The Reaction of B-Methoxydialkylboranes with Lithium Aluminum Hydride in the Presence of Olefins. A New and General Synthesis of Acyclic and Cyclic Mixed Trialkylboranes and Their Conversion into the Corresponding Trialkylcarbinols *via* Carbonylation–Oxidation

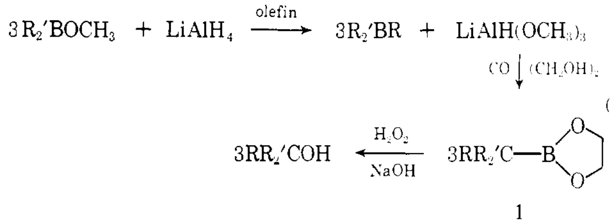
Sir:

Carbonylation–oxidation of trialkylboranes[1] provides, for the first time, a means of converting trialkylboranes into the corresponding carbon compounds while retaining all of the original structural features of the organoborane. Consequently, it now becomes highly desirable to develop procedures for the synthesis of organoboranes of known structure. Simple hydroboration[2] of an olefin provides a convenient route to organoboranes with three identical groups. We now wish to report that the treatment of readily available acyclic and cyclic B-methoxydialkylboranes[3] with lithium aluminum hydride in the presence of a wide range of olefins provides the corresponding "mixed" trialkylboranes with different groups.[4] These are readily converted into the corresponding trialkylcarbinols *via* carbonylation–oxidation (eq 1).

Table I. Preparation of Acyclic and Cyclic Mixed Trialkylboranes *via* the Reduction of B-Methoxydialkylboranes with Lithium Aluminum Hydride in the Presence of Olefins and the Conversion of the Mixed Trialkylboranes into the Corresponding Trialkylcarbinols *via* Carbonylation–Oxidation

		Trialkylborane[a,b]		Trialkylcarbinol[a,c]		
B-Methoxydialkylborane	Olefin	Yield by glpc[d] (by isolation), %	Bp, °C (mm)	Yield by glpc[d] (by isolation), %	Bp, °C (mm)	$n^{20}D$ or mp, °C
B-Methoxydi-*n*-butylborane[e]	1-Pentene	80[f]		75 (62)	142–143 (16) (139–141 (15))[g]	1.4460 (1.4420)[g]
B-Methoxydiisobutylborane	1-Pentene	87		84 (70)	74 (0.2) (77–78 (0.2))[h]	1.4420 (1.4419)[h]
B-Methoxydi-*sec*-butylborane	1-Pentene	90		88 (76)	67 (0.2)	1.4540
B-Methoxydicyclohexylborane	Isobutylene			74 (63)[i]	152–154 (0.8)[i]	1.4988[i]
B-Methoxyborinane[e]	1-Pentene	89 (67)	92–95 (20)	95 (88)[j]	83–85 (3) (96–96.5 (5))[k]	1.4656 (1.4668)[k]
	1-Octene	92[l]				
	2-Butene	(66)	64–67 (20)	90 (85)[j]	73–74 (3)	1.4705
	Cyclohexene	90 (75)	112–115 (18)	98 (90)[j]	129–130 (20) (114–115 (7))[k]	51–53 (51)[k]
	Norbornene	88 (74)	128–130 (20)	93 (82)[j]		72–73
B-Methoxyborolane	1-Butene	(56)	52–54 (20)	91 (85)[j]	110–112 (40) (193 (760))[m]	1.4539 (1.4535)[m]
	1-Octene	90[l]				
	Cyclopentene	(60)	77–78 (20)	89 (81)[j]	73–75 (1) (85–87 (3))[n]	(1.4846)[n]
B-Methoxy-9-borabicyclo-[3.3.1]nonane	1-Octene	92[o]				

[a] Structures of trialkylboranes and trialkylcarbinols are those which are expected. [b] All of the isolated trialkylboranes were identified by analyses of oxidation products and characterized by pmr and ir. [c] All of new, isolated trialkylcarbinols yielded satisfactory elemental analyses and spectral data. [d] Based on olefin or B-methoxydialkylborane. [e] A minor quantity (up to 10%) of isomeric boranes was also present. [f] In addition to the expected borane, tri-*n*-butylborane and *n*-butyldi-*n*-pentylborane were also obtained in yields of 13 and 3%, respectively. [g] A. P. Meshcheryakov, E. I. Erzyntova, and C. Kuo, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2198 (1961). [h] C. E. France and W. E. Foster, *Ind. Eng. Chem.*, **46**, 1019 (1954). [i] Values for the 2-dicyclohexylisobutylcarbinyl-1,3-dioxa-2-borolanes. [j] Based on trialkylborane. [k] F. K. Signaigo and P. L. Cramer, *J. Amer. Chem. Soc.*, **55**, 3326 (1933). [l] Yield of 1-octanol after oxidation. [m] C. R. McLellan and W. R. Edwards, Jr., *J. Amer. Chem. Soc.*, **66**, 409 (1944). [n] A. I. Chirio, *Zh. Org. Khim.*, **1**, 1984 (1965). [o] The product was identified by comparing the glpc retention time with an authentic sample prepared by the direct hydroboration of 9-BBN.



(1)

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A preliminary study on the reduction of B-methoxyborolane and B-methoxyborinane[3d] with lithium aluminum hydride in the presence of the stoichiometric quantity of 1-octene revealed that the use of a modest (33%) excess of lithium aluminum hydride, followed by oxidation, results in approximately 90% conversion of 1-octene into 1-octanol. Following this procedure no difficulty was encountered in preparing a number of representative "mixed" trialkylboranes (2–7). These "mixed" organoboranes were readily converted in high yield into the corresponding 2-trialkylcarbinyl-1,3-dioxa-2-borolanes (**1**) and trialkylcarbinols (Table I).

No sign of extensive scrambling has been observed in either the reduction–hydroboration or the carbonylation step. This is gratifying in the light of the earlier report that hydroboration with tetraethyldiborane and

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(1) H. C. Brown, *Accounts Chem. Res.*, **2**, 65 (1969), and references cited therein.

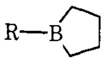
(2) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

(3) (a) H. C. Brown, A. Tsukamoto, and D. B. Bigley, *J. Amer. Chem. Soc.*, **82**, 4703 (1960); (b) B. M. Mikhailov and L. S. Vasil'ev, *Dokl. Akad. Nauk SSSR*, **139**, 385 (1961); (c) B. M. Mikhailov, L. S. Vasil'ev, and E. N. Safonova, *ibid.*, **147**, 630 (1962); (d) B. M. Mikhailov and L. S. Vasil'ev, *Zh. Obshch. Khim.*, **35**, 925 (1965); (e) unpublished results by S. K. Gupta.

(4) The reduction of alkoxydiarylboranes with lithium aluminum hydride in the presence of pyridine to form pyridine diarylborane complexes has been described: M. F. Hawthorne, *J. Amer. Chem. Soc.*, 80, 4293 (1958).

$R{-}B(CH_2CH_2CH_2CH_3)_2$

2



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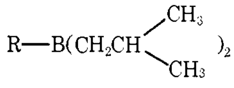
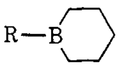


$R{-}B(CH_2CH(CH_3)_2)_2$

3



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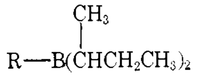
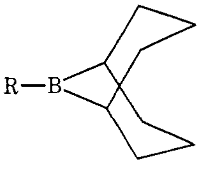


$R{-}B(CH(CH_3)CH_2CH_3)_2$

4



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tetraisopropyldiborane yielded extensively scrambled mixtures of all of the possible trialkylboranes.[5] Possibly in the present procedure the rapid *in situ* conversion of the dialkylborane intermediate into the more stable trialkylborane is primarily responsible for circumventing this difficulty.

The following procedure for the preparation of B-(*n*-pentyl)borinane and 1-(*n*-pentyl)cyclohexanol is representative. In a 300-ml three-necked flask equipped with a mechanical stirrer, a septum inlet, a thermometer well, and reflux condenser connected to a mercury bubbler were placed 7.0 g (100 mmol) of 1-pentene, 50 ml of THF, 2.28 g (20 mmol) of *n*-octane as a standard, and 24 ml of 1.38 *M* lithium aluminum hydride (33.3 mmol) in THF. To this was added over *ca.* 10 min 11.2 g (100 mmol) of B-methoxyborinane[6] at 25–30°. The uptake of 1-pentene was *ca.* 90% over in 1 hr. Two hours later, 6.9 g of 96% sulfuric acid (67 mmol) was slowly added at 0–10°, followed by the addition of *ca.* 5 ml of water and 25 ml of hexane. A clear supernatant solution resulted and the precipitate formed hail-like particles, allowing an easy transfer of the supernatant solution by means of a syringe. The precipitate was washed two–three times with hexane (10 ml each). Glpc examination of the combined solution on an SE-30 column indicated the presence of 89 mmol (89%) of B-(*n*-pentyl)borinane contaminated with *ca.* 5 mmol of B-*n*-pentyl-2-methylborolane.

One-half of the mixture was directly subjected to distillation to yield 5.4 g (71%) of *ca.* 95% pure B-(*n*-pentyl)borinane: bp 92–95° (20 mm); pmr (CCl_4, TMS) δ 0.83 (triplet, 3 H) and 1.0–1.8 (broad doublet-like multiplet, 18 H). The remaining mixture was carbonylated at 150° and 1000 psi after addition of 4.5 ml (*ca.* 75 mmol) of ethylene glycol. After a constant pressure was observed at 150° (*ca.* 3 hr), the reaction mixture was cooled and oxidized with 25 ml of 6 *N* sodium hydroxide, 25 ml of 30% hydrogen peroxide, and 25 ml of 95% ethanol at *ca.* 30° followed by heating at 50° for 1 hr. Glpc analysis indicated the presence of 1-(*n*-pentyl)cyclohexanol in 85% yield based on 1-pentene or B-methoxyborinane. 1-(*n*-Pentyl)cyclohexanol was obtained in a separate run using a distilled sample of B-(*n*-pentyl)borinane in 88% yield (95% by glpc): bp 83–85° (3 mm); $n^{20}D$ 1.4656; ir (neat) 3440 cm^{-1}; pmr (CCl_4, TMS) δ 0.9 (triplet, 3 H), 1.1–1.8 (doublet-like multiplet, 18 H), 2.2 (singlet, 1 H).

Consequently, the present results indicate that a wide variety of mixed organoboranes can be prepared and utilized without the complication of extensive disproportionation, thereby adding to the utility of the carbonylation reaction for the preparation of a wide variety of carbon structures.

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[5] R. Köster, G. Griaznow, W. Larbig, and P. Binger, *Justus Liebigs Ann. Chem.*, 672, 1 (1964).

[6] B-Methoxyborinane, bp 68–69° (90 mm), was prepared by the reaction of 1,5-bis(1′-borinyl)pentane, obtained by the hydroboration of 1,4-pentadiene followed by thermal treatment at 170°, with dry trimethyl borate in the presence of borane in THF (5 mol % in hydride) as catalyst at *ca.* 120°.[3c–e]

[7] Postdoctoral research associate on Grant No. DA 31-124 ARO(D) 453, supported by the U. S. Army Research Office (Durham).

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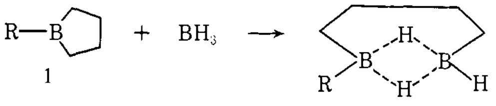
A Facile Opening of the Borolane Ring with Borane. A Simple Entry into 1,2-Tetramethylenediboranes

Sir:

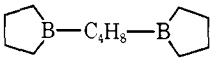
We wish to report a remarkably facile opening of the borolane ring of B-alkylborolanes (**1**) with borane (eq 1). The reaction not only indicates an unusual chemical reactivity of the borolane ring, but also provides a simple route to a novel class of compounds, the 1-alkyl-1,2-tetramethylenediboranes (**2**), with unusual and unique properties.



(1)

a, R = n-C_4H_9–
b, R = n-C_8H_{17}–

During a detailed examination of the hydroboration of 1,3-butadiene, it was discovered that the 1:1 product obtained by the addition of 1 mol of borane in tetrahydrofuran (THF) to an equimolar quantity of 1,3-butadiene is almost entirely polymeric.[1] On the other hand, the 3:2 product obtained by using only the theoretical quantity of borane, two-thirds of that utilized above, is largely a mixture of monomeric dumbbell-shaped compounds (**3**).[2] These results suggested that **3** must be susceptible to the action of borane. This observation, coupled with a new simple entry[3] into the B-alkylborolanes, led us to study this reaction of B-alkylborolanes (**1**) with borane in detail.



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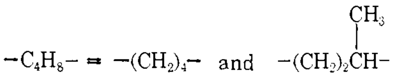

$-C_4H_8- = -(CH_2)_4-$ and $-(CH_2)_2CH(CH_3)-$

Treatment of B-(*n*-butyl)borolane (**1a**) with an equimolar quantity of borane in THF at 25° resulted in the essentially complete reaction of borane within 15 min, as revealed by the disappearance of the strong

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[1] (a) G. Zweifel, K. Nagase, and H. C. Brown, *J. Amer. Chem. Soc.*, 84, 183 (1962); (b) E. Breuer and H. C. Brown, *ibid.*, 91, 4164 (1969).

[2] H. C. Brown, E. Negishi, and S. K. Gupta, *ibid.*, 92, 2460 (1970).

[3] H. C. Brown, E. Negishi, and S. K. Gupta, *ibid.*, 92, 6648 (1970).