

19. *The Preparation of Esters of Diphenylboronous Acid.*

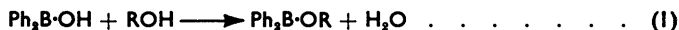
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Diphenylboronous acid and anhydride have been esterified directly by primary and secondary alcohols and phenol, to afford alkyl and phenyl diphenylboronites. Higher homologues were also obtained by alcoholysis of a lower member of the series. The procedure of widest application involved interaction of diphenylboron chloride with the alcohol, and was suitable for the preparation of methyl and *tert.*-butyl homologues. The merit of each method is discussed.

A REPRESENTATIVE series of alkyl and phenyl diphenylboronites, $\text{Ph}_2\text{B}\cdot\text{OR}$, have been prepared by methods analogous to those which have proved satisfactory for the borates, $\text{B}(\text{OR})_3$, and phenylboronates, $\text{Ph}\cdot\text{B}(\text{OR})_2$. These methods have been reviewed by Lappert.¹ Certain ethanalamine esters,^{2,3,4} including the only known diphenylboronite, and a number of mixed boronous esters $\text{R}'\text{R}''\text{B}\cdot\text{OR}$ are known.^{2,5} It was necessary to study the properties of diphenylboronites, particularly in relation to the series, $\text{B}(\text{OR})_3$, $\text{Ph}\cdot\text{B}(\text{OR})_2$, $\text{Ph}_2\text{B}\cdot\text{OR}$, Ph_3B . The starting materials, diphenylboronous acid,^{3,6} its anhydride,^{3,6} and diphenylboron chloride,⁶ were all readily available.

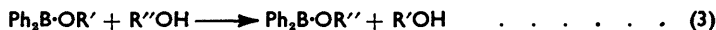
A boronous ester, $\text{Et}_2\text{B}\cdot\text{OEt}$, was first prepared by Frankland and Duppa⁷ in 1859 by controlled oxidation of triethylboron, but it was not free from diethyl ethylboronate and triethyl borate which were formed concurrently. Johnson and Van Campen⁸ prepared *n*-butyl di-*n*-butylboronite in 92% yield by controlled oxidation of tri-*n*-butylboron in the presence of water. Torssell⁵ recently obtained mixed tolylboronites by direct esterification of the hydrolysis products of the Grignard reactions between tolylmagnesium bromides and propyl borate.

A number of primary and secondary alkyl esters and the phenyl ester of diphenylboronous acid have now been prepared in 80—90% yield by direct esterification of the acid or the anhydride with the appropriate alcohols and phenol :



The results of this method are given in Table 2. The water was removed as a water-alcohol azeotrope by using excess of the alcohol. When no convenient water-alcohol azeotrope was formed, benzene was added to form a ternary azeotrope. With the higher-boiling alcohols, it was necessary to remove excess of the alcohol at reduced pressure in order to avoid the slight dephenylation which was observed to take place at a higher temperature. Reaction (2) offers the advantage of briefer reaction, because less water is formed, but neither the *tert.*-butyl nor the methyl ester could be thus prepared owing to the lack of a suitable azeotrope for the removal of water.

Alcoholysis of low-boiling esters by high-boiling alcohols has been successfully utilized to give the higher diphenylboronites in yields of 80—90% (Table 3) :



This method was very satisfactory where there was a difference of more than 20° in the boiling points of the two alcohols. Again neither the methyl ester nor the *tert.*-butyl ester

¹ Lappert, *Chem. Rev.*, 1956, in the press.

² Letsinger and Remes, *J. Amer. Chem. Soc.*, 1955, **77**, 2489.

³ Letsinger and Skoog, *ibid.*, p. 2491.

⁴ Rondestvedt, Scribner, and Wulfman, *J. Org. Chem.*, 1955, **20**, 9.

⁵ Letsinger, Skoog, and Remes, *J. Amer. Chem. Soc.*, 1954, **76**, 4047; Mikhailov and Aronovich, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1955, 946; Torssell, *Acta Chem. Scand.*, 1955, **9**, 239, 242.

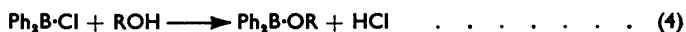
⁶ Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.

⁷ Frankland and Duppa, *Proc. Roy. Soc.*, 1859, **10**, 568.

⁸ Johnson and Van Campen, *J. Amer. Chem. Soc.*, 1938, **60**, 121.

could be obtained. There was no interaction between *tert.*-butyl alcohol and the methyl ester.

The action of diphenylboron chloride on the alcohols and phenol is the fourth method for the preparation of the esters (Table 4). The reaction proceeded to completion in an inert solvent at room temperature :



The methyl and the *tert.*-butyl ester were made in this way. For the latter, however, the yield was low (57%) when methylene dichloride or *n*-pentane was used as solvent. The reversal of the order of addition, *i.e.*, adding diphenylboron chloride to the alcohol in solvent, decreased the yield. *tert.*-Butyl diphenylboronite was not obtained by either order of addition in the absence of solvent, because of exclusive production of *tert.*-butyl chloride :



Of the methods described, the diphenylboron chloride one appears to be the best, in view of its range of application and the speed of the reaction, and because the ester is the only non-gaseous product. If, however, the ester is required in quantity, it is best obtained from the anhydride, if this method is applicable. In this way one step in the synthesis is avoided, as the chloride is most conveniently obtained from the anhydride.⁶ Alcoholysis presents a convenient method of moving up a homologous series of esters.

The preparation of esters from diphenylboron chloride does not apparently involve alkyl-oxygen fission. Hence starting from (+)-octan-2-ol and diphenylboron chloride the (–)-1-methylheptyl ester is regarded as completely retaining the configuration, whilst the ester obtained from *neopentyl* alcohol is regarded as unrearranged. The formation of the same esters having identical optical activity and characterizing constants when prepared by direct esterification and by alcoholysis indicates that boron-oxygen and not alkyl-oxygen fission is involved in both reactions. The low yield of *tert.*-butyl ester may be due to its dealkylation by hydrogen chloride formed *in situ* (6) and, secondly, the reaction possible between the hydrogen chloride and *tert.*-butyl alcohol (7) :



Reaction (7) is favoured when the diphenylboron chloride is added to the alcohol, thus explaining the decreased yield of boronite when this order of mixing is adopted. In the absence of solvent the above reactions appear to prevent completely the formation of ester. This appears to be peculiar to the *tert.*-butyl system, as a good yield of *sec.*-butyl diphenylboronite was obtained in the absence of solvent.

The diphenylboronites are slightly viscous, thermally stable, colourless liquids. The phenyl ester is very viscous and crystallizes during two weeks. The esters are hydrolysed slowly when shaken with water, and in air slowly become brown.

Many borates have been prepared by means of boron trichloride,⁹ although *tert.*-butyl alcohol gave alkyl chloride,^{9a} and several phenylboronates including the *tert.*-butyl ester have been made from phenylboron dichloride.¹⁰ Azeotropic methods and alcoholysis have been used for the preparation of the borates,¹ and also for the preparation of phenylboronates.^{10, 11}

Molecular refractivities were determined. To obtain the calculated values, Vogel's¹²

⁹ Gerrard and Lappert, *J.*, 1951, (a) 2545, (b) 1020; Edwards, Gerrard, and Lappert, *J.*, 1955, 1470; Colclough, Gerrard, and Lappert, *J.*, 1955, 907; 1956, 3006; Gerrard, Lappert, and Silver, *J.*, 3285; Abel, Edwards, Gerrard, and Lappert, *J.*, in the press.

¹⁰ Brindley, Gerrard, and Lappert, *J.*, 1956, 1540.

¹¹ Brindley, Gerrard, and Lappert, *J.*, 1955, 2956.

¹² Vogel, *J.*, 1946, 133; 1948, 616, 644, 654.

atomic (except boron) refractivities, and Torssell's¹³ value for boron (in diarylboron compounds) were used. The agreement (Table 1) confirms the value¹³ of 4.39 determined for boron in this type of compound.

TABLE 1.

R in Ph ₂ B·OR	Me	Et	Pr ^a	Bu ^a	Bu ^b	Bu ^c	Bu ^d	neo- Pentyl	n-C ₆ H ₁₁	n-C ₆ H ₁₃ ·CHMe	Ph
[R _L] _D (Found)	62.37	67.17	71.86	76.43	76.05	76.35	76.83	81.53	95.01	94.21	81.93
[R _L] _D (Calc.)	62.63	67.28	71.93	76.58	76.58	76.58	76.58	81.23	95.18	95.18	82.41

EXPERIMENTAL

Diphenylboronous acid was prepared by Letsinger and Skoog's method,³ and its anhydride and diphenylboron chloride as described by Abel *et al.*⁶ Boron was estimated acidimetrically in the presence of mannitol, after hydrolysis of the ester in water. Yields are of the pure distilled ester in each case. Rotatory powers are recorded for $l = 10$ cm.

Esterification of Diphenylboronous Acid.—The esterifications were carried out on an approximately 0.05 molar scale. The diphenylboronous acid or anhydride was heated with the appropriate alcohol, sufficient alcohol being used to remove the water formed as a water-alcohol azeotrope. The reaction vessel was fitted with a 25 cm. lagged Vigreux column and a Dean and Stark head. A thermometer incorporated in the head indicated when removal of the azeotrope was complete, and excess of alcohol was then removed. For lower-boiling alcohols, this was carried out at normal pressure, but for phenol and higher-boiling alcohols at 20 mm. in order to avoid dephenylation which occurred at a high temperature in the presence of excess of alcohol. A 30 cm. Snyder-Schriner column fitted with a heating jacket, and total-reflux partial-ratio head was used to prepare the ethyl ester, as the water-ethanol-benzene azeotrope required very efficient separation from the alcohol. The esters were finally distilled under reduced pressure in an atmosphere of nitrogen. The results are shown in Table 2; the yields are based on schemes (1) and (2).

TABLE 2.

R in Ph ₂ B·OR	Yield (%)	B. p. (°/mm.)	Found (%)		Required (%)					
			α_D^{20}	n_D^{20}	C	H	B			
Et *	80	138/10	1.005	1.5557	80.0	7.2	5.08	80.1	7.1	5.14
Pr ^a †	91	152/10	0.987	1.5458	79.7	7.7	4.88	80.4	7.6	4.83
Bu ^a *	93	158/9	0.977	1.5390	80.4	8.0	4.53	80.7	7.9	4.54
Bu ^b †	84	153/10	0.963	1.5276	79.5	8.3	4.55	80.7	7.9	4.54
Bu ^c *	86	152/10	0.961	1.5291	80.4	8.2	4.52	80.7	7.9	4.54
Bu ^d *	79	155/0.05	0.950	1.5259	81.8	9.6	3.65	81.7	9.2	3.67
n-C ₆ H ₁₁ †	84	148/0.2	0.941	1.5196	81.5	9.4	3.70	81.7	9.2	3.67
1-Methylheptyl * §	82	114/0.5	0.965	1.5370	80.7	8.3	4.25	80.9	8.3	4.28
neoPentyl †	72	140/0.05	1.084	1.6053	82.9	6.0	4.23	83.6	5.8	4.18

* Esterification of the anhydride.

§ $\alpha_D^{20} - 4.28^\circ$; from ROH, $\alpha_D^{20} + 7.28^\circ$.

† Esterification of the acid.

Alcoholysis of Diphenylboronites.—These reactions were carried out on approx. 0.05 molar scale. The higher-boiling alcohol (3 mols.) was added to the alkyl diphenylboronite (1 mol.), and the mixture was very slowly fractionated, through a vacuum-jacketed Vigreux column. The lower-boiling alcohol slowly distilled, followed by excess of the higher alcohol, the last traces of which were removed at low pressure. The crude esters were distilled at reduced pressure in nitrogen. The results are shown in Table 3; yields are based on scheme (3).

Action of Diphenylboron Chloride on Alcohols.—These reactions were carried out on an approx. 0.05 molar scale. The alcohol (1 mol.) in methylene dichloride (20 c.c.) was added dropwise ($\frac{1}{2}$ hr.) to the diphenylboron chloride (1 mol.) in methylene dichloride (20 c.c.). Hydrogen chloride was evolved and the solvent was then removed at reduced pressure. The crude ester remained as a yellow liquid and was distilled in nitrogen. The results are shown in Table 4; yields are based on scheme (4).

Addition of Diphenylboron Chloride to tert.-Butyl Alcohol in the Absence of Solvent.—Diphenylboron chloride (22.23 g., 1 mol.) was added slowly (1/4 hr.) to *tert.*-butyl alcohol (8.23 g., 1 mol.)

¹³ Torssell, *Acta Chem. Scand.*, 1954, 8, 1779.

TABLE 3.

R' in Ph ₂ B·OR'	R''OH	Yield (%) Ph ₂ B·OR''	B. p. (°/mm.)	n _D ²⁰	Found: B (%)	Calc.: B (%)
Et	Bu ⁿ OH	89	158/9	1.5383	4.4	4.5
Bu ⁿ	n-C ₈ H ₁₇ ·OH	83	160/0.3	1.5247	3.7	3.7
Pr ⁿ	n-C ₆ H ₁₃ ·CHMe·OH	92 •	152/0.5	1.5198	3.8	3.7
Bu ⁿ		83 †	140/0.05	1.5189	3.8	3.7
Et	Bu ^t CH ₂ ·OH	85	110/0.2	1.5369	4.3	4.3
Et	PhOH	88	139/0.05	1.6050	4.1	4.2

* α_D²⁰ -4.17°. † α_D²⁰ -4.14°. Both from R''OH, α_D²⁰ +7.28°.

TABLE 4.

R in Ph ₂ B·OR	Yield (%)	B. p. (°/mm.)	n _D ²⁰	d ₄ ²⁰	Found (%)			Calc (%)		
					C	H	B	C	H	B
Me •	80	132/10	1.5709	1.032	79.0	6.7	5.59	79.6	6.6	5.53
Bu ^t • §	57	142/10	1.5396	0.972	80.2	7.8	4.56	80.7	7.9	4.53
n-C ₈ H ₁₇ ·CHMe †	93	134/0.001	1.5218	—	—	—	3.69	—	—	3.67
Bu ^t CH ₂	79	116/0.5	1.5374	—	—	—	4.32	—	—	4.28
Ph	83	136/0.01	1.6062	—	—	—	4.15	—	—	4.18

• New compounds.

† α_D²⁰ -4.20°; from ROH, α_D²⁰ +7.28°.

§ Reversal of order of addition produced only 35% yield of the ester

at 0°. No evolution of gas was observed when the mixture warmed to room temperature, but a white precipitate was formed. *tert.*-Butyl chloride (7.9 g., 83%) was removed at reduced pressure and trapped at -80°; it had b. p. 53°, n_D²⁰ 1.3858 (Found: Cl, 37.6. Calc. for C₄H₉Cl: Cl, 38.9%). The residue was washed with *n*-pentane, and after desiccation at low pressure diphenylboronous anhydride (18.25 g., 95%), m. p. 114° (Found: B, 6.3. Calc. for C₂₄H₂₀OB₂: B, 6.3%), was obtained. Reversal of the order of addition produced similar results. Yields are based on scheme (5).

Addition of Diphenylboron Chloride to sec.-Butyl Alcohol in the Absence of Solvent.—Diphenylboron chloride (2.68 g., 1 mol.) was added during 15 min. to *sec.*-butyl alcohol (0.994 g., 1 mol.) at 0°. Hydrogen chloride was evolved and its removal was completed at reduced pressure. *sec.*-Butyl diphenylboronite [2.75 g., 86%, based on (4)], b. p. 149°/8 mm., n_D²⁰ 1.5310 (Found: B, 4.61%), was obtained.

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