[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Organoboron Compounds. II.[1] The Preparation of Ethylene Dialkylborinates by the Grignard Reaction

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Dibutylborinic acid and diisoamylborinic acid were prepared by the reaction of the appropriate Grignard reagents with butyl ethylene borate at low temperatures. These acids were isolated as the ethylene esters.

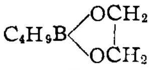
Good methods are available for the preparation of the alkylboronic acids and the trialkylborines. Thus Johnson and co-workers isolated butaneboronic acid (50% yield) from a reaction of butylmagnesium bromide with methyl borate at −75°,[2] and they obtained tributylborine (80% yield) from the reaction of butylmagnesium bromide with boron trifluoride.[3] However, no satisfactory procedure for preparing the dialkylborinic acids (R_2BOH) or their derivatives by a direct Grignard reaction has been described. These compounds have, instead, been formed from the trialkylborines. Johnson[4] employed moist air to convert tributylborine to butyl dibutylborinate while Meerwein[5] effected the oxidation of triethylborine to esters of diethylborinic acid with aldehydes. Dibutylboron bromide has been prepared by the cleavage of tributylborine with hydrogen bromide[3,6] and bromine.[3,7]

We have found that the Grignard reaction can be used directly for the preparation of an ester of dibutylborinic acid. Two modifications in the technique of the reaction were employed: (a) the organoboric acids were separated by distillation as the esters of ethylene glycol, and (b) butyl ethylene borate, $C_4H_9OBOC_2H_4O$, was used as a source of boron.

In the first reaction the conditions used by Johnson[2] for the preparation of butaneboronic acid were used. Instead of isolating the product as the solid acid, however, we distilled the organoboric acids with toluene and ethylene glycol in order to form the glycol esters, ethylene butaneboronate (I) and ethylene dibutylborinate (II). These compounds boiled sufficiently far apart that they could be separated easily by fractional distillation. I was isolated in 46% yield, and II, in 27% yield. (These yields are based on the amount of the Grignard reagent; based on the methyl borate, the yield of II was 12.5%.) This distillation technique, therefore, made feasible the isolation of the borinic acid derivative as well as the boronate ester from this Grignard reaction.

An attempt to improve the yield of the borinate by employing a two-to-one, rather than a one-to-one, mole ratio of butylmagnesium bromide to methyl borate was not very successful. In this case the yield of II was only 17% (based on either methyl borate or the Grignard reagent). It was then found that a marked improvement in the yield of the borinate could be realized by using a cyclic borate ester, butyl ethylene borate, in place of methyl borate. From a reaction of butylmagnesium bromide with butyl ethylene borate at −60° (two to one mole ratio of Grignard to borate) there was isolated a 47.4% yield of the borinic ester (II). A similar reaction between isoamylmagnesium bromide and butyl ethylene borate yielded 45% of ethylene diisoamylborinate. Only small amounts of the boronate and little, if any, trialkylborine were formed in these reactions.

Ethylene dibutylborinate oxidizes readily in air. The pure liquid becomes warm when shaken in air, and will ignite spontaneously when absorbed on cotton and exposed to the atmosphere. It can be titrated quantitatively with sodium hydroxide in the presence of mannitol, and it reduces silver ion in ammoniacal solution. A portion of the ester was converted to dibutylborinic anhydride (III) by hydrolysis to the acid and subsequent dehydration.



I

$(C_4H_9)_2BOCH_2CH_2OB(C_4H_9)_2$ (II)

$(C_4H_9)_2BOB(C_4H_9)_2$ (III)

Experimental Part

Preparation of the Borate Esters.—Butyl ethylene borate was prepared from *n*-butyl borate and ethylene glycol. The preparation of the butyl borate was carried to the point where all the water azeotrope had been removed[8] (2 moles of boric acid and 9 moles of butyl alcohol were used); then technical ethylene glycol (124 g., 2 moles) was added and the products distilled through a packed column. After removal of the butyl alcohol, the butyl ethylene borate distilled at 108° (30 mm.), weight 215 g. (75%), $n^{25}D$ 1.4280, d^{25}_4 0.9976. The percentage of boron, as determined by duplicate titrations with alkali in the presence of mannitol, was 7.10; calcd. for $C_6H_{13}O_3B$, 7.515. The low boron analysis is due, no doubt, to the presence of a small amount of butyl borate which distilled over with the ethylene ester. Ethylene glycol was absent since the ester showed no reaction with sodium metal.

Amyl ethylene borate, $n^{27}D$ 1.4343, b.p. 115° (17 mm.), was prepared in 75% yield by the same procedure. Titration showed 6.76% boron; calcd. for $C_7H_{15}O_3B$, 6.85. In this case the ethylene ester and the amyl borate boiled sufficiently far apart that a good separation could be realized. Amyl ethylene borate and other higher molecular weight alkyl ethylene esters have been described by Thomas.[9]

Methyl borate, $n^{25}D$ 1.3570, b.p. 68° (760 mm.), was prepared by the procedure of Schlesinger and co-workers.[10]

Reaction of Butylmagnesium Bromide with Methyl Borate. (a).—One-half liter of 2 *M* *n*-butylmagnesium bromide in ether was added with stirring over an eight-hour period to 112 g. (1.08 moles) of methyl borate in 200 ml. of ether at −70°. A nitrogen atmosphere was maintained

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[1] For the first paper in this series, see R. L. Letsinger and I. Skoog, *J. Org. Chem.*, **18**, 895 (1953).

[2] H. R. Snyder, J. A. Kuck and J. R. Johnson, THIS JOURNAL, **60**, 105 (1938).

[3] J. R. Johnson, H. R. Snyder and M. G. Van Campen, *ibid.*, **60**, 115 (1938).

[4] J. R. Johnson and M. G. Van Campen, *ibid.*, **60**, 121 (1938).

[5] H. Meerwein, G. Hinz, H. Majert and H. Sonek, *J. prakt. Chem.*, [2] **147**, 226 (1936).

[6] H. A. Skinner and T. Fees, *J. Chem. Soc.*, 3378 (1953).

[7] For the preparation of iodo- and chloroborines see L. H. Long and D. Rollimore, *ibid.*, 3909 (1953).

[8] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 106.

[9] L. H. Thomas, *J. Chem. Soc.*, 821 (1946).

[10] H. I. Schlesinger and co-workers, THIS JOURNAL, **75**, 213 (1953).

throughout the reaction. The white precipitate which settled out was broken up and the mixture hydrolyzed with 400 ml. of 3 *M* hydrochloric acid. Ethylene glycol (56 ml., 1.0 mole) and toluene (1 l.) were then added to the ether portion. Distillation yielded ether, a water–toluene azeotrope, a glycol–toluene azeotrope and finally toluene, respectively. The residue was fractionated through a 25-cm. helices packed column to give the portions indicated in Table I.

TABLE I

Fraction	B.p., °C.	Pressure, mm.	Wt., g.
1	55–75	66	8.45
2	75–78	66	7.75
3	78–79	66	59.10
4	64–70	1	0.75
5	70–128	1	1.15
6	128–142	1	20.80

The weight of ethylene 1-butaneboronate (fraction 3), $n^{25}\text{D}$ 1.4129, $d^{25}{}_4$ 0.9141, corresponds to a 46% yield. As fraction 2 no doubt also consists primarily of this compound, the total yield is actually somewhat greater than this.

Anal. Calcd. for $C_6H_{13}O_2B$: C, 56.33; H, 10.24. Found: C, 56.84; H, 10.31.

On hydrolysis, fraction 3 yielded a white precipitate which melted at 91–92° after recrystallization from toluene and drying over 65% sulfuric acid. The equivalent weight of this solid acid determined by titration in the presence of mannitol was 103. Butaneboronic acid is reported to melt at 92–94°,[2] and its equivalent weight is 102.

Redistillation of fraction 6 (20.8 g., 27% yield of borinate based on the Grignard reagent) yielded 13.35 g. of purified ethylene dibutylborinate; b.p. 144° (2 mm.), $n^{27}\text{D}$ 1.4343.

Anal. Calcd. for $C_{18}H_{40}O_2B_2$: C, 69.70; H, 13.00. Found: C, 70.24; H, 13.34.

(b).—An ether solution of butylmagnesium bromide (0.84 ml.) was added (2.5 hours) to 43.8 g. (0.42 mole) of methyl borate in 300 ml. of ether at −70°. This reaction differed from that previously described in that the mole ratio of Grignard reagent to methyl borate was about 2-to-1 rather than 1-to-1. The products were worked up as described in part a. Distillation data for the fractions above toluene are given in Table II. The yield of ethylene dibutylborinate (fraction 4) is 17%, based on the Grignard reagent or on the borate.

TABLE II

Fraction	B.p., °C.	Pressure, mm.	Wt., g.	$n^{25}\text{D}$
1	61–88	60	4.0	1.4165
2	78–110	35	13.2	1.4223
3	110–200	35	4.7	1.4414
4	168–169	10	10.6	1.4323

Reaction of Butylmagnesium Bromide with Butyl Ethylene Borate.—An ether solution containing 1.23 moles of butylmagnesium bromide was added to 91.6 g. (0.636 mole) of butyl ethylene borate in 1.6 l. of ether at −60° over a four-hour period. A white precipitate formed immediately and became quite thick before completion of the reaction. The products of the reaction were hydrolyzed and separated by distillation of the ethylene esters as described for the previous reactions. Distillation data are presented in Table III.

TABLE III

Fraction	B.p.	Pressure, mm.	Weight, g.
1	60	2	1.40
2	60–65	2	4.65
3	65–133	2–1	3.35
4	133–134	1	45.4

The principal product was ethylene dibutylborinate (fraction 4), which was isolated in 47.4% yield, $n^{27}\text{D}$ 1.4340, $d^{25}{}_4$ 0.8266. The equivalent weight was determined by titrating a 0.2932-g. sample of fraction 4 (weighed in a glass ampule in a nitrogen atmosphere) in a solution of 10 ml. of water and 10 ml. of methanol containing 0.50 g. of mannitol; the titration being followed by a *p*H meter. A value of 156 for the equivalent weight was found; calcd. for ethylene dibutylborinate, 155.

Anal. Calcd. for $C_{18}H_{40}O_2B_2$: C, 69.70; H, 13.00. Found: C, 69.83; H, 12.91.

Samples of fraction 4 ignited spontaneously when placed on cotton, and burned with a green flame.

In another experiment with butylmagnesium bromide, amyl ethylene borate was used in place of butyl ethylene borate. In this case, however, the separation of the products from the reaction was not satisfactory. The difficulty was probably due to the fact that the amyl alcohol–toluene azeotrope boiled at about the same point as the toluene–ethylene glycol azeotrope. This would lead to the incomplete removal of amyl alcohol and therefore the contamination of the ethylene esters of the organoboron compounds with the amyl esters.

Dibutylborinic Anhydride.—Ethylene dibutylborinate (58 g.) was shaken for a few minutes with 200 ml. of 1.87 *N* sodium hydroxide. A clear, homogeneous solution resulted. Ether (approximately 300 ml.) was added, the solution acidified to congo red end-point, and then after good mixing the ether layer was separated. It was dried with calcium sulfate and the ether distilled off. In order to dehydrate the borinic acid toluene was added to the residue and distilled at atmospheric pressure. A reduced pressure distillation then yielded 14.70 g. of material which boiled at 140° (22 mm.), $n^{25}\text{D}$ 1.4250, and 32.20 g. of material which boiled at 102° (1 mm.), $n^{25}\text{D}$ 1.4258, $d^{25}{}_4$ 0.7933. The two portions belong to the same fraction since the pressure was reduced midway to facilitate the distillation; total yield 95%.

Anal. (fraction 2) Calcd. for $C_{16}H_{36}B_2O$: C, 72.22; H, 13.63; equiv. wt., 133. Found: C, 71.92; H, 13.58; equiv. wt., 139 (by titration procedure similar to that described for the ethylene ester).

Titration of Organoboron Compounds with Ammoniacal Silver Nitrate.—The procedure of Johnson, Van Campen and Grummitt[11] was used for the reaction of ammoniacal silver nitrate with ethylene butaneboronate and ethylene dibutylborinate. In each case the amount of silver reduced by the organoboron compound was determined by separating the precipited silver, dissolving it in nitric acid and titrating with potassium thiocyanate. As a check, the unreduced silver was also determined quantitatively, and the reduced silver calculated from this value and the amount of silver nitrate initially present. Excellent agreement in values was obtained in all cases.

The amount of silver reduced by 2.279 × 10^{-3} mole of ethylene butaneboronate was 2.292 × 10^{-3} g. atom. This result is that which would be expected from the work of Johnson and co-workers,[11] who found that 1 g. atom of silver was reduced for every mole of butaneboronic acid.

On the other hand, 6.845 × 10^{-4} mole of ethylene dibutylborinate reduced only 1.211 × 10^{-3} mole of silver nitrate. That is, 0.89 g. atom of silver was reduced per mole of the borinic acid. Apparently only one of the carbon–boron bonds in the borinic acid is broken by oxidation with silver ion.

In another experiment the borinate was boiled for 40 minutes with the silver nitrate solution, instead of 20 minutes, as in the case previously described. The result was essentially the same, however; 0.90 g. atom of silver was produced per mole of the borinic acid.

Reaction of Isoamylmagnesium Bromide with Butyl Ethylene Borate.—Isoamylmagnesium bromide (0.901 mole) in ether (735 ml. of solution) was added slowly (3 hr.) to 65.6 g. (0.46 mole) of butyl ethylene borate in 1300 ml. of ether at −60°. After standing overnight, during which the

TABLE IV

Fraction	B.p., °C. (mm.)	Wt., g.	$n^{25}\text{D}$
1	51(27) –58 (12)	9.00	1.4243
2	77–93 (0.45)	6.30	1.4338
3	93–147 (.45)	3.95	1.4392
4	147–148 (.45)	36.88	1.4385

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[11] J. R. Johnson, M. G. Van Campen and O. Grummitt, THIS JOURNAL, **60**, 111 (1938).

temperature rose to 24°, the mixture was hydrolyzed and worked up as described in the previous preparations. Distillation data are given in Table IV.

Fraction 4 corresponds to a 45% yield (based on the Grignard reagent) of ethylene diisoamylborinate. For analysis the fraction was redistilled to give 27.30 g. of material boiling at 147° (0.48 mm.) to 151° (0.65 mm.), $n^{25}D$ 1.4378, d^{25}_4 0.8267.

Anal. Calcd. for $C_{22}H_{48}O_2B_2$: C, 72.14; H, 13.21; equiv. wt., 183. Found: C, 72.06; H, 12.72; equiv. wt., 181 ± 4

Hydrolysis of fraction 1 yielded 3.53 g. (3.4% yield of 3-methylbutaneboronic acid based on the Grignard reagent) of a white, solid, boronic acid, which after two recrystallizations from toluene and drying over 65% sulfuric acid in a nitrogen atmosphere melted at 64–69°. The equivalent weight of this material determined by titration in the presence of mannitol was 115, that calculated for 3-methylbutaneboronic acid, 116. Reported values for the melting point of this acid are in disagreement. Krause and Nitsche claimed the melting point to be 169°,[12] and Khotinsky and Melamed reported a value of 101°.[13]

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[12] E. Krause and R. Nitsche, *Ber.*, **54**, 2784 (1921).

[13] E. Khotinsky and M. Melamed, *ibid.*, **42**, 3090 (1909).

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC COMPANY]

Molecular Compounds. IV. The Effect of Substituents on the Equilibrium Constant for Complex Formation

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The equilibrium constants for complex formation between anthracene and a series of 1-substituted-2,4,6-trinitrobenzenes in chloroform at 23.8 ± 0.1° and between 1,3,5-trinitrobenzene and a series of substituted anilines in absolute ethanol at 25.0 ± 0.1° have been determined spectroscopically. Data available in the literature have been used to calculate the equilibrium constants for complexing between 2,4-dinitrochlorobenzene and a series of substituted anilines in absolute ethanol at both 35.0 and 45.0°. The magnitudes of the equilibrium constants within each series cannot be explained by considerations of potential energy alone, and estimation of the thermodynamic constants for the 2,4-dinitrochlorobenzene–substituted aniline equilibria shows that kinetic energy changes accompanying complex formation are not uniformly the same in this series of compounds.

In the previous papers in this series[1] measurements of the extent of molecular compound formation by the spectroscopic method were self-consistent and adequately encompassed by the Mulliken theory.[2] In accord with this theory, molecular compound formation results from donor–acceptor interaction, resulting in the formation of a charge-transfer type intermolecular bond. The specific interaction may be represented as

$$A + B \rightleftarrows (A\ B) \longleftrightarrow (A\cdot^{-} - \cdot B^{+})$$

the intermolecular bonding in the complex being due to the resonance indicated above, although the contribution of the ionic structure is undoubtedly small.

On the basis of this theory it would be anticipated that complex formation would be favored by electron-donating substituents in the donor molecule and electron-withdrawing substituents in the acceptor molecule. In the present paper we wish to report the effect of systematic substitution of both the donor and acceptor molecules on the equilibrium constant for complex formation.

The most successful correlation of structure and reactivity is due to Hammett[3] and applies to a large number of side chain reactions of *meta* and *para* substituted aromatic compounds. For such reactions

$$\log (k/k^0) = \sigma\rho$$

where k^0 and k are the rate or equilibrium constants for the unsubstituted and substituted aromatic compound, respectively, ρ is a constant characteristic of the reaction and the conditions under which it occurs, and σ depends only on the substituent group and its position. This equation holds only for the special cases where the effect of a change in structure on rate or equilibrium can be explained in terms of internal electron displacements, in terms that is of potential energies alone, and only when there is a cancellation of other effects due to the internal kinetic energies of the reactants.

The σ-constants reflect the changes in electron density on the different carbon atoms of the aromatic ring, and Jaffe[4] has shown that it is possible to correlate Hammett's σ-values with electron densities in mono-substituted benzenes as calculated by the MO method. The Hammett σ-constants thus apply to *side chain* reactions in *meta* and *para* substituted benzenes and would not apply to molecular complex formation where the electron density of the aromatic ring as a whole is presumably involved. However, it is still possible that a similar treatment, with new σ-constants reflecting the electron density of the aromatic ring as a whole, will hold for molecular compound formation provided, of course, that the other limiting conditions are met.

Results

The first system studied was complexing between anthracene and 1-substituted-2,4,6-trinitrobenzenes in chloroform at 23.8 ± 0.1°. The equilibrium constants were determined spectroscopically by methods previously described.[1a,b,5] The results are given in Table I.

In this first system the substitution was in the acceptor moiety. Table II presents the results for complexing between trinitrobenzene and a series of *meta* and *para* substituted anilines in absolute alco-

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(1) (a) S. D. Ross, M. Bassin, M. Finkelstein and W. A. Leach, THIS JOURNAL, **76**, 69 (1954); (b) S. D. Ross and I. Kuntz, *ibid.*, **76**, 74 (1954); (c) S. D. Ross and I. Kuntz, *ibid.*, **76**, 3000 (1954).

(2) R. S. Mulliken, *ibid.*, **72**, 600 (1950); **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, Chapter VII.

(4) H. H. Jaffe, *J. Chem. Phys.*, **20**, 279 (1952).

(5) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 1891 (1952).