

### 561. *Phenylchloroboronites and Phenylboronates.*

By S. H. DANDEGAONKER, W. GERRARD, and M. F. LAPPERT.

A number of new phenylchloroboronites,  $\text{Ph}\cdot\text{BCl}\cdot\text{OR}$ , and phenylboronates,  $\text{Ph}\cdot\text{B}(\text{OR})_2$ , have been prepared, including the first examples of aryl esters. Reactions of phenylchloroboronites with water, alcohols, phenols, ethers, and pyridine have been investigated. Alkyl phenylchloroboronites, except the benzyl ester, were thermally stable and the effects of various factors on the decomposition into alkyl chloride were studied. By contrast, phenyl phenylchloroboronite disproportionated when heated in a vacuum. Reactions of phenylboronates with phenylboron dichloride and with pyridine are reported; the diaryl phenylboronates formed complexes with pyridine. Infrared spectra are discussed.

IN a recent paper Brindley, Gerrard, and Lappert <sup>1</sup> described certain properties of dialkyl phenylboronates,  $\text{Ph}\cdot\text{B}(\text{OR})_2$ , and of alkyl phenylchloroboronites,  $\text{Ph}\cdot\text{BCl}\cdot\text{OR}$ ; their preparation had been considered earlier.<sup>2,3</sup> We have now extended these studies and also

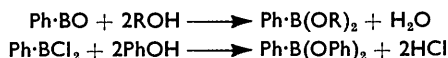
<sup>1</sup> Brindley, Gerrard, and Lappert, *J.*, 1956, 1540.

<sup>2</sup> *Idem*, *J.*, 1955, 2956.

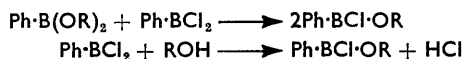
<sup>3</sup> *Idem*, *J.*, 1956, 824.

describe the preparation and properties of the corresponding phenyl and *o*-tolyl esters, e.g., PhB(OAr)<sub>2</sub> and Ph·BCl·OAr; such aryl esters have not previously been reported.

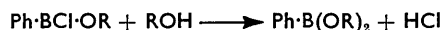
A number of new dialkyl phenylboronates as well as the diphenyl and di-*o*-tolyl esters were prepared in high yields by esterification of phenylboronic anhydride (see Table 1), and diphenyl phenylboronate was also obtained from phenylboron dichloride.



Of the phenylchloroboronites only the *n*-butyl<sup>3,4</sup> and the (+)-1-methylheptyl<sup>1</sup> esters were known. Ten alkyl phenylchloroboronites have now been prepared and also the phenyl and *o*-tolyl esters, from phenylboron dichloride and the appropriate phenylboronate or alcohol or phenol (see Tables 3 and 4).



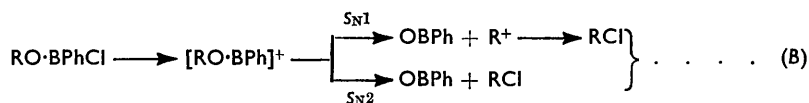
Both phenylboronates and phenylchloroboronites were readily hydrolysed. Reaction with alcohols and phenols was demonstrated for phenylchloroboronites:



It had previously been shown that *n*-butyl phenylchloroboronite was thermally stable, but that in the presence of Lewis acids it decomposed readily at 20° (reaction *A*); with the (+)-1-methylheptyl ester, (–)-2-chloro-octane was obtained.<sup>1</sup> The thermal stability of phenylchloroboronites has now been considered over a wider field. *iso*Butyl phenylchloroboronite was substantially unchanged after being heated at 160–165° for 65 hr. In the

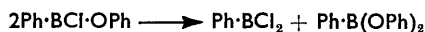


presence of a trace of ferric chloride, decomposition (*A*) was rapid at 20°, giving a mixture of *iso*- and *tert*-butyl chloride. Benzyl phenylchloroboronite was less stable; it decomposed in 24 hr. at 20°. In the  $\alpha$ -methyl ester series (Table 5) the relative rates of decomposition were R = Bu<sup>t</sup> > Pr<sup>i</sup> > Et > Me. In reaction (*A*) the rate-determining



step is the B-Cl heterolysis, followed by one of the reactions (*B*). Thus, (*a*) the rate of reaction is governed by the electron-releasing power of R, (*b*) electrophilic catalysts accelerate the reaction, and (*c*) Walden inversion of the group R occurs, if R is not hindered with respect to S<sub>N</sub>2 "in line" replacement, or else proceeds through a carbonium cation, as evident from the cited example of a Wagner–Meerwein rearrangement.

Phenyl phenylchloroboronite, in contrast to the alkyl esters did not decompose, but disproportionated when heated in a vacuum.



The application of a vacuum (to remove phenylboron dichloride) was important since this reaction is reversible, the reverse being a method of preparing the ester. A comparable difference between aryloxy- and alkoxy-boron chlorides had been noted<sup>5,6</sup> with dichloroboronites RO·BCl<sub>2</sub> and chloroboronates (RO)<sub>2</sub>B·Cl, and may be attributed to the difficulty of aromatic compared with aliphatic nucleophilic substitution.

<sup>4</sup> Mikhailov and Kostroma, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1956, **10**, 376.

<sup>5</sup> Colclough, Gerrard, and Lappert, *J.*, 1955, 907; 1956, 3006.

<sup>6</sup> Lappert, *Chem. Rev.*, 1956, **56**, 959.

Phenylchloroboronites did not react with ethers; in this they resemble the chloroboronates, but contrast with the dichloroboronites.<sup>6</sup>

*n*-Butyl phenylchloroboronite forms a 1 : 2 complex with pyridine.<sup>1</sup> This is now found also for the ethyl homologue and the aryl esters. These complexes are stable and crystalline and are easily hydrolysed.

Diaryl phenylboronates (unlike the di-*n*-butyl ester<sup>1</sup>) formed crystalline 1 : 1 complexes with pyridine. Similarly triaryl borates, in general, co-ordinate with pyridine, whereas trialkyl borates do not.<sup>5</sup>

The molar refractivities of the phenylboronates and phenylchloroboronites were in reasonable agreement with those calculated from Vogel's atomic refractivities<sup>7</sup> (except boron) and Torsell's value<sup>8</sup> of 3.94 for boron.

The infrared spectra of these compounds are, in general, consistent with established correlations between band frequencies and structures. For example, all the phenylboronates and phenylchloroboronites exhibit very strong absorption in the region of 1310—1350  $\text{cm}^{-1}$ . Werner and O'Brien<sup>9</sup> attributed such absorption by alkyl and aryl borates to B-O stretching modes and a similar assignment can be made here for the boronates and boronites. Also, all the compounds have strong absorption bands near 690—700 and 750—760  $\text{cm}^{-1}$ , showing that the out-of-plane CH modes of boron-substituted aromatic compounds fit the rules given by Randle and Whiffen.<sup>10</sup>

The spectra of all phenylchloroboronites include a band in the region 890—916  $\text{cm}^{-1}$ , at least as intense as, and usually more intense than, the strong phenyl bands at 690—700  $\text{cm}^{-1}$ , and these can be tentatively assigned to stretching of B-Cl bonds: they lie close to the frequency (958  $\text{cm}^{-1}$ ) of the degenerate stretching vibration of  $\text{BCl}_3$ ,<sup>11</sup> and fit moderately well application of Gordy's rule<sup>12</sup> to the B-Cl stretching frequency. Gordy's rule suggests a range of 750—850  $\text{cm}^{-1}$ ; it neglects interaction with neighbouring bonds and is therefore very approximate; phenylboronates have mostly only weak bands, if any, in this region but a few have bands of medium intensity (*e.g.*, diethyl and di-*tert.*-butyl phenylboronate). It is therefore advisable to assume the presence of a B-Cl bond in compounds containing boron and chlorine only when the intensity of the band near 900  $\text{cm}^{-1}$  is greater than that of the band due to a phenyl group near 700  $\text{cm}^{-1}$ .

Our observations with respect to the spectra of phenylboronates are generally similar to those by Letsinger.<sup>13</sup>

## EXPERIMENTAL

*Preparations and Techniques.*—Phenylboronic acid was obtained by Bean and Johnson's method;<sup>14</sup> the corresponding anhydride was obtained by dehydration. Phenylboron dichloride was prepared by the method of Abel, Dandegaonker, Gerrard, and Lappert.<sup>15</sup> The ethyl and *tert.*-butyl esters of phenylboronic acid were prepared by Brindley, Gerrard, and Lappert's procedure.<sup>2</sup> Analytical techniques have been described previously.<sup>1,3</sup> Boron in diaryl phenylboronates and in aryl phenylchloroboronites could not be satisfactorily analysed; the methods tried were: (a) hydrolysis to phenylboronic acid,  $\text{Ph}\cdot\text{B}(\text{OH})_2$ , and the phenol, and titration with alkali in presence of mannitol; (b) the modification proposed by Thomas<sup>16</sup> for use with triaryl borates, namely, distillation with methanol in the presence of a trace of concentrated sulphuric acid and titration of boron [as  $\text{B}(\text{OH})_3$ ] in the distillate. Method (a) gave consistently high results owing to the acid nature of the phenol, whilst in (b) the results were very low, which

<sup>7</sup> Vogel, *J.*, 1946, 133; 1948, 616, 644, 654.

<sup>8</sup> Torsell, *Acta Chem. Scand.*, 1954, **8**, 1779.

<sup>9</sup> Werner and O'Brien, *Austral. J. Chem.*, 1955, **8**, 355; 1956, **9**, 137.

<sup>10</sup> Randle and Whiffen, *Inst. of Petroleum Conference on Molecular Spectroscopy*, 1954.

<sup>11</sup> Anderson, Lassettre, and Yost, *J. Chem. Phys.*, 1936, **4**, 703.

<sup>12</sup> Gordy, *ibid.*, 1946, **14**, 305.

<sup>13</sup> Letsinger, personal communication.

<sup>14</sup> Bean and Johnson, *J. Amer. Chem. Soc.*, 1932, **54**, 4415.

<sup>15</sup> Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.

<sup>16</sup> Thomas, *J.*, 1946, 820.

we interpret as due to the non-formation of a methanol-dimethyl phenylboronate azeotrope as required by the method.

*Preparation of Phenylboronates.*—(1) Phenylboronic anhydride (2.5–5.0 g., 1 mol.), the alcohol or phenol (slightly greater than 2 mols.), and benzene or toluene (50–80 c.c.) were heated together in a flask fitted with a 15 cm. lagged Vigreux column fitted with a modified

TABLE 1. Phenylboronites, Ph·B(OR)<sub>2</sub>.

R	Yield (%)	B. p./mm.	$n_D^{20}$	$d_4$	Found (%)			Formula	Required (%)		
					C	H	B		C	H	B
Pr <sup>t</sup>	82	54°/0.05	1.4632	0.9283 <sup>c</sup>	70.1	8.3	5.2	C <sub>12</sub> H <sub>10</sub> O <sub>2</sub> B	69.9	8.2	5.2
Bu <sup>t</sup>	86	76–77°/0.03	1.4675	0.9153 <sup>c</sup>	—	—	4.6	C <sub>14</sub> H <sub>23</sub> O <sub>2</sub> B	—	—	4.6
Bu <sup>a</sup>	84	69–70°/0.03	1.4650	0.9045 <sup>c</sup>	—	—	4.6	—	—	—	4.6
<i>n</i> -C <sub>6</sub> H <sub>17</sub>	94	157–160°/0.05	1.4700	0.895 <sup>d</sup>	76.2	11.3	3.2	C <sub>22</sub> H <sub>30</sub> O <sub>2</sub> B	76.3	11.3	3.1
<i>n</i> -C <sub>6</sub> H <sub>13</sub> ·CHMe <sup>a</sup>	84	148–150°/0.05	1.4670	0.889 <sup>d</sup>	75.7	11.5	3.0	—	76.3	11.3	3.1
Cl·CH <sub>2</sub> ·CH <sub>2</sub> ...	85	109–110°/0.03	1.5135	1.102 <sup>d</sup>	48.2	5.8	4.4	C <sub>10</sub> H <sub>13</sub> O <sub>2</sub> Cl <sub>2</sub> B	48.6	5.3	4.3
Ph·CH <sub>2</sub> ...	90	190–192°/0.2	1.5745	1.110 <sup>d</sup>	79.7	6.6	3.6	C <sub>20</sub> H <sub>19</sub> O <sub>2</sub> B	79.5	6.3	3.6
Ph <sup>h</sup>	69	140–150°/0.05	M. p. 98–100°	—	76.1	5.6	—	C <sub>18</sub> H <sub>16</sub> O <sub>2</sub> B <sup>e</sup>	78.8	5.5	—
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Me	80	149–151°/0.05	1.5457 <sup>b</sup>	1.020 <sup>d</sup>	78.8	6.5	—	C <sub>20</sub> H <sub>19</sub> O <sub>2</sub> B <sup>f</sup>	79.5	6.3	—

<sup>a</sup>  $\alpha_D^{20}$  – 14.50°; from ROH,  $\alpha_D^{20}$  – 8.00°. <sup>b</sup> At 26; crystallises after some days. <sup>c</sup> At 20°. <sup>d</sup> At 16°. <sup>e</sup> Found: OPh, 68.0. Req'd.: OPh, 67.9%. <sup>f</sup> Found: O-C<sub>6</sub>H<sub>4</sub>Me, 71.1. Req'd.: O-C<sub>6</sub>H<sub>4</sub>Me, 70.9%.

TABLE 2. Phenylchloroboronites, Ph·BCl·OR (method a).

R	Yield (%)	B. p./mm.	$n_D^{20}$	$d_4$	Found (%)		Formula	Required (%)	
					Cl	B		Cl	B
Me	—	52°/4	1.5168	1.086 <sup>b</sup>	23.0	7.0	C <sub>7</sub> H <sub>9</sub> OCIB	23.0	7.0
Et	—	69–70°/10	1.5032	1.004 <sup>c</sup>	21.0	6.4	C <sub>8</sub> H <sub>10</sub> OCIB	21.1	6.4
Pr <sup>t</sup>	—	55°/0.15	1.4928	1.022 <sup>b</sup>	19.2	5.9	C <sub>9</sub> H <sub>12</sub> OCIB <sup>e</sup>	19.5	5.9
Bu <sup>t</sup>	—	52°/0.05	1.4920	1.009 <sup>b</sup>	17.9	5.4	C <sub>10</sub> H <sub>14</sub> OCIB	18.0	5.5
Bu <sup>a</sup>	94	49°/0.05	1.4898	1.007 <sup>b</sup>	17.9	5.5	—	18.0	5.5
Bu <sup>b</sup>	89	44°/0.05	1.4955	1.021 <sup>b</sup>	18.1	5.5	—	18.0	5.5
<i>n</i> -C <sub>6</sub> H <sub>17</sub>	80	112–113°/0.05	1.4900	0.976 <sup>b</sup>	14.0	4.3	C <sub>14</sub> H <sub>22</sub> OCIB	14.1	4.3
<i>n</i> -C <sub>6</sub> H <sub>13</sub> ·CHMe <sup>a</sup>	77	108–110°/0.05	1.4877	0.963 <sup>b</sup>	13.9	4.3	—	14.1	4.3
Cl·CH <sub>2</sub> ·CH <sub>2</sub> ...	81	62°/0.05	1.5265	1.158 <sup>b</sup>	17.2 <sup>d</sup>	5.2	C <sub>8</sub> H <sub>9</sub> OCl <sub>2</sub> B	17.5 <sup>d</sup>	5.3
Ph·CH <sub>2</sub> ...	81	122–123°/0.5	1.5620	1.136 <sup>c</sup>	15.3	4.7	C <sub>13</sub> H <sub>12</sub> OCIB	15.4	4.7
Ph <sup>h</sup>	62	109–110°/0.05	1.5670	1.151 <sup>b</sup>	16.5	—	C <sub>12</sub> H <sub>10</sub> OCIB <sup>f</sup>	16.4	—
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Me	95	107°/0.05	1.5620	1.156 <sup>c</sup>	15.2	—	C <sub>13</sub> H <sub>12</sub> OCIB <sup>g</sup>	15.4	—

<sup>a</sup>  $\alpha_D^{20}$  – 34.7°; from Ph·B(OR)<sub>2</sub>,  $\alpha_D^{20}$  – 14.5°. <sup>b</sup> At 20°. <sup>c</sup> At 16°. <sup>d</sup> Cl hydrolysable by cold H<sub>2</sub>O. <sup>e</sup> Found: C, 60.3; H, 6.7. Req'd.: C, 59.3; H, 6.6%. <sup>f</sup> Found: OPh, 43.8. Req'd.: OPh, 43.4%. <sup>g</sup> Found: O-C<sub>6</sub>H<sub>4</sub>Me, 47.1. Req'd.: O-C<sub>6</sub>H<sub>4</sub>Me, 46.9%. <sup>h</sup> Reaction in CH<sub>2</sub>Cl<sub>2</sub>.

TABLE 3. Phenylchloroboronites, Ph·BCl·OR (method b).

R	Yield (%)	Yield of HCl (%)	B. p./mm.	$n_D^{20}$	Found (%)				Calc. (%) <sup>a</sup>	
					C	H	Cl	B	C	H
Me	70	100	55°/5	1.5130	54.7	5.5	22.9	7.0	54.5	5.2
Et	86	98	86–87°/12	1.5030	56.7	5.6	21.0	6.6	57.2	5.9
Bu <sup>t</sup>	59	100	70–71°/0.3	1.4925	63.1	6.9	18.2	5.6	61.3	7.0
Bu <sup>a</sup>	65	99	64.5°/0.3	1.4885	62.8	7.2	17.9	5.4	61.3	7.0
<i>n</i> -C <sub>6</sub> H <sub>17</sub>	62	89	110–112°/0.05	1.4900	66.9	8.9	13.8	4.3	66.6	8.8
<i>n</i> -C <sub>6</sub> H <sub>13</sub> ·CHMe ...	83	98	107–109°/0.05	1.4863	66.5	8.8	13.9	4.3	66.6	8.8
Cl·CH <sub>2</sub> ·CH <sub>2</sub> ...	75	86	64–65°/0.05	1.5260	49.9	4.9	17.5 <sup>b</sup>	5.3	47.4	4.5
Ph·CH <sub>2</sub> ...	70	95	120–122°/0.05	1.5618	—	—	15.3	4.7	—	—
Ph	46	98	120–125°/0.2	1.5780	66.6	4.8	16.6	<sup>c</sup>	66.6	4.7
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Me	70	97	107–108°/0.05	1.5620	67.7	5.3	15.2	<sup>d</sup>	67.7	5.2

<sup>a</sup> See Table 2. <sup>b</sup> Hydrolysed by cold H<sub>2</sub>O. <sup>c</sup> Found: OPh, 42.9%. <sup>d</sup> Found: O-C<sub>6</sub>H<sub>4</sub>Me, 47.5%.

Dean and Stark still-head. The distillate comprised successively, the water-hydrocarbon azeotrope, and the bulk of the remaining hydrocarbon. The still-head was then changed for a total-reflux partial-ratio head and the remaining material was distilled in a vacuum, affording first a small fore-run and finally the pure phenylboronate. These esters (see Table 1) with the

exception of the *n*-, *sec*-, and *iso*-butyl esters, are new; the (+)-1-methylheptyl ester has previously been obtained.<sup>3</sup>

(2) Phenol (3.79 g.) in *n*-pentane (15 c.c.) was added to phenylboron dichloride (3.20 g.) at 20° during 15 min. The reaction was vigorous. *n*-Pentane was removed under reduced pressure and the residue afforded a forerun (0.40 g.), and diphenyl phenylboronate (4.40 g., 80%), b. p. 130—140°/0.05 mm. (Found: PhO, 68.9; B, 4.15%). Hydrogen chloride (1.39 g., 93%) was trapped in alkali.

*Preparation of Phenylchloroboronites*.—(a) The boronate (1 mol.) and phenylboron dichloride (1.0—2.5 g., 1 mol.) were mixed at 20°; the mixture became warm and was set aside for 1—3 hr. Distillation afforded a small forerun and then the pure *phenylchloroboronite* (see Table 2).

(b) The alcohol or phenol (1 mol.) in *n*-pentane or methylene dichloride (5—15 c.c.) was added during  $\frac{1}{2}$ —1 hr. to phenylboron dichloride (2—5 g., 1 mol.) at -80°. The mixture was allowed to attain room temperature, whereafter matter volatile at 20°/15 mm. was removed. Hydrogen chloride (95—100%) was collected in traps. The residue was fractionated and the phenylchloroboronite was obtained as the middle cut (see Table 3).

*Alcoholysis and Phenolysis of Phenylchloroboronites*.—The alcohol or phenol (1 mol.) in solvent (*n*-pentane or methylene chloride, 5—15 c.c.) was added to the appropriate phenylchloroboronite (2—10 g., 1 mol.) at 20° during 15 min. The mixture was set aside for 1—3 hr. at 20°, whereafter volatile matter was removed at 20°/15 mm. The residue was fractionated to afford the phenylboronate. Liberated hydrogen chloride was trapped. The results are in Table 4.

TABLE 4. *Solvolysis of chloroboronites, Ph·BCl·OR.*

R	Yield of HCl (%)	Ph·B(OR) <sub>2</sub>				Found (%): B
		Yield (%)	B. p./mm.	$n_D^{20}$	$d_4^{20}$	
Me .....	97	87	59°/5	1.4962	0.984	7.3
Et .....	90	92	40°/0.05	1.4785	—	6.1
Bu <sup>a</sup> .....	96	93	85°/0.05	1.4750	—	4.5
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Me ...	95	68	155—158°/0.05	1.5745	—	3.8

*Catalytic Decomposition of isoButyl Phenylchloroboronite*.—Anhydrous ferric chloride (0.01 g.) was added to the boronite (1.04 g.) at 20°. Within 10 min. the mixture became hot. After 2 hr. at 20°, volatile matter was removed at 20°/15 mm. and condensed. This (0.350 g., 64%) was a mixture of *tert*-.butyl (51%) and *isobutyl* (49%) chloride [Found: Cl hydrolysed by HNO<sub>3</sub> in 24 hr. at 20° (from Bu<sup>t</sup>Cl), 18.9; Cl, 37.9. Calc. for C<sub>4</sub>H<sub>9</sub>Cl: Cl, 38.4%]. The non-volatile residue was extracted with methylene dichloride; this extract, after removal of solvent at 20°/15 mm., comprised phenylboronic anhydride (0.52 g., 98%), m. p. 214—216° (Found: B, 10.6. Calc. for C<sub>6</sub>H<sub>5</sub>OB: B, 10.4%).

TABLE 5. *Decomposition (%) of Ph·BCl·OR.*

Time (hr.)	Ph·BCl·OMe	Ph·BCl·OEt	Ph·BCl·OPr <sup>t</sup>	Ph·BCl·OBu <sup>t</sup>
1	0	0	0.75	51.5
2	0	0.54	1.5	53.5
3	0.75	1.0	7.6	55.0
5	1.26	1.33	16.7	55.8
7	2.0	2.5	18.0	56.1
10	4.0	8.7	20.2	56.6
20	5.5	17.8	31.2	58.9
30	8.9	18.5	33.7	67.4
40	10.6	19.9	35.0	76.2
60	15.2	20.5	36.5	88.1

After *isobutyl* phenylchloroboronite (1.60 g.) had been heated at 160—165°, in the absence of a catalyst, in a sealed-tube for 65 hr., little decomposition had taken place; thus 1.32 g. (83%), b. p. 50°/0.05 mm.,  $n_D^{20}$  1.4880 (Found: Cl, 18.0; B, 5.5%), were recovered.

*Thermal Stability of Benzyl Phenylchloroboronite*.—Freshly prepared boronite (1.85 g.) was set aside for 24 hr. at 20°; a solid product had begun to separate. Distillation afforded benzyl chloride (0.98 g., 96%), b. p. 62—63°/10 mm.,  $n_D^{20}$  1.5395 (Found: Cl, 27.1. Calc. for C<sub>7</sub>H<sub>7</sub>Cl: Cl, 28.1%), and a residue of phenylboronic anhydride (0.83 g., 99%), m. p. 215—218° (Found: B, 10.3%).

*Relative Stability of the  $\alpha$ -Methyl Series of Phenylchloroboronites.*—The relative stabilities of boronites were determined by heating small (*ca.* 0.2 g.), weighed samples in sealed tubes at 160—165°. Samples were withdrawn periodically, hydrolysed in enclosed systems with cold water, and analysed for chlorine and boron by titration against carbonate-free sodium hydroxide to successively methyl-orange (HCl) and phenolphthalein [B(OH)<sub>3</sub>] end-points, the latter in presence of mannitol. The extent of decomposition was calculated from the hydrogen chloride titration and checked by considering the ratio of Cl : B. The results are in Table 5.

*Thermal Stability of Phenyl Phenylchloroboronite.*—Phenyl phenylchloroboronite (3.45 g.) was heated at 155—160°/0.05 mm. under reflux with a cold (−80°) trap in series for 9 hr., whereafter distillation of the remainder afforded diphenyl phenylboronate (2.00 g., 94%), m. p. 98—101°, b. p. 150—155°/0.05 mm. (Found : PhO, 69.5; B, 4.7%). The condensate in the cold trap was phenylboron dichloride (0.82 g., 65%), b. p. 60—62°/11 mm.,  $n_D^{20}$  1.5440 (Found : Cl, 44.0; B, 6.7. Calc. for C<sub>6</sub>H<sub>5</sub>Cl<sub>2</sub>B : Cl, 44.7; B, 6.8%).

*Lack of Reaction between Phenylchloroboronites and Ethers.*—The following 1 : 1 systems were investigated at 20° : (1) *n*-butyl phenylchloroboronite with diethyl and *n*-butyl isobutyl ether, anisole, and phenetole; (2) phenyl phenylchloroboronite with anisole and phenetole; (3) *o*-tolyl phenylchloroboronite with ethyl *o*-tolyl ether. There was no change in temperature. In system (1), in each case after 3—4 hr. under reflux, the phenylchloroboronite (75—98%) was recovered on subsequent distillation. In systems (2) and (3), the extent of recovery was 55—65%, owing to disproportionation of the aryl phenylchloroboronites, as evident from the isolation in each case of some phenylboron dichloride and diaryl phenylboronate. In none of these experiments was there evidence for the formation of alkyl chlorides.

*Pyridine Complexes of Phenylchloroboronites.*—Pyridine (slightly > 2 mol.) was added to the phenylchloroboronite (1 mol.) at −80° during 20 min., whereafter the viscous, syrupy mixture was allowed to attain room temperature and was set aside for 24 hr. at 20°. The product was washed by decantation with *n*-pentane, and residual volatile matter was removed (2 hr. at 20°/12 mm. and 5 hr. at 20°/0.05 mm.). The residue was the white hygroscopic 1 : 2 complex between the phenylchloroboronite and pyridine (see Table 6).

TABLE 6. Complexes, Ph·BCl·OR, 2C<sub>5</sub>H<sub>5</sub>N.

R	Yield (%)	M. p.	Found (%)			Required (%)		
			C <sub>5</sub> H <sub>5</sub> N	Cl	ArO	C <sub>5</sub> H <sub>5</sub> N	Cl	ArO
Et .....	99	103—107°	47.9	10.9	(B, 3.5%)	48.4	10.9	(B, 3.3%)
Ph .....	99	105—108	42.5	9.3	25.6	42.2	9.5	25.1
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Me .....	98	111—113	40.8	9.0	27.3	40.7	9.1	27.8

*Pyridine Complexes of Diaryl Phenylboronates.*—(a) Pyridine (0.88 g.) was added to diphenyl phenylboronate (3.00 g.) in methylene dichloride (10 c.c.) at −80° during 10 min. The mixture was set aside at 20° for 12 hr., whereafter volatile matter was removed at 20°/15 mm. The residue was washed several times by decantation with *n*-pentane, and residual volatile matter was removed (2 hr. at 20°/10 mm. and 5 hr. at 20°/0.05 mm.). The residue comprised the white 1 : 1 phenylboronate-pyridine complex (3.80 g., 99%), m. p. 127—130° (Found : PhO, 53.6; B, 3.2; C<sub>5</sub>H<sub>5</sub>N, 22.1. C<sub>28</sub>H<sub>20</sub>O<sub>2</sub>NB requires PhO, 53.3; B, 3.1; C<sub>5</sub>H<sub>5</sub>N, 22.4%). The complex was obtained also when the ester (1 mol.) was added to pyridine (3 mols.).

(b) By a similar technique, from pyridine (2.01 g.) and di-*o*-tolyl phenylboronate (1.70 g.) there was obtained the complex (2.10 g., 98%), m. p. 135—136° (Found : O·C<sub>6</sub>H<sub>4</sub>Me, 56.8; B, 3.16; C<sub>5</sub>H<sub>5</sub>N, 21.0. C<sub>25</sub>H<sub>24</sub>O<sub>2</sub>NB requires O·C<sub>6</sub>H<sub>4</sub>Me, 56.6; B, 2.84; C<sub>5</sub>H<sub>5</sub>N, 20.7%).

We are very grateful to Mr. H. Pyszora for carrying out the infrared measurements, determined on a Grubb-Parsons double beam spectrometer (kindly made available by the National College of Rubber Technology), with sodium chloride optics, and to Dr. L. A. Duncanson for valuable and detailed comments on these.

THE NORTHERN POLYTECHNIC, HOLLOWAY ROAD, LONDON, N.7. [Received, March 1st, 1957.]