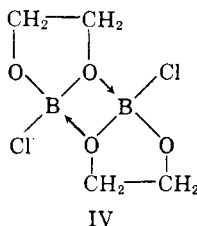
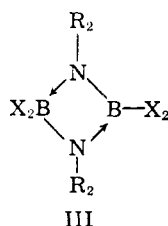


TABLE I
MOLECULAR WEIGHTS OF SOME DIOXABORINANES AND DIOXABOROLANES

Compound	Moles/L. ^a	Molecular Weight			Degree of Polymerization
		Exptl.	Calcd.		
			Monomer	Dimer	
(Ia) 2-Chloro-1,3,2-dioxaborinane	0.27	124.8	120.8	241.6	1.03
(Ib) 2- <i>n</i> -Butoxy-1,3,2-dioxaborinane	0.14	162.7	158.0	316.0	1.03
(IIa) 2-Chloro-1,3,2-dioxaborolane	0.36	208.9	106.8	212.6	1.96
(IIc) 2- <i>n</i> -Butoxy-1,3,2-dioxaborolane	0.17	182.4	143.8	287.6	1.27
(IId) 2-Dimethylamino-1,3,2-dioxaborolane	0.33	113.6	114.8	229.6	1.01

^a Moles/l. in benzene solution, moles based on monomer.

by Landesman and Williams¹⁴ have proven that all boron atoms present in these compounds are equivalent and have postulated a cyclic trimeric structure with coordinate boron-oxygen bonds for these materials. The related aminohaloborane dimers with the empirical formula R_2NBX_2 have been assigned Structure (III) with coordinate boron-nitrogen bonds.¹⁵⁻¹⁷ A comparable structure for the dimer, IIa, is represented by (IV) but on the basis of present evidence it is only possible to speculate on the structures of this dimeric derivative.



2-Dimethylamino-1,3,2-dioxaborolane, IId, was found to be monomeric in the liquid state. However, 2-*n*-butoxy-1,3,2-dioxaborolane, IIc, which was previously reported⁶ to be monomeric in cyclohexane solution, has now been found to have an intermediate degree of association in benzene at least in the concentration range indicated. The molecular weight of 2-ethoxy-1,3,2-borolane (IIb) was not determined, but on the basis of its reported boiling point⁶ it is probably dimeric or highly associated also.

The striking differences in the molecular weights of these five and six-ring derivatives are difficult to explain, and more information is needed concerning both the nature and the absolute configurations of the five and six-membered boron-oxygen-carbon ring systems.

EXPERIMENTAL

Borolanes. The preparations of 2-chloro-1,3,2-dioxaborolane^{2,6} and 2-dimethylamino-1,3,2-dioxaborolane² were as described in the literature. 2-*n*-Butoxy-1,3,2-dioxaborolane was prepared by Letsinger's method⁷ from ethylene glycol and *n*-butyl borate and also by the reaction of 2-chloro-1,3,2-dioxaborolane with *n*-butyl alcohol as described by Gerrard and Lappert.⁸ The products from both methods exhibited identical physical properties and molecular weights.

2-Chloro-1,3,2-dioxaborinane. Boron trichloride (71.70 g., 0.613 mole) was added slowly to a solution of 46.64 g. (0.613 mole) of trimethylene glycol in 200 ml. of pentane at -10° in a dry-nitrogen atmosphere. The reaction mixture was warmed to room temperature, the hydrogen chloride and pentane removed by distillation at reduced pressure, and the residue distilled to give 55.0 g. (74.3% yield) of 2-chloro-1,3,2-dioxaborinane, b.p. $28-31^\circ/0.5$ mm., n_D^{25} 1.4361.

Anal. Calcd. for $C_3H_6O_2ClB$: C, 29.83; H, 5.01; Cl, 29.4; B, 8.97. Found: C, 29.90; H, 5.40; Cl, 29.04; B, 8.84.

2-*n*-Butoxy-1,3,2-dioxaborinane. A solution of 3.77 g. (0.051 mole) of *n*-butyl alcohol in 10 ml. of pentane was added slowly to 6.14 g. (0.051 mole) of 2-chloro-1,3,2-dioxaborinane in 15 ml. of pentane at 25° in a dry-nitrogen atmosphere. The solution was stirred for 3 hr. at this temperature, the pentane removed under vacuum, and the residue distilled to give 6.34 g. (79% yield) of 2-*n*-butoxy-1,3,2-dioxaborinane, b.p. $75-80^\circ/1-2$ mm., n_D^{25} 1.4270.

Anal. Calcd. for $C_7H_{14}O_3B$: C, 53.21; H, 9.57; B, 6.84. Found: C, 53.80; H, 9.59; B, 6.95.

Molecular weight determinations. Molecular weights (Table I) were obtained in benzene using samples of about 0.5 g. in ca. 20 ml. of solvent (concentrations given in Table I) and standard cryoscopic techniques. The samples were handled and the determinations made in an atmosphere of dry, oxygen-free nitrogen. Molecular weight measurements were reproducible within 2-3% and the values given are the averages of two to four separate determinations in each case.

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Some New Orthoboric Acid Esters¹

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During the course of work on the chemical properties and hydrolytic stability of organic

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TABLE I
 NEW ORGANIC ORTHOBORATES

R in B(OR) ₃	Yield, %	B.P., (mm.)	M.P.	n_D^{25}	d_4^{20}	% B	
						Calcd.	Found
C ₄ H ₉ OC ₂ H ₅	66	161–163 ^a (0.7)		1.4327	1.0399	2.99	3.09
CH ₃ OC ₃ H ₇	74	125–128 ^b (15)		1.4257	0.9525	3.89	3.72
C ₂ H ₅ OC ₂ H ₄ OC ₂ H ₅	72	222–223 (5)		1.4247	0.9955	2.64	2.70
CH ₃ OC ₃ H ₇ OC ₃ H ₇	98 ^c	183–184 ^d (2)		1.4082	0.9774	2.39	2.40
5-CH ₃ -2-(<i>i</i> -C ₃ H ₇)C ₆ H ₃	81	170–176 (0.05)	67–69			2.36	2.33
2,6-(<i>i</i> -C ₃ H ₇) ₂ C ₆ H ₃			273–280			1.99	2.00
(C ₆ H ₅) ₂ CH	73		171–176			1.93	1.91
BrCH ₂ CH ₂		169–170 (6)				2.83	2.83

^a 140(0.5), using a regular thermometer. ^b Using a thermometer. ^c Calculated from water collected. ^d 170(2), using a thermometer.

orthoborates, we have had occasion to prepare a number of hitherto unknown compounds. We wish now to report briefly their properties. The compounds are listed in Table I. The only compound showing appreciable resistance to hydrolysis was the borate of 2,6-diisopropylphenol, doubtless owing to steric hindrance. 2,6-Di-*tert*-butylphenol could not be esterified even under the most rugged conditions, although it is possible to make a model of the trisborate and, indeed, the mixed ester, bis(diisopropyl)2,6-di-*tert*-butyl-*p*-cresyl borate, has been reported.² Tris(triphenylcarbinyl) borate could not be formed since triphenylcarbinol gave no reaction with boric acid and yielded triphenylchloromethane on treatment with boron trichloride. Benzyl alcohol and *tert*-butyl alcohol have been reported to react similarly with boron trichloride.^{3,4}

EXPERIMENTAL

General procedures. Three moles of the alcohol or phenol and 1 mole of orthoboric acid were heated in the presence of an excess of ethylbenzene or toluene.⁵ The water eliminated was continuously removed as a binary azeotrope. The more volatile borates were vacuum distilled after the solvent and unchanged alcohol or phenol had been removed by distillation. The less volatile borates were allowed to crystallize from the solvent; filtration, washing, drying, and recrystallization were all carried out in a dry box. The borates of the glycol monoethers were also prepared in good yield using excess glycol monoether in place of the inert solvent.

The melting points cited in Table I were determined in sealed tubes and are corrected. The boiling points were measured in a separate apparatus equipped with a vacuum-jacketed head and a copper-constantan thermocouple connected to a potentiometer, unless otherwise noted. Boiling points so measured are somewhat higher than those recorded with an ordinary thermometer, at low pressures (see foot-

notes *a* and *d*, Table I). Boron analyses were carried out by hydrolyzing the ester in water or aqueous acetone, adding mannitol, and titrating against 0.1*N* sodium hydroxide to the phenolphthalein end point. Procedures for boron analysis of the aryl borates are set forth below. Infrared spectra of the purified compounds showed no —OH bands, indicating absence of the parent alcohols or phenols.

Borates of the glycol monoethers. All four esters were colorless oily liquids, readily hydrolyzed by water.

Tris(thymyl)borate is a white crystalline solid, instantly hydrolyzed by water. The boron content was determined using the methanolysis procedure of Thomas.⁶

Tris(2,6-diisopropylphenyl)borate. The esterification proceeded very slowly, 12 hr. being required for complete reaction in toluene. This ester was unaffected by hot water, sodium hydroxide, or methanol. The boron content was estimated by hydrolyzing the ester in aqueous tetrahydrofuran and titrating the boric acid in the usual way. The rate of hydrolysis of this borate in aqueous acetone solution was measured as follows. A 50–100 mg. sample of the borate was weighed out. Enough 0.1*N* sodium hydroxide to neutralize exactly half the boric acid liberated from the sample on hydrolysis was added to 100 ml. of a saturated solution of mannitol in 90% v./v. acetone-water, and phenolphthalein added. The borate sample was dissolved in a volume of anhydrous acetone nine times that of the sodium hydroxide used. The two solutions were mixed (A) and continuously stirred until the color of the indicator disappeared (B). The time interval between events A and B, 118 sec. at 25° in the present case, provides a convenient measure of the hydrolytic stability of the ester.

Tris(benzhydryl) borate was recrystallized from benzene. It is insoluble in, but slowly hydrolyzed by water (14% hydrolyzed after 4 hr.). It is hydrolyzed immediately in 90% v./v. acetone-water.

Tris(2-bromoethyl) borate was prepared from 2-bromoethanol and boron trichloride, following the procedure used by Edwards, Gerrard, and Lappert⁷ for making tris(2-chloroethyl) borate. The freshly distilled material was a brown oily liquid, readily hydrolyzed by water.

Attempted preparation of tris(2,6-di-*tert*-butylphenyl) borate. 2,6-Di-*tert*-butylphenol failed to react with boric acid and with boron trichloride, even under the most rugged conditions. Thus, no reaction was observed in methylene chloride at –80°, or on passing boron trichloride gas into solution of the phenol in boiling carbon tetrachloride or hexachlorobutadiene (b.p. 220°).

Attempted preparation of tris(triphenylcarbinyl) borate. No reaction occurred on heating 3 moles of triphenyl carbinol with 1 mole of boric acid in boiling ethylbenzene.

A solution of triphenylcarbinol (25 g., 0.096 mole) in 185 ml. of methylene chloride at –80° was mixed with boron

(1) Contribution No. 36 from the Exploratory Research Laboratory, Dow Chemical of Canada, Limited, Sarnia, Ontario.

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trichloride (3.76 g., 0.032 mole) in 20 ml. of methylene chloride at -80° . After allowing the mixture to warm, the solvent was removed at the pump. The yellow-orange solid residue was recrystallized from benzene and then from carbon disulfide. Infrared analysis indicated that the compound was triphenylchloromethane. This was confirmed by hydrolyzing a weighed sample in aqueous acetone and titrating the hydrochloric acid liberated.

Anal. Calcd. for $C_{19}H_{15}Cl$: Cl, 12.7. Found: Cl, 11.9.

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Bromination of Dichlorophenylborane¹

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The direct bromination of aryldihalogenoboranes has not been investigated; this note describes the direct bromination of dichlorophenylborane.

The phenyl-attached $-BCl_2$ grouping should be considered as a second order substituent due to an electron deficiency on the boron atom. In the case of electrophilic substitution, the inductive effect should thus favor *m*-substitution of the aromatic ring.

At room temperature and in the presence of a catalyst, the addition of bromine to dichlorophenylborane results in substitution of the ring along with a small amount of a B—C cleavage. The brominated arylboron derivative was isolated and identified after hydrolysis as B-tri(*m*-bromophenyl)boroxine.

In contrast, bromination of aryldihydroxyborane rather than affording ring bromination results in cleavage of the B—C bond accompanied by replacement of the boron containing moiety by bromine,² unless the exchange of the $B(OH)_2$ -group by bromine is hindered, due to an electron deficiency of the B-attached carbon atom.³

EXPERIMENTAL⁴

About 2 g. of iron filings and a few crystals of iodine were added to 198 cc. (1.5 mole) of dichlorophenylborane and 64 cc. (1.25 moles) of bromine were added with stirring over a period of 30 min. The reaction mixture warmed slightly and stirring was continued for 8 hr. After standing overnight, the product was distilled at normal pressure. A small amount of an unidentified forerun, b.p. $35-70^{\circ}$, was discarded. Unchanged dichlorophenylborane was collected at $165-180^{\circ}$, and the main product distilled at $187-250^{\circ}$. This high boiling fraction was shaken with mercury to remove free halogen, subjected to redistillation, and 174 g. of material, b.p. $205-228^{\circ}$ was collected. The material, which

crystallized on prolonged standing, showed a melting range (in a sealed tube) of $68-72^{\circ}$. It consists of dibromobenzene (isolated after alcoholysis of the mixture) and a boron-containing substance, which was isolated after hydrolysis in the following manner: 10 g. of the distillate was hydrolyzed with 100 cc. of water; the reaction was most vigorous. A white precipitate was collected and dried *in vacuo* over phosphorus pentoxide for 2 hr. Recrystallization from *n*-heptane afforded 4.1 g. of B-tri(*m*-bromophenyl)boroxine, m.p. $176-178^{\circ}$.

Anal. Calcd. for $B_3O_3C_{18}H_{12}Br_3$: B, 5.9; C, 39.4; H, 2.2; Br, 43.7; mol. wt. 548.5. Found: B, 6.1; C, 39.1; H, 2.4; Br, 43.4; mol. wt. (cryoscopically in benzene) 563.

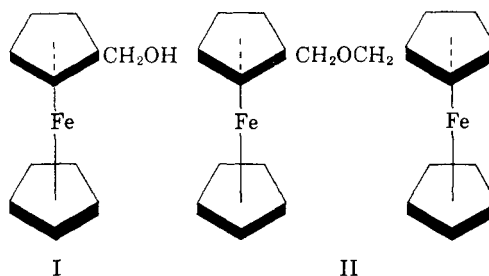
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Ethers of Bis(1-hydroxyethyl)ferrocene and 1-Hydroxybenzylferrocene

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Several workers have observed that hydroxymethylferrocene (I) is readily converted to ether II. This reaction has occurred on treatment of I with 5% acetic acid in ethanol-water,² with acidified oxidizing agents,² and with phosphorus trichloride.³ The hydrogenation of formylferrocene over Raney nickel has produced II⁴; I may have been an intermediate.



Somewhat similarly, we have apparently obtained ether IV on treatment of benzoylferrocene (III) with sodium borohydride in methanol, which is one of the common methods of reduction of ketones or aldehydes to the corresponding carbinols.⁵

Structure IV was supported by analysis and by its infrared spectrum, which showed a strong band

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