1.0	1.3	77	16	7	
	1.0	2.0	78	15	6	1
	1.2	1.2	87	7	5	1
	1.2	1.2	80	5	1	14
	1.5	1.5	89	7	3	1

[a] Acid was added at −78 °C. [b] Reaction was complete in 1 h after room temperature was attained unless otherwise stated. [c] Amount in equivalents with respect to the substrate. [d] Yields are based on ^{11}B NMR. [e] Refer to eq 4 in the text for individual products. [f] Required 16 h for the reaction to be complete after room temperature was attained. [g] About 7% of **5** and 8% of **7** were also obtained.

Transformation of the "ate" complex using 1.0 equiv of anhydrous hydrogen chloride in ether (HCl/ether) gives the methylboronate **3** as the major product (Table III), but it takes a longer time (16 h at 25 °C) for the transformation to be complete. Continuation of the reaction for a long time, at room temperature, results in a shift of the equilibrium toward the formation of methylboronate **3** and 1-hexenyllithium (eq 6). The detection of a small amount of 1-hexene, in the reaction of 1-hexenyldicyclohexylborane with methyllithium followed by treatment with hydrogen chloride, along with the 1,2-migration product[22] supports the possible formation of some 1-hexenyllithium.

Surprisingly, in the present study, the addition of a slight excess of the acid selectively shifts the equilibrium toward the formation of the desired borinic ester **2** (eq 5) and the transformation of the "ate" complex is complete in 1 h after room temperature is attained.

Thus, a maximum yield of 81% of the desired product is achieved by using 1.3 equiv of HCl/ether. It was expected that use of excess alkyllithium might improve the yield and selectivity. However, the use of an excess of methyllithium (1.2 equiv) does not improve the yield of the borinic ester **2**. Instead, the yield of the borinic ester decreased slightly and more dialkylborinate **4** formed. Apparently, the desired product **2** undergoes further reaction with the excess methyllithium to give dimethylborinate **4** (eqs 7 and 8). No dimethyl-1-hexenylborane (**5**; eq 9) is detected in this reaction.

Methanesulfonic Acid. Since the reaction with hydrogen chloride (1.0 equiv) is very slow, it was thought that a stronger acid, such as methanesulfonic acid (CH_3SO_3H), might help in reducing the reaction time and increasing the yield and selectivity. As anticipated, a good yield of the desired product was achieved. The reaction is fast (1 h at 25 °C), and the yields are also comparable in both ether and THF. However, in terms of selectivity, THF gives better results.

(22) Zweifel, G.; Fisher, R. P. *Synthesis* 1974, 339.

Table IV. Effect of Various Lewis Acids on the Product Distribution in the Reaction of 1-Hexenyldiisopropoxyborane with MeLi[a,b]

solvent	amt of MeLi, equiv[c]	amt of acid, equiv[c]	yield,[d,e] % 2	1	3	4
		CH_3COCl				
ether	1.0	1.0	86	5	7	2
	1.0	1.3	85	6	8	1
	1.0	2.0	85	6	7	2
THF	1.0	1.0	85	6	7	2
	1.0	1.3	83	7	6	3
	1.0	2.0	84	6	6	4
ether	1.2	1.2	85	5	7	3
THF	1.2	1.2	86	6	5	3
		$ClCH_2COCl$				
ether	1.0	1.0	85	6	7	2
THF	1.0	1.0	89	5	2	4
	1.0	1.3	89	5	3	3
	1.0	2.0	88	4	5	3
		$Cl_2CHCOCl$				
ether	1.0	1.0	86	7	6	1
THF	1.0	1.0	86	6	5	3
		Cl_3CCOCl				
ether	1.0	1.0	85	7	7	1
THF	1.0	1.0	85	5	8	2
		Me_3SiCl				
ether	1.0	1.0[f]	60	14	21	5
	1.0	1.3[f]	82	4	12	2
	1.0	2.0[f]	86	4	9	1
THF	1.0	1.0[g]	71	12	12	5
	1.0	1.3	80	9	8	3
	1.0	2.0	89	4	6	1
	1.0	2.5	91	6	3	

[a] Acid was added at −78 °C. [b] Reaction was complete in 1 h after room temperature was attained unless otherwise stated. [c] Amount in equivalents with respect to the substrate. [d] Yields are based on ^{11}B NMR. [e] Refer to eq 4 in the text for individual products. [f] Required 14 h for the reaction to be complete after room temperature was attained. [g] Required 4 h for the reaction to be complete after room temperature was attained.

The results in Table III indicate that the yields of the borinic ester **2** are essentially the same irrespective of the amount of CH_3SO_3H used. However, with excess acid undesired byproducts, such as methylboronate **3** and dimethylborinate **4**, also appear. This suggests that CH_3SO_3H, a stronger acid, may cleave the alkenyl carbon–boron bond of the "ate" complex **A1** to give the corresponding alkenyllithium and the alkylboronate **3** (eq 6), which in turn reacts with excess methyllithium to give dimethylborinate **4** (eq 13). As pointed out earlier, the preparation of dialkylborinic esters from the corresponding alkylboronic esters and alkyllithiums has previously been reported.[16a]

$$\underset{\mathbf{3}}{\text{MeB(O-}i\text{-Pr)}_2} + \text{MeLi} \longrightarrow \underset{\mathbf{4}}{\text{Me}_2\text{BO-}i\text{-Pr}} + \text{LiO-}i\text{-Pr} \qquad (13)$$

The amount of alkyllithium also plays an important role in this reaction. Unlike hydrogen chloride, the yield of the desired product **2** is improved by using an excess of methyllithium (1.2 equiv) when CH_3SO_3H is used to transform the "ate" complex. A maximum yield of 87% of the desired borinic ester is obtained with 1.2 equiv of methyllithium and 1.0 equiv of methanesulfonic acid. Further increase in the amount of the alkyllithium and acid does not significantly improve the yield.

Acetyl Chloride and Mono-, Di-, and Trichloroacetyl Chlorides. A comparison of HCl/ether and CH_3-

SO_3H suggests that the strength and the amount of acid play an important role in influencing the yield and the selectivity of the formation of the desired alkylalkenylborinate. Even though the use of excess of acid increases the yield, it results in the formation of other side products. Therefore, it may be desirable to use weaker acids, such as acetyl and chloroacetyl chlorides, in excess.

In the case of acetyl chloride (AcCl), the results are essentially the same in both ether and THF irrespective of the amount of AcCl used (Table IV). A maximum yield of 85% of the desired borinic ester **2** is obtained under optimized conditions.

Chloroacetyl chlorides have also been used and compared with acetyl chloride in order to explore the effect of acid strength on selectivity. The results are given in Table IV. Since it was observed in the case of AcCl that the amount of acid does not affect the yield of the desired product, only 1 equiv of the chloroacetyl chlorides was used for the transformation reaction. A slightly better yield is obtained with chloroacetyl chloride in THF. The product selectivity is not affected by the use of an excess of chloroacetyl chloride. However, with di- and trichloroacetyl chlorides, the results are essentially the same as that of AcCl in both ether and THF. Thus, it is clear that in the cases of acetyl and chloroacetyl chlorides the selectivity and the yield of the products do not depend essentially upon the nature and the amount of the acid used for transformation of the "ate" complex.

In the case of HCl/ether, isopropyl alcohol is obtained as a byproduct. It forms an azeotropic mixture with some of the borinic esters and hence increases the difficulty in the isolation of the desired product in pure form. This is avoided with acetyl chloride, since the byproduct is volatile isopropyl acetate, readily separated by distillation.

Trimethylsilyl Chloride. Another Lewis acid, trimethylsilyl chloride (Me_3SiCl), has also been examined in the present study. In this case, the amount of the acid used significantly affects the yield of the desired product. Originally, it was thought that Me_3SiCl, a weak acid, would not form side products. However, the reaction with 1.0 equiv of Me_3SiCl, in both ether and THF, gives a mixture of products with very poor selectivity. The reaction time is also longer. Addition of an excess of the acid (2.0 equiv) improves the yield of the desired product **2** with a better selectivity realized in THF than in ether (Table IV). Irrespective of the amount of the acid used, the transformation reaction is very slow in ether (14 h at 25 °C) but essentially complete in 1 h in THF after attaining room temperature. A maximum yield of 91% of the desired product **2** has been achieved with 2.0 equiv of trimethylsilyl chloride in THF.

All these studies with different acids suggest that Me_3SiCl is the most convenient and efficient reagent for the selective transformation of the "ate" complex to get the desired product. However, our further studies suggest that the experimental conditions have to be varied to achieve good yield and selectivity for reactions with other alkyllithium reagents.

Reactions with Other Alkyllithium Reagents. It was expected that conditions similar to those for MeLi would give similar results with other alkyllithium reagents, such as *n*-BuLi, *sec*-BuLi, *tert*-BuLi, and PhLi. Surprisingly, this is not the case. Individual cases show small variations and require minor modifications to obtain the desired product in good yield. Ether is the preferred solvent for AcCl as the acidic agent. All other reactions with other acids are best in THF at −78 °C.

Table V. Comparison of the Effect of Various Acidic Agents on the Product Distribution in the Reaction of 1-Hexenyldiisopropoxyborane with Various RLi[a,b]

solvent	amt of RLi, equiv[c]	acid[d]	yield,[e,f] % 2	1	3	4
		n-BuLi				
THF	1.0	HCl/ether (1.3)	81	10	2	7
	1.2	HCl/ether (1.5)	79	6	1	14
	1.0	CH_3SO_3H (1.0)	73	26	1	
	1.2	CH_3SO_3H (1.2)	75	7	10	8
ether	1.0	CH_3COCl (1.3)	85	10	5	
THF	1.0	Me_3SiCl (2.0)	90	6	4	
	1.1	Me_3SiCl (2.10)	92	4	4	
		sec-BuLi				
THF	1.0	HCl/ether (1.3)	77	16	3	4
	1.2	HCl/ether (1.5)	87	10	3	
	1.0	CH_3SO_3H (1.0)	76	12	8	4
	1.2	CH_3SO_3H (1.2)	83	6	5	7
ether	1.0	CH_3COCl (1.3)	57	43		
	1.0	CH_3COCl (2.0)	63	21	7	9
	1.2	CH_3COCl (1.6)	76	24		
	1.5	CH_3COCl (1.95)	91	7	2	
THF	1.0	Me_3SiCl (2.0)	65	35		
	1.2	Me_3SiCl (2.4)	80	17	3	
	1.5	Me_3SiCl (3.0)	95	3	2	
	1.0	Me_3SiCl (3.0)	76	13	6	5
		t-BuLi				
THF	1.0	HCl/ether (1.3)	80	9	8	3
	1.2	HCl/ether (1.5)	93			7
	1.0	CH_3SO_3H (1.0)	66	32	1	1
	1.2	CH_3SO_3H (1.2)	72	10	9	9
ether	1.0	CH_3COCl (1.3)	82	18		
THF	1.0	Me_3SiCl (2.0)	95	3	2	
		PhLi				
THF	1.0	HCl/ether (1.3)	81	19		
	1.2	HCl/ether (1.5)	93	7		
	1.0	CH_3SO_3H (1.0)	87	13		
ether	1.0	CH_3COCl (1.3)	60	40		
	1.2	CH_3COCl (1.6)	81	19		
	1.5	CH_3COCl (1.95)	88	12		
	2.0	CH_3COCl (2.6)	92	8		
THF	1.0	Me_3SiCl (2.0)	71	29		
	1.2	Me_3SiCl (2.4)	88	12		
	1.5	Me_3SiCl (3.0)	92	8		
	2.0	Me_3SiCl (4.0)	92	8		

[a] Acid was added at −78 °C. [b] Reaction was complete in 1 h after room temperature was attained. [c] Amount in equivalents with respect to the substrate. [d] Values in parentheses represent equivalents with respect to the substrate. [e] Yields are based on ^{11}B NMR. [f] Refer to eq 4 in the text for individual products.

Reactions with *n*-BuLi. The results obtained with the reaction of 1-hexenyldiisopropoxyborane with *n*-BuLi are almost the same as those obtained with MeLi. The results are given in Table V. Use of 1.0 equiv of *n*-BuLi with a slight excess of HCl/ether (1.3 equiv) gives a maximum yield of 81% of the desired ester with other side products, such as *n*-butylboronate and di-*n*-butylborinate. Reaction with excess *n*-BuLi does not improve the yield but leads to the formation of dialkylborinate, as observed earlier with MeLi.

When CH_3SO_3H is used, unlike the case with MeLi, addition of excess *n*-BuLi does not show any improvement in the yield of the desired product and the selectivity is also poor. Reactions using AcCl or Me_3SiCl give results similar to those for MeLi. A maximum yield of 90% of the desired borinic ester is obtained under optimized conditions with Me_3SiCl.

Reactions with *sec*-BuLi. Reactions with *sec*-BuLi under optimized conditions give only a 65% yield of the

desired borinic ester. Irrespective of the nature and the amount of acid used, an excess of *sec*-BuLi (1.2–1.5 equiv) is required to form the desired product in good yield. The results are summarized in Table V.

To our surprise, when HCl/ether is used for transformation of the "ate" complex, use of excess *sec*-BuLi improves the yield of borinic ester and no dialkylborinate formation is noticed. This is probably due to the large steric interactions caused by the bulkier *sec*-butyl group.

In the case of AcCl, the amount of acid strongly influences the yield and selectivity, not observed earlier with MeLi or *n*-BuLi. Reaction with 1.0 equiv of *sec*-BuLi with a slight excess of the acid (1.3 equiv) gives the desired borinic ester in poor yield but with good selectivity. The same reaction with a large excess of the acid (2 equiv) gives very low selectivity. However, with an excess of *sec*-BuLi (1.2–1.5 equiv) both the yield and the selectivity are improved. A maximum yield of 91% of the borinic ester is obtained with 1.5 equiv of *sec*-BuLi and 1.9 equiv of AcCl. Similarly, when Me_3SiCl is used, under optimized conditions an excess of *sec*-BuLi (1.5 equiv) provides an excellent yield (95%) of the desired product.

Reactions with *t*-BuLi. Reaction with *t*-BuLi gives a very good yield of the desired product with HCl/ether or Me_3SiCl as the acidic agent (refer to Table V). However, when HCl/ether is used, an excess of *t*-BuLi (1.2 equiv) is needed to achieve the maximum yield. But in the case of Me_3SiCl, even with 1.0 equiv of the alkyllithium, a 95% yield of the borinic ester is realized under optimized conditions. Reactions with CH_3SO_3H or AcCl give only a moderate yield and a poor selectivity even with excess *t*-BuLi.

Reactions with PhLi. Phenyllithium was selected as a representative aromatic organolithium reagent. Surprisingly, the reaction with PhLi shows very good selectivity in all cases. Formation of side products is not significant. The results are summarized in Table V. In all cases, except for CH_3SO_3H, an excess of PhLi is needed to get the desired product in high yield. Thus, 1.2 equiv of PhLi is needed when HCl/ether is used and 1.5 equiv in the case of Me_3SiCl and 2.0 equiv in the case of AcCl to get a maximum yield of 90–93% of the borinic ester.

Purification. Like most organoboranes, alkylalkenylborinic esters are highly sensitive to air and moisture. Therefore, proper care should be taken during the isolation of these compounds by distillation. When the reaction product mixture contains impurities, such as alkylboronate, dialkylborinate, or starting material, redistribution can occur on prolonged heating during slow fractional distillation. Hence, rapid distillation is essential to avoid this problem. The presence of any undestroyed alkyllithium also causes decomposition of the alkylalkenylborinate at higher temperature during distillation. When excess alkyllithium is neutralized with excess acid, care should be taken, since the presence of even a trace of acid leads to decomposition at higher temperature.

From all the above results, it is clear that, only when Me_3SiCl is used, (i) the yields are very high (90–95%), (ii) the selectivity is very good and side-product formation is negligible, (iii) only in the cases of *sec*-BuLi and PhLi is excess alkyllithium needed, and (iv) even when excess Me_3SiCl is used, it can be easily removed under reduced pressure prior to distillation.

Thus, the alkyl-1-alkenylborinic esters can be prepared in high yields and purity by treating alkenylboronic esters with alkyllithium reagents in THF at −78 °C using Me_3SiCl, the most convenient reagent to transform the "ate" complex to the desired product. A series of organyl-1-alkenylborinic esters have been prepared in the present study. Usually the ^{11}B NMR spectrum of the isolated borinic esters indicates only a trace amount of either alkenylboronic ester or alkylboronic ester as an impurity, an impurity which should not affect further reactions.

Reactions of 1-Alkenylboronic Esters with Representative Grignard Reagents for the Selective Preparation of Alkyl-1-alkenylborinic Esters. In organic synthesis, the Grignard reagents complement alkyllithium reagents. Unlike alkyllithium reagents, Grignard reagents are readily available in a wide variety and the preparation is usually simple. After achieving the selective preparation of alkylalkenylborinic esters from the reaction of alkenylboronic esters with alkyllithium, we turned our attention to the applicability of Grignard reagents. To our knowledge, there is no report available in the literature on the preparation of borinic esters from the corresponding boronic esters with Grignard reagents. We therefore thought that the utilization of Grignard reagents might enhance both the scope and the selectivity of the synthesis of organylalkenylborinic esters.

It has been reported in the literature[18] that the reactions of trialkoxyboranes with Grignard reagents give a mixture of products. However, our present experience with alkyllithium reagents is very useful in optimizing conditions to achieve the desired selectivity. In fact, Grignard reagents can also be used to get the desired product in good yields and selectivity, by modifying the reaction conditions. We have been successful in preparing various alkylalkenylborinic esters in even higher yields and in better selectivity using Grignard reagents with a minor modification.

Initial experiments carried out under the conditions optimized for alkyllithium gave the desired borinic esters in poor yields. Since various factors, such as alkylating agent and acid, play an important role in the product selectivity, it was necessary to undertake a systematic study for the Grignard reagent procedure. The representative Grignard reagents selected for study were EtMgBr, *i*-PrMgCl, and *i*-BuMgBr. These reagents were selected to complement the alkyllithium reagents examined earlier.

Reactions with EtMgBr. In the present study, the reaction of 1-hexenyldiisopropoxyborane with EtMgBr was selected as a model reaction. Reactions were carried out using different acids at −78 °C. The results are given in Table VI.

From these results, it is clear that the reaction with 1.0 equiv of EtMgBr gives the borinic ester selectively, but in poor yields. However, the yield is improved considerably by increasing the amount of the Grignard reagent. Thus, the desired borinic ester is obtained in >98% yield with 2.0–2.5 equiv of EtMgBr using either HCl/ether or AcCl as the acidic agent. With CH_3SO_3H, 3 equiv of the Grignard reagent is necessary to get a maximum yield of 89%.

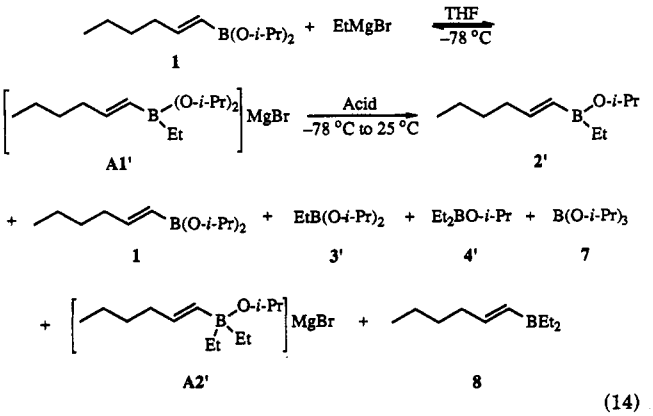
Me_3SiCl, the most convenient and efficient reagent used for alkyllithiums, gives lower yields and poorer selectivity with Grignard reagents. The yield does not improve significantly with an increase in the amount of the Grignard reagent. Instead, the side products increased. The side products, in this case, are mainly the "ate" complex **A2′** and the alkenyldialkylborane 8 in addition to a trace

Table VI. Comparison of the Effect of Various Acidic Agents on the Product Distribution in the Reaction of 1-Hexenyldiisopropoxyborane with RMgX[a,b]

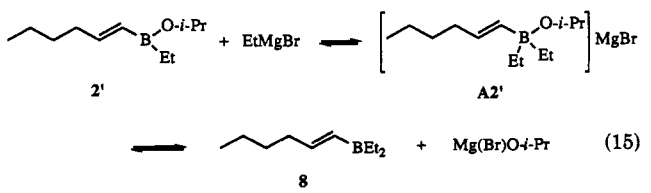
solvent	amt of RMgX, equiv[c]	acid[d]	yield,[e,f] % 2′	1	A2′	8	7
		EtMgBr					
THF	1.0	HCl/ether (1.3)	60	40			
	1.5	HCl/ether (2.0)	83	17			
	2.0	HCl/ether (2.6)	98	2			
	1.0	CH_3SO_3H (1.0)	50	50			
	1.5	CH_3SO_3H (1.0)	66	32			2
	2.0	CH_3SO_3H (2.0)[g]	84	13			
	3.0	CH_3SO_3H (3.0)[g]	89	8			
ether	1.0	CH_3COCl (1.3)	52	47			1
	1.5	CH_3COCl (1.8)	68	29			3
	2.0	CH_3COCl (2.6)	83	15			2
	2.5	CH_3COCl (3.25)	98	2			
THF	1.0	Me_3SiCl (2.0)	69	24	4	3	
	1.5	Me_3SiCl (3.0)[h]	82		11	2	
	2.0	Me_3SiCl (4.0)[i]	69		22	6	
		i-PrMgCl					
THF	2.0	HCl/ether (2.6)	95	5			
	2.0	CH_3SO_3H (2.0)	79	21			
	2.5	CH_3SO_3H (2.5)	81	19			
ether	2.0	CH_3COCl (2.6)	92	8			
THF	2.0	Me_3SiCl (4.0)	67		22	10	1
		i-BuMgBr					
THF	2.0	HCl/ether (2.6)	82	18			
	2.5	HCl/ether (3.25)	89	11			
	3.0	HCl/ether (3.9)	98	2			
	2.0	CH_3SO_3H (2.0)	59	33			8
ether	2.0	CH_3COCl (2.6)	78	22			
	2.5	CH_3COCl (3.25)	78	22			
THF	2.0	Me_3SiCl (4.0)	82		18		

[a] Acid was added at −78 °C. [b] Reaction was complete in 1 h after room temperature was attained. [c] Amount is equivalents with respect to the substrate. [d] Values in parentheses represent equivalents with respect to the substrate. [e] Yields are based on ^{11}B NMR. [f] Refer to eq 14 in the text for individual products. [g] About 3% of 4′ was also obtained. [h] About 5% of 3′ was also obtained. [i] About 3% of 3′ was also obtained.

amount of alkylboronate 3′. However, no dialkylborinate, produced in the case of alkyllithium, is detected in the reactions with the Grignard reagent. Apparently, the borinic ester 2′ (^{11}B NMR δ 47 ppm) formed reacts with excess Grignard reagent to give the more stable "ate" complex A2′ (^{11}B NMR δ −18 ppm), which in turn gives diethyl-1-hexenylborane 8 (^{11}B NMR δ 75 ppm) (eq 15).



(14)



(15)

A similar observation has been observed earlier by Kramer and Brown[17] in the alkylation of B-methoxy-9-BBN with Grignard reagents.

Reactions with *i*-PrMgCl and *i*-BuMgBr. Since 2.0 equiv of Grignard reagent is required in the case of EtMgBr to get a maximum yield, 2 equiv is also used in the reactions of *i*-PrMgCl and *i*-BuMgBr. The results are shown in Table VI. In the case of *i*-PrMgCl, the desired product is obtained in 92–95% yield with HCl/ether or AcCl. However, with CH_3SO_3H, an inferior yield is obtained. With Me_3SiCl, the desired product is obtained in low yield along with the "ate" complex A2′ and the borane 8.

In the case of *i*-BuMgBr, even with 2.0 equiv of the Grignard reagent, the desired product is obtained only in low yield in all cases. However, by using 3.0 equiv of Grignard reagent and HCl/ether, the desired borinic ester is obtained in 98% yield.

Thus, it is important to note that Grignard reagents can also be used for the preparation of alkylalkenylborinic esters from alkenylboronic esters, complementing the alkyllithium route. In this case, HCl/ether is the better acidic agent. Thus, the ethyl-, isopropyl-, and isobutyl-1-hexenylborinic esters are prepared in excellent yield from 1-hexenyldiisopropoxyborane and the corresponding Grignard reagents. The ^{11}B NMR spectrum of the isolated borinic esters indicates only a trace amount of either alkenylboronic ester or alkylboronic ester to be present as an impurity in the isopropyl and isobutyl substituted products.

Conclusion

This is the first systematic, detailed study of the reactions of alkenylboronic esters with representative organolithium and Grignard reagents. This route has been developed into a simple, efficient, general procedure for the preparation of organylalkenylborinic esters. The present study reveals that various factors, such as the nature and the amount of alkyllithium or Grignard reagent, the solvent, the reaction temperature, and the nature and the amount of acid used, play significant roles in both the yield and the selectivity of the desired product. From this detailed study, it has been established that, for the preparation of alkylalkenylborinic esters from the alkenylboronic esters in good yield and selectivity, (i) two isopropoxy groups on boron in the substrate are most favorable, (ii) THF is the best solvent, (iii) the acid should be added at −78 °C, (iv) Me_3SiCl is the most convenient and efficient acidic agent for reactions with alkyllithium reagents, and (v) HCl/ether is the most suitable reagent for reactions with Grignard reagents. The conditions have been optimized, and simple and efficient synthetic procedures are now available for the synthesis of organylalkenylborinic esters in good yields and purity. These compounds are now available for use as intermediates for organic synthesis or for conversion into other organoboranes. Further research on the application of these organylalkenylborinates as versatile intermediates to various organic transformations is in progress.

Experimental Section

General Comments. All glassware was thoroughly dried in an air oven, assembled hot and cooled under a stream of argon. The degassed, anhydrous solvents hexane and ethyl ether (Mallinkrodt) were stored over 4-Å molecular sieves under argon and used. THF was freshly distilled from sodium benzophenone

ketyl and stored under an argon atmosphere. The organolithium reagents, Grignard reagents, methanesulfonic acid, acetyl chloride, mono-, di-, and trichloroacetyl chloride, and trimethylsilyl chloride are commercial materials (Aldrich). The concentration of organolithium and Grignard reagents was standardized prior to use. The other commercial materials were distilled and then used. The boronic esters were prepared using the reported procedures.[23] The anhydrous hydrogen chloride in ether solution (1.17 M) was prepared by using a Brown[2] apparatus from hydrochloric acid and sulfuric acid[24] and standardized by titrating with a standard solution of sodium hydroxide.

The ^1H and ^{13}C NMR spectra were recorded on a 300-MHz instrument, and the chemical shift values are in δ (ppm) relative to tetramethylsilane. ^{11}B NMR spectra were also recorded on a 300-MHz instrument, and the values are in δ (ppm) relative to $BF_3{\cdot}OEt_2$. Since these compounds are highly sensitive to air and moisture, the mass spectral and elemental analyses could not be done. All the following reactions were carried out under an argon atmosphere.

General Procedure Determining the Product Selectivity for the Reaction of 1-Alkenylboronic Esters with Alkyllithium or Grignard Reagents. A simple and general procedure for the reaction of 1-alkenylboronic esters with alkyllithium or Grignard reagents is described as follows. In a 50-mL round-bottom flask fitted with a magnetic stirring bar and rubber septum, 5 mL of solvent and 2.5 mmol of 1-hexenylboronic ester are mixed and kept at −78 °C. One equivalent of alkyllithium or Grignard reagent is added dropwise using a syringe. The resulting mixture is stirred at −78 °C for 3 h. A sample is removed and checked by ^{11}B NMR to confirm the complete formation of the "ate" complex. Then, the required amount of the acid (HCl/ether, CH_3SO_3H, AcCl, $ClCH_2COCl$, $Cl_2CHCOCl$, Cl_3CCOCl, or Me_3SiCl) is added. The reaction mixture is warmed slowly to room temperature. Stirring is continued at room temperature until the decomposition of the intermediate "ate" complex is complete. The reaction mixture is analyzed by ^{11}B NMR. The percentages of the various products and the starting material obtained are estimated from the intensity of the corresponding peaks. The results are shown in Tables I–VI.

General Procedure for the Isolation of Alkyl-1-alkenylborinic Esters Using Alkyllithium. A simple and general procedure for the preparation and isolation of alkyl-1-alkenylborinic esters using alkyllithium reagents is described as follows. In a round-bottom flask fitted with a magnetic stirring bar and adapter, the required amounts of THF and alkenylboronic ester are mixed and kept at −78 °C. Then, alkyllithium (1 equiv in the cases of MeLi, *n*-BuLi, and *t*-BuLi and 1.5 equiv in the cases of *sec*-BuLi and PhLi) is added slowly using a double-ended needle. The reaction mixture is stirred for 3 h. Me_3SiCl (2 equiv with respect to alkyllithium) is then added dropwise. The reaction mixture is warmed slowly to room temperature and stirred for an additional 1 h at room temperature. The reaction mixture is diluted with anhydrous hexane. The solution is transferred to a centrifuge bottle through a double-ended needle and centrifuged. The clear organic layer is separated from the lithium chloride precipitate and transferred into another round-bottom flask using a double-ended needle. After the solvent is removed using a water aspirator (~25 mmHg), the residual material is distilled under reduced pressure.

Methyl-1-hexenylisopropoxyborane. The reaction is carried out as described above using 1-hexenyldiisopropoxyborane (10.55 g, 50 mmol), methyllithium (0.65 M, 77 mL, 50 mmol), and Me_3SiCl (12.6 mL, 100 mmol). Distillation yielded 7.1 g of product (42.5 mmol, 85%): bp 72–74 °C (15 mmHg); ^{11}B NMR (THF) δ (ppm) +46.6; ^1H NMR ($CDCl_3$) δ (ppm) 0.45 (s, 3H), 0.9 (t, 3H), 1.15–1.45 (m, 10H), 2.15 (m, 2H), 4.4 (m, 1H), 5.69 (d, 1H, J = 18 Hz), 6.55 (dt, 1H, J = 18, 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm) 13.9, 22.2, 24.5, 30.6, 35.5, 67.5, 125.0, 154.0.

(23) Brown, H. C.; Bhat, N. G.; Somayaji, V. *Organometallics* **1983**, *2*, 1311.

(24) Brown, H. C.; Rei, M. H. *J. Org. Chem.* **1966**, *31*, 1090.

***n*-Butyl-1-hexenylisopropoxyborane.** The reaction is carried out as described above using 1-hexenyldiisopropoxyborane (10.55 g, 50 mmol), *n*-butyllithium (2.2 M, 22.5 mL, 50 mmol), and Me_3SiCl (12.6 mL, 100 mmol). Distillation yielded 8.8 g of product (42 mmol, 84%): bp 106–108 °C (15 mmHg); ^{11}B NMR (THF) δ (ppm) +46.4; ^1H NMR ($CDCl_3$) δ (ppm) 0.9 (m, 8H), 1.1–1.4 (m, 14H), 2.15 (m, 2H), 4.45 (m, 1H), 5.7 (d, 1H, J = 18 Hz), 6.5 (dt, 1H, J = 18, 6.2 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm) 13.9, 22.3, 24.4, 24.6, 25.8, 27.2, 30.7, 35.7, 67.1, 124.0, 153.5.

***sec*-Butyl-1-hexenylisopropoxyborane.** The reaction is carried out as described above using 1-hexenyldiisopropoxyborane (2.11 g, 10 mmol), *sec*-butyllithium (1.35 M, 11.1 mL, 15 mmol), and Me_3SiCl (3.78 mL, 30 mmol). Distillation yielded 1.6 g of product (7.5 mmol, 75%): bp 104–106 °C (15 mmHg); ^{11}B NMR (THF) δ (ppm) +46.5; ^1H NMR ($CDCl_3$) δ (ppm) 0.9 (m, 8H), 1.1–1.5 (m, 14H), 2.25 (m, 2H), 4.45 (m, 1H), 5.75 (d, 1H, J = 17.6 Hz), 6.55 (dt, 1H, J = 17.6, 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm) 13.8, 22.3, 24.4, 24.7, 26.7, 30.7, 35.8, 66.6, 126.5, 152.9.

***tert*-Butyl-1-hexenylisopropoxyborane.** The reaction is carried out as described above using 1-hexenyldiisopropoxyborane (2.11 g, 10 mmol), *tert*-butyllithium (1.58 M, 6.3 mL, 10 mmol), and Me_3SiCl (2.52 mL, 20 mmol). Distillation yielded 1.7 g of product (8.2 mmol, 82%): bp 100–102 °C (15 mmHg); ^{11}B NMR (THF) δ (ppm) +47.8; ^1H NMR ($CDCl_3$) δ (ppm) 0.9 (m, 11H), 1.1–1.4 (m, 11H), 2.25 (m, 2H), 4.45 (m, 1H), 5.65 (d, 1H, J = 18 Hz), 6.2 (dt, 1H, J = 18 Hz, 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm) 14.0, 22.3, 24.6, 27.6, 31.1, 36.3, 67.7, 126.0, 146.8.

Phenyl-1-hexenylisopropoxyborane. The reaction is carried out as described above using 1-hexenyldiisopropoxyborane (2.11 g, 10 mmol), phenyllithium (1.88 M, 7.9 mL, 15 mmol), and Me_3SiCl (3.78 mL, 30 mmol). Distillation yielded 1.8 g of product (7.8 mmol, 78%): bp 88–90 °C (0.05 mmHg); ^{11}B NMR (THF) δ (ppm) +43.1; ^1H NMR ($CDCl_3$) δ (ppm) 0.9 (t, 3H), 1.1–1.5 (m, 10H), 2.2 (m, 2H), 4.6 (m, 1H), 6.0 (d, 1H, J = 17.8 Hz), 6.4 (dt, 1H, J = 17.8, 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm) 13.9, 22.3, 24.7, 30.8, 36.1, 68.4, 127.4, 128.7, 129.8, 134.4, 156.2.

General Procedure for the Isolation of Alkyl-1-alkenylborinic Esters Using Grignard Reagents. A simple and general procedure for the preparation and isolation of alkyl-1-alkenylborinic esters using Grignard reagents is described as follows. In a round-bottom flask fitted with a magnetic stirring bar and adapter, 20 mL of THF and 10 mmol of the alkenylboronic ester are mixed and kept at −78 °C. The required amount of Grignard reagent (2 equiv in the cases of EtMgBr and *i*-PrMgCl and 3 equiv in the case of *i*-BuMgBr) is added slowly using a syringe. The reaction is stirred at −78 °C for 3 h. Then, HCl/ether (1.3 equiv with respect to the Grignard reagent) is added dropwise. The reaction mixture is then warmed slowly to room temperature and stirred for an additional 1 h at room temperature. The reaction mixture is diluted with anhydrous hexane. The solution is transferred to a centrifuge bottle using a double-ended needle and centrifuged. The clear organic layer is transferred into another round-bottom flask using a double-ended needle. After the solvent is removed using water aspirator (~25 mmHg), the residual material is distilled under reduced pressure.

Ethyl-1-hexenylisopropoxyborane. The reaction is carried out as described above using 1-hexenyldiisopropoxyborane (2.11 g, 10 mmol), EtMgBr (1.04 M, 19.2 mL, 20 mmol), and HCl/ether (1.17 M, 22.2 mL, 26 mmol). Distillation yielded 1.6 g of product (9 mmol, 90%): bp 78–80 °C (15 mmHg); ^{11}B NMR (THF) δ (ppm) +45.9; ^1H NMR ($CDCl_3$) δ (ppm) 0.9 (m, 8H), 1.18–1.45 (m, 10H), 2.25 (m, 2H), 4.45 (m, 1H), 5.7 (d, 1H, J = 17.6 Hz), 6.5 (dt, 1H, J = 17.6, 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm) 8.6, 10.0, 13.9, 22.3, 24.8, 30.9, 35.8, 67.0, 128.0, 153.6.

Isopropyl-1-hexenylisopropoxyborane. The reaction is carried out as described above using 1-hexenyldiisopropoxyborane (2.11 g, 10 mmol), *i*-PrMgCl (1.975 M, 10.1 mL, 20 mmol), and HCl/ether (1.17 M, 22.2 mL, 26 mmol). Distillation yielded 1.67 g of product (8.6 mmol, 86%): bp 86–88 °C (15 mmHg); ^{11}B NMR (THF) δ (ppm) +46.7; ^1H NMR ($CDCl_3$) δ (ppm) 0.9 (m, 8H), 1.1–1.4 (m, 12H), 2.15 (m, 2H), 4.45 (m, 1H), 5.75 (d, 1H,

J = 17.6 Hz), 6.52 (dt, 1H, J = 17.6, 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm) 13.9, 18.7, 22.4, 24.7, 30.9, 36.0, 66.8, 124.0, 153.0.

Isobutyl-1-hexenylisopropoxyborane. The reaction is carried out as described above using 1-hexenyldiisopropoxyborane (2.11 g, 10 mmol), *i*-BuMgBr (2.075 M, 14.5 mL, 30 mmol), and HCl/ether (1.17 M, 33.3 mL, 39 mmol). Distillation yielded 1.8 g of product (8.7 mmol, 87%): bp 100–102 °C (15 mmHg); ^{11}B NMR (THF) δ (ppm) +47.0; ^{1}H NMR ($CDCl_3$) δ (ppm) 0.9 (m, 12H), 1.2–1.45 (m, 9H), 1.9 (m, 1H), 2.2 (m, 2H), 4.5 (m, 1H), 5.8 (d, 1H, J = 17.5 Hz), 6.55 (dt, 1H, J = 17.5 Hz, 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm) 14.0, 19.1, 22.4, 24.6, 24.8, 25.6, 30.9, 35.8, 67.2, 128.0, 153.9.

Acknowledgment. We wish to thank the National Science Foundation (Grant CHE-9012236) for financial support of this work.

Supplementary Material Available: ^{11}B NMR, ^{1}H NMR, and ^{13}C NMR spectra for various alkyl-1-hexenylisopropoxyboranes (alkyl = Me, *n*-Bu, *sec*-Bu, *t*-Bu, Ph, Et, *i*-Pr, *i*-Bu) (25 pages). Ordering information is given on any current masthead page.

OM920623O