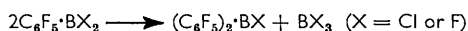


730. *Polyfluoroaryl Organometallic Compounds. Part II.*¹
Pentafluorophenylboron Halides and Some Derived Compounds

By R. D. CHAMBERS and T. CHIVERS

Pentafluorophenylboron dihalides $C_6F_5BX_2$ ($X = Cl$ or F) have been prepared by cleavage of trimethylpentafluorophenyltin, dimethylbis(pentafluorophenyl)tin and methylpentafluorophenylmercury with boron halides; and bis(pentafluorophenyl)boron chloride, $(C_6F_5)_2BCl$, can be obtained by reaction of dimethylbis(pentafluorophenyl)tin with one molecular proportion of boron trichloride. Unlike the perfluoroalkyl or perfluorovinyl compounds, the perfluoroaryl derivatives do not decompose by migration of fluorine from carbon to boron; on heating, the dihalides disproportionate



Careful hydrolysis of the di- and mono-halides gave pentafluorophenylboronic acid and bis(pentafluorophenyl)borinic acid, respectively. These acids show an unusual susceptibility to nucleophilic cleavage of the organic groups and a resistance to dehydration. The nuclear magnetic resonance (n.m.r.) spectra of pentafluorophenylboron compounds indicate π - p interaction in the trivalent boron derivatives.

INTEREST in pentafluorophenyl derivatives of metals and non-metals has recently been established; a number of derivatives have been described² and preliminary Communications include some derivatives of boron.³ We describe here the preparation and chemistry

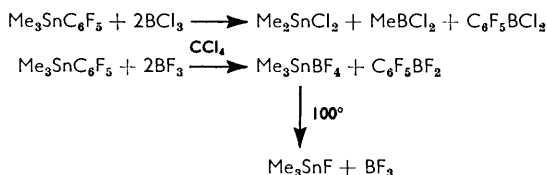
¹ Part I, R. D. Chambers and T. Chivers, *J.*, 1964, 4782.

² L. A. Wall, R. E. Donadio, and W. J. Pummer, *J. Amer. Chem. Soc.*, 1960, **82**, 4846; R. D. Chambers, G. E. Coates, J. G. Livingstone, and W. K. R. Musgrave, *J.*, 1962, 4367; J. M. Holmes, R. D. Peacock, and J. C. Tatlow, *Proc. Chem. Soc.*, 1963, 108; G. B. Deacon and R. S. Nyholm, *Chem. and Ind.*, 1963, 1803; M. A. Chaudhari, F. G. A. Stone, and P. M. Treichel, *J. Organomet. Chem.*, 1963, **1**, 98; M. D. Rausch, *J. Inorg. Chem.*, 1964, **3**, 300; J. G. Noltes and J. W. G. Van Den Hurk, *J. Organomet. Chem.*, 1964, **1**, 377.

³ R. D. Chambers and T. Chivers, *Proc. Chem. Soc.*, 1963, 208; A. G. Massey, A. J. Park, and F. G. A. Stone, *ibid.*, p. 212.

of pentafluorophenylboron halides and their derivatives. Perfluoroaryl derivatives of boron are particularly interesting, since trifluoromethylboron difluoride,⁴ the only perfluoroalkyl derivative of three-covalent boron that has been isolated, is very unstable because of the easy migration of fluorine from carbon to boron, giving boron trifluoride; this instability, although reduced, is still evident in the corresponding trifluorovinyl compounds, which also give boron trifluoride.⁵ In perfluoroarylboron compounds, this mode of decomposition may be expected to be affected by π - p interaction with boron, and especially so because there is no fluorine attached to a carbon atom that is alpha to boron.

Reactions of boron trihalides with tetra-alkyl- and tetra-aryl-tin compounds are well-known routes to the corresponding organoboron dihalides,⁶ but tetrakis(pentafluorophenyl)-tin is too unreactive to be useful as a route to pentafluorophenylboron dihalides. However, we have found that pentafluorophenyl in methylpentafluorophenyltin compounds is very susceptible to electrophilic cleavage, *e.g.*, trimethylpentafluorophenyltin reacts with two molecular proportions of boron trichloride or trifluoride giving the corresponding pentafluorophenylboron dihalides.



The reaction with boron trifluoride is particularly significant in that trimethyltin tetrafluoroborate is produced; it thus differs from the analogous reaction of trimethyltrifluoromethyltin, $\text{Me}_3\text{SnCF}_3 + \text{BF}_3 \longrightarrow \text{Me}_3\text{Sn}[\text{CF}_3 \cdot \text{BF}_3]$,⁷ indicating that pentafluorophenylboron difluoride, in contrast to trifluoromethylboron difluoride, is a weaker Lewis acid than boron trifluoride. Trifluorovinylboron dichloride has been made by Stafford and Stone,⁸ by an analogous method, and converted into the difluoride with antimony trifluoride below 0° . Pentafluorophenylboron dichloride was also conveniently fluorinated by this method, but in reaction at 45° , exchange of pentafluorophenyl occurred, giving bis-(pentafluorophenyl)antimony chloride. Pentafluorophenylboron dichloride can also be conveniently prepared by cleavage of methylpentafluorophenylmercury with boron trichloride, $\text{MeHgC}_6\text{F}_5 + \text{BCl}_3 \longrightarrow \text{MeHgCl} + \text{C}_6\text{F}_5\text{BCl}_2$. The mercurial is, in fact, useful for the preparation of a number of pentafluorophenyl metal and non-metal halides by similar reactions.^{1,9} Both pentafluorophenylboron dihalides formed solid complexes with pyridine, $\text{C}_6\text{F}_5\text{BX}_2 \cdot \text{Py}$ ($X = \text{Cl}$ or F), and it was possible to displace pentafluorophenylboron dichloride from the complex by using boron trichloride at 110° , indicating that this pentafluorophenyl compound is a weaker Lewis acid,¹⁰ but the complex of the difluoride was not stable enough when heated with boron trifluoride for the results to be meaningful.

No perfluorocarbon boronic acid has previously been characterised, and hydrolysis of pentafluorophenylboron dihalides to pentafluorophenylboronic acid required careful control in order to avoid the competing cleavage of pentafluorophenyl, to give pentafluorobenzene. However, at -78° and by using an equivalent quantity of water in acetone, pentafluorophenylboron dichloride was successfully hydrolysed to pentafluorophenylboronic

acid, $\text{C}_6\text{F}_5\text{BCl}_2 \xrightarrow{\text{H}_2\text{O}} \text{C}_6\text{F}_5\text{B}(\text{OH})_2 + 2\text{HCl}$. The hydrolytic stability of the acid itself depends on the acidity of the medium, since the acid was recovered unchanged from

⁴ T. D. Parsons, E. D. Baker, A. B. Burg, and G. L. Juvinall, *J. Amer. Chem. Soc.*, 1961, **83**, 250.

⁵ H. D. Kaesz, S. L. Stafford, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6232.

⁶ W. Gerrard, "The Organic Chemistry of Boron," Academic Press, London, 1961, p. 59, and references therein.

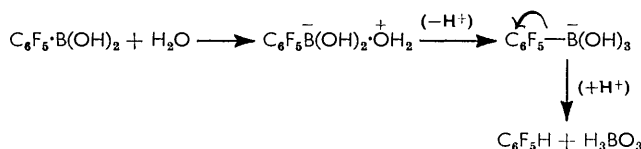
⁷ R. D. Chambers, H. C. Clark, and C. J. Willis, *J. Amer. Chem. Soc.*, 1960, **82**, 5298.

⁸ S. L. Stafford and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6238.

⁹ R. D. Chambers and J. Cunningham, unpublished results.

¹⁰ J. M. Miller and M. Onyszchuk, *Canad. J. Chem.*, 1963, **41**, 2898.

solution in acidic aqueous acetone, but in neutral or basic solutions it was rapidly hydrolysed to pentafluorobenzene and boric acid. We deduce from this that it is the anion of the boric acid that is unstable.



Although acid- and base-catalysed cleavage reactions of arylboronic acids are common,^{6,11} such ready cleavage as described above seems to be unknown; but, this increase in the already electrophilic properties of tricovalent boron, by attached pentafluorophenyl, is consistent with the observed effect of pentafluorophenyl on tin¹ and lead.⁹ The unusual susceptibility to nucleophilic attack was further reflected by the fact that we were unable to prepare a diethanolamine ester, which is normally the most convenient derivative for the characterisation of arylboronic acids.¹² Cleavage with hydrogen peroxide, a well-known reaction of arylboronic acids,¹³ was complicated in this case by competing hydrolysis but, with 85% peroxide, the reaction proceeded smoothly to give a high yield of pentafluorophenol, $\text{C}_6\text{F}_5\text{B}(\text{OH})_2 + \text{H}_2\text{O}_2 \longrightarrow \text{C}_6\text{F}_5\text{OH} + \text{H}_3\text{BO}_3$. Another difference between the properties of phenylboronic and pentafluorophenylboronic acids is that the latter is not significantly dehydrated on being heated; the ease of dehydration of substituted phenylboronic acids is obviously very susceptible to both the type and the position of the substituents,¹⁴ but the effect is not yet predictable.

It has already been mentioned that fluoroalkyl and, to a lesser extent, trifluorovinyl derivatives of tricovalent boron are unstable, in that fluorine attached to carbon atoms in the α - or β -positions to the boron can migrate^{4,5,15} and give boron trifluoride under a variety of conditions. On this basis, it seemed likely that the corresponding pentafluorophenyl derivatives would decompose, by migration of the fluorine in the pentafluorophenyl group and *ortho* to boron, to give pentafluorobenzene. Pentafluorophenylboron difluoride underwent $\sim 40\%$ decomposition to boron trifluoride on storage in a sealed tube at room temperature, and this reaction was accelerated by heating, *e.g.*, at 194° a 77% yield of boron trifluoride was obtained. However, the accompanying product was bis(pentafluorophenyl)boron fluoride. Also, in a similar manner, pentafluorophenylboron dichloride was converted to boron trichloride and bis(pentafluorophenyl)boron chloride, $2\text{C}_6\text{F}_5\cdot\text{BX}_2 \longrightarrow (\text{C}_6\text{F}_5)_2\text{BX} + \text{BX}_3$ ($\text{X} = \text{Cl}$ or F). Thus, although pentafluorophenylboron dihalides are unstable with respect to boron trihalides, the reaction involved is simple disproportionation and not the formation of tetrafluorobenzene. Pentafluorophenylboron dichloride is much less susceptible to disproportionation than the difluoride, which must be stored at -78° .

Bis(pentafluorophenyl)boron chloride was more conveniently obtained by cleavage of dimethylbis(pentafluorophenyl)tin with only *one* molecular proportion of boron trichloride, $\text{Me}_2\text{Sn}(\text{C}_6\text{F}_5)_2 + \text{BCl}_3 \longrightarrow \text{Me}_2\text{SnCl}_2 + (\text{C}_6\text{F}_5)_2\text{BCl}$. The monochloride on hydrolysis, under the conditions already described for the dihalides, gave bis(pentafluorophenyl)borinic acid but, when these particular conditions were not employed then cleavage of pentafluorophenyl occurred, as with the dihalides. Bis(pentafluorophenyl)borinic acid was unstable in neutral aqueous solution, giving pentafluorobenzene and boric acid; and the borinic acid also showed resistance to dehydration.

Fluorine-19 Nuclear Magnetic Resonance Spectra.—The fluorine-19 chemical shift for

¹¹ H. G. Kuivila and K. V. Nahabedian, *J. Amer. Chem. Soc.*, 1961, **83**, 2159, and references therein.

¹² O. C. Musgrave and T. O. Park, *Chem. and Ind.*, 1955, 1552; R. L. Letsinger and I. Skoog, *J. Amer. Chem. Soc.*, 1955, **77**, 2491.

¹³ H. G. Kuivila, *J. Amer. Chem. Soc.*, 1954, **76**, 870.

¹⁴ L. Santucci, L. Tavoletti, and D. Montalbano, *J. Org. Chem.*, 1962, **27**, 2257.

¹⁵ J. R. Phillips and F. G. A. Stone, *J.*, 1962, 94; J. M. Birchall, R. N. Haszeldine, and J. F. Marsh, *Chem. and Ind.*, 1961, 1080.

para-fluorine in pentafluorophenyl derivatives has been suggested as a possible probe for indicating $d\pi-p\pi$ interaction between pentafluorophenyl and metal atoms,¹ since it has been shown that the fluorine-19 chemical shift is sensitive to resonance interaction of a *para*-substituted group with the aromatic ring, both in fluorobenzenes¹⁶ and pentafluorobenzenes.¹⁷ Chemical shifts for *para*-fluorine in pentafluorophenylboron compounds are shown in the Table and indicate a sensitivity to $p-\pi$ interaction of pentafluorophenyl

¹⁹F chemical shifts (from CCl₃F) for pentafluorophenylboron compounds

Compound	Solvent	δ (ortho) (p.p.m.)	δ (meta) (p.p.m.)	δ (para) (p.p.m.)
C ₆ F ₅ ·BCl ₂	None	129.2	161.0	145.0
	CCl ₄ *	128.25	160.7	145.3
C ₆ F ₅ ·BCl ₂ , C ₆ H ₅ N	CHCl ₃	133.5	163.3	155.7
	Me ₂ CO	133.1	164.1	157.2
C ₆ F ₅ ·BF ₂	CCl ₄ *	127.75	160.4	143.0
C ₆ F ₅ ·BF ₂ , C ₆ H ₅ N	Me ₂ CO	132.9	163.1	155.6
C ₆ F ₅ ·B(OH) ₂	Me ₂ CO	132.9	164.1	155.4
(C ₆ F ₅) ₂ BCl	None	129.5	161.3	145.35

Measured in p.p.m. relative to CCl₃F as internal standard

* At infinite dilution.

with boron. A difference of 10 p.p.m. is observed between the shifts for *para*-fluorine in the corresponding three- and four-covalent boron derivatives *e.g.*, for C₆F₅·BCl₂ and C₆F₅·BCl₂, C₆H₅N, whereas the values for *ortho*- and *meta*-positions remain reasonably constant. Acetone will co-ordinate to boron in pentafluorophenylboronic acid, and the *para*-fluorine shift observed for the latter corresponds to a four-covalent derivative. Thus the relative deshielding of the *para*-fluorine in the three-covalent state must arise from the $p-\pi$ interaction mentioned above, and this probably contributes to the increased stability of perfluoroarylboron compounds over the corresponding perfluoro-alkyl and -vinyl derivatives, since the partial occupation of the fourth covalency of boron would make the migration of fluorine from carbon to boron less likely to occur.

EXPERIMENTAL

Cleavage of Methylpentafluorophenyltin Compounds with Boron Halides.—(a) *Trimethylpentafluorophenyltin and boron trichloride.* Boron trichloride (10.04 g., 86 mmoles) was condensed from a vacuum system into an evacuated Carius tube containing trimethylpentafluorophenyltin,¹ (14.3 g., 43 mmoles). The tube was sealed under vacuum and kept at 20° overnight. White crystals appeared after 20 min. at 20°. The tube was opened to a vacuum system and volatile material fractionated through a trap at -78° in which *pentafluorophenylboron dichloride* (10.26 g., 96%), b. p. 155° (extrapolated), was contained and was characterised by its formation of a complex with pyridine.

Pentafluorophenylboron dichloride (2.0 g., 8.0 mmoles) was condensed on to an equimolar quantity of anhydrous pyridine in dry di-*n*-butyl ether (10 ml.). A white solid was formed, which was filtered off to give *pentafluorophenylboron dichloride-1-pyridine* (1.5 g., 57%) which, after recrystallisation from benzene-cyclohexane had m. p. 140—142° (Found: C, 40.3; N, 4.4. C₁₁H₅BCl₂F₅N requires C, 40.3; N, 4.3%) and could be handled without special precautions. Volatile material that passed through the trap at -78° was methylboron dichloride, which gave an infrared spectrum that was identical with that of an authentic specimen, made by heating together trimethylboron and boron trichloride.¹⁸ The residue in the Carius tube was shown to be dimethyltin dichloride (8.96 g., 41 mmoles) by comparison of its infrared spectrum and m. p. with those of an authentic specimen; m. p. (from cyclohexane) 106—107° (lit.,¹⁹ 108°).

(b) *Dimethylbis(pentafluorophenyl)tin and excess of boron trichloride.* Boron trichloride (2.87 g., 24.6 mmoles) was condensed into a Carius tube containing dimethylbis(pentafluorophenyl)tin (1.44 g., 3.0 mmoles). The tube was sealed off under vacuum and kept at 20° for

¹⁶ R. W. Taft, F. Prosser, L. Goodman, and G. T. Davis, *J. Chem. Phys.*, 1963, **38**, 380.

¹⁷ N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Mol. Phys.*, 1964, **8**, 133.

¹⁸ A. G. Massey, *J.*, 1960, 5264.

¹⁹ Z. M. Manulkin, *Chem. Abs.*, 1947, **41**, 90.

34 hr. and then opened to a vacuum system. Volatile material was fractionated through a trap at -78° to give excess of boron trichloride (2.28 g., 19.5 mmoles), identified by its infrared spectrum; a residue (0.75 g.) containing largely dimethyltin dichloride remained in the tube, and pentafluorophenylboron dichloride (1.10 g., 74%) was contained in the trap.

(c) *Dimethylbis(pentafluorophenyl)tin and boron trichloride (1 : 1)*. Boron trichloride (3.11 g., 26.5 mmoles) was condensed into a Carius tube containing dimethylbis(pentafluorophenyl)tin (12.8 g., 26.5 mmoles) and the tube was then sealed under vacuum and allowed to reach room temperature. White crystals appeared after 30 min. at this temperature and the tube was heated to 100° for 2 hr. The tube was cooled and its contents were quickly transferred to a vacuum sublimation apparatus and sublimed ($20^\circ/0.05$ mm.) to give dimethyltin dichloride (4.0 g., 18.3 mmoles), identified by its infrared spectrum and m. p. (from cyclohexane). The residue was distilled ($68-72^\circ/0.02$ mm.) to give *bis(pentafluorophenyl)boron chloride* (3.6 g., 36%), which crystallised when cooled (Found: Cl, 9.2; F, 50.0. $C_{12}BClF_{10}$ requires Cl, 9.2; F, 49.5%).

(d) *Trimethylpentafluorophenyltin and boron trifluoride*. Boron trifluoride (1.68 g., 24.8 mmoles) was condensed into a Carius tube containing trimethylpentafluorophenyltin (2.12 g., 6.4 mmoles) in anhydrous carbon tetrachloride (10 ml.). The tube was sealed off under vacuum and allowed to reach 20° . After 1 hr. a white precipitate appeared, and after 60 hr. the tube was opened to a vacuum system and volatile material was fractionated through a trap at -78° . Excess of boron trifluoride (0.84 g., 12.4 mmoles) was obtained, and the liquid in the trap, which was a mixture of pentafluorophenylboron difluoride and carbon tetrachloride, was hydrolysed by cautious addition of water to the cooled solution. Pentafluorophenylboronic acid was obtained and identified by its m. p. and infrared spectrum (see later). The residue of trimethyltin tetrafluoroborate in the tube was heated to 100° to give boron trifluoride (0.42 g., 6.2 mmoles), and left trimethyltin fluoride (1.11 g., 6.4 mmoles), identified by comparison of its infrared spectrum with that of an authentic specimen. In a separate experiment without heat, the precipitate in the Carius tube was filtered off in a dry box, and its infrared spectrum (potassium bromide disc) showed a broad band centred at 1050 cm.^{-1} , which is characteristic of tetrafluoroborates.²⁰

Fluorination of Pentafluorophenylboron Dichloride.—(a) *At -15°* . Dry antimony trifluoride was obtained by continuous extraction into anhydrous methanol followed by distillation of the solvent under vacuum. Pentafluorophenylboron dichloride (10.7 g., 43 mmoles) was condensed into a Carius tube containing antimony trifluoride (10.7 g., 58 mmoles). The tube was sealed off under vacuum, kept at -15° for 4 hr., and then opened to a vacuum system; volatile material was fractionated through a trap at -78° , to give boron trifluoride (0.20 g., 3.0 mmoles), and pentafluorophenylboron difluoride (6.8 g., 73%), which was contained in the trap and was characterised by hydrolysis to pentafluorophenylboronic acid (see later), and by conversion into a 1 : 1 complex with pyridine. Pentafluorophenylboron difluoride (1.5 g., 6.95 mmoles) was condensed into an equimolar quantity of anhydrous pyridine in dry petroleum (b. p. $40-60^\circ$) (15 ml.). The white solid that formed was filtered off, and found to be *pentafluorophenylboron difluoride-1-pyridine*, m. p. $82-83^\circ$ (from chloroform-light petroleum) (Found: F, 45.4. $C_{11}H_5BF_7N$ requires F, 45.1%); it was slowly hydrolysed in air.

(b) *At 45°* . Pentafluorophenylboron dichloride (2.0 g., 8.1 mmoles) was condensed into a Carius tube containing antimony trifluoride (4.5 g., 25.0 mmoles). The tube was then sealed under vacuum, heated at 45° for $1\frac{1}{2}$ hr., and opened to a vacuum system; volatile material was fractionated through a trap at -78° giving boron trifluoride (0.37 g., 5.6 mmoles), and the trap contained pentafluorophenylboron difluoride (0.33 g., 18%), identified by its infrared spectrum. The residue in the Carius tube was extracted with ether (30 ml.), the solution dried ($MgSO_4$), and the solvent was removed under vacuum, to give a white solid which, on sublimation under vacuum, gave *bis(pentafluorophenyl)antimony chloride* (1.1 g., 55%), which after a second sublimation had m. p. $68-71^\circ$ (Found: C, 29.6; Cl, 7.3; F, 38.0. $C_{12}ClF_{10}Sb$ requires C, 29.4; Cl, 7.2; F, 38.7%).

Reaction of Boron Trichloride and Methylpentafluorophenylmercury.—Boron trichloride (1.25 g., 10.7 mmoles) was condensed into a Carius tube containing methylpentafluorophenylmercury²¹ (1.98 g., 5.3 mmoles) and the tube was sealed under vacuum and kept for 24 hr. at 20° . The tube was then opened to the vacuum line and volatile material was fractionated through a trap at -78° to give excess of boron trichloride (0.70 g., 6.0 mmoles) and pentafluorophenylboron dichloride (1.12 g., 84%) was contained in the trap. A white solid residue of

²⁰ D. W. A. Sharpe, "Advances in Fluorine Chemistry," vol. 1, Butterworths, London, 1960, p. 70.

²¹ R. D. Chambers, G. E. Coates, J. G. Livingstone, and W. K. R. Musgrave, ref. 2.

methylmercury(II) chloride (1.33 g., 5.3 mmoles), m. p. 170° (lit.,²² 167°), remained in the Carius tube and was identified by comparison of its infrared spectrum with that of an authentic specimen.

Pentafluorophenylboronic Acid.—Pentafluorophenylboron dichloride (10.26 g., 41.5 mmoles) was added, dropwise, to acetone (40 ml.) cooled to -78° and containing the calculated amount of water for the hydrolysis. Solvent was removed by vacuum transfer to give *pentafluorophenylboronic acid* (7.85 g., 89%) which, after sublimation (140°/0.01 mm.), had m. p. 290° (Found: F, 44.4. C₆H₂BF₅O₂ requires F, 44.6%). Neutralisation equivalents were determined by dissolving a weighed sample of the acid in 50% aqueous ethanol containing 20 times the solute weight of D-mannitol, and titrating it with standard sodium hydroxide solution to the phenolphthalein end-point. The values obtained were dependent on the previous treatment of the acid, but in no case was any significant amount of dehydration indicated: sample recrystallised from toluene (Found: Equiv. = 212.7, pentafluorophenylboronic acid requires Equiv. = 211.9; the anhydride requires Equiv. = 193.9); sample sublimed at 140°/0.01 mm. (Found: Equiv. = 207.0).

Hydrolytic Stability of Pentafluorophenylboronic Acid.—(a) Pentafluorophenylboronic acid (0.132 g., 0.62 mmoles) and water (0.76 g.) contained in a sealed, evacuated tube was set aside at 20° for 2 days. When the tube was opened to a vacuum system, volatile material was obtained and was shown by gas chromatography to be pentafluorobenzene (0.02 g., 20%).

(b) Pentafluorophenylboronic acid (0.20 g., 0.94 mmoles) was dissolved in 50% aqueous ethanol (5 ml.) and set aside at 20° for 45 min. The solvent was removed by vacuum transfer to give boric acid (0.053 g., 0.86 mmoles). The acid was more stable in aqueous acetone under similar conditions, but hydrolysis was complete after several hours.

(c) Pentafluorophenylboronic acid (0.087 g.) was dissolved in aqueous ethanol (4 ml.) to which a few drops of 2N-hydrochloric acid had been added. The solution was kept at 20° for 1 hr. The solvent was removed by vacuum transfer to give a white solid residue (0.074 g.), which from its infrared spectrum and m. p. 280—285° was mainly unchanged pentafluorophenylboronic acid.

Cleavage of Pentafluorophenylboronic Acid with 85% Hydrogen Peroxide.—Hydrogen peroxide (85%, 10.1 ml.) was added, dropwise, to pentafluorophenylboronic acid (5.4 g., 25.4 mmoles), at -78°. The reaction mixture was gradually allowed to reach room temperature, and finally heated to 50° to complete the reaction. The reaction mixture was extracted with methylene chloride (3 × 20 ml.); the organic layer was separated, dried (MgSO₄), and solvent was removed under vacuum to give crude pentafluorophenol (4.25 g., 91%), which after distillation had b. p. 143—147° (lit.,²³ 143°), identified by its infrared spectrum by comparison with the spectrum obtained from an authentic specimen.

Thermal Disproportionation of Pentafluorophenylboron Compounds.—(a) *Pentafluorophenylboron dichloride.* Pentafluorophenylboron dichloride (1.34 g., 5.4 mmoles) was heated at 220° for 25 hr. in a sealed evacuated Carius tube. The tube was cooled and the volatile material was fractionated through a trap at -78°, giving boron trichloride (0.21 g., 67%); the residue in the tube was bis(pentafluorophenyl)boron chloride (0.6 g., 59%), which on hydrolysis gave the borinic acid (see later). The material in the trap was shown, by its infrared spectrum, to be unchanged pentafluorophenylboron dichloride (0.40 g., 30%). Much less disproportionation occurred when the reaction was carried out at 130°, and at room temperature no significant reaction occurred.

(b) *Pentafluorophenylboron difluoride.* When pentafluorophenylboron difluoride (0.90 g., 4.2 mmoles) was heated at 95° for 16 hr. in an evacuated Carius tube, fractionation of the product gave boron trifluoride (0.048 g., 0.7 mmoles). The remainder of the material was re-sealed in the Carius tube and heated at 194° for a further 18 hr. Fractionation of the products gave more boron trifluoride (0.062 g., 0.9 mmoles) (total amount = 0.11 g., 77%). The white solid residue in the Carius tube, bis(pentafluorophenyl)boron fluoride, was hydrolysed to bis(pentafluorophenyl)borinic acid (0.55 g., 71%), which was identified by its infrared spectrum (see later).

Bis(pentafluorophenyl)borinic Acid.—Bis(pentafluorophenyl)boron chloride (1.38 g., 3.6 mmoles) in acetone (5 ml.) was added to acetone (10 ml.) cooled to -20° and containing the calculated amount of water for hydrolysis. The solvent was removed by vacuum transfer to give a colourless oil, which solidified after several hours under vacuum. This solid, after two

²² K. H. Slotta and K. R. Jacobi, *Chem. Abs.*, 1929, **23**, 1870.

²³ J. M. Birchall and R. N. Haszeldine, *J.*, 1959, 13.

sublimations (90°/0.05 mm.) gave white crystals of bis(pentafluorophenyl)borinic acid (0.64 g., 49%), m. p. 102° and stable in air (Found: F, 52.5%; Equiv., 356, 358. $C_{12}HBF_{10}O$ requires F, 52.5%; Equiv., 362).

We thank Professors G. E. Coates and W. K. R. Musgrave for their interest, Dr. J. W. Emsley for nuclear magnetic resonance spectra, and the D.S.I.R. for a maintenance grant (to T. C.).

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DURHAM, SCIENCE LABORATORIES,
SOUTH ROAD, DURHAM. [Received, November 6th, 1964.]
