2-Vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane. I. Synthesis and Properties[1,2]

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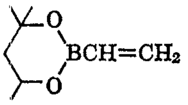
The reaction of freshly prepared vinylmagnesium chloride and 2-*n*-butoxy-4,4,6-trimethyl-1,3,2-dioxaborinane (2) at −70° followed by pyrolysis of the complex gives 2-vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane (1) in good yield. The use of aged Grignard reagent or higher temperature in the addition step leads to lower yields. Transesterification of dimethyl ethyleneboronate with 2-methyl-2,4-pentanediol gives a moderate yield of 1. The reaction of dispersed sodium and vinyl chloride with tris(2-methyl-2,4-pentanediol) biborate or 2 leads to 1 in poor yield. In contrast to other known simple esters of ethyleneboronic acid, 1 is unaffected by contact with air and gives a soluble homopolymer. Copolymers of 1 with styrene, methyl methacrylate, and acrylonitrile are described.

Our interest in esters of ethyleneboronic acid led us to prepare 2-vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane (1).

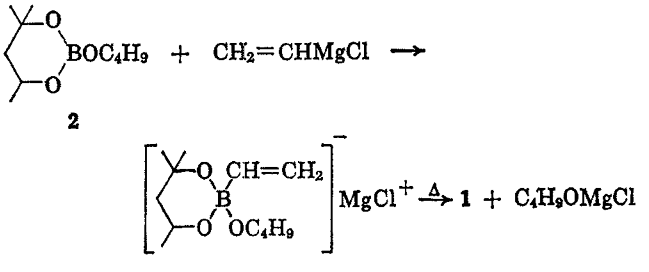


1

Simple dialkyl ethyleneboronates polymerize very readily[3,4] and the cyclic ethylene glycol ester could not even be purified.[5] Diethanolamine ethyleneboronate, however, is stable toward polymerization.[6]

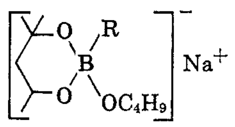
Syntheses.—Transesterification of dimethyl ethyleneboronate with 2-methyl-2,4-pentanediol gives 1 in 64% yield. Instability of the dimethyl ester and difficulties in obtaining it pure make this route unattractive.

The Grignard synthesis of 1 using vinylmagnesium chloride in THF[7] and 2-*n*-butoxy-4,4,6-trimethyl-1,3,2-dioxaborinane (2) is preferred. The complex is pyrolyzed neat or in the presence of mineral oil to give 1.



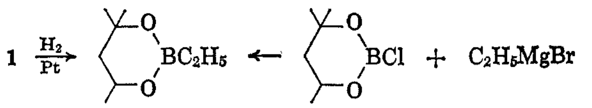
The results of a number of experiments show that the best yield (79%) is obtained at −70°, similar to the synthesis of benzeneboronic acid.[8] Higher temperatures in the addition step gave lower yields; *e.g.*, at −10° only 40% of 1 is obtained. When pentane was added in an attempt to reduce the solubility of the complex in a run at −10°, no improvement in yield was noted. The yield of 1 decreases from 79 to 23% as the age of the vinylmagnesium chloride solution increases from 4 to 120 days. This instability of vinylmagnesium chloride in THF has been noted by others.[9]

The reaction of 2, vinyl chloride, and dispersed sodium gave a low yield (9%) of 1. Analysis suggested that the desired complex 3 (R = vinyl) and/or the butoxide complex 3 (R = OC_4H_9) were formed. When tris(2-methyl-2,4-pentanediol) biborate was used in place of 2, a 22% yield of 1 was realized.[10]



3

Hydrogenation of 1 gives 2-ethyl-4,4,6-trimethyl-1,3,2-dioxaborinane (4). The latter is identical with the product obtained by treating 2-chloro-4,4,6-trimethyl-1,3,2-dioxaborinane (5) with ethylmagnesium bromide.[11]



Spectra.—The infrared spectrum of 1 shows the C=C stretching frequency at 1615 cm^{-1}, as expected for a vinyl group conjugated with boron.[12] The proton nmr spectrum of 1 shows three protons as two singlets assigned to the vinyl group at τ 4.08 (1 H) and 4.15 (2 H). A single proton gives rise to a multiplet of at least 11 lines centered at τ 5.79 and assigned to the tertiary proton. The methylene protons give an ABX pattern, part of which is obscured by the methyl resonances at τ 8.69 (7.5 protons) and 8.77 (1.5 protons). The AB part of this ABX system is centered at about τ 8.35 (J = 14 cps).

The ^{11}B chemical shifts of 1 and 2 are given in Table I. Tributyl borate and 2 show similar shielding, in accord with the Lewis acidities of tributyl borate and 2-*n*-butoxy-1,3,2-dioxaborinane.[13] Vinyl derivative 1 and dibutyl ethyleneboronate show the same shift.

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[1] Presented in part at the Pacific Southwest Regional Meeting of the American Chemical Society, Claremont, Calif., Dec 1962.

[2] Also see W. G. Woods, I. S. Bengelsdorf, and D. L. Hunter, Canadian Patents 667,401 (1963) and 686,361 (1964), to U. S. Borax and Chemical Corp.

[3] (a) D. S. Matteson, *J. Am. Chem. Soc.*, **81**, 5004 (1959); (b) B. M. Mikhailov and P. M. Aronovich, *Vysokomolekul. Soedin.*, **3**, 861 (1961).

[4] G. W. Willcockson and J. K. Sandie, U. S. Patent 3,045,039 (1962), to U. S. Borax and Chemical Corp., and unpublished observations by the authors.

[5] H. Normant and J. Braun, *Compt. Rend.*, **248**, 828 (1959).

[6] G. W. Willcockson, D. L. Hunter, and I. S. Bengelsdorf, U. S. Patent 3,069,454 (1962), to U. S. Borax and Chemical Corp.

[7] H. E. Ramsden, *et al.*, *J. Org. Chem.*, **22**, 1602 (1957).

[8] R. M. Washburn, E. Levens, C. F. Albright, F. A. Billig, and E. S. Cernak, "Metal-Organic Compounds," Advances in Chemistry Series, Vol. 23, American Chemical Society, Washington, D. C., 1959, p 102 ff.

[9] D. S. Matteson, *J. Org. Chem.*, **27**, 275 (1962).

[10] W. G. Woods and R. O. Schaeffer, U. S. Patent 3,219,682 (1965), to U. S. Borax and Chemical Corp.

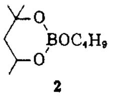
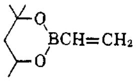
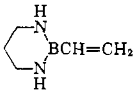
[11] W. G. Woods, to be published.

[12] D. S. Matteson, *J. Am. Chem. Soc.*, **82**, 4228 (1960).

[13] A. J. Hubert, B. Hargitay, and J. Dale, *J. Chem. Soc.*, 931 (1961).

TABLE I

^{11}B CHEMICAL SHIFTS[a]

Compd	δ, ppm[b]
$B(OC_4H_9)_3$	-0.1[c]
 **2**	-0.4
 **1**	-7.4
$(C_4H_9O)_2BCH{=}CH_2$	$-7.3\ (-12)$[d]
	-8.9[e]

[a] Determined at 19.3 Mc. [b] Relative to trimethyl borate. [c] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959). [d] Calculated from the δ_σ and δ_π values given by C. D. Good and D. M. Ritter, *ibid.*, **84**, 1162 (1962). [e] Reference 14.

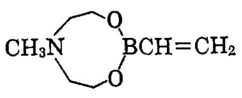
The boron atom of 2-vinyltetrahydro-1,3,2-diazaborine[14] is slightly more shielded than that in the oxygen derivatives.

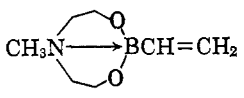
The ultraviolet spectrum of **1** shows a maximum at 198.5 mμ, whereas dibutyl ethyleneboronate absorbs at 185 mμ.[15] This bathochromic shift can be accounted for by enhanced oxygen to boron $p\pi$–$p\pi$ delocalization in **1** due to the constraint of the dioxaborinane ring. LCAO–MO calculations predict[12] a reduced $\pi \rightarrow \pi^*$ transition energy as boron–oxygen overlap is increased.

Polymerization.—Monomer **1** can be handled in contact with air without polymerization and it can be stored in the absence of inhibitors for months. As some thermal polymerization is observed when **1** is distilled, the use of phenothiazine is recommended. The homopolymer of **1** has a low molecular weight, it is soluble in organic solvents, and it is resistant to hydrolysis.

The stability of **1** is in marked contrast to the dialkyl ethyleneboronates which polymerize immediately on contact with the atmosphere to give insoluble gels.[3b] The resistance of **1** to oxygen-initiated polymerization could be taken as evidence for an initiation mechanism involving attack of oxygen on boron, as is found in the autoxidation of boron–carbon compounds.[16] A tetrahedral boron atom in **1** is sterically unfavorable and steric, noncoordinative stabilization of a vinylboron derivative has been reported.[17]

Tetrahydro-2-vinyl-6-methyl-6-aza-1,3,2-dioxaborocine (**6**) is presumed to be stabilized by an intramolecular coordinate bond between boron and nitrogen.[6] However, the C=C stretching band of **6** appears at 1611 cm^{-1}. The low intensity of the band suggests that **6** may exist as an equilibrium mixture of **6a** and **b**, with the C=C stretch of **6b** not observed. The low intensity of the C=C band of tetrahedral vinylboron derivatives has been noted.[18] An attempt to polymerize **6** under the same conditions as used for **1** gave no polymer.


6a


6b

Copolymers were prepared of **1** with styrene, methyl methacrylate, and acrylonitrile. The conversions and the observed monomer ratios are given in Table II.

TABLE II

COPOLYMERS OF 2-VINYL-4,4,6-TRIMETHYL-1,3,2-DIOXABORINANE (**1**)

Comonomer	Molar ratio, comonomer/1		%
	Initial	Copolymer	conversion
Styrene	1.53	5.6	45
Methyl methacrylate	1.54	2.24	69.4
Acrylonitrile	1.00	1.25	62.9

The reactivity of these monomers toward copolymerization with **1** is in the order: acrylonitrile > methyl methacrylate > styrene. Data at lower conversions and with various initial monomer ratios would be needed to evaluate monomer reactivity ratios.[19]

Other 2-substituted 4,4,6-trimethyl-1,3,2-dioxaborinanes have been synthesized, many of which show unusual stability. Details of this work and of derivatives of **1** will be presented elsewhere.

Experimental Section

All operations were carried out under dry nitrogen. Melting and boiling points are uncorrected. Nmr spectra were measured using Varian spectrometers operating at 19.3 Mc for ^{11}B [external $BF_3 \cdot O(C_2H_5)_2$ reference] and 60 Mc for protons (internal tetramethylsilane reference). A sample of dibutyl ethyleneboronate was kindly provided by Professor D. S. Matteson.

Vinylmagnesium Chloride in Tetrahydrofuran.—Method II of Ramsden and co-workers[7] was followed. Reactions were initiated with small volumes of vinylmagnesium chloride solution. Aging 2 weeks or longer results in a solid deposit. Several runs were made using vinylmagnesium chloride solution purchased from Metal and Thermit Corp., Rahway, N. J.

2-*n*-Butoxy-4,4,6-trimethyl-1,3,2-dioxaborinane (**2**).—A mixture of 370.6 g (5.00 moles) of *n*-butyl alcohol, 590.9 g (5.00 moles) of 2-methylpentane-2,4-diol, and 309.2 g (5.00 moles) of boric acid in 1750 ml of benzene was boiled under a Dean-Stark trap and 270.5 ml (100.2%) of water removed in 6 hr. The product was collected in three fractions: 366.5 g, bp 60.5–54.5° (0.70–0.23 mm), $n^{25}{}_D$ 1.4202, 5.43% B; 420.5 g, bp 54.5–49.5° (0.23–0.08 mm), $n^{18}{}_D$ 1.4237, 5.42% B; and 18.3 g., $n^{20}{}_D$ 1.4212 (total yield of 80.5%). (*Anal.* Calcd for $C_{10}H_{21}BO_3$: B, 5.41.) The boron-11 nmr shows a single peak (half-width = 14.7 ppm) at -18.5 ± 0.2 ppm.

2-Vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane (**1**). **A.**—A solution of 33.4 g (0.334 mole) of dimethyl ethyleneboronate and 43.5 g (0.368 mole) of 2-methyl-2,4-pentanediol in 50 ml of benzene was distilled to give 15 ml of forerun, bp 50–55° (22 mm), followed by 32.8 g (63.7%) of product, bp 57–58° (22 mm) (B, 7.00%).

The infrared spectrum (neat) showed vinyl CH at 3025 (w), CH_3 stretch at 2950 (s), CH_2 stretch at 2925 (m), C=C at 1620 (m), vinyl C—H bend at 960 (m), and unassigned at 714 cm^{-1} (s). The C=C stretch at 1615 cm^{-1} had ϵ 68.5 kg mole^{-1} cm^{-1} ($CHCl_3$).

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(14) K. Niedenzu, P. Fritz, and J. W. Dawson, *Inorg. Chem.*, **3**, 1077 (1964).

(15) A. N. Nikitina, *et al.*, *Opt. Spectr. USSR* (Eng. Transl.), **16**, 528 (1964).

(16) A. G. Davies in "Progress in Boron Chemistry," Vol 1, H. Steinberg and A. L. McCloskey, Ed., The Macmillan Co., New York, N. Y., 1964, p 277.

(17) D. S. Matteson and R. W. H. Mah, *J. Org. Chem.*, **28**, 2171 (1963).

(18) T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.*, 3103 (1961).

(19) G. E. Ham, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., 1964, pp 67 ff.

B.—In a typical experiment, vinylmagnesium chloride in THF (292 ml of a 1.71 *M* solution, 0.500 mole) and 2 (100 g, 0.500 mole) were added simultaneously to 150 ml of stirred ether at −60° over 0.5 hr. The slurry became clear at −33° as it was allowed to warm to 25°. The residue from solvent removal was heated at 0.1 mm from 65 to 175° over 2.5 hr and the pyrolysate collected at −80°. The residue (99.6 g, 150%) contains 21.5% Cl and 0.19% B. (*Anal.* Calcd for C_4H_9OMgCl: Cl, 26.68.) Redistillation gave 1, bp 45.5–42.5° (8–6.5 mm), n^{23}D 1.4272, 7.02% B, 43.5 g (56.5%).

In some cases, mineral oil was added prior to pyrolysis or the solution of the complex was added to hot mineral oil at reduced pressure. These modifications did not improve the yield. Phenothiazine should be added to the complex before pyrolysis to reduce losses due to polymerization.

C.—Vinyl chloride (8 g, 0.13 mole) was dissolved in 23.5 g (0.118 mole) of freshly distilled 2, bp 47° (22 mm), in 100 ml of ether. This solution was added to 5.1 g (0.222 g-atom) of sodium dispersed in 150 ml of ether at 0° over 1 hr. The temperature rose briefly to 35° and phenylboron dichloride (0.1 ml) or chlorobenzene (0.2 ml) failed to induce further exotherm. The slurry stood overnight, the milky solution decanted, and the residue washed with ether. The solid contained 69.2 mequiv of chloride, 22.3 mequiv of alkalinity, and 9.7 mequiv of boron. The syrup was heated to 215° (0.4 mm) to give 4.85 g of pyrolysate. The infrared spectrum showed 1 and an unknown component. Analysis by glpc gave 1.4 g (9% yield) of 1. The solid residue (24.2 g) contained 8.25 mequiv of chloride, 88.2 mequiv of alkalinity, and 82.7 mequiv of boron.

D.—A solution of vinyl chloride (11.0 g, 0.18 mole) and 46.3 g (0.125 mole) of tris(2-methyl-2,4-pentanediol) biborate[20] in 85 ml of ether was added over 2 hr to a dispersion of 5.60 g (0.25 g-atom) of sodium in 150 ml of ether at 0°. An exotherm maintained the mixture at 49° for 1 hr. The slurry was centrifuged, the solid washed with 50 ml of ether, and analysis showed 78.8 mequiv of chloride, 19.8 mequiv of alkalinity, and 9.8 mequiv of boron. The residue from the ether was heated to 210° (0.25 mm) to give 14.45 g of pyrolysate (2.27% B). Analysis by glpc (220°, 6-ft Apiezon "L" column) and infrared showed 30% 1 (22.5% yield). The residue contained tris(2-methyl-2,4-pentanediol) biborate (infrared) and analysis showed a total of 11.9 mequiv of chloride, 80.3 mequiv of alkalinity, and 138.3 mequiv of boron.

E.—An analytical sample of 1 was obtained by fractionation in an efficient column: bp 69–70° (35 mm); vp = 2 mm at 22°; n^{22}D 1.4284; d^{24} 0.894; $\lambda_{\max}^{C_6H_{12}}$ 198.5 mμ (ε 6900).

Anal. Calcd for $C_8H_{15}BO_2$: C, 62.38; H, 9.82; mol wt, 154. Found: C, 62.08; H, 9.97; mol wt, 162.

Glpc shows only a single sharp peak and the infrared spectrum was unchanged after 3 months except for a small hydroxyl band. The proton nmr spectrum[21] ($DCCl_3$) is described in the text. The boron-11 chemical shift (neat) is −25.5 ± 0.3 ppm; the chemical shift of $B(OCH_3)_3$ relative to $BF_3 \cdot O(C_2H_5)_2$ is taken as −18.1 ppm.[22]

2-Ethyl-4,4,6-trimethyl-1,3,2-dioxaborinane (4).—A solution of 30.6 g (0.199 mole) of 1 [bp 55.5° (11.5 mm)] in 75 ml of 1,2-dimethoxyethane containing 1.5 g of Adams catalyst was hydrogenated at 50 psi. Uptake of hydrogen was very rapid and exothermic (97% in 5 min). Distillation gave 2.5 g of forerun, bp 33–56.5° (22 mm), followed by 25.0 g (80.5%) of 4, bp 57.5–58.5° (22–21 mm), $n^{25.8}$D 1.4116.

Anal. Calcd for $C_8H_{17}BO_2$: C, 61.58; H, 10.98; B, 6.93. Found: C, 61.74; H, 11.04; B, 7.03 (Parr fusion).

The infrared spectrum of this material is identical with that of authentic 4.[11]

Tetrahydro-2-vinyl-6-methyl-6-aza-1,3,2-dioxaborocine (6).—Dibutyl ethyleneboronate (18.4 g, 0.100 mole) and N-methyldiethanolamine (11.9 g, 0.100 mole) in 50 ml of toluene were boiled under an efficient column; 49.6 g (107%) of toluene–*n*-butyl alcohol azeotrope was collected, bp 105.5°. Distillation gave a forerun, 1.4 g, bp 104–113° (0.10–0.12 mm), n^{21}D 1.4821, followed by 12.35 g (79.7%) of product, bp 114–119° (0.12–0.15 mm), mp 43–44°.

Anal. Calcd for $C_7H_{14}BNO_2$: C, 54.24; H, 9.10; B, 6.98; N, 9.04. Found: C, 54.23; H, 9.79; B, 6.76; N, 8.85, 8.86.

The infrared spectrum ($CHCl_3$) shows C=C stretch at 1611 cm^{-1} (ε 23.8 kg $mole^{-1}$ cm^{-1}).

Attempted Homopolymerization of 6.—A solution of 2.0 g (0.0129 mole) of 6 in 5.6 ml of benzene containing 0.024 g (0.00015 mole) of azobisisobutyronitrile (AIBN) was boiled for 88 hr. Distillation gave 1.95 g (97.5%) of recovered 6 (infrared), bp 114° (0.11 mm). The dark, tarry residue weighed 0.11 g. A sample of 6 stored for 4.5 years gave unchanged 6 on distillation.

Dibutyl ethyleneboronate has the reported[12] infrared C=C stretch at 1610 cm^{-1}, with ε 87.9 kg $mole^{-1}$ cm^{-1} ($CHCl_3$). The boron-11 chemical shift (neat) is −25.4 ppm.

Homopolymer of 1.—A solution of 10.0 g (0.065 mole) of freshly distilled 1 and 0.1 g (0.00061 mole) of AIBN in 37.5 ml of benzene was boiled for 88 hr. Evaporation gave 21.57 g of distillate shown (infrared) to contain 3.21 g (32%) unreacted 1. The viscous residue was heated at 100° (0.2 mm) for 4 hr to give 0.48 g of 1. The yellow, thermoplastic polymer weighs 6.32 g (63.2%).

Anal. Calcd for $(C_8H_{15}BO_2)_n$: C, 62.38; H, 9.82; B, 7.03. Found: C, 62.24; H, 9.98; B, 7.15; mol wt, 700 (vapor osmometric in benzene).

The infrared spectrum of a thin film was unchanged (no hydroxyl) after exposure to air at 50% relative humidity for 3 hr.

Copolymers of 1.—**Styrene** (15.5 g, 0.149 mole) and 15.0 g (0.097 mole) of 1 were boiled in 100 ml of benzene with 0.3 g (0.0018 mole) of AIBN for 136 hr to give 13.7 g (45%) solid copolymer, mp 112–125° (B, 1.47%), intrinsic viscosity (benzene) 0.106 (30.0°), 84.54% C, 8.60% H. **Methyl methacrylate** (15.0 g, 0.15 mole), 1 (15.0 g, 0.097 mole), and AIBN (0.3 g, 0.0018 mole) gave white solid (20.8 g, 69.4%, mp 85–117°), 2.86% B, intrinsic viscosity (methyl ethyl ketone) 0.090 (30.0°). **Acrylonitrile** (4.9 g, 0.092 mole), 14.2 g (0.092 mole) of 1, and 0.2 g (0.0012 mole) of AIBN boiled for 64 hr gave 12.0 g (62.9%) of off-white solid, softening 70–110°, 4.91% B, mol wt 10,860 (cryoscopic, benzene). Infrared spectra of films showed peaks found in the corresponding homopolymers.

Acknowledgment.—The authors are indebted to M. F. Hawthorne and P. A. Wegner, University of California, Riverside, for the ^{11}B nmr data. D. P. Hollis of Varian Associates kindly provided the proton nmr spectrum. Helpful discussions with Professors S. Winstein and R. O. Schaeffer are gratefully acknowledged.

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(20) BORESTER® 7, U. S. Borax Research Corp., Anaheim, Calif.

(21) See N. S. Bhacca, *et al.*, "NMR Spectra Catalog," Vol. 2, Instrument Division, Varian Associates, Palo Alto, Calif., 1963, Spectrum No. 517.

(22) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).