CCLXXX.—*Studies of the Boron–Carbon Linkage. Part I. The Oxidation and Nitration of Phenylboric Acid.*

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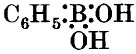
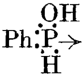
THE existence in phenylboric acid of an incomplete octet with only six electrons,



$C_6H_5{:}\underset{OH}{\underset{..}{B}}{:}OH$, renders a discussion of its structure and reactions of particular interest. The formula is not $C_6H_5{:}B{\vdots}O$ nor $C_6H_5{:}B{\rightarrow}O$, since a compound of this empirical formula and different properties is obtained on dehydrating phenylboric acid. The somewhat analogous compound phenylphosphinous acid, $PhPO_2H_2$, is monobasic and has the structure



$Ph{:}\overset{OH}{\underset{H}{\ddot{P}}}{\rightarrow}O$, but phenylboric acid cannot have the analogous constitution owing to its deficiency in valency electrons.

Phenylboric acid readily gives mercury phenyl chloride, PhHgCl, with aqueous mercuric chloride (Michaelis and Becker, *Ber.*, 1882, **15**, 182), its behaviour recalling that of triphenylbismuthine and the tolylstibines towards this reagent in alcohol (Challenger and Ridgway, J., 1922, **121**, 106). The phenyl groups of phenylphosphinous and phenylphosphinic acid, $PhPO(OH)_2$, are not eliminated by mercuric chloride (Michaelis, *Annalen*, 1876, **181**, 305; Michaelis and Becker, *loc. cit.*, p. 182), mercurous chloride being produced in the first case. This is paralleled by the non-migration of phenyl from triphenylphosphine when heated with the chlorides of bismuth, antimony, arsenic, and phosphorus (Challenger and Pritchard, J., 1924, **125**, 866).

Phenylboric acid reacts readily at the ordinary temperature with chlorine or bromine water, with iodine in potassium hydroxide, and with hydrogen peroxide, giving halogenobenzenes and phenol. The halogens appear to react in the form of the hypohalide acid, HOX. Phenylboric acid readily gives benzene when heated with 50% sodium hydroxide solution, or with water under pressure, or when boiled with concentrated hydrochloric acid.

The reactions with mercuric bromide, cupric chloride and cupric bromide are aided by heat, giving mercury phenyl bromide, chlorobenzene, and bromobenzene respectively. Cuprous halide is also produced. Thus,

(a) $PhB(OH)_2 + X_2 + H_2O = PhX + HX + B(OH)_3$
(b) $PhB(OH)_2 + HO{\cdot}OH = PhOH + B(OH)_3$
(c) $PhB(OH)_2 + HgBr_2 + H_2O = PhHgBr + HBr + B(OH)_3$
(d) $PhB(OH)_2 + 2CuX_2 + H_2O = PhX + Cu_2X_2 + HX + B(OH)_3$
(e) $PhB(OH)_2 + H_2O = PhH + B(OH)_3$

Hot copper sulphate solution gives benzene, diphenyl, and some phenol. Benzene is also produced with hot aqueous cadmium bromide and zinc chloride. The close relation of cadmium and zinc salts to those of mercury, and the instability of cadmium diphenyl and dialkyls and of zinc diphenyl to water (Hilpert and Grüttner, *Ber.*, 1913, **46**, 1683; Krause, *Ber.*, 1917, **50**, 1815), whereas mercury phenyl chloride is stable to water, would suggest the reactions

$$PhB(OH)_2 + MBr_2 + H_2O = PhMBr + HBr + B(OH)_3$$
$$PhMBr + HOH = PhH + M(OH)Br$$

where M = Cd or Zn. The stability of phenylboric acid to dilute hydrochloric acid indicates that the formation of benzene is not due to the action of the acid resulting from hydrolytic dissociation of the cadmium or zinc halide. The production of benzene by means of copper sulphate may be similarly indicated [the intermediate formation of $(PhCu)_2SO_4$ being assumed], but its non-formation with the cupric halides remains to be explained. The reason may lie in the ease with which cupric halides are reduced to the stable insoluble cuprous compounds.

A striking difference in behaviour towards phenylboric acid is exhibited by the halides of those elements in Group II which have low atomic numbers. Hot aqueous solutions of beryllium chloride and of the chlorides and bromides of magnesium and calcium do not react with the acid, although from a superficial consideration the production of benzene by way of magnesium phenyl bromide might have been expected. The non-reactivity of magnesium bromide may be associated with the necessity for the presence of ether, dimethylaniline, or other electron-donating compound for the production of organo-magnesium halides, whereas in the case of mercury or zinc, which are more plentifully furnished with electrons, this is unnecessary. Zinc ethyl iodide can be obtained with or without ether and recrystallised from ethyl iodide (Beilstein, " Organische Chemie," 4th edition, IV, 676).

The work of Gilman and Schulze (*J. Amer. Chem. Soc.*, 1926, **48**, 2463) on organo-calcium iodides appears to indicate that here also ether is necessary. Beryllium alkyl halides are formed with great difficulty by prolonged heating of beryllium with alkyl halides, ether, and a catalyst (*ibid.*, 1927, **49**, 2904).

Many reactions of boron compounds are to be ascribed to the tendency of this element to complete its octet : the formation of potassium borofluoride and of the compounds $H_3N{\rightarrow}BMe_3$ (Frankland, *Annalen*, 1862, **124**, 138), $H_3N{\rightarrow}BPh_3$, and $R_2NH{\rightarrow}BPh_3$ (Krause, *Ber.*, 1924, **57**, 813) are instances of this affinity for electrons. The formation of a complex ion when boric acid is dissolved in hydrofluoric acid (Abegg, Fox, and Herz, *Z. anorg. Chem.*, 1903, **35**, 129) is probably another example, the reaction possibly proceeding thus :

$$B(OH)_3 + HF \rightleftharpoons \overset{+}{H} + [B(OH)_3\overset{-}{F}].$$

We have observed that it is difficult to extract phenylboric acid with ether from aqueous solutions containing potassium hydrogen fluoride. Addition of calcium chloride precipitates the fluoride and the phenylboric acid is then readily extracted. Presumably a complex ion is formed which is broken up by the calcium chloride, and also by mercuric chloride, since the presence of potassium hydrogen fluoride does not prevent the precipitation of mercury phenyl chloride when mercuric chloride is added to phenylboric acid. Addition of calcium chloride or sodium chloride to aqueous mercuric chloride prevents its interaction with phenylboric acid. Here the effect is due to the excess of chlorine ions in depressing the ionisation of the mercuric chloride.

Nitration of phenylboric acid at about − 10° gives rise to much charring and production of nitrobenzene, but at − 20° it proceeds quantitatively, giving a product (A) containing 70% of m-*nitro-*

phenylboric acid which is readily obtained pure. This behaves like phenylboric acid towards most reagents and the orientation of the nitro-group has been determined by treatment with hydrogen peroxide, mercuric chloride, cupric chloride, cupric bromide, and bromine water; *m*-nitrophenol, mercury *m*-nitrophenyl chloride (Kharasch and Chalkley, *J. Amer. Chem. Soc.*, 1921, **43**, 607), *m*-chloro- and *m*-bromo-nitrobenzenes respectively were then obtained.

The mixture of bromonitrobenzenes (B) obtained from the crude nitration product (A) and cupric bromide has been analysed by the method of Francis and Hill (*J. Amer. Chem. Soc.*, 1924, **46**, 2503), giving the above figure (70%) for the proportion of *m*-nitro-compound in the original nitrated phenylboric acid. The occurrence of *o*- or *p*-substitution was also shown by the formation of some 2 : 4-dinitrobromobenzene (characterised as 2 : 4-dinitrodiphenylamine) on nitration of a portion of (B).

So far as the authors are aware, this is the first recorded instance of the successful nitration of a compound with an incomplete octet. Other examples are furnished by the nitration of phenyl derivatives of certain elements in Groups II and III and will shortly be communicated to the Society in a paper written in conjunction with Miss B. Parker, B.Sc. In no case has the orienting influence of an element of smaller atomic number than boron been investigated. A comparison of the orienting influence of boron with that of other *m*-directing groups is in progress.

The *m*-nitration of phenylboric acid may be explained by the attempt of the boron atom to complete its octet at the expense of the electrons of the benzene nucleus, thus setting up a drift from the aromatic nucleus towards the boron atom whereby the *o*- and *p*-positions are denuded of electrons, with the result that *m*-substitution occurs (see Allan, Oxford, Robinson, and Smith, J., 1926, 409). The *m*-nitration may also be regarded as arising from the fact that, since boron has a total of only 5 electrons external to the nucleus, including the three valency electrons, its nucleus may be regarded as permanently uncovered. Consequently a strong positive field is directed over the benzene nucleus, electrons being withdrawn from the *o*- and *p*-positions.

Phenylboric acid, suspended in light petroleum or in benzene–light petroleum, does not react with hydroferrichloric acid (Robinson, J., 1925, **127**, 768), and therefore is probably almost devoid of basic properties, though Robinson states that " there is a certain minimum strength of a base below which the test is not diagnostic." The above observation renders it improbable that the observed *m*-nitration is due to salt formation.

EXPERIMENTAL.

Reactions of Phenylboric Acid in which the Boron Atom is eliminated.—Chlorine and bromine water. When aqueous phenylboric acid was treated with chlorine or bromine water, a turbidity was produced and the odour of halogenobenzene, much intensified on the addition of potassium hydroxide, was observed.

Iodine. On addition of iodine in potassium iodide to aqueous phenylboric acid no reaction was observed, but a very faint odour of iodobenzene was detected after 4 months. With iodine in the presence of excess of potassium hydroxide, however, iodobenzene was readily produced.

Phenylboric acid (4 g.) in 100 c.c. of cold 20% potassium hydroxide solution was slowly treated with 16·6 g. of iodine. The odour of iodobenzene was observed in 10—15 minutes. After the mixture had been kept overnight at room temperature, extraction with ether yielded 0·8 g. of iodobenzene, characterised as the dichloride, m. p. 111° (decomp.). The alkaline solution was acidified, and sodium hydroxide added to remove iodine; steam distillation then yielded a further 1·4 g. of iodobenzene (total yield, 2·2 g.).

Sodium hydroxide. Phenylboric acid (1 g.) appeared to be unchanged after 20 hours' boiling with 50 c.c. of 5% aqueous sodium hydroxide.

When heated with a small quantity of water and excess of solid sodium hydroxide, phenylboric acid evolved benzene, which gave *m*-dinitrobenzene, m. p. 90°. Sodium borate was detected in the residue.

Water. Phenylboric acid (1·3 g.), heated with 20 c.c. of water at 140—150° for 40 hours, gave benzene (0·8 c.c.), which was identified as before.

Hydrogen peroxide. Phenylboric acid, with cold hydrogen peroxide (20 vols.), readily gave phenol, which was detected by its odour, by the precipitate with bromine water, and by the ferric chloride test.

Mercuric bromide. Phenylboric acid with hot saturated aqueous mercuric bromide gave a precipitate, m. p. 230°. After crystallisation from acetone the m. p. was 276°, which is that of mercury phenyl bromide. The replacement of $-B(OH)_2$ by $-HgX$ proceeds without abnormality and may be employed in orientation experiments. This is indicated by the production of mercury *p*-tolyl chloride, m. p. and mixed m. p. 233°, from *p*-tolylboric acid and aqueous mercuric chloride.

Cupric chloride. When cupric chloride (7 g.) in water (100 c.c.) was boiled under reflux for some hours with phenylboric acid

(2 g.), cuprous chloride was deposited. Distillation yielded chlorobenzene, b. p. 130—132°, in 85% yield. This gave *p*-chloronitrobenzene, m. p. and mixed m. p. 83°.

Cupric bromide. Cupric bromide (20·2 g.; 2 mols.) in water (100 c.c.) was boiled for 2 hours with phenylboric acid (5 g.; 1 mol.). Distillation and ether-extraction yielded 4·5 g. of an oil, which gave 2 c.c. of bromobenzene, b. p. 154—157°, on redistillation. This was characterised as 2 : 4-dinitrobromobenzene, m. p. and mixed m. p. 72°. The non-volatile solid residue (0·7 g.) contained some unchanged phenylboric acid. No diphenyl could be detected.

These reactions with cupric halides proceed normally, the halogen atom entering the nucleus at the place formerly occupied by the $-B(OH)_2$ group as indicated by the formation of pure *p*-bromotoluene when *p*-tolylboric acid is heated with aqueous cupric bromide. Similarly *p*-borobenzoic acid, $CO_2H \cdot C_6H_4 \cdot B(OH)_2$ (Michaelis, *Annalen*, 1901, **315**, 33), gives *p*-chlorobenzoic acid (m. p. and mixed m. p. 236°) with hot aqueous cupric chloride.

Copper cyanide. Cold solutions of phenylboric acid (5 g. in water, 40 c.c.) and copper sulphate (20·5 g. in water, 60 c.c.) were mixed and slowly treated with potassium cyanide (5·4 g. in water, 20 c.c.), cyanogen being evolved. After 2 hours, the mixture was heated at 100° for 40 minutes and left overnight; the odour of benzonitrile was then perceptible. Distillation gave 0·3 g. of oil, which was heated with excess of potassium hydroxide, ammonia being evolved. Acidification and recrystallisation from hot water gave benzoic acid, m. p. 120°. The yield of benzonitrile was only 7%, and no phenylboric acid was recovered, probably being lost as benzene (see p. 2172).

Cadmium bromide. Phenylboric acid (2 g.), cadmium bromide (4·8 g.; 1 mol. + 7%) and water (50 c.c.) were boiled for 6½ hours. Benzene was produced at once (total yield, 1·1 c.c.), and characterised as *m*-dinitrobenzene, m. p. and mixed m. p. 89°. Yield, 78%.

Zinc chloride. Phenylboric acid (2 g.), zinc chloride (2·4 g.; 1 mol. + 9%), and water (20 c.c.) were boiled for 5 hours. Benzene was produced at once (total yield, 1·2 c.c., *i.e.*, 84%), and characterised by its b. p. 78° and as *m*-dinitrobenzene, m. p. and mixed m. p. 90°.

Nitration of Phenylboric Acid.

Preliminary experiments showed that with nitric acid (*d* 1·42) at − 17° or with the fuming acid (*d* 1·5) at − 15° more or less charring and the production of nitrobenzene occurred, though a nitrophenylboric acid could be obtained in small amount. Charring was considerable when the temperature rose above − 10° and in such cases very little, if any, boron compound was isolated. On the other hand, when phenylboric acid (5 g.) was dissolved in 60 c.c. of nitric acid (*d* 1·42) at − 10°, and the whole poured on ice before any darkening or rise in temperature occurred, most of it was recovered unchanged.

The following method gave better results. A mixture of sulphuric acid (15 c.c.) and nitric acid (15 c.c.; *d* 1·42) was cooled to − 16°, and phenylboric acid (1 g.) slowly added during 20 minutes, the temperature rising to − 12°. The mixture, which had contained a suspended white solid throughout the reaction, was left for 3 hours before being poured on ice, the temperature then having risen to − 7°. No charring occurred. On standing overnight, the amount of solid increased and there was a slight odour of nitrobenzene. The resulting solid (C) (0·5 g.), sintering at 233° and m. p. 270° (decomp.), was separated. The acid liquor was concentrated, neutralised with sodium carbonate, faintly acidified with sulphuric acid, and repeatedly extracted with ether, yielding 0·3 g. of a solid (D), m. p. 250° (decomp.) after crystallisation from water. Seven crystallisations gave a product of constant m. p. 273°, identical with (C).

The above conditions were sometimes modified, proportionately less mixed acid being employed, and in each case the reaction mixture was kept for 3 hours before being poured on ice. For further details see p. 2179.

The m. p. of the crude nitration product varied slightly in each preparation and depended to some extent on the rate of heating. A further quantity of nitrated phenylboric acid could always be obtained from the acid liquors as already described. It had a lower m. p., the cause of which was investigated (see p. 2179), but on repeated crystallisation from water, yielded pure m-*nitrophenylboric acid*, m. p. 273° (decomp.) (Found: B, 6·5, 6·5; N, 8·7, 8·8, 9·3,* 9·8,*; H, 3·5. $C_6H_6O_4NB$ requires B, 6·5; N, 8·4; H, 3·6%).

Determination of Boron in m-*Nitrophenylboric Acid*.—*m*-Nitrophenylboric acid was heated with nitric acid (*d* 1·5) for 12 hours at 150—180° and then at 230—250° for 24 hours. The acid liquor was diluted to 100 c.c., the excess of nitric and the nitrous acid in 10 c.c. titrated with 0·1*N*-sodium hydroxide and methyl-red, and the liquid, neutral to methyl-red, gently warmed to 50°. 0·1—0·2 C.c. of 0·05*N*-sodium hydroxide was found necessary to restore neutrality. About 0·5 g. of mannitol was then added, and the boric acid titrated with 0·05*N*-sodium hydroxide and phenolphthalein.

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* The high results obtained in these cases were shown to be due to the presence of nitric oxide, which was detected by ferrous sulphate. The results for carbon were very low owing to fusion of boric oxide round particles of unburned carbon during the combustions.

Identification of the Pure Nitration Product of Phenylboric Acid as m-*Nitrophenylboric Acid.*—*Action of cupric chloride.* The pure product (0·5 g.), when boiled with a concentrated aqueous solution of cupric chloride (2 g.) for 3 hours, gave a solid, which was extracted with ether and shown to be *m*-chloronitrobenzene, m. p. and mixed m. p. 43°. No odour of nitrobenzene could be detected.

Action of mercuric chloride. The pure product, m. p. 273°, from the nitration of phenylboric acid with nitric acid (*d* 1·5) was warmed at 100° with excess of saturated aqueous mercuric chloride, giving a white crystalline precipitate, m. p. 237° after one crystallisation from alcohol. This did not depress the m. p. (237°) of an authentic specimen of mercury *m*-nitrophenyl chloride prepared from the sodium salt of *m*-nitrobenzenesulphinic acid, mercuric chloride, and acetic acid in alcohol (Kharasch and Chalkley, *J. Amer. Chem. Soc.*, 1921, **43**, 607).

Action of bromine water. *m*-Nitrophenylboric acid (3 g.) was shaken for 30 minutes with bromine water, warmed to about 100°, and treated with sodium hydroxide. Filtration gave a pale brown solid (0·3 g.), m. p. 53°, and 54° after crystallisation from aqueous alcohol. Mixed with *m*-bromonitrobenzene, it melted at 54·5—55°. Extraction of the alkaline liquor with ether gave 0·1 g. of an oily solid with the odour of nitrobenzene. On acidification of the extracted liquor, 2·8 g. of a solid, m. p. 279° (decomp.), were precipitated. With aqueous mercuric chloride, this gave mercury *m*-nitrophenyl chloride, m. p. 237°, and the 2·8 g. therefore consisted of unchanged *m*-nitrophenylboric acid.

Action of hydrogen peroxide. *m*-Nitrophenylboric acid (0·35 g.) was shaken with approximately the theoretical amount of hydrogen peroxide (20 vols.; 12 c.c.) for 30 minutes; a test portion then gave a deep orange-red colour with sodium hydroxide. (*m*-Nitrophenylboric acid gives no such colour.) After 2 days, the reaction mixture deposited a few pale yellow crystals (E), m. p. 94—95°. Extraction of the solution with ether gave a brown oil which soon solidified (F). On crystallising (E) and (F) together from water, pale yellow crystals were obtained, m. p. and mixed m. p. with *m*-nitrophenol, 95—96°.

The use of excess of hydrogen peroxide causes considerable decomposition, nitric acid being produced.

Nitration of Phenylboric Acid and Determination of the Relative Proportions of the Isomerides produced.—Phenylboric acid (20 g.) was nitrated in portions of 5 g. with 50 c.c. of nitric acid (*d* 1·41) and 50 c.c. of sulphuric acid at − 20°. After remaining for 3 hours in the freezing mixture, the product was poured on ice, the solid separated, and the acid liquor, after neutralisation with ammonium carbonate and slight acidification with sulphuric acid, extracted with ether. By using 60, 70, 100, and 120 g. of ice, 3·75, 3·05, 2·45, and 2·90 g. (in all, 12·15 g.) of precipitate (G) were obtained having m. p.'s 265—266°, 254°, 259°, and 270° respectively. In the first three cases slight darkening and a faint odour of nitrobenzene were noticed. The ethereal extracts yielded further quantities (in all, 15·1 g.) of solid (H) of m. p.'s ranging from 160° to 184°; these were obviously mixtures. The total yield of nitration product (G + H) was 27·25 g. (calc. for a mononitrophenylboric acid, 27·36 g.).

(G) was crystallised once from water, giving 8·75 g. (J) of m. p. 271—272°, whereas *m*-nitrophenylboric acid has m. p. 273°. Treatment of a trace of (J) with mercuric chloride gave a product of m. p. 207°, whereas mercury *m*-nitrophenyl chloride melts at 237°. (J) was therefore not the pure *m*-compound and was worked up later (see below). The mother-liquor from (J) was extracted with ether, and the product obtained (K, 2 g.) added to (H). There was a loss of 1·4 g. during this extraction, but the control experiment (p. 2180) shows that the result is hardly affected.

The whole of (K) + (H) (17·1 g.) was converted into bromonitrobenzenes by boiling with cupric bromide (50 g.; 2·1 mols.) and water (250 c.c.) for 6½ hours and extracted with ether, giving 19·2 g. of an oil. To ensure complete elimination of boron, this was again boiled with cupric bromide (25 g.) in water (100 c.c.). Ether extraction again gave 19·2 g. of oil (L + M), which distilled mainly from 250—259°, though a small portion (L) passed over up to 275°, leaving only a minute dark residue. The b. p.'s of *o*-, *m*-, and *p*-bromonitrobenzenes are 264°, 257°, and 259°. Both fractions were united and the whole was analysed (Found: Br, 39·4, 39·3. Calc. for $C_6H_4O_2NBr$: Br, 39·6%). The presence of *o*- or *p*-bromonitrobenzene was detected by nitration of 0·15 g. of (L) with nitric and sulphuric acids at 100°. The product, on boiling with alcoholic aniline, gave 2 : 4-dinitrodiphenylamine, which after recrystallisation had m. p. and mixed m. p. 151—152°.

The united bromonitrobenzenes (L + M) were analysed by the method of Francis and Hill, which was shown by preliminary experiments to be well suited to the analysis of mixtures of *o*-, *m*-, and *p*-bromonitrobenzenes (Found: *m*-compound, 61·0, 60·0%. Mean, 60·5%). The nitrophenylboric acid directly precipitated from the nitration mixture by water and recrystallised (J) was similarly converted into a mixture of bromonitrobenzenes (Found: *m*-compound, 93·6, 94·6. Mean, 94·1%).

The total percentage of *m*-isomeride in G + H (*i.e.*, J + K + H) may be computed thus; 8·75 g. of (J) with 94·1% of *m*-compound contain 8·23 g. of *m*-acid; 17·1 g. of (K + H) with 60·5% of *m*-compound contain 10·35 g. of *m*-acid. Therefore 25·85 g. of crude nitration product contain (8·23 + 10·35) = 18·58 g., *i.e.*, 71·9%, of *m*-nitrophenylboric acid.

This result was controlled by a further nitration of 5 g. of phenylboric acid. The solid precipitated by ice (2·65 g.) and that obtained with ether from the neutralised acid liquor (4·05 g.) were united (6·7 g.; calc., 6·8 g.) and converted into bromonitrobenzenes (7·9 g.) as before (Found: *m*-compound, 70·1, 69·9. Mean, 70·0%).

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