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.), $n^{23.5}_{\mathrm{D}}$ 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.), $n^{27.5}_{\mathrm{D}}$ 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}_{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}_{D} 1.4760 [reported[17] b.p. 89° (26 mm.), n^{22}_{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.

(3) D. S. Matteson, *J. Am. Chem. Soc.*, **82**, 4228 (1960).

(4) E. Khotinsky and M. Melamed, *Ber.*, **42**, 3090 (1909).

(5) (a) Acetyleneboronic acid and dibutyl 1-propyne-1-boronate: T. L. Heying, S. L. Clark, and H. Stange, Abstracts of Papers, 132nd National Meeting of the American Chemical Society, New York, September, 1957, p. 16-N. (b) Dibutyl vinylacetyleneboronate and 1-propyne-1-boronate: V. S. Zavgorodnii and A. A. Petrov, *J. Gen. Chem. USSR* (Engl. Transl.), **31**, 2268 (1961). (c) Possible synthesis of phenylacetyleneboronic acid: W. H. Pittman, *Dissertation Abstr.*, **20**, 4528 (1960). (d) Preparation of acetyleneboronates from ethynylsodium: G. W. Willcockson, U. S. Patent 3,036,111 (May 22, 1962). (e) Other types of ethynylboron compounds: J. Soulié and A. Willemart, *Compt. rend.*, **251**, 727 (1960); D. Giraud, J. Soulié, and P. Cadiot, *ibid.*, **254**, 319 (1962); H. Hartmann and K.-H. Birr, *Z. anorg. allgem. Chem.*, **290**, 174 (1959); earlier literature summarized in ref. 1b.

(6) L. Skattebol, E. R. H. Jones, and M. C. Whiting, *Org. Syn.*, **39**, 56 (1959).

Although the experimental procedure outlined gives approximately 60% yields of dibutyl acetyleneboronate, minor variations in the procedure may reduce the yield to 25–50%. It appears to be important that the ethynylmagnesium bromide be carefully prepared from pure acetylene and that efficient stirring and low temperature be maintained in the reaction vessel during the addition of the Grignard reagent to the methyl borate. Fractional distillation of the solvents from the product is used to avoid the possible loss of volatile dimethyl acetyleneboronate. Some variations make no difference; the reaction mixture may be acidified with either aqueous acid or anhydrous hydrogen chloride as long as the temperature is kept below −70° until excess acid is present, and the excess acid may be removed from the product either by repeated washing or by the less tedious treatment with calcium carbonate. Use of a high speed, dispersion-type stirrer[7] or simultaneous addition of the Grignard reagent and methyl borate[7] did not seem to help. When the acetylenic Grignard reagent was prepared in diethyl ether, dibutyl acetyleneboronate was obtained in about 10% yield; no evidence of any tetrabutyl acetylenebisboronate was found.

Reactions.—The reactivity of dibutyl acetyleneboronate toward electrophilic, nucleophilic and free radical reagents has been examined. Only free radical and four-center type additions have been found synthetically useful. The latter, including the Diels–Alder reaction with cyclopentadiene[1b,8] and the cycloaddition of diazo compounds,[9] are described in other papers.

Free radicals add to dibutyl acetyleneboronate without disturbing the carbon–boron bond. Bromotrichloromethane adds efficiently to dibutyl acetyleneboronate in the presence of an azonitrile initiator to form the 1:1 adduct.

$$CCl_3CH{=}CBrB(OC_4H_9)_2$$

The less active carbon tetrachloride fails to react in synthetically significant amounts. Other halogen-containing adducts include those with hydrogen bromide and bromine.

$$BrCH{=}CHB(OC_4H_9)_2 \qquad BrCH{=}CBrB(OC_4H_9)_2$$

Dibutyl 2-bromoethyleneboronate is formed on passing hydrogen bromide through dibutyl acetyleneboronate under ultraviolet light; its structure is supported by its rapid degradation to acetylene (confirmed with silver ion) by aqueous sodium bicarbonate, behavior characteristic of the known 2-chloroethyleneboronic esters.[10] Bromine adds only sluggishly to dibutyl acetyleneboronate under ordinary room illumination but rapidly when an incandescent light is placed close to the reaction mixture to form dibutyl 1,2-dibromoethyleneboronate in excellent yield. This behavior appears to be characteristic of acetylenic compounds[11] and contrasts with the exceedingly rapid, presumably electrophilic, addition of bromine to dibutyl ethyleneboronate at −70° in methylene chloride to yield dibutyl 1,2-dibromoethaneboronate.[12]

Thiols add readily to dibutyl acetyleneboronate; the 1:1 adducts have been obtained with 1-hexanethiol, thiophenol, and thiolacetic acid in the presence of azobisisobutyronitrile.

$$RSH + HC{\equiv}CB(OC_4H_9)_2 \longrightarrow RSCH{=}CHB(OC_4H_9)_2$$

The structure of the hexanethiol adduct, 2-(1-hexylthio)ethyleneboronate, is supported by deboronation with hydrogen peroxide in the presence of 2,4-dinitrophenylhydrazine to yield the 2,4-dinitrophenylhydrazone of *n*-hexylthioacetaldehyde.

$$C_6H_{13}SCH_2CH{=}NNHC_6H_3(NO_2)_2$$

Further support is provided by the degradation to acetylene with potassium hydroxide. It also appears that two moles of hexanethiol may add to dibutyl acetyleneboronate at low temperatures under ultraviolet irradiation, but the high boiling adduct decomposed on attempted distillation. The thiolacetic acid adduct appears to be unstable under the conditions used for its preparation, moderately good yields being obtained with short reaction times but decomposition and low yields resulting from longer heating. Hydrogen sulfide did not yield any adduct with dibutyl acetyleneboronate under the conditions used for the successful addition to butyl divinylborinate[13]; some decomposition to butyl borate occurred.

In summary, the reactivity of dibutyl acetyleneboronate toward free radicals is lower than that of dibutyl ethyleneboronate but is sufficient for synthetically useful results with the more active reagents. The stereochemistry of the additions has not yet been investigated.

Because of the sensitivity of dibutyl acetyleneboronate to bases, the conventional additions of nucleophilic reagents to acetylenes cannot be carried out with this compound. Sodium hydride suspended in refluxing 1,2-dimethoxyethane caused some decomposition to acetylene and black polymer. Ethynylmagnesium bromide apparently failed to add to dibutyl acetyleneboronate, no diethynyl compound being isolated after the usual work-up procedure. Dibutyl acetyleneboronate is fairly inert toward electrophilic reagents, as shown by its behavior with bromine. Attempts to form cyclic trimer or tetramer with bis(triphenylphosphine)nickel dicarbonyl or nickel acetylacetonate led only to formation of black polymer and butyl borate.

Experimental

Dibutyl Acetyleneboronate.—A solution of 0.5 mole of ethynylmagnesium bromide[6] in 600 ml. of tetrahydrofuran (sufficient to prevent crystallization of the Grignard reagent at about 30°) was added under nitrogen over a period of 40–50 min. to a vigorously stirred solution of 65 ml. of trimethyl borate in 630 ml. (1 lb.) of commercial anhydrous ether kept below −68°.[14] After stirring 1.5 hr. longer at −70°, the mixture was acidified with a slow stream of gaseous hydrogen chloride at −70° and 500 ml. of saturated aqueous sodium chloride was added, the mixture being kept near −70° during addition of the first 50 ml. but allowed to warm toward 0° after that. Approximately 0.3 g. of phenothia-

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(7) R. M. Washburn, E. Levens, C. F. Albright, and F. A. Billig, *Org. Syn.*, **39**, 3 (1959).

(8) D. S. Matteson and J. O. Waldbillig, *J. Org. Chem.*, **28**, 366 (1963).

(9) D. S. Matteson, *ibid.*, **27**, 4293 (1962).

(10) H. R. Arnold, U. S. Patents 2,402,589 and 2,402,509; W. A. Lazier and P. L. Salzberg, U. S. Patent 2,402,591; *Chem. Abstr.*, **40**, 5769 (1946).

(11) R. Daniels and L. Bauer, *J. Chem. Educ.*, **35**, 444 (1958).

(12) This compound has also been prepared and some of its reactions studied by B. M. Mikhailov and P. M. Aronovich, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 927 (1961); *Chem. Abstr.*, **55**, 24541d (1961).

(13) D. S. Matteson, *J. Org. Chem.*, **27**, 275 (1962).

(14) Tetrahydrofuran was distilled from lithium aluminum hydride. The acetylene was the purified grade (99.5%) from the Matheson Co., further dried as described in ref. 6. Methyl borate of 99.5% minimum purity as supplied by Callery Chemical Co. was used directly.

zine was added. Approximately 100 ml. of water was added to dissolve most of the precipitated salt, the aqueous phase was separated and extracted with three 100-ml. portions of 1-butanol, and the combined organic phase was stirred with 250 ml. of saturated sodium chloride while calcium carbonate was added in several portions until the pH of the aqueous phase rose to 5. The organic phase was separated and filtered. The ether and tetrahydrofuran were distilled rapidly through an efficient 30-cm. vacuum-jacketed column packed with Podbielniak nichrome helices. The pressure was lowered enough to keep the b.p. near 25–35°, maintaining rapid reflux and thus some fractionation in the column. Distillation of butanol–water azeotrope and butanol at 20 mm. followed until the pot temperature reached 100°; the vacuum pump was then used. The yield of fractionated dibutyl acetyleneboronate, b.p. 30–32° (0.3 mm.), was 53–58 g. (58–63%). The material is stable on storage at 5° under nitrogen without any radical inhibitor. An analytical sample was redistilled, b.p. 34° (0.1 mm.), n^{26}D 1.4180. The infrared spectrum (neat or in CCl_4) showed a sharp acetylenic C—H band at 3.10 μ and a C≡C band at 4.84 μ.

Anal. Calcd. for $C_{10}H_{19}BO_2$: C, 65.96; H, 10.52; B, 5.94. Found[15]: C, 66.09; H, 10.73; B, 5.94.

Dibutyl 1-Hexyne-1-boronate.—Hexynylmagnesium bromide from 41 g. of 1-hexyne and 0.5 mole of methylmagnesium bromide refluxed 18 hr. in 200 ml. of ether was added to 63 ml. of trimethyl borate in 300 ml. of ether below −55° with stirring under nitrogen. After adding 150 ml. more ether to the slurry, the previously described[3] ritual for acidification was followed. The aqueous phase was extracted with ether, the combined organic phase was washed with three 100-ml. portions of 10% sodium chloride and 300 ml. of butanol was added. Fractional distillation to separate butyl borate yielded 47 g. (39%) of dibutyl 1-hexyne-1-boronate, b.p. 85–90° (0.1 mm.), center cut n^{26}D 1.4357, C≡C band at 4.58 μ.

Anal. Calcd. for $C_{14}H_{27}BO_2$: C, 70.60; H, 11.43; B, 4.54. Found: C, 70.40; H, 11.53; B, 4.76.

Dibutyl 3,3,3-Trichloro-1-bromopropene-1-boronate.—A mixture of 1.82 g. (0.01 mole) of dibutyl acetyleneboronate and 7.5 ml. of bromotrichloromethane was heated under nitrogen with an oil bath at 95° for a total of 2.5 hr. and treated with two 0.03-g. portions of azobisisobutyronitrile after 0 and 1 hr. Distillation yielded 3.4 g. (90%) of the adduct. The analytical sample was fractionated, b.p. 102° (0.1 mm.), $n^{25.5}$D 1.4854, C=C band (neat) 6.12 μ.

Anal. Calcd. for $C_{11}H_{19}BBrCl_3O_2$: C, 34.73; H, 5.04; B, 2.84; Br + Cl, 1.624 mg. AgX/mg. sample. Found: C, 35.09; H, 5.33; B, 3.03; Br + Cl, 1.629 mg. AgX/mg. sample.

Dibutyl 2-(1-Hexylthio)ethyleneboronate.—By the above procedure, 1.82 g. of dibutyl acetyleneboronate and 1.24 g. of 1-hexanethiol at 80–85° 3 hr. with two 0.03-g. portions of azobisisobutyronitrile yielded 72% of the adduct, b.p. 120° (0.1 mm.), C=C band (neat) at 6.40 μ, strong and broad.

Anal. Calcd. for $C_{16}H_{33}BO_2S$: C, 63.99; H, 11.08; B, 3.60; S, 10.68. Found: C, 63.75; H, 11.15; B, 3.42; S, 10.87.

Dibutyl 2-Phenylthioethyleneboronate.—By the above procedure, 20.0 g. of dibutyl acetyleneboronate and 12.7 g. of thiophenol in 25 ml. of refluxing benzene 3 hr. with three 0.05-g. portions of azobisisobutyronitrile yielded 26–28 g. (86–92%) of adduct, b.p. 124–126° (0.1 mm.), $n^{23.5}$D 1.5242, strong C=C band at 6.40 μ.

Anal. Calcd. for $C_{16}H_{25}BO_2S$: C, 65.75; H, 8.62; B, 3.70; S, 10.97. Found: C, 65.88; H, 8.80; B, 3.92; S, 11.12.

Dibutyl 2-Acetylthioethyleneboronate.—By the above procedure, 7.3 g. of dibutyl acetyleneboronate and 4.2 g. of thiolacetic acid in 15 ml. of refluxing benzene 3 hr. with two 0.1-g. portions of azobisisobutyronitrile yielded 6.6 g. (64%) of adduct, b.p. 93–95° (0.1 mm.), C=O band at 5.88, C=C band at 6.39 μ.

Anal. Calcd. for $C_{12}H_{23}BO_3S$: C, 55.82; H, 8.98; B, 4.19; S, 12.42. Found: C, 55.88; H, 9.20; B, 4.42; S, 12.72.

2-Acetylthioethyleneboronic Acid.—The butyl ester was hydrolyzed by adding excess water and distilling the butanol–water azeotrope at 20 mm. The boronic acid was recrystallized twice from warm water, 54% yield, m.p. 120–122°.

Anal. Calcd. for $C_4H_7BO_3S$: C, 32.91; H, 4.83; B, 7.41; S, 21.96. Found: C, 32.69; H, 4.70; B, 7.62; S, 22.06.

(1-Hexylthio)acetaldehyde 2,4-Dinitrophenylhydrazone.—The procedure previously described[3] for deboronation with hydrogen peroxide in the presence of 2,4-dinitrophenylhydrazine was applied to 0.30 g. of dibutyl 2-(1-hexylthio)ethyleneboronate. The product was recrystallized from methanol, yield 0.20 g. (59%), m.p. 175–176°.

Anal. Calcd. for $C_{14}H_{20}N_4O_4S$: C, 49.40; H, 5.92; N, 16.46; S, 9.42. Found: C, 49.13; H, 5.74; N, 16.46; S, 9.34.

Potassium hydroxide degradation of dibutyl 2-(1-hexylthio)ethyleneboronate was carried out with excess solid potassium hydroxide as previously described[3] at 140–160°. A 70% yield of acetylene was obtained, confirmed by its reaction with silver ion.

Dibutyl 2-Bromoethyleneboronate.—Dry hydrogen bromide was slowly bubbled through 5.20 g. of dibutyl acetyleneboronate stirred in a quartz flask 2.5 hr. and irradiated with a 500-w. mercury vapor lamp. The weight gain was 2.9 g. (theoretical 2.4). Distillation yielded 4.4 g. (58%) of the adduct, b.p. 62–65° (0.1 mm.), strong C=C band at 6.30 μ.

Anal. Calcd. for $C_{10}H_{20}BBrO_2$: C, 45.67; H, 7.67; B, 4.11; Br, 30.39. Found: C, 45.49; H, 7.51; B, 4.26; Br, 30.58.

Dibutyl 1,2-Dibromoethyleneboronate.—To 1.82 g. of dibutyl acetyleneboronate in 7 ml. of methylene chloride under nitrogen was added 1.60 g. of bromine dropwise over a period of 40 min. The flask was irradiated with an incandescent lamp and kept at 24–37° with a water bath during this time. Distillation yielded 3.0 g. (88%) of the adduct, b.p. 76–80° (0.1 mm.), $n^{29.8}$D 1.4747, C=C band at 6.28 μ.

Anal. Calcd. for $C_{10}H_{19}BBr_2O_2$: C, 35.13; H, 5.60; B, 3.16; Br, 46.75. Found: C, 35.12; H, 5.88; B, 3.30; Br, 47.04.

Dibutyl 1,2-Dibromoethaneboronate.—A solution of 4.0 g. of bromine in 10 ml. of methylene chloride was added to 4.60 g. of dibutyl ethyleneboronate[3] in 10 ml. of methylene chloride stirred at −70° over a period of 20 min. Distillation yielded 7.7 g. (90%) of the adduct; center cut, b.p. 94–95° (0.1 mm.), $n^{21.3}$D 1.4732 (reported[12] b.p. 142–143° (3 mm.), n^{20}D 1.4730).

Anal. Calcd. for $C_{10}H_{21}BBr_2O_2$: C, 34.92; H, 6.61; B, 3.15 Br, 46.47. Found: C, 34.69; H, 6.19; B, 3.32; Br, 46.55.

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