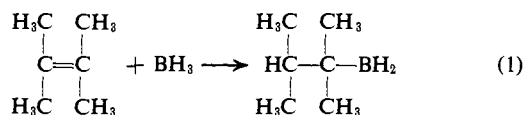G. N. Schrauzer,* R. J. Holland

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A Simple General Synthesis of Monoalkylboranes and Their Applicability for the Preparation of Mixed Organoboranes via Hydroboration

Sir:

B-Alkylcatecholoboranes (2-alkyl-1,3,2-benzodioxaboroles (**1**), readily available *via* the hydroboration of olefins with catecholborane,[1] undergo a smooth reduction with either lithium aluminum hydride (LAH) or aluminum hydride (AlH_3) to give the corresponding monoalkylboranes in nearly quantitative yield. This facile synthesis constitutes the first general preparative route to monoalkylboranes (1,2-dialkyldiboranes), and a simple new route to mixed trialkylboranes.
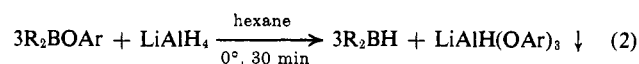
The hydroboration of 2,3-dimethyl-2-butene can be controlled to give the monoalkylborane, thexylborane (eq 1).[2] Otherwise, the synthesis of monoalkylboranes

$$\begin{array}{ccc} H_3C \ CH_3 & & H_3C \ CH_3 \\ | \ \ | & & | \ \ | \\ C{=}C & + \ BH_3 \longrightarrow & HC{-}C{-}BH_2 \quad (1) \\ | \ \ | & & | \ \ | \\ H_3C \ CH_3 & & H_3C \ CH_3 \end{array}$$
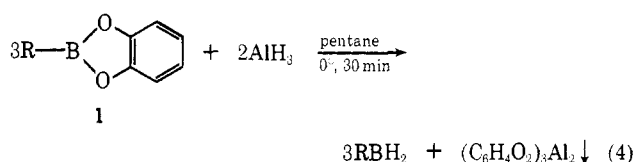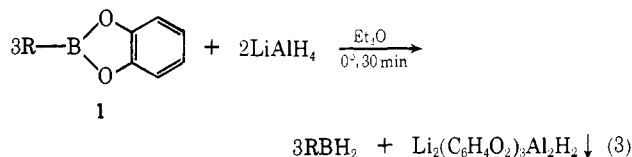
has been quite difficult. Thus, the redistribution of trialkylboranes with diborane gives the unsymmetrical 1,1-dialkyldiborane, rather than the desired 1,2-dialkyldiborane.[3] The reduction of alkylboron dihalides with metal hydrides results in the formation of a mixture of several organoboron products.[4] Recently, certain monoalkylborane addition compounds with trimethylamine have been synthesized *via* the reduction of the corresponding trialkylboroxine with LAH in the presence of the tertiary amine.[5] However, these addition compounds hydroborate olefins and dienes only at relatively high temperature.[6]

The parent monoalkylboranes, such as thexylborane, free of coordinating amine, possess highly interesting properties as reagents for selective reduction,[7] for the cyclic hydroboration of dienes,[8] the synthesis of cyclic and other ketones,[9] and the synthesis of olefins and dienes.[10] These potentialities offer major incentives for a convenient synthesis of monoalkylboranes.

Unfortunately, the methods which had proven successful (eq 2) in converting dialkylborinic acid esters to

(1) H. C. Brown and S. K. Gupta, *J. Amer. Chem. Soc.*, **93**, 1816 (1971).
(2) H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 204 (1962).
(3) H. I. Schlesinger, N. Y. Flodin, and A. B. Burg, *J. Amer. Chem. Soc.*, **61**, 1078 (1939).
(4) L. H. Long and M. G. H. Wallbridge, *J. Chem. Soc.*, 3513 (1965).
(5) M. F. Hawthorne, *J. Amer. Chem. Soc.*, **83**, 831 (1961).
(6) M. F. Hawthorne, *ibid.*, **83**, 2541 (1961).
(7) H. C. Brown and N. M. Yoon, unpublished research.
(8) H. C. Brown and C. D. Pfaffenberger, *J. Amer. Chem. Soc.*, **89**, 5475 (1967).
(9) H. C. Brown and E. Negishi, *ibid.*, **89**, 5477 (1967).
(10) G. Zweifel, N. L. Polston, and C. C. Whitney, *ibid.*, **90**, 6243 (1968).

$$3R_2BOAr + LiAlH_4 \xrightarrow[0^\circ, \ 30 \ min]{hexane} 3R_2BH + LiAlH(OAr)_3 \downarrow \quad (2)$$

dialkylboranes and their derivatives[11–13] proved unsatisfactory. Thus the treatment of dimethyl alkylboronates with LAH or AlH_3 gives the monoalkylborane in yields of only 40–45%. Utilization of the cyclic trimethylene esters[14] gives slightly improved yields, 60–68%. However, reduction of the *o*-phenylene esters of alkaneboronic acids (B-alkylcatecholboranes (**1**)) with either LAH (eq 3) or with AlH_3 (eq 4)

$$3R{-}B \overset{O}{\underset{O}{\diagdown}} \diagup \hspace{-0.2em} \bigcirc + 2LiAlH_4 \xrightarrow[0^\circ, 30 min]{Et_2O}$$

1

$$3RBH_2 + Li_2(C_6H_4O_2)_3Al_2H_2 \downarrow \quad (3)$$

$$3R{-}B \overset{O}{\underset{O}{\diagdown}} \diagup \hspace{-0.2em} \bigcirc + 2AlH_3 \xrightarrow[0^\circ, 30 min]{pentane}$$

1

$$3RBH_2 + (C_6H_4O_2)_3Al_2 \downarrow \quad (4)$$

makes available highly satisfactory routes to the monoalkylboranes. In the lithium aluminum hydride reduction a moderate excess (33%) of the reducing agent, corresponding to conversion to the $Li_2(C_6H_4O_2)_3Al_2H_2$ stage, was necessary to achieve optimum yields. The addition of an olefin to the filtrate provides the corresponding mixed trialkylborane. The structure of these mixed boranes was confirmed by glpc analysis, whenever possible, using the previously identified samples,[13] and by their transformation *via* carbonylation[15] into the corresponding trialkylcarbinylboronates. A solution of 2-*n*-butyl-1,3,2-benzodioxaborole (1.76 g, 10 mmol) in ethyl ether (10 ml) was cooled with an ice bath and a clear solution of LAH in ethyl ether (3.35 ml of 2 *M*, 6.7 mmol) added over 2 min. The mixture was stirred for 1 hr at 0° and then diluted with pentane (20 ml). A white crystalline precipitate separated. The mixture was filtered through Celite under nitrogen. Evaporation of the filtrate provided *n*-butylborane as a clear liquid: ir (CCl_4) 2550, 1590, 1480 cm⁻¹. Addition of water evolved 19.2 mmol of hydrogen gas.

Alternatively, addition of amines provides corresponding amine–monoalkylborane. Thus, 17.6 g (100 mmol) of 2-*n*-butyl-1,3,2-benzodioxaborole in 100 ml of ethyl ether was treated with 67 mmol of LAH solution as above. After 1 hr at 0°, the mixture was diluted with pentane (100 ml) and filtered. Addition of trimethylamine (150 mmol) to the filtrate provided 10.3 g (80%) of trimethylamine–*n*-butylborane: bp 48° (0.5 mm); $n^{20}D$ 1.4320.

In the above synthesis (eq 3) the lithium aryloxy-aluminohydride by-product retains reactive hydride. Consequently, it must be separated from the monoalkylborane if the latter is to be used to hydroborate olefins containing reducible functional groups. The aluminum hydride procedure (eq 4) circumvents the need for this separation. This synthetic potential is described in the following procedure. A solution of 2-*n*-butyl-1,3,2-

(11) H. C. Brown and S. K. Gupta, *ibid.*, in press.
(12) H. C. Brown, E. Negishi, and S. K. Gupta, *ibid.*, **92**, 6648 (1970).
(13) H. C. Brown and S. K. Gupta, *ibid.*, **93**, 1818 (1971).
(14) H. C. Brown and S. K. Gupta, *ibid.*, **92**, 6983 (1970).
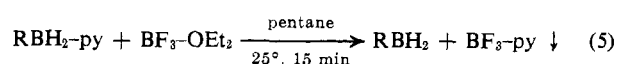(15) H. C. Brown, *Accounts Chem. Res.*, **2**, 65 (1969).

Table I. Preparation of Representative Monoalkylboranes from 2-Alkyl-1,3,2-benzodioxaboroles *via* Reaction with Lithium Aluminum Hydride or Aluminum Hydride and Their Converison into Amine–Monoalkylboranes and Mixed Trialkylboranes[a]

Monoalkylborane, RBH$_2$, R substituent	Amine–monoalkylborane			Mixed trialkylborane, RBH$_2$ + olefin	RBR'$_2$ yield,[d] %	RR'$_2$CB-(OCH$_2$)$_2$ (2) yield, %
	Yield,[c] %	Bp, °C (mm)	n^{20}D			
1-Butyl	85	48 (0.5)	1.4320[e]	Isobutylene	90	88
1-Butyl	83	48 (0.5)	1.4320[b,e]	2-Butene[b]	85	80[g]
1-Butyl	90		1.5155[f]	11-Chloro-1-hendecene	75	70
1-Butyl				4-Penten-1-ol acetate	85	70
Isobutyl	87	40 (0.5)	1.4305[e]	Isobutylene	99	
Isobutyl	93		1.5100[f]	2-Butene	90	86
Isobutyl				2-Butene[b]	90	78[g]
Isobutyl				11-Chloro-1-hendecene	75	
2-Butyl	81	36 (0.3)	1.4342[e]	Isobutylene	92	88
2-Butyl				Isobutylene[b]	86	75[g]
2-Butyl				4-Penten-1-ol acetate	80	70
Cyclopentyl	90	67 (0.5)	1.4640[e]	Isobutylene	88	
Cyclopentyl				2-Butene	85	
Cyclohexyl	90	84 (0.5)[e,h]				
exo-Norbornyl	85		1.5440[f]	Allyl ethyl ether	85	
exo-Norbornyl	95	93 (0.2)[b,e]				

[a] Unless otherwise mentioned, aluminum hydride was used as the reducing agent. [b] Lithium aluminum hydride was used as the reducing agent. [c] By isolation. [d] By glpc analysis. [e] Trimethylamine–monoalkylborane derivative. [f] Pyridine–monoalkylborane derivative. [g] The corresponding trialkylcarbinol product. [h] Mp 42°; lit.[5] mp 42°.

benzodioxaborole (1.76 g, 10 mmol) in pentane (10 ml) was treated with a clear solution of AlH$_3$ in THF[16] (7.3 ml of 1 *M*, 10% excess) at 0° under nitrogen for 30 min. After dilution with pentane (10 ml), the mixture was filtered through Celite under nitrogen. Evaporation of the solvent at 0° gave 0.68 g (97%) of a clear liquid, *n*-butylborane: ir (CCl$_4$) 2550 (B–H, terminal), 1590 (B–H–B, bridge) cm^{-1}. Upon reaction with methanol, 19.0 mmol of hydrogen gas was evolved. Glpc analysis of the reaction mixture then indicated the presence of dimethyl 1-butylboronate in 90% yield. No other organoboron compounds were discernible in the glpc chromatogram. The addition of an olefin instead of methanol to the monoalkylborane product completes the formation of the corresponding mixed trialkylborane in nearly quantitative yield. For example, *sec*-butylborane (25 mmol) prepared as described above was treated with 4-penten-1-ol acetate (6.4 g, 50 mmol). The usual carbonylation in the presence of ethylene glycol then produced the corresponding 2-trialkylcarbinyl-1,3,2-dioxaborolane in 70% yield: bp 146° (0.1 mm); n^{20}D 1.4685.

The monoalkylboranes should be utilized soon after preparation. They can be transformed into relatively stable amine derivatives by treatment either with trimethylamine or pyridine. The pyridine–monoalkylboranes permit a ready regeneration of the parent monoalkylborane upon treatment with boron trifluoride etherate[13] (eq 5).

$$\text{RBH}_2\text{–py} + \text{BF}_3\text{–OEt}_2 \xrightarrow[25°, \ 15 \ \text{min}]{\text{pentane}} \text{RBH}_2 + \text{BF}_3\text{–py} \downarrow \quad (5)$$

The preparation of several representative monoalkylborane transformation products is given in Table I.[17]

(16) N. M. Yoon and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 2927 (1968).

(17) All the compounds were analyzed by ir and nmr spectroscopy. All the new compounds, in addition, gave satisfactory elemental analyses.

The present development provides, for the first time, a general and highly straightforward synthesis of monoalkylboranes, and some of their transformation products of considerable synthetic importance.

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Geometry of the *anti*-Tricyclo[3.1.0.0^{2,4}]hexane and Cyclohexa-1,4-diene Systems

Sir:

Several examples of photoinduced dimerization of cyclopropenes are known.[1a] In particular, photolysis of 3-monosubstituted 1,2-diphenylcyclopropenes with or without sensitizer proceeds readily to afford one or two dimeric products, to which the tricyclo[3.1.0.0^{2,4}]-hexane skeleton was assigned.[1b-e] The stereochemistry of the photoproducts, however, was either undetermined or assigned only on the basis of mechanistic considerations, and, further, in some cases even proposed structures appeared to be insecure.[1e] Because of (i) the absence of unambiguous evidence to establish the stereochemistry of these compounds and (ii) our interest in the exact geometry of this intriguing tricyclo system, we have undertaken X-ray analysis of photodimers obtained from 3-carbomethoxy-1,2-diphenylcyclopropene (1).

The direct irradiation of 1 (Pyrex filter, THF solvent, 6 hr, room temperature) provided dimers A and B in 56 and 25% yields, respectively.[2] Both A and B were

(1) (a) H. H. Stechl, *Chem. Ber.*, **97**, 2681 (1964); (b) N. Obata and I. Moritani, *Bull. Chem. Soc. Jap.*, **39**, 2250 (1966); (c) J. Trotter, C. S. Gibbons, N. Nakatsuka, and S. Masamune, *J. Amer. Chem. Soc.*, **89**, 2792 (1967); (d) C. Deboer and R. Breslow, *Tetrahedron Lett.*, 1033 (1967); photolysis of triphenylcyclopropene with a sensitizer provided a cyclopropylcyclopropene derivative in addition to a normal dimer (tricyclohexane); (e) H. Dürr, *ibid.*, 1649 (1967).