Table I. The Synthesis of 2-Alkyl-1,3,2-benzodioxaboroles (**2**) from Olefins *via* Hydroboration

Alkyl substituent, R, in **2**	Method	Yield,[a] %	Bp, °C (mm)	n^{20}D	Mol wt[b]
1-Decyl	A	(98)[c]			
1-Pentyl	A[d]	90	75 (0.5)	1.4805	190 (58)
2,4,4-Trimethyl-1-pentyl	A	88	78 (0.25)	1.4890	232 (100)
Cyclopentyl	A[d]	90	72 (0.2)	1.5260	
Cyclohexyl	A	95	80 (0.4)	1.5250	
exo-Norbornyl	A	95 (98)	104 (0.5)	1.5405	
1-Butyl	B	86	65 (0.5)	1.4925	176 (38)
2-Butyl	B	94	48 (0.2)	1.4975	176 (48)
Isobutyl	B	90	56 (0.4)	1.4930	176 (33)
Cyclopentyl	B	80	72 (0.2)	1.5260	188 (42)
Cyclohexyl	B	88	88 (0.5)	1.5255	202 (48)
exo-Norbornyl	B	90	104 (0.5)	1.5400	214 (100)

[a] By isolation. The yields by glpc are given in parentheses. [b] By mass spectrometry; based on ^{11}B. The intensity of the molecular ion (M^+) is given in parentheses. [c] Determined by the alkaline hydrogen peroxide oxidation of the product and the estimation of 1-decanol formed by glpc analysis. [d] Experiments were performed in a sealed ampoule at 100° for 2 hr.

The alkaneboronic esters and acids are becoming increasingly important synthetic intermediates.[14] We are currently exploring several other transformations of alkylboroles **2**, providing us with novel applications of alkaneboronic acids and esters in organic synthesis.

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(14) D. S. Matteson, *Accounts Chem. Res.*, **3**, 186 (1970).

(15) Postdoctorate research associate on a research grant (No. GM-10937) supported by the National Institutes of Health.

Herbert C. Brown,* S. K. Gupta[15]
Richard B. Wetherill Laboratory
Purdue University, Lafayette, Indiana 47907

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New Addition Compounds of Dialkylboranes and Aluminum Methoxide. New Practical Syntheses of Dialkylboranes and of Mixed Trialkylboranes Containing Functional Groups

Sir:

Aluminum methoxide forms reasonably stable addition compounds with dialkylboranes [$(CH_3O)_3Al \cdot 3R_2BH$]. These addition compounds permit the synthesis of mixed organoboranes containing functional substituents, the synthesis of pyridine–dialkylboranes, and the synthesis of the parent dialkylboranes themselves. Consequently, these new organoborane derivatives should be exceedingly valuable for many applications of the new organoborane chemistry to organic synthesis.

With the exception of certain relatively hindered and cyclic dialkylboranes such as dicyclohexylborane,[1] disiamylborane,[1] diisopinocampheylborane,[1] bisborinane,[2] and 9-borabicyclo[3.3.1]nonane,[3] dialkylboranes have proved to be relatively unstable toward disproportionation.[4] Consequently, they have been difficult to prepare and to utilize for the synthesis of mixed trialkylboranes. One solution to this problem has been the reduction of dialkylborinic esters by lithium aluminum hydride in the presence of olefins[5] (eq 1). The

$$3R_2BOCH_3 + LiAlH_4 + 3\text{olefin} \longrightarrow 3R_2BR' + LiAlH(OCH_3)_3 \quad (1)$$

success of this procedure presumably arises from the rapid capture of the dialkylborane intermediate before it can undergo disproportionation.[5]

We were examining the reduction of the methyl esters of dialkylborinic acids with aluminum hydride[6] when we discovered that the precipitate was not the simple aluminum methoxide we had anticipated (eq 2).

$$3R_2BOCH_3 + AlH_3 \longrightarrow 3R_2BH + Al(OCH_3)_3\downarrow \quad (2)$$

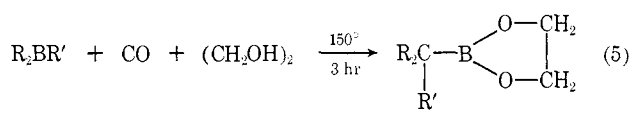
Instead, the precipitate contained all of the dialkylborane groups (eq 3). Nevertheless, this complex was

$$3R_2BOCH_3 + AlH_3 \longrightarrow [(CH_3O)_3Al \cdot 3R_2BH]\downarrow \quad (3)$$

an active hydroborating agent, reacting rapidly with an added olefin (eq 4). The purity of the mixed tri-

$$[(CH_3O)_3Al \cdot 3R_2BH] + 3\text{olefin} \longrightarrow 3R_2BR' + (CH_3O)_3Al\downarrow \quad (4)$$

alkylboranes thus prepared was determined by glpc analysis of the reaction mixtures, whenever possible, and also by the analysis of the boronates **1** produced *via* the carbonylation[7] reaction.



$$R_2BR' + CO + (CH_2OH)_2 \xrightarrow[3\ hr]{150^\circ} R_2R'C{-}B(OCH_2)_2 \quad (5)$$

1

The results are summarized in Table I. The high purities of the mixed organoboranes indicate that the formation of the aluminum methoxide addition compounds must stabilize the dialkylboranes against disproportionation. Another major advantage of the

Table I. The Hydroboration of Simple and Functionally Substituted Olefins with Dialkylborane Derivatives. Synthesis of Mixed Trialkylboranes and Trialkylcarbinylboronates

Dialkylmethoxyborane, R_2BOCH_3, R	Olefin hydroborated	Trialkylborane, R_2BR'		Boronate, **1**, $R_2R'CB(OCH_2)_2$
		Method	Yield, %[a]	Yield, %[a]
1-Butyl	1-Pentene	A	91	85
1-Butyl	1-Pentene	B	90	
1-Butyl	11-Acetoxy-1-hendecene	B	80	75[b]
Isobutyl	1-Pentene	A	95	88
Isobutyl	1-Pentene	B	90	
Isobutyl	11-Chloro-1-hendecene	A	78	60[b]
2-Butyl	1-Pentene	A	88	85
2-Butyl	1-Pentene	B	90	
Cyclopentyl	11-Dodecene nitrile	A	82	55[b,c]

[a] By glpc analysis. [b] By isolation. [c] Bp 208–210° (0.3 mm); n^{20}D 1.4920; nmr ($CDCl_3$, TMS) δ 4.10 (s, 4), 2.3 (br t, 3), 2.05–1.1 ppm (br, 38).

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(1) H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 204 (1962).

(2) H. C. Brown and E. Negishi, *J. Organometal. Chem.*, **26**, C67 (1971).

(3) E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 5280 (1968).

(4) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. I, Methuen, London, 1968, p 232, and references cited there.

(5) H. C. Brown, E. Negishi, and S. K. Gupta, *J. Amer. Chem. Soc.*, **92**, 6648 (1970).

(6) N. M. Yoon and H. C. Brown, *ibid.*, **90**, 2927 (1968).

(7) H. C. Brown, *Accounts Chem. Res.*, **2**, 65 (1969).

present procedure is the fact that it can readily be extended to the synthesis of derivatives containing reducible functional groups (Table I), in contrast to the previous method.[5]

The following procedure is representative of this new method. Diisobutylmethoxyborane (7.8 g, 50 mmol) was dissolved in ethyl ether (100 ml) and a solution of aluminum hydride in THF[6] (17.4 ml of 1 *M*, 17.4 mmol) was added to it in 10 min at 25–28° (exothermic reaction). After 30 min, a microcrystalline white solid had separated. The reaction mixture was cooled in an ice bath and then filtered through a sintered-glass funnel under the blanket of nitrogen. The solid weighed 7.6 g (92%). Upon reaction with water, it evolved 49.3 mmol of hydrogen gas.

The solid obtained above can be suspended in THF or ethyl ether (EE) and then treated with the olefin in order to accomplish the hydroboration. However, it is usually more convenient to omit the prior isolation of the solid complex (method A). Thus, diisobutylmethoxyborane (7.8 g, 50 mmol) in 100 ml of THF was treated with 17.4 mmol of aluminum hydride in THF at 25–28°. After 30 min, 11-chloro-1-hendecene (9.4 g, 50 mmol) was added. The stirring was continued for an additional 30 min. The reaction mixture was then treated with water (2 ml) and sulfuric acid (2 ml, 36 mmol). This transformed aluminum salts into crystalline aluminum sulfate. After the addition of hexane (50 ml), the clear supernatant solution was withdrawn with the aid of a hypodermic syringe. The organoborane solution was carbonylated as usual in the presence of ethylene glycol at 150° for 3 hr. After the usual work-up and distillation, boronate **1** (R = isobutyl, R′ = 11-chlorohendecanyl), 11.5 g (60%), was obtained: bp 156–158° (0.2 mm); $n^{20}\text{D}$ 1.4660; nmr ($CDCl_3$, TMS) δ 4.11 (s, 4), 3.51 (t, 2, J = 6.5 Hz), 1.26 (br s, 26), 0.87 ppm (br d, 12). *Anal.* Calcd for $C_{22}H_{44}BClO_2$: B, 2.79, Cl, 9.16: Found: B, 2.91, Cl, 9.20.

The new dialkylborane–aluminum methoxide complexes can also be used to prepare the corresponding pyridine–dialkylboranes.[8] This requires merely the addition of the theoretical quantity of pyridine (eq 6).

$$[(CH_3O)_3Al\cdot 3R_2BH] + 3py \longrightarrow (CH_3O)_3Al\downarrow + 3R_2BH{:}py \qquad (6)$$

Alternatively, the reduction of the borinic ester can be carried out in the presence of the base. The following procedure illustrates this preparation. To a stirred mixture of diisobutylmethoxyborane (7.02 g, 45 mmol), EE (90 ml), and pyridine (4 g, 50 mmol) was added a solution of aluminum hydride in THF[6] (15.75 ml of 1 *M*) at 25° in 10 min. After stirring for 30 min, pentane (50 ml) was added, and after ice-bath cooling, the reaction mixture was filtered through Celite. The filtrate was evaporated to give pyridine–diisobutylborane as a pale liquid. It was dried at 25° (0.2 mm) for 2 hr: yield 7.7 g (83%); $n^{20}\text{D}$ 1.4830; ir (neat) 4.3, 4.45, 6.15; nmr ($CDCl_3$, TMS) δ 8.86–7.22 (m, 5) and 2.26–0.26 ppm (m, 18). *Anal.* Calcd for $C_{13}H_{24}BN$: B, 5.27; N, 6.82. Found: B, 5.32; N, 6.68. Other derivatives were prepared likewise. Pyridine–di-*n*-butylborane (90% yield): $n^{20}\text{D}$ 1.4880; ir (neat) 4.3, 4.45, 6.15; nmr ($CDCl_3$, TMS) δ 8.74–7.16 (m, 5), 1.62–0.2 ppm (c, 18). *Anal.* Found: B, 5.30; N, 6.73. Pyridine–di-*sec*-butylborane (90% yield): $n^{20}\text{D}$ 1.4920; ir (neat) 4.3, 4.40, 6.20; nmr ($CDCl_3$, TMS) δ 8.66–7.20 (m, 5), 1.93–0.16 ppm (c, 18). *Anal.* Found: N, 6.42.

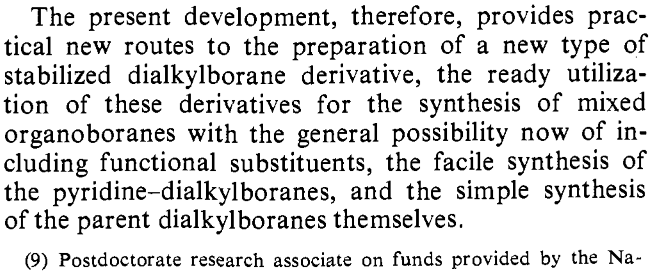
Finally, pure dialkylboranes were readily generated from the pyridine addition compounds by treatment with the theoretical quantity of boron trifluoride etherate (eq 7). If the addition is carried out in pentane

$$R_2BH{:}py + BF_3\cdot Et_2O \longrightarrow R_2BH + BF_3{:}py\downarrow \qquad (7)$$

solution, the pyridine–boron trifluoride is insoluble, and a pentane solution of the dialkylborane is obtained. It is important to utilize these as soon as possible, since the dialkylboranes undergo rapid disproportionation. When the addition of boron trifluoride etherate is performed with the prior addition of an olefin, pure mixed trialkylboranes are obtained (method B). For example, a mixture of pyridine–di-*n*-butylborane (10.25 g, 50 mmol), 11-acetoxy-1-hendecene (10.6 g, 50 mmol), and hexane (50 ml) was stirred and boron trifluoride etherate (50 mmol) was slowly added to it at 25° over 15 min. After stirring at 25° for 30 min, the clear supernatant liquid containing the organoborane was siphoned out, leaving the crystalline pyridine–boron trifluoride complex in the flask. The usual carbonylation and work-up gave boronate **1** (R = *n*-butyl, R′ = 11-acetoxyhendecanyl) in 75% yield after distillation: bp 178–180° (0.15 mm); $n^{20}\text{D}$ 1.4580; nmr ($CDCl_3$, TMS) δ 4.13 (overlapped t, 6), 2.0 (s, 3), 1.25 ppm (br, 38). *Anal.* Calcd for $C_{24}H_{47}BO_4$: C, 70.24; H, 11.46. Found: C, 70.42; H, 11.38.

The pyridine addition compounds of the dialkylboranes appear to be quite stable to disproportionation and relatively insensitive to air and moisture. Consequently, they constitute an excellent form for storing the dialkylboranes.

The potential of this new synthetic approach is indicated by the following representative synthesis.



The present development, therefore, provides practical new routes to the preparation of a new type of stabilized dialkylborane derivative, the ready utilization of these derivatives for the synthesis of mixed organoboranes with the general possibility now of including functional substituents, the facile synthesis of the pyridine–dialkylboranes, and the simple synthesis of the parent dialkylboranes themselves.

Herbert C. Brown,* S. K. Gupta[9]
Richard B. Wetherill Laboratory
Purdue University, Lafayette, Indiana 47907

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[8] Pyridine–diarylboranes have been reported previously: M. F. Hawthorne, *J. Amer. Chem. Soc.*, 80, 4293 (1958).

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