192. *The Structure and Relative Stabilities of Boric Esters of 1,2- and 1,3-Diols.*

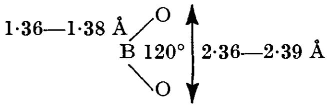
By A. J. Hubert, B. Hargitay, and Johannes Dale.

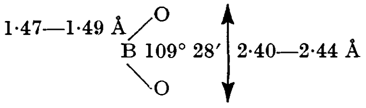
Cyclic boric esters of 1,2-diols show a much greater heat of reaction with amines than do cyclic esters of 1,3-diols and non-cyclic borates.

Isolation of the acetylation products of the mixed ester resulting from a competitive reaction between ethylene glycol and propane-1,3-diol for boric acid shows that the cyclic ester of the 1,3-diol is formed preferentially.

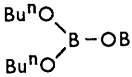
It is concluded that the five-membered ring must be strained with trigonal boron but not with tetrahedral boron, whereas the six-membered ring is unstrained in both cases. The strain in the five-membered ring approximately offsets the energy gain in ring formation, so that 1,2-diol borates, although distillable as cyclic esters, rearrange more or less to open-chain polymers on condensation. The unstrained 1,3-diol borates remain in the cyclic form.

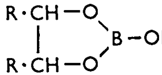
From the work of Böeseken and his collaborators[1] it is known that many 1,2- but not 1,3-diols raise the acidity and conductivity of boric acid by complex formation. On the other hand, Hermans,[2] and later other workers,[3] have shown that boric esters are formed more readily from 1,3- than from 1,2-diols. In an early stereochemical treatment Hermans[4]





suggested that the difference in stability is caused by the different O–O distances for trigonal (2·32 Å) and tetrahedral boron (2·42 Å), the first of which fits better with 1,3-diols, the latter better with 1,2-diols. Newer results[5] show that the two O–O distances are really much closer and the difference probably too small to account for such a strong effect.

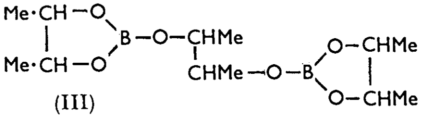

(I)


(II)

a : R = R′ = H

b : R = Me; R′ = H

c : R = R′ = Me (*meso*-form)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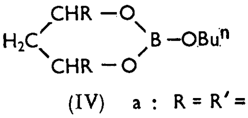
(IV) a : R = R′ = H

b : R = Me; R′ = H

In the preceding paper it was shown that 1,3-diols also give stable complexes in alkaline solution, and a more modern stereochemical analysis was given which indicated that the angular requirements of the mesomerically stabilized planar boric acid system[6] (BOC angle 120°) must be mainly responsible for the strain in the five-membered ring. This strain can be relieved by forming the borate anion whereby, not only the boron atom, but also the oxygen atoms become " tetrahedral." In the non-planar six-membered ring no strain would be expected with either trigonal or tetrahedral boron.

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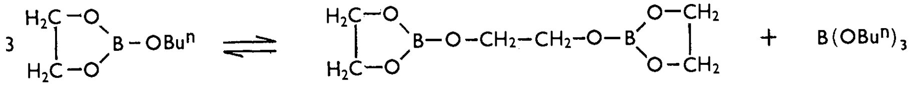
[1] Böeseken, *Adv. Carbohydrate Chem.*, 1949, **4**, 189.
[2] Hermans, *Z. anorg. Chem.*, 1925, **142**, 83.
[3] Pastureau and Veiler, *Compt. rend.*, 1936, **202**, 1683.
[4] Hermans, *Rec. Trav. chim.*, 1938, **57**, 333.
[5] Christ, Clark, and Evans, *Acta Cryst.*, 1958, **11**, 761.
[6] Lewis and Smyth, *J. Amer. Chem. Soc.*, 1940, **62**, 1529.

The expected great difference in the base-accepting power of five- and six-membered cyclic borates has now been confirmed by calorimetric measurements of the reaction with organic bases. These bases have a suitable base strength, allowing comparison, and permit work in hydroxyl-free solvents, whereby complicating solvolyses are avoided.

The borates used were of the simplest possible type, namely, (I—IV), to avoid steric effects by ring substituents. Qualitative comparison of the behaviour of these esters towards benzylamine showed that only compounds (II and III) containing the five-membered ring system gave a noticeable heat effect and a precipitate. The precipitates were too unstable to be recrystallized without decomposition. The amine and the borate contents, determined by titration (see Table 1), demonstrate that they are 1 : 1 addition compounds, although the values obtained for the mixed esters (IIa and c) are appreciably lower than the calculated values. Probably the mixed esters are in part disproportionated [7] in the liquid phase into tributyl borate and the trisdiol diborate, as shown. A part of the precipitate would then consist of the addition product of the trisdiol diborate with a lower equivalent weight (the tributyl borate gives no precipitate). This explanation is supported by the correct and even too high values obtained with tri(butane-2,3-diol) diborate (III) in which such a disproportionation cannot take place.



After the nature of the reaction had been established as addition of the amine to the boron atom, and not for example an aminolysis [8] with liberation of butanol, the heat effect was determined calorimetrically for octane solution with benzylamine and the stronger base pyrrolidine. The latter base did not give a precipitate with any of the borates, which was an advantage; the medium being homogeneous throughout the measurement, the heat of crystallization of the product did not obscure the effect. The heat of dilution of the concentrated amine in octane, separately measured, had to be subtracted from the observed heats of reaction. The results are given in Table 2.

TABLE 1. *Equivalent weight of precipitates of boric esters with benzylamine.*

Borate	Titr. HCl	Titr. NaOH	Theor.
Ethylene glycol butyl (IIa)	230	225	250
* *meso*-Butane-2,3-diol butyl (IIc)	268	263	274
meso-Butane-2,3-diol (III)	262	250	250

* Commercial butane-2,3-diol (Fluka) shown by us to contain 98·5% of *meso*-diol and 1·5% of racemate.

TABLE 2. *Thermal effect in the reaction between boric esters and amines in octane (12·5 mmoles of borate + 12·5 mmoles of amine in 96 ml. of octane).*

	Benzylamine		Pyrrolidine	
Borate	Obs. ΔH^1 (cal./mole)	$\Delta H = \Delta H^1 - \Delta H_{dil}$ [a]	Obs. ΔH^1 (cal./mole)	$\Delta H = \Delta H^1 - \Delta H_{dil}$ [b]
Tributyl (I)	+1130	−750	+770	−480
Ethylene glycol butyl (IIa)	−7750 [c]	−9630	−7100	−8350
Propane-1,2-diol butyl (IIb)	−2800 [d]	−4680	−9300	−10,550
meso-Butane-2,3-diol butyl (IIc)	−1580 [c]	−3460	−7100	−8350
meso-Butane-2,3-diol (III)	[c]		−8700	−9950
Propane-1,3-diol butyl (IVa)	+1400	−480	−650	−1900
Butane-1,3-diol butyl (IVb)	+1280	−600	+770	−480

[a] $\Delta H_{dilution} = 1800$ cal./mole. [b] $\Delta H_{dilution} = 1250$ cal./mole. [c] Solid precipitate. [d] Gelatinous precipitate.

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[7] Thomas, *J.*, 1946, 823.

[8] Goubeau *et al.*, *Z. anorg. Chem.*, 1951, **266**, 161; 1951, **267**, 27; 1952, **268**, 145.

It will be noticed that, although pyrrolidine is a stronger base than benzylamine, the borate (IIa) shows a higher apparent heat of reaction with benzylamine. This is presumably due to the additional heat of crystallization, since this complex is much less soluble than the other benzylamine complexes (with methyl substituents) and is precipitated more completely. On this basis the results obtained with pyrrolidine are more reliable, and it is seen that cyclic 1,2-diol borates are throughout far more acidic than cyclic 1,3-diol borates and open-chain borates.

To determine the relative stabilities of the boric esters as such, a mixture of one mol. of ethylene glycol and one of propane-1,3-diol was esterified with one mol. of boric acid. If now, as expected, the 1,3-diol forms preferentially the cyclic ester, a mixed ester, which might possibly in part be disproportionated into the trisdiol diborate and free ethylene glycol, should be formed. It was in fact found that, after the free hydroxyl groups had been caused to react with acetyl chloride, it was possible after mild hydrolysis to isolate as main products ethylene glycol monoacetate and ethylene chlorohydrin acetate, and only very little of the corresponding propanediol derivatives (Table 3). Acetyl chloride was chosen as reagent because neither it nor the hydrogen chloride formed attacks boric esters, and because the reaction was rapid and the products were easily separated by distillation. An analogous procedure has been used in a structural study of methyl D-glucopyranoside:[9] its boric ester was treated with benzoyl chloride and the benzoylated products were identified after hydrolysis.

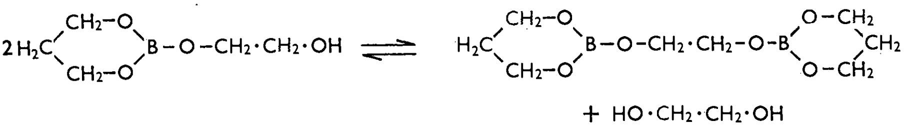
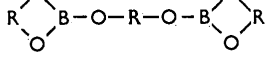
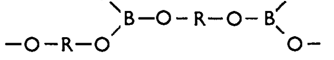


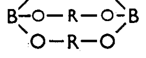
TABLE 3. *Acetylation of mixed boric esters of diols.*

Product treated with AcCl (0·5 mol.)	Isolated products (in moles)						Recovery (%)
	OH $[CH_2]_2$ Cl	OAc $[CH_2]_2$ Cl	OAc $[CH_2]_2$ OH	OH $[CH_2]_3$ Cl	OAc $[CH_2]_3$ Cl	OAc $[CH_2]_3$ OH	
Ester between ethylene glycol (1 mol.) and boric acid (0·5 mol.)	0·02	0·21	0·11				68
Ester between propane-1,3-diol (1 mol.) and boric acid (0·5 mol.) ...				0·03	0·02	0·24	58
Mixed ester between ethylene glycol (0·5 mol.), propane-1,3-diol (0·5 mol.), and boric acid (0·5 mol.) ...	0·01	0·17	0·19		0·01	0·04	84
Mixture of free ethylene glycol (0·5 mol.) and propanediol (0·5 mol.)...	0·10	0·04	0·04	0·01	0·01	0·24	88

To make sure that the ethylene glycol derivatives were not formed by a secondary exchange, a mixture of the two free diols was treated with acetyl chloride sufficient for only one partner: propanediol monoacetate was the main product. As a further check on the method and as an aid in the identification of the products, the borates of each of the diols alone were tested. The results are included in Table 3, and it is evident from the results of the competitive reaction that boric acid forms the six-membered ring much more easily than the five-membered one.


(A)


(B)


(C)

The main reason for the greater heat effect with amines is clearly that the strain in the five-membered ring can be relieved by converting the planar trigonal into the tetrahedral

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[9] Sugihara and Petersen, *J. Amer. Chem. Soc.*, 1956, **78**, 1760.

boron atom. The strain seems approximately to cancel the energy gain on cyclization, as can be seen from the fact that whereas tris-(1,3-diol) diborates remain liquid indefinitely, and therefore are assigned the structure (A), the corresponding 1,2-diol borates, although distillable, become very viscous or even glassy after condensation (cf. Thomas [7]). The structure (A) must therefore in this case be in equilibrium with open-chain polymer structures such as (B).

Several of these esters have been prepared (see Table 4). The contribution of the polymer structure seems to diminish with increasing substitution, presumably because of increasing steric difficulties brought about by the methyl groups in the network structure. A similar trend is observed in the cryoscopic molecular-weight determinations of ethylene-glycol butyl borate (IIa) and the tri(propane-1,2-diol) diborate. The former has a much too high molecular weight in concentrated benzene solution which drops off towards the normal value on dilution, whereas with the latter a constant normal value is obtained even at higher concentrations (Table 5). Similarly, a comparison of the heats of dilution in octane shows that the five-membered ring structure (IIa) with a value of 2200 cal./mole must be more " associated " in the liquid state than in dilute solution. The value 1130 cal./mole obtained with the six-membered ring structure (IVa) indicates a smaller structural change on dilution.

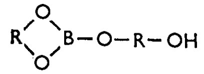
TABLE 4. *Trisdiol diborates.*

Diol	Equivalent weight Theor.	Equivalent weight Found	
$HO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	101	103	Glass
$HO{\cdot}CHMe{\cdot}CH_2{\cdot}OH$	122	125	Gelatinous liquid
$HO{\cdot}CHMe{\cdot}CHMe{\cdot}OH$ (*meso*)	143	143	Very viscous liquid
$HO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	122	121	Liquid

TABLE 5. *Molecular-weight determinations by cryoscopy in benzene.*

(IIa):	Concn. (g./100 ml.)	4·17	2·77	2·08	1·39	1·04	0 (extrap.)	Theor.
	M	208	198	188	176	171	154	144
$(\text{–}O{\cdot}CHMe{\cdot}CH_2{\cdot}O\text{–})_3B_2$:	Concn. (g./100 ml.)	6·75	4·50	3·38			0 (extrap.)	Theor.
	M	254	253	255			254	244

The ease with which boric acid esters form and rearrange explains why predominantly polymeric esters can be distilled completely in the form of their most volatile structure, with continuous displacement of the equilibrium.



The observation was also made that bisdiol borates, although they can sometimes be isolated by crystallization,* cannot be distilled as such, but disproportionate, whereby the diol distils first, and the trisdiol diborate (A) afterwards. The only mixed esters which can be distilled are of the diol alkyl type (II and IV) in which the alcohol must be of such a size that the mixed ester is more volatile than the trialkyl borate.

The triply-bridged cage structure (C) proposed by Dupire [13] seems impossible for steric reasons for 1,2- and 1,3-diols, and improbable even for 1,4-diols, since molecular models

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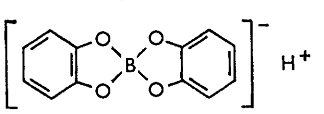
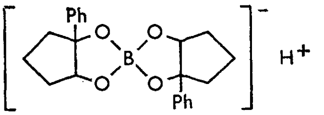
* The compounds assigned the annexed " acid " structures by Meulenhoff [10] and by Maan [11] are probably simple bisdiol borates in as much as the open structure of a crystalline bis-(2,2,5,5-tetramethylhexane-3,4-diol) borate has been proved by the presence of an OH absorption band in the infrared spectrum.[12]





[10] Meulenhoff, *Z. anorg. Chem.*, 1925, **142**, 373.

[11] Maan, *Rec. Trav. chim.*, 1929, **48**, 332.

[12] Dale, preceding papers.

[13] Dupire, *Compt. rend.*, 1936, **202**, 2086.

show that the structure (A) with seven-membered rings and the structure (B) are much less strained. Several attempts to distil tri(butane-1,4-diol) diborate were unsuccessful, indicating that in this case the structure is completely polymeric (B). However, substituted 1,4-diols may well be more difficult to accommodate sterically in structure (B), and definitely in structure (C). The distillable tris-(2,5-dimethylhexane-2,5-diol) diborate which was obtained by Steinberg and Hunter [14] and for which the cage structure was proposed, has therefore probably the structure (A). This is supported by the finding that seven-membered cyclic benzeneboronates are stable and even preferred structures in certain cases.[15]

EXPERIMENTAL

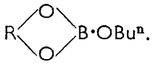
Tributyl Borate (I).—The ester was prepared from butan-1-ol and boric acid by azeotropic distillation of the water with excess of butan-1-ol [16] and purified by vacuum-distillation.

Diol Butyl Borates (II *and* IV).—The mixed esters were prepared by the method used by Letsinger and Skoog [17] for the preparation of ethylene glycol butyl borate. Equimolar quantities of diol and tributyl borate were mixed; the butanol formed by alcoholysis of the tributyl borate was distilled off through a Vigreux column, and the mixed ester finally distilled at reduced pressure. Data for the products are given in Table 6. The equivalent weights were determined by potentiometric titration with sodium hydroxide in the presence of mannitol.

Attempts to prepare the analogous ester with butane-1,4-diol led only to a polymer.

Bisdiol Borates.—A mixture of 2 mol. of ethylene glycol or propane-1,3-diol and 1 mol. of boric acid was heated in chloroform, and the calculated quantity of water removed by azeotropic distillation. After evaporation of the chloroform a viscous residue was obtained (cf. Blau, Gerrard, and Lappert [18]) which was soluble in chloroform and benzene. When distilled, disproportionation took place, as the diol and then the trisdiol diborate were obtained, neither of which was soluble in chloroform or benzene in the case of ethylene glycol.

Trisdiol Diborates.—These esters were obtained by esterification of 2 mol. of boric acid with 3 mol. of diol.[13,19,20] The water was removed by azeotropic distillation with chloroform or benzene. The esters were distilled at reduced pressure. The infrared spectra showed the absence of hydroxyl groups. Data for the products are given in Table 4.

TABLE 6. *Diol butyl borates* .

R	B. p./mm.	Equivalent weight Theor.	Equivalent weight Found	
$\cdot CH_2\cdot CH_2\cdot$	97°/11	144	147	Viscous liquid
$\cdot CHMe\cdot CH_2\cdot$	98°/11	158	153	Liquid
$\cdot CHMe\cdot CHMe\cdot$	92°/13	172	173	Liquid
$\cdot CH_2\cdot CH_2\cdot CH_2\cdot$	98°/12	158	164	Liquid
$\cdot CHMe\cdot CH_2\cdot CH_2\cdot$	101°/13	172	178	Liquid

Isolation of Addition Compounds of Benzylamine with Boric Esters.—When a solution of a 1,2-diol borate in pentane or hexane was mixed with one of benzylamine in the same solvent, a precipitate was formed. This was unstable and had to be filtered off quickly,[7] washed with pentane, then dried for 15 min. in an oil-pump vacuum. Attempts to recrystallize the substances resulted in decomposition. The amine content was determined by titration with 0·1N-hydrochloric acid; then mannitol was added and the boron content determined by back-titration with 0·1N-sodium hydroxide (Table 1).

When ethylene glycol butyl borate (IIa) was treated with dry ammonia, a solid was obtained which rapidly liquefied (decomposition) *in vacuo* or if heated at ordinary pressure.

Calorimetric Measurements.—A very simple calorimeter consisting of a 250 ml. Dewar flask,

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[14] Steinberg and Hunter, *Ind. Eng. Chem.*, 1957, **49**, 174.

[15] Sugihara and Bowman, *J. Amer. Chem. Soc.*, 1958, **80**, 2443.

[16] *Org. Synth.*, 1957, Coll. Vol. II, p. 106.

[17] Letsinger and Skoog, *J. Amer. Chem. Soc.*, 1954, **76**, 4174.

[18] Blau, Gerrard, and Lappert, *J.*, 1957, 4116.

[19] Morell and Lathrop, *J. Amer. Chem. Soc.*, 1945, **67**, 879.

[20] Garner and Lucas, *J. Amer. Chem. Soc.*, 1950, **72**, 5497.

a Beckmann thermometer, a known resistance, and a stirrer, was used. The resistance was used for the calibration by passing a current through it for a short period. The reproducibility was ±5%.

Octane (96 ml.) containing the boric ester (12·5 mmoles) was introduced into the Dewar flask. Then a very thin-walled sealed glass phial containing the amine (12·5 mmoles) and octane (1 ml.) was immersed in the solution and thermal equilibrium established during 30 min. while stirring. The phial was then broken with the stirrer and the temperature variation with time followed. After a very sharp rise (or fall) the temperature became fairly constant and diminished (or increased) by only 0·01—0·02°/min. Identical measurements with the amine in the absence of borate allowed a correction for the heat of dilution of the amine in octane to be applied. The results are given in Table 2.

In the same way the heat of dissolution, or dilution, of some boric esters (12·5 mmoles) in octane (100 ml.) was determined. The value obtained for ethylene glycol butyl borate (IIa) was +2200 cal./mole; for propane-1,3-diol butyl borate (IVa) it was +1130 cal./mole.

Molecular-weight Determinations.—Cryoscopic measurements were carried out in a classical Beckmann apparatus with benzene as a solvent and naphthalene for the calibration. The results are given in Table 5.

Acetylation of Bisdiol Borates.—0·5 Mol. of boric acid was esterified with a total of 1·0 mol. of diol by azeotropic distillation of the water with chloroform. When 1·5 mol. of water had been collected, the solution had become homogeneous and was left to cool to room temperature. 0·5 mol. of acetyl chloride in chloroform was slowly added. Hydrogen chloride was evolved and the solution became warm. After complete addition, the solution was refluxed for 5 min., then cooled and washed with sodium hydrogen carbonate, and the chloroform was evaporated. The residue was fractionally distilled on a spinning band column at reduced pressure. Elemental analysis, infrared spectrum, and b. p. determination at atmospheric pressure were used for the identification of each fraction. In a first experiment ethylene glycol was used alone to facilitate the identification of the acetylated products, then propane-1,3-diol alone, and finally the mixture of both. The results are presented in Table 3 together with the results of an acetylation experiment on an equimolar mixture of the diols in the absence of boroic acid and with acetyl chloride sufficient for only one partner.

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