

the isomeric thiophosphate in the product.¹³ It is possible that some of the initially formed thionophosphate has rearranged during the distillation.¹⁴ However, the thiophosphate should have b.p. 122° (20 mm.).¹⁶

(13) L. J. Bellamy, "Infrared Spectra of Complex Molecules," second edition, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 322, attributes the 7.7 to 8.0 μ region to the P=O bond.

(14) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 5.

(15) Pischimuka, *J. Russ. Phys. Chem. Soc.*, **44**, 1406 (1912).

Acknowledgment.—This investigation was supported in part by American Petroleum Institute Project 48B. The authors would like to express their thanks to Messrs. W. C. Jones, H. C. Reeder, H. C. Williams and H. T. Taylor of The Humble Oil and Refining Co. for help with the butene analyses.

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[CONTRIBUTION FROM THE STAMFORD LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID CO.]

The Synthesis of *p*-Vinylphenylboronic Acid and Some of its Derivatives

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RECEIVED AUGUST 14, 1958

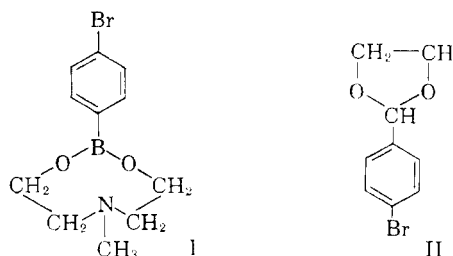
The synthesis of *p*-vinylphenylboronic acid, iminodiethyl *p*-vinylphenylboronate, *p*-vinylphenylboroxine and di-*n*-butyl *p*-vinylphenylboronate is described. These compounds are new monomers.

A wide variety of boron compounds may be classed as either demonstrated or potential monomers. Polymers of such compounds contain boron atoms whose bonds either form part of the polymer skeleton as in glycol borates, or are non-integral to the polymer skeleton. Molecules containing a polymerizable vinyl group and a boron moiety unaffected by vinyl polymerization conditions could lead to the latter type of polymer. Representative compounds of this type include β -chlorovinylboronic,¹ allylboronic,² and styrylboronic acids,³ B-tri-(β -chlorovinyl)borazine,⁴ potassium tetrasterylborate⁵ and the vinylborines.⁶ No detailed information regarding the polymerization of this monomer class has, however, been reported.

The synthesis of a boron-containing vinyl monomer was undertaken to provide information relating to the electronic influence of boron on a reactive vinyl group under polymerization conditions. Factors such as air-oxidative stability and hydrolytic stability, coupled with the known behavior of styrene under a wide variety of conditions, led to our choice of *p*-vinylphenylboronic acid as a model compound for this study. Accordingly, this paper presents the synthesis of this monomer and some of its derivatives. In an attempt to obtain *p*-(β -hydroxyethyl)-phenylboronic acid as a precursor of the desired monomer, N-methyliminodiethyl *p*-bromophenylboronate (I) was prepared from *p*-bromophenylboronic acid.⁶ Attempts to form a Grignard reagent from I failed as did also attempts to form the lithium or sodium derivatives by reaction of I with the metals in ether.

A similar approach employing 2-*p*-bromophenyldioxolane (II) also failed because of resistance to Grignard-reagent formation. A "direct reaction"

was attempted with this halide but no significant metal consumption occurred under these conditions.⁷



Since a procedure was desired which could lead to relatively large amounts of monomer, failure of I and II to easily form Grignard reagents prompted an approach avoiding such unreactive halides. Although arylboronic acids are known to undergo electrophilic displacement reactions resulting in cleavage of the aryl-boron bond,⁸ no information regarding similar displacements by free radicals was available. In the hope that such a displacement by a bromine atom would not be significantly competitive with α -hydrogen abstraction from a *p*-ethylphenyl-substituted boron-containing group, bromination of N-methyliminodiethyl *p*-ethylphenylboronate by N-bromosuccinimide was attempted. N-Methyliminodiethyl *p*-ethylphenylboronate was prepared from *p*-bromoethylbenzene as starting material. When brominated with N-bromosuccinimide, it afforded only a brown tar from which no brominated ester could be recovered. Bromination under the same conditions, however, of *p*-ethylphenylboroxine (III) led in excellent yield to the expected *p*- α -bromoethylphenylboroxine.

Recently, Torssell⁹ reported brominating *p*-tolylboronic acid with N-bromosuccinimide and isolating *p*- ω -bromotolylboronic acid and not the corresponding boroxine.

(7) Unpublished work by R. A. Clarke and S. J. Groszos of these laboratories has shown that alkyl and aryl halides react with metallic magnesium in refluxing *n*-butyl borate to form, respectively, di-*n*-butylalkyl- and or -arylboronates.

(8) A. D. Ainsley and F. J. Challenger, *J. Chem. Soc.*, 2171 (1930).

(9) K. Torssell, *Arkiv Kemi*, **10**, 507 (1957).

(1) H. R. Arnold, U. S. Patent 2,402,590, June 25, 1946.

(2) W. L. Ruigh, C. E. Erickson, F. Gunderloy and M. Sedlak, WADC Technical Report 55-26, Part II.

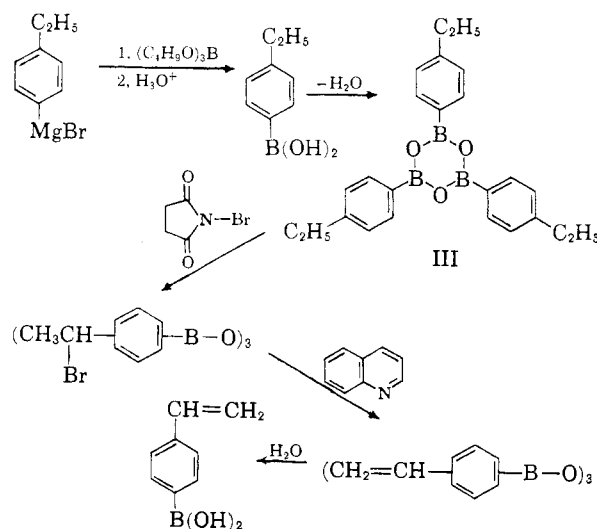
(3) V. A. Sazonova and N. Ya. Kronrod, *Zhur. Obshchei Khim.*, **26**, 1876 (1956).

(4) W. L. Ruigh, A. D. Olin, N. G. Steinberg and P. A. Van Der Meulen, WADC Technical Report 55-26, Part IV.

(5) T. D. Parsons, M. B. Silverman and D. M. Ritter, *This Journal*, **79**, 5091 (1957).

(6) F. R. Bean and J. R. Johnson, *ibid.*, **54**, 4415 (1932).

Our observations have been that if the water formed (by conversion of boronic acid to boroxine in the refluxing solvent) during the bromination is not removed by azeotropic distillation, the reaction mixture becomes transiently colored due to the presence of molecular bromine and the yield of *p*- α -bromoethylphenylboroxine is lowered. In any event, whether water is removed or not, brominated boroxine and not boronic acid is obtained as the major reaction product. This reaction is analogous to the bromination of *o*- and *m*-tolylboronic acids which give the corresponding ω -bromotolylboroxines and not boronic acids.⁹ The lowered yield of bromoboroxine from a reaction mixture containing water is hardly surprising in view of the availability of cationic bromine from *N*-bromosuccinimide in hydroxylic solvents.¹⁰ In addition to facilitating polar reactions of *N*-bromosuccinimide, water also enhances the rate of brominative displacement in arylboronic acids since in "20%" aqueous acetic acid the rate is ten times that in "50%" acetic acid.¹¹



Dehydrobromination of *p*-(α -bromoethyl)-phenylboroxine to *p*-vinylphenylboroxine occurred smoothly in quinoline. Recrystallization of *p*-vinylphenylboroxine from water afforded pure *p*-vinylphenylboronic acid which was converted by conventional methods to di-*n*-butyl and iminodiethyl *p*-vinylphenylboronates.

The behavior under polymerization conditions and its theoretical implications for the several monomers described will be published separately. It will suffice, therefore, to mention this behavior only briefly. *p*-Vinylphenylboronic acid and boroxine polymerize readily in the presence of α, α' -azodiisobutyronitrile or other free-radical initiators as does di-*n*-butyl *p*-vinylphenylboronate. This ester, in striking contrast to styrene, is unreactive to cationic initiation by boron trifluoride. Similarly, *p*-vinylphenylboronic acid and boroxine, while not completely unreactive to boron trifluoride, are considerably more resistant to polymerization by this initiator than styrene.

(10) S. Weinstein, I. Goodman and R. Boschan, *THIS JOURNAL*, **72**, 2311 (1950).

(11) H. G. Kuivila and E. K. Easterbrook, *ibid.*, **73**, 4629 (1951).

Experimental¹²

***N*-Methyliminodiethyl *p*-Bromophenylboronate (I).**—*p*-Bromophenylboronic acid (15.0 g., 0.075 mole) was azeotroped in 200 ml. of toluene with 10.0 g. (0.083 mole) of *N*-methyl-diethanolamine until water no longer appeared in the condensate. The hot toluene solution was filtered, and deposited white crystalline ester on cooling. Evaporation of the mother liquors to 50 ml. gave a second crop. The crude ester was twice recrystallized from acetone to give 18.5 g., 86% of theory, m.p. 149–150°. *Anal.* Calcd. for $C_{11}H_{15}NO_2Br$: C, 46.52; H, 5.32; N, 4.93; Br, 28.14. Found: C, 46.94, 46.67; H, 5.77, 5.37; N, 4.78; Br, 28.08; B, 2.86, 2.99.

2-*p*-Bromophenyldioxolane (II).—To 87 g. (0.47 mole) of *p*-bromobenzaldehyde in 200 ml. of toluene was added 30 g. (0.48 mole) of ethylene glycol and 0.5 g. of *p*-toluenesulfonic acid. The solution was azeotropically distilled. When water no longer condensed, the solution was cooled and made slightly alkaline with ethanolic potassium hydroxide. The toluene solution then was washed with water, separated, and dried over anhydrous potassium carbonate. Vacuum evaporation of the toluene left a residue of essentially pure 2-*p*-bromophenyldioxolane, b.p. 107° (2 mm.). *Anal.* Calcd. for $C_8H_7O_2Br$: C, 47.18; H, 3.96; Br, 34.89. Found: C, 46.92; H, 4.15; Br, 35.06.

The product did not react with magnesium or lithium in ether solution. Attempts to react it with magnesium metal in refluxing *n*-butylborate resulted in failure to consume significant amounts of metal over a 12-hour period.

***p*-Ethylphenylboronic Acid.**—*p*-Ethylbromobenzene (555 g., 3.0 moles) was added dropwise to 73 g. (3.15 moles) of magnesium in 1 l. of anhydrous ether. After completion of reaction, the ether solution of *p*-ethylphenylmagnesium bromide was added dropwise under nitrogen pressure to a solution of 913 g. (3.98 moles) of *n*-butyl borate in 800 ml. of anhydrous ether cooled to -70° in a Dry Ice-acetone-bath. After addition of the Grignard solution was completed, the reaction mixture was allowed to remain at room temperature for 12 hours before decomposition.

The reaction mixture was decomposed by the addition of 1 l. of 10% sulfuric acid. The ether layer was separated and evaporated on a water-bath. Following the ether removal, the butanol-water system was made alkaline with aqueous sodium hydroxide and the butanol removed by distillation *in vacuo*. Water was added from time to time to maintain a volume of 3 l. When the butanol had been removed, the aqueous solution was acidified with hydrochloric acid, and the resultant precipitate of *p*-ethylphenylboronic acid filtered and recrystallized once from hot water; yield 378 g., 84% of theory, m.p. 149–150°; reported¹³ m.p. 108–111°. *Anal.* Calcd. for $C_8H_9BO_2$: C, 64.06; H, 7.39; B, 7.21. Found: C, 64.24; H, 7.61; B, 7.02.

***p*-Ethylphenylboroxine.**—*p*-Ethylphenylboronic acid (284 g., 1.9 moles) was refluxed in 1 l. of toluene in a flask fitted with a Dean and Stark trap to remove water. When water no longer appeared in the condensate, the toluene was removed by vacuum evaporation to yield crystalline *p*-ethylphenylboroxine, m.p. 194–195°, which was used directly for subsequent steps.

***p*-(α -Bromoethyl)-phenylboroxine.**—*p*-Ethylphenylboroxine (147 g., 0.372 mole) was dissolved in 3.25 l. of anhydrous carbon tetrachloride. *N*-Bromosuccinimide (200 g., 1.125 moles) was added and the reaction mixture heated to reflux. Benzoyl peroxide, 1.0 g., then was added to initiate reaction. It is noteworthy that in the absence of benzoyl peroxide, no reaction occurs over a period of 8 hours, while in the presence of an initiating amount of benzoyl peroxide bromination is complete in 3 hours. After completion of reaction, the succinimide was removed by filtration, washed with small portions of carbon tetrachloride and the solvent removed by evaporating the filtrate in a water-bath. Cooling the residue gave a pale tan crystalline mass of crude *p*-(α -bromoethyl)-phenylboroxine which on recrystallization from 1:1 benzene-cyclohexane yields 212 g. (90% of theory) of cream-colored product. An additional recrystallization

(12) All melting points were taken on a Fisher-Johns melting point block and are uncorrected. Boiling points are uncorrected. Microanalyses were run by the microanalytical group of these Laboratories. The semi-micro method by which these compounds were analyzed for boron is scheduled for publication in the "Microchemical Journal."

(13) N. N. Melnikov and M. S. Rokitskaya, *J. Gen. Chem. (USSR)*, **8**, 1768 (1938).

affords white product, m.p. 183.5–184°. *Anal.* Calcd. for $C_{24}H_{24}O_3Br_3B_3$: C, 45.56; H, 3.82; Br, 37.90; B, 5.13. Found: C, 45.51; H, 3.97; Br, 38.16; B, 5.09.

***p*-Vinylphenylboronic Acid.**¹⁴—*p*-(α -Bromoethyl)-phenylboroxine (10 g., 0.0155 mole), was placed in a 150-ml. erlenmeyer flask to which 20 g. of freshly distilled quinoline was added. The reaction mixture was heated at 130–140° for 0.5 hour with occasional stirring. During reaction the flask was protected by a calcium sulfate drying tube. At the end of the reaction time, the flask was cooled and the contents poured into 200 ml. of water. The reaction mixture was acidified with aqueous hydrochloric acid and extracted with ether. The ether was evaporated on the water-bath and the residual light orange solid was recrystallized from hot water in the presence of a small amount of charcoal. The yield of colorless *p*-vinylphenylboronic acid was 5.3 g. (74%), m.p. 179–182° dec. *Anal.* Calcd. for $C_8H_9O_2B$: C, 64.93; H, 6.13; B, 7.31. Found: C, 64.93, 64.20; H, 6.08, 6.43; B, 6.53, 7.07.

Iminodiethyl *p*-Vinylphenylboronate.—*p*-Vinylphenylboronic acid (5.0 g., 0.034 mole) was azeotroped in 200 ml. of toluene containing 3.6 g. (0.034 mole) of diethanolamine for 2 hours. At the end of this time, the reaction mixture was cooled and filtered. Recrystallization of the colorless product from acetone yielded 7.3 g. (99% of theory) of long glistening needles, m.p. 236–237° dec. *Anal.* Calcd. for $C_{12}H_{16}O_2NB$: C, 66.39; H, 7.43; N, 6.45; B, 4.98. Found: C, 66.42; H, 7.41; N, 6.44; B, 5.06.

(14) During the preparation of this manuscript a paper by H. R. Snyder, M. S. Konecky and W. J. Lennarz, *THIS JOURNAL*, **80**, 3611 (1958), has appeared in which salient features of the infrared spectra of *p*-vinylboronic acid and its boroxine have been discussed.

***p*-Vinylphenylboroxine.**—*p*-Vinylphenylboronic acid (10 g., 0.068 mole) was refluxed in 200 ml. of toluene until water no longer evolved. Evaporation of the toluene to a volume of 20 ml. led to the deposition of 8.4 g. of pale tan crystals of *p*-vinylphenylboroxine; yield 97%. Two recrystallizations of a small sample of the product from toluene afforded colorless needles, m.p. 195–196°. *Anal.* Calcd. for $C_{24}H_{24}B_3O_3$: C, 73.93; H, 5.43; B, 8.33. Found: C, 73.94; H, 5.45; B, 8.54.

Di-*n*-butyl *p*-Vinylphenylboronate.—*p*-Vinylphenylboronic acid (15.0 g., 0.10 mole) was azeotroped in 100 ml. of 1-butanol for several hours. The butanol was removed by distillation followed by vacuum evaporation at 100°. The residue was distilled and the yield of di-*n*-butyl *p*-vinylphenylboronate, b.p. 130° (1 mm.), was 14.4 g. (55%). *Anal.* Calcd. for $C_{16}H_{26}O_2B$: C, 73.84; H, 9.69; B, 4.16. Found: C, 73.21; H, 9.31; B, 4.09.

Polymerization of *p*-Vinylphenylboronic Acid and Derivatives.—Homopolymerization of *p*-vinylphenylboronic acid, *p*-vinylphenylboroxine or iminodiethyl *p*-vinylphenylboronate is accomplished readily by treating chloroform or methylene chloride solutions of the monomer with boron trifluoride diethyl etherate at 0–20°. The amount of catalyst required for complete conversion of monomer to polymer is high, of the order of 20–30 mole %. Di-*n*-butyl *p*-vinylphenylboronate does not form solid polymer under these conditions.

p-Vinylphenylboroxine in toluene solution or di-*n*-butyl *p*-vinylphenylboronate may be polymerized readily by 0.3 mole % free radical initiator such as α, α' -azodiisobutyronitrile or di-*t*-butyl peroxide at 80–100°

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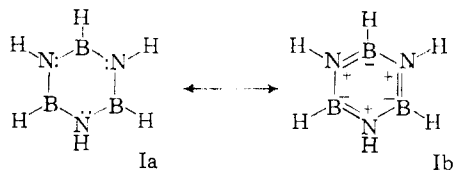
Organoboron Compounds. II. The B-Alkylation of N-Trisubstituted Borazoles

By JANET HALL SMALLEY AND STANLEY F. STAFIEJ

RECEIVED JULY 22, 1958

The reaction of N,N',N'' -triphenyl- and trimethylborazole with several Grignard and lithium reagents has been examined. From these reactions B-tri-alkylated and arylated borazoles have been isolated when three moles of the reagent to one mole of the borazole was used. From N,N',N'' -triphenylborazole, B-mono- and disubstituted derivatives were obtained in good yields when the mole ratios of starting material to reagent were 1:1 and 1:2. The partially B-substituted N,N',N'' -triphenylborazoles in turn were further alkylated to give unsymmetrically substituted compounds. The reaction of N,N',N'' -trimethylborazole with fewer than three molar equivalents of a Grignard reagent is more complex, resulting in mixtures of mono-, di- and trisubstituted products. These results represent the first examples of the substitution of B-H containing borazoles by alkyl or aryl groups, *via* Grignard or lithium reagents.

The structure of borazole has been represented as a resonance hybrid in which the electron pairs on the nitrogen atoms are neither completely localized, as shown in structure Ia, nor completely shared by overlap with the vacant p-orbitals of the boron atoms, as shown in structure Ib, but have some intermediate electron distribution.¹ Substituents on the ring alter this electron distribution in a manner which depends on the electrical character of the substituents and their location on the ring (on boron or on nitrogen). The variation in electronic structure of substituted borazoles is manifested in some of their physical properties.²



bution in a manner which depends on the electrical character of the substituents and their location on the ring (on boron or on nitrogen). The variation in electronic structure of substituted borazoles is manifested in some of their physical properties.²

(1) E. Wiberg, *Naturwiss.*, **35**, 182, 212 (1948).

(2) For a comparison of the far ultraviolet spectra of borazole, B-trimethyl-, B-trichloro- and N-trimethylborazole, see C. W. Rector,

It might be expected that substituents would also affect the chemical behavior of the ring system, and that differences in substituents would be reflected in differences in reactivity. With this thought in mind, a study of the chemical behavior of B-H containing borazoles toward selected reagents was initiated. It has now been found that the B-H hydrogen atoms in these compounds can be replaced by the alkyl or aryl groups of Grignard or lithium reagents to give B-substituted products. An examination of the product composition, obtained from those reactions that lead to partial substitution, reveals that the rate of displacement depends on the nature of the groups attached to the nitrogen atoms of the ring and also on the degree of B-substitution. The present paper describes the results of this study with two members of this class of substituted borazoles, N,N',N'' -triphenylborazole (II) and N,N',N'' -trimethylborazole (V).

Compound II, which has not previously been re-

G. W. Schaeffer and J. R. Platt, *J. Chem. Phys.*, **17**, 460 (1949). For differences in B-N bond lengths of several substituted borazoles, see S. H. Bauer, *THIS JOURNAL*, **60**, 524 (1938), and K. P. Coffin and S. H. Bauer, *J. Phys. Chem.*, **59**, 193 (1955).