standard deviations of those in I. However, the removal of the outer phenyl rings and the substitution of bulkier mesityl groups for phenyl groups in the inner positions upon going from I to II result in two large differences in twist angles. The torsion angle about the central bond in the butadiene portion [C(5)–C(3)–C(4)–C(6)] is much smaller in II (18°) than in I (33°) while the best plane of the mesityl ring makes an angle of 54° with the C(7)–C(5)–C(3) plane compared to 43 and 31° in I. There are also slight differences in bond angles at carbon atoms C(4), C(5), and C(1) consistent with the different substituents in I and II.

The determination of the structures of I and II establishes these compounds as models whose spectra and dipole moments may assist in the assignment of structures to other allene dimers. The isomer of II obtained from it by iodine-catalyzed rearrangement must also have trans chlorines (the mesityl groups are outward rather than inward), and the other 1,2-dichloro-3,4-bis(2,4,6-trimethylbenzylidene)cyclobutane, which has one mesityl inward and one outward, probably has trans chlorines as well on the basis of the nmr signals of the ring protons.[4]

The principal dimer of 1-chloro-3-methyl-1,2-butadiene was originally assigned a structure with trans chlorines on the basis of ozonization to yield *dl*-2,3-dichlorosuccinic acid. However, a preliminary report by Bertrand and coworkers[7] suggested that some of the meso acid might also be formed. The dipole moment observed for this dimer, 2.63 D, was in poor accord with the values calculated for the structure with trans (1.44 D) or cis chlorines (3.50 D). If the ring structure of this dimer resembles that of I with an expected contribution of 2.14 D for the C–Cl bonds, the observed value and the value for the trans structure are in much better agreement. The definitive paper from Bertrand's group has now appeared[8] and there is agreement that ozonization of this dimer yields only *dl*-2,3-dichlorosuccinic acid and none of the meso isomer. The trans structure thus appears to be established.

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(7) M. Bertrand, H. Reggio, and G. Leandri, *C. R. Acad. Sci., Ser. C*, **259**, 827 (1964).

(8) R. Maurin, G. Leandri, and M. Bertrand, *Bull. Soc. Chim. Fr.*, 530 (1971).

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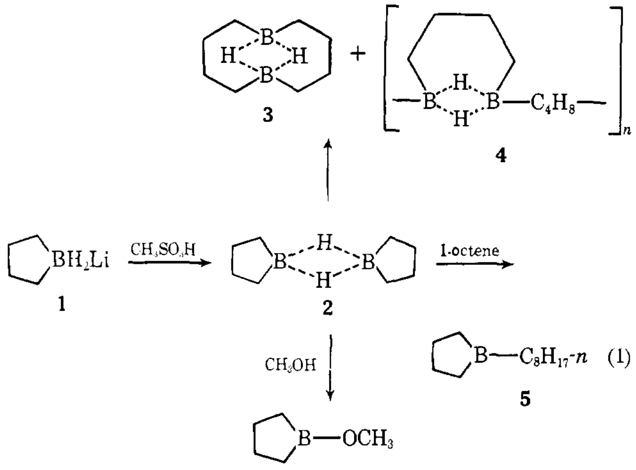
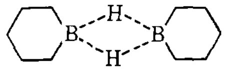
Bisborolane. A Highly Elusive Bisboracyclane

Sir:

The reaction of lithium tetramethyleneborohydride (**1**) with methanesulfonic acid produces the hitherto elusive bisborolane (**2**) as a fugitive species. In the absence of trapping reagents, the intermediate is rapidly transformed into 1,6-diboracyclodecane (**3**) and a polymer (**4**). However, addition of 1-octene or methanol immediately following the generation produces *B*-(*n*-octyl)borolane (**5**) or *B*-methoxyborolane (**6**), respectively. Thus, the results of these reactions (eq 1) provide the first unambiguous demonstration of the independent existence of bisborolane (**2**).



Bisborinane (**7**) is a thermally stable bisboracyclane.[1] However, the five-membered analog, bisborolane (**2**), has been highly elusive. Thus, the hydroboration of 1,3-butadiene does not yield **2** as a final product.[2] Instead, the product is a polymer largely represented by **4**, which undergoes methanolysis rapidly and yet hydroborates olefins only sluggishly at room temperature.[2a] On heating, **4** is converted to an unusually stable tetraalkyldiborane, **3**, which reacts neither with olefins nor with methanol at detectable rates at 25°.[2b]



7

Earlier, Köster[3] assigned the bisborolane structure **2** to the product obtained in the reduction of *B*-chloroborolane with lithium aluminum hydride. However, the properties reported for the product are identical with those of the highly stable species obtained in the hydroboration of 1,3-butadiene,[4] recently shown to have the structure **3**.[2b,5] Therefore, the reduction product isolated must also be **3**. The first indication that bisborolane (**2**) must be an active hydride species capable of reacting readily with olefins was realized in the reduction of *B*-methoxyborolane (**6**) with lithium aluminum hydride in the presence of olefins.[6] In this reaction, the olefins underwent rapid hydroboration to form the corresponding *B*-alkylborolanes in high yields. These results strongly support the formation of **2** as an intermediate capable of rapid hydroboration of olefins. However, the synthesis of free bisborolane as a distinct species with independent existence has not yet been demonstrated.

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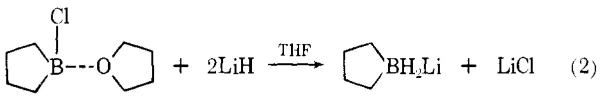
(3) R. Köster and G. Benedikt, *Angew. Chem.*, **75**, 346 (1963).

(4) (a) R. Köster, *ibid.*, **72**, 626 (1960); (b) R. Köster, *Advan. Organometal. Chem.*, **2**, 257 (1964).

(5) D. E. Young and S. G. Shore, *J. Amer. Chem. Soc.*, **91**, 3497 (1969).

(6) H. C. Brown, E. Negishi, and S. K. Gupta, *ibid.*, **92**, 2460, 6648 (1970).

Free *B*-chloroborolane is a rather unstable species with respect to polymerization.[7] However, with tetrahydrofuran (THF) it forms a more stable, distillable 1:1 complex **8**: bp 40–42° (0.9 mm); pmr (CCl_4, TMS) δ 0.63 (t, J = 7 Hz, 4 H), 1.47 (m, 4 H), 2.13 (m, 4 H), and 4.27 (t, J = 7 Hz, 4 H). *Anal.* Calcd for $C_8H_{16}BClO$: Cl, 20.3. Found: Cl, 19.9. Treatment of **8** with sodium methoxide provides a 95% yield of *B*-methoxyborolane (**6**).[9] Freshly distilled **8** reacts readily with 2 mol equiv of lithium hydride in THF (eq 2) to produce a solution containing lithium tetramethyleneborohydride (**1**), ir (THF) ν 2180 (broad and strong) cm^{-1}, Li:active hydride = 1:2.1. Methanolysis of **1** followed by treatment with methanesulfonic acid forms *B*-methoxyborolane (85% yield).



8 **1**

The reaction of lithium tetramethyleneborohydride (**1**) with an equimolar quantity of methanesulfonic acid at 25° is essentially instantaneous, as indicated by the evolution of the calculated amount of hydrogen. If an equimolar quantity of 1-octene were present, 88% of the 1-octene was utilized in 1 hr at 25°, forming *B*-(*n*-octyl)borolane. On the other hand, if the 1-octene was added 15 min after the addition of methanesulfonic acid, the uptake of 1-octene was less than 5%. In this experiment 1,6-diboracyclodecane (**3**) was the major product (59% yield). At this time the reaction mixture still retained 38% active hydride in spite of the failure to take up more 1-octene. Examination of the mixture by ir indicated the presence of a strong band at 1570 cm^{-1} in addition to the absorption at 1610 cm^{-1} for **3**. No other noticeable bands were observable in the 2600–1500-cm^{-1} region. Clearly, the remaining active hydride species is a tetraalkyldiborane, which readily undergoes methanolysis, but does not hydroborate olefins. These chemical and physical properties closely parallel those of **4**,[2a] strongly suggesting that the two species are essentially identical.

Preparation of a solution containing bisborolane (**2**) was achieved by lowering the reaction temperature to −25°. At this temperature, the reaction of **1** with methanesulfonic acid was complete in only 1 min. Immediate addition of 1-octene resulted in an uptake of 79%. Moreover, immediate addition of methanol produced *B*-methoxyborolane (**6**) in 73% yield.

The experimental results of the hydroboration of 1-octene with the product derived from **1** and methanesulfonic acid are summarized in Table I and Figure 1. The results clearly demonstrate the formation of bisborolane (**2**) as a fugitive reactive species.

The highly labile nature of bisborolane (**2**) in THF precludes its observation by ir in this solvent at room temperature. However, **2** appears more stable in diethyl ether. Thus, a reaction product derived from **1** in diethyl ether and methanesulfonic acid and kept at room temperature for 15 min (time required for ir examination) was still capable of hydroborating 1-octene to the extent of 45%. Of the only two noticeable bands in the 2600–1500-cm^{-1} region of the ir spectra, the intensity of the band at 1570 cm^{-1} relative to that of the 1610-cm^{-1} band decreased considerably after the hydroboration. Therefore, the normal 1570-cm^{-1} band may be assigned tentatively to the double hydrogen bridge stretching of bisborolane.

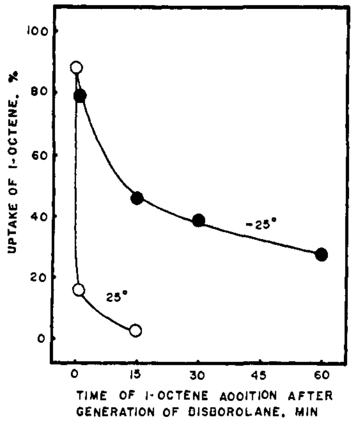


Figure 1. Hydroboration of 1-octene with bisborolane generated by the reaction of lithium tetramethyleneborohydride with methanesulfonic acid in tetrahydrofuran at 25° (○) and −25° (●).

Table I. Hydroboration of 1-Octene with Bisborolane Generated by the Reaction of Lithium Tetramethyleneborohydride with Methanesulfonic Acid in Tetrahydrofuran

Temp,[a] °C	Time,[b] min	Uptake of 1-octene,[c] %	**3**,[c] %	Residual hydride,[d] %
25	*In situ*	88[e]	10	[f]
25	0	16	49	31
25	15	<5	59	38
−25	0	79	11	8
−25	15	46	30	27
−25	30	39	41	23
−25	60	28	49	23

[a] Lithium tetramethyleneborohydride in THF (0.5 *M*) was treated with the calculated quantity of methanesulfonic acid at the temperature indicated. [b] 1-Octene added after indicated time following completion of hydrogen evolution. [c] Analysis by glpc after 1 hr at 25°. [d] Analysis for residual hydride after 1 hr at 25°. [e] A 90% yield of 1-octanol was observed after oxidation. [f] Not determined.

We have thus completed the preparation and characterization of three representative types of products, **2**, **3**,[2b] and **4**,[2a] which are derived from 1,3-butadiene and contain tetramethylene and H–B< moieties in the 1:1 ratio. This should clarify the existing confusion regarding these highly intriguing species.

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(7) As pointed out by Kovredov and Zakharkin,[8] *B*-chloroborolane is quite unstable with respect to polymerization in the presence of hydride-containing species. Even in their absence it was not feasible, in our hands, to syphon out the initially mobile distillate with a syringe equipped with a 20-gauge needle 1 hr after distillation.

(8) A. I. Kovredov and L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 50 (1964).

(9) The complex **8** also undergoes a slow polymerization. However, it remains essentially (>90%) monomeric for at least a few hours at 25° (by glpc analysis of the methanolysis product using the block and column temperature of 50°).

(10) Postdoctoral Research Associate on Grant No. DA 31-124 ARO(D) 453, supported by the U. S. Army Research Office (Durham).