721. *Cyclic Boronates and their Amine Complexes.*

By Arthur Finch and J. C. Lockhart.

Cyclic phenylboronates have been prepared in high yield by a simplified process. The differences in stability of their amine complexes are discussed with reference to ring size and to substituent effects.

In contrast to aryl esters, methyl borate is the only simple aliphatic ester of boric acid which forms isolable solid complexes with strongly basic amines,[1, 2] though evidence also exists for the formation of unstable amine adducts of ethyl borate.[1, 3] It is reasonable to assume that steric factors are in part responsible for the failure of higher aliphatic esters to give stable adducts.[2]

That cyclic boron esters give more stable complexes is indicated by thermal measurements.[4] In the present work we have used cyclic esters (I—VII) of phenyl- and propylboronic acid because of their greater potential Lewis acidity.

Phenyl-1,3,2-dioxaborolans (I—III) and -dioxaborinans (V, VI) were rapidly formed by shaking equimolar mixtures of phenylboronic anhydride and the appropriate diol at room temperature (Table 1). Formation of 5- or 6-membered rings by this method was too fast for relative rates of reaction to be measured. No evidence was obtained for cyclisation of butane-1,4-diol or pentane-1,5-diol under these conditions.

Complexes of boron ring compounds and amines, made by mixing the components in 1 : 1 ratio and dilution with hexane, are listed in Table 2. This stoicheiometry consistently gave 1 : 1 complexes, save for ester (III) the complex from which gave analyses for approximately a 2 : 1 amine–ester adduct; this was converted in a vacuum into the 1 : 1 adduct. Attempts to make a 2 : 1 amine–ester complex from cyclohexylamine and ester (I) gave products of non-stoicheiometric composition which in a vacuum passed slowly over into the 1 : 1 form. Goubeau and Link [5] noted similar variable nitrogen : boron ratios in complexes of methyl borate and alkylamines. Neither dibutyl phenylboronate (VIII) nor 2-propyl-1,3,2-dioxaborinan (VII) formed a stable amine adduct at room temperature; nor did triethylamine under similar conditions with esters (I—VIII).

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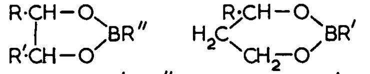
[1] Gould and Urs, *J. Amer. Chem. Soc.*, 1952, **74**, 2948.
[2] Brown and Fletcher, *J. Amer. Chem. Soc.*, 1951, **73**, 2808.
[3] Landesman and Williams, *J. Amer. Chem. Soc.*, 1961, **83**, 2663.
[4] Hubert, Hargitay, and Dale, *J.*, 1961, 931.
[5] Goubeau and Link, *Z. anorg. Chem.*, 1951, **267**, 27.

All the adducts dissociated on being heated and in solution; most of them were hygroscopic, decomposing rapidly in moist air. Complex formation is clearly an equilibrium process, and discussion of the relative stabilities of different complexes must include the effect of structures of reactants and products. Four such effects are here considered:



	R	R′	R″
(I)	H	H	Ph
(II)	Me	H	Ph
(III)	Me	Me	Ph
(IV)	H	H	Pr

	R	R′
(V)	H	Ph
(VI)	Me	Ph
(VII)	H	Pr

$Ph\cdot B(OBu^n)_2$ (VIII)

(*a*) Ring size. Complexes from five-membered ring esters are formed in greater yield and are more stable with respect to dissociation than the six-membered analogues. Amine adducts of ester (I) were especially stable, being less hygroscopic and less soluble in benzene. This greater general stability is attributable to the release, by formation of a tetrahedral configuration round the boron atom, of internal strain (*I*-strain [6]) inherent in the planar dioxaborolan structure. The dioxaborinans are presumably puckered, so that no appreciable relief of *I*-strain would be expected on change from sp^2- to sp^3-boron co-ordination. Qualitative estimation of exothermic heats of complex formation also give the expected order: -olan > -inan.

(*b*) Ring substituents. In the five-membered ring series, the exothermic heats of mixing of the two reactants are in the order: (I) > (II) > (III). The stabilities of the resultant complexes are in a similar order: (I) > (II) ~ (III). Thus 4-methyl- (II) and 4,5-dimethyl-2-phenyl-1,3,2-dioxaborolan (III) are evidently weaker Lewis acids than the unmethylated compound (I). There are two possible explanations: (i) electron-releasing effects, and (ii) steric hindrance by the methyl groups to formation of the transition state; that methyl groups do not cause strain in the complex itself is shown by models.

(*c*) Boron substituents. 2-Propyl- and 2-butoxy-1,3,2-dioxaborolan, unlike the corresponding dioxaborinans, give amine adducts; absence of major difference in acidity can therefore be inferred, although tri-isopropylborane is known to form amine complexes [7] and tri-n-butyl borate does not.[2] Phenyl substituents, however, confer greater acidity, even the esters with 6-membered rings (V and VI) giving isolable adducts, owing to the electrophilic property of the aromatic nucleus. Models show that steric hindrance is in the order: BuO < Pr > Ph. The order of acid-strengthening effects of substituents on boron is, however, found to revert to Ph > Pr > BuO, suggesting greater importance of the electronic than of the steric effect.

(*d*) Amines. For the amine component steric considerations are very important. The strongly hindered triethylamine does not form an adduct with any boron compound considered here. Strong steric effects have been noted by, for example, Brown [7] and by Brown and Sujishi [8] who explained the order of base-strength, quinuclidine > trimethylamine > triethylamine (reference acid trimethylboron), on this basis. Similarly the lack of complex-formation in the system between triethylamine and phosphorus trichloride [9] indicates the operation of a steric effect, since the electron-donating tendency of the ethyl groups would increase the basicity of the nitrogen. Thus the importance of steric effects in boron and in analogous systems may be assumed.

EXPERIMENTAL

Cyclic Phenylboronates.—These were made by two methods. (*a*) Azeotropic removal of water and toluene from an equimolar mixture of a diol and phenylboronic anhydride followed

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[6] Brown, Fletcher, and Johanneson, *J. Amer. Chem. Soc.*, 1951, **73**, 212.

[7] Brown, *J. Amer. Chem. Soc.*, 1945, **67**, 374, 1452.

[8] Brown and Sujishi, *J. Amer. Chem. Soc.*, 1948, **70**, 2878.

[9] Holmes, *J. Amer. Chem. Soc.*, 1960, **82**, 5285.

by fractional distillation afforded the desired ring compounds. (*b*) Equimolar mixtures of diol and phenylboronic anhydride liquefied when shaken at room temperature for a few minutes, forming the ring compound and water; the water was separated mechanically and the cyclic phenylboronate, after being shaken with magnesium sulphate, had an infrared spectrum identical with that of the fractionally distilled material. The *compounds* obtained are shown in Table 1.

Cyclic Propylboronates.—These were available from previous work.[10]

Amines.—These were dried and fractionally distilled before use.

Complexes.—Equimolar mixtures of amine and boronate were made at room temperature. Heat was evolved when complexes were formed. An equivalent volume of hexane was then added. White crystals separated rapidly with five-membered ring esters, and on cooling to *ca.* −80° for the six-membered analogues. These were filtered off, washed with hexane and kept at *ca.* 20 mm. to remove solvent. Usually the 1 : 1 complex was formed, but the 2 : 1 cyclohexylamine–ester (III) complex was formed preferentially. A 2 : 1 mixture of cyclohexylamine and ester (I) gave a mixture of 1 : 1 and 2 : 1 complexes, according to analytical data. These higher amine complexes lost amine at *ca.* 0·1 mm. and formed the usual 1 : 1 adduct.

TABLE 1.

Compound	Diol	Method	Yield (%)	B. p./mm.	d^{25}	Found (%)			Formula	Required (%)		
						C	H	B		C	H	B
(I)	$(CH_2{\cdot}OH)_2$	*a*	80	56°/0·5	1·060	—	—	—	—	—	—	—
		b	95			65·6	6·3	7·2	$C_8H_9BO_2$ ‡	64·9	6·1	7·3
(II)	$HO{\cdot}CHMe{\cdot}CH_2{\cdot}OH$	*a*	60	54—56°/0·5	1·038	—	—	—	—	—	—	—
		b	90			65·3	6·7	6·6	$C_9H_{11}BO_2$	66·7	6·8	6·7
(III) *	$(CHMe{\cdot}OH)_2$	*a*	85	68°/0·8	1·089	—	—	—	—	—	—	—
		b	93			—	—	6·2	$C_{10}H_{13}BO_2$	—	—	6·2
(V) †	$HO{\cdot}[CH_2]_3{\cdot}OH$	*b*	90		1·051	—	—	6·8	$C_9H_{11}BO_2$	—	—	6·7
(VI) *	$HO{\cdot}[CH_2]_2{\cdot}CHMe{\cdot}OH$	*a*	73	75—76°/0·5	1·081	—	—	—	—	—	—	—
		b	95	75—76°/0·5		—	—	6·2	$C_{10}H_{13}BO_2$	—	—	6·2

* Sugihara and Bowman, *J. Amer. Chem. Soc.*, 1958, **80**, 2443. † Pearn, unpublished work.
‡ Found: *M*, 156 (cryoscopically in benzene). Calc.: *M*, 148.

TABLE 2.

Amine–ester adducts.

Compound *		M. p.	Required (%)		Formula	Found (%)	
			Amine	B		Amine	B
IA	1 : 1	108·5°	40·1	4·4	$C_{14}H_{12}BNO_2$	40·3	4·34
	2 : 1	104	57·3	3·1	$C_{20}H_{15}BN_2O_2$	49·0	3·9
IIA	1 : 1	85—86	38·0	4·15	$C_{15}H_{14}BNO_2$	† 38·2	4·25
IIIA	2 : 1		53·2	2·9	$C_{22}H_{19}BN_2O_2$	50·1	3·1
VA	1 : 1	73—76	38·0	4·1	$C_{15}H_{14}BNO_2$	34·6	3·8
VIA	1 : 1	57—59	36·1	3·9	$C_{16}H_{16}BNO_2$	34·4	4·05
IVA	1 : 1	65·5	46·5	5·1	$C_{11}H_{24}BNO_2$	45·3	5·0
IB	1 : 1	86—88	42·0	4·2	$C_{15}H_{18}BNO_2$	42·7	4·4
VB	1 : 1	74—75	40·0	4·0	$C_{16}H_{20}BNO_2$	40·8	4·1
IC	1 : 1	—	36·5	4·65	$C_{13}H_{20}BNO_2$	36·5	4·65
IIC	1 : 1	—	33·9	4·3	$C_{14}H_{22}BNO_2$	34·6	4·35
IIIC	1 : 1	—	32·6	4·15	$C_{15}H_{24}BNO_2$	32·6	4·2
VC	1 : 1	Indefinite	33·9	4·3	$C_{14}H_{22}BNO_2$	34·7	4·4
IVC	1 : 1	—	42·8	5·45	$C_{10}H_{22}BNO_2$	43·1	5·35

* A, B, C refer to cyclohexylamine, benzylamine, and piperidine, respectively. † PhBO estimated spectrophotometrically in dilute acid solution, 44·0% (Reqd.: 43·7%).

Catalysis.—The presence of moisture assisted the formation of the complexes of esters (V) and of (VI) (cf. Gould and Urs).[1]

Dissociation.—Most of the complexes dissociated readily on dissolution in hexane, benzene, ether, Nujol, etc. The most stable [derived from ester (I)] were insufficiently soluble for

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[10] Chainani and Finch, unpublished work.

molecular-weight studies. Cryoscopy, in benzene, of the less stable cyclohexylamine–4-methyl-2-phenyl-1,3,2-dioxaborolan complex gave only half the calculated molecular weight, indicating dissociation into two species. The infrared spectra in hexane, benzene, and Nujol showed the two species to be the initial reagents, amine and phenylboronate.

Some complexes were too unstable for melting-point determination. The *complexes* obtained are listed in Table 2.

Heats of Mixing.—The temperature rise on addition of the stoicheiometric quantity of cyclohexylamine to the boron ring compound in a Dewar vessel was measured with a sensitive mercury thermometer under identical conditions for compounds (I—III) and (V, VI). The observed order was: I > II > III > V > VI.

Infrared Spectra.—Infrared spectra of cyclic boronates in benzene solution and as liquid films and of complexes in Nujol were recorded on a Perkin–Elmer model 137 Infracord, over the range 4000—700 cm.$^{-1}$. The N–H stretching modes for the amines (3500—3300 cm.$^{-1}$) do not appear in the spectra of the complexes. A band of moderate intensity near 2180 cm.$^{-1}$ was observed in spectra of all complexes: it is provisionally assigned to an NH motion (NH_2^+ and NH^+).[11] More precise measurements will be reported elsewhere.

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[11] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen & Co. Ltd., London, 2nd edn., 1958, p. 260.