Organoboron Compounds. Part VI.[1] Photochemical Reactions of Aryl and Alkyl Halides with Boron Halides

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The photolysis of aryl iodides in the presence of boron halides results in the formation of arylboron dihalides and diarylboron halides by free-radical substitution reactions. Hydrolysis of the products gives the corresponding boronic and borinic acids. Alkyl iodides and di-iodo-compounds behave in a similar manner. The photolysis and subsequent hydrolysis of mixtures of bromo- or chloro-benzene with boron tribromide also affords boronic acids; the by-products indicate that the dibromoboryl ($Br_2B\cdot$) radical takes part in these reactions.

THE usual methods of preparing boronic and borinic acids and their derivatives involve reactions of boron halides or trialkyl borates with organometallic reagents, or of boron halides or diborane with unsaturated compounds.[2] All these reactions appear to proceed by polar or four-centre mechanisms in which the nucleophilic organic groupings add to the electrophilic boron compounds. To see if carbon–boron bonds could also be formed by free-radical processes, we examined some reactions of boron halides with free aryl and alkyl radicals in the liquid phase.

The reactions were brought about by ultraviolet irradiation of mixtures of boron halides and iodo-compounds. This method of generating free radicals avoids the possibility that polar reactions might occur if nitrogen- or oxygen-containing,[3] or organometallic,[4] free-radical sources were used in the presence of the boron halides. We found, for example, that benzoyl peroxide reacted with boiling boron tribromide to give bromobenzene (18·5%) but were unable to isolate any product containing the phenyl–boron bond. There is considerable evidence that photolysis of aryl iodides by ultraviolet light gives free aryl radicals having similar chemical properties to those of radicals produced by other procedures.[4,5] The irradiation of a mixture of boron tri-iodide and iodobenzene for 48 hr. gave, after distillation and hydrolysis, phenylboronic anhydride (64%). A similar reaction with boron tribromide gave phenylboronic anhydride (40%) and 4-biphenylylboronic acid (0·4%) while boron trichloride gave only phenylboronic anhydride (4·4%). The low yield in the last reaction may be due partly to the high volatility of the boron trichloride. At the temperature used (110° ± 20°) the amount of mixing of the reactants would be small. Although the highest yield of phenylboronic anhydride was obtained from boron tri-iodide, the tribromide was chosen for later experiments as it is cheaper and more readily available. The addition of silver powder has been recommended[4] to remove the iodine liberated in the photolysis of iodobenzene but we found that there was little difference between reactions performed in the presence, and in the absence, of silver. Several observ-

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[3] *E.g.*, G. H. Williams, *Chem. and Ind.*, 1961, 1286.

[4] J. M. Blair, D. Bryce-Smith, and B. W. Pengilly, *J. Chem. Soc.*, 1959, 3174.

[5] W. Wolf and N. Kharasch, *J. Org. Chem.*, 1961, **26**, 283; N. Kharasch, W. Wolf, T. J. Erpelding, P. G. Naylor, and L. Tokes, *Chem. and Ind.*, 1962, 1720; N. Kharasch and L. Göthlich, *Angew. Chem. Internat. Edn.*, 1962, **1**, 459.

ations indicate that the above reactions do involve phenyl radicals despite the presence of the highly electrophilic boron halides. First, iodobenzene did not react with boron tribromide when heated under reflux in the dark for 12 hr. in the presence of silver powder, indicating that ultraviolet light is necessary to bring about the reaction. Secondly, the isolation of 4-biphenylylboronic acid from the hydrolysed products of the reaction between iodobenzene and boron tribromide indicates that some phenylation of the aromatic nucleus of the intermediate phenylboron dibromide has occurred. The formation of biaryls is a characteristic reaction of aryl radicals in the presence of aromatic compounds.[6] The photolysis of iodobenzene in the presence of phenylboron dichloride and of phenylboron dibromide for 40 and 50 hr., respectively, provided two further examples of such phenylations. The main products, obtained by distillation, were diphenylboron chloride (23·4%) and diphenylboron bromide (27%). After hydrolysis of the distillation residues, small amounts of 3- and 4-biphenylylboronic acid (0·16 and 1·6%, respectively) were obtained from the former and of the 4-isomer (0·9%) from the latter reaction. Despite a careful search, we were unable to obtain any of the 2-biphenylylboronic acid from either reaction. This suggests that the steric effects of the $-BCl_2$ and $-BBr_2$ groups hinder substitution in the 2-position of the phenylboron dihalides just as those of the $-CCl_3$ group affect the phenylation of benzotrichloride.[6] The photolysis of mixtures of other iodo-compounds with boron tribromide for periods of 45—76 hr. was next examined, the products being isolated after hydrolysis. The following boronic acids or boronic anhydrides were obtained from the corresponding iodides: *p*-tolyl- (24%), *p*-chlorophenyl- (10%), *m*-chlorophenyl- (13·5%), 4-biphenylyl- (44%), *n*-butyl- (6·1%), and *p*-iodophenyl- (18·6%). 1-Iodonaphthalene afforded only 2-naphthylboronic acid (25%), the 1-naphthyl radical or the intermediate 1-naphthylboron dibromide having rearranged to the 2-isomer during reaction. The following diboronic acids resulted from similar photolyses (for periods of 36—60 hr.) with di-iodo-compounds: *p*-phenylene- (9%), 4,4′-biphenylylene- (3%), and 1,10-decamethylene- (12·5%). The above yields reflect in some cases the difficulty of isolation of the boron compounds rather than the efficiency of the reactions. The range of usable iodo-compounds is limited by the need to effect the photolyses in the liquid phase. Thus 4,4′-di-iodobiphenyl (m. p. 202°) required a reaction temperature of *ca.* 200°, which resulted in inefficient mixing with the boron tribromide (b. p. 91°).

All the products described above are those which would be expected to be formed by the radicals resulting from the homolysis of the carbon–iodine bond in the various iodo-compounds. The photolytic reactions of bromobenzene and of chlorobenzene with boron tribromide were rather more complicated however. From the former we obtained, after irradiation for 50 hr. and subsequent hydrolysis, phenylboronic anhydride (25·5%), *p*-bromophenylboronic acid (3·2%), and a little *p*-phenylenediboronic acid (0·3%), and from the latter, after 74 hr., phenylboronic anhydride (9%) and *p*-chlorophenylboronic acid (5·6%). In each case the main reaction appears to involve the photolysis of the aryl halide, the resulting phenyl radicals reacting subsequently with boron tribromide to form phenylboron dibromide. The dissociation energies [7] of the carbon–halogen bonds in the halogenobenzenes indicate that the homolysis of the carbon–chlorine and carbon–bromine bonds should be more difficult to effect than that of the carbon–iodine bond. This is in agreement with the yields of phenylboronic anhydride isolated from the above reactions which were much lower than that obtained from the corresponding reaction of iodobenzene. The minor products must be formed by a different route. We suggest that the boron tribromide itself is photolysed to some extent forming dibromoboryl ($Br_2B\cdot$) radicals which react with the aromatic compounds present. The excess of bromo- and chloro-benzene give *p*-bromo- and *p*-chloro-phenylboron dibromide, respectively, which on hydrolysis form the corresponding boronic acids. In the reaction with bromobenzene the phenylboron dibromide resulting from the main photochemical process is partly converted into *p*-phenylenebis(boron dibromide) and thence to the diboronic acid. This explanation is supported by the isolation of *p*-phenylenediboronic acid in small (1·9%) yield from the photolysis (for 48 hr.) and subsequent hydrolysis of a mixture of phenylboron dibromide and boron tribromide. The photolysis of a mixture of bromobenzene and boron trichloride for 30 hr. gave, after hydrolysis, only a little phenylboronic anhydride (3·3%). *p*-Bromophenylboronic acid could not be isolated, indicating that photolysis of boron trichloride does not take place under these conditions. A mixture of fluorobenzene and boron tribromide on being photolysed for a short period (8 hr.) and then hydrolysed gave some phenylboronic anhydride (0·65%) showing that the carbon–fluorine bond is photolysed to some extent.

Authentic specimens of all the boronic acids and anhydrides obtained in these experiments were made by reactions between methyl borate and the appropriate Grignard reagents. The m. p.s of the boronic acids and of their anhydrides are notoriously unreliable when determined by conventional methods.[2] We obtained reproducible values by melting the acids, or preferably the anhydrides, in evacuated capillaries. The values thus obtained were often even higher than those resulting from the tedious "instant immersion" technique [8] and it is clear that previous difficulties have been due largely to aerial oxidation of the boron compounds during heating. The boronic acids were further characterised by the formation of their esters with di-(2-hydroxy-

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ethyl)amine [9,10] or with 2,2-dimethylpropane-1,3-diol.[1] The ultraviolet absorption spectra of the biphenylylboronic acids were in close agreement with those [11] of the corresponding biphenylcarboxylic acids; likewise phenylboronic anhydride and benzoic acid [12] show similar ultraviolet absorption.

We investigated briefly the photolysis of mixtures of iodobenzene with halides of other elements. No recognisable products were obtained with silicon tetrabromide or stannic bromide, but phosphorus trichloride and tribromide gave phenylphosphonous dichloride (8·5%) and dibromide (11·5%), respectively, after irradiation for 50—53 hr.

EXPERIMENTAL

Melting points were determined in Pyrex capillaries evacuated to 0·1 mm. Nitrogen was determined by the Kjeldahl method and boron by photometric titration in aqueous ethanol with 0·1N-sodium hydroxide in the presence of a large excess of mannitol, with Thymol Blue–Cresol Red indicator.

Authentic Boronic Acids and Anhydrides.—(*a*) 4-*Biphenylylboronic acid.* The Grignard reagent from 4-bromobiphenyl (23·3 g.), magnesium turnings (2·6 g.), and tetrahydrofuran (kept over potassium hydroxide pellets for 2 days, then distilled from sodium; 120 ml.) was added dropwise with stirring to a solution of trimethyl borate (freshly distilled; 14 ml., 12·9 g.) in dry ether (100 ml.) at such a rate that the temperature did not rise above −70°. Next day the mixture was added with stirring to ice (100 g.) and concentrated sulphuric acid (5 ml.) and shaken repeatedly with ether. Evaporation of the ethereal extract gave a solid which crystallised from aqueous ethanol giving 4-biphenylylboronic acid (15·05 g., 76%), m. p. 264—266° (lit.,[13] m. p. 232—234°) (Found: B, 5·5. Calc. for $C_{12}H_{11}BO_2$: B, 5·45%).

(*b*) *Others.* The following acids and anhydrides were prepared similarly from the corresponding aryl bromides, the acids being dehydrated by heating at 110° or by sublimation at 260°/0·001 mm.: 3-biphenylylboronic acid (80%), m. p. 208—210° (lit.,[13] m. p. 207—208°) (Found: B, 5·45. Calc. for $C_{12}H_{11}BO_2$: B, 5·45%); 2-biphenylylboronic acid (35%; the mixture of Grignard reagent and methyl borate was heated under reflux for 1 hr.) (Found: B, 5·6%; it was necessary to use Thymolphthalein as indicator) which lost water at 122—125° forming 2-biphenylylboronic anhydride, m. p. 194—196° (lit.,[13,14] m. p. 195°); 1-naphthylboronic anhydride (46·5%), m. p. 218—220° (lit.,[13] for acid, m. p. 219°); 2-naphthylboronic anhydride (40%), m. p. 286—288° (lit.,[13] for acid, m. p. 280°); *p*-iodophenylboronic acid (14% from *p*-di-iodobenzene), m. p. 286°, which gave p-*iodophenylboronic anhydride*, m. p. 344—347° (Found: B, 4·75; I, 55·1. C_6H_4BIO requires B, 4·7; I, 55·25%). The following were prepared similarly from the corresponding aryl iodides in ether as solvent in the formation of the Grignard reagents: *p*-chlorophenylboronic anhydride (50%), m. p. 307—309° (lit.,[8] for acid, m. p. 306—307°) (Found: Cl, 25·5; B, 7·65. Calc. for C_6H_4BClO: Cl, 25·65; B, 7·8%); *m*-chlorophenylboronic anhydride (56%), m. p. 189—191° (lit.,[8] for acid, m. p. 189—190°) (Found: Cl, 25·6; B, 7·65%). Phenylboronic anhydride had m. p. 220—222° (lit.,[15] m. p. 223—224°), *p*-tolylboronic anhydride had m. p. 262—264° (lit.,[16] m. p. 259°), and *p*-bromophenylboronic anhydride had m. p. 322—324° (lit.,[17] for acid, m. p. 312—315°).

Ultraviolet Absorption.—Phenylboronic anhydride has $\lambda_{max.}$ 2680 (log ε 2·82), 2735 (2·90), and 2800 Å (2·80) in cyclohexane and $\lambda_{max.}$ 2615 (log ε 2·56), 2670 (2·64), and 2740 Å (2·54) in ethanol. 2-, 3-, and 4-Biphenylylboronic acids have $\lambda_{max.}$ 2460 (log ε 4·15), 2510 (4·24), and 2600 Å (4·41), respectively, in light petroleum (b. p. 100—120°).

2,2-*Dimethylpropane*-1,3-*diol Boronates.*—A mixture of the boronic acid (0·005 mole), 2,2-dimethylpropane-1,3-diol (0·005 mole), and benzene (50 ml.) was heated under reflux until evolution of water was complete (*ca.* 6 hr.). After removal of the solvent under reduced pressure the resulting 2,2-dimethylpropane-1,3-diol boronate (50—95% yield) was crystallised from light petroleum (b. p. 80—90°) at low temperature or, if liquid, was distilled under reduced pressure. The following esters were prepared by this procedure: the 4-*biphenylylboronate*, m. p. 108—109° (Found: C, 77·0; H, 7·4; B, 4·0. $C_{17}H_{19}BO_2$ requires C, 76·7; H, 7·2; B, 4·05%); the 3-*biphenylylboronate*, m. p. 85—87° (Found: B, 4·0%); the 2-*biphenylylboronate*, b. p. 110°/0·07 mm. (Found: B, 4·1%); and the p-*iodophenylboronate*, m. p. 118—118·5° (Found: B, 3·35; I, 40·1. $C_{11}H_{14}BIO_2$ requires B, 3·4; I, 40·2%).

Di-(2-*hydroxyethyl*)*amine Boronates.*—Solutions of the boronic acid (0·005 mole) and of redistilled di-(2-hydroxyethyl)amine (diethanolamine) (0·005 mole) in hot acetone were mixed and cooled giving the crystalline boronate in 65—80% yield. The following esters were prepared by this procedure: the 2-*biphenylylboronate*, m. p. 184—186° (Found: N, 5·1. $C_{16}H_{18}BNO_2$ requires N, 5·25%); the p-*chlorophenylboronate*, m. p. 250·5—251·5° (Found: B, 4·7; Cl, 16·1; N, 6·2. $C_{10}H_{13}BClNO_2$ requires B, 4·8; Cl, 15·7; N, 6·2%); the m-*chlorophenylboronate*, m. p. 207—209° (Found: B, 4·7; Cl, 15·5; N, 6·1%); the 2-*naphthylboronate*, m. p. 250—252° (Found: N, 5·8. $C_{14}H_{16}BNO_2$ requires N, 5·8%); and the 1-naphthylboronate, m. p. 243—244° (lit.,[9] m. p. 242—243°) (Found: N, 5·8%).

Phenylboron Dibromide.—Prepared by the method [18] previously used for phenylboron dichloride, boron tribromide being substituted for boron trichloride, this (100%) had b. p. 42—44°/0·2 mm. (lit.,[19] b. p. 80°/8 mm.). Treatment with water followed by heating at 110° gave phenylboronic anhydride, m. p. 220—222°.

Photochemical Reactions.—These were effected in a long quartz test-tube (2 × 17 cm.) fitted with a ground socket by which was attached a long water-cooled reflux condenser. Dry nitrogen was passed into the top of the condenser to

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exclude air and moisture. The inner surface of the test-tube was rubbed continuously with glass wool [4] attached to a glass stirrer which passed down the inner tube of the condenser. The test-tube was irradiated with a "Hanovia" S 500 medium pressure mercury-vapour lamp mounted 3 cm. away and the assembly was surrounded by aluminium foil to reflect the ultraviolet light. The temperature of the tube was kept at 110° ± 20° by air-cooling. In the reactions involving boron trichloride a condenser cooled with a mixture of acetone and solid carbon dioxide was used.

The identities of the reaction products described below were established by (*a*) the comparison of their infrared spectra (recorded for Nujol mulls or for liquid films with a Perkin-Elmer "Infracord" model 137 spectrophotometer) with those of authentic specimens, and (*b*) the absence of m. p. depressions on admixture with authentic specimens. All operations involving boron halides were performed under dry nitrogen.

Iodobenzene and Boron Tribromide.—Purified [4] iodobenzene (10 g.) and boron tribromide (10 g.) were irradiated for 48 hr. Distillation of the dark reaction mixture under reduced pressure gave a dark red liquid, b. p. 40—45°/0·4 mm. and a less-volatile residue. Both were shaken separately with water and ether, and the ethereal extracts were evaporated under reduced pressure. The solid resulting from the hydrolysis of the distillate crystallised from water to give phenylboronic acid which on being dried at 110° afforded phenylboronic anhydride (1·66 g., 40%), m. p. 220—222° (authentic, m. p. 220—222°) (Found: B, 10·3. Calc. for C_6H_5BO: B, 10·4%). This formed 2,2-dimethylpropane-1,3-diol phenylboronate, m. p. 65·5° (plates from aqueous methanol) (lit.,[1] m. p. 65—65·5°). The solid obtained from the hydrolysis of the distillation residue crystallised from water or from aqueous ethanol giving 4-biphenylylboronic acid (0·03 g., 0·4%) as plates, m. p. 261—263° (authentic, m. p. 264—266°). This formed 2,2-dimethylpropane-1,3-diol 4-biphenylylboronate, m. p. 107—108° (authentic, m. p. 108—109°).

From a similar reaction in which silver powder was added at intervals during the irradiation period, phenylboronic anhydride (39%) and 4-biphenylylboronic acid (0·3%) were isolated. When the irradiation time was reduced to 10 hr., only phenylboronic anhydride (16·5%) was obtained.

Iodobenzene and Boron Trichloride.—Iodobenzene (50 g.) and boron trichloride (25 g.) were irradiated for 48 hr. Distillation afforded unchanged boron trichloride (12 g.), b. p. 13°, and a liquid, b. p. 68—75°/15 mm., which was added to ice (50 g.). The resulting solid crystallised from water and when dried at 110° formed phenylboronic anhydride (0·97 g., 4·4%), m. p. 221—223°. The addition of silver powder did not affect the yield of the anhydride.

Iodobenzene and Boron Tri-iodide.—Iodobenzene (10 g.) and boron tri-iodide (2·1 g.) were irradiated for 48 hr., silver powder being added at intervals. The reaction mixture was added to ice (75 g.) and ether, and the ethereal extract was evaporated. The resulting solid crystallised from water and on drying at 110° gave phenylboronic anhydride (0·355 g., 64%), m. p. 220—221°.

Iodobenzene and Phenylboron Dichloride.—Iodobenzene (30 g.) and phenylboron dichloride [18] (19 g.) were irradiated for 40 hr., silver powder being added from time to time. Distillation of the mixture under reduced pressure gave unchanged starting materials, b. p. 35—45°/1 mm., followed by diphenylboron chloride (5·6 g., 23·4%), b. p. 110°/0·5 mm. (lit.,[20] b. p. 98°/0·1 mm.). Hydrolysis of the latter with moist nitrogen gave diphenylborinic anhydride, m. p. 114—115° (lit.,[20] m. p. 116°), which was dissolved in methanol and treated with a saturated methanolic solution of 8-hydroxyquinoline until no more precipitation occurred. The yellow precipitate was crystallised from methanolic tetrahydrofuran giving the 8-hydroxyquinoline ester of diphenylborinic acid, m. p. 205° (lit.,[21] m. p. 204—205°) (Found: N, 4·2. Calc. for $C_{21}H_{16}BNO$: N, 4·55%). The residue from the distillation of the reaction mixture was shaken with 2N-sodium hydroxide and ether, and the aqueous solution was acidified with 2N-hydrochloric acid and shaken with ether. Evaporation of the ethereal extract gave a gum, part of which was soluble in boiling water, and part in boiling toluene. On cooling, these solutions deposited crystals of, respectively, 3-biphenylylboronic acid (0·04 g., 0·16%), m. p. 207—209° (authentic, m. p. 208—210°), and 4-biphenylylboronic acid (0·4 g., 1·6%), m. p. 263—265° (authentic, m. p. 264—266°).

Iodobenzene and Phenylboron Dibromide.—Iodobenzene (20 g.) and phenylboron dibromide (17·8 g.) were irradiated for 50 hr. Distillation under reduced pressure gave a mixture of unchanged starting materials, b. p. 70—75°/18 mm., followed by diphenylboron bromide (4·88 g., 27%), b. p. 110—112°/0·05 mm. (lit.,[22] b. p. 110°/0·01 mm.). Hydrolysis of the latter with moist nitrogen gave diphenylborinic anhydride, m. p. 114—116° (lit.,[20] m. p. 116°). The residue from the distillation was shaken with water and ether. Evaporation of the ethereal extract gave 4-biphenylylboronic acid (0·13 g., 0·9%) as plates, m. p. 262—264° (authentic, m. p. 264—266°), from water. This formed 2,2-dimethylpropane-1,3-diol 4-biphenylylboronate, m. p. 107—109° (authentic, m. p. 108—109°).

p-*Iodotoluene and Boron Tribromide.*—*p*-Iodotoluene (10 g.) and boron tribromide (10 g.) were irradiated for 45 hr. and then poured on ice (150 g.). The mixture was made alkaline with 2N-sodium hydroxide, washed with ether (3 × 25 ml. portions), filtered, and acidified with 2N-hydrochloric acid. The resulting precipitate crystallised from water giving *p*-tolylboronic acid (1·3 g., 24%) which on being dried at 110° formed *p*-tolylboronic anhydride, m. p. 263—264° (authentic, m. p. 262—264°). This gave di-(2-hydroxyethyl)amine *p*-tolylboronate, m. p. 235—238° (lit.,[10] m. p. 232—233°) (Found: N, 6·9. Calc. for $C_{11}H_{16}BNO_2$: N, 6·85%).

p-*Chloroiodobenzene and Boron Tribromide.*—*p*-Chloroiodobenzene (10 g.) and boron tribromide (10 g.) were irradiated for 76 hr. and then treated as described above for *p*-iodotoluene. The product crystallised from water giving *p*-chlorophenylboronic acid (0·63 g., 10%) as plates which on sublimation at 260°/0·01 mm. gave *p*-chlorophenylboronic anhydride, m. p. 308—309° (authentic, m. p. 307—309°). This formed di-(2-hydroxyethyl)amine *p*-chlorophenylboronate, m. p. 251—253° (authentic, m. p. 250·5—251·5°).

m-*Chloroiodobenzene and Boron Tribromide.*—A mixture of *m*-chloroiodobenzene (10 g.) and boron tribromide (10 g.) was irradiated for 48 hr. and treated as described for *p*-iodotoluene. *m*-Chlorophenylboronic acid (0·84 g., 13·5%) crystallised from water in plates which on sublimation at 260°/0·001 mm. gave *m*-chlorophenylboronic

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anhydride m. p. 188—190° (authentic, m. p. 189—191°). This formed di-(2-hydroxyethyl)amine *m*-chlorophenylboronate, m. p. 207—209° (authentic, m. p. 207—209°).

4-*Iodobiphenyl and Boron Tribromide*.—4-Iodobiphenyl (8·4 g.) and boron tribromide (10 g.) were irradiated for 51 hr., silver powder being added from time to time. Treatment as for *p*-iodotoluene gave 4-biphenylylboronic acid (2·6 g., 44%) which crystallised from aqueous ethanol as plates, m. p. 263—265° (authentic, m. p. 264—266°).

1-*Iodonaphthalene and Boron Tribromide*.—1-Iodonaphthalene (10·16 g.) and boron tribromide (10 g.) were irradiated for 54 hr., silver powder being added from time to time, and treated as for *p*-iodotoluene. 2-Naphthylboronic acid (1·71 g., 25%) crystallised from benzene and was converted by sublimation at 260°/0·001 mm. into 2-naphthylboronic anhydride, m. p. 287—288° (authentic, m. p. 286—288°). This gave di-(2-hydroxyethyl)amine 2-naphthylboronate, m. p. 250—252° (authentic, m. p. 250—252°).

1-*Iodobutane and Boron Tribromide*.—1-Iodobutane (10 g.) and boron tribromide (10 g.) were irradiated for 48 hr. Treatment as for *p*-iodotoluene gave n-butylboronic acid (0·25 g., 6·1%) which was isolated by ether-extraction and crystallised from water in plates, m. p. 92—95° (lit.,[23] m. p. 92—94°) (Found: B, 10·45. Calc. for $C_4H_{11}BO_2$: B, 10·6%).

p-*Di-iodobenzene and Boron Tribromide*.—*p*-Di-iodobenzene (13·2 g.) and boron tribromide (30 g.) were irradiated for 60 hr., silver powder being added from time to time, and treated as for *p*-iodotoluene. The resulting precipitate was extracted with ether and the insoluble residue was crystallised from water to give *p*-phenylenediboronic acid (0·6 g., 9%) as an infusible solid. This formed bis-(2,2-di-methylpropane-1,3-diol) *p*-phenylenediboronate, m. p. 233—235° (lit.,[24] m. p. 233—233·5°). Evaporation of the above ethereal extract gave *p*-iodophenylboronic acid (1·84 g., 18·6%) which crystallised, m. p. 284—285° (authentic, m. p. 286°) from water, and which sublimed at 260°/0·001 mm. giving *p*-iodophenylboronic anhydride, m. p. 344—346° (authentic, m. p. 344—347°). This formed 2,2-dimethylpropane-1,3-diol *p*-iodophenylboronate, m. p. 117—118° (authentic, m. p. 118—118·5°).

4,4′-*Di-iodobiphenyl and Boron Tribromide*.—4,4′-Di-iodobiphenyl (4·06 g.) and boron tribromide (20 g.) were irradiated for 36 hr. at 200° and treated as for *p*-iodotoluene. 4,4′-Biphenylylenediboronic acid [25] (0·075 g., 3%) was obtained as an infusible solid which gave bis-(2,2-dimethylpropane-1,3-diol) 4,4′-biphenylylenediboronate, m. p. 248—250° (lit.,[25] m. p. 250—251°) (Found: B, 5·85. Calc. for $C_{22}H_{28}B_2O_4$: B, 5·7%).

1,10-*Di-iododecane and Boron Tribromide*.—1,10-Di-iododecane (15·76 g.) and boron tribromide (30 g.) were irradiated for 53 hr., silver powder being added from time to time, and treated as for *p*-iodotoluene. Crystallisation from dioxan gave 1,10-decamethylenediboronic acid [25] (1·15 g., 12·5%) which formed bisdi-(2-hydroxyethyl)amine 1,10-decamethylenediboronate, m. p. 216° (lit.,[25] m. p. 216—218°).

Bromobenzene and Boron Tribromide.—Bromobenzene (10 g.) and boron tribromide (10 g.) were irradiated for 50 hr. and then distilled under reduced pressure giving unchanged starting materials followed by a liquid, b. p. 40—45°/0·2 mm. which was added to ice (150 g.). Extraction with ether afforded a solid which when crystallised from water and dried at 110° gave phenylboronic anhydride (1·05 g., 25·5%), m. p. 220—222°. The residue from the above distillation was shaken with water and ether. The solid which remained undissolved was *p*-phenylenediboronic acid (0·01 g., 0·3%) which gave bis-(2,2-dimethylpropane-1,3-diol) *p*-phenylenediboronate, m. p. 232—234° (lit.,[24] m. p. 233—233·5°). Evaporation of the ethereal extract gave *p*-bromophenylboronic acid (0·26 g., 3·2%) which crystallised from water and which sublimed at 260°/0·01 mm. to form *p*-bromophenylboronic anhydride, m. p. 320—323° (authentic, m. p. 322—324°). This gave di-(2-hydroxyethyl)amine *p*-bromophenylboronate, m. p. 272—273° (lit.,[10] m. p. 272·5—273°).

Repetition of this reaction with an irradiation time of 7 hr. gave only phenylboronic anhydride (4%).

Phenylboron Dibromide and Boron Tribromide.—Phenylboron dibromide (11·9 g.) and boron tribromide (20 g.) were irradiated for 48 hr. and then distilled under reduced pressure to remove unchanged starting materials. The residue was treated with water and the resulting solid crystallised from water giving *p*-phenylenediboronic acid (0·15 g., 1·9%) which formed bis-(2,2-dimethylpropane-1,3-diol) *p*-phenylenediboronate, m. p. 233—235° (lit.,[24] m. p. 233—233·5°).

Chlorobenzene and Boron Tribromide.—Chlorobenzene (15 g.) and boron tribromide (20 g.) were irradiated for 74 hr. Distillation under reduced pressure yielded unchanged starting materials and a liquid, b. p. 43—64°/0·1 mm., which was added to ice (200 g.) and shaken with ether. Evaporation of the ethereal extract under reduced pressure and crystallisation of the residue from water followed by drying at 110° gave phenylboronic anhydride (0·74 g., 9%), m. p. 220—222°. The residue from the distillation of the reaction mixture was shaken with water and ether. Evaporation of the ethereal extract gave *p*-chlorophenylboronic acid (0·7 g., 5·6%) which crystallised from water and which sublimed at 260°/0·01 mm. to give *p*-chlorophenylboronic anhydride, m. p. 306—308° (authentic, m. p. 307—309°).

Repetition of this reaction with an irradiation time of 7 hr. gave only phenylboronic anhydride (1%).

Fluorobenzene and Boron Tribromide.—Fluorobenzene (15 g.) and boron tribromide (25 g.) were irradiated for 8 hr., silver powder being added from time to time, and poured into ice (200 g.) and extracted with ether. Evaporation of the ethereal extract gave a solid which on crystallisation from water and drying at 110° afforded phenylboronic anhydride (0·068 g., 0·65%), m. p. 220—222°.

Bromobenzene and Boron Trichloride.—Bromobenzene (40 g.) and boron trichloride (25 g.) were irradiated for 30 hr., silver powder being added from time to time, and then added to ice (200 g.) and shaken with ether. Evaporation of the ethereal extract under reduced pressure, crystallisation of the residue from water, and drying at 110° gave phenylboronic anhydride (0·72 g., 3·3%), m. p. 221—222°.

Iodobenzene and Phosphorus Trichloride.—Iodobenzene (25 g.) and phosphorus trichloride (13·75 g.) were irradiated for 50 hr., silver powder being added from time to time. Distillation under reduced pressure afforded unchanged starting materials and phenylphosphonous dichloride (1·52 g., 8·5%), b. p. 60—64°/0·5 mm. (lit.,[26] b. p. 68—70°/1 mm.) (Found: P, 17·0. Calc. for $C_6H_5Cl_2P$: P, 17·3%).

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Iodobenzene and Phosphorus Tribromide.—Iodobenzene (45 g.) and phosphorus tribromide (54 g.) were irradiated for 53 hr., silver powder being added from time to time. Distillation gave unchanged starting materials followed by phenylphosphonous dibromide (6·12 g., 11·5%), b. p. 90°/0·05 mm. (lit.,[27] b. p. 75—80°/0·005 mm.) (Found: P, 11·3. Calc. for $C_6H_5Br_2P$: P, 11·55%).

Reaction of Benzoyl Peroxide with Boron Tribromide.—Benzoyl peroxide (crystallised from chloroform and dried at 20°/10 mm.; 5 g.) was added in portions to boiling boron tribromide (25 g.). The mixture was heated under reflux for 3 hr. and distilled giving unchanged boron tribromide (20·5 g.), b. p. 20°/18 mm., and bromobenzene (0·6 g., 18·5%), b. p. 40—43°/18 mm.

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