Norborneneboronates[1]

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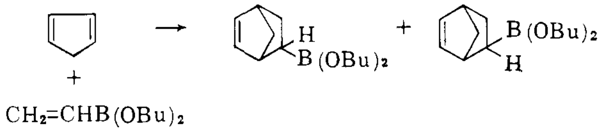
The Diels–Alder reaction of dibutyl ethyleneboronate and cyclopentadiene yields the *endo-* and *exo*-5-norbornene-2-boronic esters in the ratio 2:3. This ratio is subject to steric control and changes to 63% *endo* when ethyleneboronic acid is used, 73% *exo* when the di-*tert*-butyl ester is used. The product ratios are kinetically controlled. Highly purified samples of the *endo*-norborneneboronic acid and of both the *endo-* and the *exo-o*-phenylenediamine derivatives have been prepared. Some other Diels–Alder reactions of α,β-unsaturated boronic esters have been examined briefly.

The evident π-electron-withdrawing power of the boronic ester group has led to the prediction[2] that ethyleneboronic esters should behave as dienophiles. In addition to confirming this theoretical prediction, the Diels–Alder reactions of ethyleneboronic acid derivatives with cyclopentadiene provide the two diastereoisomeric 5-norbornene-2-boronic acids, which may be anticipated to be useful in stereochemical studies of electrophilic displacements of boron from saturated carbon.

Results

Dibutyl ethyleneboronate and excess cyclopentadiene heated under reflux with a bath at 90–100° gave a good yield of a mixture of dibutyl *endo-* and *exo*-5-norbornene-2-boronates. Different proportions of *endo* and *exo* isomers were obtained when ethyleneboronic acid was used in place of the ester. The more abundant and less soluble isomer, *endo*-5-norbornene-2-boronic acid, was readily freed from the *exo* isomer by recrystallization. It was initially postulated that the less bulky boronic acid group would lead to a higher proportion of the *endo* adduct than would the butyl ester; the correctness of this assumption is established below. Product rich in *exo* isomer was obtained from di-*tert*-butyl ethyleneboronate.



For analysis of the reaction mixtures, deboronation with alkaline hydrogen peroxide was chosen. The deboronation products, *endo-* and *exo*-dehydronorborneol, have been clearly characterized[3] and separated by gas chromatography.[4] Retention of configuration at the asymmetric carbon atom was expected and observed (see Discussion). Gas chromatography of the dehydronorborneols from deboronation of the crude Diels–Alder adducts yielded the *endo*/*exo* ratios summarized in Table I.

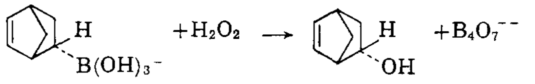
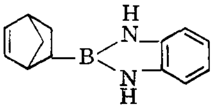


TABLE I

R in $(RO)_2$-$BCH=CH_2$	Ratio of *endo/exo*	Bath temp., °C. (approx.)[a]	Solvent	Time, hr.	Yield, %
H	1.70	80	Benzene	4.5	62[b]
H	1.50	110	Diglyme	4	30[b]
n-C_4H_9	0.64	100	None	4	83
n-C_4H_9	.51	25	None	22	15
t-C_4H_9	.37	120	None	7.5	65
t-C_4H_9	.22	85	None	3.5	1

[a] The actual reaction temperatures are lower by unknown and variable amounts, since a variable excess of refluxing cyclopentadiene was present; these figures are of qualitative significance only. [b] Converted to butyl ester (liquid) before isolation to avoid isomer separation.

Although the pure *endo*-boronic acid was easily isolated by recrystallization, the *exo* isomer was not because of its greater solubility in the solvents tried. To obtain a pair of pure *endo* and *exo* diastereoisomers the *o*-phenylenediamine derivatives[5] were prepared.



The *exo* derivative was the less soluble and was purified by repeated recrystallization. The pure *endo* derivative was obtained by starting with boronic acid that was 94% *endo*. The infrared spectra of the derivatives, shown in Fig. 1, indicated that each isomer was free of the other to the limit of sensitivity of the measurement, estimated to be about 1%. Conversion to dehydronorborneol and gas chromatography indicated the *exo* sample contained less than 1% *endo*. An *endo* sample showing a small amount of *exo* content by infrared was hydrolyzed to boronic acid which contained 3% *exo*. These analyses also establish the stereospecificity of the deboronation with hydrogen peroxide.

The generality of Diels–Alder reactions of unsaturated boron compounds has been explored briefly. The dibutyl ethyleneboronate adduct with perchlorocyclopentadiene was formed in high yield at 115°. Isoprene failed to add to dibutyl ethyleneboronate at reflux temperature but at 140° in a sealed tube yielded the adduct, dibutyl 1-methylcyclohexene-4-boronate. This structure is supported by hydrogen peroxide deboronation to 1-methylcyclohexen-4-ol. Gas chromatography did not indicate the presence of any

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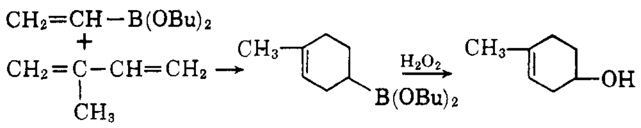
[1] Supported by National Science Foundation grants G 9916 and G 19906.

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

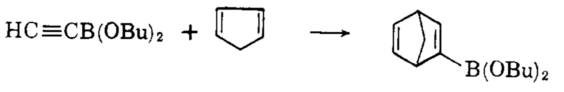
[3] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950). The published infrared spectrum of *endo*-dehydronorborneol reveals contamination with a substantial fraction of *exo* isomer and *vice versa*, but the data are adequate for positive identification of the isomers.

[4] G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 183 (1962).

[5] (a) R. L. Letsinger and S. B. Hamilton, *ibid.*, **80**, 5411 (1958); (b) M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3076 (1958).



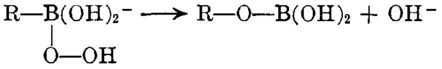
isomeric alcohol from the expected by-product, dibutyl 1-methylcyclohexene-5-boronate, but this isomer has not been proved absent. Anthracene did not react with dibutyl ethyleneboronate at 200°. The reaction of cyclopentadiene with butyl divinylborinate has been reported.[6] Dibutyl acetyleneboronate reacts with cyclopentadiene in refluxing chlorobenzene (approx. 130°) to yield dibutyl norbornadiene-2-boronate.[7]



Although the conversion obtained was only 25%, much of the unchanged acetyleneboronic ester could be recovered. The conversion was not improved by running the reaction in a sealed tube. Use of a higher boiling solvent, cumene, increased the conversion to 49% but caused by-product formation. Evidence for the norbornadiene structure includes the infrared spectrum and hydrogen peroxide deboronation to 5-norbornene-2-one, isolated as the 2,4-dinitrophenylhydrazone.[3]

Discussion

The assignment of the *endo* and *exo* configurations to the two 5-norbornene-2-boronic acids and their derivatives is firmly established by the stereospecific deboronations with hydrogen peroxide. The mechanism of the deboronation process is probably similar to that found with benzeneboronic acid.[8] Retention of con-



$$R{-}\underset{\displaystyle O{-}OH}{B}(OH)_2^- \longrightarrow R{-}O{-}B(OH)_2 + OH^-$$

figuration of the carbon atom is expected in this process.[9] Even if the mechanistic details were somewhat different from the path postulated, the history of electrophilic substitution at saturated carbon implies that a stereospecific inversion of configuration is unlikely but retention is common.[10]

The increasing proportion of *exo* adduct with increasing bulkiness of the dialkoxyboryl group is in accord with the presently accepted mechanism of the Diels–Alder reaction[11] and, like the steric control of the hydroboration of norbornene,[9] provides further support for the identification of the *endo* and *exo* isomers. That the *endo/exo* ratios in Table I are kinetically controlled was shown by the failure of either dibutyl *endo*- or *exo*-5-norbornene-2-boronate to isomerize at 120° and of the *exo* acid to isomerize in refluxing benzene. In considering the steric effect of the dihydroxyboryl group a further complication, the possible equilibration of the acid with anhydride (boroxine) and water, should be considered. However, the anhydride ring is probably less bulky than the di-*n*-butoxyboryl group and would thus qualitatively resemble the acid. Furthermore, anhydride formation was probably suppressed by the addition of water to the reaction mixtures, and the absence of polymer formation implies that little of the unstable ethyleneboronic anhydride[12] could have been present. The *endo/exo* ratios are smaller than might have been predicted from those of the isoelectronic acrylic acid derivatives.[3] However, boron is larger than carbon, which may lead to greater steric repulsion and/or less favorable *p*-orbital interaction with the diene in the transition state leading to *endo* product. In terms of free energies of activation, the difference between the 85/15 *endo/exo* ratio from the condensation of methyl acrylate[3] and the 63/37 ratio from ethyleneboronic acid is small. The limited, qualitative data on the temperature dependence of the isomer ratios suggest that the heats of activation slightly favor the *exo* condensation of the *n*-butyl ester, considerably favor the *exo* condensation of the *t*-butyl ester; these results are in accord with the concept of steric control of the isomer ratio formulated above.

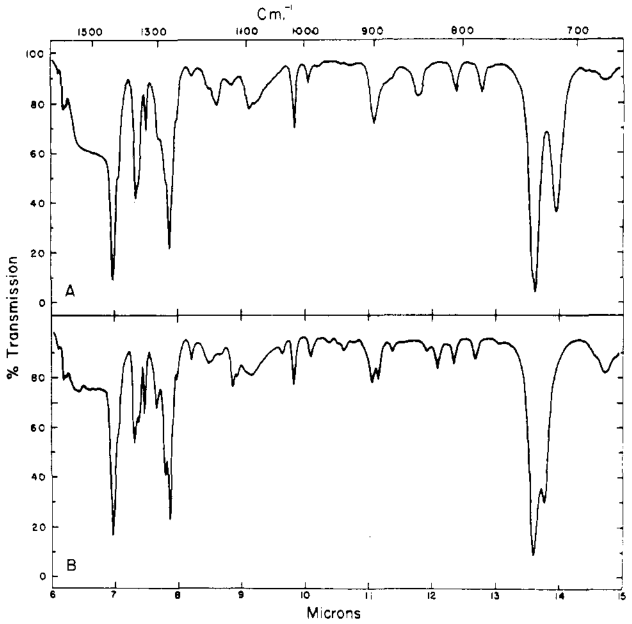


Fig. 1.—Infrared spectra of *o*-phenylenediamine derivatives of 5-norbornenyl-2-boronic acids, 0.05 g./ml. in CS_2, 0.1-mm. cell, taken with a Beckman IR-5. Curve A is *exo*, B is *endo*.

The accuracy of the analysis for *endo/exo* isomer ratios is undoubtedly sufficient for the present qualitative discussion, although it has not been quantitatively checked. An independent qualitative check on the isomer ratios has been carried out by converting the crude Diels–Alder adducts to the *n*-butyl ester form and examining the infrared spectra. The relative position of each entry in Table I was confirmed by this method. There is actually little reason to doubt the inherent accuracy of the hydrogen peroxide deboronation method, since there is evidence that the process is quantitative in general[13] and good yields of purified dehydronorborneols have been obtained in the present work. The dehydronorborneols were isolated from

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

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

[8] H. G. Kuivila and A. G. Armour, *ibid.*, **79**, 5659 (1957).

[9] A detailed discussion of this point has been presented by H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961).

[10] D. J. Cram, D. A. Scott, and W. D. Nielsen, *ibid.*, **83**, 3696 (1961) and preceding papers.

[11] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[12] D. S. Matteson, *J. Org. Chem.*, **27**, 3712 (1962).

[13] H. C. Brown, *Tetrahedron*, **12**, 117 (1961).

the crude reaction mixtures by sublimation before being gas chromatographed, but negligible isomer fractionation would be expected in this procedure.

Although the infrared spectra of the *o*-phenylenediamine derivatives shown in Fig. 1 indicate the purity of the samples and their diastereoisomeric relationship, the band shifts are too complex and most of the shifted bands too weak to assign any definite correlations with the *endo* and *exo* structures. The most characteristic bands seem to be a sharp peak at 12.0–12.1 μ in the *endo* series, weak or absent in the *exo*, and a somewhat broader band at 11.7–11.8 μ in the *exo* series, usually weaker or absent in the *endo*. The compounds examined include the boronic acids, *n*-butyl ester, *o*-phenylenediamine derivatives, 5-norbornene-2-carboxylic acids,[3] and dehydronorborneols. The strong band at 13.8–14.3 μ usually appeared at shorter wave lengths with the *endo* than the *exo* isomers, but the shift was very slight between the *n*-butyl boronic esters and was reversed with the carboxylic acids.

The activity of ethyleneboronic acid and its derivatives as dienophiles appears to correlate well in a qualitative fashion with simple molecular orbital calculations.[2,14a,b] These calculations imply chemically significant electron withdrawal from the vinyl group by the vacant p-orbital of boron, for which there is now considerable experimental support.[2,14] Present data are sufficient for qualitative placement of the ethyleneboronic esters in the series of reactivity toward cyclopentadiene. While dibutyl ethyleneboronate evidently reacts many times more slowly than methyl acrylate[3] with cyclopentadiene, in contrast to the surprisingly close rates observed for the boronic ester and ethyl acrylate with diazo compounds,[14a] it also appears from the drastic synthetic conditions generally required for weakly active dienophiles[15] that the activating effect of the dialkoxyboryl group is moderately strong.

Experimental

Di-*n*-butyl 5-Norbornene-2-boronates.—A 10.9-g. sample of dibutyl ethyleneboronate[2] was heated with an oil bath at 94–104° and five 2.5-ml. portions of cyclopentadiene (monomer) were added at approximately 0.8-hr. intervals. The total time was 4.3 hr. A reflux condenser and a nitrogen atmosphere were used. Distillation yielded 12.3 g. (83%) of dibutyl 5-norbornene-2-boronates (61% *exo*), b.p. 65–68° (0.05 mm.). The analytical sample was fractionated at 75–76° (0.1 mm.).

Anal. Calcd. for $C_{15}H_{27}BO_2$: C, 72.01; H, 10.88; B, 4.32. Found[16]: C, 71.81; H, 11.07; B, 4.53.

A solution of 2.28 g. of dibutyl ethyleneboronate and 2 g. of cyclopentadiene kept at 25° for 22 hr. yielded 0.41 g. (15%) of the adduct (66% *exo*).

A sample of the *endo* isomer was prepared by treating a portion of 94% *endo*-5-norborneneboronic acid with excess butanol, distilling the butanol–water azeotrope (20 mm.) and then the butyl ester.

Anal. Found: C, 71.79; H, 11.10; B, 4.50.

A sample enriched in *exo* isomer was prepared by treating 7.5 g. of 73% *exo*-*t*-butyl ester with 4 ml. of water and 30 ml. of 1-butanol and distilling as described above. The differences in the infrared spectra of the above samples were in agreement with the differing *endo*/*exo* ratios.

Anal. Found: C, 71.67; H, 11.20; B, 4.65.

Di-*tert*-butyl *exo*-5-Norbornene-2-boronate.—By the procedure described above for the *n*-butyl ester, 10.1 g. of di-*t*-butyl ethyleneboronate[12] and six 3-ml. portions of cyclopentadiene at equal intervals over a period of 7.5 hr. at 95–125° yielded 8.9 g. (65%) of the adduct, b.p. 49–53° (0.1 mm.), 73% *exo*.

Anal. Found: C, 72.20; H, 10.95; B, 4.43.

***endo*-5-Norbornene-2-boronic Acid.**—A suspension of 3.6 g. of ethyleneboronic acid[2,12] and 0.5 ml. of water in 25 ml. of benzene was refluxed under nitrogen 4.5 hr. During this time five 2-ml. portions of cyclopentadiene were added at approximately equal intervals. In one run, the acid was converted to the *n*-butyl ester, isolated by distillation in 62% yield and found to be 63% *endo*. In another, the benzene solution was concentrated and the residual boronic acid was recrystallized twice from ether, m.p. 105° dec.; this material was 94% *endo*. A similar sample (checked by infrared) was analyzed.

Anal. Calcd. for $C_7H_{11}BO_2$: C, 60.93; H, 8.04; B, 7.84. Found: C, 60.73; H, 8.24; B, 7.96.

***exo*-5-Norbornene-2-boronic Acid** (73%).—Treatment of the *n*-butyl ester derived from the *t*-butyl ester with water and removal of the butanol as the azeotrope led to the boronic acid, 73% *exo*, in 90% yield. The analytical sample was recrystallized once from water.

Anal. Found: C, 60.58; H, 7.89; B, 8.11.

Repeated fractional crystallization from ether or acetone–water concentrates the *exo*-boronic acid in the mother liquor to 80–90% purity and, starting from a 60% *exo* mixture, serves as the most convenient source of this material.

***o*-Phenylenediamine Derivative of *exo*-5-Norbornene-2-boronic Acid.**—A solution of 0.50 g. of dibutyl 5-norbornene-2-boronate, 61% *exo*, and 0.22 g. of *o*-phenylenediamine in 6.5 ml. of toluene was distilled at atmospheric pressure to remove butanol and toluene. Sublimation of the solid residue at 110° (0.1 mm.) yielded 0.42 g. (84%) of the derivative of the mixture. Five recrystallizations from carbon tetrachloride followed by sublimation yielded the pure *exo* derivative, m.p. 138–141° dec.; the infrared spectrum of this material is shown in Fig. 1.

Anal. Calcd. for $C_{13}H_{15}BN_2$: C, 74.32; H, 7.20; B, 5.15; N, 13.33. Found: C, 73.98; H, 7.19; B, 5.30; N, 13.46.

***o*-Phenylenediamine Derivative of *endo*-5-Norbornene-2-boronic Acid.**—A solution of 0.76 g. of *endo*-5-norbornene-2-boronic acid (94%) and 0.6 g. of *o*-phenylenediamine in toluene was distilled at atmospheric pressure to remove water and toluene. Sublimation of the residue at 110° (0.1 mm.) yielded 1.16 g. (90%) of the derivative, which was then dissolved in approx. 50 ml. of hot petroleum ether (b.p. 30–60°), cooled to 5°, and seeded with both the *exo* derivative and *o*-phenylenediamine. After removal of the first crop of impure material, concentration of the mother liquor and sublimation of the residue yielded 0.59 g. of the pure *endo* derivative, m.p. 94–98°; the infrared spectrum is shown in Fig. 1.

Anal. Found: C, 74.53; H, 7.26; B, 5.13; N, 13.34.

Determination of *endo*/*exo* Ratios.—The butyl esters were converted to the boronic acids before analysis to avoid interference by butanol in the isolation of the dehydronorborneols. Addition of 2 ml. of water/g. of ester and concentration at 20 mm. gave 90–98% yields of boronic acid residue. A suspension of 1 g. of norborneneboronic acid in 30 ml. of water was treated with 0.9 ml. of 30% hydrogen peroxide and 2.5 ml. of 2.5% potassium hydroxide at 0°, then allowed to stand overnight at room temperature. The solution was treated with 10 ml. of 5% sodium hydroxide and saturated with sodium chloride, then extracted with three 25-ml. portions of ether. After drying over magnesium sulfate the ether was evaporated and the residue was sublimed to yield 72–90% of the dehydronorborneols, which were analyzed by gas chromatography on a Ucon Polar on firebrick column.[4] Analysis of the *o*-phenylenediamine derivatives was less satisfactory. The sample which was 99% *exo* was treated directly with alkaline hydrogen peroxide to yield 15% of *exo*-dehydronorborneol and much residue. The *endo* derivative was not analyzed directly but hydrolyzed to the acid first.

Regeneration of *endo*-5-Norbornene-2-boronic Acid from the *o*-Phenylenediamine Derivative—An 0.85-g. sample of the *o*-phenylenediamine derivative from 94% *endo*-boronic acid was hydrolyzed by treatment with 15 ml. of 5% aqueous sodium hydroxide at 50° for 3 hr. Removal of non-acidic material by extraction with ether was followed by addition of hydrochloric acid, which precipitated 0.39 g. (70%) of the boronic acid, found by analysis to be 97% *endo*.

Thermal Stabilities.—Samples of 94% dibutyl *endo*- and 73% *exo*-norborneneboronates heated at 116–120° 6 hr. under nitrogen showed no detectable isomerization when examined by infrared.

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(14) (a) D. S. Matteson, *J. Org. Chem.*, **27**, 4293 (1962); (b) C. D. Good and D. M. Ritter, *J. Am. Chem. Soc.*, **84**, 1162 (1962); (c) T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.*, 3103 (1961).

(15) H. L. Holmes, *Org. Reactions*, **4**, 60 (1948).

(16) Microanalyses by Galbraith Laboratories, Knoxville, Tenn.

Refluxing moist 73% *exo*-boronic acid 4.5 hr. in benzene followed by conversion to the butyl ester for infrared comparison showed no change in the isomer ratio but a trace of decomposition to butyl borate.

Dibutyl 1,4,5,6,7,7-Hexachloro-5-norbornene-2-boronate.—Heating 7 g. of perchlorocyclopentadiene with 4.6 g. of dibutyl ethyleneboronate at 110–115° under nitrogen for 20 hr. followed by two simple distillations yielded 9.35 g. (82%) of the adduct, b.p. 147–151° (0.1 mm.). A center cut was analyzed, b.p. 150–151° (0.1 mm.), $n^{23.5}\text{D}$ 1.5043.

Anal. Calcd. for $C_{15}H_{21}BCl_6O_2$: C, 39.43; H, 4.63; B, 2.37; Cl, 46.56. Found: C, 39.69; H, 4.45; B, 2.52; Cl, 46.66.

Dibutyl Norbornadiene-2-boronate.—A solution of 1.82 g. of dibutyl acetyleneboronate[7] in 7.5 ml. of chlorobenzene was heated to vigorous reflux, 3 ml. of cyclopentadiene was added, and refluxing under nitrogen was continued 15 hr. Distillation yielded 1.1 g. of impure recovered dibutyl acetyleneboronate followed by 0.65 g. (25%) of dibutyl norbornadieneboronate, b.p. 80–85° (0.3 mm.). The analytical sample was redistilled through a short column, b.p. 74–75° (0.1 mm.), $n^{27.5}\text{D}$ 1.4634, twin C=C infrared peaks at 6.33 and 6.47 μ (in CCl_4).

Anal. Calcd. for $C_{15}H_{25}BO_2$: C, 72.59; H, 10.15; B, 4.36. Found: C, 72.72; H, 10.12; B, 4.46.

When the reaction was carried out in refluxing cumene (approx. 150°) the yield of dibutyl norbornadieneboronate was increased to 49% but considerable higher boiling residue was formed and distillation of the product failed to yield a pure sample; however, the reactivity of the material toward air (gum formation on storage) has not been ruled out as the cause of the 3% low carbon content found. Carrying out the reaction in a sealed tube at 140° gave a 25% conversion and offered no advantage.

Treatment of the norbornadieneboronic ester with hydrogen peroxide and 2,4-dinitrophenylhydrazine in acidic aqueous ethanol[2] yielded 40% of twice crystallized 2,4-dinitrophenylhydrazone of 5-norbornene-2-one, m.p. 169–172° (reported m.p. 175°).[3]

Dibutyl 1-Methylcyclohexene-4-boronate.—A mixture of 4.2 g. of dibutyl ethyleneboronate, 4.4 ml. of isoprene, and 0.01 g. of phenothiazine was heated in a sealed tube at 130–140° for 20 hr. Distillation yielded 4.87 g. (85%) of the adduct, b.p. 73–77° (0.08 mm.). An analytical sample was redistilled, b.p. 76–78° (0.08 mm.), $n^{25}\text{D}$ 1.4486.

Anal. Calcd. for $C_{15}H_{29}BO_2$: C, 71.43; H, 11.59; B, 4.29. Found: C, 71.35; H, 11.35; B, 4.41.

Conversion of the butyl ester to the boronic acid followed by treatment with alkaline hydrogen peroxide yielded 58% of 1-methylcyclohexen-4-ol, b.p. 80–87° (20 mm.), $n^{25}\text{D}$ 1.4760 [reported[17] b.p. 89° (26 mm.), $n^{22}\text{D}$ 1.4803]. Gas chromatography under the conditions which separated the dehydronorborneols yielded only one peak except for a few per cent impurity believed to be butanol. The alcohol was converted to its 3,5-dinitrobenzoate, m.p. 104–106° after several recrystallizations (reported[17] m.p. 107°).

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[17] E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 615 (1949).

Dibutyl Acetyleneboronate: Preparation and Some Additions of Free Radicals[1]

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Dibutyl acetyleneboronate has been prepared *via* the addition of ethynylmagnesium bromide to methyl borate. The ethynyl–boron linkage is stable in neutral or acidic hydroxylic solvents but is rapidly cleaved by bases as mild as sodium bicarbonate. Reagents that are reactive in radical-catalyzed additions to unsaturated systems generally add efficiently to the acetyleneboronic ester to yield the substituted ethyleneboronic ester.

The successful preparation of ethyleneboronic esters and their utility in the synthesis of new types of organoboron compounds[3] led us to extend our work to the corresponding acetylenic series. Although the general synthesis of boronic acids[4] and the necessary alkyl borates and Grignard reagents have been known for a long time, reports of acetyleneboronic acid derivatives have been confined to recent preliminary announcements and a patent.[1b,5]

Synthesis.—The first attempted preparation was that of dibutyl 1-hexyne-1-boronate, which was obtained in 40% yield from treatment of methyl borate with 1-hexynylmagnesium bromide followed by the usual acidification and esterification with butanol.

$$C_4H_9C{\equiv}CMgBr + B(OCH_3)_3 \longrightarrow \longrightarrow C_4H_9C{\equiv}CB(OC_4H_9)_2$$

One seemingly innocuous traditional step in work-up procedure,[3] neutralization of excess acid with sodium bicarbonate, was omitted when it was observed that the final water wash was nearly neutral. The initial results would have been discouraging if this step or any other base treatment had been included.

A good preparation of ethynylmagnesium bromide in tetrahydrofuran has been described recently.[6] This material was used for the preparation of dibutyl acetyleneboronate, $HC{\equiv}CB(OC_4H_9)_2$. Washing with water saturated with sodium chloride proved inefficient for removing excess mineral acid remaining from acidification of the reaction mixture. Addition of sodium bicarbonate led to a sudden increase in the rate of effervescence as the pH of the aqueous phase rose past 7 and only a low yield of acetyleneboronic ester survived. With pure samples of the boronic ester, it was shown that aqueous sodium bicarbonate, magnesium hydroxide, ammonia, or sodium hydroxide catalyzed rapid decomposition to acetylene, confirmed by precipitation of silver acetylide when the gas was led into aqueous silver nitrate. However, dibutyl acetyleneboronate is stable in the presence of calcium carbonate and in neutral or moderately acidic hydroxylic solvents.

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[1] (a) Supported by National Science Foundation grants G9916 and G19906; (b) Preliminary communication: D. S. Matteson and K. Peacock, *J. Am. Chem. Soc.*, **82**, 5759 (1960).

[2] National Defense Education Act Fellow, 1959–1962.

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