Preparation of 1,1,3,3-Tetraacetoxy-2-oxa-1,3-diborapropane (Boron Acetate)

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BORON ACETATE denotes the crystalline product obtained from the reaction of orthoboric acid and acetic anhydride. Some investigators (*1, 8*) contend that this product has a boron-to-acetate ratio of 1 to 3, and a structure corresponding to $\mathrm{B(OOCCH_3)_3}$. Others (*2, 4, 6, 7*) claim that it has a boron-to-acetate ratio of 1 to 2 and a structure of $\mathrm{(CH_3COO)_2B\text{-}O\text{-}B(OOCH_3)_2}$. Both structures have been named according to several systems: boron triacetate, triacetyl borate, and triacetoxyborane for $\mathrm{B(OAc)_3}$; pyroboron tetraacetate, tetraacetyl diborate, and tetraacetoxy diboroxane for $\mathrm{(AcO)_2B\text{-}O\text{-}B(OAc)_2}$. The product which Hayter and others (*6*) obtained from the reaction of orthoboric acid and acetic anhydride was pyroboron tetraacetate. However, Dukelski (*3*) indicates that the boron triacetate structure may exist under certain conditions.

EXPERIMENTAL

Reaction of Methyl Borate and Acetic Anhydride. Methyl borate (34 grams, 0.33 mole) was heated to gentle reflux, and acetic anhydride (204 grams, 2.0 moles) was added slowly over a period of 1 hour. The reflux temperature dropped to 57° C. (methyl acetate boiling point 57.1° C.), and methyl acetate was removed rapidly without allowing the head temperature to rise. Sixty-six grams (90% yield) of methyl acetate was collected. When the residue was cooled, a white precipitate of boron acetate formed. The compound was recovered and washed with cold dry ether. The combined precipitates weighed 21.0 grams ($\mathrm{B{:}CH_3COO}$ = 1:1.86).

Reaction of Ethyl Borate and Acetic Anhydride. Ethyl borate (43.8 grams, 0.3 mole) and acetic anhydride (204 grams, 2.0 moles) were refluxed for 1 hour. During this period the vapor temperature stabilized at 77° C. (ethyl acetate boiling point, 77° C.). A total of 79 grams of ethyl acetate (100% yield) was removed during 2 hours by distillation through a 10-inch Vigreux column. The reaction mixture was cooled to 0° C., and the product (61.5 grams) crystallized out ($\mathrm{B{:}CH_3COO}$ = 1:1.91).

Attempted Reaction of Boric Anhydride and Amyl Acetate. Boric anhydride (14 grams, 0.2 mole) and amyl acetate (88 grams, 0.68 mole) were stirred and refluxed for 4 hours. Most of the boric anhydride dissolved. The mixture was then distilled at 45-mm. pressure. Decomposition and precipitation of boric anhydride took place throughout the distillation. Eighty grams of amyl acetate was collected (40° to 45° C. at 45-mm. pressure). The residue was boric anhydride. No evidence of boron acetate or amyl borate was found.

Reaction of Boric Acid and Ketene. Boric acid (10 grams, 0.16 mole) was suspended by rapid stirring in a mixture of 150 ml. of acetone and 150 ml. of tetrahydrofuran. During a 6-hour period, ketene (168 grams, 4.0 moles) was passed into the reaction mixture which was held at reflux (56° C.). After 1 hour of ketene addition, the suspended solids were completely dissolved and the reaction mixture became clear. After another 2 hours of ketene addition, the product began to precipitate from the reaction mixture. Ketene addition was continued for another 3 hours to ensure complete reaction. The reaction mixture was cooled and filtered and 22 grams of product was collected ($\mathrm{B{:}CH_3COO}$ = 1:1.84).

Reaction of Boron Trichloride and Silver Acetate. Boron trichloride (12.2 grams, 0.104 mole) was added to 300 ml. of dioxane. Silver acetate (55.0 grams, 0.329 mole) was added in small portions to the rapidly stirred solution of boron trichloride. The reaction mixture was held at 30° C. by the application of external cooling. After the addition of the silver acetate was complete, analysis of a filtered aliquot of the reaction mixture revealed that no boron trichloride remained. The reaction mixture was filtered and the filtrate concentrated by vacuum distillation. Addition of diethyl ether to the concentrated filtrate caused precipitation of approximately 1 gram of material ($\mathrm{B{:}CH_3COO}$ = 1:1.73).

Attempted Reaction of Boron Trichloride and Sodium Acetate. Boron trichloride (23.4 grams, 0.20 mole) was dissolved in 300 ml. of dioxane. Addition of sodium acetate (52.3 grams, 0.65 mole) to the rapidly stirred reaction mixture failed to produce any temperature rise. The reaction mixture was allowed to stand at room temperature for 2 weeks. Analysis of a filtered aliquot of the reaction mixture indicated that no boron trichloride had reacted.

RESULTS AND DISCUSSION

The reactions for the synthesis of boron acetate investigated during this study are:

$$\mathrm{2B(OMe)_3 + 5Ac_2O \rightarrow (AcO)_2B\text{-}O\text{-}B(OAc)_2 + 6AcOMe} \tag{1}$$

$$\mathrm{2B(OEt)_3 + 5Ac_2O \rightarrow (AcO)_2B\text{-}O\text{-}B(OAc)_2 + 6AcOEt} \tag{2}$$

$$\mathrm{2B_2O_3 + 6AcO\text{-}Am \rightarrow (AcO)_2B\text{-}O\text{-}B(OAc)_2 + Ac_2O + 2B(O\text{-}Am)_3} \tag{3}$$

$$\mathrm{2B(OH)_3 + 6CH_2{=}C{=}O \rightarrow (AcO)_2B\text{-}O\text{-}B(OAc)_2 + Ac_2O} \tag{4}$$

$$\mathrm{2BCl_3 + 6AcOAg \rightarrow (AcO)_2B\text{-}O\text{-}B(OAc)_2 + Ac_2O + 6AgCl} \tag{5}$$

$$\mathrm{2BCl_3 + 6AcONa \rightarrow (AcO)_2B\text{-}O\text{-}B(OAc)_2 + Ac_2O + 6NaCl} \tag{6}$$

Reactions 1 and 2 were easily driven to completion by removing the low boiling alkyl acetates formed as by-products. If a slight excess of acetic anhydride is used, all the alkoxy groups react, and can be removed from the reaction mixture by distillation as the alkyl acetate. However, the product obtained from this type of reaction analyzed properly for the structure $\mathrm{(AcO)_2\text{-}B\text{-}O\text{-}B(OAc)_2}$. Hence, boron triacetate may be formed as an intermediate product which decomposes to yield pyroboron tetraacetate and acetic anhydride. Other mechanisms are possible; nevertheless, all the alkoxy groups in the borate ester react and are displaced.

In the attempted Reaction 3, most of the boric anhydride dissolved in amyl acetate, which is worth noting.

Reaction 4 has not been reported specifically in the literature. However, Hagemeyer (*5*) states that acetylated boric acids are formed when boric acid is brought into contact with a ketene. Several solvents—chloroform, diethyl ether, acetone, and tetrahydrofuran—and several binary mixtures of these solvents were used. Although products which analyzed properly for the pyroboron tetraacetate structure were isolated several times, the reactions were not clear-cut, and yielded partially acetylated products.

The metathetical type Reaction 5 was slightly exothermic. It was carried out at 25° C. by adding the silver salt to boron trichloride dissolved in diethyl ether or dioxane. However, only small amounts of materials were isolated which had boron-to-acetate ratios in the range of 1 to 2.

Reaction 6 was attempted by adding the sodium salt to

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solutions of boron trichloride at 25° C., using dioxane and acetic acid as solvents. There were no indications of reaction. Analysis of the reaction mixtures indicated the presence of unreacted boron trichloride.

All the products of the new reactions were similar to those obtained by known reactions, and in no case analyzed properly for the structure $B(OOCCH_3)_3$. Although boron triacetate was never isolated, it may have been formed as an intermediate; but it was unstable and decomposed to yield acetic anhydride and pyroboron tetraacetate:

$$2B(OAc)_3 \rightarrow (AcO)_2B\text{-}O\text{-}B(OAc)_2 + Ac_2O$$

Boron and acetate content were determined by a titrimetric method similar to the one reported by Gerrard and Wheelans (*4*).

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Physical Properties of Organoboron Compounds

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IN A PREVIOUS publication (*5*) the Lorentz-Lorenz molar refraction, R_L, was evaluated for a number of organoboron compounds using literature data (*12*) for density and refractive index. A plot of the observed molar refraction, $R_{\text{obsd.}}$, *vs.* the number of carbon atoms in a single alkyl group, n, for six homologous series of compounds showed a linear relationship, and equations of the type $R_{\text{obsd.}} = a\ n + b$ were derived for the six series reported. It now becomes necessary to correct the equations previously reported, in view of the fact that some of the densities and refractive indices were incorrectly given in the review article (*12*). The corrected equations are listed below in Table I (numbers 1 to 6) along with some new equations (numbers 7 to 16) for other homologous series not previously reported. All equations were derived by the method of least-squares. The numbers in parentheses following the general formulas for series 7 to 16 give reference to the original articles from which representative compounds were selected. The n in Equations 8, 9, and 10 refer to the number of CH_2 groups in the compounds concerned, rather than to the number of carbon atoms in a single alkyl group. An estimation of the contribution by a CH_2 group to molar refraction may be found by dividing the slope of each equation by the number of alkyl groups given in the general formula. The mean value from the 16 series listed is 4.64 cc. per mole, which is the accepted value for R_{CH_2} as evaluated for long homologous series. The molar refraction, or electronic polarization, is taken as some measure of the deformation of the valence electron clouds in the presence of external electrical fields or to fields which result from the presence of strongly polar groups within the molecule. The loosening up of the electron sheaths is demonstrated in going from a cyclic to an open structure—i.e., from series 15 to 16—the value of R_{CH_2} increasing accordingly from 4.60 to 4.72 cc. per mole.

The molar volumes at temperature t, V^t_m, were evaluated for members of the series listed in Table I. The plot of V^t_m *vs.* the number of carbon atoms in a single alkyl group, n, also shows linearity, and equations of the type $V^t_m, = c\ n + d$ can be derived. V^t_m among isomeric compounds differed at most by only a few per cent, thus the average value of this property was used in derivations. The resulting equations are given in Table II for the corresponding series listed in Table I. The last equation, 17, is for the series RBF_2. This series was not included in Table I, since refractive indices for representative compounds were not reported (*12*). An estimation of the contribution by the CH_2 group to V^t_m is given in the last column.

Table I. Equations for Molar Refractions

	Series	$R_{\text{obsd.}} = an + b$
1	$B(OR)_3$	$= 13.87n + 10.74$
2	$ClB(OR)_2$	$= 9.22n + 14.05$
3	$ROBCl_2$	$= 4.57n + 17.47$
4	BR_3	$= 13.97n + 6.73$
5	$C_6H_5B(OR)_2$	$= 9.29n + 34.29$
6	$C_6H_4CH_3B(OR)_2$	$= 9.36n + 39.09$
7	$(C_6H_5)_2BOR$ (*1*)	$= 4.67n + 57.85$
8	$B[O(CH_2)_nCl]_3$ (*2*)	$= 13.96n + 24.98$
9	$ClB[O(CH_2)_nCl]_2$ (*2*)	$= 9.71n + 22.06$
10	$Cl(CH_2)_nOBCl_2$ (*2*)	$= 4.42n + 22.83$
11	$C_6H_5B(OR)Cl$ (*8*)	$= 4.61n + 38.16$
12	$C_6H_4O_2BOR$ (*9*)	$= 4.65n + 33.01$
13	$(ROBO)_3$ (*13*)	$= 13.90n + 20.38$
14	$(RBO)_3$ (*15*)	$= 14.01n + 16.92$
15	$(BNHRNR)_3$ (*4*)	$= 27.61n + 34.39$
16	$B(NHR)_3$ (*4*)	$= 14.15n + 16.54$

Table II. Equations for Molar Volumes

Series	$V^t_m = cn + d$	V_m for CH_2 group
1	$V^{20}_m = 50.02n + 68.53$	$50.02/3 = 16.67$
2	$V^{20}_m = 33.37n + 73.44$	$33.37/2 = 16.69$
3	$V^{20}_m = 16.45n + 77.95$	$16.45/1 = 16.45$
4	$V_m^{22\text{-}25} = 50.20n + 43.85$	$50.20/3 = 16.73$
5	$V^{20}_m = 34.13n + 118.6$	$34.13/2 = 17.07$
6	$V^{25}_m = 35.01n + 133.2$	$35.01/2 = 17.51$
7	$V^{20}_m = 17.25n + 174.6$	$17.25/1 = 17.25$
8	$V^{20}_m = 49.84n + 95.40$	$49.84/3 = 16.61$
9	$V^{20}_m = 34.30n + 84.90$	$34.30/2 = 17.15$
10	$V^{20}_m = 15.00n + 90.73$	$15.00/1 = 15.00$
11	$V^{20}_m = 16.82n + 126.6$	$16.82/1 = 16.82$
12	$V^{20}_m = 16.76n + 111.3$	$16.76/1 = 16.76$
13	$V^{20}_m = 53.62n + 87.50$	$53.62/3 = 17.87$
14	$V^{25}_m = 49.87n + 90.20$	$49.87/3 = 16.62$
15	$V^{20}_m = 105.0\ n + 104.7$	$105.0\ /6 = 17.50$
16	$V^{20}_m = 55.32n + 60.50$	$55.32/3 = 18.44$
17	$V^{25}_m = 15.75n + 61.98$	$15.75/1 = 15.75$

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