and the residue taken up in benzene and chromatographed on alumina. Recrystallization from benzene yielded one gram of yellow crystals, 18%, m.p. 279–281°.

Anal. Calcd. for $C_{43}H_{32}Fe$: C, 85.96; H, 5.71. Found: C, 85.59; H, 5.96.

The infrared spectrum of this product was identical with that of triphenylmethylferrocene prepared by the method of Nesmeyanov,[12] except for the absence of the monosubstitution bands at 9 and 9.95 μ.

Spectra. The spectra used in this work were obtained with a Perkin-Elmer Model 137 Infracord instrument with sodium chloride optics, employing potassium bromide pellets.

Acknowledgment. The authors would like to acknowledge financial assistance from the University of North Carolina Research Council, the Du Pont Co., and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

CHAPEL HILL, N.C.

[CONTRIBUTION FROM THE MOORE LABORATORY, ROYAL HOLLOWAY COLLEGE, UNIVERSITY OF LONDON]

Boron Ring Compounds. A New Series

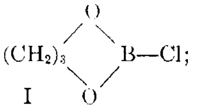
ARTHUR FINCH, J. C. LOCKHART,[1] AND JOY PEARN[2]

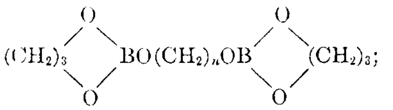
Received February 6, 1961

The preparation and characterization of the boron-containing heterocycle, 2-chloro-1,3,2-dioxaborinane, and of related compounds are described. Isolation of the mixed ester, 2-(3′-chloropropyl)-1,3,2-dioxaborinane, in addition to the expected tris(3-chloropropyl) borate and boric oxide, from the pyrolysis of 2-chloro-1,3,2-dioxaborinane, is discussed.

Cyclic esters of chloroboronic acid are of interest because they are thermodynamically more stable than noncyclic esters, and yet contain a reactive center, the B—Cl bond. Both the susceptibility of this B—Cl link to nucleophilic attack, and its chlorinating function, enable the synthesis and study of new boron-containing heterocycles. In this paper, a survey of reactions of 2-chloro-1,3,2-dioxaborinane and its pyrolytic decomposition is made.

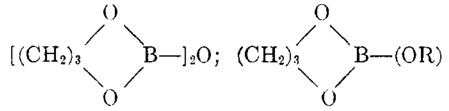
The reaction of boron trichloride and trimethylene glycol at low (*ca.* −80°) temperatures, and in various proportions, has been investigated. 2-Chloro-1,3,2-dioxaborinane I and diborate IIa were obtained using appropriate ratios of glycol to boron trichloride. A further excess of glycol produced IIa but no tris-(3-hydroxypropyl) borate III was isolated.


I


IIa. $n = 3$
b. $n = 2$

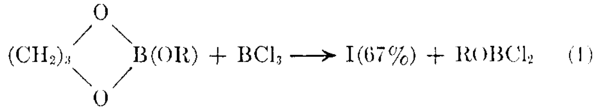
$B[O(CH_2)_3OH]_3$
III

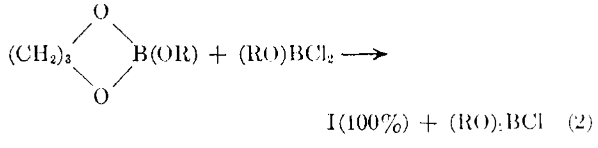
I was further characterized by the preparation of the anhydride IV, several esters V, and another diborate IIb.

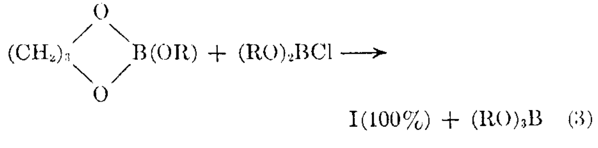

IV V

R is a. n-C_3H_7 c. $Cl(CH_2)_2$
b. n-C_4H_9 d. $Cl(CH_2)_3$

The ester 2-(3′-chloropropyl)-1,3,2-dioxaborinane Vc is of special interest, as it was isolated from the pyrolysis of I. The reactions of this ester with the chlorinating species boron trichloride, (3-chloropropyl) dichloroborinate, and di(3-chloropropyl) chloroboronate led to high yields of I, in accordance with the following equations:


$$(CH_2)_3O_2B(OR) + BCl_3 \longrightarrow I(67\%) + ROBCl_2 \quad (1)$$


$$(CH_2)_3O_2B(OR) + (RO)BCl_2 \longrightarrow I(100\%) + (RO)_2BCl \quad (2)$$


$$(CH_2)_3O_2B(OR) + (RO)_2BCl \longrightarrow I(100\%) + (RO)_3B \quad (3)$$

These reactions presumably take place *via* a 4-center bridge complex involving the (vacant) boron P_z orbital. For example, the transition state in Equation 3 is represented as shown below, with the direction of subsequent disproportionation towards removal of the comparatively volatile I and simultaneous production of the thermodynamically stable ester, tris(3-chloropropyl) borate VI.

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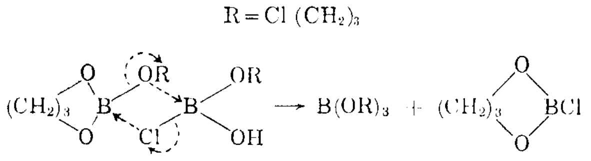
(1) Holder of an I.C.I. Research Fellowship.

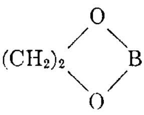
(2) Holder of a D.S.I.R. Postgraduate Studentship.



VI

Pyrolysis. The orthobaric pyrolysis of I at *ca.* 100°, with subsequent low-pressure fractionation of the products, was studied. The salient features were: (a) no loss of weight; (b) ultimate production of trisester VI, in yields of up to 25%, and boric oxide; concomitant formation of the mixed ester Ve; (c) production only of boron-containing compounds.

Pyrolysis of the five-membered ring analogue, 2-chloro-1,3,2-dioxaborolane has been shown to yield boric oxide and the corresponding trisester, tris(2-chloroethyl) borate.[3] This was explained by the intermediacy of 2-chloroethyl metaborate, which is known to give the observed pyrolysis end-products on distillation:

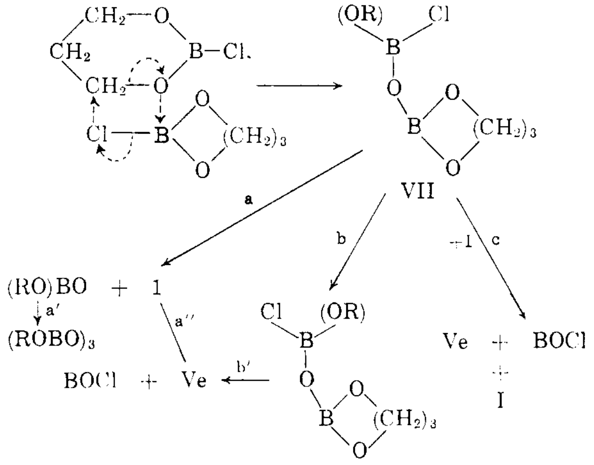


$$\longrightarrow [Cl(CH_2)_2OBO] \longrightarrow [Cl(CH_2)_2O]_3B + B_2O_3 \quad (4)$$

The formation in the borinane pyrolysis of the mixed ester Ve, 2-(3-chloropropyl)-1,3,2-dioxaborinane, indicates greater complexity, since no corresponding mixed ester was detected in the borolane reaction. However, intermediate production of the metaborate may still be assumed.[4] The presence of metaborate in the pyrolysate, prior to distillation, has now been confirmed by comparison of the infrared spectrum of the pyrolysate with that of metaborate independently synthesised by standard procedures from boric acid and 3-chloropropanol. Inspection of infrared spectra taken on samples of I after varying periods of pyrolysis showed *ca.* 40% metaborate present after two hours, *ca.* 80% after twenty-four hours, and *ca.* 100% after four weeks. At no time was the spectrum of the pyrolysis end-product, trisester, VI, observed. Hence further decomposition of metaborate to VI occurred only on distillation.

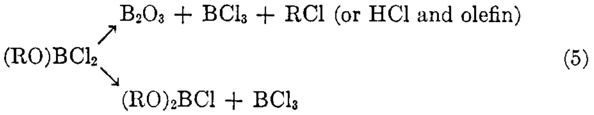
The state of molecular aggregation of the metaborate is of interest. Metaborates are known to have the trimeric boroxole structure $(BORO)_3$[5] and the infrared spectrum of the pyrolysate indicates that it is this form which is present. Attempts to isolate mixed ester Ve from I and synthesized metaborate under pyrolysis conditions were unsuccessful. Consequently should metaborate be a precursor in the formation of Ve (as shown in the Scheme, Aa″) then the monomeric form only is involved, at the expense of trimerisation to boroxole (route Aa′).

Scheme A



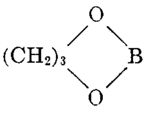
The preliminary step is formation of the intermediate VII from two molecules of I. This then disproportionates to give metaborate and I (Scheme Aa) which can in turn disproportionate to give one molecule of boron oxychloride and one of Ve (route a″). Finally, reaction of I with VII will also result in these products (c).

BOCl is well known as a product of organoboron pyrolyses, and its decomposition is conventionally written: BOCl → $BCl_3 + B_2O_3$. The boron trichloride then reacts either with Ve (equation 1) or with metaborate to give, in either case, 3-chloropropyl dichloroborinate $(RO)BCl_2$. The decomposition of these compounds is well known,[6] and takes the alternative paths:



$$(RO)BCl_2 \begin{cases} \nearrow B_2O_3 + BCl_3 + RCl \text{ (or HCl and olefin)} \\ \searrow (RO)_2BCl + BCl_3 \end{cases} \quad (5)$$

The former may be disregarded since (a) no weight-loss is observed; (b) only boron-containing compounds are formed; (c) the second mode is characteristic for the closely-similar 2-chlorethyldichloroborinate. Formation of dialkyl chloroboronate $(RO)_2BCl$ may therefore be assumed. It is possible that under pyrolysis conditions this compound forms directly, without intermediate production of $(RO)BCl_2$, *via* ring-opening of Ve:



$$B(OR) + BCl_3 \longrightarrow B(OR)_2Cl + BOCl \quad (6)$$

That no $(RO)_2BCl$ is isolated on distillation is readily explicable, as (a) reaction with Ve (Equa-

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(3) J. A. Blau, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 4116 (1957).

(4) A. Finch, J. C. Lockhart, and J. Pearn, *Chem. & Ind.*, 471 (1960).

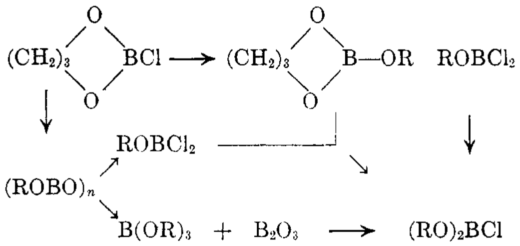
(5) G. L. O'Connor and H. R. Nace, *J. Am. Chem. Soc.*, 77, 1578 (1955); M. F. Lappert, *J. Chem. Soc.*, 2790 (1958).

(6) E. W. Abel, J. D. Edwards, and M. F. Lappert, *J. Chem. Soc.*, 501 (1957).

tion 3) is quantitative and (b), we have shown that it reacts with metaborate, largely in accordance with the equation:

$$(RO)BO + (RO)_2BCl \longrightarrow (RO)_3B + BOCl$$

We conclude, therefore, that the pyrolysis may be represented by the following general scheme:



Diborate (IIb). I, (13.2 g.) and ethylene glycol (3 ml.) were warmed at 20° under a −80° reflux after initial mixing at −80°. Hydrogen chloride evolved (3.75 g., Calcd. Found: 3.60 g.) was collected at −180°. IIb was obtained (9.09 g., 72%), b.p. 122° (0.01 mm.) n_{D}^{25} 1.4540.

Anal. Calcd. for $C_8H_{16}O_6B_2$: C, 41.70; H, 7.00; B, 9.42. Found: C, 39.14; H, 6.74; B, 9.84.

Anhydride IV. Water (2.0 ml. in 40 ml. ethyl ether) was added to I (15.0 g.) in methylene chloride (20 ml.). Solvents and excess I were pumped off at 20° (0.01 mm.) leaving a colorless liquid, b.p. 115–117° (0.01 mm.), n_{D}^{25} 1.4528, in 78% yield.

Anal. Calcd. for $C_6H_{12}B_2O_5$: C, 38.7; H, 6.51; B, 11.6. Found: C, 39.1; H, 6.51; B, 11.4.

Esters V. All were prepared by addition of the calculated quantity of cooled alcohol to a slight excess of I in cold methylene chloride solution; volatile materials were removed by distillation. The data is collected in the table below:

Compound		C	H	B	Cl	B.P. (Mm.)	n_{D}^{25}
Va	Calcd.:	50.1	9.1	7.5		29–30 (0.08)	1.4205
	Found:	50.0	8.95	7.5			
Vb	Calcd.:	53.2	9.5	6.86		37–38 (0.05)	1.4305
	Found:	52.4	9.7	6.46			
Vc	Calcd.:	36.6	6.1	6.58	21.6	48 (0.01)	1.4510
	Found:	36.7	6.1	6.64	21.5		
Vd	Calcd.:	40.4	6.78	6.06	19.87	66–67 (0.15)	1.4505
	Found:	40.7	6.93	6.00	19.80		

Infrared spectra. A detailed study of the B—Cl and ring-skeletal vibrations in this type of ring-compound is in preparation. Measurements on 2-chloro-1,3,2-dioxaborinane using a Hilger H-800 (potassium bromide region), and a Perkin-Elmer Infracord (rock-salt region), lead to tentative assignment of the B—Cl vibration to a band near 550 wave numbers.[7]

EXPERIMENTAL

Distillations were carried out at lowest possible temperatures in specially-designed apparatus capable of evacuation to 10^{-2} mm. In a typical run, approximately 10 g. could be distilled through a column, condensed by a −80° reflux, and separated into several fractions with *ca.* 0.3 g. "apparatus loss." Moisture was rigorously excluded.

2-Chloro-1,3,2-dioxaborinane, I. Trimethylene glycol (30.2 ml., 0.41 mole) was slowly added with shaking to boron trichloride (50 g., 0.43 mole) in methylene chloride (30 ml.) cooled to −80° by an acetone–Dry Ice bath, and under a Dry–Ice reflux. The resulting liquid was allowed to warm to room temperature overnight. Distillation afforded I in yields of up to 85%.

Anal. Calcd. for $C_3H_6O_2BCl$: C, 29.94; H, 5.02; Cl, 29.46; B, 8.99. Found: C, 30.73; H, 5.08; Cl, 29.17; B, 9.00. B.p. 20° (0.01 mm.); n_{D}^{25} 1.4340.

Trimethylene diborate (IIa). Glycol (50 g., 0.63 mole) was treated with boron trichloride (50 g., 0.43 mole) as before, giving 69 g. of distillate boiling from 110–130°. Repeated redistillations gave a sharp fraction, b.p. 125° (0.05 mm.), n_{D}^{25} 1.4520.

Anal. Calcd. for $C_8H_{16}O_6B_2$: C, 44.4; H, 7.4; B, 8.82. Found: C, 44.76; H, 7.69; B, 8.75.

Reaction of Ve *with boron trichloride.* The ester Ve (7.1 g. was mixed at −80° with boron trichloride (6.8 g.), allowed to warm slowly, and refluxed under a Dry-Ice condenser for 1 hr. Distillation gave I (3.2 g., 66%), n_{D}^{25} 1.4365, the infrared spectrum being identical with that of a pure sample, together with 4.4 g. of liquid, b.p. 31° (0.5 mm.) and 1.2 g. of a fraction boiling in the range 48–120° (0.3 mm.). Boron trichloride was recovered (4.1 g.).

Reactions of Ve *with (3-chloropropyl) dichloroborinate.* Ester (6.0 g.) and dichloroborinate (6.0 g., obtained by Lappert's procedure,[6] n_{D}^{25} 1.4467) were mixed at −80°, refluxed at room temperature for 2 hr., and distilled to give I (6.1 g.), b.p. 21° (0.01 mm.), boron trichloride (0.3 g.), and 2.5 g. of liquid distilling at 97–100°, (0.01 mm.), identified as tris-ester VI. A middle fraction, boiling-range 30–90° (0.05 mm.), amounted to 2.5 g. (Found: easily hydrolysable chlorine, 21.4%: B, 5.4%.)

Reaction of Ve *with di(3-chloropropyl) chloroboronate.* Ester (4.2 g.) and dichloropropyl chloroboronate (5.5 g., made by Lappert's method, n_{D}^{25} 1.4599) were mixed at −80°, refluxed for 30 min. at 50°, and slowly distilled, giving I (2.8 g.), and trisester VI (5.7 g.), b.p. 98° (0.05 mm.).

Pyrolysis: (a) *at 60°.* When I (28 g.) was heated at 60° for 15 hr. 24.8 g. was recovered on distillation, showing the great thermal stability of this compound.

(b) *at 100°.* Weighed quantities of I were heated at 100 ±3° for 15 hr. under reflux, contact with moisture being prevented by a mercury cut-off. No loss of weight was observed on heating. The products were separated by distillation at low pressure. The first fraction, b.p. 73–76° (0.4 mm.), in up to 10% yield gave, on redistillation, the pure ester Ve, b.p. 67–68°, n_{D}^{25} 1.4470. The second fraction, b.p. 102–120° (1 mm.) gave, on redistillation, pure trisester VI, b.p. 98° (0.05 mm.). The residue in the flask was mostly boron oxide (no easily hydroysable chlorine, and a boron content of 29.2% calcd.: 31%).

Preparation and decomposition of 3-chloropropyl metaborate. Boric acid (10.3 g.) and trimethylene chlorohydrin, after pumping at 20° (0.05 mm.) gave a sample of metaborate, n_{D}^{25} 1.4645.

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[7] A. Finch, P. J. Hendra, and J. Pearn, unpublished work.

Anal. Calcd. for $C_3H_6O_2BCl$: C, 29.94; H, 5.02; Cl, 29.46; B, 8.99. Found: C, 30.76; H, 5.27; Cl, 30.80; B, 8.99.

Distillation of the metaborate (7.02 g.) under reduced pressure gave a fraction (0.6 g.) containing very little boron (*ca.* 0.8%), b.p. 35° (0.05 mm.), and, after prolonged heating, a fraction (3.13 g.), b.p. 100–120° (0.05 mm.), (B content, 4.0%), n_D^{25} 1.4585. This fraction on redistillation gave pure trisester, VI. The residue in the flask (2.0 g.) contained boron, (18.3%).

Reaction of metaborate with I. I (4.7 g.) and 3-chloropropyl metaborate (4.9 g.) were subjected to pyrolysis conditions (100°) for 15 hr. There was no loss of weight. I was recovered (3.4 g., b.p. 20° (0.05 mm.)), and trisester VI (2.7 g.). No trace of the mixed ester Ve was found in this or two checking runs. Reaction of metaborate with 3-chloropropyl dichloroborinate. Metaborate (3.5 g.) and dichloroborinate (4.1 g.) were mixed at −80° and heated at 20° for 90 min. Boron trichloride evolved (0.7 g.) was trapped at −180° (boron: chlorine ratio found 1:9.5; calcd., 1:9.8). Much of the distillate had a wide boiling range, but one sharp fraction (0.6 g., n_D^{25} 1.4575) corresponding to trisester VI was obtained.

Acknowledgment. It is a pleasure to thank Dr. P. J. Hendra for helpful discussions, and Messrs. B. Smethurst and R. Lane for technical assistance. Partial support from the European Research Office, U. S. Department of the Army, is also gratefully acknowledged.

ENGLEFIELD GREEN, SURREY, U. K.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

New Heteroaromatic Compounds. XV.[1] Halogenation of 2-Methyl-2,1-borazaronaphthalene

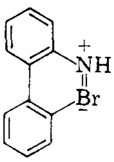
MICHAEL J. S. DEWAR AND ROY DIETZ

Received February 6, 1961

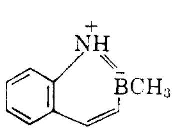
Bromination of 2-methyl-2,1-borazaronaphthalene gives a mixture of the 3-bromo derivative together with *o*-amino-ω-bromostyrene, chlorination gives analogous products. The first step in these reactions seems to be the formation of a π-complex involving the 3,4-bond; the possibility that similar π-complexes may be formed as intermediates in the substitution of other aromatic compounds is discussed.

Derivatives of 10,9-borazarophenanthrene undergo halogenation,[2] nitration,[2] and Friedel-Crafts acetylation[3] in the 6- and 8-positions, as predicted by the simple perturbation form of the MO theory that has proved a good semiquantitative guide to the orientation of substitution in other aromatic systems.[4]

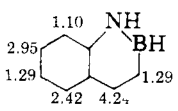
By an unfortunate coincidence the most reactive positions in 10,9-borazarophenanthrenes (I) are those *ortho* and *para* to the imino group; electrophilic attack would therefore be expected to take place preferentially in those positions even if central boron-containing ring were nonaromatic. This difficulty does not arise in the case of 2,1-borazaronaphthalenes, *e.g.*, II.[5] Here one would predict attack mainly in the benzenoid ring if the compound is aromatic, the corresponding π-activation energies[4] being shown in III; the predicted order of reactivity is 8 > 3 = 6 > 5 ⟫ 4. If the compound were nonaromatic, the preferred point of attack should certainly be the styrene-like 3,4-bond and the reaction should lead to addition rather than substitution, particularly for the reactions of II with halogens.



I



II



III

2-Methyl-2,1-borazaronaphthalene was brominated and chlorinated in acetic acid or carbon tetrachloride using standard solutions of halogen to ensure addition of one mole. The uptake of halogen was in all cases rapid and quantitative at room temperature. The nonbasic material was purified by chromatography and yielded in each case only one product, C_9H_9NBS (X = Cl, Br), whose ultraviolet spectrum (Fig. 1) resembled closely that of II. The infrared spectra resembled that of II in the region most characteristic of aromatic substitution (1660–2000 cm.$^{-1}$). It therefore seemed likely that the compounds were the 3-chloro and 3-bromo derivatives of II.

The basic products from the halogenations consisted of compounds C_8H_8NX (X = Cl, Br) whose ultraviolet spectra (Fig. 2) resembled that of 2-aminostyrene, but whose infrared spectra, unlike

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[1] Previous paper, S. S. Chissick, M. J. S. Dewar, and P. M. Maitlis, *J. Amer. Chem. Soc.*, *in press*.

[2] M. J. S. Dewar and V. P. Kubba, *Tetrahedron*, **7**, 213 (1959) *J. Org. Chem.*, **25**, 1722 (1960).

[3] M. J. S. Dewar and V. P. Kubba, *J. Amer. Chem. Soc.*, *in press*.

[4] M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956); M. J. S. Dewar and P. M. Maitlis, *J. Chem. Soc.*, 2521 (1957); M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3357 (1952).

[5] M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 2728 (1959).