2-Vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane. II. Derivatives[1]

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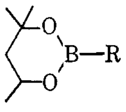
The title compound (1) has been converted to 2-(1′,2′-dibromoethyl)-, 2-(3′-thianonyl)-, and 2-(2′,2′-dichlorocyclopropyl)-4,4,6-trimethyl-1,3,2-dioxaborinane by treatment with bromine, 1-hexanethiol, and dichlorocarbene, respectively. The dibromide readily eliminates vinyl bromide and hydrogen bromide on hydrolysis. Spectral evidence indicates that the dichlorocarbene adduct reacts with base to give 1-chloroallene. Diels-Alder adducts of 1 with hexachlorocyclopentadiene and with cyclopentadiene are described. The latter is shown by hydrogenation, oxidation, and nmr spectroscopy to be a 57:43 mixture of the *exo* and *endo* isomers. Ethyl diazoacetate and 1 provides a boron-substituted pyrazoline.

The synthesis of 2-vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane (1) and its unusual stability toward polymerization have been described.[1a] It was of interest to prepare derivatives of 1 to ascertain whether they also possess unusual stability. Of further interest was the hitherto unexplored addition of dichlorocarbene to a vinyl group bonded to boron.

Derivatives 2-7 were synthesized from 1 by straightforward methods.

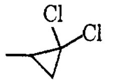


1, R = $CH{=}CH_2$

2, R = $CHBrCH_2Br$

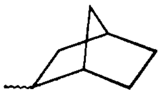
3, R = $(CH_2)_2S(CH_2)_5CH_3$

4, R =

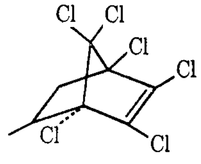


5, R =

6, R =



7, R =

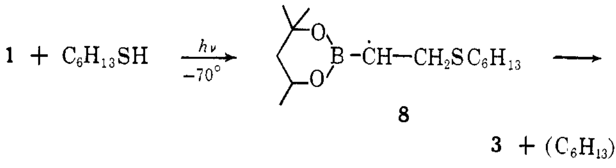


Bromination.—Addition of bromine to 1 proceeds readily to give 2 in 91% yield. The conditions are those used to brominate dibutyl ethyleneboronate.[2] The dibromide 2 exhibits a proton nmr spectrum consistent with the assigned structure. Hydrolysis quantitatively produces one equivalent of hydrogen bromide and one equivalent of boric acid. In practice, the

$$2 + 3H_2O \longrightarrow HBr + B(OH)_3 + CH_2{=}CHBr + (CH_3)_2C(OH)CH_2CH(OH)CH_3$$

hydrogen bromide can be titrated with sodium hydroxide to the methyl red end point, mannitol added, and the boron determined by continuing the titration to the phenolphthalein end point. Treatment of 2 with excess aqueous sodium hydroxide and trapping the volatiles gave vinyl bromide in 93.5% yield. Vinyl bromide is obtained when di-*n*-butyl 1,2-dibromoethaneboronate is treated with sodium butoxide or dilute sulfuric acid.[3] Similarly, ethylene is produced from the hydrolysis of (2-chloroethyl)dichloroborane, tris(2-chloroethyl)borane,[4] or dibutyl 2-bromoethaneboronate.[5] The mechanism of these deboronohalogenations is known to involved a stereospecific *trans* elimination.[6] Steric hindrance apparently does not prevent this type of reaction with 2 or with bis(diisobutylcarbinyl) 2-bromoethaneboronate, indicating that a tetracoordinate boron intermediate is not involved.[5]

1-Hexanethiol Addition.—Di-*n*-butyl ethyleneboronate rapidly adds 1-hexanethiol in the presence of ultraviolet light.[7] The same reaction with 1 proceeds more slowly and gives a considerably lower yield of the adduct (3) (51.5 *vs.* 93%[7]). Gas is evolved during this reaction and some di-*n*-hexyl sulfide is formed. The proton nmr spectrum of the product is consistent with structure 3. The lower reactivity of 1 in this free-radical addition may indicate a reduced stability of the intermediate α radical 8 compared with that derived from di-*n*-butyl ethyleneboronate, $[(BuO)_2\dot{B}CHCH_2SC_6H_{13}]$. Reduced volume for electron delocalization in 8 due to the axial methyl group might account for this reduced reactivity.



Dichlorocarbene Additions.—A low yield of 4 (4%) results when sodium trichloroacetate[8] is decomposed in the presence of an equimolar amount of 1. A much better yield (61%) is realized when an excess of 1 is employed with phenyltrichloromethylmercury[9] as the source of dichlorocarbene.

The product exhibits a strong infrared band at 766 cm^{-1} diagnostic of the CCl_2 group.[10] The proton nmr spectrum of 4 shows the typical pattern for the tri-

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[1] (a) Part I: W. G. Woods, I. S. Bengelsdorf, and D. L. Hunter, *J. Org. Chem.*, **31**, 2766 (1966). (b) Presented in part at the Pacific Southwest Regional Meeting of the American Chemical Society, Claremont, Calif., Dec 1962.

[2] D. S. Matteson and K. Peacock, *J. Am. Chem. Soc.*, **82**, 5759 (1960).

[3] B. M. Mikhailov and P. M. Aronovich, *Izv. Akad. Nauk. SSSR Otd. Khim. Nauk*, No 5, 927 (1961).

[4] M. F. Hawthorne and J. A. DuPont, *J. Am. Chem. Soc.*, **80**, 5830 (1958).

[5] D. S. Matteson and J. D. Leidtke, *J. Org. Chem.*, **28**, 1924 (1963).

[6] D. S. Matteson and J. D. Liedtke, *J. Am. Chem. Soc.*, **87**, 1526 (1965).

[7] (a) D. S. Matteson, *ibid.*, **81**, 5004 (1959); (b) *ibid.*, **82**, 4228 (1960).

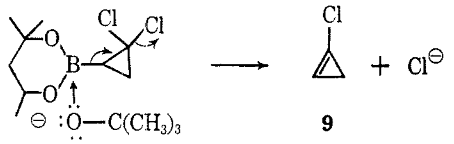
[8] W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959).

[9] D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

[10] S. W. Tobey and R. West, *Tetrahedron Letters*, **No. 18**, 1179 (1963).

methyldioxaborinane ring, plus an obscured multiplet in the region τ 8.27–9.22 (three protons). The proton on the carbon α to boron appears as a quartet (τ ~9.0, J = 9–12 cps), as expected for an electropositive substituent on a dichlorocyclopropane ring.[11] The two β protons (τ 8.3–8.8) are in the same region as the corresponding protons in 1,1-dichloro-2-trimethylsilylcyclopropane.[11]

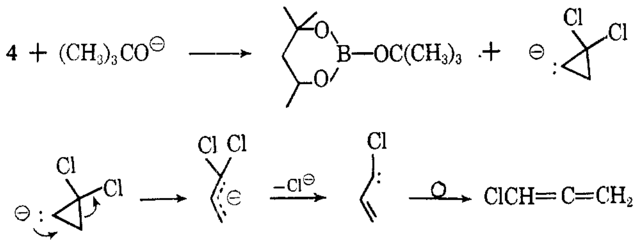
Because of the known facility by which β-haloalkylboron derivatives undergo elimination, it was of interest to treat **4** with a nucleophilic reagent. 1-Chlorocyclopropene (**9**) would be the product expected from simple β elimination in this case.



9

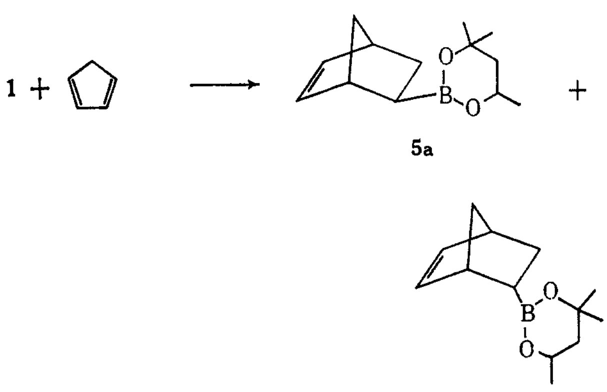
A mixture of potassium *t*-butoxide (free of *t*-butyl alcohol) in toluene was treated with an equimolar amount of **4**. Rapid distillation gave a distillate shown by infrared spectra, proton nmr spectra, and gas chromatography to contain toluene, *t*-butyl alcohol, and 1-chloroallene. The 1-chloroallene (low yield) was identified unequivocally by comparison of its proton nmr spectrum[12] and gas chromatographic retention times (four different columns) with those of an authentic sample dissolved in a toluene–*t*-butyl alcohol mixture.

The 1-chloroallene could arise by isomerization of **9**, since the opening of a substituted cyclopropene ring to give an allene is known.[13] It is not necessary to postulate **9** as the primary product, however, since a path to 1-chloroallene *via* a cyclopropyl anion is feasible.



Further work is necessary in order to elucidate this mechanism.

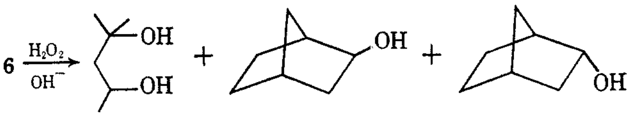
The Diels–Alder reaction of **1** with cyclopentadiene gives a mixture of the *exo* (**5a**) and *endo* (**5b**) isomers. The vinyl region in the proton nmr spectrum of **5** shows a triplet superimposed on a double quartet. This same pattern appears in the nmr spectrum of mixtures of *exo*- and *endo*-2-trimethylsilylbicyclo[2.2.1]hept-5-ene;[14] the triplet is assigned to the *endo* and the double quartet to the *exo* isomer. In the present case, integration shows that 57% of **5a** (*exo*) is present. The upfield region reveals two sets of patterns for the methyl groups on the dioxaborinane ring. Assigning the more shielded pattern to the *endo* isomer[14] suggests that 43% of **5b** is present.



5a

5b

Conformation of this isomer distribution provided by hydrogenation of **5** to give **6** followed by oxidation to give a mixture of 2-methyl-2,4-pentanediol, *exo*-norborneol, and *endo*-norborneol. Comparison of the infrared spectrum of this mixture with that of a synthetic mixture indicates an *exo* to *endo* ratio of 52 ± 5 to 48 ± 5.



It is of interest that the **5a**:**5b** ratio is similar to the *exo*:*endo* ratio expected at 150° for the dibutyl ethyleneboronate–cyclopentadiene adduct.[15] Since di-*t*-butyl ethyleneboronate has been found to give less *endo* isomer,[15] the steric requirement of the 4,4,6-trimethyl-1,3-dioxypropylene group of **1** appears to be about equivalent to that of two di-*n*-butoxy groups in Diels–Alder additions.

Hexachlorocyclopentadiene forms adduct **7** with **1** in a yield of 87%. The proton nmr spectrum shows the easily recognized pattern for the trimethyldioxaborinane ring, plus a singlet at τ 9.01. This absorption is assigned to the proton on the carbon α to boron by analogy with the cyclopropane system above and from the known upfield shifts of the *exo* C-2 proton with decreasing substituent electronegativity in related derivatives.[16] The two protons at C-3 appear at τ 7.73–7.79. Extrapolation of Williamson's data to the electronegativity of boron suggests that these protons shoud lie in the τ 7.2–7.4 region.[16]

Reactions with Diazo Compounds.—When an ethereal solution of diazomethane was treated with an equimolar amount of **1**, polymethylene was formed. This behavior is commonly observed with boron compounds and is associated with the Lewis acidity of the boron atom.[17]

The reaction of **1** and ethyl diazoacetate goes very slowly in ether solution at room temperature; heating at 50–90° (neat) for 7.5 hr results in the disappearance of infrared absorptions due to the starting materials. These observations indicate that **1** reacts much more slowly with ethyl diazoacetate than does dibutyl ethyleneboronate.[18] It is tempting to attribute this

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[11] K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *J. Am. Chem. Soc.*, **86**, 762 (1964).

[12] E. B. Whipple, J. H. Goldstein, and L. Mandell, *J. Chem. Phys.*, **30**, 1109 (1959).

[13] V. K. Jones and A. J. Deutschman, Jr., *J. Org. Chem.*, **30**, 3978 (1965).

[14] H. G. Kuivila and C. R. Warner, *ibid.*, **29**, 2845 (1964).

[15] D. S. Matteson and J. O. Waldbillig, *ibid.*, **28**, 366 (1963).

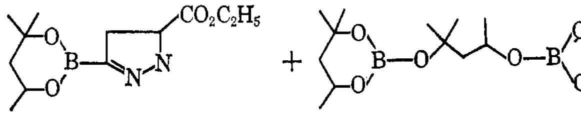
[16] K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963).

[17] C. E. H. Bawn and A. Ledwith, in "Progress in Boron Chemistry," Vol. I, H. Steinberg and A. L. McCloskey, Eds., The Macmillan Co., New York, N. Y., 1964, p 345.

[18] D. S. Matteson, *J. Org. Chem.*, **27**, 4293 (1962).

reduced reactivity to steric interference of the axial methyl group of **1**. However, Matteson observed only a modest decrease in rate with di-*t*-butyl ethyleneboronate compared with the di-*n*-butyl ester. The proposed transition state[18] has negative charge delocalized onto the boron atom and steric interference with delocalization by the axial methyl group of **1** is a possibility. The product from the reaction of **1** and ethyl diazoacetate was isolated as a distillable liquid, whose infrared spectrum and elemental analysis suggested a mixture of predominantly pyrazoline **10** with a lesser amount of tris(2-methyl-2,4-pentanediol) biborate (**11**). Survival of a significant proportion of **10** above about 175° shows a striking stability toward disproportionation compared with that of the analogous dibutoxyboryl derivative. This resistance to disproportionation is marked in 2-substituted 4,4,6-trimethyl-1,3,2-dioxaborinane derivatives and appears to be steric in origin.

$\mathbf{1} + N_2CHCO_2C_2H_5 \rightarrow$



10 **11**

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were taken as neat liquids or as Nujol mulls.

2-(1′,2′-Dibromoethyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (2).—Bromine (20.3 g, 0.127 mole) in 50 ml of methylene chloride was added in 45 min to 18.65 g (0.121 mole) of **1** in 100 ml of methylene chloride at −70°. Distillation gave a total of 34.70 g (91.4%) of product: 13.10 g, bp 66.5–67° (0.5–0.3 mm), n^{24}D 1.4925; 8.75 g, bp 67–69° (0.3 mm), n^{24}D 1.4909; and 12.85 g, bp 69–67.5° (0.3–0.25 mm), n^{24}D 1.4912. The infrared spectra of the three fractions were identical.

Anal. (last fraction). Calcd for $C_8H_{15}BBr_2O_2$: C, 30.62; H, 4.82; B, 3.45; Br, 50.92; HBr, 25.78. Found: C, 31.21; H, 5.05; B, 3.43; Br, 50.60; HBr, 25.45 (by hydrolysis).

Treatment of 8.16 g (0.0260 mole) of **2** with 15 ml of 3 *M* sodium hydroxide solution gave 2.60 g (93.5%) of vinyl bromide in an attached trap cooled to −80°. The infrared spectrum (gas cell) was identical in all respects to that of an authentic sample.

A freshly distilled sample of **2**, bp 75–76° (0.42–0.45 mm), was utilized for the proton nmr spectrum (neat, τ): $(CH_3)_2$ singlet at 8.79; CH_3 doublet at 8.74 (J = 6 cps); CH_2 as an AB multiplet at 7.95–8.60 and another at 6.1–6.9; a symmetrical multiplet (1H) is centered at 5.73 and a partially concealed multiplet appears at 8.92 (1H).

2-(3′-Thianonyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (3).—1-Hexanethiol (9.9 g, 0.0837 mole) was added to 11.10 g (0.0721 mole) of **1** in a quartz flask (0°). The solution was stirred at −80° and irradiated for 7 hr with a 140-w Hanovia ultraviolet lamp. Gas bubbles appeared during the reaction and the solution became cloudy. Distillation gave 8.00 g of a forerun, bp 52–53° (13–12 mm), $n^{22.5}$D 1.4547, shown by infrared and gas chromatographic analysis to contain 14% **1**, 30.5% 1-hexanethiol, and some dihexyl sulfide. Unreacted **1** then was obtained, bp 63–93° (7.2–0.08 mm), $n^{22.5}$D 1.4487, 2.04 g. The desired product was collected in two portions: 5.73 g, bp 93–97° (0.08 mm), $n^{22.5}$D 1.4630; and 5.42 g, bp 96–100.5° (0.10–0.08 mm), $n^{22.5}$D 1.4633.

Anal. (final fraction). Calcd for $C_{14}H_{29}BO_2S$: C, 61.76; H, 10.74; S, 11.78. Found: C, 62.21; H, 10.97; S, 11.88.

The infrared spectrum of **3** showed no vinyl absorption at 1620 cm^{-1} and gas chromatographic assay of the product fractions indicated a total yield of 10.1 g (51.5% yield, 72% conversion).

The proton nmr spectrum showed a multiplet (1H) at τ 5.87, methyl protons (9H) at 8.77 and 8.87, an AB multiplet (2H) at 8.05–8.7, a methyl (3H) at 9.12 superimposed on a multiplet (2H) at 8.9–9.33 (J = 6 cps), four protons as a multiplet centered at 7.53, and eight protons near 8.60.

2-(2′,2′-Dichlorocyclopropyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (4).—(a)[19] The procedure of Wagner[8] was followed. A mixture of 27.0 g (0.175 mole) of freshly distilled **1** [bp 64° (28 mm)] and 32.5 g (0.175 mole) of purified sodium trichloroacetate in 75 ml of 1,2-dimethoxyethane was boiled under reflux. A white solid deposited after 20 min; after 21 hr, filtration gave 163 mmoles (93%) of sodium chloride. Removal of solvent from the filtrate and distillation of the residue gave 23.1 g (85.6%) of recovered **1**, bp 42.5–44° (6.3–5.9 mm), n^{25}D 1.4267, identified by its infrared spectrum. An intermediate fraction of 1.6 g, bp 44–35° (5.9–1.0 mm), n^{25}D 1.4328, appeared by its infrared spectrum to be a mixture of **1** and ethyl trichloroacetate. The product was collected in two fractions: 0.75 g, bp 64–71° (0.8 mm), n^{25}D 1.4466; and the analytical fraction of about 1 g, bp 71.0–71.5° (0.85–0.92 mm), n^{25}D 1.4560 (4.2% yield, 29.5% conversion).

Anal. Calcd for $C_9H_{15}BCl_2O_2$: C, 45.62; H, 6.38; B, 4.57; Cl, 29.93. Found: C, 45.86; H, 6.43; B, 4.47; Cl, 30.00.

The product exhibited no infrared absorption near 1620 cm^{-1}. The proton nmr spectrum ($DCCl_3$) showed a multiplet (1H) centered at τ 5.80, with small impurities at 6.62 and 6.97. A multiplet (4H) at τ 8.0–8.7 is partially obscured by the methyl proton peak. The major methyl singlet (7.5H) is found at τ 8.72 with the remaining methyl protons (1.5) at 8.80. A multiplet at τ 8.83–9.24 (1H) accounts for the remaining hydrogen atom.

(b) A mixture of 19.8 g (0.050 mole) of phenyltrichloromethylmercury,[20] 23.1 g (0.150 mole) of **1**, and 0.05 g of phenothiazine in 25 ml of benzene was boiled under reflux. A white solid separated after 30 min; after 42 hr, the mixture was filtered and the solid washed with benzene to give 15.00 g (95.9%) of phenylmercuric chloride, mp 255–256°. Distillation of the filtrate gave four fractions: 1.42 g, bp 87–85° (1.3–1.2 mm), n^{25}D 1.4601; 3.30 g, bp 85–87° (1.2–1.1 mm), n^{25}D 1.4614; 2.03 g, bp 87–92° (1.1–1.0 mm), n^{25}D 1.4627; and 0.52 g, bp 92–96° (1.0 mm), n^{25}D 1.4641, for a total yield of 7.27 g (61.4% yield).

The infrared spectra of all the fractions were identical with that of the material prepared by method a. A calibrated spectrum of the third fraction showed C—H stretching frequencies at 2925 and 2967 cm^{-1} (CCl_4). Redistillation gave an analytical sample, bp 87–89.5 (1.5 mm).

Anal. Calcd for $C_9H_{15}BCl_2O_2$: mol wt, 236.9. Found: mol wt, 232 (vapor osmometric in benzene).

Reaction of 4 with Potassium *t*-Butoxide.—A slurry of 1.00 g (0.0089 mole) of potassium *t*-butoxide in 20 ml of dry toluene (*t*-butanol-free) was cooled to 0° and 1.6 g (0.0068 mole) of **4** added to give an amber solution. Rapid heating under a short-path still head gave 0.4 ml of an initial fraction, bp 80–105°, followed by 2.4 ml of toluene, bp 105–109.5°. The inital fraction showed the presence of *t*-butyl alcohol and toluene in its infrared spectrum, plus peaks at 3.25, 5.78, 9.6, 10.55, and 12.35 μ. A calibrated spectrum showed a peak at 1735 ± 5 cm^{-1}. This solution reduced aqueous potassium permanganate in acetone to give manganese dioxide. A dark precipitate (silver metal?) formed with ethanolic silver nitrate. The proton nmr spectrum showed toluene at τ 7.66 (methyl) and 3.83 (aromatics), *t*-butyl alcohol at 8.64 (methyls) and 7.24 (hydroxyl), and an impurity (doublet) at 6.22 (J = 2.2 cps). A doublet appears at τ 5.05 (J = 6.3 cps) with a related triplet at 4.04 (J = 6.2 cps). The latter triplet has a relative area of 0.024 compared to 0.037 for the doublet. Gas chromatograms were run on 6 ft × $^1/_4$ in. columns at 92° using 25 psi of helium carrier gas pressure. Area ratios indicated 4 to 7% of 1-chloroallene in the initial distillate fraction. The results are given in Table I, along with the data using the synthetic mixture of toluene, *t*-butyl alcohol, and 1-chloroallene described below.

1-Chloroallene was prepared by the isomerization of propargyl chloride.[21] The product, bp 46°, exhibited an infrared spectrum

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[19] W. G. Woods and I. S. Bengelsdorf, U. S. Patent 3,219,683 (1965), to U. S. Borax and Chemical Corp.

[20] D. Seyferth and J. M. Burlitch, *J. Organometallic Chem.*, **4**, 127 (1965).

[21] T. L. Jacobs and W. F. Brill, *J. Am. Chem. Soc.*, **75**, 1314 (1953).

(gas) identical with that reported.[22] A synthetic mixture of 0.2053 g of 1-chloroallene, 0.7500 g of *t*-butyl alcohol, and 4.0733 g of toluene was prepared; the results of gas chromatographic analysis are given in Table I. The proton nmr spectrum displayed *t*-butyl alcohol methyl protons at τ 8.83, toluene methyl at 7.82, hydroxy proton at 7.44, and the aromatic protons as a multiplet centered at 2.93. 1-Chloroallene gives rise to a doublet at τ 5.22 (J = 6.2 cps) and a triplet at 4.21 (J = 6.2 cps). A solution of 1-chloroallene in carbon tetrachloride shows the double (2H) at τ 4.88 ($J = 6.2 \pm 0.1$ cps), and the triplet (1H) at 3.98 ($J = 6.3 \pm 0.1$ cps), illustrating the solvent effect on the chemical shifts.[12] A small impurity (propargyl chloride) appeared at τ 5.96 (doublet, J = 2.5 cps) and at 7.62 (very weak triplet, J = 2.5 cps).

TABLE I

GAS CHROMATOGRAPHIC DATA

Column packing[a]	Retention time, min 1-Chloro-allene	 *t*-Butyl alcohol	 Toluene
2% Versamid[b]	1.0	1.3	1.8
	(1.0)[c]	(1.2)[c]	(1.9)[c]
Carbowax 1000	4.3	5.5	12.1
	(4.4)	(5.7)	(12.8)
Carbowax 4000 dioleate	4.2	5.0	12.8
	(4.7)	(5.6)	(14.3)
Silicone oil	3.7	3.0	15.5
	(3.7)	(3.0)	(16.1)

[a] Firebrick support. [b] Silanized. [c] Data for the synthetic mixture given in parentheses.

endo-, exo-**2-(4′,4′,6′-Trimethyl-1′,3′,2′-dioxaborinanyl)bicyclo[2.2.1]hept-5-ene** (**5**).—A solution of 7.00 g (0.0455 mole) of **1** in 3.45 g (0.0522 mole) of freshly distilled cyclopentadiene (bp 40°) was heated at 150–153° for 15 hr in a sealed tube. Distillation gave 1.18 g of forerun, bp 72–66° (0.95–0.55 mm), $n^{23.5}\mathrm{D}$ 1.4711, shown by infrared spectra and gas chromatography to be a mixture of dicyclopentadiene, unreacted **1**, and product. The product (7.82 g, 78.2%) was collected in two fractions: 6.67 g, bp 66–62° (0.55–0.30 mm), $n^{23.5}\mathrm{D}$ 1.4683; and 1.15 g, bp 62–63° (0.25 mm), $n^{23.5}\mathrm{D}$ 1.4693. Gas chromatography at 160° on an Apiezon column showed two closely spaced components in comparable amount plus a trace of dicyclopentadiene.

Anal. Calcd for $C_{13}H_{21}BO_2$: C, 70.93; H, 9.62. Found: C, 71.14; H, 9.55.

The proton nmr spectrum presented two sets of methyl groups which appear at τ 8.81 and 8.88 (J = 4.5 cps) and at 8.76 and 8.84 (J = 5.5 cps). Relative peak height measurements indicated that the more shielded methyl protons comprise 43% of the mixture. A multiplet (1H) is centered at τ 9.03 with some near 9.43. A complex multiplet (4H) appears at τ 8.0–8.7. Two broadened peaks (2H) are found at τ 7.12 and 7.23. A single proton multiplet is centered at τ 5.93. The vinyl region (2H) shows a triplet (τ 4.13, J = 2 cps) superimposed on a double quartet centered at 4.04. Integration of the vinyl region[14] shows 43% *endo* isomer.

endo-, exo-**2-(4′,4′,6′-Trimethyl-1′,3′,2′-dioxaborinanyl)bicyclo[2.2.1]heptane** (**6**).—To 35 ml of cyclohexane containing 0.5 g of freshly reduced platinum oxide was added 2.10 g (0.00954 mole) of **5**. Hydrogenation at 27.5–30° (atm press) resulted in the rapid and nearly quantitative uptake of hydrogen. Distillation gave 2.0 g (94.5%) of **6**, bp 71–65° (0.7–0.15 mm), $n^{22}\mathrm{D}$ 1.4637. The product did not decolorize bromine in carbon tetrachloride and exhibited a single peak under the same gas chromatographic conditions that resolved the isomers of **5**.

Anal. Calcd for $C_{13}H_{23}BO_2$: C, 70.29; H, 10.44. Found: C, 70.59; H, 10.46.

A 1.65-g (0.00743 mole) sample of **6** was dissolved in 5 ml of tetrahydrofuran and 3 ml of 3 N sodium hydroxide and 1.7 ml of 30% hydrogen peroxide added at 0°. After 30 min of stirring at 0° and 1 hr at room temperature, 50 ml of water was added; the mixture extracted with two 25-ml portions of ether. The aqueous phase was saturated with sodium chloride and extracted with 50 ml of ether. The combined extracts were dried over magnesium sulfate and filtered; the filtrate was evaporated. The liquid residue was heated at 90° (100 mm) and collected on the cold finger of a sublimation apparatus. The infrared spectrum of this material was essentially the same as that of a synthetic mixture of 27.0 mole % *exo*-norborneol, 25.4 mole % *endo*-norborneol, and 47.5 mole % 2-methyl-2,4-pentanediol.

endo-**2-(4′,4′,6′-Trimethyl-1′,3′,2′-dioxaborinanyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene** (**7**).—A mixture of 11.35 g (0.0737 mole) of **1** and 22.4 g (0.0821 mole) of hexachlorocyclopentadiene was heated 22.5 hr at 107 to 157°. Distillation of the solid gave 2.8 g of liquid forerun, bp 80–139° (0.2–0.3 mm), $n^{22}\mathrm{D}$ 1.5525. A portion of the 30.15 g of residue was sublimed at 138–149° (0.2–0.08 mm) to give two fractions, mp 85–87 and 92–93°. The remaining 23.3 g of residue was distilled to give 13.30 g, bp 133–146° (0.12 mm), mp 86–89°, followed by 7.80 g of the analytical sample, bp 144–147° (0.12 mm), mp 89–90°, for a calculated yield of 86.7%.

Anal. Calcd for $C_{13}H_{15}BCl_6O_2$: C, 36.58; H, 3.54; Cl, 49.85. Found: C, 36.99; H, 3.61; Cl, 50.27.

Fractional sublimation of this material after crystallization from benzene gave successive fractions with mp 89–91, 90–91, 90.5–92, and 90–93°, respectively. The first two fractions were combined for the proton nmr spectrum (dilute in CCl_4) which displayed methyl protons at τ 8.81 (1.5H) and 8.74 (7.5H, J = 4.5 cps). A singlet (1H) appears at τ 9.01. An AB multiplet at τ 8.3–8.7 contains 2H; 1H is found as a symmetrical multiplet centered at τ 5.87. Two protons appear at τ 7.73 and 7.79, with possible satellites at 7.54 and 7.95.

Reaction of 1 with Diazomethane.—To 48 ml of an ethereal diazomethane solution (0.306 M, 0.0147 mole) was added 2.26 g (0.0147 mole) of **1**. Reaction commenced after about 1 min (exotherm) and a precipitate formed. Filtration and washing with ether gave 0.15 g (73%) of a tough polymer, whose infrared spectrum suggested polymethylene plus impurities. This polymer contained boron which was not extractable with methanol.

Reaction of 1 and Ethyl Diazoacetate.—A solution of 2.50 g (0.0219 mole) of ethyl diazoacetate in 5 ml of ether was added to 3.10 g (0.0201 mole) of **1** in 5 ml of ether. After 7 hr at 25°, an infrared spectrum showed mainly **1** with small, new bands at 3.0, 5.78, 7.6, 9.2, 11.35, and 12.6 μ. The ether was removed and the neat oil heated for 2 hr at 50–55° and then 30 min at 55–85°. Weaker bands due to starting materials and strong, new bands appeared at 5.76, 6.95, 8.55, 8.98, 9.7, and 10.9 μ. An additional 5 hr at 90° gave a syrup whose infrared spectrum showed no **1** and a small diazo peak at 4.75 μ. Distillation of the viscous, amber product gave a forerun with bp up to 110° (3.5 mm) followed by 0.8 g, bp 115–160° (2.5–4.4 mm). The product (2.8 g, 50%) was collected at bp 157–175° (3.4–3.1 mm), $n^{25}\mathrm{D}$ 1.4565. The infrared spectrum shows ester C=O at 5.74, N—H at 3.0, and *no* B—N near 6.55[23] μ; tris(2-methyl-2,4-pentanediol) biborate absorptions also are present.

Anal. Calcd for $C_{12}H_{21}BN_2O_4$: C, 53.75; H, 7.89; B, 4.04; N, 10.45; O, 23.87. Calcd for $C_{12}H_{21}BN_2O_4$ (85%) + $C_{18}H_{38}B_2O_6$ (15%): C, 54.45; H, 8.18; B, 4.29; N, 8.88; O, 24.17. Found: C, 53.43, 53.83; H, 8.28, 8.15; B, 4.54, 4.81; N, 8.96, 8.73; O, 24.79, 24.48 (by difference).

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