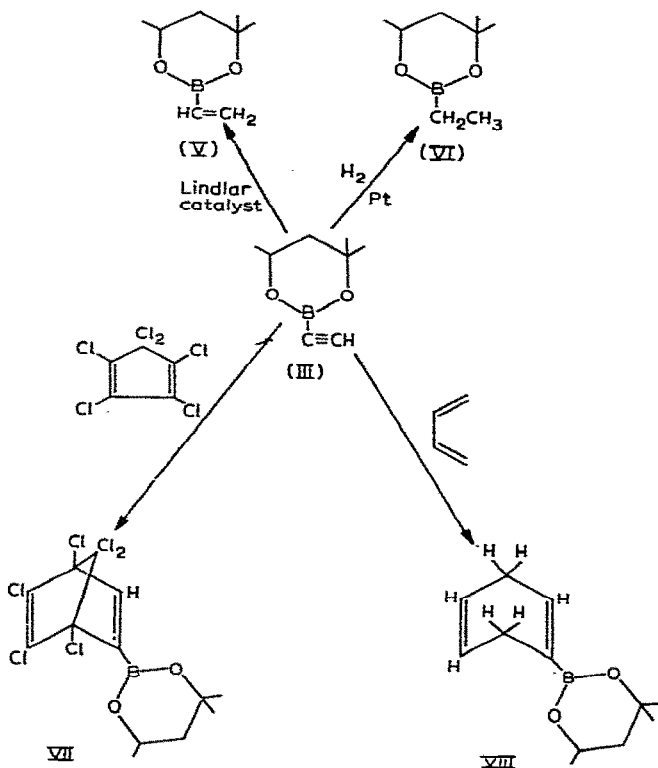


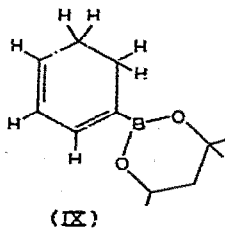


Selective reduction of substituted B-ethynyl compounds to the B-vinyl analogs has been reported<sup>6</sup>. Similar reduction of (III) (Lindlar catalyst) affords an alternative route to (V). Hydrogenation over Adams' catalyst converts (III) to the 2-ethyl derivative (VI). Both (V) and (VI) were identified by infrared spectra<sup>1,7</sup>.

The Diels-Alder adduct of (III) with hexachlorocyclopentadiene (VII) is a high-boiling oil. In addition to the readily identifiable dioxaborinane hydrogens, the proton NMR spectrum of (VII) shows a vinyl proton at  $\tau$  2.80 ppm. The infrared spectrum reveals a doublet for C=C at 1610(m) and 1575(m)  $\text{cm}^{-1}$ . In contrast, the Diels-Alder adduct with butadiene (VIII), shows only a singlet at 1625  $\text{cm}^{-1}$ . Since a doublet is found in the C=C region for the Diels-Alder adduct of cyclopentadiene and dibutyl acetyleneboronate<sup>5</sup>, a question arose as to the possibility of isomerization



of (VIII) to the conjugated isomer (IX). However, ultraviolet evidence supports the



unconjugated structure (VIII) with  $\lambda_{\max}$  at 193.0  $m\mu$  ( $\epsilon = 8680$ ) and 221.5  $m\mu$  ( $\epsilon = 2500$ ). The  $\lambda_{\max}$  for 1,4-cyclohexadiene<sup>8</sup> is reported as 220  $m\mu$  (with no extinction coefficient given) and that for 1,3-cyclohexadiene<sup>9</sup> as 256  $m\mu$  ( $\epsilon = 8000$ ). Conclusive evidence favoring (VIII) is obtained from the NMR spectrum. The vinyl hydrogen on the carbon atom adjacent to boron occurs as a singlet at  $\tau$  3.58 ppm with small splittings, the two isolated vinyl protons as a singlet at  $\tau$  4.38 ppm (also with slight splitting), and the allylic protons as a singlet at  $\tau$  7.37 ppm. One would expect the three vinyl hydrogens in (IX) to be almost equivalent and the methylene protons to give a complex multiplet rather than the singlet observed. The NMR spectrum of 4-vinylcyclohexene (X) illustrates the multiplet expected from adjacent nonequivalent methylene groups<sup>10</sup>. Also, the ring vinyl protons in (X) occur as a singlet at  $\tau$  4.32 ppm in comparison with  $\tau$  4.38 ppm in (VIII).

#### EXPERIMENTAL

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Perkin Elmer Infracord, Beckman DK-2A, and Varian A60 instruments were used to determine infrared, ultraviolet, and NMR spectra (tetramethylsilane as reference), respectively. All reactions were carried out in a nitrogen atmosphere.

#### 2-Ethynyl-4,4,6-trimethyl-1,3,2-dioxaborinane (III)

A. From 2-chloro-4,4,6-trimethyl-1,3,2-dioxaborinane (Ia)<sup>11</sup>. Simultaneously to 630 ml of dry ether at  $-70$  to  $-75^\circ$  was added 68.0 g (0.415 mole) of (Ia) and 0.415 mole of ethynylmagnesium bromide<sup>12</sup>. The addition required 45 min. Stirring was continued 6 h at  $-70^\circ$  and the mixture left overnight to warm to room temperature. The solvent was evaporated (60 mm) and the residue pyrolyzed to yield 38.0 g of brown liquid, b.p.  $40-80^\circ$  (9–15 mm). This was distilled to yield 18.5 g (29%) of product, b.p.  $77-84^\circ$  (9.5 mm). Two successive distillations, b.p.  $55-56^\circ$  (1.3 mm),  $n_D^{21}$  1.4481, failed to yield pure material, though strong absorption for  $C\equiv CH$  was noted in the infrared spectrum. (Found: C, 61.74; H, 8.83; B, 7.51.  $C_8H_{13}BO_2$  calcd.: C, 63.20; H, 8.62; B, 7.12%.)

B. From 2-n-butoxy-4,4,6-trimethyl-1,3,2-dioxaborinane. The above procedure was repeated on a 0.5 mole scale using 100 g (0.50 mole) of (Ib)<sup>1</sup> in place of (Ia). Pyrolysis yielded 32.6 g, b.p.  $48-69^\circ$  (1.0–1.25 mm),  $n_D^{25}$  1.4311. Redistillation through an 18-inch column packed with nichrome helices gave 8.95 g (12%) of (III), b.p.  $52^\circ$  (1.85–2.10 mm),  $n_D^{25}$  1.4397;  $\nu_{\max}$  (neat,  $cm^{-1}$ ):  $C\equiv CH$ , 3285(m);  $C\equiv C$ , 2092(s); NMR spectrum, neat ( $\tau$ ): tertiary H, 5.49–6.08 (multiplet);  $C\equiv CH$ , 7.68 (singlet);  $CH_2$ , 7.90–8.47 (multiplet);  $(CH_3)_2$ , 8.74 (singlet);  $CH_3$ , 8.80 (doublet) ( $J = 6$  c.p.s.), in a ratio of 1:1:2:7.3:1.5. The  $^{11}B$  NMR spectrum was run at 19.3 mc (neat). The ultraviolet spectrum of (III) in cyclohexane shows  $\lambda_{\max}$  202.5  $m\mu$  ( $\epsilon = 1590$ ). (Found: C, 63.48, 63.40; H, 8.77, 8.80; B, 6.89, 7.05.  $C_8H_{13}BO_2$  calcd.: C, 63.20; H, 8.62; B, 7.12%.)

The final fraction gave 12.1 g (12%) of starting (Ib), b.p.  $73-75^\circ$  (2.25–1.70 mm),  $n_D^{25}$  1.4228.

#### Dimethyl acetyleneboronate (IV)

A sample of (IV) which had been stored for several years at  $5^\circ$  was distilled,

b.p. 60–61° (264 mm),  $n_D^{25}$  1.3914. The infrared spectrum was identical to that of a freshly prepared sample with  $C\equiv C$  stretch at 2087  $cm^{-1}$  and  $\equiv C-H$  stretch at 3297  $cm^{-1}$ . The  $^{11}B$  NMR spectrum (neat) was run at 19.3 mc. The ultraviolet spectrum of (IV) exhibits a  $\lambda_{max}$  at 202.0  $m\mu$  ( $\epsilon=934$ ) in cyclohexane solution.

#### Hydrolysis of (III) and (IV)

Cyclohexane solutions of (III) ( $1.00 \times 10^{-3}M$ ) and (IV) ( $1.65 \times 10^{-3}M$ ) were shaken vigorously with a small drop of water and the optical density at 202.0  $m\mu$  followed as a function of time. The results are given in Table 1\*. As the hydrolysis proceeds, a peak at 195.1  $m\mu$  appears which increases in intensity initially and then disappears.

TABLE 1

HYDROLYSIS OF (III)			HYDROLYSIS OF (IV)		
Time (min)	O.D. at 202.0 $m\mu$	$M \times 10^3$	Time (min)	O.D. at 202.0 $m\mu$	$M \times 10^3$
0	1.59	1.00	0	1.54	1.65
5	1.56	0.98	2	1.53	1.64
22	1.43	0.90	8	1.36	1.44
37	1.14	0.72	13	1.09	1.17
55	0.789	0.50	19	0.747	0.80
70	0.560	0.35	25	0.470	0.50
			31	0.211	0.23

#### 2-Vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane (V)

A mixture of 1.52 g (0.010 mole) of (III), 15 ml of cyclohexane, and 100 mg of 5% palladium on calcium carbonate poisoned catalyst (Engelhard Industries, Newark, New Jersey) was hydrogenated at 20 p.s.i. until the theoretical amount of hydrogen had been absorbed (3 h). The catalyst was removed by filtration and the solvent evaporated (aspirator) to yield 1.45 g (97%) of (V) as a pale yellow liquid. The infrared spectrum is identical to that of an authentic sample prepared from (Ib) and vinylmagnesium chloride<sup>1</sup>.

#### 2-Ethyl-4,4,6-trimethyl-1,3,2-dioxaborinane (VI)

A solution of 1.52 g (0.010 mole) of (III) in 25 ml of dry ethylene glycol dimethyl ether with 100 mg of Adams' catalyst was hydrogenated at 50 p.s.i. (25°). The theoretical volume was absorbed in 2 min; removal of catalyst and evaporation of the solvent left 1.55 g of (VI) (infrared)<sup>1</sup>.

\* As pointed out by a referee, plots of these data show an apparent zero order dependence on the ester concentration following an induction period. We feel that this probably is fortuitous. The kinetic situation is complex, with consecutive and/or competitive hydrolysis and cleavage, and the hydrolysis step may be reversible. Several other runs with varying initial concentrations of (III) and (IV) consistently showed that the 202  $m\mu$  peak for (III) decreases more slowly than that of (IV). In the closed cells used for these measurements, no decrease in optical density of (IV) was observed in 1.3 h in the absence of added water. This established that oxidation is not involved.

*2-(4,4,6-Trimethyl-1,3,2-dioxaborinan-2-yl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (VII)*

A neat solution of 3.04 g (0.020 mole) of (III) and 4.26 g (0.020 mole) of hexachlorocyclopentadiene was heated 15 h at 130–137° and the dark, viscous oil distilled. Starting (III) was recovered in 11% yield (0.34 g), b.p. 38–60° (0.20 mm), followed by an intermediate fraction, 0.40 g, b.p. 60–147° (0.2 mm). The product was then collected, 4.93 g (68%), b.p. 147–157° (0.20–0.39 mm) as a very viscous yellow oil. A sample was redistilled for analysis, b.p. 149–151° (0.25 mm),  $n_D^{25}$  1.5097;  $\nu_{\max}$  (neat,  $\text{cm}^{-1}$ ): C=C 1610(m), 1575(m); NMR spectrum,  $\text{CCl}_4$  ( $\tau$ ): BC=CH, 2.80 (singlet); tertiary H, 5.34–5.83 (multiplet);  $\text{CH}_2$ , 8.02–8.17 (multiplet);  $(\text{CH}_3)_2$ , 8.51 (singlet);  $\text{CH}_3$ , 8.55 (doublet) ( $J = 5.8$  cps), in an area ratio of 1 : 1 : 2 : 9 (methyls not completely resolved). (Found: C, 37.03; H, 3.06; B, 2.79; Cl, 49.80.  $\text{C}_{13}\text{H}_{13}\text{BCl}_6\text{O}_2$  calcd.: C, 36.76; H, 3.08; B, 2.55; Cl, 50.08%.)

*1-(4,4,6-Trimethyl-1,3,2-dioxaborinan-2-yl)-1,4-cyclohexadiene (VIII)*

A solution of 2.00 g (0.0130 mole) of (III) and 0.71 g (0.013 mole) of butadiene was heated in a sealed tube at 134–138° for 15 h. The orange liquid obtained was distilled to yield 1.17 g (59%) of starting (III), b.p. 61–75° (1.25 mm), and 0.96 g (36%) of the diene adduct, b.p. 100–106° (1.25 mm),  $n_D^{24}$  1.4737. Redistillation gave 0.62 g, b.p. 85–87° (0.45 mm),  $n_D^{25}$  1.4767,  $\nu_{\max}$  (neat,  $\text{cm}^{-1}$ ): C=C 1625(s);  $\lambda_{\max}$  (in  $\text{C}_6\text{H}_{12}$ ) ( $m\mu$ ): 193.0 ( $\epsilon = 8680$ ), 221.5 (2500); NMR spectrum, neat ( $\tau$ ): *cis*-BC=CH, 3.58 [primarily singlet with slight splitting ( $J = 1.0$  cps)]; *cis*-HC=CH,  $\tau$ -value [singlet with additional splitting ( $J \sim 1.5$  cps)]; tertiary H, 5.59–6.68 (multiplet); C=CCH<sub>2</sub>, 7.37 (singlet, with only very slight evidence of splitting); borinane CH<sub>2</sub>, 8.04–8.52 (multiplet);  $(\text{CH}_3)_2$ , 8.77 (singlet);  $\text{CH}_3$ , 1.18 (doublet) ( $J = 6$  cps) with an area ratio of 1 : 2 : 1 : 4 : 2 : 9. (Found: C, 70.06; H, 9.42; B, 5.46.  $\text{C}_{12}\text{H}_{19}\text{BO}_2$  calcd.: C, 69.92; H, 9.29; B, 5.25%.)

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## SUMMARY

2-Ethynyl-4,4,6-trimethyl-1,3,2-dioxaborinane (III) was prepared and characterized by infrared, proton NMR, and <sup>11</sup>B NMR spectroscopy. Qualitative hydrolysis studies indicate that (III) is less reactive than dimethyl acetyleneboronate. Catalytic hydrogenation of (III) to form the corresponding ethyl and vinyl analogs, and Diels–Alder adducts of (III) with hexachlorocyclopentadiene and butadiene are reported.

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