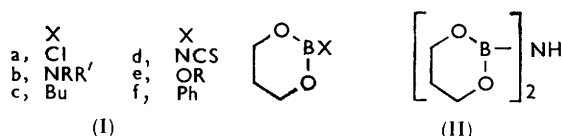


270. Boron Ring Compounds. Part II.¹ Some New 2-Substituted 1,3,2-Dioxaborinans.

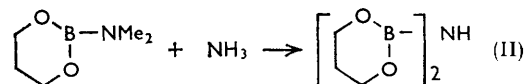
By ARTHUR FINCH, P. J. GARDNER, J. C. LOCKHART, and E. J. PEARN.

Use has been made of the reactive halogen in 2-chloro-1,3,2-dioxaborinan¹ (Ia) to prepare new dioxaborinans. Other syntheses of 2-alkyl and 2-phenyl compounds are described. Anomalous reactions of methanol and butane-1-thiol with compound (Ia) are interpreted.

SOME new compounds (Ib–e) with the 1,3,2-dioxaborinan skeleton have been prepared by nucleophilic substitution of the labile halogen in the dioxaborinan (Ia). Substitution with alkylamines to give compounds (Ib) was successful when at least two molar equivalents of amine were used, precipitating the hydrogen chloride formed as amine hydrochloride. Use of one equivalent of amine gave no identifiable products on distillation. This is in accord with certain previous findings on reaction of amines with the boron-

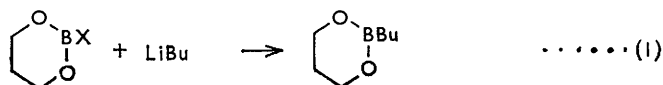


chlorine link.² Triethylamine or a second mole of the substituting amine is required to break the complex initially formed with one mole of amine. Ammonia itself did not give the corresponding amine compound (Ib; R' = R'' = H), nor was it obtained by transamination³ or use of sodamide. An undistillable material, probably the bis(dioxaboraninyl) compound (II) was obtained from the transamination reaction of ammonia with 2-dimethylaminodioxaborinan. This compound showed infrared absorption in the N-H stretching frequency region.



Simple nucleophilic substitution with butanethiol could not be achieved, for the conditions used resulted in pyrolysis. A mixture of thiol and compound (Ia) at 100°/1 atm. gave the pyrolysis product, 3-chloropropyl metaborate, previously noted.¹ Heating at reduced pressure resulted in another known pyrolysis product,⁴ 2-3'-chloropropoxy-1,3,2-dioxaborinan, but no hydrogen chloride was evolved and no boron-sulphur bond was formed. Formation of 2-butylthio-1,3,2-dioxaborolan in low yield has been reported⁵ in a similar reaction at high temperatures with the chloroborolan, which is apparently less readily pyrolysed.

Several routes to a carbon-boron link were attempted: reaction of butyl-lithium with the amine (Ia; R = R' = H) gave a good yield of 2-butyl-dioxaborinan (Ic); reaction



with tripropylboron gave a very low yield of the 2-propyl derivative. The 2-alkylborolans⁶ and -borinans have previously been made from the alkylboronic acid and the

¹ Part I, Finch, Lockhart, and Pearn, *J. Org. Chem.*, 1961, **26**, 3250.

² Brown, J. F., *J. Amer. Chem. Soc.*, 1952, **74**, 1219; Goubeau, Rahty, and Becker, *Z. anorg. Chem.*, 1954, **275**, 161.

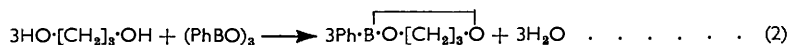
³ English, McCloskey, and Steinberg, *J. Amer. Chem. Soc.*, 1961, **83**, 2122.

⁴ Finch, Lockhart, and Pearn, *Chem. and Ind.*, 1960, 471.

⁵ Blau, Gerrard, and Lappert, *J.*, 1960, 667.

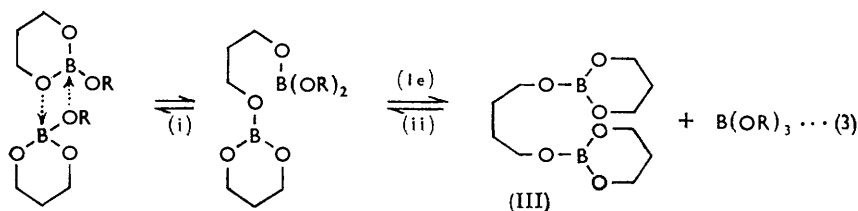
⁶ Torsell, *Acta Chem. Scand.*, 1954, **8**, 1779.

appropriate 1,2- or 1,3-diol, water being removed as the toluene azeotrope.⁷ 2-Phenyldioxaborinan (If) has been similarly prepared from phenylboronic anhydride and propane-1,3-diol (reaction 2). Complex formation with these alkyl and aryl ring compounds is in progress.

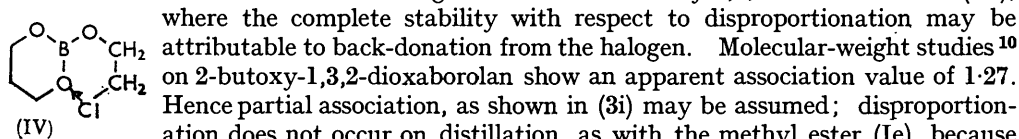


Formally analogous to reaction (1) is the metathetical reaction of chloroborinan (Ia) with potassium thiocyanate in 1,2-dimethoxyethane⁸ to give the thiocyanato-compound (Id). This had the infrared absorption expected for a covalent isothiocyanate rather than a thiocyanate.⁹ Lappert and Pyszora^{9a} recently prepared a series of boron isothiocyanates with a characteristic, very broad band at 2083—2101 wave numbers, and a half-band width 150—170 wave numbers. This band appears in the spectrum of the new compound (Id).

Addition of cyclohexanol to the chloroborinan (Ia) gave, on distillation, the corresponding ester (Ie; R = C₆H₁₁) as expected from previous work¹ with 2-chloroethanol, 3-chloropropanol, and butan-1-ol. Methanol, however, gave, on distillation, almost quantitative yields of methyl borate and trimethylene diborate (III); no methyl ester (Ie; R = Me) was isolated. However, if a mixture of methanol and chloroborinate was evacuated under a condenser cooled to -80°, so as to remove hydrogen chloride but not methyl borate, the liquid residue had a molecular weight of 103.5. The methyl ester (Ie; R = Me) should have a molecular weight of 116, the diborate 243.6. The reaction may take place as shown (reaction 3), the equilibrium depending on (a) the volatility of

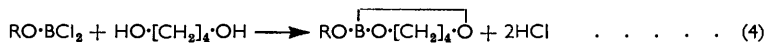


the trialkyl borate and (b) the nature of the alkyl group R. Reaction of the chloro-compound (Ia) with ethanol likewise produced no ethyl ester (Ie; R = Et) on distillation; instead, diborate could be distilled off in good yield. This may be contrasted with the reaction of 2-chloroethanol which gives 2-2'-chloroethoxy-1,3,2-dioxaborinan¹ (IV),



where the complete stability with respect to disproportionation may be attributable to back-donation from the halogen. Molecular-weight studies¹⁰ on 2-butoxy-1,3,2-dioxaborolan show an apparent association value of 1.27. Hence partial association, as shown in (3i) may be assumed; disproportionation does not occur on distillation, as with the methyl ester (Ie), because of the much lower volatility of butyl than of methyl borate. Stability to disproportionation is in the sequence Me < Et < Pr < Bu < Cl·[CH₂]₂ < Cl·[CH₂]₃.

Attempts were made to extend esterification studies to the seven-membered dioxaborepan system. The methyl and the 2-chloroethyl ester were obtained by reaction of butane-1,4-diol with the appropriate dichloroborinate (4), but neither ester was stable



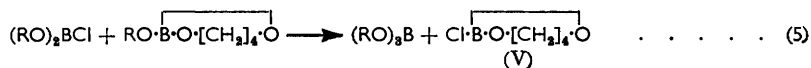
⁷ Letsinger and Skoog, *J. Amer. Chem. Soc.*, 1954, **76**, 4174; Finch and Chainani, Annual Technical Status Report, 1960, European Research Office, U.S. Dept. of the Army.

⁸ Brennan, Dahl, and Schaeffer, *J. Amer. Chem. Soc.*, 1960, **82**, 6248.

⁹ (a) Lappert and Pyszora, *Proc. Chem. Soc.*, 1960, 350; (b) Caldow and Thompson, *Spectrochim. Acta*, 1958—9, **13**, 214; Lieber, Rao, and Ramachandran, *ibid.*, p. 296.

¹⁰ Hubert, Hargitay, and Dale, *J.*, 1961, 931; Brotherton and McCloskey, *J. Org. Chem.*, 1961, **26**, 1668.

on distillation. In general, the dioxaborepan system is more readily disproportionated than the borolan or borinan analogue. Thus the 2-chloro-1,3,2-dioxaborepan (V) could not be made by reaction of boron trichloride and butane-1,4-diol, or from 2-methoxy-1,3,2-dioxaborepan and chlorodimethoxyboronate, which might be expected to undergo reaction (5) with the facility of similar reactions in the borinan series.¹



EXPERIMENTAL

2-Dimethylamino-1,3,2-dioxaborinan.—Dimethylamine (13.8 g.) and 2-chloro-1,3,2-dioxaborinan (13 g.) were mixed at -180° and allowed to warm under a condenser kept at -80° . A white solid was precipitated. The mother-liquor, mostly 2-dimethylamino-1,3,2-dioxaborinan, had b. p. $24^\circ/0.1$ mm., n_D^{25} 1.4330 (14 g., 93%) (Found: C, 46.3; H, 9.1; N, 11.0%; *M*, 128, 132. $C_5H_{12}BNO_2$ requires C, 46.5; H, 9.3; N, 10.9%; *M*, 128.9). The solid was dimethylamine hydrochloride, m. p. 169° (9 g., 96%).

2-Diethylamino-1,3,2-dioxaborinan.—Diethylamine (25 ml.) and chloroborinan (Ia) (15 g.) were treated as for the dimethylamino-compound. The diethylamino-compound had b. p. $33-34^\circ/0.01$ mm., n_D^{25} 1.4365 (14.9 g., 76%) (Found: C, 53.7; H, 10.0; N, 9.0; B, 7.1%; *M*, 150. $C_7H_{16}BNO_2$ requires C, 53.9; H, 10.3; N, 9.0; B, 6.9%; *M*, 157). Diethylamine hydrochloride was recovered (13.2 g., 97%).

2-Ethylamino-1,3,2-dioxaborinan.—Ethylamine (25 ml.) and chloroborinan (17 g.) gave the ethylamino-compound, b. p. $24^\circ/0.05$ mm., n_D^{25} 1.4340 (13.8 g., 70%) (Found: C, 46.5; H, 9.1; N, 11.0; B, 8.4. $C_5H_{12}BNO_2$ requires C, 46.5; H, 9.3; N, 10.9; B, 8.3%). Ethylamine hydrochloride (11.6 g., 100%) was recovered.

Reaction of Ammonia with Chloroborinan (Ia).—Chloroborinan (8.6 g.) and liquid ammonia (20 ml.) were sealed in a glass tube and left at room temperature for 2 days. Ammonium chloride was identified but no other nitrogen-containing compound was isolated by the usual methods.

Reaction of Ammonia with 2-Dimethylamino-1,3,2-dioxaborinan.—2-Dimethylamino-borinan (10 g.) was sealed off with a ten-fold excess (20 ml.) of sodium-dried ammonia and shaken. Ammonia was evaporated off at a low temperature, then dimethylaminoborinan (2.7 g.) was recovered (confirmed by its infrared spectrum). The residual liquid was distilled but appeared to decompose, leaving a residue (Found: C, 18.4; H, 6.3; N, 20.7; B, 13.5%). A second experiment gave a residual clear yellow liquid which was not distilled (Found: C, 39.8; H, 7.4; N, 8.2; B, 11.7. Calc. for $C_6H_{13}B_2NO_4$: C, 39.0; H, 7.1; N, 7.6; B, 11.6%). This had a characteristic infrared N-H stretching band and was probably bis(dioxaborinanyl)-amine (II).

Reaction of Butanethiol with Chloroborinan.—(a) Chloroborinan (20 g.) and butane-1-thiol were refluxed at 0.1 mm. under a condenser cooled to -80° . No hydrogen chloride was evolved. On distillation of the mixture chloroborinan (18.9 g.) was recovered and 2-3'-chloropropoxy-1,3,2-dioxaborinan⁴ (3.97 g.), b. p. $65^\circ/0.1$ mm., was identified by its infrared spectrum. (b) The chloroborinan (14 g.) and butane-1-thiol (16 ml.) were heated at 100° for 25 hr. No hydrogen chloride was evolved. The infrared spectrum of the residue when butanethiol was pumped off corresponded exactly to that of 3-chloropropyl metaborate,¹ which cannot be distilled without decomposition.

2-Butyl-1,3,2-dioxaborinan.—An ether solution (50 ml.) of chloroborinan (16 g.) was added dropwise to a solution of butyl-lithium (18.0 g.) in ether under nitrogen. Heat was evolved and the mixture was cooled in ice. A white precipitate was formed. The ether was removed on a water-pump and the remaining liquid distilled at $80-100^\circ/15$ mm. (12.0 g., 66%). 2-Butyl-1,3,2-dioxaborinan was redistilled at $166^\circ/760$ mm. and had n_D^{25} 1.4205 (Found: C, 58.5; H, 10.1; B, 8.3. $C_7H_{15}BO_2$ requires C, 59.2; H, 10.6; B, 7.6%). The residue was impure lithium chloride but contained some boron.

2-Phenyl-1,3,2-dioxaborinan.—Phenylboronic anhydride (23.5 g.) and trimethylene glycol (19 g.), reacting in toluene (75 ml.) according to Letsinger and Skoog's⁷ procedure, gave 2-phenyl-1,3,2-dioxaborinan (32.6 g., 90%), b. p. $70-75^\circ/0.2$ mm., which was a super-cooled

liquid at room temperature and could be maintained for weeks in this form (Found: C, 66.1; H, 6.8; B, 6.9%; *M*, 170. $C_9H_{11}BO_2$ requires C, 66.7; H, 6.8; B, 6.7%; *M*, 162).

2-Isothiocyano-1,3,2-dioxaborinan.—A solution of potassium thiocyanate (12 g.) in 1,2-dimethoxyethane⁸ was added dropwise to the 2-chloroborinan (Ia) (15 g.) in solvent (20 ml.). An immediate precipitate and heat of reaction were observed. After being shaken for 30 min. the mixture was filtered. The residue (9.5 g.) was mostly potassium chloride. The filtrate was pumped to remove solvent, and the residual *2-isothiocyano-1,3,2-dioxaborinan* was distilled (b. p. 62—64°/0.2 mm.). Redistillation (b. p. 58—60°/0.01 mm.) gave a yellow liquid (Found: C, 33.8; H, 4.3; N, 9.7; B, 7.3; S, 22.4; NCS, 38.1. $C_4H_6BNO_2S$ requires C, 33.6; H, 4.2; N, 9.8; B, 7.6; S, 22.4; NCS, 40.6%).

2-Cyclohexyloxy-1,3,2-dioxaborinan.—Esterification of chloroborinan with cyclohexanol in the manner previously described¹ gave an 84% yield of *2-cyclohexyloxy-1,3,2-dioxaborinan*, b. p. 64—65°/0.05 mm., n_D^{25} 1.4608 (Found: C, 57.8; H, 9.2; B, 6.0. $C_9H_{17}BO_3$ requires C, 58.7; H, 9.3; B, 5.9%).

Reaction of Methanol and Chloroborinan.—A mixture of compound (Ia) (10.4 g.) and methanol (2.8 g.) was pumped at 0°/26 mm. under a condenser at -80°. Hydrogen chloride (2.7 g. Calc., 3.2 g.) was collected. The condenser was then taken away and trimethyl borate removed (2.6 g. Calc., 3.0 g.) (Found: B, 10.2. Calc. for $C_3H_9BO_3$: B, 10.4%), b. p. 69—70° (lit., 68°), n_D^{25} 1.379 (lit., 1.362). The residue was mostly trimethylene diborate,¹ identified by its infrared spectrum (3000—400 wave numbers), b. p. 120—125°/0.05 mm., and n_D^{25} 1.4500 (lit.,¹ b. p. 125°/0.05 mm., n_D^{25} 1.4520) (Found: C, 43.8; H, 7.7; B, 9.3%; *M*, 240.6. Calc. for $C_9H_{18}O_6B_2$: C, 44.4; H, 7.4; B, 8.9%; *M*, 243.6).

2-2'-Chloroethoxy-1,3,2-dioxaborepan.—To 2-chlorethyl dichloroborinate¹¹ (15.1 g.) (Found: B, 6.55; easily hydrolysed Cl, 41.6. Calc. for $C_2H_4BCl_2O$: B, 6.7; Cl, 43.5%) was added at 0° butane-1,4-diol (8.2 ml.). Hydrogen chloride (94%) was removed and the residual viscous *borepan* analysed without distillation (Found: C, 39.1; H, 6.6; B, 6.3; easily hydrolysed Cl, 0. $C_6H_{10}BClO_3$ requires C, 41.3; H, 5.8; B, 6.2%; easily hydrolysed Cl, 0).

2-Methoxy-1,3,2-dioxaborepan.—Dichloromethoxyborinate¹² (13.5 g.) (Found: B, 9.3; Cl, 59.7. Calc. for $C_5H_{11}BO_3$: B, 9.6; Cl, 62.9%) and butane-1,4-diol (10.6 ml.), by a similar reaction, gave a pale yellow plastic *methoxy-compound* (Found: C, 46.2; H, 8.5; B, 8.3; Cl, 0. $C_5H_{11}BO_3$ requires C, 46.2; H, 8.5; B, 8.3%; Cl, 0).

Reaction of Methoxyborepan with Chlorodimethoxyboronate.—*Borepan* (4.1 g.) was added to the chlorodimethoxyboronate (4.9 g.) at -80°. After the mixture had warmed to room temperature volatile materials were removed. No methyl borate was detected. The residue had a boron content of 10.8%.

Molecular weights were determined cryoscopically. The infrared absorption spectra of some of the compounds described will be reported later.

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¹¹ Edwards, Gerrard, and Lappert, *J.*, 1955, 1470.

¹² Gerrard and Lappert, *J.*, 1951, 2545.