

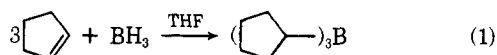
# Hydroboration. XL. Hydroboration of Alkenes and Alkynes with Monochloroborane Etherates. Convenient Procedures for the Preparation of Dialkyl-, Monoalkyl-, and Dialkenylchloroboranes and Their Derivatives<sup>1</sup>

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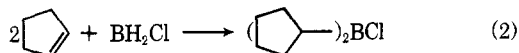
Contribution from the Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907. Received May 19, 1975

**Abstract:** The reactions of monochloroborane tetrahydrofuranate ( $\text{BH}_2\text{Cl}\cdot\text{THF}$ ) and monochloroborane ethyl etherate ( $\text{BH}_2\text{Cl}\cdot\text{EE}$ ) with alkenes and alkynes have been studied to establish their hydroborating characteristics. The reaction of  $\text{BH}_2\text{Cl}\cdot\text{THF}$  with alkenes in tetrahydrofuran (THF) is slow and gives a mixture of products. On the other hand,  $\text{BH}_2\text{Cl}\cdot\text{EE}$  hydroborates a variety of alkenes (in the stoichiometric 1:2 ratio) in ethyl ether (EE) rapidly and quantitatively at 0 °C to give the corresponding dialkylchloroborane ( $\text{R}_2\text{BCl}$ ) cleanly. This reaction exhibits an unusually powerful directive effect resulting in the formation of the major product (the less hindered derivative) in exceptionally high isomeric purity. A representative series of  $\text{R}_2\text{BCl}$  and their derivatives were synthesized and isolated by this reaction. This reaction provides a valuable route to these derivatives. The reaction of  $\text{BH}_2\text{Cl}$  with alkenes in 1:1 ratio in EE at 0 °C produces a mixture of  $\text{RBHCl}$  and  $\text{R}_2\text{BCl}$ . But the reaction can be controlled to obtain  $\text{RBHCl}$  cleanly by adding 1.2–2.0 equiv of tetrahydrofuran to the reaction mixture. Several representative  $\text{RBHCl}$  derivatives were synthesized and isolated as their trimethylamine complexes.  $\text{RBHCl}$  and their amine complexes constitute new classes of organoboron compounds.  $\text{RBHCl}$  reacts with  $\text{HCl}$  in EE at 25 °C to give  $\text{RBCl}_2$  and undergoes alcoholysis to produce  $\text{RB(OR')}_2$ . The reaction of alkynes with  $\text{BH}_2\text{Cl}$  (2:1) in tetrahydrofuran is slow. The corresponding reaction in EE is extremely fast at 0 °C and in the case of internal alkynes, produces dialkenylchloroboranes cleanly. In the case of terminal alkynes, the dialkenylchloroboranes are formed relatively cleanly only if 30–40% excess alkyne is used. Representative dialkenylchloroboranes were synthesized and isolated by this procedure. This reaction provides the first general method for the syntheses of this class of compounds. The dihydroboration of alkynes with  $\text{BH}_2\text{Cl}$  (1:1) is slow in tetrahydrofuran, but rapid and complete in EE. In the reaction of internal alkynes with  $\text{BH}_2\text{Cl}$  (1:1) in tetrahydrofuran at 0 °C, the formation of the intermediate product, alkenylchloroborane, in good yield is observed after 1 h of reaction. The observed yield of the alkenylchloroborane in the corresponding reaction involving terminal alkynes is low. The reaction of  $\text{BH}_2\text{Cl}$  in EE with alkynes (1:1) is so fast that the formation of the intermediate alkenylchloroborane cannot be detected.

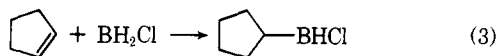
Hydroboration of alkenes with borane–tetrahydrofuran ( $\text{BH}_3\cdot\text{THF}$ ) generally produces the corresponding trialkylborane quantitatively (eq 1).<sup>3</sup> This reaction is useful to ob-



tain partially alkylated boron derivatives only in very limited cases.<sup>3</sup> In the reaction of alkenes with monochloroborane ( $\text{BH}_2\text{Cl}$ ) one would expect to obtain the partially alkylated boron derivative, dialkylchloroborane ( $\text{R}_2\text{BCl}$ ), as the end product (eq 2). One could hope to control this reaction to



provide the corresponding monoalkylboron derivative also (eq 3). Similarly, the monohydroboration of alkynes with



$\text{BH}_2\text{Cl}$  would provide methods for the synthesis of the corresponding alkenylboron derivatives. In analogy with the numerous synthetic uses of the trialkylboranes,<sup>3</sup> these partially alkylated and alkenylated boron derivatives would also be expected to provide potentially valuable intermediates in organic synthesis.

The monochloroborane–ether addition compounds were discovered by Brown and Tierney.<sup>4</sup> Since then some studies of the hydroboration of alkenes with  $\text{BH}_2\text{Cl}\cdot\text{THF}$  have been reported independently by Zweifel<sup>5</sup> and Pasto.<sup>6</sup> Zweifel prepared the solution of  $\text{BH}_2\text{Cl}$  in tetrahydrofuran (THF) by the reaction of borane in THF with 1 equiv of  $\text{HCl}$  in THF. Convincing ir spectral evidence has been provided to

substantiate the formation of  $\text{BH}_2\text{Cl}$ . The rate of reaction of various olefins with  $\text{BH}_2\text{Cl}$  in THF (olefin: $\text{BH}_2\text{Cl}$  = 2:1) at 0 °C was reported by Zweifel. The reaction was found to be slow and incomplete. Depending on the structure of the olefin, 24–88% reaction was observed in 24 h. From the rate and stoichiometry of the olefin utilized, Zweifel concluded that the reaction proceeded fairly rapidly to the monoalkylchloroborane stage. The second stage, i.e., the formation of the dialkylchloroborane ( $\text{R}_2\text{BCl}$ ), was very slow. The apparently clean formation of monoalkylchloroborane ( $\text{RBHCl}$ ) was utilized to synthesize *n*-hexylboronic acid in 67% yield by hydrolyzing the reaction mixture of 1-hexene and  $\text{BH}_2\text{Cl}$  (1:1) in THF after 12 h at 0 °C. In these studies no attempt was made to establish the formation of  $\text{R}_2\text{BCl}$ .

Pasto's group prepared  $\text{BH}_2\text{Cl}$  according to the procedure of Brown and Tierney<sup>4</sup> by the reaction of  $\text{BCl}_3$  with  $\text{BH}_3$  in THF. (In certain experiments,  $\text{BCl}_3$  in tetrahydropyran was added to  $\text{BH}_3$  in THF.) When excess 2-methylpropene was treated with  $\text{BH}_2\text{Cl}$  in THF for 6 h at 25 °C, only 56% alcohol was obtained upon oxidation of the reaction mixture. On oxidizing a reaction mixture of 1-hexene and  $\text{BH}_2\text{Cl}$  in 2:1 ratio in THF, after 72 h of reaction at 25 °C, the authors obtained hexanols in only 42% yield. Considerable olefin remained at the end of this period. This led them to believe that the reaction proceeds only to the monoalkylchloroborane ( $\text{RBHCl}$ ) stage, which was presumed to have been confirmed by methanolizing the reaction mixture and analyzing for the dimethyl alkylboronate formed by <sup>11</sup>B NMR.

It should be commented here that solvolysis of the reaction mixture followed by the identification of the solvolysis product is not conclusive evidence for the existence of

Table I. Rate of Reaction of Olefins with Monochloroborane in Tetrahydrofuran (BH<sub>2</sub>Cl:Olefin = 1:2)

BH <sub>2</sub> Cl concn, M	Olefin	Temp, °C	Time, h	Olefin reacted, %
0.5	1-Hexene	25	1.0	46
			6.0	72
			24.0	86
1.0	1-Hexene	0	0.5	55
			1.0	69
			8.0	86
			24.0	90
1.6	1-Hexene	0	1.0	77
			6.0	93
			24.0	95
1.0	1-Hexene	25	1.0	88
			6.0	97
			24.0	99
1.0	<i>cis</i> -3-Hexene	25	1.0	85
			6.0	94
			24.0	95
1.6	<i>cis</i> -3-Hexene	25	1.0	94
			3.0	96
			24.0	98

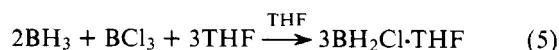
RBHCl in solution, owing to the possible equilibrium shown below (eq 4). All three species would give the same product on solvolysis. However, both Zweifel and Pasto relied on this method to conclude that RBHCl was formed cleanly by the reaction of olefins with BH<sub>2</sub>Cl in THF.



Since we felt that the possible potential of BH<sub>2</sub>Cl as a hydroborating agent had not been adequately defined by these earlier studies, we undertook a study of the reaction of BH<sub>2</sub>Cl with alkenes under controlled conditions in different solvents, analyzing for all the products formed, so that a clear understanding of the hydroboration of alkenes with BH<sub>2</sub>Cl could be achieved. It was felt desirable to extend this study to include alkynes also since no work had been previously described on the hydroboration of alkynes with BH<sub>2</sub>Cl.

## Results and Discussion

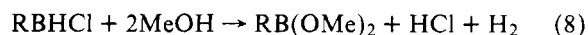
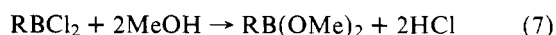
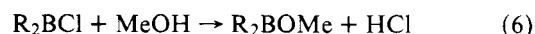
**Hydroboration of Alkenes with BH<sub>2</sub>Cl in THF.** The BH<sub>2</sub>Cl in THF solution was prepared by absorbing the stoichiometric quantity of boron trichloride into a solution of diborane in THF (eq 5). The <sup>11</sup>B NMR spectrum of the solution displayed a symmetrical triplet at -4.2 ppm (relative to BF<sub>3</sub>·EE) with *J*<sub>BH</sub> = 132 Hz. Proton heteronuclear spin decoupling produced a singlet showing that BH<sub>2</sub>Cl is the only boron containing species present in solution. The reagent was estimated to be >97% pure.



The rate of reaction of 1-hexene and *cis*-3-hexene with BH<sub>2</sub>Cl in THF was studied. The general procedure was to add 10 mmol of the olefin to 5 mmol of BH<sub>2</sub>Cl in sufficient THF, containing a known amount of *n*-octane (internal standard for GC analysis), so that the desired concentration of the reagent was obtained. The reaction mixture was stirred at 0 or 25 °C, as desired, and the rate of disappearance of olefin was followed by analyzing aliquots of the reaction mixture by GC at various times of the reaction. The results are given in Table I.

The reaction was fairly slow at 0 °C in agreement with the observations of previous workers, but on raising the reaction temperature to 25 °C and using higher concentrations of the reagents, both 1-hexene and *cis*-3-hexene reacted more than 95% in less than 6 h. This was encouraging.

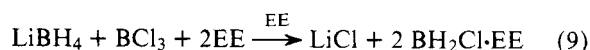
Therefore, we investigated the products formed in this reaction. For this purpose, 1-butene and *cis*-2-butene were used as the representative olefins so that the *B*-methoxyborane products obtained by the methanolysis of the reaction mixture could be analyzed by GC.<sup>7</sup> The general procedure was to add 5 mmol of butene to 2.5 mmol of BH<sub>2</sub>Cl in sufficient THF containing a known amount of tridecane (internal standard for GC analysis) so that the desired concentrations were obtained. The reaction mixture was stirred at 0 or 25 °C, as desired, for the specified period of time. The reaction products were methanolized by adding excess methanol. The HCl produced by the methanolysis of the chloroboranes was neutralized with triethylamine, and the reaction mixture was analyzed for the products, tributylboranes, methyl dibutylborinate, and dimethyl butylboronates by GC using a SE-30 column.<sup>7</sup> The results are given in Table II. The R<sub>2</sub>BOMe and RB(OMe)<sub>2</sub> were produced by the methanolysis of the corresponding alkylchloroboranes (eq 6-8). Therefore, the amount of the individual *B*-methoxyboranes provided a direct measure of the corresponding dialkyl- or monoalkylboron compounds formed in the reaction. The data in Table II establish that the major products in the reaction of BH<sub>2</sub>Cl with olefins in THF are the trialkylboranes and the monoalkylboron compounds and not the desired dialkylchloroboranes.



It is known that in the presence of boron hydrides, alkylboranes undergo equilibration to produce a mixture of products.<sup>8</sup> It is conceivable that alkylchloroborane compounds can also undergo such equilibration in the presence of boron hydrides. Since the time required for the completion of the reaction of BH<sub>2</sub>Cl with olefins in THF is quite long, there is always present sufficient free boron hydride species to cause the equilibration. Therefore, the reason for obtaining a mixture of products is probably the very low reactivity of BH<sub>2</sub>Cl in THF and the consequent low rate and long reaction times.

It occurred to us that the reason for this very low reactivity of BH<sub>2</sub>Cl in THF could be the strong complexation of the reagent with the highly basic THF rendering the boron atom much less reactive toward the alkenes. Therefore, we undertook to investigate the reaction of olefins with BH<sub>2</sub>Cl in a less basic solvent, such as diethyl ether.

**Hydroboration of Alkenes with BH<sub>2</sub>Cl in Diethyl Ether (EE).** Solutions of BH<sub>2</sub>Cl in EE were prepared by the reaction of LiBH<sub>4</sub> in EE with BCl<sub>3</sub> in EE at 0 °C (eq 9). The



lithium chloride is insoluble in EE and therefore settled on keeping the mixture at 0 °C, leaving a clear solution of BH<sub>2</sub>Cl. The hydride strength of BH<sub>2</sub>Cl was determined by hydrolyzing and measuring the hydrogen evolved. The chloride was estimated by hydrolysis, followed by the titration of the HCl produced with NaHCO<sub>3</sub> solution using methyl orange as indicator. The solution of BH<sub>2</sub>Cl in EE remained stable at 0 °C (cold room) for several weeks. The <sup>11</sup>B NMR spectrum of BH<sub>2</sub>Cl in EE solution displayed a symmetrical triplet at -5.0 ± 0.3 ppm (relative to BF<sub>3</sub>·EE) with *J*<sub>BH</sub> = 136 Hz. (The downfield shift in the <sup>11</sup>B resonance of BH<sub>2</sub>Cl in EE compared with that of BH<sub>2</sub>Cl in THF is indicative of the fact that the complexation is weaker in EE than in THF.) Proton heteronuclear spin decoupling produced a singlet, indicating that monochloroborane was the only

**Table II.** Methanolysis Products from the Reaction of 2.5 mmol of  $\text{BH}_2\text{Cl}$  with 5.0 mmol of Olefins in Tetrahydrofuran

Olefin (M)	$\text{BH}_2\text{Cl}$ , M	Temp., °C	Time, h	Products, <sup>a</sup> mmol			Yield, %	
				$\text{R}_3\text{B}$	$\text{R}_2\text{BOMe}$	$\text{RB(OMe)}_2$	B	R group
1-Butene (4)	2.0	0	6	0.76	0.45	0.98	88	83
1-Butene (2)	1.0	25	12	1.20	0.20	0.60	80	92
<i>cis</i> -2- Butene (2)	1.0	25	12	1.30	0.01	0.80	85	95

<sup>a</sup> R, 1-butyl in the case of 1-butene; R, 2-butyl in the case of *cis*-2-butene.

**Table III.** Rate of Reaction of 1-Hexene (1.0 M) with  $\text{BH}_2\text{Cl}$  (0.5 M) in Diethyl Ether at 0 °C

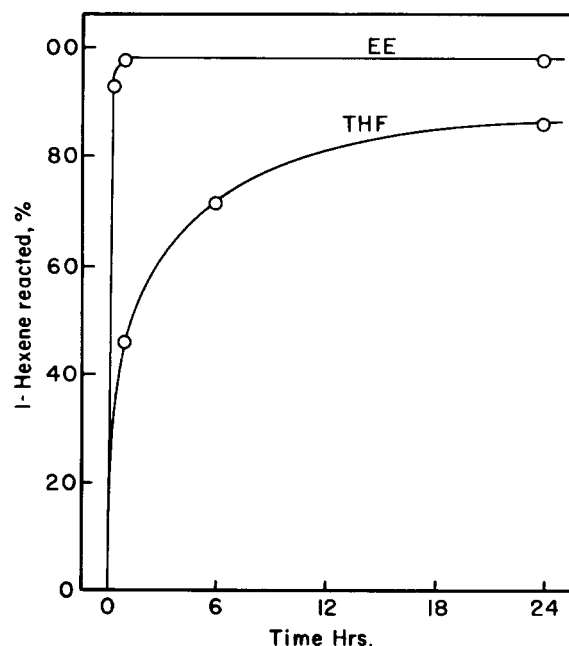
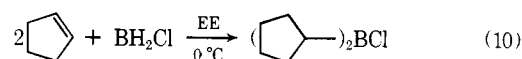
Time, h	1-Hexene reacted, %
0.25	93
1.0	98
24.0	98

**Table IV.** Rates of Reaction of Representative Alkenes (1.0 M) with  $\text{BH}_2\text{Cl}$  (0.5 M) in Diethyl Ether at 0 °C

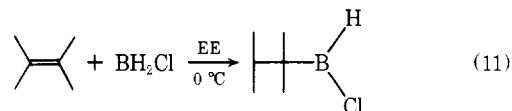
Alkene	Time, h	Alkene reacted, %
1-Hexene	0.25	93
	1.0	98
<i>cis</i> -3-Hexene	0.25	87
	1.0	98
Norbornene	0.25	92
	1.0	99
2-Methyl-2-butene	0.25	88
	1.0	98
Cyclopentene	0.25	95
	1.0	99
Cyclohexene	0.25	83
	1.0	94
	2.0	99
Styrene	0.25	50
	3.0	82
	8.0	92
	16.0	99
Tetramethylethylene	0.25	50
	20.0	50

species present in solution. The purity of the solution was estimated to be >98%.

The rate of reaction of 1-hexene (1.0 M) with  $\text{BH}_2\text{Cl}$  (0.5 M) in EE at 0 °C was measured. The reaction was carried out by adding  $\text{BH}_2\text{Cl}$  in EE to a solution of 1-hexene (1:2) in EE and stirring at 0 °C. The reaction mixture contained a known amount of *n*-octane to serve as the internal standard for GC analysis. Aliquots were withdrawn at intervals and analyzed for residual 1-hexene by GC. The results are given in Table III. The rate data in EE and THF for the reaction of 1-hexene with  $\text{BH}_2\text{Cl}$  are compared in Figure 1. As expected, the reaction is very fast in EE, being complete in less than 1 h at 0 °C even under these relatively dilute reagent concentrations. The dramatic increase in the rate of reaction in EE over that in THF is well brought out in Figure 1. Encouraged by these results, we went on to study the rate of reaction of a series of representative olefins with  $\text{BH}_2\text{Cl}$  in EE under the same conditions as those used for the study with 1-hexene. The results of this investigation are given in Table IV. In the cases of 1-hexene, *cis*-3-hexene, 2-methyl-2-butene, cyclopentene, and norbornene, 2 mol of olefin per mol of  $\text{BH}_2\text{Cl}$  was used up in 1 h. The reactions with cyclohexene and styrene were slower, requiring 2 and 16 h, respectively. In these cases, the products of the reactions are the dialkylchloroboranes ( $\text{R}_2\text{BCl}$ ), which were isolated and characterized in a number of cases (eq 10). (See the section on the synthesis of dialkylchloro-

**Figure 1.** Rate of reaction of 1-hexene (1.0 M) with  $\text{BH}_2\text{Cl}$  (0.5 M) in tetrahydrofuran (THF) and diethyl ether (EE) at 0 °C.

boranes and their derivatives.) In the case of tetramethylethylene, 1 mol of olefin per mol of  $\text{BH}_2\text{Cl}$  was utilized in 15 min. No more olefin was consumed over a considerably additional period of time, indicating that the probable product in this case is the monoalkylchloroborane (eq 11). These



results clearly establish that the hydroboration of alkenes with  $\text{BH}_2\text{Cl}$  in EE is a very facile and general reaction.

**Directive Effect in the Hydroboration of Alkenes with  $\text{BH}_2\text{Cl}$  in Diethyl Ether.** The directive effect in the hydroboration with  $\text{BH}_2\text{Cl}$  in EE was examined using a representative series of alkenes. The reaction was carried out using 1.0 M olefin and 0.5 M  $\text{BH}_2\text{Cl}$  in EE at 0 °C and allowing the reaction to proceed until the hydroboration was complete. The reaction mixture was then oxidized with  $\text{NaOH-H}_2\text{O}_2$  using ethanol as the cosolvent. The isomeric alcohols formed were analyzed by GC. The results are given in Table V along with the data on the directive effect of  $\text{BH}_3\cdot\text{THF}$ .<sup>9</sup> The results show that  $\text{BH}_2\text{Cl}\cdot\text{EE}$  exhibits a far more powerful directive effect than  $\text{BH}_3\cdot\text{THF}$ . Therefore, the alkylboron derivatives obtained by the hydroboration with  $\text{BH}_2\text{Cl}\cdot\text{EE}$  are of far higher isomeric purity than by the hy-

**Table V.** Directive Effects in the Hydroboration of Alkenes with  $\text{BH}_2\text{Cl}\cdot\text{EE}$  and  $\text{BH}_3\cdot\text{THF}$ 

Alkene	Products	Relative yield of products	
		$\text{BH}_2\text{Cl}\cdot\text{EE}^a$	$\text{BH}_3\cdot\text{THF}^b$
1-Hexene	1-Hexanol	>99.5	94
	2-Hexanol	< 0.5	6
2-Methyl-1-butene	2-Methyl-1-butanol	>99.9	99
	2-Methyl-2-butanol	< 0.1	1
Norbornene	<i>exo</i> -2-Norbornanol	>99.8	99
	<i>endo</i> -2-Norbornanol	< 0.2	1
2-Methyl-2-butene	3-Methyl-2-butanol	99.7	98
	2-Methyl-2-butanol	0.3	2
1-Methylcyclopentene	<i>trans</i> -2-Methylcyclopentanol	>99.8	98.5
	1-Methylcyclopentanol	<0.2	1.5
Styrene	2-Phenylethanol	96	81 <sup>c</sup>
	1-Phenylethanol	4	19 <sup>c</sup>
$\alpha$ -Methylstyrene	2-Phenyl-1-propanol	100	100
	2-Phenyl-2-propanol	0	0
2-Pentene	2-Pentanol	58 <sup>d</sup>	55 <sup>d</sup>
	3-Pentanol	42 <sup>d</sup>	45 <sup>d</sup>
4-Methyl-2-pentene	4-Methyl-2-pentanol	60 <sup>d</sup>	57 <sup>d</sup>
	2-Methyl-3-pentanol	40 <sup>d</sup>	43 <sup>e</sup>
4,4-Dimethyl-2-pentene	4,4-Dimethyl-2-pentanol	79 <sup>d</sup>	58 <sup>e</sup>
	2,2-Dimethyl-3-pentanol	21 <sup>d</sup>	42 <sup>e</sup>

<sup>a</sup> Total yields were  $95 \pm 5\%$ . <sup>b</sup> Reference 9a,b. <sup>c</sup> Reference 9c. <sup>d</sup> Cis olefin. <sup>e</sup> Trans olefin.

droboration with borane itself. Earlier, Zweifel<sup>5</sup> and Pasto<sup>6</sup> had reported that the directive effect of  $\text{BH}_2\text{Cl}\cdot\text{THF}$  is not significantly different from that of  $\text{BH}_3\cdot\text{THF}$ . We have discussed the significance of our results of the directive effect of  $\text{BH}_2\text{Cl}\cdot\text{EE}$  in our preliminary report of this study.<sup>1</sup>

**Synthesis of Dialkylchloroboranes and Methyl Dialkylborinates.** The results presented in Table IV suggest that the hydroboration of olefins with  $\text{BH}_2\text{Cl}$  in EE would provide a convenient method for the preparation of dialkylchloroboranes. Since the chloroboranes are easily solvolyzed by the addition of water or alcohols, this method could also be adopted to the preparation of dialkylborinic acids and their esters (eq 12 and 13).



Accordingly, a series of representative dialkylchloroboranes and/or the corresponding methyl dialkylborinates were synthesized and isolated using this facile reaction of  $\text{BH}_2\text{Cl}$  in EE with olefins. The results are summarized in Table VI.

Although 0.5 M  $\text{BH}_2\text{Cl}$  and 1.0 M olefin concentrations were used previously for the rate studies, it was later found that the actual reagent concentrations were not critical. In fact, we have used  $\text{BH}_2\text{Cl}$  solutions varying in strengths

**Table VI.** Synthesis of Dialkylchloroboranes and Methyl Dialkylborinates by the Hydroboration of Representative Olefins with Monochloroborane in Diethyl Ether at 0 °C

Dialkylchloroborane <sup>a</sup> or methyl dialkylborinate <sup>b</sup>	Yield, %	Bp, °C (mm)	$n_D^{20}$
Di- <i>n</i> -hexylchloroborane	84 <sup>c</sup>	74–75 (0.3)	
Methyl di- <i>n</i> -butylborinate	93 <sup>d</sup>	56–58 (5.0)	1.4144
	77 <sup>c</sup>		
Methyl di- <i>sec</i> -butylborinate	99 <sup>d</sup>		
Methyl diisobutylborinate	96 <sup>d</sup>		
Dicyclopentylchloroborane	80 <sup>c</sup>	68–69 (1.0)	
Methyl dicyclopentylborinate	84 <sup>c</sup>	82–84 (2.0)	1.4705
Methyl di- <i>exo</i> -norbornylborinate	83 <sup>c</sup>	96–100 (0.5)	1.5044

<sup>a</sup>  $\text{R}_2\text{BCl}$  was characterized by methanolysis followed by the identification of the  $\text{R}_2\text{BOMe}$  formed by  $^1\text{H}$ NMR. <sup>b</sup> Characterized by  $^1\text{H}$  NMR,  $\text{B}-\text{OCH}_3$  proton resonance at  $\delta$  3.65–3.68 (3 H) in  $\text{CCl}_4$ . <sup>c</sup> Isolated. <sup>d</sup> GC.

from 0.5 to 1.5 M for the preparative purposes. It was also established that clear stock solutions of  $\text{BH}_2\text{Cl}$  in EE need not be used. The required amount of  $\text{BH}_2\text{Cl}$  in EE is prepared as and when needed, according to eq 9, and the hydroboration is carried out by adding the olefin to this solution of  $\text{BH}_2\text{Cl}$  in EE containing the suspended LiCl. This procedure is actually recommended for the synthesis and isolation of the product. (The solid LiCl did not cause any difficulties while isolating the product by distillation.)

Since the reaction goes to essential completion in practically all cases, the crude product obtained by removing the solvent can usually be used directly for further synthetic applications. In these cases, the use of a clear solution of  $\text{BH}_2\text{Cl}$  in EE might be desirable.

The redistribution of trialkylboranes with  $\text{BCl}_3$  and boric acid esters, generally at elevated temperatures in the presence of boron hydrides, provides the basis for the methods, generally used in the past, for the synthesis of dialkylchloroboranes and dialkylborinic acid esters, respectively.<sup>10–12</sup> Unfortunately, these methods are often difficult and inconvenient to apply, especially for the synthesis of relatively large amounts of these compounds required as synthetic intermediates. The present procedure is very simple and provides a convenient general synthesis of dialkylchloroboranes and borinic acid derivatives. Subsequent to this development, many interesting applications of these compounds as intermediates in organic synthesis have been developed.<sup>13–18</sup>

**Controlled Hydroboration of Alkenes with  $\text{BH}_2\text{Cl}$ .** If the hydroboration of alkenes with  $\text{BH}_2\text{Cl}$  could be controlled to stop cleanly at the monoalkylation stage of  $\text{BH}_2\text{Cl}$ , it would, in principle, provide a synthesis of monoalkylchloroboranes ( $\text{RBHCl}$ ), a new class of organochloroboranes. The  $\text{RBHCl}$  could be potential intermediates for the synthesis of alkylidichloroboranes, alkylboronic acids and derivatives, monoalkylboranes, unsymmetrical dialkylchloroboranes and their derivatives, etc. Therefore, a study was undertaken to learn how to control the hydroboration of alkenes with  $\text{BH}_2\text{Cl}$  in order to obtain the  $\text{RBHCl}$  cleanly.

Previous workers have reported that the hydroboration of alkenes with  $\text{BH}_2\text{Cl}$  in THF stops at the monoalkylation stage to form  $\text{RBHCl}$ .<sup>5,6</sup> But their conclusion was based on fragmentary indirect evidence only. Since the hydroboration with  $\text{BH}_2\text{Cl}$  in THF is a very slow reaction, we decided to approach the synthesis of  $\text{RBHCl}$  starting with  $\text{BH}_2\text{Cl}$  in EE where the reaction is fast. The reaction of butene with  $\text{BH}_2\text{Cl}$  in 1:1 ratio was studied in EE. The procedure was to add 5 mmol of butene as gas to 5 mmol of  $\text{BH}_2\text{Cl}$  and a known amount of tridecane (internal standard for GC analysis) in EE at the desired reaction temperature and then to stir for the specified period of time. The initial concentration was 0.5 M in each reactant. The reaction mixture was

**Table VII.** Methanolysis Products of the Reaction of 5 mmol of Butenes (0.5 M) with 5 mmol of  $\text{BH}_2\text{Cl}$  (0.5 M) in Diethyl Ether at Low Temperatures

Butenes	Temp, °C	Time, h	$\text{BuB}(\text{OCH}_3)_2$ , mmol (% yield)	$\text{Bu}_2\text{-BOCH}_3$ , mmol	% reaction
1-Butene	0	0.5	3.24 (65)	0.85	99
	-20	1.0	4.1 (82)	0.40	98
<i>cis</i> -2-Butene	0	0.5	trace	2.40	96
	-20	1.0	3.8 (76)	0.61	100
	-30	6.0	3.65 (73)	0.38	88
	-30	24.0	4.78 (96)	0.12	100
Isobutylene	0	0.5	1.1 (22)	2.0	101

then methanolized using excess methanol and analyzed by GC for dimethyl butylboronate and methyl dibutylborinate. The latter is produced by the methanolysis of the dibutylchloroboranes. Methanolysis of the  $\text{BuBHCl}$  will give the boronate. However, it must be cautioned here that the formation of dimethyl butylboronate need not necessarily mean that the  $\text{BuBHCl}$  exists as such in the solution, without equilibration (see eq 4). However, in the absence of data as to the importance of such equilibration, the amount of boronates found is taken as a measure of the  $\text{BuBHCl}$ . The results are given in Table VII. From the results obtained, it is concluded that at 0 °C in EE simple terminal olefins, like 1-butene, give predominantly the monoalkylated product. Terminal olefins with a substituent on the double bond, like isobutylene, give largely the dialkylated products and minor amount of the desired monoalkylated products. The worst case is the internal olefins, like *cis*-2-butene, which give the dialkylated products exclusively. The yield of the monoalkylated product increases with lower reaction temperatures. Thus, at around -30 °C, *cis*-2-butene gives 96% of the monoalkylated product in 24 hr. It must be mentioned here that the maintenance of a -30 °C bath for 24 h needs special equipment. Consequently, this might not prove to be a convenient procedure for the synthesis of  $\text{RBHCl}$ . Therefore, we directed our attention to the development of an improved procedure not requiring low temperatures for extended periods of time.

The behavior of *cis*-2-butene is worth special comment here. In general, the steric requirements of the reactants and products affect the course of the hydroboration reaction.<sup>9b</sup> Therefore, from simple steric considerations, one would expect monoalkylation of  $\text{BH}_2\text{Cl}$  to take place more predominantly with *cis*-2-butene than with 1-butene. In actual fact, the exact opposite is true and the dialkylated product is formed almost exclusively with *cis*-2-butene at 0 °C. This can be explained if we consider the steric requirements of the starting borane,  $\text{BH}_2\text{Cl}$ , the intermediate  $\text{RBHCl}$ , and the final product,  $\text{R}_2\text{BCl}$ .  $\text{BH}_2\text{Cl}$  is the least hindered of the three species. All of the three species are coordinated with the ether molecule, the strength of the complex being determined by the steric nature of the alkyl group. The stronger the complexation with the ether, the lesser the reactivity of  $\text{BH}_2\text{Cl}$  and  $\text{RBHCl}$  toward olefins. In the case of 1-butene, in the intermediate species *n*- $\text{BuBHCl}$ , the alkyl group is sufficiently small so that it is still fairly strongly complexed with the ether molecule. Consequently, the tendency to undergo further reaction with another molecule of olefin is greatly diminished. Therefore, the olefin preferentially reacts with the  $\text{BH}_2\text{Cl}$  etherate to form more *n*- $\text{BuBHCl}$ , giving predominantly the monoalkylated species as the end product. In *sec*- $\text{BuBHCl}$ , the alkyl group is very bulky and therefore has little or no tendency to form a complex with the ether. As a result, *sec*- $\text{BuBHCl}$  exists largely as the open molecule, much more reactive toward the olefin than  $\text{BH}_2\text{Cl}$ , which is relatively strongly

**Table VIII.** Rate of Reaction of  $\text{BH}_2\text{Cl}$  with 1-Octene and *cis*-2-Octene in Diethyl Ether in the Presence of Varying Amounts of Tetrahydrofuran at 0 °C

Concentrations, M				Octene reacted, %	
Reactant $\text{BH}_2\text{Cl}$	THF	1-Octene	Time, h	1-Octene	<i>cis</i> -2-Octene
1.0	1.0	1.0	0.25	99	99
			1.00	100	100
1.0	1.2	1.0	0.25	98	86
			0.50	100	96
			1.00	100	100
1.0	2.0	1.0	0.25	89	63
			1.00	99	86
			3.00	100	100

complexed with the ether. Therefore, as soon as any *sec*- $\text{BuBHCl}$  is formed, it preferentially reacts with the olefin to form *sec*- $\text{Bu}_2\text{BCl}$ . The steric requirements of isobutylene appear to be between those of 1-butene and 2-butene. This interpretation provides a reasonable explanation for the observed results.

If the above reasoning is valid, a fairly strong complexing agent, such as THF, added in adequate quantity to the reaction mixture, would complex both  $\text{BH}_2\text{Cl}$  and the  $\text{RBHCl}$  to the same degree, so that the reactivity of the species would then be determined essentially by their steric requirements. In that event,  $\text{BH}_2\text{Cl}$  would be more reactive with the olefin than  $\text{RBHCl}$ , and then it should be possible to obtain  $\text{RBHCl}$  cleanly. Therefore, we studied the rate and the products formed in the reaction of olefin with  $\text{BH}_2\text{Cl}$  (1:1) in EE in the presence of varying amounts of THF. 1-Octene and *cis*-2-octene were chosen as the representative olefins for the rate studies. The general procedure was to add 5 mmol of the octene to a solution of 5 mmol of  $\text{BH}_2\text{Cl}$  in sufficient EE containing 2.5 mmol of *n*-decane (internal standard for GC analysis) and the specified quantity of THF at 0 °C ( $\text{BH}_2\text{Cl}$  and THF were stirred together for 15 min before adding the octene) so that the desired concentrations of the reactants were obtained. The mixture was stirred at 0 °C, and aliquots were withdrawn at intervals and analyzed for the residual octene by GC. The results are given in Table VIII. When the  $\text{BH}_2\text{Cl}$  and the olefin concentrations are 1.0 M, both 1-octene and *cis*-2-octene react completely in less than 1 h if the THF concentration is 1.0–1.2 M. When the THF concentration is 2.0 M, 1-octene still reacts almost completely in 1 h, but *cis*-2-octene needs 3 h for complete reaction.

For the product studies, the butenes were used as the representative olefins so that the products could be analyzed by GC. The procedure was to react 5 mmol of olefin (1.0 M) with  $\text{BH}_2\text{Cl}$  (1.0 M) in EE containing 0.5 mmol of tri-decane (internal standard for GC analysis) and the desired

**Table IX.** Methanolysis Product of the Reaction of Butenes with  $\text{BH}_2\text{Cl}$  in Diethyl Ether in the Presence of Varying Amounts of Tetrahydrofuran at 0 °C (Butene: $\text{BH}_2\text{Cl}$  = 1:1)

Butene	Reactant concentrations, M			Time, h	$\text{BuB}(\text{OCH}_3)_2$ yield, <sup>a</sup> %
	$\text{BH}_2\text{Cl}$	THF	Olefin		
1-Butene	1.0	1.0	1.0	1.0	94
	1.0	1.2	1.0	1.0	96
	1.0	2.0	1.0	3.0	97
<i>cis</i> -2-Butene	1.0	1.0	1.0	1.0	90
	1.0	1.2	1.0	1.0	94
	1.0	2.0	1.0	3.0	93
Isobutylene	1.0	1.2	1.0	1.0	96

<sup>a</sup>GC yield.

amount of THF at 0 °C for the specified period of time, after which the reaction mixture was methanolized using excess methanol and analyzed for the dimethyl butylboronate by GC. The amount of the boronate is a measure of the monoalkylated products formed in the reaction. The results are given in Table IX. The data suggest that, in general, for the synthesis of RBHCl, BH<sub>2</sub>Cl and olefin concentrations of 1.0 M and THF concentrations of 1.2–2.0 M in EE may be used at 0 °C. Reaction periods of 1–3 h may be sufficient depending on the amount of THF used. It may be noted here that these conditions are much superior to the earlier recommendations<sup>5</sup> (12 h for 1-hexene) and also to the reaction conditions required for pure EE (24 h at –30 °C).

**Synthesis of Monoalkylchloroborane–Trimethylamine Complexes.** As discussed earlier, the identification of the RB(OCH<sub>3</sub>)<sub>2</sub> obtained by the methanolysis of the reaction mixture should not be taken as a conclusive proof for the existence of RBHCl cleanly in the reaction medium (see eq 4). Therefore, it was decided to isolate and characterize the RBHCl as such, if possible, or as the stable adducts with tertiary amines like pyridine, trimethylamine, etc. For these studies, the reactions were carried out under the conditions of 1.0 M in BH<sub>2</sub>Cl and the olefin, 2.0 M in THF, EE solvent, 0 °C, and 4 h of reaction period. In an experiment using 1-pentene, the ir spectrum of the reaction mixture displayed a single absorption band at 2460 cm<sup>–1</sup> with a minor shoulder at 2500 cm<sup>–1</sup>. A solution of BH<sub>2</sub>Cl under identical conditions displayed a symmetrical doublet at 2450 and 2500 cm<sup>–1</sup>. The peak at 2460 cm<sup>–1</sup> in the ir spectrum of the reaction mixture is due to the B–H stretching in RBHCl, the shoulder being due to the small amount of unreacted BH<sub>2</sub>Cl present. On evaporating the solvent from the reaction mixture at 0 °C at low pressure (5 mm), a white solid started depositing on the sides of the flask, presumably BCl<sub>3</sub>·THF, resulting from the disproportionation of RBHCl. Based on this observation, the attempts to isolate the RBHCl·THF were abandoned. In another experiment using 1-hexene as the olefin, 30% excess pyridine was added to the reaction mixture to complex the RBHCl. The solvent and the excess pyridine were removed under low pressure. The <sup>1</sup>H NMR and ir spectra of the crude product indicated that it was >90% pure *n*-HexBHCl·Py. However, the product decomposed while attempting to purify the material by distillation.

The isolation of RBHCl as the trimethylamine adduct proved successful. The hydroboration was carried out on a 100-mmol scale. After 4 h of reaction, 130 mmol of trimethylamine was passed into the reaction mixture at 0 °C and stirred for 1 h at 0 °C, followed by 1 h at 25 °C. The solvent and the excess amine were removed under vacuum. The product was then distilled at low pressure. A small quantity of a white solid sublimed from the reaction mixture initially. This was discarded. Then the RBHCl·NMe<sub>3</sub> complex distilled and was collected. Trimethylamine complexes of *n*-pentyl-, cyclopentyl-, and 2-methyl-1-butylchloroborane were synthesized and characterized. The results are given in Table X. The products were characterized by ir, <sup>1</sup>H NMR, <sup>11</sup>B NMR, and elemental analysis. The monoalkylchloroborane–amine complexes constitute a new class of compounds not synthesized previously.

As we have seen earlier, these monoalkylchloroboranes are easily methanolized to form the dimethyl alkylboronate, providing an extremely simple synthesis of alkylboronic acid derivatives. The RBHCl formed in solution by this method reacts with 1 equiv of HCl in EE at 25 °C to liberate hydrogen quantitatively in 5 min. The obvious product in this reaction is the corresponding alkylchloroborane (eq 14). Unfortunately, this valuable product could not be iso-

**Table X.** Synthesis of Monoalkylchloroborane–Trimethylamine Complexes (RBHCl·NMe<sub>3</sub>) by the Monoalkylation of BH<sub>2</sub>Cl

RBHCl·NMe <sub>3</sub> <sup>a</sup>	Yield, %	Bp, °C (mm)	Ir (B–H), cm <sup>–1</sup>
1-Pent-BHCl·NMe <sub>3</sub> <sup>b</sup>	81	93–96 (0.1)	2413
<i>n</i> -Pent-BHCl·NMe <sub>3</sub>	78	115–118 (0.15)	2406
2-Me-1-Bu-BHCl·NMe <sub>3</sub>	81	94–98 (0.15)	2407

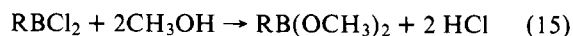
<sup>a</sup> All compounds gave correct elemental analysis and the expected <sup>1</sup>H NMR spectra (see Nair Ravindran, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1972). <sup>b</sup> <sup>11</sup>B NMR: broad doublet at –5.8 ± 0.5 ppm relative to BF<sub>3</sub>·EE. Heteronuclear spin decoupling gave a broad singlet.

**Table XI.** Reaction of Monoalkylchloroboranes (RBHCl) with HCl<sup>a</sup> in Diethyl Ether at 25 °C to Form the Alkylchloroboranes (RBCl<sub>2</sub>)

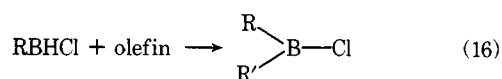
RBHCl	Time, h	Hydrogen evolved, %	Yield of RBCl <sub>2</sub> , % <sup>b</sup>
1-Hex-BHCl	5	100	95
3-Hex-BHCl	5	100	94
2-Me-1-Pent-BHCl	5	99	100

<sup>a</sup> RBHCl:HCl = 1:1. <sup>b</sup> Determined as RB(OCH<sub>3</sub>)<sub>2</sub> by GC following methanolysis of RBCl<sub>2</sub>.

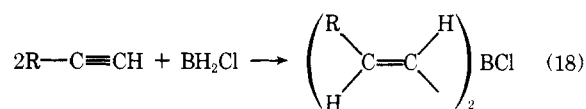
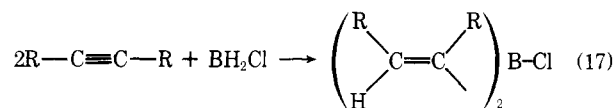
lated by distillation from the reaction medium because, during distillation, it reacts with the THF, producing complex cleavage products. However, on methanolysis after the reaction with HCl, the corresponding dimethyl alkylboronate is obtained in nearly quantitative yield (eq 15), thereby



showing that no disproportionation of the monoalkylboron compound to dialkyl- and trialkylboron compounds had occurred during the reaction with HCl at 25 °C. Reactions of HCl with 1-hexyl-, 3-hexyl-, and 2-methyl-1-pentylchloroborane were studied to demonstrate the generality of this reaction, and the results are presented in Table XI. Another valuable use of RBHCl would be to hydroborate another olefin with it to obtain unsymmetrical dialkylchloroboranes (eq 16). This has not yet been explored.



**Monohydroboration of Alkynes with BH<sub>2</sub>Cl Etherates. General Considerations.** If the reaction of alkynes with BH<sub>2</sub>Cl in 2:1 ratio of the reagents goes cleanly, the expected product is the monohydroboration product, dialkenylchloroboranes (eq 17 and 18). Since the dialkenylboron



compounds themselves can undergo further hydroboration to produce dibora compounds, the above reaction need not go cleanly in all cases to give the desired dialkenylchloroborane. Whether the reaction gives the dialkenylchloroboranes cleanly or not is easily studied by following the stoichiometry of hydride and alkyne disappearance during the reaction. If the alkynes undergo monohydroboration cleanly

**Table XII.** Reaction of Alkynes<sup>a</sup> with BH<sub>2</sub>Cl<sup>b</sup> (2:1) in Tetrahydrofuran at 0 °C

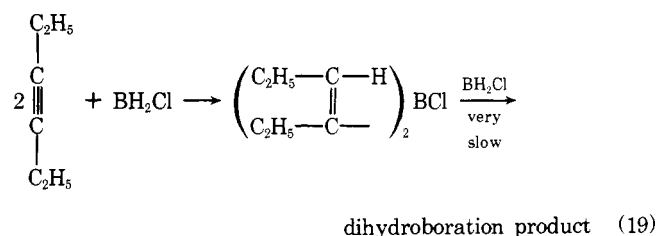
Alkyne	Time, h	Aliquot, ml	Hydride reacted, mmol	Alkyne reacted, mmol	Maximum yield of dialkenylchloroborane expected, %
1-Hexyne	0.25	2	0.6	0.59	29
	0.50	2	0.83	0.77	35
	1.00	2	1.10	1.01	46
	2.00	2	1.40	1.21	51
	4.00	2	1.69	1.31	47
	8.00	2	1.87	1.41	47
	20.00	2	2.00	1.40	40
3-Hexyne	0.50	2	1.69	1.61	77
	2.00	2	1.70	1.74	85
	4.00	2	1.75	1.77	88
	24.00	2	2.00	1.95	95

<sup>a</sup> 1.0 M alkyne. <sup>b</sup> 0.5 M BH<sub>2</sub>Cl.

to form the dialkenylchloroborane, one hydride per alkyne (2 alkynes per BH<sub>2</sub>Cl) should be utilized. If the reaction gives a mixture of alkenylboron and dibora compounds (via dihydroboration of the alkyne), more than one hydride per alkyne should be utilized. Moreover, in this case, there should be unreacted alkyne left in the reaction mixture when all the hydride is utilized in a reaction employing the alkyne and BH<sub>2</sub>Cl in 2:1 ratio. Therefore, the determination of the stoichiometry of the hydride uptake per alkyne will give a good indication whether the reaction goes cleanly to give the monohydroboration product or not. Accordingly, such a stoichiometric study of the hydroboration of alkynes with BH<sub>2</sub>Cl·THF and BH<sub>2</sub>Cl·EE was undertaken.

**Reaction of Alkynes with BH<sub>2</sub>Cl·THF. Rate and Stoichiometry.** First the reaction of alkynes with BH<sub>2</sub>Cl in 2:1 ratio was studied. The reaction was carried out by adding BH<sub>2</sub>Cl to alkyne in THF and stirring at 0 °C. The solution was 0.5 M in BH<sub>2</sub>Cl and 1.0 M in alkyne and contained 8% THP by volume. A known amount of *n*-octane was added to serve as internal standard for GC analysis. Known aliquots of the reaction mixture were withdrawn at intervals and analyzed for residual alkyne by GC and for residual hydride by hydrolyzing and measuring the hydrogen evolved. The results are given in Table XII. The reaction is somewhat slow, but in both cases, the hydride utilization is complete in about 24 h at 0 °C. When all the hydride was used up for the reaction, about 30% 1-hexyne and 2.5% 3-hexyne remained unreacted. This suggests that in the case of 3-hexyne, the corresponding dialkenylchloroborane is produced in 95% yield, whereas in the case of 1-hexyne, the corresponding dialkenylchloroborane is obtained in 40% yield only at the end of the reaction. The data show that in the case of 1-hexyne, the maximum amount of the dialkenylchloroborane (~50%) is present in the reaction mixture after 2 h of reaction when 70% of the hydride is utilized.

In the case of 3-hexyne, it appears that the alkyne is far more reactive to BH<sub>2</sub>Cl than the initial reaction product. As a result, the reaction proceeds satisfactorily to the clean formation of the desired dialkenylchloroborane (eq 19). On



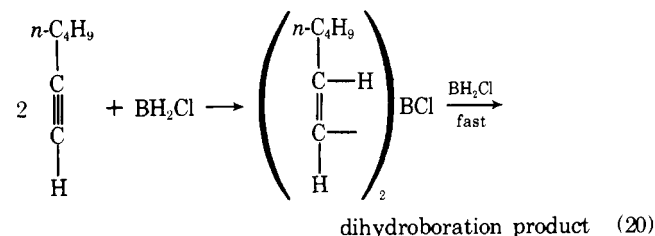
the other hand, in the case of 1-hexyne, the initially formed product is apparently more active toward the reagent than

**Table XIII.** Reaction of 1-Hexyne<sup>a</sup> with BH<sub>2</sub>Cl<sup>b</sup> (3:1) in Tetrahydrofuran at 0 °C

Time, h	Aliquot, ml	Hydride reacted, mmol	Alkyne reacted, mmol	Maximum yield of dialkenylchloroborane expected, % <sup>c</sup>
0.25	2.0	1.63	1.34	53
1.0	2.0	1.79	1.40	51
5.0	2.0	1.98	1.52	53

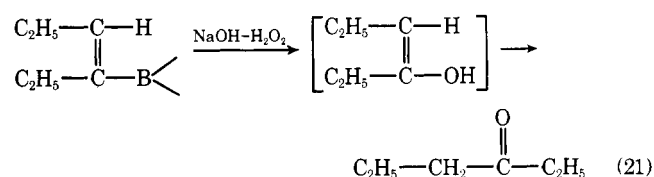
<sup>a</sup> 1.5 M 1-hexyne. <sup>b</sup> 0.5 M BH<sub>2</sub>Cl. <sup>c</sup> Based on BH<sub>2</sub>Cl.

the residual alkyne. Therefore, 1-hexyne undergoes dihydroboration preferentially (eq 20).



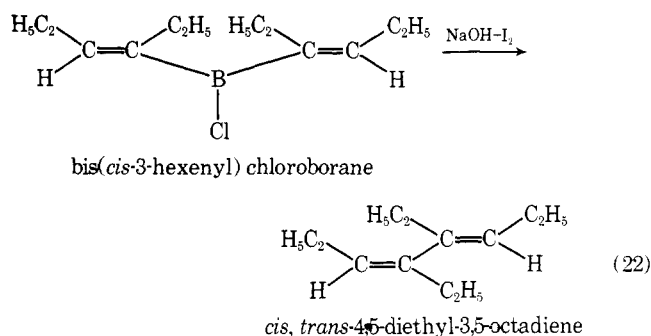
It was thought possible that the use of a large excess of 1-hexyne in the reaction might repress the second stage and give the monohydroboration product predominantly. Therefore the experiment was repeated using 1-hexyne and BH<sub>2</sub>Cl in the ratio 3:1 (50% excess 1-hexyne). The results are given in Table XIII. The reaction went faster, being complete in about 5 h. However, the yield of the monohydroboration product did not improve substantially.

**Characterization of the Product of the Reaction of 3-Hexyne with BH<sub>2</sub>Cl (2:1) in Tetrahydrofuran.** The stoichiometric results discussed above strongly suggest that the dialkenylchloroborane is formed cleanly by the reaction of 3-hexyne with BH<sub>2</sub>Cl (2:1) in THF at 0 °C. This was confirmed in the following manner. Oxidation of the reaction mixture with NaOH-H<sub>2</sub>O<sub>2</sub> produced 3-hexanone in 98% yield (GC), showing that all the 3-hexyne was converted into the alkenylboron compound (eq 21). Treatment of the



reaction mixture with NaOH-I<sub>2</sub> in THF at 0 °C produced *cis,trans*-4,5-diethyl-3,5-octadiene in 84% yield (GC).<sup>19</sup>

This clearly establishes that the product in the reaction of 3-hexyne with  $\text{BH}_2\text{Cl}$  in 2:1 ratio in THF is the expected dialkenylchloroborane (eq 22). However, no attempt was



made to isolate the dialkenylchloroborane in this case.

**Monohydroboration of Alkynes with  $\text{BH}_2\text{Cl}$  in Diethyl Ether. Rate and Stoichiometric Study.** The reaction was studied using 1-hexyne, cyclohexylethyne, phenylethyne, and 3-hexyne. Experiments were carried out using the stoichiometric quantity, as well as 10, 20, 30, and 40% more of the alkyne than that required stoichiometrically for monohydroboration with  $\text{BH}_2\text{Cl}$ .

The general procedure was to add the  $\text{BH}_2\text{Cl}$  in EE to a solution of the required amount of alkyne and a known amount of *n*-octane (internal standard for GC analysis) in EE at 0 °C. (One experiment was carried out at -78 °C using stoichiometric quantity of 1-hexyne.) The reaction mixture was 0.87 M in  $\text{BH}_2\text{Cl}$ . After a specific reaction period, aliquots of the reaction mixture were analyzed for the residual alkyne by GC and for residual hydride by hydrolyzing and measuring the hydrogen evolved. The results are given in Table XIV. Except in the case of phenylethyne, the hydride loss was complete in less than 15 min at 0 °C. (Even at -78 °C, the hydride loss was complete in less than 15 min in the case of 1-hexyne.) In the case of phenylethyne, 1 h was required for the complete loss of hydride at 0 °C. From the relative amounts of alkyne and hydride reacted, it is concluded that the stoichiometric reaction at 0 °C produced dialkenylchloroborane in almost quantitative yield (95%) in the case of 3-hexyne. Under stoichiometric reaction conditions at 0 °C, the expected yields of the corresponding dialkenylchloroborane were 58, 76, and 70% in the case of 1-hexyne, cyclohexylethyne, and phenylethyne, respectively. Lowering the reaction temperature did not improve the yield of the monohydroboration product, as indicated by the fact that only 60% of the product was formed in the reaction of 1-hexyne at -78 °C, but the use of excess

alkyne did increase the yield of the desired monohydroboration product. Thus, in reactions involving 40% excess 1-hexyne and phenylethyne and 30% excess cyclohexylethyne, the desired monohydroboration product was formed in essentially quantitative yield. This result may be compared with the corresponding reaction in THF, where the use of 50% excess 1-hexyne produced only 53% monohydroboration product.

**Synthesis of Dialkenylchloroboranes.** From the results described above, it is obvious that the synthesis of dialkenylchloroboranes can be achieved by the monohydroboration of the corresponding alkynes with  $\text{BH}_2\text{Cl}$  in EE at 0 °C using the stoichiometric amount of an internal alkyne or a terminal alkyne in an excess of 30–40%. Accordingly, a representative series of dialkenylchloroboranes was synthesized by this method, and the products were isolated by distillation. The experimental procedure is quite simple. The  $\text{BH}_2\text{Cl}$  in EE was added to a solution of stoichiometric quantity of 3-hexyne or 40% excess 1-hexyne, as the case may be, in EE at 0 °C and stirred for 30 min. The solvent and the excess alkyne were removed under vacuum and the dialkenylchloroborane was purified by distillation at low pressure. The products were characterized by  $^1\text{H}$  NMR and elemental analysis. The results are given in Table XV. The reaction was so clean that the crude product obtained by removing the solvent gave a clean  $^1\text{H}$  NMR spectrum. However, it must be mentioned here that the dialkenylchloroboranes do not seem to be very stable compounds suitable for storing. On keeping, they start turning yellow and finally red. Freshly distilled samples were colorless.

The only dialkenylchloroborane reported previously is diethenylchloroborane, which was obtained in 35% yield by the fractionation of a mixture of products from the reaction of tetraethenyltin with  $\text{BCl}_3$  at 60 °C for 1.5 h.<sup>20</sup> Obviously, the method developed here is definitely superior owing to its simplicity and generality.

The dialkenylchloroboranes undergo the usual reactions of vinylboranes.<sup>3</sup> For example, they undergo protonolysis with acetic acid to give olefins and oxidation by  $\text{NaOH-H}_2\text{O}_2$  to give the corresponding carbonyl compounds. The most useful reaction of these compounds is their ready conversion to stereochemically pure dienes by the Zweifel reaction with  $\text{I}_2/\text{NaOH}$ <sup>19</sup> (eq 22).

**Dihydroboration of Alkynes with  $\text{BH}_2\text{Cl}$  Etherates. General Considerations.** The dihydroboration of alkynes with  $\text{BH}_2\text{Cl}$  would produce *B*-chlorodibora compounds. Since  $\text{BH}_2\text{Cl}$  is a difunctional hydroborating agent, these products could have cyclic structures. The stoichiometry of the reaction is one alkyne per  $\text{BH}_2\text{Cl}$ . The initial product in the reaction of alkynes with  $\text{BH}_2\text{Cl}$  in 1:1 ratio might be the

Table XIV. Reaction of Alkynes with  $\text{BH}_2\text{Cl}$  (5 mmol) in Diethyl Ether at 0 °C ( $\sim 0.87$  M  $\text{BH}_2\text{Cl}$ )

Alkyne	Amount of alkyne used, mmol	Time, h	Hydride reacted, mmol	Alkyne remaining, mmol	Alkyne reacted, mmol	Maximum yield of the dialkenyl chloroborane expected, %
1-Hexyne	10	0.25	10	2.1	7.9	58
	10 <sup>a</sup>	0.25 <sup>a</sup>	10 <sup>a</sup>	2.0 <sup>a</sup>	8.0 <sup>a</sup>	60 <sup>a</sup>
	12	0.25	10	3.0	10	80
	13	0.25	10	3.6	9.4	88
	14	0.25	10	3.8	10.2	100
Cyclohexylethyne	10	0.25	10	1.2	8.8	76
	12	0.25	10	2.5	9.5	90
	13	0.25	10	3.0	10.0	100
Phenylethyne	10	1.00	10	1.5	8.5	70
	13	1.00	10	3.6	9.4	88
	14	1.00	10	4.2	9.8	96
	10	0.25	10	0.25	9.75	95

<sup>a</sup> At -78 °C.

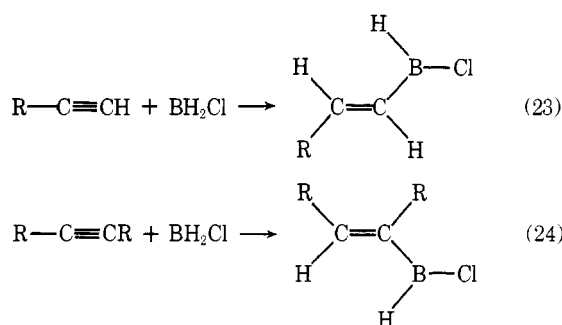


**Table XV.** Synthesis of Dialkenylchloroboranes by the Monohydroboration of Alkynes with  $\text{BH}_2\text{Cl} \cdot \text{EE}$ 

Alkyne	Dialkenyl-chloroborane <sup>a</sup>	Isolated yield, %	Bp, °C (mm)
1-Hexyne	Bis( <i>trans</i> -1-hexenyl)-chloroborane	81	79–81 (0.05)
3,3-Dimethyl-1-butyne	Bis( <i>trans</i> -3,3-dimethyl-1-butenyl)-chloroborane	80	52–53 (0.09)
Cyclohexylethyne	Bis( <i>trans</i> -2-cyclohexyl-1-ethenyl)-chloroborane	76	122–124 (0.025)
3-Hexyne	Bis( <i>cis</i> -3-hexenyl)-chloroborane	88	66–68 (0.10)

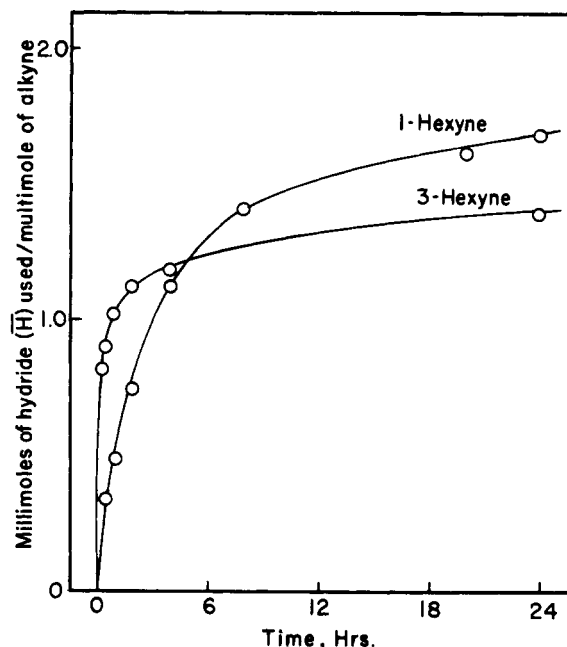
<sup>a</sup> The stereochemistry of the products was determined by  $^1\text{H}$  NMR. The isolated dialkenylchloroboranes all gave correct elemental analyses.

monohydroboration product, alkenylchloroborane (eq 23 and 24), which could be trapped as a suitable derivative if the second stage, i.e., the formation of the dihydroboration product, is considerably slower than the first step. This alk-



enylchloroborane could be a valuable intermediate for the synthesis of alkylalkenylchloroboranes and mixed dialkenylchloroboranes. From a study of the rate and stoichiometry of the hydride and alkyne uptake in the 1:1 reaction of alkyne with  $\text{BH}_2\text{Cl}$ , it might be possible to see whether the reaction goes stepwise cleanly and whether the intermediate alkenylchloroborane could be trapped or not. Therefore, such a study was undertaken using 1-hexyne and 3-hexyne as the typical alkynes.

**Dihydroboration of Alkynes with  $\text{BH}_2\text{Cl}$  (1:1) in Tetrahydrofuran. Rate and Stoichiometric Study.** The reaction was carried out by adding alkyne to  $\text{BH}_2\text{Cl}$  (1:1) in THF and stirring the mixture at 0 °C. (The solution contained a known amount of *n*-octane to serve as internal standard for

**Figure 2.** Rate of hydride uptake by 1-hexyne and 3-hexyne (0.5 M each) with  $\text{BH}_2\text{Cl}$  (0.5 M) in THF at 0 °C.

GC analysis.) The reaction mixture was 0.5 M in each reactant. Aliquots were withdrawn at intervals and analyzed for residual hydride (by hydrolyzing and measuring the hydrogen evolved) and alkyne (by GC). The results are given in Table XVI and plotted in Figure 2. The complete hydroboration to form the dihydroboration product is slow and incomplete in both cases. Under the reaction conditions, only 69% and 40% dihydroboration occurred in the case of 1-hexyne and 3-hexyne, respectively, after 24 h reaction at 0 °C. The initial stage of the reaction is much faster in both cases, being more so in the case of 3-hexyne. The maximum yield of monohydroboration product in the case of 1-hexyne was 57% (contaminated with 9% dihydroboration product) after 2 h of reaction. In the case of 3-hexyne, the maximum yield of the monohydroboration product was 86% (contaminated by 8% dihydroboration product) after 1 h of reaction. In this case, in 15 min reaction, the monohydroboration product was formed in 82% yield with virtually no contamination from the dihydroboration product. From the graphical representation of the data in Figure 2, it is seen that the reaction goes stepwise in the case of 3-hexyne, forming first the monohydroboration product cleanly, followed by the

**Table XVI.** Reaction of Alkynes<sup>a</sup> with  $\text{BH}_2\text{Cl}$ <sup>b</sup> (1:1) in Tetrahydrofuran at 0 °C

Alkyne	Time, h	Aliquot, ml	Hydride reacted, mmol	Alkyne reacted, mmol	Max yield of products expected, %	
					Monohydroboration product	Dihydroboration product
1-Hexyne	0.5	2.0	0.35	0.33	31	2
	1.0	2.0	0.50	0.47	44	3
	2.0	2.0	0.75	0.66	57	9
	4.0	2.0	1.13	0.79	45	34
	8.0	2.0	1.42	0.92	42	50
	20.0	2.0	1.63	1.00	37	63
	24.0	2.0	1.69	1.00	31	69
3-Hexyne	0.25	2.0	0.82	0.82	82	0
	0.50	2.0	0.90	0.86	82	4
	1.00	2.0	1.02	0.94	86	8
	2.0	2.0	1.13	0.98	83	15
	4.0	2.0	1.19	1.00	81	19
	24.0	2.0	1.40	1.00	60	40

<sup>a</sup> 0.5 M alkyne. <sup>b</sup> 0.5 M  $\text{BH}_2\text{Cl}$ .

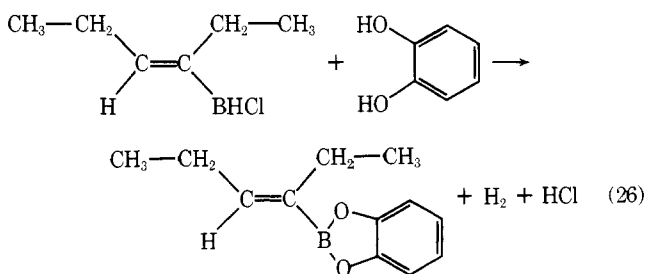
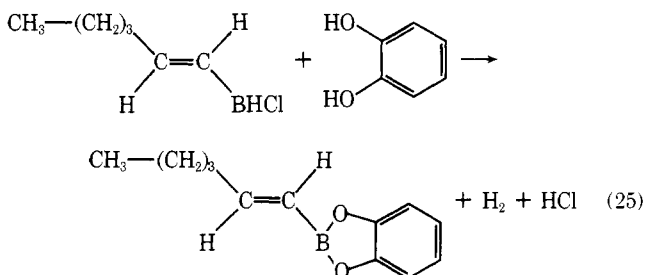
Table XVII. Reaction of Alkynes<sup>a</sup> with BH<sub>2</sub>Cl<sup>b</sup> (1:1) in Diethyl Ether at 0 °C

Alkyne	Time, h	Aliquot, ml	Hydride reacted, mmol	Alkyne reacted, mmol	Max yield of products expected, %	
					Monohydroboration product	Dihydroboration product
1-Hexyne	0.25	1.0	1.90	1.0	10	90
	1.0	1.0	1.92	1.0	8	92
	1.0 <sup>c</sup>	1.0	2.0	1.0	0	100
Cyclohexylethyne	0.25	1.0	2.0	1.0	0	100
Phenylethyne	0.25	1.0	1.92	1.0	8	92
	1.0	1.0	1.94	1.0	6	94
	1.0 <sup>c</sup>	1.0	1.98	1.0	2	98
3-Hexyne	0.25	1.0	1.53	1.0	47	53
	1.00	1.0	1.60	1.0	40	60
	1.00 <sup>c</sup>	1.0	1.81	1.0	19	81

<sup>a</sup> 1.0 M alkyne. <sup>b</sup> 1.0 M BH<sub>2</sub>Cl. <sup>c</sup> The reaction mixture was first stirred at 0 °C for 1 h followed by another 1 h at 25 °C.

slow dihydroboration stage. In the case of 1-hexyne, the reaction is not proceeding in such clean stepwise manner.

**Characterization of the Monohydroboration Product in the Reaction of 1-Hexyne and 3-Hexyne with BH<sub>2</sub>Cl (1:1) in Tetrahydrofuran at 0 °C.** The 1:1 stoichiometry of hydride and alkyne uptake in the reaction does not tell the nature of the monohydroboration product unambiguously, because this stoichiometry corresponds to the formation of both alkenylchloroborane and dialkenylchloroborane. That the monohydroboration product in this reaction was the alkenylchloroborane was proved by making the catechol derivative of the alkenylchloroborane (by reacting it with catechol) and identifying by GC (eq 25 and 26). The catechol deriva-



tives were prepared by quenching the reaction mixture in a solution of catechol in THF after 2 and 3 h reaction with BH<sub>2</sub>Cl in the case of 3-hexyne and 1-hexyne, respectively. The catechol derivatives<sup>21</sup> of the alkenylchloroboranes were analyzed by GC. The yields of the catechol derivatives were 84% in the case of 3-hexyne and 44% in the case of 1-hexyne. The corresponding yields expected based on the stoichiometric results were 83% in the case of 3-hexyne and 51% in the case of 1-hexyne. From these observations, it is concluded that monoalkenylchloroboranes are formed as a result of the initial reaction of alkynes with BH<sub>2</sub>Cl in 1:1 ratio in THF at 0 °C.

**Dihydroboration of Alkynes with BH<sub>2</sub>Cl (1:1) in Diethyl Ether. Rate and Stoichiometric Study.** Reactions of 1-hexyne, cyclohexylethyne, phenylethyne, and 3-hexyne were investigated in this study. The reaction was carried out by adding the alkyne to BH<sub>2</sub>Cl (1:1) in EE and stirring the

mixtures at 0 °C. The solution was 1.0 M in each reactant. Aliquots were withdrawn and analyzed for residual alkyne by GC and residual hydride by hydrolyzing and measuring the hydrogen evolved. The results are given in Table XVII. The reaction was extremely fast in the case of terminal alkynes studied and fairly fast in the case of internal alkyne, 3-hexyne. In the case of terminal alkynes, more than 95% hydride reacted in less than 15 min, indicating that the monohydroboration product, alkenylchloroborane, underwent further hydroboration as soon as it was formed. In the case of 3-hexyne also, the second stage of the reaction was so facile that more than 50% of the alkenylchloroborane formed underwent further hydroboration in 15 min. However, thereafter the reaction slowed down. In the case of terminal alkynes, the dihydroboration went to completion, but not in the case of 3-hexyne under the reaction conditions. Based on these findings, it is recommended that, for effecting complete dihydroboration of terminal alkynes, stoichiometric amounts of the alkyne and BH<sub>2</sub>Cl be mixed at 0 °C in EE and stirred for 1 h at 25 °C. In the case of internal alkynes, the same procedure should be followed using 10% excess BH<sub>2</sub>Cl. <sup>1</sup>H NMR spectra of the crude products, obtained by removing the solvent from the reaction mixture, did not show the presence of vinyl protons, indicating that complete dihydroboration has taken place under these reaction conditions. However, the products in these reactions were not isolated and characterized.

## Experimental Section

**Materials.** Reaction vessels and other glass equipment used for the experiments were thoroughly dried in an oven and cooled under a stream of dry nitrogen just prior to use. The tetrahydrofuran was distilled over LiAlH<sub>4</sub> and stored over Type 5A molecular sieves under nitrogen. Analytical grade diethyl ether was stored over Type 4A molecular sieves under nitrogen before use. Reagent grade methanol was used after storing over Type 3A molecular sieves without further purification. LiBH<sub>4</sub> was obtained from Ventron Corp. Alfa Products. The BCl<sub>3</sub> and HCl gas were obtained from Matheson Gas Co. and were certified >99% pure. Most of the hydrocarbons used as internal standards for GC analysis and the gaseous olefins used were from Phillips '66 Petroleum Co. and were labeled >99% pure. The liquid olefins used for these studies were commercial products of the highest purity available. Their refractive indices and spectral characteristics were checked before using for the experiments. In cases where the commercial products were of lesser quality, the materials were purified by distillation before use. All other chemicals were checked and made sure that they were of satisfactory quality before using them for the experiments.

**Gas Chromatographic Analysis.** GC analyses were carried out on either a Varian 1200 or a 1400 Series temperature programmed gas chromatograph equipped with a flame ionization detector and provided with temperature controllers for the injector and the de-

tektor. All the GC yields were determined utilizing a suitable internal standard and authentic synthetic mixtures. The yields reported here are actual rather than normalized yields. The following columns were generally used: column A, 5% SE-30 on Aeropak 30, 5 ft  $\times$  0.125 in.; column B, 5% SE-30 on Aeropak 30, 2 ft  $\times$  0.125 in.; column C, 30% adiponitrile on Firebrick, 3 ft  $\times$  0.125 in.; column D, 5% Carbowax 20M-TPA on Varaport 30, 12 ft  $\times$  0.125 in. The precautions recommended for the GC analysis of organoboranes<sup>7</sup> were religiously followed whenever such compounds were analyzed.

**Spectral Measurements.** <sup>11</sup>B NMR spectra were taken using a Varian XL-100 nuclear magnetic resonance spectrometer equipped with a boron probe. A Varian T-60 NMR spectrometer was used for obtaining proton magnetic resonance spectra. Infrared spectra were taken with a Perkin-Elmer 700 ir spectrometer.

**Preparation of Stock Solution of Diborane in THF.** Diborane was generated according to the reported procedure by Brown and co-workers.<sup>22,23</sup> Generally, solutions of strength 2–3 M in BH<sub>3</sub>·THF were prepared and stored under nitrogen in a cold room. Such solutions showed no measurable loss of hydride activity over many months.

**Preparation of BH<sub>2</sub>Cl in THF Solution.** BH<sub>3</sub> (180 mmol) in THF (80 ml) was taken in a 200-ml round-bottom flask, provided with a rubber stoppered side arm and fitted with a dry ice-acetone condenser connected to a mercury bubbler. The contents of the flask were cooled to –10 °C using an ice-salt bath. Meanwhile 90 mmol of BCl<sub>3</sub> was condensed in a stoppered centrifuge tube fitted with an outlet tube attached to a Tygon tubing. The centrifuge tube was kept cooled around –20 °C, and a very slow stream of nitrogen was kept flowing through the system (at this temperature, the evaporation of BCl<sub>3</sub> is negligible). Then under a flow of nitrogen, the rubber stopple was removed from the side arm of the flask and quickly the free end of the Tygon tubing was attached to it. The BCl<sub>3</sub> tube was allowed to warm up to room temperature slowly, letting the BCl<sub>3</sub> distill slowly into the flask, the contents of which were kept vigorously stirring. The stirring was continued for 1 h after all the BCl<sub>3</sub> had distilled into the flask. The Tygon tube was disconnected from the side arm of the flask while the nitrogen was still flowing and quickly stoppered. The solution of BH<sub>2</sub>Cl was kept in the cold room for overnight. The next morning, the active hydride concentration was determined by hydrolyzing an aliquot and measuring the hydrogen evolved. The chloride was analyzed by hydrolyzing an aliquot and titrating the HCl produced with NaHCO<sub>3</sub> using methyl orange indicator. The  $\bar{H}/\bar{Cl}$  ratio was found to be 2.03 ( $\bar{H}/\bar{Cl}$  expected for BH<sub>2</sub>Cl = 2). The strength of the solution was determined as 3.30 M in BH<sub>2</sub>Cl. The <sup>11</sup>B NMR spectrum of the solution showed it to be >97% pure. (Symmetrical triplet at –4.2 ppm relative to BF<sub>3</sub>·OEt<sub>2</sub> with  $J_{BH}$  = 132 Hz. Proton heteronuclear spin decoupling produced a singlet.) The solution was stored in a cold room. An aliquot of the solution analyzed after 2 months gave the strength as 3.36 M. During the course of the work, stock solutions of different strengths were prepared and used at different times.

**Preparation of LiBH<sub>4</sub> Solution in Diethyl Ether.** Fifteen grams of commercial lithium borohydride (~95%) was added to 500 ml of EE in a 1-l. flask at 0 °C under nitrogen and stirred at 25 °C for 2 h. Most of the solid went into solution. However, some white material always remained insoluble. The mixture was left undisturbed for a few hours when the insoluble material settled, leaving a clear supernate. (In certain experiments, the solution was filtered under nitrogen to get rid of the suspension.) The clear solution was analyzed by injecting an aliquot into a hydrolyzing mixture of glycerin and water, kept at 0 °C, and measuring the hydrogen gas evolved. Repeated analysis was necessary to obtain consistent results. The solution was found to be 1.23 M in LiBH<sub>4</sub>. (This is very near the saturation point at 25 °C.) During the course of the work, LiBH<sub>4</sub> solutions of different strengths were prepared and used at different times.

**Preparation of BCl<sub>3</sub> Solution in Diethyl Ether.** EE (500 ml) was taken in a 1-l. flask, provided with a rubber stopple inlet tube and fitted with a connecting tube attached to a mercury bubbler. The contents of the flask were cooled to 0 °C while stirring. BCl<sub>3</sub> gas was slowly passed into the flask through a broad gauge stainless steel hypodermic needle inserted through the rubber stopple and connected to the pressure regulator of the BCl<sub>3</sub> tank through a

Tygon tubing. After passing the BCl<sub>3</sub> for a few minutes, an aliquot of the solution was removed and analyzed for the BCl<sub>3</sub> content by hydrolyzing and titrating the HCl produced with NaHCO<sub>3</sub> using methyl orange indicator. If necessary, more BCl<sub>3</sub> was passed to obtain a more concentrated solution. This was continued until the desired concentration of BCl<sub>3</sub> was obtained. A solution prepared this way was 1.505 M in BCl<sub>3</sub>. (It was found that BCl<sub>3</sub>·OEt<sub>2</sub> separated out from the solution at around 1.6 M at 0 °C.) The BCl<sub>3</sub> solution in EE is found to remain practically stable over several days in a cold room (99% strength maintained after 43 days). During the course of the work, stock solutions of different strengths were prepared and used at different times.

**Preparation of BH<sub>2</sub>Cl Solution in Diethyl Ether.** In a 1-l. round-bottom flask, oven dried, fitted with a rubber stoppered side arm, and a connecting tube attached to a mercury bubbler, was taken, under an atmosphere of nitrogen, at 0 °C, 526 mmol of BCl<sub>3</sub> in EE (350 ml). The solution was stirred at 0 °C using a magnetic stirrer. While stirring, 526 mmol of LiBH<sub>4</sub> in EE (428 ml) was slowly added to the flask through the rubber stoppered side arm using a large hypodermic syringe. The stirring was continued at 0 °C for 2 h after the addition of LiBH<sub>4</sub> was over. Afterwards, the mixture was allowed to stand undisturbed for a few hours so that the LiCl settled, leaving a clear supernate of BH<sub>2</sub>Cl in EE. An aliquot of the clear supernate was analyzed for the hydride content by hydrolyzing and measuring the hydrogen evolved. The chloride was estimated by hydrolyzing an aliquot and titrating the HCl produced with NaHCO<sub>3</sub> using methyl orange indicator. The solution was 2.72 M in hydride and 1.38 M in chloride ( $\bar{H}/\bar{Cl}$  = 1.97, expected  $\bar{H}/\bar{Cl}$  = 2). This will correspond to the presence of BHCl<sub>2</sub> as impurity to the extent of 1%. The solution was 1.36 M in BH<sub>2</sub>Cl. The <sup>11</sup>B NMR spectrum of the solution showed it to be >98% pure. (Symmetrical triplet at –5.0  $\pm$  0.3 ppm relative to BF<sub>3</sub>·OEt<sub>2</sub> with  $J_{BH}$  = 136 Hz. Proton heteronuclear spin decoupling produced a singlet.) The solution was stored under nitrogen in a cold room where it was found to remain stable for several weeks (virtually no change in strength after 43 days). During the course of the work, stock solutions of different strengths were prepared and used at different times.

**Preparation of HCl Solution in Diethyl Ether.** The experimental setup and procedure was the same as in the preparation of BCl<sub>3</sub> solution in EE. The BCl<sub>3</sub> tank was substituted by an HCl tank. The strength of the solution was determined by withdrawing an aliquot and diluting with water followed by titration with standard NaHCO<sub>3</sub> using methyl orange indicator. The solution was 2.56 M in HCl. It was stored in a cold room where it remained for months without any perceptible loss of acidity. During the course of the work, stock solutions of different strengths were prepared and used at different times.

**General Procedure for the Determination of the Rates of Reactions of Olefins with BH<sub>2</sub>Cl (BH<sub>2</sub>Cl:Olefin = 1:2).** The general procedure was to add 5 mmol of BH<sub>2</sub>Cl solution to 10 mmol of olefin (in some experiments different quantities of the reagents were used) in sufficient solvent (THF or EE as the case may be) containing a known quantity of a saturated hydrocarbon (generally 5 mmol of *n*-octane or *n*-decane to serve as internal standard for GC analysis) so that the desired reagent concentrations were obtained. The reaction mixture was stirred at the desired temperature (0 °C, ice bath; 25 °C, water bath at room temperature) using a magnetic stirrer. Aliquots of the reaction mixture were withdrawn at specified intervals and quenched in an ice-water mixture in a small vial. The acidic materials in the mixture were destroyed using aqueous NaOH at 0 °C. The organic materials in the vial were extracted into pentane or EE and analyzed by GC for the amount of unreacted olefin remaining. Generally a SE-30 (column A) or adiponitrile (column C) columns were used for the analysis. From the amount of residual olefin remaining, the percentage of olefin reacted was calculated for each interval. The detailed experimental procedures for the determination of the rates of reactions of 1-hexene with BH<sub>2</sub>Cl in THF and BH<sub>2</sub>Cl in EE are described as typical examples.

**Rate of Reaction of 1-Hexene (1.0 M) with BH<sub>2</sub>Cl (0.5 M) in THF at 0 °C.** A clean 100-ml flask, oven dried, equipped with a side arm fitted with a Silicone rubber stopple, a magnetic stirring bar, and a connecting tube attached to a mercury bubbler, was cooled under a stream of nitrogen. The reaction flask was immersed in an ice bath. THF (4.79 ml) was injected into the flask

through the rubber stopple using a hypodermic syringe, followed by 10 mmol of 1-hexene (1.26 ml) and 10 mmol of *n*-octane (1.63 ml). The mixture was stirred for 15 min at 0 °C. Then 5 mmol of  $\text{BH}_2\text{Cl}$  in THF (2.32 ml) was added slowly to the flask while stirring the contents at 0 °C. Now the total volume was 10 ml (0.5 M  $\text{BH}_2\text{Cl}$ , 1.0 M in 1-hexene). One-milliliter aliquots were withdrawn at 1, 6, and 24 h after the addition of  $\text{BH}_2\text{Cl}$  and analyzed for the residual 1-hexene by GC as described in the general procedure. From these data the rate of reaction was calculated.

**Rate of Reaction of 1-Hexene (1.0 M) with  $\text{BH}_2\text{Cl}$  (0.5 M) in Diethyl Ether at 0 °C.** The experimental setup and procedure was exactly as in the above case. EE (3.44 ml) was used instead of THF as the solvent and 5 mmol of  $\text{BH}_2\text{Cl}$  in EE (3.67 ml) was used instead of the  $\text{BH}_2\text{Cl}$  in THF. The aliquots were withdrawn and analyzed at 15 min and 1 and 24 h after the addition of  $\text{BH}_2\text{Cl}$ . 1-Hexene (98%) reacted in 1 h. The experiment was repeated using the representative olefins listed in Table IV.

**Analysis of the Methanolysis Products of the Reaction of Butenes with  $\text{BH}_2\text{Cl}$ .** The experiment using 1-butene (4 M) and  $\text{BH}_2\text{Cl}$  (2 M) in THF at 0 °C is described as the typical example. A clean 100-ml flask, oven dried, equipped with a side arm capped with a tight fitting Silicone rubber stopple, a magnetic stirring bar, and connected to a mercury bubbler through a connecting tube with a stopcock closing the mouth of the flask, was cooled to 0 °C using an ice-water bath, under a stream of nitrogen. THF (0.42 ml), 0.5 mmol of *n*-octane (0.0814 ml, internal standard for GC analysis), and 2.5 mmol of  $\text{BH}_2\text{Cl}$  in THF (0.75 ml) were introduced into the flask through the rubber stopple using a hypodermic syringe. The total volume of the mixture was 1.25 ml. The contents of the flask were stirred for 5 min at 0 °C. The stopcock on the connecting tube was then closed, and 5 mmol of 1-butene was introduced into the flask as gas (123 ml at 24 °C and 751 mm) using a gas syringe developed in this laboratory for accurately transferring known amounts of gaseous materials.<sup>24</sup> The reaction mixture was stirred for 6 h at 0 °C. The stopcock was then opened, and 1 ml of dry methanol was injected into the flask for methanolizing the reaction products. After 15 min, 3 mmol (~0.5 ml) of dry triethylamine was added to the flask in order to neutralize the HCl formed as a result of the methanolysis of the chloroboranes. The mixture was diluted with 5 ml of EE and stirred for 5 min at 25 °C. A small sample of the clear supernate of the reaction mixture was analyzed by GC for *n*-BuB(OMe)<sub>2</sub>, *n*-Bu<sub>2</sub>BOMe, and *n*-Bu<sub>3</sub>B using SE-30 column (column B). The GC retention times and response ratios of these materials had been determined earlier under identical conditions using authentic samples. *n*-BuB(OMe)<sub>2</sub> (0.98 mmol), 0.45 mmol of *n*-Bu<sub>2</sub>BOMe, and 0.76 mmol of *n*-Bu<sub>3</sub>B were found to be present in the reaction mixture.

When the experiments were done using *cis*-2-butene and isobutylene, 0.5 mmol of tridecane was used as the internal standard instead of *n*-octane. When the reactions were done in EE, the required amount of EE was used in place of the THF and  $\text{BH}_2\text{Cl}$  in EE was employed instead of  $\text{BH}_2\text{Cl}$  in THF. In the reaction of butenes with  $\text{BH}_2\text{Cl}$  in 1:1 ratio in EE, 5 mmol of butenes and 5 mmol of  $\text{BH}_2\text{Cl}$  were used. The cooling baths at -20 and -30 °C were prepared by mixing dry ice with a water solution of calcium chloride of appropriate concentrations.<sup>25</sup>

**Directive Effect in the Hydroboration of 1-Hexene with  $\text{BH}_2\text{Cl}$  in Diethyl Ether.** A clean 100-ml flask, dried in an oven, equipped with a side arm fitted with a Silicone rubber serum stopple, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler, was cooled under a stream of nitrogen. The flask was immersed in an ice bath and charged with 10 mmol of 1-hexene (1.26 ml), 10 mmol of *n*-octane (1.63 ml, internal standard for GC analysis), and 1.1 ml of dry ether.  $\text{BH}_2\text{Cl}$  (5 mmol) in EE (6 ml) was then slowly added to the flask, while stirring the reaction mixture at 0 °C. After 1 h reaction time, the organochloroboranes formed in the reaction mixture were oxidized by adding 6 ml of 3 M aqueous NaOH and 2 ml of 30%  $\text{H}_2\text{O}_2$ , followed by 30 ml of 95% ethanol as a cosolvent. After stirring for 1 h at 25 °C, the oxidation was completed by warming the reaction mixture to 50 °C and stirring for 15 min. The organic layer was then analyzed by GC for the amounts of 1-hexanol and 2-hexanol formed in the reaction using a Carbowax column (column D). The total yield of the alcohols was 96.3%, of which 99.5% was 1-hexanol and 0.5% was 2-hexanol.

The experiment was repeated using the representative olefins

listed in Table V and analyzing for the corresponding alcohols produced.

**Synthesis of Dialkylchloroboranes and Methyl Dialkylborinates.** The syntheses of dicyclopentylchloroborane and methyl dicyclopentylborinate are described as typical procedures. A clean 100-ml flask, oven dried, fitted with a side arm capped with a rubber serum stopple, a magnetic stirring bar, and a connecting tube attached to a mercury bubbler, was cooled in an ice bath under a stream of dry nitrogen. The flask was then charged with 25 mmol of  $\text{BCl}_3$  in EE (1.58 M).  $\text{LiBH}_4$  (25 mmol) in EE (1.45 M) was slowly added to the  $\text{BCl}_3$  in the flask over a period of 15–20 min, while stirring the contents of the flask at 0 °C. The mixture was stirred at 0 °C for 15 min. Cyclopentene (100 mmol) was slowly added to the mixture in the flask ( $\text{BH}_2\text{Cl}$  in EE containing suspended lithium chloride), and stirring was continued at 0 °C for 1 h. The solvent was then removed under vacuum using a water aspirator, and the dicyclopentylchloroborane was isolated by distillation at 68–69 °C (1.00 mm) in 80% yield.

The methyl dicyclopentylborinate was synthesized as follows. The above procedure was followed. After 1 h of reaction between  $\text{BH}_2\text{Cl}$  and cyclopentene, 100 mmol of methanol was added and stirred for 15 min at 0 °C. The ether, excess methanol, and the HCl (formed by the methanolysis of the dicyclopentylchloroborane) were removed under vacuum using a water aspirator. The methyl dicyclopentylborinate was isolated by distillation at 82–84 °C (2.0 mm) in 84% yield.

**Rate of Reaction of Octenes with  $\text{BH}_2\text{Cl}$  (1:1) in Diethyl Ether in the Presence of Varying Amounts of THF at 0 °C.** The experiment using 1.0 M  $\text{BH}_2\text{Cl}$ , 1.2 M THF, and 1.0 M 1-octene is described as a typical example. A clean 100-ml flask, oven dried, equipped with a side arm fitted with a rubber stopple, a magnetic stirring bar, and a connecting tube attached to a mercury bubbler, was cooled in an ice bath under a stream of nitrogen.  $\text{BH}_2\text{Cl}$  (5 mmol) in EE (3.2 ml), 6 mmol of THF (0.5 ml), and 2.5 mmol of *n*-decane (0.488 ml, internal standard for GC analysis) were introduced into the flask through the rubber stopple using hypodermic syringe. The mixture was stirred for 15 min at 0 °C. 1-Octene (5 mmol, 0.78 ml) was then added, and stirring was continued at 0 °C. Aliquots were withdrawn at 15 min and 1 h after the addition of 1-octene and analyzed for the residual 1-octene by GC, after destroying the chloroboranes in the aliquot using aqueous NaOH at 0 °C. It was found that 99 and 100% 1-octene had reacted in 15 min and 1 h, respectively. The experiment was repeated using other concentrations of the reagents and also using *cis*-2-octene instead of 1-octene.

**Analysis of the Methanolysis Products of the Reaction of Butenes with  $\text{BH}_2\text{Cl}$  (1:1) in Diethyl Ether in the Presence of Varying Amounts of THF at 0 °C.** The experiment employing 1-butene (1.0 M), THF (1.2 M), and  $\text{BH}_2\text{Cl}$  (1.0 M) is described as a typical example. The experimental setup was the same as in the case of reaction of 1-butene (4 M) with  $\text{BH}_2\text{Cl}$  (2 M) in THF at 0 °C, described earlier.  $\text{BH}_2\text{Cl}$  (5 mmol) in EE (3.8 ml), 6 mmol of THF (0.5 ml), 0.7 ml of EE, and 0.5 mmol of tridecane (0.122 ml, internal standard for GC analysis) were introduced into the flask and stirred for 15 min at 0 °C. 1-Butene (5 mmol) (124.5 ml at 26 °C and 748 mm) was introduced into the flask as gas using the gas syringe as described in the earlier experiment. The reaction mixture was stirred for 1 h at 0 °C. Methanol (2 ml) was then added to methanolize the products. After stirring for 15 min, 6 mmol (~0.8 ml) of  $\text{Et}_3\text{N}$  was added to neutralize the HCl, and the clear supernate was analyzed by GC for *n*-BuB(OCH<sub>3</sub>)<sub>2</sub>, *n*-Bu<sub>2</sub>BOCH<sub>3</sub>, and *n*-Bu<sub>3</sub>B. It was found that *n*-Bu<sub>2</sub>BOCH<sub>3</sub> was formed in 96% yield. Only trace amounts of *n*-Bu<sub>2</sub>BOCH<sub>3</sub> were found. No *n*-Bu<sub>3</sub>B was detected. The experiment was repeated at other reagent concentrations and also using the other butenes.

**Synthesis of Monoalkylchloroborane-Trimethylamine Complexes.** A clean 250-ml flask, oven dried, equipped with a side arm fitted with a Silicone rubber stopple, a magnetic stirring bar, and a connecting tube attached to a mercury bubbler through a stopcock, was cooled in an ice bath under a stream of nitrogen.  $\text{BH}_2\text{Cl}$  (100 mmol) in EE (80 ml) and 200 mmol of THF (16.24 ml) were introduced into the flask and stirred for 15 min at 0 °C. 1-Pentene (100 mmol, 10.95 ml) was added to the flask slowly and stirring was continued at 0 °C for 4 h after the addition of 1-pentene was over. *n*-Pentylchloroborane was formed in the solution.  $\text{Me}_3\text{N}$  (130 mmol) was absorbed into the solution at 0 °C from a tube in which

the amine had been condensed previously. Stirring was continued for 1 h at 0 °C, followed by 1 h at 25 °C. The solvent, THF, and the excess  $\text{Me}_3\text{N}$  were removed under vacuum using a water aspirator. A small amount of a white suspension was present in the crude product. On distillation under vacuum, this solid material sublimed and came out first. This was discarded. The pure *n*-pentylchloroborane-trimethylamine complex distilled at 93–96 °C (0.1 mm). The material was obtained in 81% yield.

Trimethylamine complexes of cyclopentylchloroborane and 2-methyl-2-butylchloroborane were synthesized in the same way.

**Reaction of Monoalkylchloroborane ( $\text{RBHCl}$ ) with  $\text{HCl}$  in Diethyl Ether.** The experiment with *n*-Hex-BHCl is described as a typical example. A clean 100-ml flask, oven dried, equipped with a Silicone rubber stopple, a magnetic stirring bar, and a reflux condenser connected to a gas buret through a dry ice-acetone trap, was cooled in an ice bath under a stream of nitrogen.  $\text{BH}_2\text{Cl}$  (5 mmol) in EE (3.7 ml), 6 mmol of THF (0.5 ml), and 2.5 mmol of *n*-nonane (0.09 ml, internal standard for GC analysis) were introduced into the flask and stirred for 15 min at 0 °C. 1-Hexene (5 mmol, 0.63 ml) was added, and stirring was continued at 0 °C for 1 h. *n*-Hexylchloroborane was formed in the reaction mixture. The contents of the flask were brought to 25 °C by immersing the flask in a water bath at room temperature and stirred at 25 °C for 5 min.  $\text{HCl}$  (5 mmol) in EE (2 ml) was then added, and stirring was continued at 25 °C. The hydrogen evolved was measured using the gas buret. Hydrogen (5 mmol, 100%) evolved in 5 min.  $\text{CH}_3\text{OH}$  (2 ml) was then added, and the methanolized reaction mixture was neutralized with 0.8 ml of  $\text{Et}_3\text{N}$ , and the product was analyzed by GC using a SE-30 column (column B). *n*-Hex-B( $\text{OCH}_3$ )<sub>2</sub> was formed in 95% yield. The product was identified by comparing the retention time with the authentic *n*-Hex-B( $\text{OCH}_3$ )<sub>2</sub>.

**Reaction of Alkynes with  $\text{BH}_2\text{Cl}$  (2:1) in THF at 0 °C.** The experiment with 1-hexyne is described as a typical example. A clean 100-ml flask, oven dried, equipped with a side arm fitted with a Silicone rubber stopple, a magnetic stirring bar, and a connecting tube attached to a mercury bubbler was cooled to 0 °C under a stream of nitrogen. 1-Hexyne (30 mmol, 3.45 ml), 30 mmol of *n*-octane (4.89 ml, internal standard for GC analysis), and 14.7 mmol of THF were introduced into the flask through the rubber stopple using a hypodermic syringe.  $\text{BH}_2\text{Cl}$  (15 mmol) in THF (6.96 ml) was added to the flask and stirred at 0 °C. The reaction mixture was 1.0 M in 1-hexyne and 0.5 M in  $\text{BH}_2\text{Cl}$ . Two-milliliter aliquots were withdrawn at intervals and analyzed for residual hydride by hydrolyzing and measuring the hydrogen evolved. The residual 1-hexyne present in another aliquot, withdrawn simultaneously, was determined by GC, after destroying the chloroboranes using aqueous NaOH. The experiment was repeated using 3-hexyne instead of 1-hexyne.

**Reaction of 1-Hexyne with  $\text{BH}_2\text{Cl}$  (3:1) in THF at 0 °C.** The reaction was carried out exactly as in the above case using 45 mmol of 1-hexyne (7.34 ml), 45 mmol of *n*-octane (5.17 ml, internal standard for GC analysis), 10.53 ml of THF, and 15 mmol of  $\text{BH}_2\text{Cl}$  in THF (6.96 ml). The reaction mixture was 1.5 M in 1-hexyne and 0.5 M in  $\text{BH}_2\text{Cl}$ .

**Oxidation of the Reaction Product of 3-Hexyne with  $\text{BH}_2\text{Cl}$  (2:1) in THF by  $\text{NaOH-H}_2\text{O}_2$  and Analysis of the Oxidation Product.** The experimental setup was exactly as in the above case. 3-Hexyne (100 mmol, 11.4 ml) and 73.6 ml of THF were introduced into the flask, then 50 mmol of  $\text{BH}_2\text{Cl}$  in THF (15 ml) was added to the flask and stirred for 24 h at 0 °C (total volume = 100 ml). Meanwhile, another reaction flask was set up as in the above case, except that the connecting tube was replaced by a reflux condenser attached to a mercury bubbler. The reaction mixture (10 ml) was then transferred to the second flask and 10 mmol of *n*-dodecane (internal standard for GC analysis) was added. Oxidation was carried out by adding 3.5 ml of 3 N NaOH, followed by 1.5 ml of 30%  $\text{H}_2\text{O}_2$  and stirring for 2 h at 25 °C. Oxidation was completed by heating the reaction mixture at 50 °C for 15 min. The organic layer was then analyzed by GC for 3-hexanone (SE-30 Column A). 3-Hexanone was formed in 98% yield.

**Reaction of the Product from 3-Hexyne with  $\text{BH}_2\text{Cl}$  (2:1) in THF with  $\text{NaOH-I}_2$  to Form *cis,trans*-4,5-Diethyl-3,5-octadiene.** The experimental setup was the same as above. 3-Hexyne (20 mmol, 2.28 ml), 10 mmol of *n*-octane (1.63 ml, internal standard for GC analysis), and 11.5 ml of THF were taken in the flask and stirred at 0 °C.  $\text{BH}_2\text{Cl}$  (10 mmol, 4.6 ml) was then added, and stirring

was continued for 24 h at 0 °C. NaOH (16 ml, 3 N) was then added to the flask, and, while stirring, 12 mmol of  $\text{I}_2$  in 20 ml of THF was slowly added. Stirring was continued after the addition of  $\text{I}_2$  for 1 h at 0 °C. The excess iodine was then destroyed using aqueous sodium thiosulfate. The organic layer was then analyzed by GC (SE-30, column A) for *cis,trans*-4,5-diethyl-3,5-octadiene, which was formed in 84% yield. [The authentic sample of the diene was isolated in another experiment and performed the same way without using *n*-octane by distillation at 34 °C (1 mm). The diene was identified by  $^1\text{H}$  NMR:  $\delta$  5.1 (q, 2 H), 1.8–2.4 (m, 8 H), and 0.8–1.1 (m, 12 H).]

**Reaction of Alkynes with  $\text{BH}_2\text{Cl}$  in EE.** The experiment using 1-hexyne is described as the typical example. A clean 100-ml flask, oven dried, equipped with a side arm fitted with a rubber stopple, a magnetic stirring bar, and a connecting tube attached to a mercury bubbler, was cooled in an ice bath under a stream of nitrogen. 1-Hexyne (10 mmol, 1.15 ml) and 5 mmol of *n*-octane (0.814 ml, internal standard for GC analysis) were introduced into the flask. The mixture was stirred and 5 mmol of  $\text{BH}_2\text{Cl}$  in EE (3.7 ml) was added, and stirring was continued at 0 °C. (The solution was 0.88 M in  $\text{BH}_2\text{Cl}$ .) An aliquot was withdrawn after 15 min and analyzed for residual hydride by hydrolyzing and measuring the hydrogen evolved. The residual alkyne present in another aliquot was analyzed by GC (SE-30, column A) after destroying the chloroboranes using aqueous NaOH at 0 °C. The experiment was repeated using 12, 13, and 14 mmol of 1-hexyne. Reactions of cyclohexylethyne, phenylethyne, and 3-hexyne were also studied in the same manner. One experiment using 10 mmol of 1-hexyne was carried out at –78 °C when a dry ice-acetone bath was used as the cooling bath.

**Synthesis of Dialkenylchloroboranes.** Synthesis of bis(*cis*-3-hexenyl)chloroborane is described as the typical example. The reaction flask was set up as described in the previous experiment. The flask was cooled to 0 °C, and 100 mmol of 3-hexyne (11.4 ml) was added, followed by 50 mmol of  $\text{BH}_2\text{Cl}$  in EE (37 ml). The reaction mixture was stirred for 30 min at 0 °C. The solvent was then removed using a water aspirator, and the product, bis(*cis*-3-hexenyl)-chloroborane, was purified by distillation at 66–68 °C (0.1 mm Hg). The product, obtained in 88% yield, was identified by  $^1\text{H}$  NMR.

For the synthesis of dialkenylchloroboranes derived from terminal alkynes, the same procedure was employed, but a 40% excess alkyne was used.

The corresponding *B*-methoxy derivatives were prepared by adding a drop of methanol to a drop of dialkenylchloroborane in  $\text{CCl}_4$  taken in an NMR tube (5-mm o.d.). The *B*-methoxy derivatives were identified by  $^1\text{H}$  NMR of the sample ( $\text{BOCH}_3$  proton resonance at  $\delta$  3.7).

**Reaction of Alkynes with  $\text{BH}_2\text{Cl}$  (1:1) in THF at 0 °C.** The experiment using 1-hexyne is described as a typical example. The reaction flask was set up as in the previous experiment. The flask was cooled to 0 °C.  $\text{BH}_2\text{Cl}$  (15 mmol) in THF (6.95 ml), 15 mmol of *n*-octane (2.445 ml, internal standard for GC analysis), and 18.88 ml of THF were introduced into the flask. While stirring the mixture, 15 mmol of 1-hexyne (1.725 ml) was added. The reaction mixture was 0.5 M in reactants. Aliquots (2 ml) were withdrawn at intervals, and residual hydride and alkyne were determined, as described in similar previous experiments. The experiment was repeated using 15 mmol of 3-hexyne in place of 1-hexyne.

**Characterization of the Alkenylchloroborane as the Catechol Derivative.** The reaction flask was set up as in the above experiment. The flask was cooled to 0 °C.  $\text{BH}_2\text{Cl}$  (5 mmol) in THF (2.32 ml), 5 mmol of *n*-octane (0.185 ml, internal standard for GC analysis), and 6.3 ml of THF were introduced into the flask and stirred at 0 °C. 3-Hexyne (5 mmol, 0.57 ml) was added, and stirring was continued at 0 °C for 2 h. After 2 h, 6 mmol of catechol in 5 ml of THF was added, followed by 5 mmol of  $\text{Et}_3\text{N}$ . The mixture was stirred for 1 h at 25 °C. The supernate was then analyzed by GC for the catechol ester of *cis*-3-hexenylboronic acid (SE-30, column A). The authentic sample was prepared as described in an earlier publication.<sup>21</sup> The yield of the product was 84%.

The experiment was repeated using 5 mmol of 1-hexyne in place of 3-hexyne. The reaction mixture was quenched with catechol after 3 h of reaction between 1-hexyne and  $\text{BH}_2\text{Cl}$ . The yield of the catechol ester of the *trans*-1-hexenylboronic acid was 44%.

**Reaction of Alkynes with  $\text{BH}_2\text{Cl}$  (1:1) in EE.** The experiment

using 1-hexyne is described as the typical example. The reaction flask was set up as in the previous experiment.  $\text{BH}_2\text{Cl}$  (10 mmol) in EE (7.4 ml) and 1.4 ml of EE were introduced into the flask. The mixture was stirred at 0 °C, and 10 mmol of 1-hexyne (1.15 ml) was added, and stirring was continued at 0 °C. (The mixture was 1.0 M in reactants.) Aliquots (1 ml) were withdrawn at 15 min and 1 h and analyzed for residual hydride by hydrolyzing and measuring the hydrogen evolved. Another aliquot taken at 15 min at 0 °C was analyzed for the presence of residual 1-hexyne by GC. After 1 h at 0 °C, the reaction mixture was brought to 25 °C. After 1 h at 25 °C, another 1-ml aliquot was analyzed for the residual hydride. The experiment was repeated using cyclohexylethyne, phenylethyne, and 3-hexyne.

## References and Notes

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# Hydroboration. XLI. Hydroboration of Alkenes and Alkynes with Dichloroborane Etherates. Convenient Procedures for the Preparation of Alkyl- and Alkenyldichloroboranes and Their Derivatives<sup>1</sup>

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**Abstract:** Reactions of alkenes with dichloroborane ethyl etherate ( $\text{BHCl}_2\cdot\text{EE}$ ) and alkynes with dichloroborane tetrahydrofuranate ( $\text{BHCl}_2\cdot\text{THF}$ ) and  $\text{BHCl}_2\cdot\text{EE}$  were investigated in detail. The hydroboration of alkenes with  $\text{BHCl}_2\cdot\text{EE}$  in ether or pentane is slow and incomplete. However, the reaction goes to completion when neat reagents are allowed to react, but the resulting product is predominantly the dialkylchloroborane ( $\text{R}_2\text{BCl}$ ) and not the expected alkyldichloroborane ( $\text{RBCl}_2$ ). In the presence of 1 mol equiv of boron trichloride in pentane, the alkenes and  $\text{BHCl}_2\cdot\text{EE}$  react quantitatively to give the expected products  $\text{RBCl}_2$  and boron trichloride ethyl etherate ( $\text{BCl}_3\cdot\text{EE}$ ) cleanly. A series of alkyldichloroboranes and their derivatives have been synthesized and isolated by this new convenient procedure. Similarly, the reactions of alkynes with  $\text{BHCl}_2\cdot\text{THF}$  and  $\text{BHCl}_2\cdot\text{EE}$  are also slow and incomplete and give mixed products. As in the case of alkenes, the alkynes also react with  $\text{BHCl}_2\cdot\text{EE}$  quantitatively in the presence of 1 mol equiv of  $\text{BCl}_3$  in pentane to yield the expected alkenyldichloroborane cleanly. These developments provide for the first time convenient low-temperature procedures for the general syntheses of alkyl- and alkenyldichloroboranes and their derivatives.

## Introduction

Hydroboration of alkenes with borane-tetrahydrofuran ( $\text{BH}_3\cdot\text{THF}$ ) produces trialkylboranes.<sup>3</sup> The dialkyl- and dialkenylboron derivatives are easily prepared by the hydroboration of alkenes and alkynes, respectively, with monochloroborane ethyl etherate ( $\text{BH}_2\text{Cl}\cdot\text{EE}$ ).<sup>4</sup> However, no such convenient simple procedures are available for the preparation of monoalkyl- and monoalkenylboron derivatives. The hydroboration of alkenes and alkynes with a monofunctional borane,  $\text{HBX}_2$ , might produce such monoorganoboron compounds. In view of the synthetic utility of the triorganoboranes<sup>3</sup> and diorganoboron derivatives,<sup>5–9</sup> it is to be anticipated that the monoorganoboron derivatives should also find useful applications in organic syntheses. There-

fore, the reactions of dichloroborane etherates with alkenes and alkynes were investigated in detail, and the results of that study are reported here.

Dichloroborane etherates were first reported by Brown and Tierney.<sup>10</sup> A few scant investigations of the reactions of a few alkenes with  $\text{BHCl}_2\cdot\text{THF}$  have been reported by other workers<sup>11,12</sup> who have found that the reactions were extremely slow. Thus, in the reaction of  $\text{BHCl}_2\cdot\text{THF}$  with 1-hexene at 25 °C after 4 h, only 40% olefin underwent hydroboration, according to Zweifel,<sup>11</sup> and only 15% 1-hexanol was obtained after oxidation, according to Pasto and Balasubramanian.<sup>12</sup> Similarly, only 50% reaction was observed for 2-methylpropene in 24 h and only 27% reaction with styrene in 72 h. Therefore, the reaction of  $\text{BHCl}_2$  in