Organoboron Compounds. Part VII.¹ Photochemical Reactions of Boron Halides with Aromatic Hydrocarbons and Aromatic Ethers

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The u.v. irradiation and subsequent hydrolysis of a mixture of boron tri-iodide and benzene, and of mixtures of boron tribromide and benzene, or toluene, or biphenyl, or naphthalene results in the formation of the corresponding arylboronic acids. The initial reaction products, the arylboron dihalides, appear to be formed by photolysis of the boron trihalides followed by reaction of the resulting dihalogenoboryl radicals with the aromatic compounds. The reaction induced by visible light between benzene and boron tribromide gives low yields (after hydrolysis) of phenylboronic acid and *p*-phenylenediboronic acid and may occur *via* a loosely bound complex of the reactants. Naphthalene reacts with boron tribromide on irradiation with u.v. light to give, after hydrolysis, 2-naphthylboronic acid. A similar, but much less efficient, reaction occurs when these reactants are heated together in the dark. Irradiation and subsequent hydrolysis of a mixture of diphenyl ether and boron tribromide gives 10-hydroxy-10-bora-9-oxa-aro-anthracene; the corresponding reaction with 4-bromodiphenyl ether gives only a trace of 3-bromo-10-hydroxy-10-bora-9-oxa-aro-anthracene, the major product being 4-phenoxyphenylboronic acid. Irradiation of a mixture of phosphorus tribromide and benzene gives phenyl-phosphonous dibromide in low yield.

IN Part VI of this series ¹ we described the formation of organoboron compounds by the u.v. irradiation of mixtures of boron trihalides and aryl halides. Most of the products appeared to result from reactions of the aryl radicals formed by the photolysis of the aryl halides, but some of the minor products obtained from those reactions involving the less-easily photolysed aryl halides could not be accounted for in this way. Thus, boron tribromide and bromobenzene afforded, after hydrolysis, a little $(3\cdot 2\%)$ p-bromophenylboronic acid while a similar reaction with chlorobenzene gave a somewhat larger yield (5.6%) of p-chlorophenylboronic acid. We suggested that these products were formed by the photolysis of the boron tribromide and reaction of the resulting dibromoboryl (Br_2B) radicals with the excess of aryl halide present. This explanation was supported by our finding that the photolysis of a mixture of phenylboron dibromide and boron tribromide gave, after hydrolysis, a small (1.9%) yield of p-phenylenediboronic acid. As no other reactions involving dihalogenoboryl radicals have been reported we have examined the

¹ Part VI, R. A. Bowie and O. C. Musgrave, J. Chem. Soc. (C), 1966, 566.

photolysis of mixtures of boron tribromide with various aromatic compounds in order to learn more about the processes involved.

Benzene and boron tribromide did not react when boiled together in the dark for 50 hr. but on irradiation for 48 hr. with the unfiltered light from a 500 w mediumpressure mercury-vapour lamp, followed by distillation, gave phenylboron dibromide (20% based on BBr₃). Alternatively, hydrolysis of the crude reaction mixture with ice gave phenylboronic acid (25%) which was converted into phenylboronic anhydride for identification purposes. The latter isolation procedure resulted in the more efficient recovery of the organoboron compound and was adopted in subsequent experiments. Boron tri-iodide is more easily photolysed than is boron tribromide, being decomposed to some extent even by visible light. The much higher (48%) yield of phenylboronic anhydride obtained when a solution of the tri-iodide in benzene was irradiated with u.v. light shows that the scission of the boron-halogen bond is the crucial step in the reaction. The continuous absorption shown 2

² R. S. Sharma, Bull. Acad. Sci. United Provinces Agra Oudh, Allahabad, 1933, **3**, 87. aromatic hydrocarbons examined. Prolonged (70 hr.) heating in the dark with an excess of boron tribromide gave, after hydrolysis, a small yield (6.7%) of 2-naphthylboronic acid; the same product was obtained in much higher yield (36.4%) when the reaction was effected photochemically.

Diphenyl ether and boron tribromide had previously¹⁰ been shown to react slowly at 170-180° to form a phenoxyphenylboron dibromide but the photochemical reaction between these compounds took a different course. Hydrolysis of the irradiated reaction mixture gave 10-hydroxy-10-bora-9-oxa-aro-anthracene (I; X = H) in



10% yield which, on sublimation, underwent dehydration to give the corresponding borinic anhydride. 4-Bromodiphenyl ether and boron tribromide behaved in a similar manner to give, as the minor product, a trace (1.1%) of 3-bromo-10-hydroxy-10-bora-9-oxa-aro-anthracene (I; X = Br) which was also converted into a borinic anhydride by sublimation. The structure of the latter compound follows from the close resemblance of its i.r. and u.v. absorption spectra to those of the anhydride derived from the unbrominated borinic acid (I; X = H). The major product of the photochemical reaction was 4-phenoxyphenylboronic acid which clearly results from the photolysis of the aryl halide and subsequent reaction of the 4-phenoxyphenyl radical with boron tribromide. Authentic specimens of 4- and 3-phenoxyphenylboronic acid were prepared for comparison purposes by reaction of the appropriate Grignard reagents with trimethyl borate.

The photolysis of iodobenzene in the presence of phosphorus tribromide results in the formation of phenylphosphonous dibromide.¹ We have now found that on irradiation with u.v. light phosphorus tribromide reacts with benzene to give a small (5%) yield of phenylphosphonous dibromide. As phosphorus tribromide undergoes photolysis under such conditions to give dibromophosphinyl (Br₂P·) radicals¹¹ it seems likely that the product results from attack by these radicals on the benzene.

EXPERIMENTAL

The arrangements for effecting the photochemical reactions, and the methods used for the analysis of the products and for the preparation of derivatives are described in Part VI.¹ In addition the boron contents of some of the boronic acids were determined by potentio-

7 L. R. Koller, 'Ultraviolet Radiation,' John Wiley, New York, 1965, 2nd edn., p. 99. ⁸ R. A. Bowie and O. C. Musgrave, Proc. Chem. Soc., 1964, 15.

- 9 A. Finch, P. N. Gates, and D. Steele, Trans. Faraday Soc., 1965, **61**, 2623. ¹⁰ Z. J. Bujwid, W. Gerrard, and M. F. Lappert, *Chem. and*
- Ind., 1959, 1091.
 - ¹¹ B. Fontal and H. Goldwhite, Chem. Comm., 1965, 111.

by gaseous boron tribromide below about 2770 Å appears to be a consequence of the photodissociation of the compound, presumably into bromine atoms and dibromoboryl radicals. The start of the continuum corresponds to a bond-dissociation energy with an upper limit of *ca.* 103 kcal. mole⁻¹ which is compatible with the average thermochemical bond energy (88 \pm 1.5 kcal. mole⁻¹) recently calculated ³ for the B-Br bond in boron tribromide. As quite a large proportion of the u.v. radiation from a medium-pressure mercury-vapour $lamp^4$ has wavelengths <2770 Å we consider it to be highly likely that the dibromoboryl radical is the reactive species in the photochemical reaction between benzene and boron tribromide.⁵ The complete absence of reaction observed when boron trichloride was substituted for the tribromide can be attributed to the greater energy required to cause homolysis of the B-Cl bond. The mercury-vapour lamp used provides no radiation in the region below about 2200 Å where gaseous boron trichloride shows ⁶ continuous absorption.

Benzene and boron tribromide also reacted, much less efficiently, when subjected to prolonged (200 hr.) illumination with the light from an ordinary tungsten-filament lamp. After hydrolysis, phenylboronic anhydride (7%) and p-phenylenediboronic acid (2.4%) were obtained, indicating that small amounts of phenylboron dibromide and p-phenylenedi(boron dibromide) had been formed. Although such an incandescent lamp radiates mainly visible and i.r. light it also supplies a small amount of near-u.v. light 7 with wavelengths between 3200 and 4000 Å. Pure benzene and pure boron tribromide do not absorb in this region however, both compounds showing significant absorption only at wavelengths below about 2800 Å, and simple photolysis of the boron tribromide clearly cannot occur under these conditions. A solution of boron tribromide in benzene immediately develops a very weak absorption maximum at 4650 Å followed, on keeping in the dark, by rather stronger maxima at 3150 and 4350 Å (both with $E_{1 \text{ cm.}}^{1\%}$ ca. 0.5 after 24 hr.). In a preliminary communication ⁸ we attributed these changes to complex formation between the two substances, and spectroscopic examination⁹ of solutions of boron tribromide in benzene has demonstrated the existence of a loose 1:1 complex. Presumably it is the absorption of light by this complex which leads to the formation of phenylboron dibromide and, eventually, of p-phenylenedi(boron dibromide), though the reaction path is obscure.

The u.v. irradiation of mixtures of boron tribromide with toluene and with biphenyl gave respectively p-tolylboron dibromide (23%) and, after hydrolysis, a mixture of 3- and 4-biphenylylboronic acid (25.5%). Naphthalene proved to be the most reactive of the

⁶ D. J. Knowles and A. S. Buchanan, Inorg. Chem., 1965, 4, 1799.

³ A. Finch, P. J. Gardner, and I. J. Hyams, Trans. Faraday

Soc., 1965, 61, 649.
 ⁴ J. G. Calvert and J. N. Pitts, 'Photochemistry,' John Wiley, New York, 1966, p. 695.
 ⁵ Cf. D. Bryce-Smith, Ann. Reports, 1964, 61, 334.

metric titration with 0.1M-aqueous sodium hydroxide in the presence of mannitol, with a glass electrode. M.p.s were determined in Pyrex capillaries evacuated to 0.1 torr. The identities of the reaction products were established (a) by the comparison of their i.r. spectra (recorded for Nujol mulls or for liquid films with a Perkin-Elmer ' Infracord ' model 137 spectrophotometer) with those of authentic specimens, and (b), where appropriate, by the absence of m.p. depressions on admixture with authentic specimens. U.v. spectra were measured with Hilger 'Ultrascan' and Perkin-Elmer model 137UV spectrophotometers. All operations involving boron halides were performed under dry nitrogen.

Photochemical Reactions

Benzene and Boron Tribromide.—(a) A mixture of benzene (8.8 g.) and boron tribromide (10 g.) was irradiated for 48 hr. and then added to ice (75 g.). Extraction with ether afforded a solid which when crystallised from water and dried at 110° gave phenylboronic anhydride (1.04 g., 25%), m.p. 221-222° (lit., 1 m.p. 220-222°) which formed 2,2-dimethylpropane-1,3-diol phenylboronate, m.p. 65° (lit.,¹² m.p. 65-65.5°) (Found: B, 5.75. Calc. for C₁₁H₁₅-BO₂: B, 5.7%).

Distillation of a similar irradiated reaction mixture gave phenylboron dibromide (1.98 g., 20%), b.p. 40°/0.1 torr (lit.,¹ b.p. 42-44°/0·2 torr.).

(b) A mixture of benzene (8.8 g.) and boron tribromide (10 g.) was illuminated with light from a 200 w standard gas-filled tungsten lamp for 200 hr. and then added to ice (100 g.) and shaken with ether. The insoluble solid thereby obtained was p-phenylenediboronic acid (0.08 g., 2.4%) which formed di-(2,2-dimethylpropane-1,3-diol) p-phenylenediboronate, m.p. 232-234° (lit.,¹³ m.p. 233-233.5°). The ethereal extract afforded phenylboronic anhydride (0.29 g., 7%), m.p. 220-222°.

Benzene and Boron Tri-iodide .--- A mixture of benzene (8.8 g.) and boron tri-iodide (4.29 g.) was irradiated for 48 hr. and then treated as described above in (a). The resulting phenylboronic anhydride (0.55 g., 48%) had m.p. 220-221°.

Toluene and Boron Tribromide .--- A mixture of toluene (10 g.) and boron tribromide (10 g.) was irradiated for 62 hr. Distillation under reduced pressure gave unchanged starting materials and p-tolylboron dibromide (2.4 g., 23%), b.p. 120°/0.2 torr (lit.,14 b.p. 145°/25 torr) which was added to ice (100 g.). Extraction with ether afforded a solid which after crystallisation from water and sublimation at 240°/01 torr gave p-tolylboronic anhydride m.p. 260-262° (lit.,¹ m.p. 262-264°).

Biphenyl and Boron Tribromide.—A mixture of biphenyl (6.2 g.) and boron tribromide (10 g.) was irradiated for 76 hr. and then added to ice (150 g.). The solution was basified with 2M-sodium hydroxide and shaken for 1 hr., washed with ether $(3 \times 25 \text{ ml. portions})$, and then acidified with 2M-hydrochloric acid when a mixture of 3- and 4-biphenylylboronic acid (2.02 g., 25.5%), m.p. 248-252° was precipitated. The i.r. absorption was indistinguishable from that of an authentic mixture, m.p. 242-246° of the 3-isomer (70%) and the 4-isomer (30%). Attempted separations of the mixture of acids and of their mixed 2,2-dimethyl-

propane-1,3-diol boronates by crystallisation and by t.l.c. were unsuccessful.

Naphthalene and Boron Tribromide.-(a) A mixture of naphthalene (7.5 g.) and boron tribromide (10 g.) was irradiated for 50 hr. and treated as described above for biphenyl. The resulting 2-naphthylboronic acid (2.5 g., 36.4%) sublimed at $260^{\circ}/0.001$ torr to form 2-naphthylboronic anhydride, m.p. 285-286° (lit.,¹ m.p. 286-288°) which gave di-(2-hydroxyethyl)amine 2-naphthylboronate, m.p. 251-252° (lit., 1 m.p. 250-252°) (Found: N, 5.75. Calc. for C₁₄H₁₆BNO₂: N, 5.8%).

(b) A mixture of naphthalene (5 g.) and boron tribromide (20 g.) was heated under reflux for 70 hr. in the dark and then treated as described in (a). The resulting 2-naphthylboronic acid (0.45 g., 6.7%) formed 2-naphthylboronic anhydride, m.p. 285-287° and di-(2-hydroxyethyl)amine 2-naphthylboronate m.p. 250-252°.

Diphenyl Ether and Boron Tribromide.--- A mixture of diphenyl ether (6.8 g.) and boron tribromide (20 g.) was irradiated for 48 hr. and then treated as described above for biphenyl. Crystallisation of the resulting solid from aqueous ethanol gave nearly pure 10-hydroxy-10-bora-9-oxa-aro-anthracene (I; X = H) (0.8 g., 10%) as needles, m.p. 270–273°, ν_{max} 3300 (OH); 1910, 1780, and 1680vw, and 748s cm.⁻¹ (o-disubstituted benzene). The i.r. absorption was identical with that of an authentic specimen of the borinic acid prepared by the method of Davidson and French.¹⁵ Repeated sublimation of the product, m.p. 270-273°, at 220-240°/0.1 torr gave the pure borinic anhydride as needles, m.p. 288.5-289° (lit.,15 for the borinic acid, m.p. 285°; lit.,¹⁶ for the anhydride in air, m.p. 273—275°), λ_{max} (in cyclohexane) 2310 (log ε 5.050), 2490 (4.307), 2670 (3.408), 2775 (3.448), 3110 (4.023), 3230 (4.210), λ_{infl} , 2405 (log ε 4.670), 2690 (3.375), 2985 (3.627), 3170 (4.033). This was identical with (a) a resublimed authentic specimen of the borinic anhydride kindly provided by Dr. H. J. Roth ¹⁶ and (b) a specimen of the borinic anhydride prepared by subliming the authentic borinic acid ¹⁵ at 240°/0·1 torr. Both the borinic acid and its anhydride were unaffected by exposure to atmospheric oxygen for several years.

4-Bromodiphenyl Ether and Boron Tribromide.--- A mixture of 4-bromodiphenyl ether (12.5 g.) and boron tribromide (20 g.) was irradiated for 48 hr. and treated as described above for biphenyl. The resulting solid crystallised from aqueous ethanol to give, as the less-soluble product, 3-bromo-10-hydroxy-10-bora-9-oxa-aro-anthracene (I; X = Br) (0.15 g., 1.1%) which on sublimation at 260°/0.01 torr formed the corresponding bromoboronic anhydride, m.p. 221-223° (Found: Br, 30.1. $C_{24}H_{14}B_2Br_2O_3$ requires Br, 30.05%), λ_{\max} (in cyclohexane) 2380 (log ε 5.06), 2760 (3.47), and 3210 (4.22), $\lambda_{infl.}$ 2480 (log ε 4.70), 2650 (3.55), 2830 (3.37), 3100 (4.03), 3170 (4.11), and 3290 Å (3.92). Evaporation of the mother-liquors from the above crystallisation afforded the more-soluble product which crystallised from aqueous ethanol to give 4-phenoxyphenylboronic acid (0.35 g., 3.5%), m.p. 133-134° (authentic, see below, m.p. 134-135°).

Benzene and Phosphorus Tribromide.---A mixture of benzene (26 g.) and phosphorus tribromide (54 g.) was irradiated for 48 hr. Distillation gave phenylphosphonous

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 H. J. Roth and B. Miller, Arch. Pharm., 1964, 297, 524.
- ¹² R. A. Bowie and O. C. Musgrave, J. Chem. Soc., 1963, 3945. ¹³ O. C. Musgrave, Chem. and Ind., 1957, 1152.

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dibromide (2·04 g., 5%), b.p. 92—94°/0·05 torr (lit.,¹⁷ b.p. 75—80°/0·005 torr) (Found: P, 11·2. Calc. for $C_6H_5Br_2P$: P, 11·55%).

4-Phenoxyphenylboronic Acid.—Prepared by the usual procedure ¹ from trimethyl borate and 4-phenoxyphenylmagnesium bromide in ether at -70° this (49%) crystallised from ethanol as needles, m.p. 134—135° (lit.,¹⁸ m.p. 123—124°). On being dried at 110°/0.4 torr it gave the corresponding anhydride, m.p. 149—150° (Found: B, 5.55. C₁₂H₉BO₂ requires B, 5.5%), while with di-(2-hydroxy-ethyl)amine ¹ it gave di-(2-hydroxyethyl)amine 4-phenoxy-phenylboronate as needles, m.p. 217—219° (from acetone) (Found: N, 5.2. C₁₆H₁₈BNO₃ requires N, 4.95%).

3-Phenoxyphenylboronic Acid.—Prepared in a similar manner ¹ from trimethyl borate and 3-phenoxyphenyl-magnesium bromide in ether and tetrahydrofuran at -70°

this (60%) crystallised from water. On being dried at 110°/0·4 torr it gave the corresponding anhydride, m.p. 147—148° (Found: B, 5·5. $C_{12}H_9BO_2$ requires B, 5·5%); di-(2-hydroxyethyl)amine converted it into di-(2-hydroxyethyl)amine 3-phenoxyphenylboronate which crystallised from acetone as needles, m.p. 198—200° (Found: N, 5·0. $C_{16}H_{18}BNO_3$ requires N, 4·95%).

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