fractions being collected. The first fraction weighed 5 g. and distilled at 119–120° (1 mm.), while the second fraction distilled at 115° (0.4 mm.), n^{20}_D 1.5504, d^{20}_{20} 1.3952, and weighed 38.5 g. This second fraction represents a 75% yield of 2-(*m*-bromophenoxy)-tetrahydropyran. The method used to prepare this compound follows closely that for the *o*-bromo[18] and *p*-bromo[17] isomers.

Anal. Calcd. for $C_{11}H_{13}BrO_2$: Br, 31.08; *MR*D, 58.12. Found: Br, 30.60, 30.55; *MR*D, 58.75.

***m*-Hydroxybenzoic Acid.**—Eight and sixty-five hundredths gram of *m*-bromophenol was treated with 0.11 mole of *n*-butyllithium for 4 hr. at 20°. The reaction was terminated by pouring it jet-wise into a stirred slurry of Dry Ice and ether. After the mixture had warmed to room temperature, it was hydrolyzed by the addition of 50 ml. of 10% hydrochloric acid. The aqueous layer was separated and was washed twice with 50-ml. portions of ether which were combined with the main portion. The ether solution was extracted with three 25-ml. portions of 10% sodium hydroxide which were combined and acidified with concentrated hydrochloric acid. The solid which precipitated was dried and sublimed under vacuum twice to give 2.3 g. (33.3%) of material melting at 196–198° (lit. value, 201°).

Acknowledgments.—We wish to thank Mr. Robert McCord and Mr. E. Miller Layton, Jr., of the Ames Laboratory of the Atomic Energy Commission for the infrared spectra.

We also wish to acknowledge the financial support of the Division of Biology and Medicine of the United States Atomic Energy Commmission which has made this work possible. The results of the biological testing of these compounds will be reported by Dr. Otho D. Easterday of the Brookhaven National Laboratory.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF KANSAS]

Benzenediboronic Acids

BY DONALD R. NIELSEN AND WILLIAM E. MCEWEN

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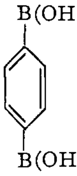
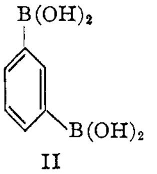
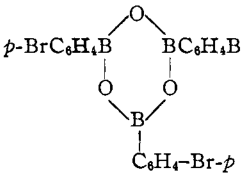
Benzene-1,4-diboronic acid (I) and benzene-1,3-diboronic acid (II) have been synthesized and characterized by conversion to the respective tetra-*n*-butyl esters and bis-(dichloroboryl)-benzenes.

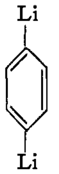
Although more than 70 aliphatic and aromatic monoboronic acids have been described in the literature, there is no report of the synthesis of diboronic acids.[1] As part of a broad investigation of the physical and chemical properties of bifunctional organoboron compounds, syntheses of benzene-1,4-diboronic acid (I) and benzene-1,3-diboronic acid (II) have now been devised.


I


II

Benzene-1,4-diboronic acid (I) has been prepared in low yield by four different methods. When a mixture of *p*-bromophenylboronic anhydride (III), dispersed sodium and methyl borate in hexane was heated for two hours, then hydrolyzed, benzene-1,4-diboronic acid (I) was obtained in 4% yield. Reaction of di-*n*-butyl *p*-bromophenylboronate, magnesium and methyl borate in refluxing 1,2-dimethoxyethane for 30 hours gave, after hydrolysis of the reaction mixture, a 10% yield of I. The yield of benzene-1,4-diboronic acid (I) amounted to 26% in a reaction in which methyl borate, which had been frozen and pulverized, was added to a suspension of *p*-dilithiobenzene (IV) in petroleum ether at −30°, followed by hydrolysis of the reaction mixture. The dilithio compound IV was prepared by metal–halogen exchange between *n*-butyllithium and *p*-dibromobenzene according to the procedure of Gilman, Langham and Moore.[2] It is noteworthy that the yield of I is considerably below that of terephthalic acid, which may be obtained in 66–89% yield by an analogous carbonation reaction of the exchange mixture.


III


IV

The best yield of I was obtained by use of the Grignard reaction. A mixture of *p*-dibromobenzene and two equivalents of magnesium in tetrahydrofuran was refluxed for a period of seven hours, then methyl borate was added to the reaction mixture maintained at about −30°. After hydrolysis of the reaction products, the resulting acids were esterified with *n*-butyl alcohol and the esters fractionated. There was obtained tetra-*n*-butyl benzene-1,4-diboronate (V) in 35% yield, together with di-*n*-butyl *p*-bromophenylboronate (5%) and di-*n*-butyl phenylboronate (19%). Hydrolysis of the butyl esters gave quantitative yields of the respective arylboronic acids. The prolonged period of heating is evidently necessary for the formation of the dimagnesium Grignard compound in moderately satisfactory yield, since the yield of benzene-1,4-diboronic acid (I) dropped to 10% when the mixture of *p*-dibromobenzene and magnesium was heated for only 2.5 hours prior to the reaction with methyl borate. Extended refluxing of a solution of *p*-dibromobenzene in ethyl ether

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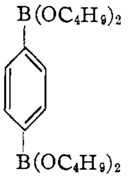
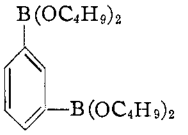
(1) M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956).

(2) H. Gilman, W. Langham and F. W. Moore, THIS JOURNAL, **62**, 2327 (1940).

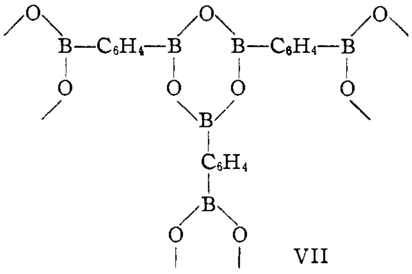
has been reported to give the dimagnesium Grignard reagent in yields of only 4–23%.[3-5]


V

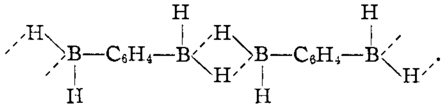
Benzene-1,3-diboronic acid (II) was obtained in 10% yield after hydrolysis of the product obtained by addition of methyl borate to the halogen-metal exchange mixture from *m*-dibromobenzene and *n*-butyllithium. By use of the dimagnesium Grignard compound of *m*-dibromobenzene instead of the dilithio derivative, however, the diboronic acid II was obtained in 36% yield. The acid was isolated by conversion to its tetra-*n*-butyl ester VI, purification of the latter compound by distillation, then hydrolysis of the ester.


VI

Both of the diboronic acids I and II proved to have exceptionally high melting points. Neither compound melted at temperatures up to 420°. It is thought that the acids gradually lose water upon being heated and form polymers of the type shown in structure VII. The structures of the acids were established by application of Melnikov's procedure.[6] Treatment of benzene-1,4-diboronic acid (I) with bromine water gave *p*-dibromobenzene and boric acid. A similar reaction of benzene-1,3-diboronic acid (II) gave *m*-bromophenylboronic acid plus boric acid.


VII

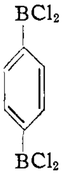
Since the diboronic acids proved to be virtually infusible, and since the respective tetra-*n*-butyl esters were liquids, an attempt was made to prepare solid derivatives of the acids having convenient melting points. The tetrachlorides were chosen because our future plans include attempts to prepare polymers of the type shown in structure VIII (or polymers which would result upon disproportionation of VIII) by reduction of the tetrachlorides.

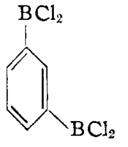

VIII

Inasmuch as the diboronic acids were isolated and purified most conveniently by way of their tetra-*n*-butyl esters, a method for the direct conversion of the esters to the halides was desired. In a model experiment it was found that di-*n*-butyl phenylboronate could be converted to the known phenyldichloroborane by reaction with phosphorus pentachloride. The stoichiometry was established as

$$C_6H_5B(OC_4H_9)_2 + 2PCl_5 \longrightarrow C_6H_5BCl_2 + 2POCl_3 + 2C_4H_9Cl$$

Treatment of tetra-*n*-butyl benzene-1,4-diboronate (V) with four equivalents of phosphorus pentachloride gave 1,4-bis-(dichloroboryl)-benzene (IX), m.p. 93–96°, in 84% yield. An analogous reaction with tetra-*n*-butyl benzene-1,3-diboronate (VI) gave 1,3-bis-(dichloroboryl)-benzene (X), m.p. 54–56°, in 58% yield. Both of the tetrachlorides underwent very rapid hydrolysis upon contact with moist air.


IX


X

Experimental[7]

General Experimental Precautions.—All preparations of organoboron compounds were carried out in an atmosphere of dry, oxygen-free nitrogen. All transfer operations involving air-sensitive or moisture-sensitive organoboron compounds were carried out in a dry-box in an atmosphere of pure nitrogen.

Benzene-1,4-diboronic Acid (I). A. Use of 1,4-Dilithiobenzene (IV).—To a solution of 52.0 g. (0.22 mole) of *p*-dibromobenzene in 500 ml. of petroleum ether was added a solution containing 0.50 mole of *n*-butyllithium in petroleum ether. The mixture was heated with stirring for 20 hours. An insoluble solid began to form immediately after the addition of the *n*-butyllithium, and the solid increased in amount as the exchange reaction progressed.

The mixture was placed in an acetone–Dry Ice-bath, and 52 g. (0.50 mole) of methyl borate, which had been frozen and pulverized, was added. The reaction mixture was allowed to warm slowly to room temperature, then hydrolyzed and acidified by the addition of dilute hydrochloric acid. The layers were separated, and the aqueous layer was extracted with ether. The combined ether–petroleum ether solution was concentrated almost to dryness. A solid which had precipitated was collected by filtration, washed with petroleum ether and recrystallized from water. There was obtained 9.45 g. (26%) of benzene-1,4-diboronic acid (I), which did not melt up to a temperature of 420°.

Anal. Calcd. for $C_6H_8B_2O_4$: C, 43.47; H, 4.87; B, 13.06. Found: C, 43.41; H, 4.83; B, 13.28.

Further concentration of the combined ether–petroleum ether filtrate and wash solution left a residue consisting of a colorless solid and a yellow liquid. The solid was collected by filtration and dissolved in ether. Addition of ethanolamine caused a solid product to precipitate. This was recrystallized from benzene, giving a small amount of

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(3) R. Quelet, *Bull. soc. chim.*, **41**, 933 (1927).

(4) Y. S. Zalkind and P. V. Raginova, *J. Russ. Phys. Chem. Soc.*, **59**, 1013 (1927).

(5) H. Gilman, H. J. Beaber and H. L. Jones, *Rec. trav. chim.*, **48**, 597 (1929).

(6) N. N. Melnikov, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1766 (1938); *C. A.*, **33**, 4908 (1939).

(7) All m.p.'s are corrected and all b.p.'s are uncorrected. Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

aminoethyl di-*p*-bromophenylborinate, m.p. 235.6–237.2°, reported[8] m.p. 236–237°.

Anal. Calcd. for $C_{14}H_{14}BBr_2NO$: C, 43.91; H, 3.69; B, 2.83; Br, 41.74; N, 3.66. Found: C, 44.19; H, 3.50; B, 3.16; Br, 41.75; N, 3.62.

In a second run, liquid methyl borate was used in place of solid methyl borate. Benzene-1,4-diboronic acid was obtained in 23% yield.

When the exchange mixture, prepared as described above, was added to powdered Dry Ice, then acidified with dilute hydrochloric acid, there was obtained terephthalic acid in 66% yield and *p*-bromobenzoic acid in 13% yield. Gilman, Langham and Moore[2] obtained terephthalic acid in 89% yield in a similar experiment.

B. **Use of the Dimagnesium Grignard Compound of *p*-Dibromobenzene.**—A solution of 36.7 g. (0.155 mole) of *p*-dibromobenzene in 250 g. of anhydrous tetrahydrofuran was added over a period of 35 minutes to 7.45 g. (0.31 g. atom) of magnesium, reaction proceeding vigorously throughout this period. After all of the *p*-dibromobenzene had been added, the mixture was heated to 60–64° for seven hours. During the initial stages of the reaction a colorless solid precipitated, and the amount of this solid increased as the reaction progressed. The mixture was placed in an acetone–Dry Ice-bath, and 27 g. (0.26 mole) of methyl borate was added. The mixture was allowed to warm gradually to room temperature, then hydrolyzed and acidified with dilute hydrochloric acid. After ether extraction of the acid solution and distillation of solvent from the extract, an excess of 1-butanol was added to the residue. The mixture was distilled until the temperature of the distillate, which remained at 90–92° during distillation of the water–butanol azeotrope, rose to 115°. Distillation of the residue at reduced pressure gave 13.9 g. of *n*-butyl borate, b.p. 63–85° (0.1 mm.), and 6.93 g. (19%) of di-*n*-butyl phenylboronate, b.p. 85–90° (0.1 mm.). A dark solid distillation residue became colorless on addition of water. Recrystallization of this solid from water gave 12.31 g. of benzene-1,4-diboronic acid (I) contaminated with some *p*-bromophenylboronic acid. The mixture of acids was esterified with 1-butanol by distillation of the water–butanol azeotrope as described above; then the esters were purified by distillation. There was obtained 2.53 g. (5%) of crude di-*n*-butyl *p*-bromophenylboronate, b.p. 87–130° (0.4 mm.), and 17.9 g. (35%) of tetra-*n*-butyl benzene-1,4-diboronate (V), b.p. 160–176° (0.4 mm.).

Anal. Calcd. for $C_{22}H_{40}B_2O_4$: C, 67.72; H, 10.33; B, 5.55. Found: C, 67.85; H, 10.11; B, 5.83.

Each of the butyl esters cited above underwent rapid hydrolysis on contact with water to give the respective boronic acids and *n*-butyl alcohol in quantitative yield.

C. **Use of Grignard Reagent Prepared from Di-*n*-butyl *p*-Bromophenylboronate.**—A mixture of 64.0 g. (0.204 mole) of di-*n*-butyl *p*-bromophenylboronate, 21.0 g. (0.20 mole) of methyl borate, 200 ml. of 1,2-dimethoxyethane and 5.0 g. (0.208 g. atom) of magnesium turnings was refluxed for 30 hours. The mixture was hydrolyzed by addition of dilute hydrochloric acid and extracted with ether. The residue obtained upon distillation of the ether was crystallized from water, giving 3.38 g. (10%) of benzene-1,4-diboronic acid (I).

D. **Use of *p*-Bromophenylboronic Anhydride (III), Sodium and Methyl Borate.**—*p*-Bromophenylboronic anhydride (III) was prepared by dehydration of *p*-bromophenylboronic acid in an evacuated desiccator over concentrated sulfuric acid for one day. A mixture containing 8.0 g. (0.044 mole) of *p*-bromophenylboronic anhydride, 7.8 g. (0.295 g. atom) of dispersed sodium and 400 ml. of hexane was stirred for three hours at room temperature without any apparent reaction taking place. After addition of 15.4 g. (0.148 mole) of methyl borate, the mixture was heated to 75° for two hours. Hydrolysis of the reaction mixture with dilute hydrochloric acid and use of an isolation procedure similar to that described above gave 0.28 g. (4%) of benzene-1,4-diboronic acid (I).

Proof of Structure of Benzene-1,4-diboronic Acid (I).—A solution of 1.00 g. (0.00604 mole) of benzene-1,4-diboronic acid in dilute sodium hydroxide was neutralized to the phenolphthalein end-point with dilute hydrochloric acid. The mixture was cooled, and an excess of bromine in potassium bromide solution was added. The mixture was allowed to stand for several hours, then 1.06 g. (0.0045 mole, 75%) of *p*-dibromobenzene was collected by filtration. After two crystallizations from ethanol its m.p. was 90–92°, and its infrared absorption spectrum in chloroform solution was identical with that of a corresponding solution of authentic *p*-dibromobenzene.

***p*-Bromophenylboronic Acid.**—This acid was prepared by a modification of the procedure of Konig and Scharrnbeck.[9] To *p*-bromophenylmagnesium bromide prepared from 11.3 g. (0.485 g. atom) of magnesium, 114.3 g. (0.485 mole) of *p*-dibromobenzene and 600 ml. of anhydrous ether, cooled in an acetone–Dry Ice-bath, was added 50.5 g. (0.485 mole) of methyl borate. The mixture was allowed to warm to room temperature, refluxed for 30 minutes, then hydrolyzed by addition of dilute hydrochloric acid and extracted with ether. Concentration of the ether solution and crystallization of the residue from water gave 51.9 g. (53%) of *p*-bromophenylboronic acid, m.p. 273–281°; reported[9] m.p. 266° for *p*-bromophenylboronic acid and m.p. 280° for *p*-bromophenylboronic anhydride.

In a second run, the crude acid from the ether extract was added to 110 ml. of *n*-butyl alcohol and distilled. After removal of the water–butanol azeotrope (b.p. 92°) and excess alcohol, the residue was distilled at reduced pressure. There was obtained a 57% yield of di-*n*-butyl *p*-bromophenylboronate, b.p. 122–126° (2 mm.).

1,4-Bis-(dichloroboryl)-benzene (IX).—To 88.9 g. (0.426 mole) of phosphorus pentachloride was added a solution of 41.7 g. (0.107 mole) of tetra-*n*-butyl benzene-1,4-diboronate (V) in 126 g. of carbon tetrachloride, and the mixture was refluxed for seven hours. Distillation of the carbon tetrachloride[10] (together with the by-products, *n*-butyl chloride and phosphorus oxychloride) and sublimation of the residue at 0.5 mm. pressure gave 21.5 g. (0.09 mole, 84%) of 1,4-bis-(dichloroboryl)-benzene (IX). After a second sublimation the material melted at 93–96° in a sealed tube.

Anal. Calcd. for $C_6H_4B_2Cl_4$: C, 30.08; H, 1.68; B, 9.03; Cl, 59.20. Found: C, 30.16; H, 1.86; B, 8.94; Cl, 58.85.

The compound is extremely sensitive to moisture and is hydrolyzed almost instantly on contact with moist air.

Benzene-1,3-diboronic Acid (II). A. Use of the Dimagnesium Grignard Compound of *m*-Dibromobenzene.—A solution of 38.8 g. (0.165 mole) of *m*-dibromobenzene in 410 g. of anhydrous tetrahydrofuran was added over a period of five hours to 8.15 g. (0.34 g. atom) of magnesium. After addition of the *m*-dibromobenzene, the mixture was maintained at a temperature of about 40° and stirred for another five hours. The mixture was then cooled in an acetone–Dry Ice-bath, and 40 g. (0.384 mole) of methyl borate was added. After being allowed to warm gradually to room temperature, the reaction mixture was hydrolyzed by addition of dilute hydrochloric acid and extracted with ether. The residue obtained on distillation of the ether was esterified with *n*-butyl alcohol by the azeotropic method cited for the preparation of tetra-*n*-butyl benzene-1,4-diboronate (V). Distillation at reduced pressure yielded only *n*-butyl borate and a small amount of di-*n*-butyl phenylboronate. The process of esterification of the residue and removal of esters by distillation at reduced pressure was repeated until no more ester distilled. The distillate was collected in four fractions: (1) *n*-butyl borate, b.p. 58–77° (0.1 mm.), 19.61 g.; (2) di-*n*-butyl phenylboronate, b.p. 77–100° (0.1 mm.), 9.97 g. (26%); (3) di-*n*-butyl *m*-bromophenylboronate, b.p. 100–123° (0.1 mm.), 3.56 g. (7%); (4) tetra-*n*-butyl benzene-1,3-diboronate, b.p. 170–181° (0.1 mm.), 22.9 g. (36%). The last fraction was analyzed.

Anal. Calcd. for $C_{22}H_{40}B_2O_4$: C, 67.72; H, 10.33; B, 5.55. Found: C, 67.89; H, 10.26; B, 5.68.

The identity of the major constituent of each of the distillation fractions was established by hydrolysis and isolation of the acid component of the ester. For example, hydrolysis of a portion of fraction 4 was effected by heating the ester in water until it dissolved, then collecting the acid which

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[8] R. L. Letsinger and I. H. Skoog, THIS JOURNAL, **77**, 2491 (1955).

[9] W. Konig and W. Scharrnbeck, *J. prakt. Chem.*, **128**, 153 (1930).

[10] Much of the phosphorus pentachloride remained unchanged after the period of refluxing. It was only after the mixture had been concentrated to about 100 ml. that all of the phosphorus pentachloride was consumed.

crystallized on cooling of the solution. After the product, benzene-1,3-diboronic acid (II), had been recrystallized from water and dried in an evacuated desiccator, it did not melt up to 420°.

Anal. Calcd. for $C_6H_8B_2O_4$: C, 43.47; H, 4.87; B, 13.06. Found: C, 43.71; H, 4.99; B, 12.77.

B. **Use of 1,3-Dilithiobenzene.**—To a solution of 15.9 g. (0.068 mole) of *m*-dibromobenzene in 300 ml. of petroleum ether was added 100 ml. of a petroleum ether solution containing 0.135 mole of *n*-butyllithium. The mixture was stirred for five hours, the temperature being maintained at about 34°. To the resulting mixture, cooled in an acetone–Dry Ice-bath, was added 14.0 g. (0.135 mole) of methyl borate. The mixture was allowed to warm gradually to room temperature, hydrolyzed with dilute hydrochloric acid and extracted with ether. After distillation of the ether and petroleum ether, the residue was digested with hot water and filtered. From the filtrate there was obtained 1.1 g. (10%) of benzene-1,3-diboronic acid (II).

When the exchange mixture was caused to react with carbon dioxide, rather than with methyl borate, isophthalic acid could be isolated in 30% yield.

Proof of Structure of Benzene-1,3-diboronic Acid (II).—The method used was the same as that described for the proof of structure of benzene-1,4-diboronic acid (I). However, in this experiment *m*-bromophenylboronic acid, m.p. 169–173° (reported[11] m.p. 170°), was isolated instead of *m*-dibromobenzene. The infrared spectrum of a chloroform solution of the product was identical with that of a chloroform solution of authentic *m*-bromophenylboronic acid.

In an independent experiment it was shown that *m*-bromophenylboronic acid is not cleaved by bromine water under the conditions used for the proof of structure of benzene-1,3-diboronic acid (II).

***m*-Dibromobenzene.**—This compound was prepared in 51% yield by a modification of the method of Mathieson and Newberry.[12] A cold solution of *m*-bromobenzenediazonium bisulfate was added to a suspension of cuprous bromide in water, through which a vigorous current of steam was being passed. Mathieson and Newberry[12] obtained *m*-dibromobenzene in 25% yield by adding cuprous bromide to *m*-bromobenzenediazonium bisulfate at 75°.

***m*-Bromophenylboronic Acid.**—The acid, m.p. 161–166°, was obtained in 46% yield from *m*-dibromobenzene, the procedure being the same as that employed for the preparation of *p*-bromophenylboronic acid.

1,3-Bis-(dichloroboryl)-benzene (X).—Tetra-*n*-butyl benzene-1,3-diboronate was caused to react with phosphorus pentachloride in the same manner as described for the preparation of bis-1,4-(dichloroboryl)-benzene (IX). After distillation of the carbon tetrachloride and the by-products *n*-butyl chloride and phosphorus oxychloride at atmospheric pressure, the residue was distilled *in vacuo*. There was obtained a 58% yield of 1,3-bis-(dichloroboryl)-benzene (X), b.p. 82–84° (1.2 mm.). After two sublimations at 50 mm. pressure, the colorless sublimate had a m.p. of 54–56° in a sealed tube.

Anal. Calcd. for $C_6H_4B_2Cl_4$: C, 30.08; H, 1.68; B, 9.03; Cl, 59.20. Found: C, 29.98; H, 1.78; B, 9.23; Cl, 58.95.

Phenyldichloroborane.—Di-*n*-butyl phenylboronate was prepared by the method of Torssell.[13] To a stirred suspension of 57.0 g. (0.274 mole) of phosphorus pentachloride in 130 g. of carbon tetrachloride was added 32.1 g. (0.137 mole) of di-*n*-butyl phenylboronate. A mildly exothermic reaction occurred, but only a small amount of the phosphorus pentachloride was consumed. Distillation of the solvent was commenced and as the distillation proceeded the remainder of the phosphorus pentachloride was consumed. After removal of solvent and the by-products *n*-butyl chloride and phosphorus oxychloride, the residue was distilled *in vacuo*. There was obtained 17.2 g. (79%) of phenyldichloroborane, b.p. 65–67° (14 mm.); reported b.p. 175°[14] and 178°[15] (760 mm.).

Anal. Calcd. for $C_6H_5BCl_2$: C, 45.37; H, 3.17; B, 6.81; Cl, 44.65. Found: C, 45.61; H, 3.44; B, 6.56; Cl, 44.84.

In order to determine the yields of by-products, the reaction was repeated without a solvent. To 130 g. (0.625 mole) of phosphorus pentachloride was added 68.5 g. (0.292 mole) of di-*n*-butyl phenylboronate. Much heat was evolved as the reagents were mixed, but not all of the phosphorus pentachloride was consumed until the mixture had been heated at about 70° for an additional two hours. Fractional distillation of the liquid product gave 53.1 g. (0.574 mole, 98%) of *n*-butyl chloride, b.p. 74–78°; 73.3 g. (0.479 mole, 82%) of phosphorus oxychloride, b.p. 90–105°; and 33.1 g. (0.208 mole, 71%) of phenyldichloroborane, b.p. 63–70° (14 mm.).

The crude *n*-butyl chloride was washed with dilute sodium carbonate solution, dried over anhydrous sodium sulfate, redistilled, converted to the Grignard reagent in ether solution and added to powdered carbon dioxide. *n*-Valeric acid was obtained by acidification of the mixture and extraction with ether. A portion of the acid was converted to the *p*-bromophenacyl ester, m.p. 73.6–75.2°, and another portion to the α-naphthalide, m.p. 112.4–113.8°, by conversion to the acid chloride and reaction of the latter with 1-aminonaphthalene.

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The Mechanism of Fluorination. III.[1] Fluorine Atom Reactions. The Olefin Dimerization Reaction[2,3]

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A general mechanism is presented for the reactions of elemental fluorine with perhalo-olefins. This mechanism accounts for the formation of dimer addition products by the diffusion-controlled combination of free radicals which are produced in pairs with the intermediate formation of fluorine atoms. This process appears to be unique with fluorine. The important new steps in the mechanism are tested by reactions of fluorine with mixtures of perhalo-olefins of different reactivities and with an olefin and chloroform. The results obtained are shown to support the proposed mechanism and to demonstrate the very great and indiscriminate reactivity of fluorine atoms.

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[1] Preceding paper in this series, W. T. Miller, Jr., S. D. Koch, Jr., and F. W. McLafferty, THIS JOURNAL, **78**, 4992 (1956).

[2] Presented at the 118th Meeting of the American Chemical Society, Chicago, Ill., Sept., 1950 (Abstracts of Papers, p. 23L).

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