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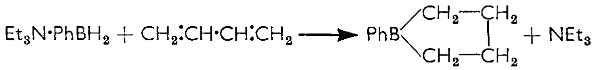
70. *Heterocyclic Organoboron Compounds. Part III.*[1] *Synthesis of Phenylboracyclopentane and the Infrared Spectra of this and other Phenylboron Compounds.*

By N. N. GREENWOOD and J. C. WRIGHT.

An improved synthesis of phenylboracyclopentane by the reaction of phenylborane–triethylamine with butadiene is reported, but the preparation of this compound from phenylboron difluoride and 1,4-dilithiobutane could not be confirmed. The infrared spectrum of phenylboracylcopentane is analysed in detail and shown to be consistent with the proposed structure. The spectra of phenylboron difluoride and phenylborane–triethylamine are also recorded and assignments made.

PHENYLBORACYCLOPENTANE has been prepared by Mikhailov and Dorokhov[2] who reacted 1,2-diphenyldiborane with butadiene at —30°. A disproportionation reaction to give triphenylboron reduced the yield of the desired heterocycle. In the present work 1-phenylboracyclopentane was prepared by passing butadiene into a solution of phenylborane–triethylamine[3,4] in refluxing benzene. By this means, the secondary reaction was suppressed and the yield improved, but some polymeric material was also produced.



The product, m. p. —19°, was isolated by low-pressure distillation and identified by elemental analysis (C,H,B), infrared spectroscopy, and chemical reactions. Oxidative hydrolysis with neutral aqueous hydrogen peroxide yielded boric acid and a 1 : 1 mixture of phenol and butane-1,4-diol and boric acid. Phenylboracyclopentane formed a 1 : 1 crystalline adduct, m. p. 99°, with ammonia, but did not interact with either triethylamine or water at room temperature.

When the hydroboronation was attempted in the absence of solvent, or in light petroleum (b. p. 100—120°) at 70°, only polymeric material was recovered. Pyrolysis of this did not produce volatile material and exposure of the solution to air produced a light coloured, unreactive material which was insoluble in all common solvents and very resistant to chemical attack. Thus, concentrated nitric and sulphuric acids and potassium hydroxide solution slowly formed a surface film which prevented further attack, but chlorosulphonic acid caused extensive charring.

An earlier route to phenylboracyclopentane had been published by Torssell[5] who

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[1] Part II, N. N. Greenwood, J. H. Morris, and J. C. Wright, *J.*, 1964, 4753.

[2] B. M. Mikhailov and V. A. Dorokhov, *Doklady Akad. Nauk, S.S.S.R.*, 1960, **133**, 119.

[3] M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1961, **83**, 831.

[4] M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1958, **80**, 4291.

[5] K. Torssell, *Acta Chem. Scand.*, 1954, **8**, 1779.

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reacted phenylboron difluoride with 1,4-dilithiobutane. However, subsequent work [6] suggested that all previous attempts to prepare phenylboron difluoride had probably been unsuccessful and this rendered uncertain the nature of the product previously considered to have been phenylboracylopentane. An attempt was therefore made to repeat Torssell's preparation of phenylboron difluoride, and also to react authentic phenylboron difluoride with dilithiobutane. Reaction of diphenylzinc with boron trifluoride–diethyl ether under the appropriate conditions [5] yielded no phenylboron difluoride but only a mixture of decomposition products, some of which contained phenyl–boron bonds but which did not have the required elemental analysis or infrared spectrum.

An authentic sample of phenylboron difluoride, prepared by reacting phenylboron dichloride with antimony trifluoride,[6] was treated with 1,4-dilithiobutane in ether. There was no apparent reaction at —5° during two hours or at 20° during a further two hours, and even after the mixture had been refluxed overnight most of the phenylboron difluoride was recovered unchanged. There was also some lithium tetrafluoroborate and a small amount of a liquid which decomposed readily to phenylboronic anhydride. This was probably ethoxyphenylboron fluoride formed by reaction with the solvent:

$$\mathrm{PhBF_2 + Et_2O \longrightarrow PhB(OEt)F + EtF}$$
$$\mathrm{3PhB(OEt)F \longrightarrow (PhBO)_3 + 3EtF}$$

The analogous reactions with phenylboron dichloride and ethoxyphenylboron chloride are well known at elevated temperatures [7,8] and have now been found to occur rapidly at room temperature in the presence of lithium salts. Boron–fluorine bonds are normally more stable to solvolysis than boron–chlorine bonds, but catalytic reaction in the presence of the dilithio-reagent and lithium tetrafluoroborate again appears to occur.

Infrared Spectra.—The infrared spectrum of liquid phenylboracyclopentane was measured on a Perkin-Elmer 125 spectrophotometer in the region 400—4000 cm.$^{-1}$, and the principal bands are listed in Table 1. Of these, thirty-two can be assigned as fundamental modes or combination bands of monosubstituted benzene on the basis of both position and intensity [9] and a further thirty-seven bands (including ^{10}B–^{11}B pairs) are associated with the heterocyclic ring. The structure of the compound is thus established since virtually all the observed infrared bands can be assigned and there are no bands corresponding to unreacted C=C bonds or to methyl groups.

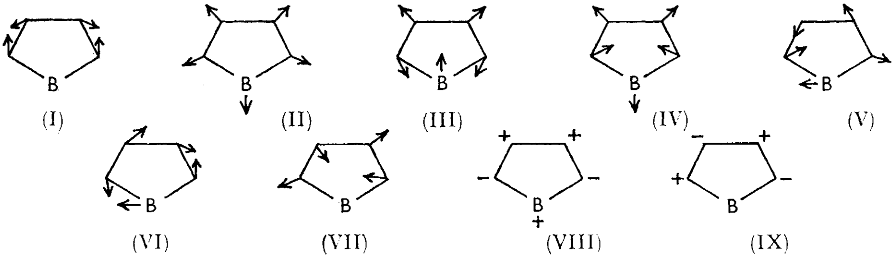

FIG. 1. Fundamental vibration modes of the boracyclopentane ring; (I), A_1 stretch (1012 cm.$^{-1}$); (II), A_1 ring-breathing (925, 932 cm.$^{-1}$); III, A_1 stretch (643, 655 cm.$^{-1}$); (IV), A_1 deformation (601, 605 cm.$^{-1}$); (V), B_1 stretch (1104, 1111 cm.$^{-1}$); (VI), B_1 stretch (1046, 1050, cm.$^{-1}$); (VII) B_1 deformation (866 or 886 cm.$^{-1}$); (VIII), B_2 deformation (568, 578 cm.$^{-1}$); (IX), A_2 deformation (probably $<$400 cm.$^{-1}$).

The infrared spectrum of the boracyclopentane ring under low resolution has been reported briefly [10] but no assignments have been made. It is expected to be similar to

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[6] P. A. McCusker and H. S. Makowski, *J. Amer. Chem. Soc.*, 1957, **79**, 5185.
[7] S. H. Dandegaonker, W. Gerrard, and M. F. Lappert, *J.*, 1957, 2893.
[8] S. H. Dandegaonker, W. Gerrard, and M. F. Lappert, *J.*, 1957, 2872.
[9] R. R. Randle and D. H. Whiffen, *Mol. Spectroscopy*, 1955, 111.
[10] A. Finch, P. J. Hendra, and J. Pearn, *Spectrochim. Acta*, 1962, **18**, 51.

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TABLE 1.

Infrared spectrum of liquid phenylboracyclopentane in the region 400—4000 cm.$^{-1}$ (for description of modes *a*—*y* see ref. 9)

ν (cm.$^{-1}$)	Rel. ε	Assignment
465	40	PhX ring out-of-plane deform. (*y* mode)
503	20	PhX ring in-plane deform. (*t* mode)
568	90	^{11}B hetero-ring out-of-plane deform. (mode VIII)
578	45	^{10}B hetero-ring out-of-plane deform. (mode VIII)
601	65	^{11}B hetero-ring in-plane deform. (mode IV)
605	30	^{10}B hetero-ring in-plane deform. (mode (IV)
618	30	Ph ring in-plane deform. (*s* mode)
643	120	^{11}B hetero-ring sym. stretch (mode III)
655	30sh	^{10}B hetero-ring sym. stretch (mode III)
677	65	CH$_2$ rock(?)
694	155	Ph ring out-of-plane deform. (*v* mode)
739	165	CH(Ph) out-of-plane deform. (*f* mode)
774	40	CH$_2$ rock (or PhX in-plane deform., *r* mode)
811	90	PhX ring in-plane deform. (*r* mode); (or hetero mode VII)
852	35sh	CH(Ph) out-of-plane deform. (*g* mode)
866	50	Hetero-ring in-plane deform. (mode VII) (?)
886	55	Hetero-ring in-plane deform. (mode (VII) (?)
898	40sh	CH(Ph) out-of-plane deform. (*i* mode)
925	135	^{11}B hetero-ring breathing (mode II)
932	150	^{10}B hetero-ring breathing (mode II)
973	40	CH(Ph) out-of-plane deform. (*j* mode)
981	40	CH(Ph) out-of-plane deform. (*h* mode)
988	40	Combination band(?)
1000	110	Ph ring A_1 stretch (*p* mode)
1012	115	Hetero-ring A_1 stretch (mode I)
1024	130	CH(Ph) in-plane deform. (*b* mode)
1046	130	^{11}B hetero-ring B_1 stretch (mode VI)
1050	90sh	^{10}B hetero-ring B_1 stretch (mode (VI)
1075	60	^{11}B–Ph stretch (*q* mode)
1082	55	^{10}B–Ph stretch (*q* mode)
1104	45	^{11}B hetero-ring antisym. stretch (mode V)
1111	40	^{10}B hetero-ring antisym. stretch (mode V)
1157	85	CH(Ph) in-plane deform. (*c* mode)
1186	135sh	CH(Ph) in-plane deform. (*a* mode)
1194	130	CH$_2$ twist
1229	170	CH$_2$ twist
1244	70	CH(Ph) in-plane deform. (*e* mode)
1275	90sh	(2 × 643)
1290	250	CH$_2$ wag
1320	250	C–C(Ph) B_1 stretch (*o* mode)
1337	195	CH$_2$ wag
1379	120	CH$_2$ wag
1411	95	(601 + 811)
1434	160	CH$_2$ scissors
1449	115	C–C(Ph) B_1 stretch (*n* mode)
1465	95	CH$_2$ scissors
1479	55	CH$_2$ scissors
1490	90	C–C(Ph) A_1 stretch (*m* mode)
1520	25	(601 + 925)
1540	25	(739 + 811); (601 + 932)
1568	30	C–C(Ph) B_1 stretch (*l* mode)
1594	155	C–C(Ph) A_1 stretch (*k* mode)
1613	45sh	(601 + 1012); (568 + 1046) (?)
1643	30	(643 + 1000); (618 + 1024); (601 + 1046)
1662	25	C–C(Ph) B_1 stretch (*o* mode) (?) or (739 + 925) (?)
1774	20	The four combination bands of CH(Ph) out-of-plane deformations
1819	30	
1893	25	
1908	20	
1958	30	
2030	10	Overtones and combinations of bands between 900—1400 cm.$^{-1}$
2124	10	
2224	10	
2304	10	
2583	15	
2740	35	(?)
2824	140	CH$_2$ sym. stretch (C·CH$_2$ groups)
2856	160	CH$_2$ sym. stretch (B·CH$_2$ groups)
2915	155sh	CH$_2$ antisym. stretch (C·CH$_2$ groups)
2938	160	CH$_2$ antisym. stretch (B·CH$_2$ groups)
3009	100	Combination bands (?)
3019	110	
3024	110	The five CH(Ph) stretches
3049	130	
3070	150	
3091	155	
3137	20	

that of tetrahydrofuran.[11,12] The CH$_2$ symmetric stretching mode occurs about 85 cm.$^{-1}$ below the antisymmetric mode and the methylene groups which are attached only to carbon atoms absorb at a lower frequency than those attached to boron.[1] A similar differentiation occurs for the antisymmetric mode though here the two bands are not completely resolved

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[11] N. Baggett, S. A. Barker, A. B. Foster, R. H. Moore, and D. H. Whiffen, *J.*, 1960, 4565, and refs. therein.

[12] H. Tschamler and H. Voetter, *Osterreich. Akad. Wissen., Sitzungsber.* [IIb], 1952, **161**, 302.

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and the C·CH$_2$ vibrations appear as a shoulder on those of the B·CH$_2$ groups. The CH$_2$ scissors, wagging, and twisting modes have characteristic positions and intensities but the rocking modes at 677 and 774 cm.$^{-1}$ are less definitely assigned.

A planar five-membered heterocyclic ring should have five fundamental stretching modes, two in-plane deformations, and two out-of-plane deformations (Fig. 1). Of these, only the A_2 mode is infrared-inactive, but even this becomes allowed if the ring assumes its more natural puckered form (C_2).

The A_1 ring-breathing mode (II) is assigned to the strong doublet at 932, 925 cm.$^{-1}$. This can be compared with values of 913 cm.$^{-1}$ for tetrahydrofuran [12] and 1000 cm.$^{-1}$ for the phenyl ring. The band at 1012 cm.$^{-1}$ shows no isotope splitting and is therefore assigned to the A_1 stretching mode (I); it is essentially a C–C stretching mode. The third A_1 stretching mode is essentially a symmetric BC$_2$ stretch and is assigned to the strong doublet at 655, 643 cm.$^{-1}$ (cf. 668, 660 cm.$^{-1}$ in azaboratricycloundecane [1]).

The BC$_2$ antisymmetric stretching modes are expected [1] near 1100 cm.$^{-1}$ and, since the B_1 ring-stretching modes (V) and (VI) incorporate this motion, they are assigned to the bands at 1111, 1104 and 1050, 1046 cm.$^{-1}$, respectively, the choice between alternative assignments being made on the basis of relative intensities.

The deformation modes are more difficult to assign. By analogy with similar systems, the B_2 out-of-plane deformation (VIII) is expected to be strong and to occur in the range 500—600 cm.$^{-1}$; the bands at 578, 568 cm.$^{-1}$ are therefore assigned to this mode. This would leave the sharp band at 605, 601 cm.$^{-1}$ for the A_1 in-plane deformation (IV) and one of the bands at 886 and 866 cm.$^{-1}$ for the B_1 in-plane deformation (VII), which does not involve movement of the boron atom. It is unlikely that the A_2 deformation occurs at such a high frequency as this and it is expected to lie below 400 cm.$^{-1}$. All other bands in the spectrum are accounted for except the curious weak peak at 2740 cm.$^{-1}$.

The infrared spectrum of phenylboron difluoride was examined on a Unicam S.P. 100 spectrophotometer and is recorded in Table 2. The phenyl bands are easily recognized, as also is the B–Ph stretching mode at 1300, 1292 cm.$^{-1}$. The symmetric and antisymmetric BF$_2$ stretching modes are unusually close together [13,14] but are assigned with some confidence both on account of their intensity and their ^{10}B–^{11}B structure. There

TABLE 2.

Infrared spectrum of phenylboron difluoride (in CCl$_4$) in the region 380—4000 cm.$^{-1}$.

ν (cm.$^{-1}$)	Rel. ε	Assignment	ν (cm.$^{-1}$)	Rel. ε	Assignment
539	15	^{11}BF$_2$ in-plane deform. (scissors)	1352	580	^{10}B–F$_2$ sym. stretch
547	10	^{10}BF$_2$ in-plane deform. (scissors)	1382	210	^{11}B–F$_2$ antisym. stretch
559	100	Ph–X (*t* mode)	1397	130	^{10}B–F$_2$ antisym. stretch
643	270	Ph–X (*y* mode)	1447	200	C–C B_1 stretch (*n* mode)
660	100	^{11}BF$_2$ out-of-plane deform.	1484	10	(2 × 742)
671	85	^{10}BF$_2$ out-of-plane deform.	1504	50	C–C A_1 stretch (*m* mode)
694	270	Ph ring out-of-plane deform. (*v* mode)	1610	150	C–C A_1 stretch (*k* mode)
			1675	10	C–C B_1 stretch (*o* mode)
963	10	CH out-of-plane deform. (*j*, *h* modes)	1789	10	The four combination bands of CH out-of-plane deformations
			1834	10	
1027	75	CH in-plane deform. (*b* mode)	1911	10	
1079	100	CH in-plane deform. (*d* mode)	1972	10	
1163	15	CH in-plane deform. (*c* mode)	2073	10	(?)
1189	15	CH in-plane deform. (*a* mode)	3010	10	The five CH stretches
1261	15	CH in-plane deform. (*e* mode)	3043	20	
1292	70	^{11}B–Ph stretch (*q* mode)	3070	20	
1300	45sh	^{10}B–Ph stretch (*q* mode)	3094	25	
1344	620	^{11}B–F$_2$ sym. stretch	3122	10	

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[13] A. J. Banister, N. N. Greenwood, B. P. Straughan, and J. Walker, *J.*, 1964, 995.

[14] F. K. Butcher, W. Gerrard, M. Howarth, E. F. Mooney, and H. A. Willis, *Spectrochim. Acta*, 1963, **19**, 905.

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are no bands between 380 and 539 cm.$^{-1}$ so the BF_2 scissoring mode, which has been observed [13] between 470—490 cm.$^{-1}$, is assigned to the doublet at 547, 539 cm.$^{-1}$. As shown in Fig. 2(a) this mode involves motion of the boron atom against the phenyl ring and is thus coupled to the phenyl *t* mode at 559 cm.$^{-1}$ (cf. PhF 519 cm.$^{-1}$). The fact that these modes (and the B–Ph stretching mode at 1300, 1292 cm.$^{-1}$) absorb at somewhat higher frequencies than usual suggests that there is some double-bonding by delocalization both of the π-electron cloud on the phenyl ring and of the p_π non-bonding electron pairs on the fluorine atoms through the " vacant " p_π orbital on the boron atom. This explanation would predict that the out-of-plane deformation of the BF_2 and B–Ph groups Fig. 2(b) would also move to higher frequencies, and this is observed. Thus, the BF_2 out-of-plane deformation at 671, 660 cm.$^{-1}$ occurs close to the value of 688, 663 cm.$^{-1}$ in the compound $Me_2N{\cdot}BF_2$, where similar π-bonding occurs,[13] and the phenyl *y* mode occurs at 643 cm.$^{-1}$, well above the normal range [9] of 450—500 cm.$^{-1}$.

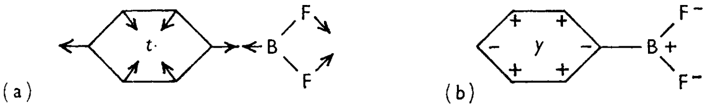

Fig. 2. Coupling of the phenyl and BF_2 deformation modes.

Phenylborane–triethylamine differs from the previous compounds discussed in having 4-co-ordinate boron. The Infracord spectrum is somewhat complicated because of the large number of different groups present, but a reasonably complete assignment is possible. The phenyl and ethyl modes are easily recognized by comparison both with other phenyl compounds and with triethylamine itself, and call for little further comment. The antisymmetric BH_2 stretching mode at 2440, 2380 cm.$^{-1}$, the symmetric BH_2 stretching mode at 2320, 2300 cm.$^{-1}$, and the BH_2 scissoring mode at 1152 cm.$^{-1}$ are normal, and the BH_2 wagging mode [15] occurs at 955 cm.$^{-1}$. As expected, the N–C antisymmetric stretch (1017 cm.$^{-1}$) has moved to lower frequencies than in the parent triethylamine and occurs at the same position as in triethylamine–borane itself.[16] The B–N stretch at 1217, 1205 cm.$^{-1}$ also occurs close to the more easily recognized B–N stretch at 1190, 1180 cm.$^{-1}$ in triethylamine–borane,[16] and is well within the range for 4-co-ordinate boron–nitrogen compounds.[17] The B–Ph stretch occurs at 1112, 1105 cm.$^{-1}$, suggesting that this mode is not sensitive to whether the boron atom is 3- or 4-co-ordinate. Only when this mode is strengthened by π-bonding, as in phenylboron difluoride, or is coupled to heterocyclic ring modes, as in phenylboronic anhydride, is the frequency appreciably altered.

EXPERIMENTAL

Standard vacuum-line and glove-box procedures were used. Solvents were dried by conventional methods, fractionated, and sealed to avoid atmospheric contamination. Large-scale preparations were carried out in Quickfit apparatus under a stream of dry, oxygen-free nitrogen. Mercury-sealed stirrers were replaced by a Vibromixer model E1, an airtight seal being effected by means of a shaped neoprene sleeve (Helvin H.V. 2311, Hellerman Ltd., Crawley, Sussex.) This enabled distillation under reduced pressure to be performed without removing the stirrer from the flask. The analytical techniques have been described previously.[1]

Phenylborane–triethylamine was prepared by reducing a solution of diethoxyphenylborane, $PhB(OEt)_2$ (19·5 g.),[4] in ether (60 ml.) with a slurry of lithium aluminium hydride (2·9 g.) in ether (300 ml.) in the presence of triethylamine (30 g.), first at −70° and then at 0° overnight. The mixture was added to ice (500 g.), filtered, and the ether layer collected. After two further extractions of the aqueous layer with ether, the combined ether solutions were dried ($MgSO_4$),

[15] L. J. Bellamy, W. Gerrard, M. F. Lappert, and R. L. Williams, *J.*, 1958, 2412.
[16] N. N. Greenwood and J. H. Morris, unpublished observations.
[17] N. N. Greenwood and K. Wade, *J.*, 1960, 1130.

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concentrated under reduced pressure, and cooled to −78°; white needles of phenylborane–triethylamine separated (8·7 g., 41%). The diethoxyphenylborane was obtained by slow fractionation of a mixture of phenylboronic anhydride (51·5 g.), dry benzene (320 g.), and absolute ethanol (140 g.). The water–benzene–ethanol azeotrope (b. p. 64°) distilled first, followed by the excess of benzene at 80°. The pressure was then reduced and diethoxyphenylborane (50 g., 57%) collected at 36°/0·2 mm.

Phenylboracyclopentane.—Phenylborane–triethylamine (6·0 g.) and benzene (15 ml.), in a 100 ml. flask fitted with a gas inlet tube and a water condenser surmounted by a cold-finger condenser maintained at −78°, were heated under reflux in a nitrogen atmosphere and butadiene (4 g.) passed in slowly. The flask was cooled, attached to the vacuum line, and fractions voltile at 0 and 20° removed and shown by infrared analysis to be butadiene, benzene, and triethylamine only. Prolonged distillation at room temperature under reduced pressure yielded phenylboracyclopentane (2·8 g., 62%), m. p. −19° (Found: C, 83·4; H, 9·3; B, 7·4. Calc. for $C_{10}H_{13}B$: C, 83·5; H, 9·0; B, 7·5%). The solid remaining in the flask appeared to be polymeric by-products; it was not the phenylboracylcopentane–triethylamine complex since it did not dissociate or decompose on heating.

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Diphenylzinc was prepared by a Grignard reaction on anhydrous zinc chloride in ether. The solvent was removed under reduced pressure and the diphenylzinc sublimed at 120° from the magnesium chloride–bromide mixture; m. p. 107° (lit.,[18] 107°). Reactions of this with boron trifluoride–diethyl ether did not yield phenylboron difluoride, but a moisture-sensitive liquid of similar boiling point. Hydrolysis of the product and treatment with mercury(II) chloride [19] yielded phenylmercury(II) chloride, m. p. 251°. This reaction indicates the presence of Ph–B bonds and the hydrolysate also contained fluoride ions, but the infrared spectrum of the product had little resemblance to that of authentic phenylboron difluoride. It appeared to be a mixture of decomposition products, as previously suggested.[6]

Phenylboron difluoride (b. p. 81°/440 mm.) was prepared [6] in 86% yield by direct reaction of phenylboron dichloride (58·4 g., 0·37 mole) with antimony trifluoride (68 g., 0·45 mole) in the absence of solvent. The dichloride, b. p. 63°/15 mm. (Found: Cl, 44·4. Calc. for $C_6H_5BCl_2$: Cl, 44·6%), was initially prepared by the reaction of phenylboronic anhydride with boron trichloride.[20] Better yields (70%) were obtained from the reaction of tetraphenyltin with boron trichloride.[21–23]

Ethereal solution of 1,5-dilithiopentane and 1,4-dilithiobutane were prepared [24] by reaction of lithium metal with the corresponding bromides, at −30° and then at 0°, and were filtered through glass wool to remove lithium bromide and unreacted lithium before use. When the dilithio-reagents were added to an ethereal solution of phenylboron dichloride at 0° the same volatile products were obtained as from the prolonged reaction of dichloride with ether itself at 60°.[7] Thus, phenylboron dichloride (15·6 g.) was mixed, with considerable evolution of heat, with ether (50 ml.) and the ethereal solution of the dilithio-reagent added at 0°. Distillation at reduced pressure yielded ethoxyphenylboron chloride (15 g.), b. p. 87—91°/12 mm. Reaction of the dilithio-reagents with an ethereal solution of phenylboron difluoride also failed to yield a heterocyclic boron compound.

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[22] K. Niedenzu and J. W. Dawson, *J. Amer. Chem. Soc.*, 1960, **82**, 4223.
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