rene-derived cyclopropyl esters, the syn and anti forms proved to be inseparable, thus frustrating any attempts to determine the absolute configurations of the products. However, because of the chemical shift dispersion of key signals for the diastereomers, the NMR shift experiment could be carried out successfully on the mixtures to determine enantiomeric excess (ee) values.

Ethyl *syn*-3-methyl-*syn*-2-phenylcyclopropanecarboxylate (*cis*-β-methylstyrene product): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.32–7.15 (5 H), 4.05 (q, 2 H), 2.63 (t, 1 H), 2.06 (t, 1 H), 1.76 (m, 1 H), 1.30 (d, 3 H), 1.18 (t, 3 H).

Ethyl *anti*-3-methyl-*anti*-2-phenylcyclopropanecarboxylate (*cis*-β-methylstyrene product): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.32–7.15 (5 H, 4.14 (q, 2 H), 2.75 (dd, 1 H), 2.82 (m, 1 H), 2.71 (m, 1 H), 1.29 (t, 3 H), 0.89 (d, 3 H).

Ethyl *syn*-2-benzylcyclopropanecarboxylate (allylbenzene product): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35–7.19 (5 H), 4.12 (q, 2 H), 2.93 (dd, 1 H), 2.83 (dd, 1 H), 1.78 (m, 1 H), 1.52 (m, 1 H), 1.23 (t, 3 H), 1.10 (m, 1 H), 0.84 (dd, 1 H).

Ethyl *anti*-2-benzylcyclopropanecarboxylate (allylbenzene product): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35–7.19 (5 H), 4.16 (q, 2 H), 2.76 (dd, 1 H), 2.57 (dd, 1 H), 1.68 (m, 1 H), 1.52 (m, 1 H), 1.23 (t, 3 H), 1.09 (m, 1 H), 0.82 (m, 1 H).

Procedure for Competition Reactions. All reactions were performed at 60 °C unless indicated otherwise. RhTTPI or RhTMPI (1.7×10^{-3} mmol) in CH_2ClCH_2Cl (1 mL) was added to a premixed solution of olefins (5.3 mmol each). Octane (0.53 mmol) was added to the reaction mixture, and the solution was equilibrated to the reaction temperature. EDA (0.53 mmol) was added, and the reaction was continued until nitrogen evolution was no longer observed. Most of the equivalents of EDA that were not accounted for in the cyclopropane products appeared as dimer products. We have subsequently found that this side reaction can be suppressed almost completely by lowering the temperature to 25 °C. The cyclopropane products are stable under the reaction conditions.

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Selective Preparation of Borinic Esters from Grignard Reagents and Selected Trialkoxyboranes

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The reaction of trialkoxyboranes with ethylmagnesium bromide was investigated for the selective alkylation to the symmetrical borinic esters, R_2BOR'. Triisopropoxyborane was found to react cleanly with 2 equiv of the Grignard reagent to form diethylisopropoxyborane at −40 °C. The selectivity of this reaction is largely controlled by the stability of the bromomagnesium diethyldiisopropoxyborate, $MgBr[Et_2B(O^iPr)_2]$. Triisopropoxyborane was found to be the most selective borane examined, yielding symmetrical borinic esters for primary and aryl derivatives with high selectivities. Secondary alkyl groups showed lower selectivities. This reaction has been developed into a general procedure for preparation of diorganylalkoxyboranes from readily available organomagnesium reagents, especially for those containing organic groups which are not accessible via hydroboration.

Recently there has been renewed interest in borinic acids and esters as intermediates for tertiary alcohols,[1,2] ketones,[3,4] α-haloborinic esters,[5] lithium dialkylborohydrides,[6] and new types of dialkylboranes.[7] The utility of these boron compounds has largely been limited by their availability as the pure compounds. A variety of methods have been used to prepare these compounds:[8] conversion of the trialkylboranes to borinic esters by reactions with alcohols[9] or aldehydes[10] and redistribution of the trialkylboranes with trialkoxyboranes[11] or trihaloboranes followed by reaction with an alcohol.[12-14] However, these reactions suffer from some limitations on the preparative scale.[11,13,15] Borinic esters and acids can also be prepared starting with a monohaloborane[16] followed by stepwise hydroboration of the alkyldihaloborane.[17] Generally these methods are limited to those types of organic groups that can be prepared by the hydroboration reaction. The selective stepwise addition of organolithium reagents has presented a simpler synthesis of borinic derivatives, although one is still limited by the availability of the corresponding organolithium reagents.[18] Grignard reagents are more easily prepared, and their use would considerably simplify the preparation of borinic esters. The synthesis of borinic acids, anhydrides, and esters from the Grignard reagents was explored sometime ago. The majority of these products were diarylborinic derivatives.[19-21] These air-

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sensitive diarylboranes were isolated as the stable ethanolamine complexes.[22,23] Relatively few dialkylborinic acids or esters have been prepared from organometallic reagents.[24,25] Unsymmetrical borinic products have also been prepared from boronic esters and Grignard reagents.[26-29] Unfortunately, the reactions of Grignard reagents with various boron compounds frequently show little selectivity, forming mixtures of products.[30]

Results and Discussion

Triisopropoxyborane and ethylmagnesium iodide were mixed in a 1:1 ratio, at −78 °C for 1 h, and then the mixture was allowed to slowly warm to room temperature (eq 1).

$$B(O^iPr)_3 + EtMgI \xrightarrow[Et_2O]{\text{−78 °C to room temp}} \xrightarrow{HCl/Et_2O} Et_2BO^iPr + B(O^iPr)_3 \quad (1)$$

Analysis by ^{11}B NMR spectroscopy after protonation with anhydrous hydrogen chloride showed essentially only two boron species to be present, starting material and a borinic ester, in an approximate 1:1 ratio. This reaction was remarkable in its selectivity, forming the borinic ester rather than the intermediate boronic ester. The addition of 2 equiv of the Grignard reagent to triisopropoxyborane gave a product mixture composed of 91% borinic ester, 2.5% triethylborane, 1.5% boronic ester, and 5% starting material. This reaction is unusual for its selectivity in the formation of the borinic ester via a Grignard reagent. We began a systematic investigation of this reaction to better understand the factors that control the alkylation of boron using Grignard reagents in the hope of developing this reaction into a convenient method for the preparation of borinic esters.

Initially, we chose ethylmagnesium bromide as a representative Grignard reagent. Preliminary results indicated that there is a wide range of selectivity toward the dialkylation with various boron compounds and that reaction conditions strongly influenced this selectivity. The reactions of the Grignard reagent with these boron compounds form a variety of ethylboranes as well as possible tetracoordinate anionic complexes. These anionic complexes can be protonated with anhydrous hydrogen chloride, forming the tricoordinate boranes.[31] In general, these reactions form only small amounts of the tetraalkylborates when diethyl ether is used as the solvent. The compositions of these reaction mixtures are readily determined by their chemical shifts of the boron-containing components, and the relative amounts can be estimated from either the peak heights or areas in the ^{11}B NMR spectrum for the starting material, boronic and borinic esters, and triethylborane. This technique appears to give good mass balances and was confirmed to give accurate estimations, ±3%, for compounds with similar peak widths using weighed mixtures of authentic boranes.[32,33]

Table I. Effect of Temperature

$$B(O^iPr)_3 + 2EtMgBr \xrightarrow[Et_2O]{\text{isothermal}} \xrightarrow{HCl/Et_2O} Et_2BO^iPr$$

temp, °C/ time, h	Et_3B	Et_2BO^iPr	$EtB(O^iPr)_2$	$B(O^iPr)_3$
0/0.25	22	57	5	16
−30/2	7	88	3	2
−40/1	3	93	3	1
−50/1.5	3	93	2	2
−78/3.5	0	0	5	95

Table II. Effects of the Halide in EtMgX

$$B(O^iPr)_3 + 2EtMgX \xrightarrow[Et_2O]{\text{−40 °C/1 h}} \xrightarrow{HCl/Et_2O} Et_2BO^iPr$$

Grignard reagent	Et_3B	Et_2BO^iPr	$EtB(O^iPr)_2$	$B(O^iPr)_3$
EtMgCl	3	76	10	11
EtMgBr	3	93	3	1
EtMgI	6	67	16	11

Table III. Effects of the Trialkoxyborane

$$B(OR)_3 + 2EtMgBr \xrightarrow[Et_2O]{\text{−40 °C/1 h}} \xrightarrow{HCl/Et_2O}$$

$B(OR)_3$	Et_3B	Et_2BOR	$EtB(OR)_2$	$B(OR)_3$
BCl_3[a]	37	11	7	44
BF_3[a]	21	12	29	38
$B(OMe)_3$	46	14	30	10
$B(OEt)_3$	45	25	4	26
$B(O^nPr)_3$	33	27	6	34
$B(O^iPr)_3$	3	93	3	1
$B(O^nBu)_3$	23	30	6	41
$B(O^sBu)_3$	13	64	3	20
$B(O^iBu)_3$	7	85	0	8
$B(O^tBu)_3$	2	5	0	93
$B(OBz)_3$	20	60	0	20
$B(OC_6H_{11}\text{-}c)_3$	0	76	9	15

[a] Products analyzed after methanolysis.

The preliminary reactions were carried out at −78 °C, stirred for 1 h, and then allowed to warm slowly to room temperature. Different selectivities were frequently observed for the formation of the borinic ester. Maintaining the reaction for a longer period of time (3.5 h) at −78 °C before protonation with anhydrous hydrogen chloride showed only minimal alkylation, forming less than 5% of the boronic ester, $EtB(O^iPr)_2$, as the only product. Thus, the selectivity of the alkylation is due to reactions which occur at temperatures greater than −78 °C. Apparently the difficulties in obtaining reproducible selectivities were due to variations in warming the reaction to room temperature. To overcome these variations, a series of isothermal reactions were examined in which the reactions were terminated with hydrogen chloride in ether at the indicated temperature. As expected, the selectivity increased with lower temperatures. The highest selectivity to the borinic ester was found at −40 °C, reacting to completion within 10 min. The effects of temperature on this reaction are summarized in Table I.

The reaction of 2 equiv of ethylmagnesium bromide and triisopropoxyborane at −40 °C in diethyl ether gave higher selectivities of the borinic ester, 93%, than in tetrahydrofuran, 67%. In addition, the reaction in tetra-

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hydrofuran was considerably slower, requiring 5 h, while the reaction in ether was complete within 10 min. The halide group also affects both the reactivity and the selectivity to the borinic ester. Ethylmagnesium chloride and iodide showed lower selectivities and required longer reaction times than the corresponding bromide. The effects of the halide on the selectivity are summarized in Table II.

A variety of trialkoxyboranes and several trihaloboranes were examined for selective alkylation to the borinic derivatives, using isothermal reaction conditions as developed above. The results of these reactions are summarized in Table III. It is apparent that there is a wide range of selectivities toward the diethylation using ethylmagnesium bromide in ether at −40 °C. The most selective alkylations were found with triisopropoxyborane. Good results were also observed using triisobutoxyborane and tris(cyclohexyloxy)borane. The other boranes showed much lower selectivities to the borinic esters.

We sought to better understand this reaction and the factors which control the selectivity. The possible reaction sequence to the borinic ester is summarized in eqs 2–8.

$$B(OR')_3 + RMgBr \rightarrow \underset{1}{MgBr[RB(OR')_3]} \quad (2)$$

$$\underset{1}{MgBr[RB(OR')_3]} \rightleftharpoons \underset{2}{MgBr(OR')} + RB(OR')_2 \quad (3)$$

$$\underset{2}{RB(OR')_2} + RMgBr \rightarrow \underset{3}{MgBr[R_2B(OR')_2]} \quad (4)$$

$$\underset{3}{MgBr[R_2B(OR')_2]} \rightleftharpoons MgBr(OR') + \underset{4}{R_2BOR'} \quad (5)$$

$$\underset{4}{R_2BOR'} + RMgBr \rightarrow \underset{5}{MgBr[R_3BOR']} \quad (6)$$

$$\underset{5}{MgBr[R_3BOR']} \rightleftharpoons MgBr(OR') + \underset{6}{R_3B} \quad (7)$$

$$\underset{6}{R_3B} + RMgBr \rightarrow \underset{7}{MgBr[R_4B]} \quad (8)$$

Assuming that the addition of the Grignard reagent to a boron compound is irreversible, the addition of the ethylmagnesium bromide to the trialkoxyborane rapidly and irreversibly forms the bromomagnesium ethyltrialkoxyborate, 1 (eq 2). This tetracoordinate complex is expected to be unreactive to further alkylation with a Grignard reagent. Elimination of bromoalkoxymagnesium would form the boronic ester. This reaction may best be described as an acid/base equilibrium between the boronic ester, 2, and bromoalkoxymagnesium (eq 3). The liberated boronic ester would be susceptible to additional attack by another 1 equiv of the Grignard reagent, forming the bromomagnesium diethyldialkoxyborate, 3 (eq 4). This addition complex would also be expected to be in equilibrium between the borinic ester, 4, and bromoalkoxymagnesium. Successive alkylation would give rise to triethylborane (6) (eqs 6 and 7) and possibly tetraethylborate (7) (eq 8). Thus, the tricoordinate boranes, 2, 4, and 6, are expected to react readily with the Grignard reagent while the tetracoordinate borates, 1, 3, and 5, are expected to be unreactive.

The reaction of triisopropoxyborane and ethylmagnesium bromide in a 1:1 ratio at −40 °C forms the borinic ester and starting material in an approximate 1:1 ratio, but little of the boronic ester is found. This suggests that the rate-determining step is the initial attack of the Grignard reagent on the trialkoxyborane. The boronic ester rapidly reacts with another 1 equiv of the Grignard reagent to give the borinic ester. The reaction in a 1:2 ratio cleanly yields the diethylisopropoxyborane with greater than 90% selectivity. Under the same conditions, an excess of the Grignard reagent (1:3 ratio) also proceeds with relatively good selectivity, giving 75% of the borinic ester and only 25% triethylborane. If this reaction is allowed to warm to room temperature, triethylborane is formed with a selectivity greater than 97%. Clearly, the formation of triethylborane from diethylisopropoxyborane and the Grignard reagent is being inhibited by some factor(s). In contrast, the reaction of isolated diethylisopropoxyborane and ethylmagnesium bromide at −40 °C for 1 h resulted in approximately 50% conversion to triethylborane. More triethylborane is formed using isolated borinic ester than reacting 3 equiv of ethylmagnesium bromide with triisopropoxyborane. Since Grignard reagents are unreactive toward tetracoordinate boron species and can only react with a tricoordinate borane, such as 2, 4, or 6, the formation of the triethylborane must proceed via uncomplexed boranes. The above experiments suggest that the selectivity to the borinic ester must be due to the formation of a relatively stable $MgBr[Et_2B(O^iPr)_2]$. This tetracoordinate complex is formed in the reaction of the boronic ester and Grignard reagent and is in equilibrium with the bromoalkoxymagnesium and borinic ester, 4. As the reaction proceeds, the formed bromoalkoxymagnesium shifts eq 5 toward the "ate" complex, 3, protecting the borinic ester from further alkylation. In contrast, the isolated borinic ester readily reacts with the Grignard reagent to form triethylborane, since there is no bromoalkoxymagnesium present to complex to the borinic ester and hinder the formation of the trialkylborane. As the reaction proceeds, the liberated bromoalkoxymagnesium can form the "ate" complex, 3, protecting the remaining borinic ester from alkylation. Additional support for the importance of the "ate" complex is seen in the reaction of a trihaloborane with ethylmagnesium bromide at −40 °C. The ethylhaloborates are expected to be formed as intermediates. These "ate" complexes would be expected to eliminate the relatively nonbasic halide, forming a tricoordinate ethylborane which would be susceptible to further reaction with the Grignard reagent. As expected, the trihaloboranes show low selectivity to the diethylborane, forming a variety of ethylated boron compounds.

The selectivity of alkylation to the borinic ester can be effected through a number of reactions and equilibria. Perhaps most important is the stability of the dialkyldialkoxyborate, 3. If this complex is stable under reaction conditions, further reaction with the Grignard reagent is prevented, allowing selective formation of the borinic ester. Thus, factors that adversely affect the stability of 3 give rise to the trialkylborane and tetraalkylborate species. The trialkoxyborane and boronic ester must readily react with the Grignard reagent and, in contrast to the borinic ester, should not form a stable "ate" complex which would inhibit further reaction with the Grignard reagent. In the reaction of triisopropoxyborane and ethylmagnesium bromide, the position of the equilibrium in eq 3 apparently favors the boronic ester, 2. This boronic ester readily reacts with a second equivalent of the Grignard reagent forming the "ate" complex, 3. The alkoxy group strongly influences the selectivity of the alkylation as summarized in Table III. The solubility of the bromoalkoxymagnesium would be expected to affect the equilibria in eqs 3, 5, and 7. A small alkoxy group, such as in bromomethoxymagnesium, was found to be less soluble than a larger branched alkoxy group such as isopropoxy, although neither of these magnesium salts are especially soluble in ether at −40 °C. The differences in the solubilities of the boron containing species are demonstrated in the reactions of trimethoxy-

borane and triisopropoxyborane with 2 equiv of ethylmagnesium bromide in ether at −40 °C. The reaction of trimethoxyborane and ethylmagnesium bromide formed a large amount of a white insoluble material at −40 °C, while triisopropoxyborane formed only a small amount of solid material. These solids were isolated and washed with cold ether at −40 °C. The solid and supernatant fractions were protonated with anhydrous hydrogen chloride and analyzed by ^{11}B NMR spectroscopy. All boron containing materials precipitated from solution in the trimethoxyborane reaction. In contrast, the triisopropoxyborane reaction revealed that all boron containing products were soluble at −40 °C and no boron was found in the precipitate. Since the trialkoxyboranes, triethylborane, and boronic and borinic esters are soluble in ether at this temperature, the solid materials must be various ionic "ate" complexes. This suggests that the intermediates must be soluble in order to form the borinic ester selectively. If the reaction mixture is not protonated, but allowed to warm to room temperature, the ^{11}B NMR spectroscopy shows a complete absence of the "ate" complexes. The dialkylborinic esters are known to be weak Lewis acids,[34] and the bromoalkoxymagnesium compounds are also expected to be weak Lewis bases. As a consequence, the addition complexes would not be expected to be especially stable, eliminating the alkoxy group and liberating the borinic ester on warming. The thermal elimination of the more basic lithium isopropoxide to form borinic esters has been demonstrated to occur at or slightly above room temperature.[35] The diarylborinic esters are stronger Lewis acids. In contrast, the anionic "ate" complexes are observed at room temperature in the ^{11}B NMR spectrum.

The steric bulk of an alkoxy group can be expected to effect both the ease of attack at the boron by the Grignard reagent and the stability of the "ate" complex. For example, the sterically bulky tri-*tert*-butoxyborane is unreactive toward ethylmagnesium bromide at −40 °C, forming approximately 5% of the borinic ester after 1 h. The alkoxy group may also effect the solubilities of the bromoalkoxymagnesium and "ate" complexes as well as the stability of the tetracoordinate complexes. Thus, the alkoxy groups may affect the selectivity of the reaction in a number of subtle ways. In general, the primary alkoxy groups showed little selectivity to the borinic esters. Secondary alkoxy groups and those with substitution at the β-position (isopropoxy, isobutoxy, benzyloxy, and cyclohexyloxy) gave much improved selectivities. Triisopropoxyborane was found to be the most generally useful reagent, followed by triisobutoxyborane for the selective formation of symmetrical borinic esters.

Triisopropoxyborane was examined with a variety of Grignard reagents for selective alkylation. The reaction conditions and results are summarized in Table IV. The reactivity and selectivity are dependent on the Grignard reagent. Small alkyl groups are more reactive and require lower temperatures to achieve good selectivity. In general, primary alkyl and aryl groups were the most selective. The secondary alkyl groups showed slightly lowered selectivities. The sterically bulky *tert*-butylmagnesium bromide reacted very slowly with triisopropoxyborane, forming only the boronic ester. Other trialkoxyboranes were examined for this reaction, of which trimethoxyborane and triethoxyborane showed promise. However, approximately 15% of the *tert*-butyl group underwent isomerization.[36,37] As a result, this reaction was not investigated further.

Table IV. Alkylation of Triisopropoxyborane with Various Grignard Reagents

$$B(O^iPr)_3 + 2RMgBr \xrightarrow{Et_2O} \xrightarrow{HCl/Et_2O}$$

Grignard reagent	temp, °C/ time, h	R_3B	R_2B-O^iPr	RB-$(O^iPr)_2$	$B(O^iPr)_3$
MeMgBr	−45/2	5	83	2	10
EtMgBr	−40/3	0	93	2	4
^{i}PrMgBr	−35/24	12	85	3	0
1-pentylMgBr	−40/3	4	90	2	4
2-pentylMgBr	−15/40	11	75	14	0
^{t}BuMgBr	RT/71	0	0	92	8
PhMgBr	0/1	0	100	0	0
p-$CH_3OC_6H_4MgBr$	0/2	0	100	0	0

Table V. Isolated Isopropoxydiorganylboranes

borinic ester	yield, %	bp, °C (mmHg)	n^{20}_D
dimethylisopropoxyborane	71	52–54 (758)	1.3612
diethylisopropoxyborane	68	85–86 (749)	1.3826
diisopropylisopropoxyborane	56	48–49 (25)	1.3890
bis(1-pentyl)isopropoxyborane	77	95–97 (5)	1.4143
diphenylisopropoxyborane	60	130–132 (2.5)	1.543
dianisylisopropoxyborane	58	122–126 (0.075)	1.559

The diorganylisopropoxyboranes were isolated in moderate to good yields for a variety of Grignard reagents. These results are summarized in Table V. These isolated borinic esters gave spectral and physical properties in excellent agreement with previously reported compounds and related analogues.

Experimental Section

General Comments. All glassware was dried at 130 °C for at least 4 h, assembled hot, and cooled under a stream of dry nitrogen. All reactions were carried out under a static pressure of nitrogen. Anhydrous ethyl ether (Mallinckrodt or Aldrich) was used as received and stored under nitrogen. Tetrahydrofuran was distilled from sodium benzophenone ketyl and stored under a nitrogen atmosphere. The Grignard reagents were prepared using standard procedures from the corresponding bromides (Aldrich). The concentrations of the Grignard reagents were estimated prior to use by the procedure of Watson and Eastham.[38] The trihaloboranes and trialkoxyboranes are available from commercial sources or were prepared from the boric acid and alcohol.[39] The anhydrous hydrogen chloride in ether solution (ca. 3 M) was prepared using a Brown squared apparatus from hydrochloric acid and concentrated sulfuric acid.[40] This ether solution was standardized by titration with a standardized base. The boranes and Grignards were handled under a nitrogen atmosphere using hypodermic syringes and double-ended needles.[41]

Spectra were obtained in an inert atmosphere. The ^1H NMR spectra were recorded on Varian EM-390 (90 MHz) and Chemagnetics A-200 (199.4229 MHz) spectrometers. The ^{13}C NMR spectra were also obtained on a Chemagnetics A-200 spectrometer (50.1500 MHz). Chemical shifts, in $CDCl_3$, are in δ relative to tetramethylsilane for ^1H and ^{13}C NMR spectra. ^{11}B NMR spectra were recorded on a Chemagnetics A-200 spectrometer (63.9837 MHz), and all chemical shifts are in δ relative to boron trifluoride etherate as external standard. All yields reported as isolated materials having purities greater than 95% based on ^{11}B, ^1H, and ^{13}C NMR spectroscopy. The major impurities are attributed to diethyl ether, 2-propanol, and boronic acids for those compounds with low boiling points. Products with lower volatilities contained

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similar amounts of impurities due to the presence of coupling products formed in the Grignard reagent preparation, borinic acid, and traces of boronic derivatives. Gas chromatographic analyses were obtained on a Hewlett-Packard 5890 instrument with flame ionization detector using a 5.25 ft. by $^1/_8$ in. column packed with 3% Carbowax 20M on Chromosorb G. The yields were determined using decane or nonane as the internal standard, and integrations were obtained using a Hewlett-Packard 3390A digital integrator. Infrared spectra were obtained with a Perkin-Elmer 1750 FT-IR instrument. EI mass spectra data were recorded on a Finnigan 3000 mass spectrometer operating at 70 eV. Microanalysis were performed by Desert Analytics, Tuscon, AZ. Samples were sent sealed in nitrogen-filled vials.

General Procedure for the Reaction of Boron Compounds with Grignard Reagents. To a 50-mL flask fitted with a septum-covered side arm, magnetic stirring bar, and gas-inlet adapter was added 5 mL of solvent and 2.5 mmol of trialkoxyborane or boron trihalide. The reaction flask was cooled to the desired reaction temperature using either a dry ice/acetone bath or a regulated refrigerated cold bath. The Grignard reagent, 5 mmol, was slowly added dropwise via a syringe. The reaction mixture was stirred for the indicated time and then terminated by the addition of 5 mmol of anhydrous hydrogen chloride either after the reaction mixture was allowed to warm to room temperature or at the reaction temperature. The reaction was analyzed by ^{11}B NMR spectroscopy for product composition. The extent of the reaction can be estimated using the ratio of peak areas in the ^{11}B NMR spectroscopy for the trialkylborane, starting material, and borinic and boronic esters. This method appears to give satisfactory results for boron species with similar peak widths. Comparison of this method with weighed mixtures of the pure authentic boron products and starting materials agreed within ±3%. Nöth and Wrackmeyer have also reported using ^{11}B NMR spectroscopy to determine the ratios of boron containing materials in equilibrium mixtures.[42] This method has been used to estimate the concentration of organolithium compounds by reacting them with trialkoxyboranes and analyzing by ^{11}B NMR spectroscopy.[43] Results for these reactions are shown in Tables I–IV.

Reaction of Diethylisopropoxyborane with Ethylmagnesium Bromide. To a 50-mL flask fitted with a magnetic stirring bar and gas-inlet adapter was added 4 mL of diethyl ether and 2.5 mmol of pure diethylisopropoxyborane (2.5 mmol, 0.35 mL), which gave an initial concentration of 0.5 M. The reaction flask was cooled to −40 °C, and 1 equiv of ethylmagnesium bromide (2.5 mmol, 1.0 mL, 2.5 M) was added slowly to the solution by means of a syringe over a period of 1–2 min. The reaction mixture was stirred at −40 °C for 1 h. The reaction was terminated with the addition of 1 equiv of hydrogen chloride in ether and allowed to warm to room temperature, and the clear supernatant solution was removed by syringe for analysis by ^{11}B NMR spectroscopy. The reaction after 1 h showed approximately 50% conversion to triethylborane.

Reaction of Triisopropoxyborane with Ethylmagnesium Bromide (1:3). Triisopropoxyborane (2.5 mmol, 0.58 mL) was reacted with 7.5 mmol of ethylmagnesium bromide (2.95 mL) in 5 mL of ether at −40 °C as described above. The reaction was stirred for 1 h and terminated with the addition of 7.5 mmol of anhydrous hydrogen chloride in ether. A sample was removed for analysis by ^{11}B NMR spectroscopy after warming to room temperature. The average of three reactions showed approximately 75.5% conversion to diethylisopropoxyborane and 24.5% triethylborane, ±6%.

Isolation of Insoluble Salts. Ethylmagnesium bromide was reacted with either triisopropoxyborane or trimethoxyborane, 2.5 mmol, in diethyl ether (0.5 M, initial concentration) at −40 °C, as described in the above general procedure. There was a rapid formation of a precipitate on addition of the 5 mmol of ethylmagnesium bromide in both reactions. The reaction mixture was stirred for 0.5 h at −40 °C, and then the clear supernatant solution was removed via double-ended needle and analyzed by ^{11}B NMR spectroscopy. The reaction with trimethoxyborane showed no boron containing materials in this clear solution either before or after protonation. In contrast, the reaction with triisopropoxyborane showed large amounts of boron containing materials in the supernatant with similar ratios as shown in Table III. These ratios did not change after protonation. The solid materials from both reactions were isolated after removal of the reaction solution and washed with ether (2 × 1 mL) via double-ended needle at −40 °C. These solids were protonated with anhydrous hydrogen chloride, and the insoluble magnesium salts were removed prior to analysis by ^{11}B NMR spectroscopy. The reaction with trimethoxyborane showed a mixture of boron containing products in approximately the same ratios as shown in Table III. However, no boron-containing materials were detected in the solid formed in the reaction of triisopropoxyborane and ethylmagnesium bromide.

General Procedure for the Isolation of Dialkylisopropoxyboranes. To a 250-mL flask with a septum-covered side-arm flask, magnetic stirring bar, and gas-inlet adapter was added 30 mmol (5.64 g, 6.84 mL) of triisopropoxyborane and 60 mL of anhydrous ether. The reaction mixture was cooled to the temperature indicated in Table IV using a dry ice/acetone or regulated low-temperature bath. Two equivalents of the Grignard reagent, 60 mmol, were added dropwise via a double-ended needle from a graduated cylinder over a period of 30–40 min, resulting in the formation of a white precipitate. The reaction was stirred for the indicated time. The reaction mixture was then cooled to −78 °C for 0.5 h without stirring to separate the solid material from the supernatant, which was transferred via double-ended needle to another flask. The solid material was then washed with cold ether at −78 °C (3 × 30 mL), and each wash was analyzed by ^{11}B NMR spectroscopy. The ether extracts were combined and then cooled to −78 °C for 0.5 h without stirring, during which time additional solid material precipitated. The clear supernatant solution was then transferred to the distillation flask along with a 15-mL cold ether wash of this solid. The diethyl ether was removed by atmospheric distillation, and then the dialkylisopropoxyborane was distilled at the indicated temperature and pressure.

General Procedure for the Isolation of Diarylisopropoxyboranes. The reaction was carried out as described above by slowly adding 50 mmol of the arylmagnesium bromide to 25 mmol (5.64 g, 6.84 mL) of triisopropoxyborane in 60 mL of anhydrous ether at 0 °C. The reaction mixture was stirred for the indicated time and then allowed to warm to room temperature with stirring for an additional 1 h. The reaction was then protonated with 50 mmol of anhydrous hydrogen chloride in ether at 0 °C. The mixture was transferred to a filter apparatus via double-ended needle under nitrogen. The magnesium salts were separated and then washed with ether (3 × 20 mL). The ether extracts were combined with the filtrate, and the volatiles were removed under reduced pressure yielding an oil. The addition of 40 mL of pentane precipitated the remaining soluble magnesium salts. These solids were removed by filtration under nitrogen and washed with pentane (3 × 10 mL). The volatiles were removed under reduced pressure, and the borinic ester was isolated by simple distillation.

Preparation of Dimethylisopropoxyborane.[18] This material was prepared on a 25-mmol scale by reacting methylmagnesium bromide (16.8 mL, 50 mmol) with 25 mmol of triisopropoxyborane at −78 °C for 1 h and then allowing it to warm slowly to room temperature. The volatile materials were transferred bulb to bulb from the reaction flask under reduced pressure and condensed at −78 °C in a solution of 80 mmol of lithium isopropoxide in ether. The ether was removed under reduced pressure at 0 °C to yield the solid "ate" complex. The lithium dimethyldiisopropoxyborate was thermally decomposed under vacuum (0.1 mmHg) and the dimethylisopropoxyborane was collected in a cold trap at −78 °C, giving 1.96 g (71% yield), n^{20}_D 1.3612, of dimethylisopropoxyborane. Spectroscopic data are in agreement with expected and previously reported values.[18,35,44] ^{11}B NMR (neat): δ +52.9 (s). ^{1}H NMR (neat): δ 4.38 (septet, 1 H, J = 6.1 Hz), 1.14 (d, 6 H, J = 6.1 Hz), 0.29 (b, 6 H). ^{13}C NMR ($CDCl_3$): δ 67.4, 24.2, 5.1 (b). IR (neat): 2976, 2933, 2881, 1466, 1372, 1332, 1281, 1132 cm^{-1}. Mass spectrum (m/z): 99 (M − 1, 2), 85 (M − 15, 23), 60 (13), 57 (10), 55 (12), 45 (62), 43 (100), 41 (71).

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Preparation of Diethylisopropoxyborane.[45,46] This material was prepared on a 30-mmol scale by reacting ethylmagnesium bromide (24.0 mL, 60 mmol) with 30 mmol (7.0 mL) of triisopropoxyborane at −40 °C for 3.0 h. The borinic ester was isolated in a 68% yield: bp 85–86 °C (749 mmHg); n^{20}_D 1.3826. Spectroscopic data are in agreement with previously reported values or similar related compounds.[45-47] ^{11}B NMR (neat): δ +53 (s). ^{1}H NMR ($CDCl_3$): δ 4.38 (m, 1 H, J = 6.1 Hz), 1.20 (m, 4 H, J = 3.6 Hz), 1.18 (d, 6 H, J = 6.1 Hz), 0.85–0.89 (m, 6 H, J = 3.6 Hz). ^{13}C NMR ($CDCl_3$): δ 66.68, 24.66, 10.75, 7.68. IR (neat): 2962, 2935, 2879, 1462, 1382, 1371, 1360, 1338, 1245, 1125 cm^{-1}. Mass spectrum (m/z): 129 (M + 1, 1), 99 (M − 29, 40), 85 (M − 43, 16), 57 (100), 56 (76), 45 (35), 43 (90), 41 (58).

Preparation of Diisopropylisopropoxyborane.[48] This borinic ester was prepared using the above general procedure reacting isopropylmagnesium bromide (26.8 mL, 60 mmol) with 30 mmol of triisopropoxyborane (7.0 mL) at −30 °C for 24 h and then allowing the reaction mixture to warm to room temperature. The borinic ester was isolated after the addition of 60 mmol of hydrogen chloride in ether using a procedure similar to that used for the diarylisopropoxyboranes. The diethyl ether was removed by simple distillation and the diisopropylisopropoxyborane isolated by distillation under reduced pressure, yielding 3.3 g (56% isolated yield): bp 48–49 °C (25 mmHg); n^{20}_D 1.3890. Spectroscopic data are in agreement with expected values and the closely related methyl ester.[49] ^{11}B NMR (neat): δ +53 (s). ^{1}H NMR ($CDCl_3$): δ 4.42 (septet, 1 H, J = 6.1 Hz), 1.15 (d, 6 H, J = 6.1 Hz), 1.24 (septet, 2 H, J = 7.1 Hz), 0.87 (d, 12 H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 66.20, 24.83, 18.22, 15.0 (b). IR (neat): 2975, 2949, 2868, 1467, 1390, 1371, 1315, 1294, 1245, 1123 cm^{-1}. Mass spectrum (m/z): 156 (M^+, <1), 114 (M − 42, 2), 113 (M − 43, 9), 71 (61), 70 (16), 59 (8), 55 (9), 45 (52), 43 (100), 41 (52).

Preparation of Bis(1-pentyl)isopropoxyborane. This preparation was carried out as described above on a 30 mmol scale by reacting 1-pentylmagnesium bromide (30.0 mL, 60 mmol) with 30 mmol (7.0 mL) of triisopropoxyborane at −40 °C for 5 h, and then the reaction mixture was allowed to warm to room temperature. The borinic ester was isolated without protonation with hydrogen chloride as described above to give 5.1 g (77% isolated yield) of bis(1-pentyl)isopropoxyborane: bp 95–97 °C (5 mmHg); n^{20}_D 1.4143. ^{11}B NMR (neat): δ +53 (s). ^{1}H NMR ($CDCl_3$): δ 4.40 (septet, 1 H, J = 6.1 Hz), 1.4–1.2 (m, 12 H), 1.17 (d, 6 H, J = 6.1 Hz), 0.91–0.79 (m, 10 H). ^{13}C NMR ($CDCl_3$): δ 66.84, 35.25, 24.77, 24.02, 22.68, 20.20 (b), 14.02. IR (neat): 2959, 2925, 2860, 1466, 1371, 1332, 1125 cm^{-1}. Mass spectrum (m/e): 142 (1), 99 (2), 71 (21), 59 (53), 57 (56), 45 (72), 43 (100), 41 (69). Anal. Calcd for $C_{13}H_{29}BO$: C, 73.59; H, 13.78. Found: C, 73.34; H, 13.83.

Preparation of Diphenylisopropoxyborane.[18] The reaction of 60 mmol (32.0 mL) of phenylmagnesium bromide with 30 mmol (7.0 mL) of triisopropoxyborane at 0 °C for 2 h is described in the above general procedure. The insoluble magnesium salts were separated by filtration following addition of 60 mmol of hydrogen chloride in ether. The volatile materials were removed from the filtrate under reduced pressure yielding a yellow oil. The remaining magnesium salts were precipitated from this oil by the addition of 40 mL of pentane and removed by filtration under an inert atmosphere. The diethyl ether was removed by simple distillation followed by vacuum distillation of the borinic ester yielding 4.1 g (60% isolated yield) of diphenylisopropoxyborane: bp 130–132 °C (2.5 mmHg); n^{20}_D 1.5428. Spectroscopic data are in agreement with previously reported values.[18] ^{11}B NMR (neat): δ +45.1 (s). ^{1}H NMR ($CDCl_3$): δ 7.59 (m, 4 H), 7.23 (m, 6 H), 4.54 (septet, 1 H, J = 6.1 Hz), 1.22 (d, 6 H, J = 6.1 Hz). ^{13}C NMR ($CDCl_3$): δ 137.88 (b), 133.69, 129.66, 127.40, 69.32, 24.66. IR (neat): 3073, 3051, 3014, 2975, 2928, 1598, 1438, 1364, 1332, 1264, 1116 cm^{-1}. Mass spectrum is in agreement with previously reported values.[50]

Preparation of Dianisylisopropoxyborane. Triisopropoxyborane (25 mmol, 5.8 mL) was reacted with 50 mmol of anisylmagnesium bromide (34.5 mL) in ether at 0 °C for 1 h and then allowed to warm to room temperature over a period of 1 h following the above general procedure. The reaction mixture was then protonated with 50 mmol of hydrogen chloride in ether (17 mL), and the reaction mixture was filtered to remove magnesium salts under an inert atmosphere. The volatile materials were removed under reduced pressure yielding a yellow oil. Pentane was added to this oil while the mixture was stirred to precipitate the remaining magnesium salts, which were removed by filtration under a nitrogen atmosphere. The volatiles were removed under reduced pressure, and the anisole borinic ester was isolated by simple vacuum distillation to yield an oil 4.12 g (58% isolated yield) of dianisylisopropoxyborane: bp 122–126 °C (0.05–0.1 mmHg); n^{20}_D 1.559. The related dianisylborinic acid[51] and its corresponding amino acid complexes have previously been reported.[22,52] Spectroscopic date for these related compounds are in agreement with the following data. ^{11}B NMR (neat): δ +44.6 (s). ^{1}H NMR ($CDCl_3$): δ 7.57 (d, 4 H, J = 8.7 Hz), 6.90 (d, 4 H, J = 8.7 Hz), 4.63 (septet, 1 H, J = 6.1 Hz), 3.77 (s, 6 H), 1.27 (d, 6 H, J = 6.1 Hz). ^{13}C NMR ($CDCl_3$): δ 161.04, 135.73, 129.67 (b), 113.05, 68.94, 54.61, 24.83. IR (neat): 3062, 3026, 2973, 2933, 2837, 1601, 1569, 1511, 1463, 1408, 1371, 1324, 1283, 1243, 1174, 1116, 1034 cm^{-1}.

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Registry No. B(O-*i*-Pr)$_3$, 5419-55-6; EtMgBr, 925-90-6; EtMgCl, 2386-64-3; EtMgI, 10467-10-4; BCl_3, 10294-34-5; BF_3, 7637-07-2; B(OMe)$_3$, 121-43-7; B(OEt)$_3$, 150-46-9; B(OPr)$_3$, 688-71-1; B(OBu)$_3$, 688-74-4; B(O^{s}Bu)$_3$, 22238-17-1; B(O^{i}Bu)$_3$, 13195-76-1; B(O^{t}Bu)$_3$, 7397-43-5; B(OBz)$_3$, 2467-18-7; B(OC$_6$H$_{11}$-*c*)$_3$, 2467-16-5; MeMgBr, 75-16-1; ^{i}PrMgBr, 920-39-8; (1-pentyl)MgBr, 693-25-4; (2-pentyl)MgBr, 57325-22-1; ^{t}BuMgBr, 2259-30-5; PhMgBr, 100-58-3; *p*-$CH_3OC_6H_4MgBr$, 13139-86-1; BMe_3, 593-90-8; Me_2BO^iPr, 95407-90-2; Et_2BO^iPr, 74953-03-0; $^iPr_2BO^iPr$, 115307-73-8; B^iPr_3, 1776-66-5; (1-pentyl)$_2$BO^{i}Pr, 138152-38-2; (1-pentyl)$_3$B, 21969-29-9; (2-pentyl)$_2$BO^{i}Pr, 138152-39-3; (2-pentyl)B(O^{i}Pr)$_2$, 138152-40-6; ^{t}BuB(O^{i}Pr)$_2$, 86595-34-8; Ph_2BO^iPr, 69737-51-5; (*p*-$CH_3OC_6H_4)_2BO^iPr$, 138152-41-7; LiO^{i}Pr, 2388-10-5.

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