Contribution to the Chemistry of Boron, 136 [1]

A Reinvestigation of the Existence of 1,3,2-Dioxaborinium(1+) Cations

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1,3,2-Dioxaborinium(1+) Salts, 2-Perchlorato-1-oxa-3-oxonia-2-borato-cyclohexadienes,
2-Triflato-1-oxa-3-oxonia-2-borato-cyclohexadienes

It is shown that the previously reported 1,3,2-dioxaborinium salts containing tri-coordinated boron are in fact tetracoordinated coordination compounds. The same holds for the corresponding triflates.

Introduction

The chemistry of boron cations was a field long neglected [2]. Meanwhile, many cations containing tetracoordinated boron have been reported [3] and their chemistry has been explored. In addition there exists scattered information relating to tri- [4–8] and dicoordinated [9, 10] boron cations. Unlike carbenium ion chemistry their role in boron chemistry is not yet well understood. This situation, however, will quickly change as their chemical behaviour is being studied.

Having evaluated some governing factors relating to the stability of dicoordinated cations of boron [9] we became interested in those of coordination number 3 because their stability should also depend on mesomeric effects. Such effects could prevail in tricoordinated 1,3,2-dioxaborinium(1+) salts **1** which were isolated as perchlorates and hexachloroantimonates [5–7]. One important argument for the presence of a tricoordinated boron atom in these compounds was an ^{11}B NMR signal at ~ 26 ppm which is typical for a CBO_2 structural unit [11].

Results

Since the triflate group is an exceptionally good leaving group we turned our attention to the preparation of the triflates **6a** and **6b**. However, these compounds (Table I) contain tetracoordinated boron by ^{11}B NMR evidence. Therefore we repeated the preparation of **5a** and **5b**. Although we could easily obtain these compounds [12], they exhibited, in our hands, ^{11}B NMR data for tetracoordinated boron in CH_2Cl_2 or benzene solution. Therefore

they have to be described by formula **2** rather than by **1**. Evidence for this structure rests also on the IR spectra which show well defined bands at 1010 and 1145 cm^{-1} typical for a monodentate ClO_4^- species of local C_{3v} symmetry. In addition, a band of medium intensity is found at 918 cm^{-1} , which is also indicative of coordinated ClO_4^- of C_{3v} symmetry [14].

FORMULAE 1

	R ¹	R ²	X
5a	C ₆ H ₅	C ₆ H ₅	ClO ₄
5b	C ₆ H ₅	CH ₃	ClO ₄
6a	C ₆ H ₅	C ₆ H ₅	SO ₃ CF ₃
6b-H ₂ O	C ₆ H ₅	CH ₃	SO ₃ CF ₃

Since **5a** and **5b** show low solubility in CH_2Cl_2 their ^{11}B NMR spectra were also recorded in acetonitrile solution, and again only tetracoordinated boron (Table I) was observed. It is likely, therefore, that this solvent coordinates to **1** thus leading to **3** [14]. This assumption rests on the fact that the acetonitrile solutions show high electrical conductivity as well as a $\delta^{35}\text{Cl}$ shift typical of an ionic

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Table I. NMR data of 1,3,2-dioxa-bora-cyclohexadiene-compounds **5** and **6**; δ -values in ppm.

	$\delta^{11}\text{B}$	Solvent	$\delta^{19}\text{F}$	Solvent	$\delta^1\text{H}$	Solvent
5a	5.6 8.1	CH_3CN CH_2Cl_2				
5b	5.5 6.8	CH_3CN CH_2Cl_2				
6a	8.6	CH_2Cl_2				
6b H_2O	6.5	CH_2Cl_2	— 77.09	CDCl_3	2.3 (S, CH_3) 7.26–7.98 (M, C_6H_5) 10.95 (S H_2O) ^a	CDCl_3
$\text{C}_6\text{H}_5\text{B}(\text{OH})_2$	29.4	CH_2Cl_2				
	compound ratio		$\delta^{11}\text{B}$		Intensity ratio	
$\text{C}_6\text{H}_5\text{B}(\text{OH})_2 + \text{BzacH}^b$	1:1		29.9	6.8	(2:1)	
	1:2		29.1	6.7	(1:1)	
	1:3		29.9	6.8	(1:1)	

^a This signal disappears on addition of D_2O ; ^b BzacH = benzoylacetone; solvent CH_2Cl_2 .

perchlorate (found: $\delta^{35}\text{Cl} = 1000$ ppm, $h(1/2)$ 65 Hz, literature [13]: $\delta^{35}\text{Cl} = 1000$ ppm) [13]. Evidence for coordination of acetonitrile is obtained also from ^1H NMR spectra of a 1:1 solution of **5a** and CH_3CN in CDCl_3 which shows a 9 Hz downfield shift for the signal of acetonitrile although part of the perchlorate precipitates from the solution, and this may have changed the stoichiometry.

In the solid state, however, the structure of **5a** and **5b** is best represented by **4**. The compounds hydrolyse fairly readily in CH_2Cl_2 solution. Thus the ^{11}B NMR signals reported previously for **5a** and **5b** are most likely due to phenylboronic acid [13].

The triflates **6a** and **6b**, prepared in analogy to the perchlorates, are sharp melting, powdery solids and are more soluble in dichloromethane than the corresponding perchlorates. They show ^{11}B chemical shifts (Table I) typical for tetracoordinated boron. All NMR data for **6a** are in accord with a structure containing a coordinated triflate group in analogy to **4**. Therefore, the comparison of the perchlorates and triflates very strongly point to the conclusion that none of these compounds is truly ionic, *i.e.* are salts of a 1,3,2-dioxaborinium(1+) cation. However, the electronegative group $\text{X} = \text{ClO}_4$ or SO_3CF_3 may be readily replaced by a suitable base, the compounds thus acting as a tricoordinate boron cationic species with a loosely coordinated anion. This situation thus resembles the highly reactive compounds $\text{CpM}(\text{CO})_2\text{BF}_4$ ($\text{M} = \text{Mo}, \text{W}$) [16].

The formation of compounds **5** and **6** seems to occur in two steps. ^{11}B NMR signals in an approximately 1:1 ratio are recorded on addition of the diketone to a solution of phenylboronic acid (see Table I), one at $\delta^{11}\text{B} = 27$, the other at 6,8 ppm. Since this intensity ratio changes in favour of the high field signal at higher diketone ratios an equilibrium situation (1) is indicated. The addition of either HClO_4 or HOSO_2CF_3 then produces the ^{11}B NMR signal of **5a** and **6a** respectively, according to (2a, b). In contrast, **6b** could only be isolated as a hydrate, and we assume that this compound has the constitution of the intermediate **7** [15].

FORMULAE II

Experimental

All manipulations were carried out under rigorously dry conditions in a nitrogen atmosphere using standard high vacuum or Schlenk tube techniques. Solvents were carefully dried and stored under dinitrogen. Most of the starting materials are commercially available and were used as such. Anhydrous perchloric acid was prepared by extracting a mixture of oleum and 70% perchloric acid in dichloromethane [17]. The solution obtained was standardized by base titration.

IR-spectra: Perkin-Elmer 325, Nujol/hostaflon mulls; NMR: Jeol FX 90 and Bruker WP 200; standards for $\delta^1\text{H}$: tetramethylsilane;

^{11}B : $\text{F}_3\text{B}\cdot\text{O}(\text{C}_2\text{H}_5)_2$ ext.; $\delta^{35}\text{Cl}$: 1 M NaClO_4 solution, ext.

General method: A two necked, round bottomed

flask (100 ml) fitted with a dropping funnel and reflux condenser was charged with dibenzoylmethane, phenylboronic acid and 25 ml CH_2Cl_2 . This flask was immersed in an ice-salt bath and the mixture stirred magnetically. A solution of triflic acid (or HClO_4) in CH_2Cl_2 was added dropwise, and a yellow powder starts separating after addition of $\sim 1/5$ of the acid. Having completed the addition stirring was continued for another 2 h, the solid filtered, washed with 20 ml of CH_2Cl_2 and dried *in vacuo*.

Results are summarized in Table II.

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Table II. Preparative and analytical results for the perchlorates and triflates, **5** and **6**.

	Reactants (g (mmol))		Acid	CH_2Cl_2 ml	yield g (%)	m.p. [°C]
	$\text{PhB}(\text{OH})_2$	Diketone				
2-Perchlorato-2,4,6-triphenyl-1-oxa-3-oxonia-2-borata-cyclohexadien(3,5) (5a)	.600 (5.00)	1.11 (4.95)	.498 (4.96)	10	1.57 (78)	111 ^a
2-Perchlorato-2,4-diphenyl-6-methyl-1-oxa-3-oxonia-2-borata-cyclohexadien(3,5) (5b)	.600 (5.00)	.810 (4.96)	.498 (4.96)	10	1.48 (85)	114 ^b
2-Triflato-2,4,6-triphenyl-1-oxa-3-oxonia-2-borato-cyclohexadien(3,5) (6a)	.695 (5.80)	1.27 (5.66)	.850 (5.67)	60	2.32 (89)	94 dec.
2-Aquo-2,4-diphenyl-6-methyl-1-oxa-3-oxonia-2-borata-cyclohexadienyl(3,5)-trifluorsulfonat (6b)	.690 (5.75)	.940 (5.76)	.850 (5.67)	60	2.18 (95)	74

Analysis (calcd (found))

	Formula	mol. weight	C [18]	H	B	S	Cl
5a	$\text{C}_{21}\text{H}_{16}\text{BClO}_6$	410.6	61.43 (48.29)	3.93 (4.11)	— —	— —	— —
5b	$\text{C}_{16}\text{H}_{14}\text{BClO}_6$	348.5	55.14 (49.19)	4.05 (4.01)	3.10 (2.83)	— —	10.17 (10.2)
6a	$\text{C}_{22}\text{H}_{16}\text{BF}_3\text{O}_5\text{S}$	460.2	57.42 (40.78)	3.50 (3.63)	2.35 (2.04)	6.97 8.23	— —
6b	$\text{C}_{17}\text{H}_{16}\text{BF}_3\text{O}_6\text{S}$	398.1	49.06 (48.44)	3.88 (4.21)	— —	— —	— —

^a Lit. [5] m.p. 100 °C; ^b Lit. [5] m.p. 104 °C.

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