value of 7.7 dynes/cm. is found. Further substitution of this value into equation I provides an expression showing the variation of bond order "n" with bond distance "d." This expression is found to be

$$n = 1.16d^{1.5} \qquad \text{(III)}$$

From this equation, it is evident that the character of a B–N bond absorbing at 6.8 μ does not vary drastically with the bond distance. In order to obtain single or triple bond orders, *i.e.*, $n < 1.5$ or $n > 2.5$, it is necessary to have single bond lengths less than 1.18 Å. or triple bonds greater than 1.68 Å., respectively. Either case seems highly improbable, so one may assume that, if the bond at 6.8 μ indicates a stretching of boron–nitrogen, there must be a double bond involved.

In summation, the present investigation: (a) provides evidence corroborating a theory involving electronic shifts in the structures of aminoboranes, (b) contributes evidence for the assumption of double bond character and ethylene-like structures of this particular boron–nitrogen system, (c) describes an experimental procedure for the preparation of unsymmetrical tetraorgano substituted aminoboranes.

Acknowledgment is gratefully accorded to Dr. Carl F. Prenzlow for his assistance in making the calculations cited in this paper. The analyses recorded herein were made by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y., and the Galbraith Laboratory, Knoxville, Tenn.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON STATE UNIVERSITY]

Radical-catalyzed Additions to α,β-Unsaturated Boronic Esters[1,2]

BY DONALD S. MATTESON

RECEIVED JANUARY 30, 1960

Dibutyl ethyleneboronate, propene-2-boronate and 1-propene-1-boronate have been synthesized and their reactions with free radicals investigated. Bromotrichloromethane adds readily to the double bond of each of the three esters, carbon tetrachloride to the first two, and hexyl mercaptan to the only one tested, the first. The 1:1 adducts obtained represent the first general synthesis of aliphatic boronic esters (and their derivatives) containing other non-hydrocarbon functional groups. The first transfer constant in the reaction of dibutyl ethyleneboronate with carbon tetrachloride (calculated by means of a convenient new equation valid for dilute solutions) is 3.3 ($\pm$0.7) $\times 10^{-3}$, which provides strong evidence that the intermediate radical is stabilized by carbon–boron π-bonding. Simple molecular orbital calculations with appropriately selected parameters for boron predict accurately the qualitative chemical and spectral behavior of the α,β-unsaturated boronic esters and acids.

Study of α,β-unsaturated organoboron compounds may furnish useful information on two types of problems: the synthesis of organoboron compounds which contain other functional groups, discussed immediately below, and the determination of the strength of carbon–boron π-bonding, discussed under Transfer Constants and Molecular Orbital Calculations.

The number of known organoboron compounds containing other functional groups is severely restricted because of the ease with which carbon–boron bonds are broken by bases, oxidizing agents or acids and because of the small number of methods for making carbon–boron bonds, which ordinarily require the use of a Grignard reagent or other conditions incompatible with most types of functional groups.[3] The introduction of other functional groups after a boronic acid group is already present is a well-known practice in the aromatic series,[3,4] and in the present work is extended to aliphatic compounds by starting with α,β-unsaturated boronic esters, readily synthesized from the recently available vinyl-type Grignard reagents.[5] The selection of ethyleneboronic acid and its dibutyl ester as the starting point was dictated by anticipated reactivity and experimental convenience. The double bond of previously known α,β-unsaturated boronic acids is made unreactive by the presence of a phenyl,[6] a chloro[7] or two methyl groups[8] at the β-position. Known α,β-unsaturated organoboron compounds in which the double bond should be highly reactive (and in which it shows some evidence of conjugation with the vacant p-orbital of the boron atom) include vinyldimethylboron, trivinylboron and several related compounds,[9] as well as vinylboron difluoride,[10] all of which require vacuum techniques for handling.

Ethyleneboronic acid,[11] $CH_2{=}CHB(OH)_2$, was

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(1) Preliminary Communication: D. S. Matteson, THIS JOURNAL, **81**, 5004 (1959).

(2) Supported in part by National Science Foundation Grant G 9916.

(3) M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956).

(4) (a) H. R. Snyder, A. J. Reedy and W. J. Lennarz, THIS JOURNAL, **80**, 835 (1958); (b) K. Torssell, *Arkiv Kemi*, **10**, 507 (1957).

(5) (a) H. Normant, *Compt. rend.*, **239**, 1510 (1954); (b) H. E., Ramsden, J. R. Leebrick, S. D. Rosenberg, E. H. Miller, J. J. Walburn, A. E. Balint and R. Cserr, *J. Org. Chem.*, **22**, 1602 (1957).

(6) (a) N. N. Melnikov and M. S. Rokitskaya, *J. Gen. Chem. U.S.S.R.*, **8**, 1768 (1938); *C. A.*, **33**, 4790 (1939); (b) V. A. Sazonova and N. Ya. Kronrod, *J. Gen. Chem. U.S.S.R.* (English translation), **26**, 2093 (1956).

(7) (a) 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; *C. A.*, **40**, 5769 (1946). (b) Chlorovinylboron compounds have failed to undergo attempted free radical addition of such reagents as thiolacetic acid (H. R. Arnold, private communication); (c) A. E. Borisov, *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, 402 (1951); *C. A.*, **46**, 2995 (1952).

(8) R. L. Letsinger and I. H. Skoog, *J. Org. Chem.*, **18**, 895 (1953).

(9) T. D. Parsons and D. M. Ritter, THIS JOURNAL, **76**, 1710 (1954); T. D. Parsons, M. B. Silverman and D. M. Ritter, *ibid.*, **79**, 5091 (1957).

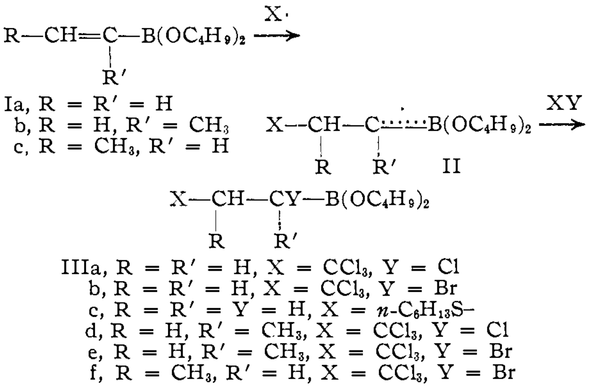
(10) (a) B. Bartocha, F. E. Brinckman, H. D. Kaesz and F. G. A. Stone, *Proc. Chem. Soc.*, 116 (1958); (b) D. M. Ritter, private communication (1959).

(11) During the course of this investigation, similar preparation of all the α,β-unsaturated boronic acids and esters reported in the present article was announced without experimental details by H. Normant and J. Braun, *Compt. rend.*, **248**, 828 (1959); *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1397 (1959); *C. A.*, **54**, 1266 (1960).

prepared by the addition of vinylmagnesium chloride[5b] to trimethyl borate below −50°, and then by hydrolysis. Uncontrollable polymerization or oxidation of much of the boronic acid occurred during the final stages of the isolation procedure, but could be avoided by *in situ* conversion to the dibutyl ester Ia.

In the presence of azobisisobutyronitrile as the initiator, carbon tetrachloride adds to dibutyl ethyleneboronate (Ia) or to dibutyl propene-2-boronate (Ib) to form dibutyl 1,3,3,3-tetrachloropropane-1-boronate (IIIa) or 2,4,4,4-tetrachlorobutane-2-boronate (IIId), respectively, presumably *via* a radical of the type II (Chart I).

CHART I



Ia, $R = R' = H$
b, $R = H, R' = CH_3$
c, $R = CH_3, R' = H$

IIIa, $R = R' = H, X = CCl_3, Y = Cl$
b, $R = R' = H, X = CCl_3, Y = Br$
c, $R = R' = Y = H, X = n\text{-}C_6H_{13}S\text{-}$
d, $R = H, R' = CH_3, X = CCl_3, Y = Cl$
e, $R = H, R' = CH_3, X = CCl_3, Y = Br$
f, $R = CH_3, R' = H, X = CCl_3, Y = Br$

The small transfer constants[12] (see below) makes a large excess of carbon tetrachloride necessary for good yields of 1:1 adducts. Dibutyl 1-propene-1-boronate, as is typical of non-terminal olefins, does not react efficiently with carbon tetrachloride. The more active[12] bromotrichloromethane adds in excellent yield to all three esters (I). Light-catalyzed addition of hexyl mercaptan to Ia, carried out at −70° to avoid any possibility of ester interchange,[7a] proceeded rapidly and efficiently. Other substances tested for possible addition to the double bond of dibutyl ethyleneboronate (Ia) included chloroform and aldehydes, the former yielding telomers and the latter proving unreactive.

For proof of structure, oxidation of either of the α-haloalkaneboronic esters IIIa or IIIb with hydrogen peroxide in the presence of 2,4-dinitrophenylhydrazine yielded the 2,4-dinitrophenylhydrazone of 3,3,3-trichloropropionaldehyde.

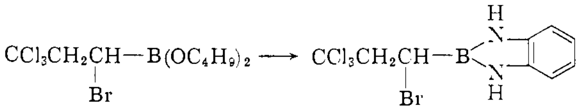
$$CCl_3CH_2CHClB(OC_4H_9)_2 \longrightarrow CCl_3CH_2CH{=}NNHAr$$

The structure proof for dibutyl 3-thianonane-1-boronate (IIIc) rests on the fact that a sulfide group and a boronic ester group separated by two carbon atoms should be capable of undergoing an elimination reaction in the presence of a base, Z^-

$$RSCH_2CH_2BZ_2 \xrightarrow{Z^-} RSCH_2CH_2BZ_3^- \longrightarrow RS^- + CH_2{=}CH_2 + BZ_3$$

Solutions of alkali in hydroxylic solvents failed to cause elimination, but the adduct IIIc was successfully degraded to ethylene in the presence of solid potassium hydroxide at 125°.

The stability of the α-haloalkaneboronic esters (IIIa,b,d,e,f) may be contrasted to that of fluoromethylboron difluoride,[13] which is reported to be unstable at room temperature (perhaps because it is a strong Lewis acid), but qualitatively resembles that of the known α-haloalkylsilicon compounds.[14] The α-halogen of compounds such as the carbon tetrachloride adduct IIIa is easily hydrolyzed, and neutralization of the ester with sodium bicarbonate appears to involve hydrolysis of both the ester and the α-chloro group. However, if contact with base is avoided and the α-haloalkaneboronic ester is instead hydrolyzed with cold water, hydrolysis of the α-halogen does not occur. Thus, 1-bromo-3,3,3-trichloropropane-1-boronic acid was prepared from the ester IIIb and purified by recrystallization from water. This acid polymerized with evolution of hydrogen bromide either on storage or on attempted recrystallization from hot methylcyclohexane. The ester IIIb also was converted to its *o*-phenylenediamine derivative[15] without affecting the α-bromine atom, again by employing temperatures near 0°, and the product was purified by sublimation.



The other classes of boronic esters, including the unsaturated esters I and the mercaptan adduct IIIc, underwent similar transformations of the ester group without difficulty.

Transfer Constants

The first transfer constant,[12a] C_1, in the reaction of carbon tetrachloride with dibutyl ethyleneboronate (Ia) is $3.3 \times 10^{-3} \pm 0.7 \times 10^{-3}$; with dibutyl propene-2-boronate (Ib), approximately 2.8×10^{-2}. Since transfer constants beyond C_1 are not of present interest, the traditional methods of data evaluation[12a] have been avoided. Instead, a convenient integrated equation valid for dilute solutions of the unsaturated reactant has been derived for finding C_1 from the quantities of reactants and products.

In the addition of a reagent XY to a vinyl monomer M, the intermediate radical XM· may react either with XY to yield the 1:1 adduct XMY (and X·) or with M to yield XM_2·, the ratio of the two rate constants being defined as C_1.[12a] If M is sufficiently dilute, XM_2· leads almost exclusively to the telomer XM_2Y, and the concentration of the solvent XY is a constant. These conditions lead to the equations

$$C_1 = ([M]/[XY])(d[XMY]/d[XM_2Y]) \qquad (1)$$

and

$$d[XMY] + 2d[XM_2Y] = -d[M] \qquad (2)$$

which may be combined and rearranged to

$$d[XMY] = -C_1[XY]d[M]/(2[M] + C_1[XY]) \qquad (3)$$

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[12] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957: (a) pp. 240–265; (b) pp. 47–53, 117–126, 132–140, 157–158.

[13] J. Goubeau and K. H. Rohwedder, *Ann.*, **604**, 168 (1957).

[14] P. D. George, M. Prober and J. R. Elliott, *Chem. Revs.*, **56**, 1065 (1956).

[15] (a) M. J. S. Dewar, V. P. Kubba and R. Pettit, *J. Chem. Soc.*, 3076 (1958); (b) R. L. Letsinger and S. B. Hamilton, THIS JOURNAL, **80**, 5411 (1958); (c) E. Nyilas and A. H. Soloway, *ibid.*, **81**, 2681 (1959).

and integrated to

$$[\mathrm{XMY}] = {}^1/_2C_1[\mathrm{XY}] \ln \left(\frac{2[\mathrm{M}]_0 + C_1[\mathrm{XY}]}{2[\mathrm{M}] + C_1[\mathrm{XY}]}\right) \quad (4)$$

where $[\mathrm{M}]_0$ and $[\mathrm{M}]$ are the initial and final concentrations of M, respectively. Integration of eq. 2, then simultaneous solution with eq. 4, yields

$$[\mathrm{XM_2Y}] = {}^1/_2([\mathrm{M}]_0 - [\mathrm{M}]) - {}^1/_4C_1[\mathrm{XY}] \ln \left(\frac{2[\mathrm{M}]_0 + C_1[\mathrm{XY}]}{2[\mathrm{M}] + C_1[\mathrm{XY}]}\right) \quad (5)$$

Although C_1 may be found by successive approximations from either eq. 4 or 5, the two results will not agree if the material balance is not quantitative. If, as appears likely in the present work, the compound lost is mainly M (Ia or Ib, volatile and hydrolyzable), it can be shown that eq. 4 yields a grossly low value of C_1 but the value from eq. 5 is only slightly too high.

It turns out to be experimentally impractical to work with M in such high dilution that formation of the higher telomer $\mathrm{XM_3Y}$ is truly negligible as assumed in deriving eq. 5. In fact, under the present experimental conditions it appears likely that up to 25% of the product assumed to be $\mathrm{XM_2Y}$ is actually $\mathrm{XM_3Y}$ (although $\mathrm{XM_4Y}$ appears to be negligible) if C_2 is, as usual,[12a] about 5 times C_1. However, the error in the calculated C_1 from this source appears to be less than 5%, since the hypothetical assumption that all $\mathrm{XM_2\cdot}$ radicals yield not $\mathrm{XM_2Y}$ but exclusively $\mathrm{XM_3Y}$ allows derivation of an equation analogous in form to eq. 5, and substitution of the experimental data into this hypothetical equation yields, as a result of partial mutual cancellation of false assumptions, values of C_1 only about 15% higher than those from eq. 5. Most of the total uncertainty in C_1 (±20%) arises from the usual errors inherent in determining product yields.

Interpretation.—The transfer constant C_1 is a function of the free energy difference between two transition states, and is useful for the present discussion only because it reflects qualitatively the otherwise inaccessible value of the delocalization energy of the radical $\mathrm{XM\cdot}$. Stable $\mathrm{XM\cdot}$ and $\mathrm{XM_2\cdot}$ radicals tend to have a stable transition state (compared to that for reaction of $\mathrm{XM\cdot}$ with XY) connecting them, resulting in a value of C_1 unusually low for the given solvent XY.[12] For example, C_1 for carbon tetrachloride with propylene is near 1, but with styrene is 6×10^{-4}.[12a] Electron-withdrawing substituents, as in allyl chloride, will relatively retard the reaction of $\mathrm{XM\cdot}$ with carbon tetrachloride and also lead to a low C_1.[12a] However, the inductive effect of a boron atom would be electron-donating, and the low values of C_1 for the boronic esters must result from radical stabilization due to electron delocalization as expressed by the canonical structures

$$\mathrm{CCl_3CH_2CH{-}B(OC_4H_9)_2} \longleftrightarrow \mathrm{CCl_3CH_2\overset{+}{C}H{-}\overset{-}{B}(OC_4H_9)_2}$$

The magnitude of the delocalization energy appears to be in the range 8–20 kcal./mole, *i.e.*, a sizable fraction of that[12b] of a benzyl-type radical.

The above conclusion is further supported in a qualitative fashion by the observed facile polymerization of ethyleneboronic acid and related compounds in the presence of oxygen, which would be unlikely if the intermediate radicals were not resonance-stabilized.[12]

Molecular Orbital Calculations[16]

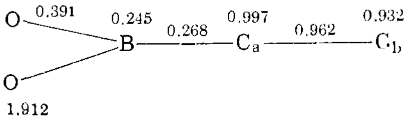
Simple molecular orbital calculations[17a] have been carried out for ethyleneboronic acid, with variation of the parameters for boron through suitable ranges. The values yielding good correlation of calculated quantities with the observed spectra and radical stabilities then are used to predict further properties.

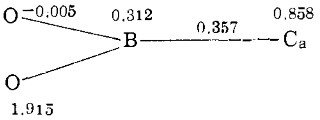
The effects of varying boron parameters on the calculated relative stability of the radical $\mathrm{XCH_2{-}\dot{C}H{-}B(OR)_2}$ and on the π-electron densities and C–C bond order of ethyleneboronic acid are summarized in Table I. (Varying the parameters for oxygen, holding all others constant, affects the calculated results only slightly, the electron-accepting power of the $\mathrm{-B(OR)_2}$ group and the radical stability both increasing if the coulomb integral α_O is increased, decreasing if the exchange integral $\beta_\mathrm{B-O}$ is increased.) Since, as discussed above under Transfer Constants, the delocalization energy of $\mathrm{XCH_2{-}\dot{C}H{-}B(OR)_2}$ is substantial, Table I suggests that the values selected for α_B and $\beta_\mathrm{B-C}$ should not be too low. An upper limit of $\beta_\mathrm{B-C} = 0.7\ \beta_\mathrm{C-C}$, similar to the ratio of the central to the terminal bond of butadiene, is suggested by Mulliken, Rieke and Brown's[18,17a] correlation of β with bond length. The values $\alpha_\mathrm{B} = \alpha_\mathrm{C} - \beta_\mathrm{C-C}$, $\beta_\mathrm{B-C} = 0.7\ \beta_\mathrm{B-C}$ and the other parameters mentioned in Table I lead to the following molecular diagrams for ethyleneboronic acid and $\mathrm{XCH_2{-}\dot{C}H{-}B(OH)_2}$, respectively.

TABLE I

α_B [a]	$\beta_{\mathrm{B-C_a}}$ [b]	Radical stabilization [c]	C–C π-bond order	π-Electron density C_a	C_b
−0.5	0.7	0.129	0.945	1.021	0.879
−1	.7	.098	.962	0.997	.932
−1.5	.7	.076	.973	.973	.977
−2	.7	.057	.978	.946	1.015
−1	.5	.060	.981	.976	0.988
−1	.9	.128	.936	1.025	0.863

[a] Tabulated as $-\lambda$ from the expression $\alpha_\mathrm{B} = \alpha_\mathrm{C} - \lambda\beta_\mathrm{C-C}$. In all calculations, $\alpha_{\mathrm{C_a}} = \alpha_\mathrm{C} - 0.1\lambda\beta_\mathrm{C-C}$, $\alpha_{\mathrm{C_b}} = \alpha_\mathrm{C}$, and except as otherwise noted, $\alpha_\mathrm{O} = \alpha_\mathrm{C} + 3\ \beta_\mathrm{C-C}$. [b] $\beta_\mathrm{C-C} = 1$; arbitrarily, $\beta_\mathrm{B-O} = \beta_\mathrm{C-C}$ [c] The energy required to break the π-bond in ethylene when $\mathrm{X\cdot}$ is added is $|2\beta|$; in ethyleneboronic esters, somewhat less; the difference is tabulated.





The energy levels for the boronic acid are (in units of β) 3.4637, 3 and 1.0309 for the filled and −0.7657 for the lowest unfilled orbital; for the radical, 3.4625 and 3 for the filled, 0.1624 for the half-filled orbital.

Further justification for the above selection of α_B not lower than $\alpha_\mathrm{C} - \beta_\mathrm{C-C}$ is provided by comparison with literature calculations on styrene and

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[16] (a) The author wishes to thank Dr. E. L. Wagner for numerous helpful discussions. (b) Calculations were performed by the Washington State University Computing Center on an IBM 650 Computer.

[17] B. Pullman and A. Pullman, "Les Théories Électroniques de la Chimie Organique," Masson et Cie, Paris, 1952: (a) pp. 176–216; (b) pp. 293, 636.

[18] R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941).

benzyl radical.[17b] Since these have been made assuming all exchange integrals equal, $\beta_{B-C} = 0.9\,\beta_{C-C}$ is used for this comparison (see Table I). The free valences of the terminal carbon atoms for styrene and ethyleneboronic acid are 0.821 and 0.796, respectively, and the radical stabilizations are 0.296 β and 0.128 β.

The parameters chosen for deriving the above molecular diagram also are consistent with spectral data. Propene-2-boronic acid shows only end absorption in the ultraviolet down to 205 mμ, in accord with the calculated value 1.8 β for the π–π^* transition when contrasted to the 1.4 β calculated for butadiene with the central bond parameter chosen as $2^{-1/2}\,\beta$. (The reported[8] ultraviolet spectrum of 2-methyl-1-propene-1-boronic acid, ϵ_{max} 1000 at 223 mμ, appears anomalous.) The infrared spectra of ethyleneboronic acid and its derivatives show definite evidence of conjugation, the C=C stretching band appearing at 1625–1605 cm.$^{-1}$, in accord with the calculated bond order, 0.962; the corresponding bond order for butadiene is 0.943, infrared frequency, 1597 cm.$^{-1}$.[19] The C–H bending bands of the terminal methylene group of ethyleneboronic acid derivatives appear at higher frequencies (see Experimental) than in ordinary olefins, as is characteristic when a double bond is conjugated with a group that withdraws electrons by π-delocalization.[19]

Table I indicates that lowering the electronegativity of the boron atom decreases the stability of the radical $XCH_2–\dot{C}H–B(OR)_2$. This effect could be achieved in practice by substituting a less electronegative element for the oxygen, and would result in improved reactivities and transfer constants for synthetic purposes. However, drastic changes in other parameters invalidate this generalization in certain situations, such as when the β_{B-O} of Table I is replaced by a considerably smaller value presumably appropriate for β_{B-CH_3} (*e.g.*, 0.25 β_{C-C}) in vinyldimethylboron, leading to the high radical stabilization 0.242 β if $\alpha_{CH_3} = \alpha_C$, $\alpha_B = \alpha_C - 1.5\,\beta_{C-C}$ and $\beta_{B-C} = 0.7\,\beta_{C-C}$. Dropping out the hyperconjugation ($\beta_{B-CH_3} = 0$) reduces the calculated radical stabilization to 0.103 β.

The trends in Table I and the above discussion actually apply to any compounds of the vinylmetallic type. For example, vinylsilicon compounds should have parameters α_{Si} and β_{Si-C} (involving a *d* orbital of Si) smaller than the corresponding α_B and β_{B-C}. Consequently, the intermediate radicals of the type $XCH_2\dot{C}H–SiZ_3$ should be more reactive than $XCH_2\dot{C}H–BZ_2$, as is indicated qualitatively by the published synthetic chemistry.[14]

On the basis of the calculated electron densities, ethyleneboronic acid derivatives would be expected to be dienophiles, to react with electrophilic reagents at C_a, and, provided side reactions at the boron atom do not prevent it, react with nucleophilic reagents at C_b.

Experimental[20]

Preparation of α,β-Unsaturated Boronic Acid Dibutyl Esters (I).—Vinylmagnesium halides were prepared by the usual method.[5b] A solution of the vinylmagnesium halide prepared from 12.16 g. (0.5 gram-atom) of magnesium and an excess of the appropriate vinyl-type halide in 150 ml. of tetrahydrofuran was kept warm enough to prevent crystallization and added dropwise over a period of 10–15 min., under nitrogen, to a vigorously stirred solution of 54.5 g. (0.55 mole) of trimethyl borate in 250 ml. of dry ether kept below −50°. The mixture was allowed to warm to about 20° to assure completion of the reaction, then cooled and stirred at −70° to −60° during the addition of 25 ml. of water. A 0.15-g. portion of phenothiazine was added. Beginning with the mixture at −70°, a solution of 20 ml. of hydrochloric acid and 35 ml. of phosphoric acid in 250 ml. of water was added dropwise. The mixture was stirred vigorously and allowed to warm gradually to about 0° during this addition; a slow rate of temperature rise helped prevent the mixture from congealing to a gummy mass impossible to stir. After all the solid material dissolved, the two phases were separated, and the aqueous solution was extracted with three 100-ml. portions of 1-butanol. The combined organic phases were washed with two 100-ml. portions of 10% sodium chloride solution, then 50 ml. of sodium chloride solution and enough solid sodium bicarbonate to raise the *p*H to 5. The organic phase was dried by freezing at −78° and the collected ice crystals were rinsed with 200–300 ml. of cold ether. Distillation through a 12-in. packed column at reduced pressure separated solvents, butanol–water azeotrope and high-boiling impurities from the desired boronic ester, which was collected in a receiver containing 10 mg. of phenothiazine. Preparation of analytical samples required treatment of the esters with butanol before refractionation.

Dibutyl Ethyleneboronate (Ia).—Vinylmagnesium chloride was converted to dibutyl ethyleneboronate on twice the described scale; yield 134 g. (72%), b.p. 35–40° (0.1 mm.), $n^{24.5}_{D}$ 1.4167; purity checked by analysis, found[21]: C, 65.12; H, 11.22. Analytical sample: b.p. 89° (14 mm.), $n^{25.8}_{D}$ 1.4160; infrared spectrum, significant bands only,[19,22] neat, cm.$^{-1}$: vinyl C–H stretch 3050(m); C=C stretch, 1610(m); vinyl C–H bend, 965(m) and 1010(m) with overtones 1930(w) and 2030(w); unassigned, 710(s), 730(s).

Anal.[20b] Calcd. for $C_{10}H_{21}BO_2$: C, 65.24; H, 11.50; B, 5.88. Found: C, 64.97; H, 11.64; B, 6.06.

Dibutyl Propene-2-boronate (Ib).—Isopropenylmagnesium bromide was converted to dibutyl propene-2-boronate in 62% yield, b.p. 65-67° (2 mm.). Analytical sample: b.p. 96° (14 mm.), $n^{25.8}_{D}$ 1.4190; infrared spectrum, significant bands,[19,22] neat, cm.$^{-1}$: =C–H stretch, 3050(m); C=C stretch, 1625(m); $=CH_2$ bend, 923(m) with overtones 1840–1850(w); unassigned, 2015(w).

Anal. Calcd. for $C_{11}H_{23}BO_2$: C, 66.69; H, 11.70; B, 5.46. Found: C, 66.47; H, 11.98; B, 5.56.

Dibutyl 1-Propene-1-boronate (Ic).—Propenylmagnesium bromide was converted to dibutyl 1-propene-1-boronate in 70% yield. Analytical sample: b.p. 99.5–100.5° (12 mm.), $n^{22.2}_{D}$ 1.4254; infrared spectrum, significant bands,[19,22] neat, cm.$^{-1}$: C=C, 1620(m) with shoulder, 1630(m); unassigned, 2020(w); =C—H bending bands evidently in region 980–1080, not clearly distinguishable. The double absorption at 1620–1630 suggests that the sample is a mixture of *cis* and *trans* isomers.

Anal. Calcd. for $C_{11}H_{23}BO_2$: C, 66.69; H, 11.70; B, 5.46. Found: C, 66.54; H, 11.88; B, 5.62.

Dibutyl 1,3,3,3-Tetrachloropropane-1-boronate (IIIa) (Transfer Constant).—A solution of 9.21 g. (0.05 mole) of dibutyl ethyleneboronate (Ia) in 3077 g. (20 moles) of carbon tetrachloride refluxed 24 hours under nitrogen and

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[19] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 34–53.

[20] (a) All m.p.'s are corrected. (b) Analyses by Galbraith Laboratories, Knoxville, Tenn., unless otherwise noted. Liquid analytical samples were distilled through a short column. (c) Infrared spectra were determined on a Perkin–Elmer model 21 or on a Beckman IR-5.

[21] Analysis by Weiler and Strauss, Oxford, England.

[22] An unassigned strong absorption appeared at 730–750 cm.$^{-1}$ (unless masked by a solvent) in all the α,β-unsaturated boron compounds examined. Very strong boronic acid or ester group absorption occurred as expected in the region 1200–1500 cm.$^{-1}$, with occasional strong bands from 980–1200 cm.$^{-1}$; these were not examined in detail. Other bands omitted include medium or weak unassigned absorptions and C–H stretch.

treated with three 0.1-g. portions of azobisisobutyronitrile after 0, 2 and 4 hr. yielded on simple distillation (oil-bath heat) 0.45 g. of Ia and 0.14 g. of tetramethylsuccinonitrile, b.p. 35–60° (0.1 mm.), 8.50 g. (50%) of the 1:1 adduct IIIa, b.p. 100–120° (0.1 mm.), and 4.89 g. of undistilled residue, presumably largely 1:2 telomer; $C_1 = 3.55 \times 10^{-3}$ by eq. 5. In similar fashion, 10 moles of carbon tetrachloride led to $C_1 = 3.04 \times 10^{-3}$ and 7.8 moles, when the telomeric product was distilled, to 4.0×10^{-3}.[23] For synthetic purposes, a solution of 9.2 g. of Ia and 0.5 g. of azobisisobutyronitrile in 150 ml. of carbon tetrachloride was added over a period of 40 hr. to 250 ml. of refluxing carbon tetrachloride; yield of IIIa, 45%; analytical sample: b.p. 90–95° (0.07 mm.), $n^{29.3}\mathrm{D}$ 1.4565; infrared spectrum in general accord with the assigned structure.

Anal. Calcd. for $C_{11}H_{21}BCl_4O_2$: C, 39.10; H, 6.27; B, 3.20; Cl, 41.97. Found: C, 39.49, 39.42; H, 6.68, 6.44; B, 3.46; Cl, 41.67.

An attempted purification of the 1:2 telomer by molecular distillation led to decomposition.

Dibutyl 2,4,4,4-tetrachlorobutane-2-boronate (IIId) was prepared by the first method used for IIIa above from 9.90 g. of dibutyl propene-2-boronate (Ib), 1538 g. of carbon tetrachloride and 0.5 g. of azobisisobutyronitrile; recovery of Ib 2.94 g., yield of IIId 9.08 g., residue 1.8 g.; analytical sample: b.p. 93–95° (0.07 mm.), $n^{22.5}\mathrm{D}$ 1.4642.

Anal. Calcd. for $C_{12}H_{23}BCl_4O_2$: C, 40.95; H, 6.59; B, 3.07; Cl, 40.30. Found: C, 40.92; H, 6.69; B, 3.29; Cl, 40.37.

Dibutyl 1-Bromo-3,3,3-trichloropropane-1-boronate (IIIb).—A solution of 9.21 g. of dibutyl ethyleneboronate (Ia) and 0.04 g. of azobisisobutyronitrile in 40 g. of bromotrichloromethane was heated under nitrogen to 85°, where an exothermic reaction took place, and the product isolated by distillation in 94% yield; analytical sample: b.p. 95–96° (0.08 mm.), $n^{27}\mathrm{D}$ 1.4710, infrared spectrum in accord with assigned structure.

Anal. Calcd. for $C_{11}H_{21}BBrCl_3O_2$: C, 34.55; H, 5.53; B, 2.83; Br + Cl, 1.6148 mg. silver halide/mg. sample. Found: C, 34.82; H, 5.67; B, 3.13; Br + Cl, 1.6143 mg. silver halide/mg. sample.

Dibutyl 2-bromo-4,4,4-trichlorobutane-2-boronate (IIIe).—By the method above, 4.95 g. of dibutyl propene-2-boronate, 0.01 g. of azobisisobutyronitrile and 20 g. of bromotrichloromethane led to IIIe in 90% yield; analytical sample: b.p. 112° (0.1 mm.), $n^{24.4}\mathrm{D}$ 1.4786.

Anal. Calcd. for $C_{12}H_{23}BBrCl_3O_2$: C, 36.36; H, 5.85; B, 2.73; Br + Cl, 1.559 mg. silver halide/mg. sample. Found: C, 36.44; H, 5.91; B, 2.92; Br + Cl, 1.555 mg. silver halide/mg. sample.

Dibutyl 1-Bromo-2-methyl-3,3,3-trichloropropane-1-boronate (IIIf).—From 4.95 g. of dibutyl 1-propene-1-boronate (Ic), 0.02 g. of azobisisobutyronitrile and 20 g. of bromotrichloromethane heated 2 hr. at 95–105° without evidence of exothermic reaction, 2.4 g. of Ic was recovered and 4.0 g. of IIIf was obtained; analytical sample: b.p. 112–115° (0 08 mm.).

Anal. Calcd. for $C_{12}H_{23}BBrCl_3O_2$: C, 36.36; H, 5.85; B, 2.73; Br + Cl, 1.559 mg. silver halide/mg. sample. Found: C, 36.01; H, 5.90; B, 3.00; Br + Cl, 1.538 mg. silver halide/mg. sample.

Dibutyl 3-Thianonane-1-boronate (IIIc).—A 6.4-g. (0.055-mole) sample of 1-hexanethiol and a 9.21-g. (0.05-mole) sample of dibutyl ethyleneboronate (Ia) were each chilled below 0°, then stirred together and irradiated with a 500 watt Hanovia mercury vapor lamp at −70° under a carbon dioxide atmosphere in an open beaker. After about 5 min. the mixture solidified and stirring was stopped; irradiation was continued for 75 min. The product (IIIc) was distilled immediately, b.p. 120–125° (0.1 mm.), yield 14.1 g. (93%); analytical sample: b.p. 115–118° (0.07 mm.), $n^{29.5}\mathrm{D}$ 1.4501; infrared spectrum in accord with the assigned structure.

Anal. Calcd. for $C_{16}H_{35}BO_2S$: C, 63.56; H, 11.67; B, 3.58; S, 10.61. Found C, 63.26; H, 11.70; B, 3.89; S, 10.81.

3,3,3-Trichloropropionaldehyde 2,4-Dinitrophenylhydrazone (Structure Proof of IIIa and IIIb).—A solution of 0.20 g. of 2,4-dinitrophenylhydrazine in 1.5 ml. of sulfuric acid, 5 ml. of water and 10 ml. of methanol was mixed with 2.5 ml. of 30% hydrogen peroxide and added to 0.34 g. of dibutyl 1,3,3,3-tetrachloropropane-1-boronate (IIIa). Crystallization of the product, which began almost immediately, was allowed to proceed at room temperature for 24 hr. The yield of the yellow 2,4-dinitrophenylhydrazone of 3,3,3-trichloropropionaldehyde was 0.25 g. (73%), m.p. 110–115° with evolution of hydrogen chloride (confirmed by reaction with *p*H paper and with silver nitrate) to yield the orange 2,4-dinitrophenylhydrazone of 3,3-dichloroacrolein, solidifies, m.p. 156–158° (reported[24] m.p. 164–165°). An analytical sample was recrystallized twice from methanol and once from ethanol with as little heating as possible, dried at room temperature, m.p. 109–112° (−HCl); 161–163°.

Anal.[21] Calcd. for $C_9H_7Cl_3N_4O_4$: C, 31.65; H, 2.06; Cl, 31.14; N, 16.41. Found: C, 31.61; H, 2.16; Cl, 31.00; N, 16.25.

Similar degradation of the bromotrichloromethane adduct IIIb was carried out at 0–5° and the product isolated within 48 hr., before it became gummy due to a side reaction involving bromide ion, in 30% yield, identity confirmed by mixture m.p. Since it has been alleged that the 2,4-dinitrophenylhydrazone of 3,3,3-trichloropropionaldehyde melts at 173° (taken at 10°/min.),[25] an independent synthesis of this compound also was performed. The 1:1 adduct of carbon tetrachloride and vinyl acetate[24] was treated with a solution of 2,4-dinitrophenylhydrazine in sulfuric acid–water–methanol to yield the same product as that from the degradation of IIIa, confirmed by mixture m.p.

Degradation of Dibutyl 3-Thianonane-1-boronate (IIIc) **to Ethylene.**—One millimole (0.30 g.) of dibutyl 3-thianonane-1-boronate heated with 1.0 g. of potassium hydroxide pellets at 110–127° for 2.5 hr. yielded 0.8 millimole of ethylene, identified by its infrared spectrum.

3-Thianonane-1-boronic Acid.—A suspension of 0.75 g. of dibutyl 3-thianonane-1-boronate (IIIc) in 10 ml. of water was stirred during the distillation of the water and the butanol (formed by hydrolysis) under reduced pressure at 0–15°. The residue, 3-thianonane-1-boronic acid, was recrystallized twice from acetone–water, final yield 0.18 g., m.p. 74–78°.

Anal. Calcd. for $C_8H_{19}BO_2S$: C, 50.53; H, 10.07; B, 5.69; S, 16.87. Found: C, 50.90; H, 9.97; B, 5.94; S, 17.02.

1 - Bromo - 3,3,3 - trichloropropane-1-boronic acid was prepared by similar hydrolysis of 0.96 g. of dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate (IIIb) with 20 ml. of water and the product crystallized once by dissolving in water at 40° and cooling to 5°, dried 1 hr. under vacuum, yield 0.18 g., m.p. 76–80°.

Anal. Calcd. for $C_3H_5BBrCl_3O_2$: C, 13.33; H, 1.86. B, 4.00; Br + Cl, 2.287 mg. silver halide/mg. sample. Found: C, 13.62; H, 2.05; B, 4.17; Br + Cl, 2.264 mg. silver halide/mg. sample.

***o*-Phenylenediamine Derivative of Dibutyl 1-Bromo-3,3,3-trichloropropane-1-boronate** (IIIb).—A mixture of 0.38 g. of dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate (IIIb), 0.11 g. of *o*-phenylenediamine and 10 ml. of toluene was stirred and distilled under reduced pressure below room temperature. The residue was sublimed first at 75° (0.05 mm.), 0.07 g. in 50 hr., then at 100° (0.05 mm.), 0.17 g. in 24 hr. (total yield 70%). The second fraction was resublimed at 85° (0.05 mm.), m.p. 117–121° dec. The compound decomposed in about a day if stored in contact with air.

Anal. Calcd. for $C_9H_9BrCl_3N_2$: C, 31.58; H, 2.65; B, 3.16; Br + Cl, 1.804 mg. silver halide/mg. sample; N, 8.19. Found: C, 31.05; H, 2.85; B, 3.39; Br + Cl, 1.781 mg. silver halide/mg. sample; N, 8.30.

Ethyleneboronic Acid.—A 1.84-g. sample of dibutyl ethyleneboronate (Ia) was treated with 10 ml. of 5% aqueous sodium hydroxide. The butanol formed was removed by extraction with ether, the sodium ethyleneboronate solution was nearly saturated with sodium chloride and acidified with phosphoric acid, and the ethyleneboronic

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[23] The value reported previously[1] was erroneous and should have been the above figure.

[24] M. S. Kharasch, O. Reinmuth and W. H. Urry, This Journal, **69**, 1105 (1947).

[25] J. Harmon, U. S. Patent 2,396,261, Mar. 12, 1946; *C. A.*, **40**, 3466 (1946).

acid was extracted with ether. A small amount of phenothiazine was kept present during all operations to inhibit air oxidation and polymerization. The ether solution was dried over magnesium sulfate and concentrated on the steam-bath. On cooling, ethyleneboronic acid crystallized, yield 0.25 g. (35%). This product was recrystallized twice from ether–pentane, with addition of a trace of phenothiazine to the solution each time, and the volatile ethyleneboronic acid was dried less than 5 min. at 0.1 mm. and room temperature, m.p. 84–85°, polymerization following melting within a few seconds; infrared spectrum, significant bands,[19,22] in chloroform, cm.$^{-1}$: O–H stretch, 3635(m); C=C stretch, 1605(m); vinyl C–H bend, 965(ms) and 1000(m), with overtone, 1940(w).

Anal. Calcd. for $C_2H_5BO_2$: C, 33.42; H, 7.01; B, 15.05. Found: C, 33.44; H, 7.36; B, 15.36.

Propene-2-boronic acid was prepared in a similar manner, m.p. 97–98°, polymerizes. Two attempts to prepare an analytical sample yielded impure material.

Anal. Calcd. for $C_3H_7BO_2$: C, 41.94; H, 8.21; B, 12.60. Found: C, 40.49, 40.71; H, 7.82, 8.19; B, 13.02, 12.43.

Phenothiazine inhibited air oxidation and polymerization of propene-2-boronic acid, but hydroquinone was practically ineffective. If about a gram of the purified boronic acid without inhibitor was dried under vacuum and then exposed to air, after about a minute the material became hot, turned brown, and polymerized. The ultraviolet spectrum of propene-2-boronic acid in water or in isoöctane showed only end absorption; in water (Beckman DU): ϵ_{225} 56, ϵ_{220} 170, ϵ_{210} 3000; infrared spectrum, significant bands,[19,22] cm.$^{-1}$, in chloroform: O–H stretch, 3635(m); C=C stretch, 1610(m); =CH$_2$ bend, 940(ms) (partially masked by chloroform); unassigned, 980(ms), 850(mw), 1700(w), 1845(ww), 1890(ww); in KBr: OH stretch, 3100-3450(ms); C=C stretch, 1615(m); =CH$_2$ bend, 930(m); unassigned, 875(m), 1702(m), 2050(w).

The *o*-phenylenediamine derivative of ethyleneboronic acid was prepared by the usual method[15b] but purified by sublimation at 50° (0.07 mm.), yield 60%, m.p. 116–124°. An analytical sample was resublimed, m.p. 122–124°; infrared spectrum, significant bands,[19,22] in Nujol, cm.$^{-1}$: N–H stretch, 3375(m); C=C stretch, 1595(m); vinyl C–H bend, 1010(m) and 950(ms), possible overtones, 1750(w), 1810(w), 1850(w). Instead of the strong bands characteristic of B–O groups,[22] a complex system of medium bands attributable to the aromatic system was observed in this region.

Anal. Calcd. for $C_8H_9BN_2$: C, 66.73; H, 6.30; B, 7.51, N, 19.46. Found: C, 67.01; H, 6.52; B, 7.83; N, 19.49.

PULLMAN, WASH.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

Hydroboration. V. A Study of Convenient New Preparative Procedures for the Hydroboration of Olefins

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The simple hydroboration procedure previously developed, the addition of boron trifluoride etherate to a mixture of sodium borohydride and olefin in diglyme solution, has been expanded to alternative procedures involving other solvents (ethyl ether, tetrahydrofuran and triglyme), other hydride sources (lithium borohydride, potassium borohydride, lithium aluminum hydride, lithium hydride, sodium hydride, pyridine-borane and trimethylamine-borane) and other Lewis acids, (boron trifluoride, boron trichloride, aluminum chloride plus methyl borate, aluminum chloride, titanium tetrachloride, hydrogen chloride, sulfuric acid and alkyl halides). In the course of these studies the practicality has been demonstrated of a number of convenient new hydroboration procedures, utilizing various solvents, hydride sources and appropriate acids.

The hydroboration reaction provides a convenient new route from olefinic and acetylenic derivatives to organoboranes[4,5] and to the many derivatives to which organoboranes can be converted.[6]

In our original study[4] we utilized the action of aluminum chloride on a mixture of olefin and sodium borohydride in diglyme[7] solution to achieve hydroboration of the olefin at temperatures of 25–75° (1).

$$9RCH{=}CH_2 + 3NaBH_4 + AlCl_3 \longrightarrow 3(RCH_2CH_2)_3B + 3NaCl + AlH_3 \quad (1)$$

Later we discovered that diborane adds to olefins in ether solvents with remarkable ease at 25°, and that hydroboration could be achieved rapidly and quantitatively by adding boron trifluoride etherate to a solution of sodium borohydride and olefin in diglyme[5] (2).

$$12RCH{=}CH_2 + 3NaBH_4 + 4BF_3 \longrightarrow 4(RCH_2CH_2)_3B + 3NaBF_4 \quad (2)$$

This procedure is a highly convenient one and we have utilized it in the extensive studies of the hydroboration reactions on which we have been engaged. However, it appears that the unavailability of the solvent abroad has resulted in difficulties in applying the reaction to synthetic problems. Thus Dulou and Chrétien-Bessière reported that in order to circumvent this difficulty they generated diborane from the reaction of lithium aluminum hydride with boron trifluoride in ether solution[8] and passed the gas into an ether solution of the olefin.[9] Sondheimer and his co-workers found it possible to avoid the external generation of diborane by adding lithium aluminum hydride to a solution of the olefin and boron trifluoride in ether solution.[10]

Since the original discovery of the alkali metal

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(7) Diglyme is diethylene glycol dimethyl ether; triglyme, triethylene glycol dimethyl ether.

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