Organoboron Compounds. On the Reaction of Phenylboronic Acid with Diols and Diamines

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In previous papers¹⁾ the present authors showed that when polyvinylalcohol (PVA) is treated with phenylboronic acid, it is readily converted into polyvinylboronic ester, which is characterized by being soluble in some organic solvents, insoluble in water, and capable of being transformed into colorless strong films or fibers with a water resistance superior to that of PVA itself. The dyeing property of PVA can be improved by this esterification in some respects²⁾.

From these facts, it can be expected that by introducing boron into polymeric substances, remarkable specialities will appear in its properties. However, relatively little is known of polymeric substances which contain boron, especially in the main chain of polymers. It is the main object of this experiment to devise a method of preparing such polymeric substances, containing boron atoms bonded directly to a nitrogen or carbon atom in the main chain of polymers. In order to prepare these substances, phenylboronic acid was heated at 120~200°C with organic reagents containing a reactive hydrogen atom until any water or hydrogen chloride formed as a by-product was eliminated. In general, it is preferable to use bifunctional organic reagents such as glycol and diamines with at least one hydrogen atom on each terminal carbon or nitrogen atom, since the acid reacts with them to give linear polymers. Beside these reactants, organosilane compounds such as diphenylsilanediol and dichlorodiphenylsilane were used.

Experimental

Preparation of Phenylboronic Acid³⁾.—From bromobenzene and methylborate, phenylboronate was prepared, and after hydrolysis phenylboronic acid was obtained. Yield, 82%; m. p., 214°C.

Preparation of Phenylboronic Anhydride.—Phenylboronic acid can easily be converted to the anhydride by azeotropic distillation of water with toluene.

Preparation of Phenylboronic Dichloride.—A mixture of phenylboronic anhydride (32 g., 0.31 mol.) and phosphorus pentachloride (74 g., 0.36 mol.) was melted at 160°C and heated under reflux at 120~130°C for 24 hr. Subsequent distillation gave phosphorus oxychloride as a forerun. The main fraction, after redistillation, consisted of

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1) S. Kato, Y. Tsuzuki and S. Kitajima, This Bulletin, 34, 1107 (1961); S. Kato, *Waseda Applied Chem. Soc. Bulletin*, 28, 28 No. 5, (1961).

2) S. Kato and Y. Tsuzuki, This Bulletin, 33, 1741 (1960).

3) "Organic Syntheses", Vol. 39 (1959), p. 3.

phenylboronic dichloride. Yield, 4.9 g. (11%); b. p., 48∼50°C/5 mmHg.

Preparation of Diphenylsilanediol. — Into a heterogeneous mixture of 26 ml. of toluene, 54 ml. of *tert*-amyl alcohol and 220 ml. of water was stirred drop by drop 67 g. of diphenyldichlorosilane dissolved in 26 ml. of toluene. The solution was maintained at 25°C with a cooling bath. About one-half hour was required for the addition of the chloride, after which the solution was stirred for ten minutes. The solution was then filtered by suction. The crystals obtained were washed with water until they became free of acid, and were then dried in air and recrystallized from warm ethyl methyl ketone. Yield, 49 g.; (90%) m. p., 143°C.

Reaction of Phenylboronic Acid with Diamines. —All the following reactions were carried out in an atmosphere of dry oxygen-free nitrogen.

a-1) With Ethylenediamine. — Ethylenediamine (1.34 ml., 1.2 g., 0.02 mol.), together with a 5% excess of phenylboronic acid, was placed in a 50 ml. three-necked Claisen flask with a receiver, a thermometer, and an inlet for dry oxygen-free nitrogen. Reaction took place spontaneously with the evolution of heat. The flask was heated in a silicone oil-bath. At about 140°C (bath temperature), reaction set in. Water distilled off freely during the first hour and very slowly during the succeeding two hours at 120°C (inner temperature). The flask was provided with a very fine capillary, and heating was continued in vacuum (5 mmHg) for about half an hour, the temperature of the bath being raised to 160∼170°C. During this period a little distillate was collected. The residue, which was a glassy, granular, slightly brown substance, was readily soluble in hot water, absolute methyl and ethyl alcohol, but insoluble in carbon tetrachloride, chloroform, dimethylformamide, ethyl ether, benzene, xylene, aceton and dioxane. This polymer-like substance melts at 80°C and can be drawn out into thread at that temperature, but it seems to be readily hydrolyzed by atmospheric moisture. Analysis indicates that this crude substance contains 23.52% nitrogen, 38.20% carbon and 7.20% hydrogen.

a-2) About 2.8 g. (ca. 002 mol.) of phenylboronic acid and 1.34 ml. (0.02 mol.) of ethylenediamine were simultaneously added to 40 ml. of toluene. Reaction took place spontaneously with evolution of heat. The mixture was then refluxed for an hour. The water formed in this reaction was distilled by means of water-toluene azeotropic distillation. After removal of the residual toluene at 5 mm., no further distillation took place up to the bath temperature of 180°C. The residue showed the same properties as were found in a-1).

b) With Trimethylenediamine. — In a two-necked flask equipped with a condenser and a nitrogen inlet were placed about 2.8 g. (ca. 0.02 mol.) of phenylboronic acid and 1.48 g. (1.67 ml., 0.02 mol.) of trimethylenediamine (b. p. 135∼136°C/738 mmHg). The flask was thoroughly swept with dry nitrogen and was heated first at 130∼150°C for 13 hr., and then at 150∼190°C for the succeeding two hours under 5 mmHg. During the heating at 140∼160°C, water was distilled, and the viscosity of the reaction mixture increased greatly. When this viscous liquid was heated under 5 mmHg, there remained a bright brittle material in the bottom of the flask. The appearance and solubility were the same as with a). Analysis showed that this crude substance contained 12.27% nitrogen, 30.67% carbon and 6.21% hydrogen.

c) With Hexamethylenediamine.—A mixture of 2.8 g. (ca. 0.02 mol.) of phenylboronic acid and 2.4 g. (0.02 mol.) of hexamethylenediamine was heated to 190∼195°C under atmospheric pressure for six hours and then for two and one-half hours at 210°C under 5 mmHg. About 3.2 g. of microcrystalline powder were obtained.

d) With p-Phenylenediamine.—In a mortar 3.8 g. (0.03 mol.) of phenylboronic acid and 3.3 g. (0.03 mol.) of *p*-phenylenediamine (m. p. 145∼147°C) were triturated. This mixture was placed in a flask filled with dry nitrogen and heated to 210°C for twenty minutes. At about 150°C reaction set in; water distilled off during this period. Heating was continued for an additional ten minutes under reduced pressure. The final residue, which was a light brown, resinous mass, was soluble in hot water and alcohols, but insoluble in warm benzene, carbon tetrachloride and chloroform. This substance became dark brown on standing in the air.

Esterification of Phenylboronic Acid with Glycols. — *a) With Ethylene Glycol.*—An attempt to condense phenylboronic acid with ethylene glycol was unsuccessful.

b) With Tetramethylene Glycol. — Phenylboronic acid (2.5 g., ca. 0.02 mol.) and tetramethylene glycol (1.8 ml., ca. 0.02 mol.) were heated together in a nitrogen atmosphere from 120°C to 130°C for ten hours. Additional heating was continued below 140°C under reduced pressure for an hour. The final residue was a brittle, transparent solid which could be drawn out into thread from a molten condition. This thread seemed to be easily hydrolyzed by moisture in the air. Analysis indicated that this substance contained 64.7% carbon and 8.13% hydrogen.

c) With Pentamethylene Glycol.—About 2.5 g. of phenylboronic acid and 2.08 ml. (0.02 mol.) of pentamethylene glycol was added to 50 ml. of toluene. This mixture was refluxed for an hour, followed by removal of the water as a ternary azeotrope. The product showed the same properties as were found in b) above.

d) With Diphenylsilanediol.—A mixture of 4.32 g. (0.02 mol.) of diphenylsilanediol and 2.6 g. of phenylboronic acid was heated in a reaction flask equipped with a condenser, a thermometer and an inlet for dry oxygen-free nitrogen. The mixture was heated for 24 hr. at 190∼200°C and for a further hour at 200°C under a pressure of 6 mmHg. The resulting resinous substance was a light yellow, glassy solid melting at about 90°C. This substance is soluble in benzene, ethyl methyl ketone, alcohol, etc., slightly soluble in carbon tetrachloride, and insoluble in water. When molten, this material can be drawn out into elastic threads. A flame test showed that this substance contains boron.

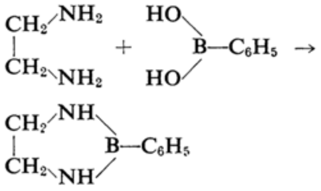
e) With Dichlorodiphenylsilane.—To a reaction vessel equipped with a thermometer, a nitrogen inlet tube extending to the bottom of the flask, and a glass tube leading to an 1 N sodium hydroxide solution, were added 3.8 g. (0.03 mol.) of phenylboronic acid and 6.7 g. (0.03 mol.) of dichlorodiphenylsilane. The reaction mass was heated in an atmosphere of nitrogen for 20 hr. at 190~200°C and then for an hour at 210°C under a pressure of 5 mmHg. The hydrogen chloride evolved during the reaction hours was absorbed in 100 ml. of an 1 N sodium hydroxide solution. Titration of the sodium hydroxide solution with a 1.011 N hydrochloric acid solution indicated that this reaction proceeded to the extent of 70% of the theoretical. About eight grams of the resinous mass were obtained. This residue showed the same properties as observed in experiment d).

f) An attempt to get phenylboron dichloride to react with bifunctional substances by way of interfacial polycondensation was unsuccessful.

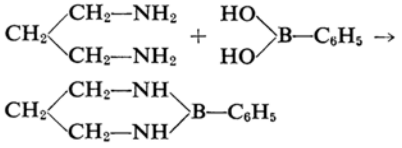
Discussion

It is a well-known fact that if a 5- or 6-ring can be formed by esterification, the intramolecular reaction usually prevails over the inter-molecular reaction; in the case of 6- and 7-membered rings, both a monomolecular ring and linear polymers of a medium molecular weight are produced. It follows from this well-established fact that three of the reagents used, i. e., ethylenediamine, trimethylenediamine and ethylene glycol, might react with phenylboronic acid to give reaction products of the intra-molecular type:

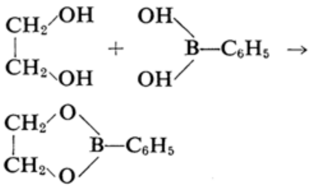
(1)



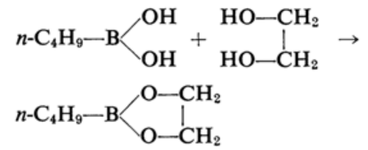
(2)



(3)



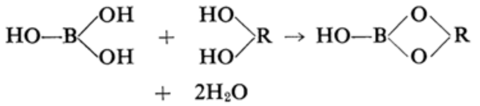
However, two of these three cyclic structures, 1 and 2, do not appear to have the indicated structures, since they could be drawn out into threads. Lestinger and Skoog⁴⁾ obtained the ethylene glycol ester of *n*-butylboronic acid by the addition of ethylene glycol and toluene to a concentrated aqueous solution of *n*-butylboronic acid, followed by removal of the water as a ternary azeotrope.



On the other hand, the ethylene glycol ester of phenylboronic acid could not be obtained by the same method. The reason for this is partly that phenylboronic acid is more easily deboronated by heating with water⁵⁾:

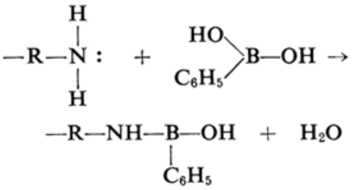
$$C_6H_5B(OH)_2 + H_2O \rightarrow C_6H_6 + B(OH)_3$$

Therefore, the following side reaction seems to accompany the main reaction:



Thus, the reaction product between phenylboronic acid and glycols must be a mixture of products of the linear and cyclic types.

The reaction of phenylboronic acid with diamines can be formulated as follows:



In this reaction the nitrogen atom of the diamine donates a pair of electrons to the boron atom. This results in a partial polarization of each atom, and the positive charge on the nitrogen atom will facilitate the removal of hydrogen atom as a proton. On the other hand, the negative charge on the boron atom promotes the removal of the hydroxyl group as a hydroxyl ion. Thus, the reaction proceeds with the formation of water, and the nitrogen-boron bond may be produced as a covalent bond.

Becher and his co-workers⁶⁾ investigated the Raman and ultraviolet spectra of methylamino- and diethylaminoboron and showed that the boron-nitrogen bond has a considerable double bond character. The infrared absorption

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4) R. L. Lestinger and I. H. Skoog, *J. Am. Chem. Soc.*, **76**, 4176 (1955).

5) A. D. Ainley and F. Challenger, *J. Chem. Soc.*, **1930**, 219.

6) H. J. Becher et al., *Z. anorg. u. allgem. Chem.*, **286**, 133 (1952).

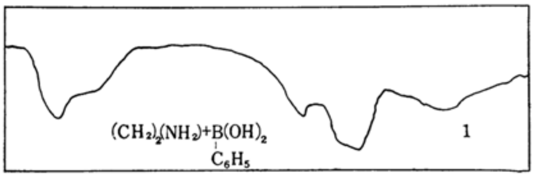

Fig. 1

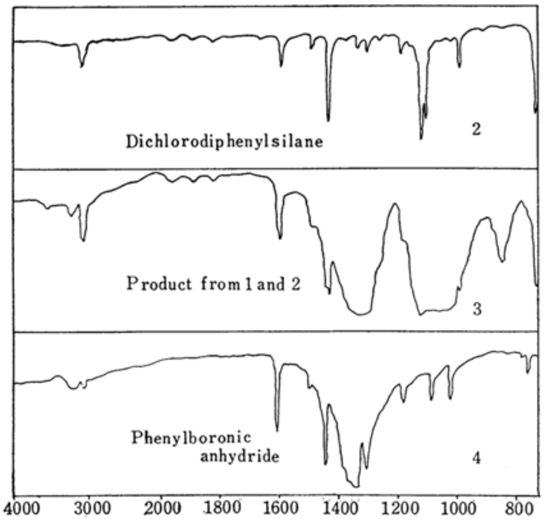

Fig. 2

spectra of the derivatives of phenylboronic acid condensed with a diamine as well as with an organo-silicone are shown in Figs. 1—4. As regards the compounds formed from phenylboronic acid and ethylenediamine (Fig. 1), perhaps the most striking feature in the generally, weak absorption spectrum is a broad band in the region of 1300∼1400 cm^{-1}. The same absorption band occurred with *N, N, N*-trimethylborazol⁷⁾. It seems certain that the band is associated with the B–N group (1330 ∼1380 cm^{-1}) and the B–O group (1330∼1390 cm^{-1}). Figure 2 shows the absorption spectrum of dichlorodiphenylsilane, while Fig. 4 is that of phenylboronic anhydride. Figure 3 is also the spectrum of the compound formed from these two. The three bands at 850, 1000 ∼1100 and 1300∼1350 cm^{-1} seen in Fig. 3 are characteristic of this condensed compound. The band at 850 cm^{-1}, which can not be found in either of the parent spectra, suggests the formation of some new bond during the reaction. Moreover, the broad and strong band in the 1000∼1100 cm^{-1} region is probably connected with the stretching vibration of the Si–O–B bond, the band of which casually comes near the 1100 cm^{-1} absorption due to the ether linkage C–O–C. In conclusion, the most notable feature observed in this spectrum is that the polymer formed from phenylboronic acid and dichlorodiphenylsilane shows a very strong band in the 1000∼1100 cm^{-1} range; this band is probably due to Si–O–B absorption, and therefore the product must be polyborosiloxane.

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7) Sadtler, Standard Spectra, No. 11868.