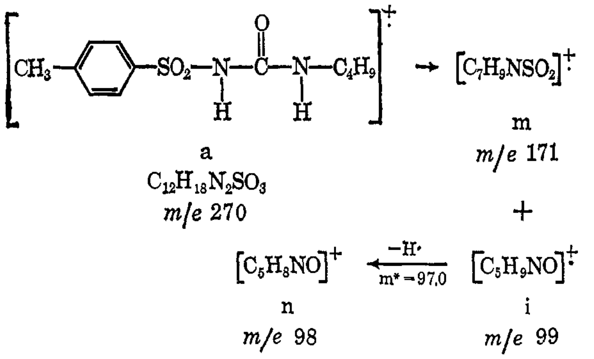

scheme were assessed from the m/e 107 and 108 peaks rather than from the m/e 99 peak.

Experimental Section

Mass Spectra. Low-resolution mass spectra were recorded using an Atlas CH4 instrument equipped with a TO4 direct inlet source and the high-temperature inlet system. High-resolution mass measurements were performed by peak matching using two MS-9 instruments employing the direct insertion system. Source temperatures on the two instruments were 180–200 and 200–230°.

Deuterated Tolbutamide. Sodium tolbutamide was dissolved in D_2O and concentrated by evaporation of solvent. Additional D_2O was added to bring the solution to the original volume and the solution was again concentrated. This process was repeated four times. The solution was then acidified with DCl and the deuterated tolbutamide was filtered, washed with D_2O, and dried overnight at 50° under high vacuum. The nmr spectrum of this material showed about equal absorptions assigned to both types of N–H groups in this molecule.

4,4,6-Trimethyl-1,3,2-dioxaborinane. A Stable Dialkoxyborane

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Contribution from the U. S. Borax Research Corporation, Anaheim, California.

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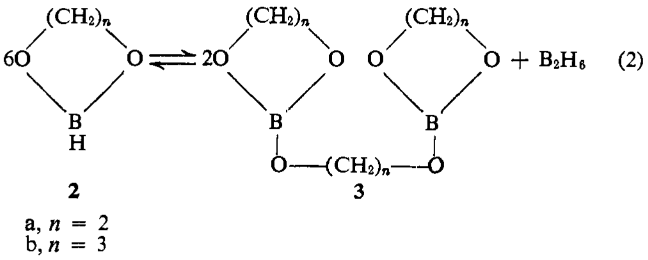
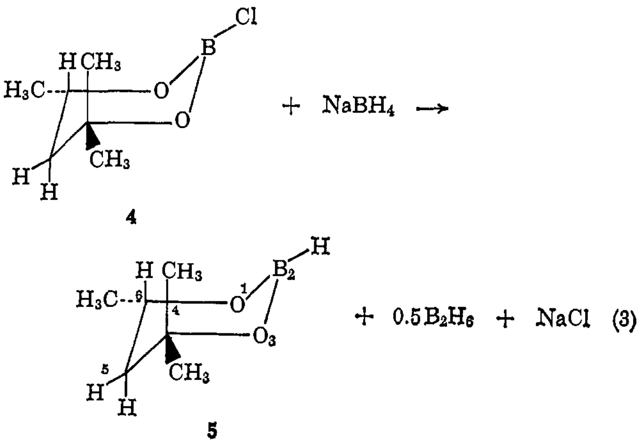
Abstract: 4,4,6-Trimethyl-1,3,2-dioxaborinane (**5**) was prepared by reduction of the 2-chloro derivative (**4**) with sodium borohydride or lithium aluminum hydride, and from reaction of diborane and tris(2-methyl-2,4-pentanediol)biborate (**6**). Five-bond HCCOBH proton–proton coupling (J = 1.6 cps) was observed for **5**, but disappeared in the nmr spectrum of the 2-*d* compound. Hydroborations of cyclohexene, 1-octene, and allyl methyl sulfide with **5** gave the corresponding 2-alkyl compounds; **5** gave exclusively terminal addition with 1-alkenes and with 1-alkynes. The nmr spectra of the 1-alkene-1-boronates (**11** and **12**) from **5** with 1-hexyne and 1-heptyne constitute direct evidence for stereospecific *cis* addition in the hydroboration of acetylenes. A selective Raney nickel type hydrogenation catalyst was produced from nickel acetate and **5**. Reaction of **5** with dimethylamine gave the 2-dimethylamino derivative (**14**) and with ammonia gave the bis-2-amino compound (**13**); trimethylamine did not form a complex with **5**.

Interesting stability is exhibited by 2-vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane with respect to other ethyleneboronates.[1] Evidence from our laboratories indicates unusual stability associated with other 2-substituted 4,4,6-trimethyl-1,3,2-dioxaborinanes.[2] Consequently, it was of interest to prepare 4,4,6-trimethyl-1,3,2-dioxaborinane (**5**), the parent member of this system. The instability of dimethoxyborane[3] (**1**), 1,3,2-dioxaborolane[4] (**2a**), and 1,3,2-dioxaborinane[5] (**2b**) toward disproportionation has been well documented (see eq 1 and 2). The extent to which **5** is stabilized toward disproportionation, therefore, was of prime concern.

$$\underset{\mathbf{1}}{6(CH_3O)_2BH} \rightleftharpoons 4(CH_3O)_3B + B_2H_6 \qquad (1)$$



Synthesis. 4,4,6-Trimethyl-1,3,2-dioxaborinane (**5**) was prepared from 2-chloro-4,4,6-trimethyl-1,3,2-dioxaborinane (**4**) by reduction with sodium borohydride in tetraglyme (eq 3). The yield based on **4** was near



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[1] W. G. Woods, I. S. Bengelsdorf, and D. L. Hunter, *J. Org. Chem.*, **31**, 2766 (1966).

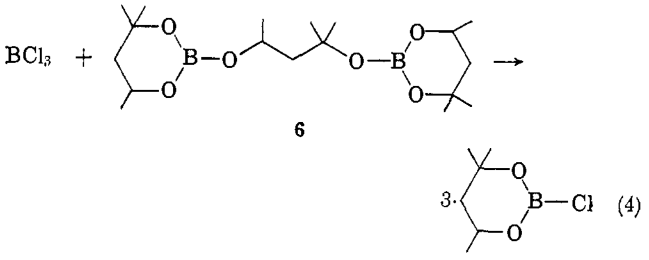
[2] (a) W. G. Woods and I. S. Bengelsdorf, *ibid.*, **31**, 2769 (1966); (b) W. G. Woods and P. L. Strong, *J. Organometal. Chem.*, in press.

[3] A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **55**, 4020 (1933).

[4] S. H. Rose and S. G. Shore, *Inorg. Chem.*, **1**, 744 (1962).

[5] G. E. McAchran, Ph.D. Thesis, Ohio State University, 1964.

50%, whether 1 or 0.5 molar equiv of sodium borohydride was employed. Prior distillation of **4** is not required; material prepared *in situ* from boron trichloride and tris(2-methyl-2,4-pentanediol)biborate (**6**) may be used directly (eq 4).[6] Lithium aluminum hydride reduction of **4** in bis(2-ethoxyethyl) ether provided only a 17% yield of **5**. The stoichiometry (eq 5) was designed to utilize all of the hydridic hydrogen in this case. A similar reduction of **4** with lithium aluminum deuteride at a lower temperature and over a longer period provided 4,4,6-trimethyl-1,3,2-dioxaborinane-2-*d* (**7**) in comparable yield (21%).



6

4

$$4 + {}^1/_4\mathrm{LiAlH_4} \longrightarrow 5 + {}^1/_4\mathrm{LiAlCl_4} \qquad (5)$$

An alternative route to **5** from diborane and **6** was suggested by the isolation of pure **2b** (unspecified yield) by the reverse of reaction 2.[5] Only 7% of **5** resulted when diborane was generated *in situ* from sodium borohydride and acetic acid[7] in the presence of **6**. An improved yield (14%) resulted when excess diborane was passed through an ethereal solution of **6** at atmospheric pressure.

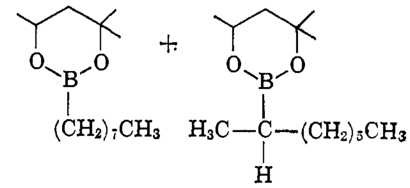
Characterization. Dioxaborinane **5** was identified by its elemental analysis, molecular weight (monomer), and infrared and nmr spectra. The BH stretching frequency of **5** (2550 cm^{-1}) and the B–D of **7** (1901 cm^{-1}) are as expected for dialkoxyboranes.[8] Proton nmr spectra of **4**, **5**, and **7** are quite diagnostic. The methyl groups at C-4 appear as a sharp singlet near τ 8.7, while that at C-6 (equatorial) records as a doublet (τ 8.8, $J = 6$ cps). The C-6 proton (axial) is a complex multiplet of at least 13 lines centered near τ 5.6 in **4** and τ 5.8 in **5** and **7**. The proton on the boron atom of **5** was located with difficulty as a broad quartet centered near τ 6.3 with $J_{\mathrm{BH}} = 173 \pm 3$ cps. The latter is in excellent agreement with the J_{BH} value of 171 cps found in the boron-11 spectrum of **2b**.[5] The methylene protons at C-5 comprise the AB portion of an ABX system in the τ 7.9–8.4 region.

Long-Range Coupling. The low-field portion of the C-5 methylene multiplet for **4** and **7** consists of a quartet. This quartet, shown for **7** in Figure 1A, is assigned to the equatorial proton at C-5. The coupling constant with the axial proton at C-6 is 3.6 cps, in agreement with the reported values for vicinal axial–equatorial coupling in 1,3-dioxanes.[9] A geminal coupling constant of $J = 14.1$ cps for the C-5 methylene group of **5** is in the expected range.[10] In the case of **5**, a further splitting of each member of the quartet ($J = 1.58$ cps) is observed (see Figure 1B). Such five-bond proton–proton couplings in oxygenated, saturated systems have been reported.[11,12] 4-Phenyl-1,3-dioxane shows an equatorial–equatorial HCOCCH coupling of 0.9 cps.[11] Values for the rigid 2,8,9-trioxaadamantane (1.25 cps) and 2,6,7-trioxabicyclo[2.2.1]octane (1.7 cps) are somewhat higher.[12] The conformational rigidity of **5** might contribute to the enhanced coupling compared with 4-phenyl-1,3-dioxane. In addition, a boron atom with a vacant 2p orbital may be a better transmitter of through-bond, long-range coupling than a saturated carbon atom.

Stability. In contrast to the previously known dialkoxyboranes, **5** is a colorlesss liquid which shows marked stability toward disproportionation. Rose and Shore[4] noted strong absorption due to diborane in the infrared spectrum of all samples of **2a**. Diborane absorptions are barely detectable in the infrared spectrum of **5** after 24 hr at room temperature, with no appreciable increase after 48 hr. Whereas **5** can be distilled without disproportionation at 50° (50 mm), and with only slight disproportionation at 118–124° (760 mm), **1**,[3] **2a**,[4] and **2b**[5] must be handled under vacuum below room temperature. At ambient temperature, **2a** forms a glassy solid[4] and **1** is converted to trimethylborate,[3] whereas **5** remains unchanged after 1 month. These results suggest that the equilibrium between **5**, diborane, and **6** strongly favors **5**. The low yields of **5** realized from treatment of **6** with diborane probably were due to failure to achieve equilibrium.

Hydroboration Reactions. Selectivity and reduced reactivity of **5** relative to diborane or alkylboranes was anticipated due to back π bonding from oxygen to boron. Hydroboration of 1-octene with **5** at 100° proceeded to give addition of boron at the terminal position (28% yield); **8** was the only observable product. The nmr spectrum exhibits a multiplet upfield from the main absorption which is assigned to the two hydrogens adjacent to boron. No multiplet for a tertiary hydrogen as expected for **9** is observed. Terminal addition with the bulky **5** is not surprising since disiamylborane[13] gives 99% of the terminal adduct. Similar results were obtained in the hydroboration of allyl methyl sulfide which gave 2-[1-(4-thiapentyl)]-4,4,6-trimethyl-1,3,2-dioxaborinane (**10**).

$$5 + \mathrm{H_2C{=}CH(CH_2)_5CH_3} \longrightarrow$$



8 **9**

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(6) G. H. Birum and J. L. Dever (to Monsanto Chemical Co.), U. S. Patent 3,064,032 (1962).

(7) H. C. Brown, E. J. Mead, and C. J. Shoaf, *J. Am. Chem. Soc.*, **78**, 3613 (1956).

(8) H. Steinberg, "Organoboron Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1964, p 871.

(9) (a) C. Barbier, J. Delman, and J. Rauft, *Tetrahedron Letters*, No. 45, 3339 (1964); (b) J. Delman and C. Barbier, *J. Chem. Phys.*, 41, 1106 (1964).

(10) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p 85.

(11) K. C. Ramey and J. Messick, *Tetrahedron Letters*, No. 49, 4423 (1956).

(12) E. J. Boros, K. J. Coskran, R. W. King, and J. G. Verkade, *J. Am. Chem. Soc.*, **88**, 1140 (1966).

(13) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 192.

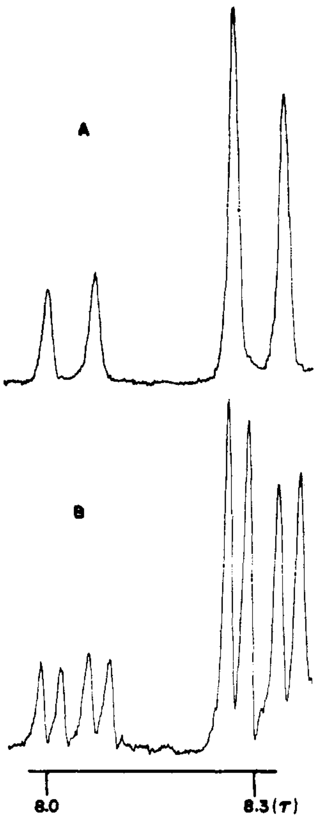
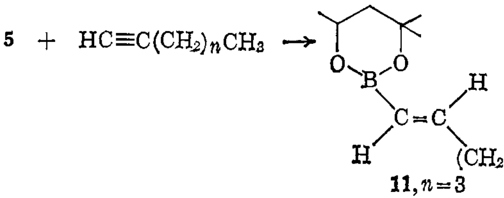


Figure 1. Proton nmr pattern of the equatorial C-5 proton of **7** (A) and of **5** (B).

Cyclohexene and **5** provided the 2-cyclohexyl derivative in 57% yield.

Direct evidence for *cis* addition in the hydroboration of alkynes was obtained by reaction of **5** with 1-hexyne and 1-heptyne. Previous evidence for the stereochemistry of acetylene hydroborations has been indirect, involving protonolysis of the vinylboron product and assuming retention of configuration.[14] Vinylboranes from addition of disiamylborane[15] or trimethylamine *t*-butylborane[16] to 1-alkynes exhibit strong infrared absorption near 1000 cm^{-1} attributed to *trans* olefinic protons.



11, $n = 3$
12, $n = 4$

The infrared spectrum of **11** shows comparable absorption at 995 cm^{-1}; however, its nmr spectrum is particularly definitive (Figure 2). The olefinic proton β to boron, split by the α-vinyl proton and the two allylic protons, appears as two triplets (J = 6.4 cps) at τ 3.32 and 3.62. The other olefinic proton α to boron and split by the β-vinyl proton occurs as a doublet (J = 17.4 cps) at τ 4.72, and shows fine structure suggesting allylic coupling (J = 1.5 cps). Integration gives the predicted 1:1 ratio and the coupling constants are of the proper order of magnitude for the *trans* product.[10,17] The heptenyl product (**12**) exhibits parallel infrared and nmr spectra. Since **11** is the expected product from *cis* addition during hydroboration, the nmr spectrum gives strong support to previous assignments of stereochemistry based on protonolysis. The possibility that any *cis* product formed during the hydroboration could have isomerized under the reaction conditions is unlikely at the moderate temperature (100°) used in the synthesis of **11**. A *cis–trans* equilibrium would have to be so in favor of the *trans* that any *cis* isomer was undetectable by nmr.

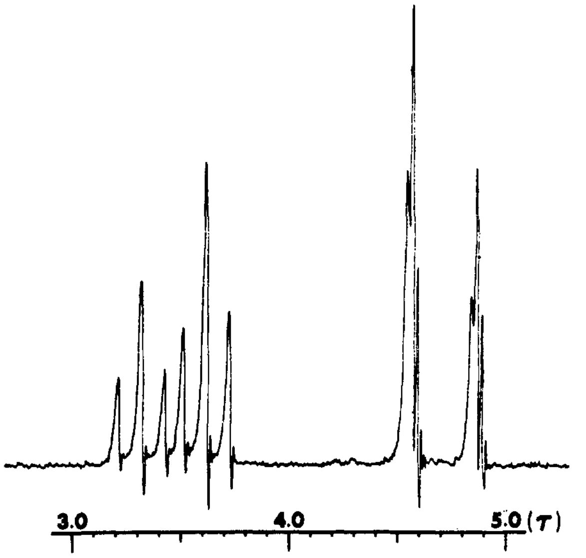


Figure 2. Vinyl proton nmr pattern of 2-(*trans*-1-hexenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (**11**).

An attempt was made to prepare some of the *cis* isomer by exposure of **12** to ultraviolet light. Irradiation of **12** for 3 days failed to yield any detectable change in its infrared spectrum. A similar unsuccessful attempt to isomerize a *trans*-substituted vinylboron derivative was attributed to a large energy difference between the *cis* and *trans* isomers.[18]

Metal Salt Reductions with 5. The black solid from reduction of nickel acetate in ethanol with sodium borohydride is an efficient catalyst for hydrogenation of alkynes to alkenes.[19] When dialkoxyborane **5** reacts with nickel acetate in N,N-dimethylacetamide, a black solid is produced which catalyzes the hydrogenation of phenylacetylene to styrene. Also, copper acetylacetonate in benzene, stannous chloride in ethanol, and aqueous solutions of silver nitrate and copper sulfate are reduced by **5**.

Amine Reactions. Rose and Shore[4] isolated the solid amine complexes of 1,3,2-dioxaborolane with ammonia and trimethylamine. McAchran[5] obtained the trimethylamine and trimethylphosphine adducts of 1,3,2-dioxaborinane at −65° and pointed out their instability above that temperature. In contrast, no solid complex was obtained from ammonia and **5** in ether at −78°; after warming to room temperature, bis(2-amino-4,4,6-trimethyl-1,3,2-dioxaborinane) (**13**) is obtained.

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(14) Reference 13, p 227.

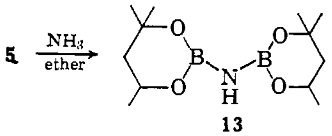
(15) Reference 13, p 233.

(16) M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2541 (1961).

(17) D. Seyferth and L. G. Vaugh, *J. Organometal. Chem.*, 1, 138 (1963).

(18) M. F. Lappert and B. Prokai, *ibid.*, **1**, 384 (1964).

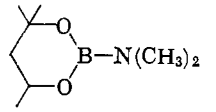
(19) C. A. Brown and H. C. Brown, *J. Am. Chem. Soc.*, **85**, 1003, 1005 (1963).



13

A white solid separated when **5** was added to liquid ammonia. At room temperature, this solid was slowly converted to **13**. It appears that the complex of **5** was produced in liquid ammonia, but it subsequently eliminated hydrogen to form 2-amino-4,4,6-trimethyl-1,3,2-dioxaborinane. The latter then reacted with itself to form **13** and ammonia, in agreement with previous attempts to isolate 2-amino-1,3,2-dioxaborinane.[20] In contrast to the intractable bis(2-amino-1,3,2-dioxaborinane),[20] **13** can be distilled and obtained in pure form, which is additional evidence for the stability of the 4,4,6-trimethyl-1,3,2-dioxaborinane system.

A solid complex was not observed from dimethylamine and **5** in ether at −78°. However, distillation provided the substitution product **14**. Reaction of **5** with trimethylamine under the same conditions resulted in isolation of unreacted **5**. Lack of reaction with trimethylamine (no replaceable hydrogens) may have been due to the size of the tertiary amine compared to ammonia. Since the axial methyl group in **5** interferes sterically with a tetrahedral configuration of the boron atom, ammonia and dimethylamine complexes are readily converted to the less hindered trigonal state by evolution of hydrogen. Similar considerations account for the unusual stability of **5** toward disproportionation.



14

Experimental Section[21]

Perkin-Elmer-Infracord and Varian A-60 instruments were used to determine infrared and nmr spectra (tetramethylsilane as reference), respectively. Boiling points are uncorrected. Sealed ampoule experiments were run with external nitrogen pressure of 400–500 psi. Ether was dried by distillation from lithium aluminum hydride. All operations were performed under dry nitrogen.

4,4,6-Trimethyl-1,3,2-dioxaborinane (5). (a) 2-Chloro-4,4,6-trimethyl-1,3,2-dioxaborinane (**4**) was prepared from 230 g (0.622 mole) of tris(2-methyl-2,4-pentanediol)biborate (**6**) and 50 ml (71.7 g, 0.613 mole) of boron trichloride.[6,22] This material was used without distillation and added in 3 hr to a mixture of 35.3 g (0.933 mole) of sodium borohydride in 250 ml of dry tetraglyme at 0–10°. The diborane which formed was passed into 200 ml of acetone. The reaction mixture was allowed to warm to room temperature overnight and distilled to yield 119 g (50%) of product, bp 30–70° (50 mm). Redistillation gave the analytical sample, bp 55–56° (61 mm); n^{24}D 1.4031; $\nu_{\max}^{\text{neat}}$ (cm^{-1}), BH 2550 (s); nmr spectrum (neat, τ), 5.50–6.10 (multiplet), 7.94–8.38 (multiplet), 8.72 (singlet), 8.77 (doublet, J = 6 cps), with an area ratio of 1:2:6:3, plus a broad quartet centered at 6.29 ± 0.05 ppm (J = 173 ± 3 cps).

Anal. Calcd for $C_6H_{13}BO_2$: C, 56.30; H, 10.23; B, 8.45; mol wt, 128. Found: C, 56.28; H, 10.43; B, 8.47; mol wt, 121.

(b) Freshly distilled **4** (104 g, 0.64 mole, bp 62–54° [0.9–0.4 mm]) was added to 24.3 g (0.64 mole) of sodium borohydride in 250 ml of tetraglyme as in a. Warming the resulting mixture to about 130° at 1 mm gave 39.1 g (48%) of **5** (infrared) in an attached trap at −80°.

(c) Diborane (0.64 mole), generated in b above, was passed into a solution of 73.0 g (0.200 mole) of tris(2-methyl-2,4-pentanediol)biborate in 200 ml of ether. Distillation gave 7.98 g (14%) of **5**, bp 50° (44 mm), identified by its infrared spectrum.

(d) To 22.2 g (0.060 mole) of tris(2-methyl-2,4-pentanediol)biborate in 50 ml of dry tetraglyme was added 6.84 g (0.018 mole) of sodium borohydride (foam, exotherm). Glacial acetic acid (11.9 g, 0.198 mole) was added dropwide over 45 min. Hydrogen evolved rapidly and foaming was a problem. Distillation gave 1.50 g (7%) of **5**, bp 50–52° (52 mm), followed by 16.2 g, bp 90–92° (30 mm), n^{25}D 1.4130.

(e) Freshly distilled **4** (6.85 g, 0.0422 mole, bp 58–54° [1.1–0.4 mm]) was added to a stirred slurry of 0.500 g (0.0132 mole) of lithium aluminum hydride in 35 ml of dry bis(2-ethoxyethyl) ether at 10–15°. The mixture was heated for 1 hr at 40° and then for 0.75 hr at 100°. Distillation gave 0.9 g (16.7%) of **5**, bp 40–60° (3–7 mm), identified by its infrared spectrum.

4,4,6-Trimethyl-1,3,2-dioxaborinane-2-*d* (7). To a stirred slurry of 1.01 g (0.0241 mole) of lithium aluminum deuteride in 50 ml of bis(2-ethoxyethyl) ether at 10° was added slowly 12.0 g (0.0739 mole) of **4**; the initial 2 ml of **4** gave some exotherm. The mixture was stirred overnight at room temperature and then heated 1 hr at 80°. About 4 ml of liquid was removed from the white slurry at 3-mm pressure during slow warming to 80°. Redistillation gave about 2 g (21%) of crude **7**, bp 51–54° (47.7 mm). Redistillation gave the spectral sample, bp 49.5–49.8° (45 mm), n^{25}D 1.4042. The infrared spectrum (neat) showed a strong B–D stretch at 1901 cm^{-1} and only a trace of B–H at 2550 cm^{-1}. The proton nmr spectrum (neat, τ) displays a singlet at 8.75 (6 H), a doublet (3 H) at 8.83 (J = 6 cps), a multiplet plus impurities (3.2 H) at 7.9–8.6, including two doublets (J_{AB} = 14.1 cps) at 8.01 and 8.26 (J_{AX} = 3.58 ± 0.08 cps), and a complex multiplet (1.3 H) centered at 5.80.

Stability Studies of 5. The infrared spectrum of a sample stored 1 month at room temperature in a stoppered flask was identical with that of a freshly distilled sample. Distillation at atmospheric pressure of a 3.34-g sample of **5** gave 2.33 g (70%) of pure product, bp 118–124°. An infrared spectrum of the residue indicated a mixture of **5**, **6**, and bis(2-methyl-2,4-pentanediol)boric anhydride. Infrared examination of the vapor showed very weak bands for diborane in the 1500–1600 cm^{-1} region only after 24 hr at room temperature. The intensity of these bands had not increased after 48 hr. Slow hydrolysis with hydrogen evolution was noted in samples of **5** stored over a period of months.

2-Octyl-4,4,6-trimethyl-1,3,2-dioxaborinane (8).[23] A mixture of 50 ml of dry ether, 4.43 g (0.0346 mole) of **5**, and 3.90 g (0.0346 mole) of 1-octene was sealed in a 150-ml ampoule and heated 3 days at 100°. Distillation gave 2.31 g (28%) of **8**, bp 91–98° (0.7–0.9 mm). An analytical sample was prepared by redistillation, bp 84–89° (0.7 mm), n^{25}D 1.4322. The infrared spectrum shows no absorption for C=C at 1600 cm^{-1} or for BH at 2500 cm^{-1}. The nmr spectrum (neat, τ) shows a tertiary H at 5.51–6.07 (multiplet), BCH_2 at 9.10–9.55 (multiplet), and a complex pattern at 8.03–9.10, all in an area ratio of 1:2:26. An unresolved $(CH_3)_2$ singlet appears at 8.73 and the CH_3 doublet is centered at 8.78 (J = 6 cps).

Anal. Calcd for $C_{14}H_{29}BO_2$ (240.2): C, 70.00; H, 12.17; B, 4.51. Found: C, 69.88; H, 12.08; B, 4.40.

2-[1-(4-Thiapentyl)]-4,4,6-trimethyl-1,3,2-dioxaborinane (10). A solution of 4.06 g (0.0317 mole) of **5**, 2.70 g (0.0317 mole) of allyl methyl sulfide (freshly distilled), and 10 ml of dry ether was sealed in an ampoule and heated 4 days at 110°. Distillation yielded 1.06 g (15%) of **10**, bp 88–89° (1.1 mm). Redistillation gave 0.77 g, bp 94–97° (1.3 mm), n^{22}D 1.4600. The proton nmr spectrum (neat, τ) shows tertiary H at 5.70–6.13 (multiplet), SCH_2 at 7.45–7.76 (multiplet), SCH_3 at 8.03 (singlet), CH_2 (borinane and 2-propyl) at 8.08–8.58 (multiplet), $(CH_3)_2$ at 8.77 (singlet), CH_3 at 8.83 (doublet, J = 6 cps), and BCH_2 at 9.13–9.50 (multiplet), in an area ratio of 1:2:3:4:7.7:1.5:1.5, respectively.

Anal. Calcd for $C_{10}H_{21}BO_2S$: C, 55.53; H, 9.79; S, 14.83. Found: C, 55.43; H, 9.84; S, 14.73.

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[20] A. Finch, P. J. Gardner, J. C. Lockhart, and E. J. Pearn, *J. Chem. Soc.*, 1428 (1962).

[21] The microanalytical work was performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Schwarzkopf Laboratories, Woodside, N. Y. Some boron analyses were carried out by aqueous mannitol titrations.

[22] The proton nmr spectrum of a freshly distilled sample of 4, bp 62° (4 mm), shows (neat, τ) a singlet (9 H) at 8.68; a doublet (3 H) at 8.73 (J = 6.3 cps); a complex multiplet (2.6 H) at 7.85–8.55, including two doublets (J_{AB} = 14.5 cps) at 7.92 and 8.17 (J_{AX} = 3.6 cps); and a complex multiplet (1 H) centered at 5.62.

[23] This compound is disclosed by F. J. Dykstra, U. S. Patent 3,148,961 (Sept 15, 1964); no physical properties are given.

2-Cyclohexyl-4,4,6-trimethyl-1,3,2-dioxaborinane. A sealed ampoule containing 5.97 g (0.0465 mole) of **5**, 3.82 g (0.0465 mole) of cyclohexene (redistilled), and 50 ml of dry ether was heated 2 days at 110° and then 1 day at 210°. Distillation gave 5.55 g (57%) of product, bp 65–79° (0.8–1.0 mm). This was redistilled to give the analytical sample, bp 62–63° (0.6–0.8 mm), $n^{25}D$ 1.4482. The nmr spectrum (neat, τ) shows tertiary H (borinane ring) at 5.58–6.25 (multiplet). The remaining protons appear as a complex pattern at 8.00–9.50, with an area ratio of 27 relative to that of the tertiary protons. The incompletely resolved $(CH_3)_2$ singlet appears at 8.72, and the CH_3 doublet is centered at 8.77 (J = 6 cps).

Anal. Calcd for $C_{12}H_{23}BO_2$ (210.1): C, 68.57; H, 11.03; B, 5.15. Found: C, 68.81; H, 11.23; B, 5.31.

2-(*trans*-1-Hexenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (11). A solution of 6.05 g (0.0473 mole) of **5** (bp 50° (44 mm]) and 5.00 g (0.0610 mole) of 1-hexyne (bp 71°) in 50 ml of dry ether was heated (sealed tube) at 98–100° for 15 hr. Removal of the ether left 7.52 g of crude product, whose infrared spectrum and glpc pattern showed unreacted **5** and the desired **11** (C=C at 1640 cm^{-1} and 995 cm^{-1}). Two impurities with lower retention times than **11** amounted to about 4 and 0.7% of the area of the peak due to **11**. Distillation gave 0.70 g, bp 69–74° (0.17 mm), $n^{25}D$ 1.4432; 1.78 g, bp 74–87° (0.17–0.21 mm), $n^{25}D$ 1.4440; and 0.85 g, bp 87–90° (0.21–0.20 mm), $n^{25}D$ 1.4420 (total yield 33.5%). Redistillation of the center fraction gave the analytical sample, bp 68° (0.08 mm), $n^{25}D$ 1.4440.

Anal. Calcd for $C_{12}H_{23}BO_2$ (210.1): C, 68.58; H, 11.03; B, 5.14. Found: C, 68.38; H, 11.07; B, 5.18.

Glpc analysis of this product gave a pattern identical with that of the crude material. The nmr spectrum (neat, τ) displays two triplets (1 H) at 3.32 and 3.62 (J = 6.4 cps) and a doublet (1 H) at 4.72 (J = 17.4 cps) (see Figure 2); the latter have triplet fine structure (J = 1.5 cps). A complex multiplet is centered at 5.82 (1 H) and a broad multiplet (4 H) extends from 7.65 to 8.47. The dioxaborinane methyls appear at 8.77 (6 H) and 8.81 (doublet, J = 5.8 cps, 3 H), over a broad group (4 H) at 8.47–8.86. An unsymmetrical doublet is found at 9.00 and 9.12 (3 H). Integration gives area ratios of 1.06:0.97:1:4.1:13.6:2.6, respectively.

2-(*trans*-1-Heptenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (12) was prepared similarly from 2.70 g (0.021 mole) of **5**, 2.04 g (0.021 mole) of 1-heptyne (redistilled, bp 96–99°), and 35 ml of ether. Heating for 2 days at 110° and then 1 day at 210° gave 3.62 g (69%) of **12**, bp 79–87° (0.6–0.7 mm). Redistillation yielded an analytical sample, bp 73–76° (0.15 mm); $n^{25}D$ 1.4460; $\nu_{\max}^{\text{neat}}$ (cm^{-1}), BC=CR (*trans*) 1625 (s), 998 (s). The nmr spectrum (neat) showed vinyl H at 3.53 (two triplets, J = 5.8 cps) and at 4.77 (doublet, J = 17.4 cps), tertiary H at 5.46–6.17 (multiplet), and the remaining protons at 7.66–9.44 (multiplet) in an area ratio of 1:1:1:22, respectively. The $(CH_3)_2$ singlet at 8.76 and the CH_3 doublet centered at 8.81 (J = 6 cps) are incompletely resolved. One node of the latter is resolved and integrates for 1.5 hydrogens.

Anal. Calcd for $C_{13}H_{25}BO_2$: C, 69.65; H, 11.25; B, 4.83. Found: C, 69.34; H, 11.19; B, 5.01.

Attempted Isomerization of 12. About 0.5 g of **12** was sealed under nitrogen in an 8 mm o.d. quartz tube and irradiated with a 140-w Hanovia lamp. Infrared spectra after 16 and 72 hr showed no change. The product (orange) was transferred to a quartz flask with 50 ml of dry hexane and irradiated (nitrogen) from the bottom for 3 days; an infrared spectrum of the residual brown oil showed it to be unchanged **12**.

Hydrogenation of Phenylacetylene over a Nickel Catalyst from 5 and Nickel Acetate. To a saturated solution of nickel acetate tetrahydrate in 50 ml of N,N-dimethylacetamide was added 500 mg (3.90 mmoles) of **5**. Most of the N,N-dimethylacetamide was removed with a pipet, and the black solid washed by decantation with cyclohexane (two 50-ml portions). Phenylacetylene (2 g, 0.0196 mmole) was added followed by 50 ml of cyclohexane. Hydrogenation for 3.5 hr at 50 psi (hydrogen absorption had ceased) was followed by filtration and distillation to yield 1.28 g (64%) of styrene, bp 62–71° (50 mm), contaminated with a small amount of N,N-dimethylacetamide (infrared).

Bis(2-amino-4,4,6-trimethyl-1,3,2-dioxaborinane) (13). (a) An excess of ammonia was condensed from sodium at −78° into a solution of 3.97 g (0.030 mole) of freshly distilled **5** in 50 ml of dry ether. The solution was held at −78° for 2 hr and allowed to warm to room temperature overnight. Distillation gave a small amount of white sublimate followed by 1.30 g (46%) of product, bp 102–104° (0.5 mm). Redistillation yielded the analytical sample, bp 90° (0.1 mm); $n^{22}D$ 1.4393; $\nu_{\max}^{\text{neat}}$ (cm^{-1}) 3440, NH (m).

Anal. Calcd for $C_{12}H_{25}B_2NO_4$: C, 53.17; H, 9.37; B, 8.03. Found: C, 53.47; H, 9.47; B, 8.21.

(b) To 15 ml of dry ammonia at −78° was added 4.05 g (0.0316 mole) of freshly distilled **5** over a 10-min period. A white solid formed immediately with no detectable gas evolution. The mixture was kept at −78° for 0.5 hr and then overnight at room temperature. Attempted sublimation failed, and an infrared spectrum of the cloudy residual liquid was identical with that of **13** from procedure a above.

2-Dimethylamino-4,4,6-trimethyl-1,3,2-dioxaborinane (14). To a solution of 4.32 g (0.0336 mole) of **5** (freshly distilled) in 50 ml of dry ether at −78° was condensed an excess of dimethylamine (dried over sodium). The colorless solution was allowed to warm to room temperature overnight. Distillation yielded 3.60 g (62%) of **14**, bp 69–88° (53–50 mm). Redistillation gave the analytical sample, bp 88–89° (50 mm); $n^{25}D$ 1.4262 (no absorption at 2500 cm^{-1} for BH in the infrared spectrum). The nmr spectrum, 30% CCl_4-(τ), shows tertiary H at 5.63–6.22 (multiplet), $N(CH_3)_2$ at 7.52 (singlet), CH_2 at 8.20–8.58 (multiplet), $(CH_3)_2$ at 8.80 (singlet), and CH_3 at 8.85 (doublet, J = 5.8 cps) in an area ratio of 1:6:2:9, respectively.

Anal. Calcd for $C_8H_{18}BNO_2$ (171.0): C, 56.17; H, 10.61; B, 6.32. Found: C, 56.32; H, 10.42; B, 6.46.

An attempted reaction of trimethylamine with **5** in ether produces no solid at −78°; distillation gives recovered **5**, plus some residual bis(2-methyl-2,4-pentanediol)boric anhydride (by infrared spectra).

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