Tetrahedron Letters 51 (2010) 6181–6185

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Diverse reactivity of 2-formylphenylboronic acid with secondary amines: synthesis of 3-amino-substituted benzoxaboroles

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ARTICLE INFO

Article history:
Received 5 July 2010
Revised 25 August 2010
Accepted 20 September 2010
Available online 25 September 2010

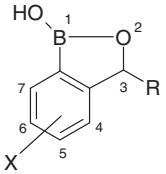
Keywords:
Boronic acids
Benzoxaboroles
Boroxins
Secondary amines
Crystal structure

ABSTRACT

In the reaction of 2-formylphenylboronic acid with secondary amines different products are formed depending on the structure of the amines. For aliphatic amines the reaction proceeds with the formation of 3-amino-substituted benzoxaboroles or with the formation of complexed boroxins. A crystal structure of the benzoxaborole with a thiomorpholinyl substituent was determined.

1. Introduction

Boronic acids, $RB(OH)_2$, are compounds of great interest due to their numerous applications in organic synthesis, catalysis, supramolecular chemistry, biology, and medicine.[1,2] Only recently has growing attention been paid to their derivatives, benzoxaboroles **I**, due to their new medical applications as potent antifungal drugs.[3] They have also been tested for the treatment of periodontal disease,[4] psoriasis,[5] and malaria together with other parasites.[6] Moreover, chiral (*S*)-3-aminomethylbenzoxaborole was found to be efficacious against Gram negative bacteria.[6]



I

Benzoxaboroles reveal high receptor activity toward polyols due to the formation of anionic form of cyclic esters derived from saccharides in neutral or slightly alkaline media.[7] Another very important application of benzoxaboroles is their use in Suzuki coupling to give *ortho*-substituted benzyl alcohols.[8]

A comprehensive review on the chemistry, structure, and applications of benzoxaboroles has been published.[9] The main methods for their synthesis (Scheme 1) are based on the formation of the appropriate *ortho*-boronobenzyl alcohols by the introduction of a hydroxymethyl group into the boronic acid molecule (method A), by the reaction of 2-formylboronic acid with nucleophiles (method B), or by the introduction of a boronic group into benzyl alcohol (method C). Depending on the particular systems, appropriate protection of functional groups in the substrates can be applied.[9] Recently, 3-amido-substituted benzoxaboroles were obtained in high yields as the products of the reaction of 2-formylphenylboronic acid with isonitriles (Scheme 1, method B, X: CONHR).[10] Reactions with activated olefins can lead to benzoxaboroles with olefinic substituents (Scheme 1, method B, X: $C(=CH_2)R$ and $CH_2C(CH_2)R$).[11]

The properties of a benzoxaborole strongly depend on the substituents. The influence of the substituents on the phenyl ring has been widely investigated from the point of view of the biological activity of the compounds.[6] The introduction of a substituent to an oxaborole ring, that is, at position 3 has influence on the geometry of the whole molecule, which was proved by a combination of experimental and theoretical methods.[12,13] However, in comparison with the numerous examples of molecular structures known for compounds with a carbon substituent at position 3,[9] there is only one example of a 3-amino-substituted compound.[14]

2-Formylphenylboronic acid reacts with primary amines yielding *ortho*-iminomethylphenylboronic acids, which can be

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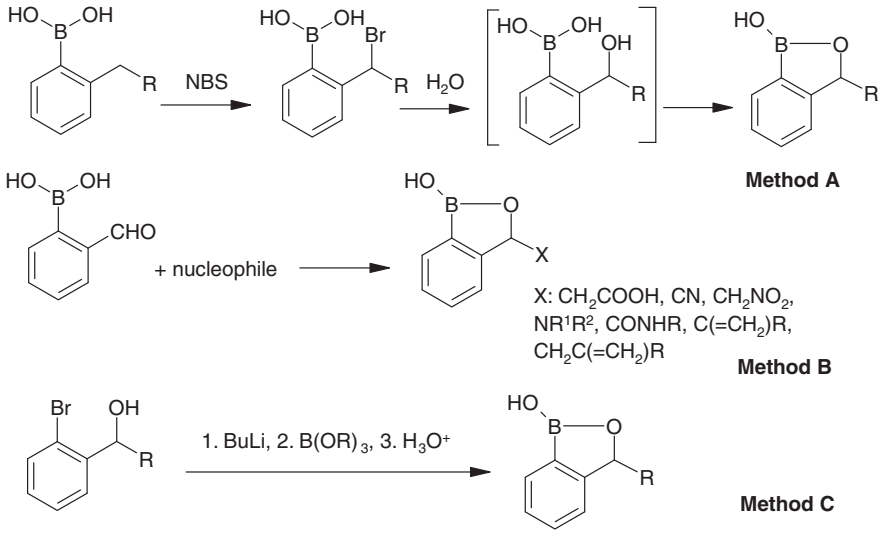
0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.09.091



Scheme 1. The main methods for the synthesis of benzoxaboroles: from *o*-(bromomethyl)phenylboronic acid (**A**), from *o*-formylphenylboronic acid (**B**) or from a benzyl alcohol (**C**).

subsequently reduced to aminomethyl derivatives.[15] Aminomethylarylboronic acids are currently the established standards for the recognition of sugars, so their synthesis, characterization, and receptor activity have been widely investigated.[1,16] Methods for the synthesis of these compounds have been reviewed.[15] Recently, self-assembling systems containing 2-formylphenylboronic acids, primary amines, and diols were described.[17,18]

The aim of the present work was to investigate a new method for the synthesis of 3-amino-substituted benzoxaboroles and the properties of the compounds obtained.

The reaction of 2-formylphenylboronic acid with secondary amines was investigated in solution (acetone-d_6 or acetonitrile-d_3) by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy. The results are collected in Table 1. On the basis of these results, one can divide the reactivity of the systems investigated into three groups (Scheme 2).

For the reactions with morpholine, thiomorpholine, piperidine, pyrrolidine, *N*-ethylbenzylamine, and dibenzylamine, the signal of the aldehyde proton completely disappeared (entries a–d, h, and i), whereas new signals at ca. δ 3 (broad) and at δ 5.8–6 appeared. The ^{1}H signal at ca. δ 6 originates from the CH protons in the oxaborole ring and at ca. δ 3 from water. In the ^{13}C NMR spectra, new signals appeared at ca. δ 96 and δ 153, while the signal at δ 196 due to the aldehyde carbon was no longer present. Assignment of the signals in the ^{13}C spectra can be done on the basis of HSQC and HMBC correlation spectra which have been reported for several benzoxaboroles (Table 2).[12] In some cases a ^{13}C signal at δ 77 was observed, which can be attributed to the hemiaminal **1′**. Due to the presence of the boronic acid group, hemiaminals can be stabilized by the formation of intramolecular hydrogen bonds.[20] This signal slowly disappears in time, while that at δ 95 increases. The products were identified as 3-amino-substituted benzoxaboroles **1**. The presence of only one signal due to the three-coordinated boron atom in the ^{11}B NMR spectra confirms the proposed reaction (pathway I). Several aminobenzoxaboroles were obtained in this way by the preparative scale reactions.[21]

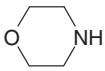
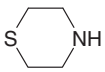
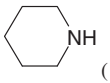
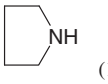
For the reaction of 2-formylphenylboronic acid with diethylamine, di-isopropylamine, and dicyclohexylamine (entries e–g) a new ^{1}H NMR signal at ca. δ 3.8 appeared, while the signal of the aldehyde proton moved to higher values and split into two. The signals of the aromatic protons were broadened. The signal at δ 3.8 originates from the hydroxy groups in water. This was proved by the addition of water to a sample, which increased the intensity of this signal with a small shift to ca. δ 3.5. In the ^{13}C NMR spectra, signals corresponding to the benzoxaborole unit (at ca. δ 96 and δ 153) were not observed and those of an aldehyde carbon were present. In the ^{11}B NMR spectra, signals corresponding to three- and four-coordinate boron atoms were observed. The most probable explanation is the formation of a boroxin **2** complexed by the amine molecule (pathway II). This type of reaction has been described as a 'ligand facilitated trimerization'[22] Complexes of boroxins with amines are dynamic systems,[23] and the signals observed are usually averages due to three- and tetra-coordinate boron atoms.[24] However, in our investigated systems separate signals were observed. A possible explanation is that the exchange is slowed down by the additional interactions between the carbonyl and amine groups resulting in broadening of the signals in the ^{11}B NMR spectra. Additional signals in the ^{11}B NMR spectra may also originate from hemiaminals or imino derivatives,[25] the formation of which cannot be excluded.

Numerous examples of the crystal structures of such complexes have been described in the literature for several phenylboronic acids.[24,26] Attempts to obtain crystals of the complexes of 2-formylphenylboronic anhydride with amines for X-ray determination failed, but the products obtained in the preparative reactions[21] were identified by elemental analysis and NMR.

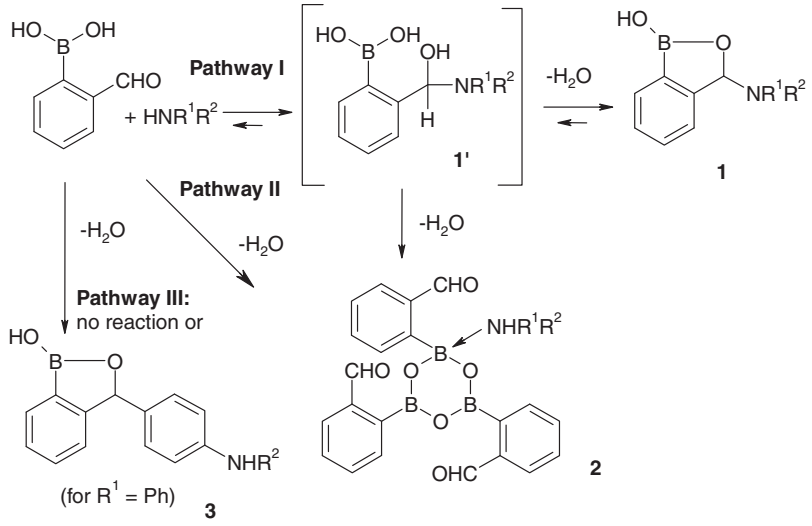
The third group of reagents were aromatic secondary amines (entries j and k), for which only signals due to unreacted substrates were observed (pathway III). The reaction of 2-formylphenylboronic acid with *N*-ethylaniline has recently been investigated and the unexpected product of a C-addition was obtained (**3**, Scheme 2). However, it was obtained in low yield in methanol.[12] In acetone only traces of this product were found (Table 1, entry j).

On the basis of the above results, the reaction course can be described as outlined in Scheme 2. For sufficiently strong nucleophiles the hemiaminal **1′** is formed, which can react to form a benzoxaborole or a complex of boroxin. Formation of **1′** was proved by the presence of a ^{13}C signal at δ 77 (C–OH) in the reaction mixture, which disappeared upon the formation of benzoxaborole. For the basic amines, a boroxin complex is formed in solution, while for weaker amines the formation of a benzoxaborole is observed. Aminobenzoxaboroles are stable in the solid state but in solution slowly decompose with the precipitation of a complexed boroxin. This was observed during attempted crystallization of compounds **1**: the products after the crystallization contained an increased amount of complexed boroxin. Weak bases (aromatic amines) form neither benzoxaboroles nor

Table 1
NMR signals (δ, ppm) for the spectra of the reaction mixture of 2-formylphenylboronic acid and secondary amine (1:1 molar ratio) in acetone-d_6 at rt[a]

Entry	Amine (pK_a)[19]	^{1}H NMR[b]		^{13}C NMR (amine signals are underlined)	^{11}B NMR
		3–6 ppm region	10–11 ppm region		
0	None	–	10.2 10.1[c]	130, 132, 133, 135, 141, 196 130, 133, 134, 135, 140, 196[c]	30.5 30.7[c]
a	 (8.39)	3.1 (broad), 5.8	–	48, 67, 96, 123, 129, 130, 131, 153	32.1
b	 (9.13)	3.2 (broad), 5.8	–	28, 50, 98, 123, 128, 130, 131, 153	32.7
c	 (11.12)	3.1 (broad), 5.8	–	25, 27, 47, 77, 97, 121, 127, 130, 131, 153	32.3
d	 (11.27)	6.0[c]	–	25, 47, 93, 123, 128, 130, 153[c]	9.7, 28.9[c]
e	Et_2NH (10.98)	4.1, 6.0[d] 3.8, 6.0[c]	11.1[d] (weak) 11.0[c]	14, 15, 42, 44, 77, 95, 122, 128, 130, 131, 155[d] 15, 43, 44, 97, 124, 127, 129, 131, 132, 156[c]	16.5, 32.1[c]
f	iPr_2NH (10.96)	3.8	11.0, 11.1	22, 46, 126, 129, 132, 135, 142, 196	8.6, 21.2, 30.5 8.3, 20.2, 30.0[c]
g	CHx_2NH (10.40)	3.7 3.7[c]	11.1, 11.2	25, 26, 33, 53, 117, 126, 133, 135, 142, 196[c]	9.1, 21.0, 30.6
h	$PhCH_2N(Et)H$ (9.65)	4.4 (broad) 6.0,	10.2 (trace)	13, 15, 43, 52, 54, 77, 94, 122, 123, 127, 128, 141, 154	32.7
i	$(PhCH_2)_2NH$ (8.76)	3.1 (broad), 5.8	–	53, 77, 93, 122, 123, 127, 128, 141, 157	32.8
j	PhN(Et)H (5.12)	6.1 (trace)	10.2	n.i.[e]	30.6
k	Ph_2NH (1.78)	–	10.2	n.i.[e]	30.6

[a] Frequencies: 300, 96.2 and 128.3 MHz for ^{1}H, ^{13}C and ^{11}B, respectively. Number of decimal places in chemical shift values was reduced for clarity, exact values are given in Supplementary data.
[b] Signals of the amine groups and aromatic protons not shown.
[c] In acetonitrile-d_3.
[d] Immediately after mixing of the reagents.
[e] Not investigated.



Scheme 2. Reactions of 2-formylphenylboronic acid with secondary amines.

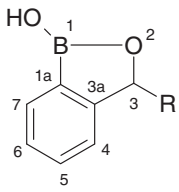
complexed boroxins, but can undergo electrophilic aromatic substitution (pathway III, Scheme 2).

2. Crystal structure

The crystal structure of 1,3-dihydro-1-hydroxy-3-(thiomorpholin-4-yl)-2,1-benzoxaborole **1b** was determined by the single crystal X-ray diffraction.[27] The molecular structure of this compound with the atom numbering scheme used is shown in Figure 1.

Compound **1b** crystallizes in the monoclinic system in the $P2_1/n$ space group. The main structural feature is a centrosymmetric dimer formed via relatively strong O–H···O hydrogen bonds (Fig. 1). This dimeric motif can be described with an $R_2^2(8)$ graph set[28] and is found to be typical for most of the previous structurally characterized benzoxaboroles.[9] The fused six- (phenyl) and five- (borole) membered rings are flat with the largest deviation from the least square plane being only 0.033(1) Å. The boron center shows ideal trigonal coordination (the sum of the angles at the boron atom is

Table 2
Assignments of the signals in ^{13}C NMR spectra

	Carbon atom	R = Ph (Ref. 12)[a]	R = NR^1R^2 (this work)
	**1a**	Not detected	
	3	83.61	93–98
	3a	158.48	153–157
	4	123.22	121–126
	5	131.87	128–132
	6	128.21	
	7	131.24	

[a] In $CDCl_3$, 125.1 MHz.

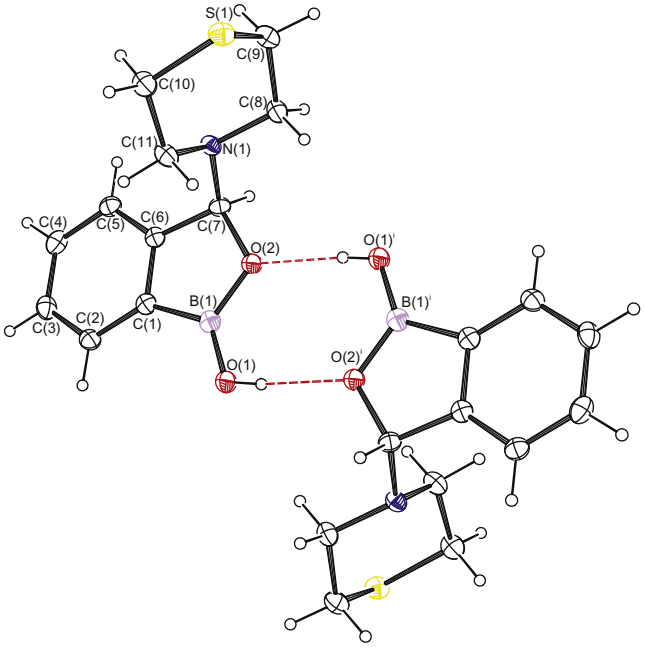


Figure 1. The hydrogen bonded dimeric structure of 1,3-dihydro-1-hydroxy-3-(4-thiomorpholinyl)-2,1-benzoxaborole (**1b**). Thermal ellipsoids are drawn with 50% probability. The intermolecular O–H···O hydrogen bonds are depicted with dashes.

360.0(2)°) and the O(1)–H(1) group is in plane with the fused ring system. In contrast to morpholine derivative **1a**, where the hydrogen-bonded dimer is described as involving interacting parallel planes of benzoxaborole units shifted by ca. 0.5 Å,[9,14] in the case of **1b**, the H-bonded dimer is flat with the largest deviation from planarity around 0.05 Å. This decreases significantly the hydrogen bond length to 2.728(2) Å for the O···O separation from that observed for **1a** [2.797(2) Å]. The comparison between the relevant bonds around the boron atom shows that in the case of **1b** all the bonds are significantly shorter than in **1a**. Similar to **1a**, the thiomorpholine ring in **1b** adopts a chair conformation and is almost perpendicular to the plane of the central dimeric ring. The observed discrepancies in the geometry of a molecule of **1b** compared to that of **1a** indicate that the borole fragment is extremely sensitive to modifications introduced by substituents.[9] This example shows that both steric and electronic factors are important but a weak interaction should not be precluded.

In conclusion, on the basis of NMR results, we have described the diverse reactivity of 2-formylphenylboronic acid with secondary amines as a function of their basicity and structure. Substituted benzoxaboroles are the main products of the reactions with amines of moderate basicity, while with strong Lewis bases complexes of boroxin are formed. With aromatic amines, the formation of C-alkylated products is the dominant reaction.

Acknowledgments

This work has been supported by the European Union in the framework of the European Social Fund through the Warsaw University of Technology Development Programme and by scholarships awarded by the Center of Advanced Studies for Andrzej Sporzyński at the University of Twente and for Agnieszka Adamczyk-Woźniak.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.09.091.

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21. (a) *Typical procedure for the synthesis of aminobenzoxaboroles* **1**: Na_2SO_4 (5.5 g) was added to a solution of 2-formylphenylboronic acid (1.0 g, 6.7 mmol) and morpholine (0.58 g, 6.7 mmol) in Et_2O (50 mL). The reaction mixture was stirred for 24 h at room temperature. After this time, the Na_2SO_4 was removed by filtration and another portion of Na_2SO_4 (5.5 g, 40 mmol) was added to the resulting clear solution. The reaction mixture was stirred for an additional 24 h. After this time the Na_2SO_4 was removed by filtration and the organic filtrate was slowly evaporated to dryness. The resulting yellowish crystalline solid was ground and was washed with hexane (2 mL) to wash out the remaining morpholine. The hexane was decanted and the solid was dried to give the desired product **1a** as a cream powder (1.32 g, 89%); (b) *Typical*

procedure for the synthesis of complexes **2**: Na_2SO_4 (3.0 g) was added to a solution of 2-formylphenylboronic acid (0.75 g, 5.0 mmol) and diethylamine (0.12 g, 1.7 mmol) in Et_2O (50 mL). The reaction mixture was treated as above to give 0.73 g (90%) of **2e** as an oil.

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27. Crystallographic data for compound **1b** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 782356) and can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44(0) 1223 336033 or deposit@ccdc.cam.ac.uk).
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