Aminoboronic Acids

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Synthesis of Aminoboronic Acid Derivatives from Amines and Amphoteric Boryl Carbonyl Compounds

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Dedicated to Professor K. Barry Sharpless on the occasion of his 75th birthday

Abstract: *Herein, we demonstrate the use of α-boryl aldehydes and acyl boronates in the synthesis of aminoboronic acid derivatives. This work highlights the untapped potential of boron-substituted iminium ions and offers insights into the behavior of N-methyliminodiacetyl (MIDA) boronates during condensation and tautomerization processes. The preparative value of this contribution lies in the demonstration that various amines, including linear and cyclic peptides, can be readily conjugated with boron-containing fragments. A mild deprotection of amino MIDA-boronates enables access to α- and β-aminoboronic acids in high chemical yields. This simple process should be applicable to the synthesis of a wide range of bioactive molecules as well as precursors for cross-coupling reactions.*

As part of a research program aimed at new amphoteric molecules, we have been exploring bifunctional structures which combine nucleophilic (Nu) and electrophilic (E) functional groups. Our general strategy has depended on finding appropriate kinetic barriers against unwanted Nu/E reactivity.[1] Using this logic, we have succeeded in combining amine and aldehyde groups within aziridine aldehydes,[2] and boroalkyl and aldehyde groups within α-boryl aldehydes.[3] We became interested in developing a general synthesis of aminoboronic acids. Preparation of aminoboronic acid derivatives from amphoteric boryl carbonyls was envisioned to proceed through the intermediacy of fundamentally interesting, yet unexplored, borylated iminium ions (Figure 1).

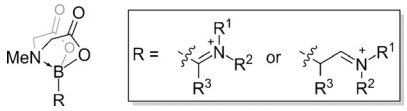

Figure 1. Borylated iminium ions.

Boron is distinguished for its capacity to reversibly interact with n-donor heteroatoms. This property has found applications in analyte sensing, catalysis, and drug discovery.[4] Creative ways to temporarily protect boronic acids also rely on this property.[5] We were determined to use the *N*-methyliminodiacetyl (MIDA) group to explore polar reactivity in the vicinity of boron. MIDA-boronates,[6] which have garnered a great deal of attention in the realm of cross-coupling applications,[7] have recently allowed us to generate acyl boronates[8] and α-boryl aldehydes. These bench-stable reagents offer a means to produce both B-C-N and B-C-C-N motifs in one-step, motifs which are sought-after frameworks as both synthetic building blocks and bioactive molecules. Moreover, with recent advances in high-throughput protein profiling technologies of electrophilic compounds, screening platforms such as EnPlex[4g] require access to diverse and heteroatom-rich boron-containing peptidomimetics. Herein, we demonstrate the synthesis of aminoboronic acid derivatives and propose a late-stage borylation strategy through the intermediacy of boron-containing iminium ions.

Since the pioneering work of Matteson, Lienhard, and co-workers,[9] α-aminoboronic acids have been widely used as protease inhibitors. There are few methods that enable the convergent synthesis of these compounds,[10] however, the majority of available protocols are based on S_N2 reactions of the boron-functionalized halomethyl species.[11] While useful, these electrophiles can lead to side-products with non-amine nucleophiles. Additionally, the use of common nucleophilic components, such as lithium amides, often requires cryogenic conditions with rigorous exclusion of water.[4h,11a]

To streamline the synthesis of aminoboronic acids, we sought to combine boryl carbonyl systems with amine fragments through condensation. Typically, carbonyl systems bearing metalloids such as silicon in acylsilanes, undergo Brook rearrangement during condensation with amines (Figure 2a).[12] The recent report of a bora-Brook rearrangement by Nozaki and co-workers (Figure 2b)[13] has extended this concept to boron-containing compounds, whereby the higher affinity of sp^2-hybridized boron atoms for an oxygen versus carbon atom provides the driving force for the isomerization. A related rearrangement from carbon to nitrogen atoms has also been noted in the decomposition of tricoordinate boron in α-boryl amines (Figure 2c).[9c] In our quest to preserve the C–B bond and gain entry to heteroatom-rich aminoboronic acid derivatives, we sought to use tetracoordinate boryl

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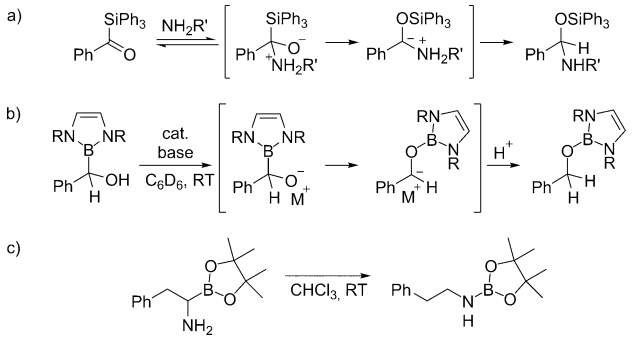


Figure 2. a) C→O silyl migration in acylsilanes upon condensation with amines. b) Base-catalyzed C→O boryl migration in α-borylbenzyl alcohols. c) C→N boryl migration in aminoboronates.

carbonyl reagents for the efficient formation of boron-containing iminium ions.

We began our investigation with the condensation between the MIDA-protected acyl boronate **1** and aniline, which led to observation of the imine **2** (Figure 3a). The

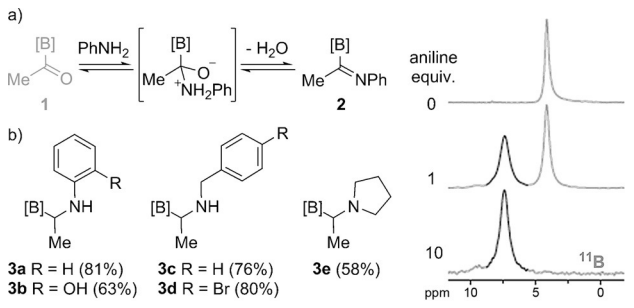


Figure 3. a) Tracking boryl imine formation through ^{11}B NMR analysis of 1.0 equiv of the acyl boronate **1** with 1.0 equiv of aniline, 3 Å MS, and 1.0 equiv of AcOH in CD_3CN at room temperature for 8 h. Quantitative conversion into **2** was achieved by heating the reaction mixture to 45 °C with a total of 10.0 equiv of aniline for 8 h. b) α-Amino MIDA-boronate derivatives synthesized through a one-pot reductive amination using 1.5 equiv of amine, 3 Å MS, 1.0 equiv of AcOH, and 1.5 equiv of $NaBH(OAc)_3$ in MeCN (0.05 M) at room temperature for 16 h. [B] = *N*-methyliminodiacetyl boronate, MS = molecular sieves.

reaction was monitored by ^{11}B NMR spectroscopy, thus revealing a downfield shift of **1** at 4.2 ppm to a signal at 7.4 ppm corresponding to the borylated imine species **2**. Upon quantitative conversion into **2** with excess aniline, we proceeded to investigate the feasibility of reductive amination through the intermediacy of borylated iminium ions. A survey of reaction conditions compatible with C(sp^2)–B(MIDA) boronates and organotrifluoroboronates[5b,14] led us to use $NaBH(OAc)_3$ to accomplish the in situ reduction of **2** to the α-amino MIDA-boronate **3a** in 81% yield (Figure 3b). Additional examples of primary and secondary amine inputs were also shown to undergo reductive amination with **1** to the corresponding α-boryl amines (**3b–e**), with no evidence of overalkylation or boryl migration.

Having accessed α-amino MIDA-boronates through reductive conjugation with acyl boronates, we used α-boryl aldehydes as a means to access the much less explored class of β-aminoboronic acids.[4c,15] However, our mechanistic studies uncovered an unusual phenomenon. On the basis of bond dissociation energies, the imine species was expected to be more stable than the aldehyde against boryl tautomerization (Figure 4a). In reality, the opposite was observed: the boryl

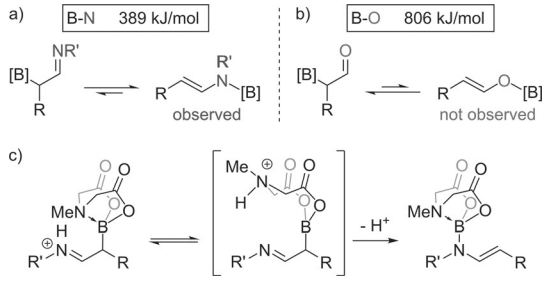


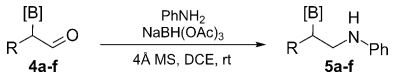
Figure 4. a) C→N boryl migration is observed in α-boryl imines. b) C→O boryl migration is not observed in α-boryl aldehydes. c) Proposed hemilability in borylated iminium ions initiated by an intramolecular proton transfer followed by C→N boryl migration.

substituent underwent facile migration from carbon to nitrogen atoms in the case of α-boryl imines, but remained bound to the carbon atom in the case of α-boryl aldehydes (Figure 4b). Despite the notion that the MIDA group offered adequate protection from 1,2-boryl migrations in acylboronates, the facile formation of *N*-boryl enamines[16] suggests that 1,3-boryl migration might be due to hemilability of the MIDA nitrogen coordination to boron (Figure 4c).

We were able to prevent the undesired C→N boryl migration by trapping the short-lived borylated iminum ions in situ with $NaBH(OAc)_3$. By using this method, various substituted α-boryl aldehydes (**4a–f**) were reacted with aniline and reduced to furnish β-amino MIDA-boronates (**5a–f**) in good to excellent yields as stable crystalline solids (Table 1). X-ray quality crystals of **5c** were obtained by slow evaporation in acetone (see the Supporting Information).[17]

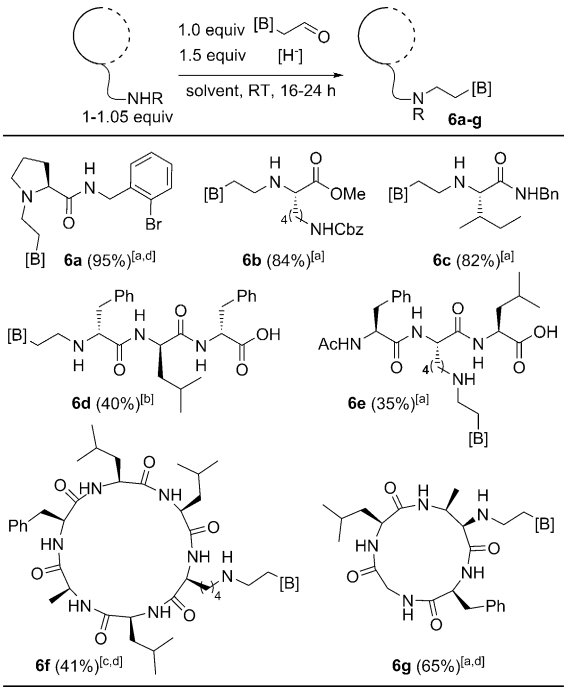
Having developed a procedure to access β-amino MIDA-boronates, we turned our attention to more challenging amine inputs such as amino acids and peptides. Using the aldehyde **4a**, we prepared various peptide conjugates in acetonitrile at

Table 1: Preparation of β-amino MIDA-boronates.[a]

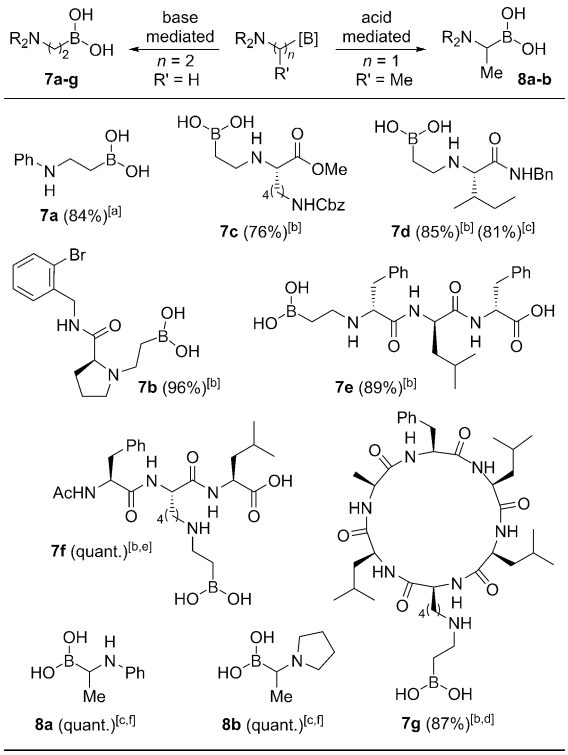


Boryl aldehyde	R	Product	Yield [%][b]
4a	H	**5a**	82
4b	isobutyl	**5b**	83
4c	cyclohexyl	**5c**	84
4d	benzyl	**5d**	86
4e	phenethyl	**5e**	86
4f	phenyl	**5f**	54

[a] Reactions were carried out using 0.2–1.0 mmol of α-boryl aldehyde, 1.1 equiv of aniline, 1.5 equiv of $NaBH(OAc)_3$, 1,2-dichloroethane (DCE; 0.04 M) with 4 Å MS at room temperature. [b] Yield is that of the isolated product. No boryl migration was observed with the exception of **4f** where 22% of *N*-boryl enamine was isolated.



Scheme 1. Boron-containing peptides prepared by reductive amination. Reactions were carried out using 1–1.05 equiv of amine, 1.0 equiv of α-boryl aldehyde (**4a**), and 1.5 equiv of reducing agent at room temperature in 0.04 M solutions. [a] MeCN, $NaBH(OAc)_3$. [b] 1:1 $MeCN/H_2O$, $NaBH_3CN$. [c] MeCN, $NaBH(OAc)_3$, 1.5 equiv of Et_3N. [d] Isolated as a formate salt. Cbz = carboxybenzyl.



Scheme 2. Deprotection of α- and β-amino MIDA-boronates. [a] 3.0 equiv of 1 M $NaOH_{(aq)}$ in THF (0.04 M). [b] 6 equiv of $NaHCO_3$ in MeOH (0.04 M). [c] 6.0 equiv of 3 M $HCl_{(aq)}$ in CD_3CN (0.1 M). [d] Isolated as formate salt. [e] Characterized as 1:1 mixture with free MIDA. [f] Characterized as HCl salt.

room temperature, and they were isolated in high purity using reverse-phase flash chromatography (Scheme 1).

Our study included functionalization of amino groups in amino-acid derivatives (**6a–c**) and linear tripeptides (**6d–e**). Further driven by the ongoing interest in boron-containing cyclic peptidomimetic inhibitors of serine proteases,[18] we turned to boroalkylation of cyclic peptides. Some of the known inhibitors of this type are equipped with amino boronate groups at the P1 position.[19] Access to boropeptide conjugates of this kind would be particularly streamlined if a mild late-stage conjugation of macrocycle side chains became available. As an example of our approach, a homodetic 18-membered cyclic peptide was prepared and successfully boroalkylated at its lysine side chain to give the conjugate **6f**. Given the conformational rigidity of α3β motifs and their importance in drug discovery,[20] we also evaluated boroalkylated 13-membered rings. The compound **6g** was derived from the corresponding azide using our previously described method for the introduction of amine side chains into 13-membered rings.[21]

With MIDA-protected boron conjugates in hand, we sought to remove the MIDA group to access the free boronic acid derivatives. Treatment of β-amino MIDA-boronates with base at room temperature,[3] followed by purification by reverse-phase chromatography afforded the β-aminoboronic acids **7a–g** in moderate to excellent yields (Scheme 2). However, in the case of the α-aminoboronic acids **8a** and **8b**, a 3.0 M HCl solution was used instead for quantitative MIDA removal because of the propensity for 1,2-boryl migration under basic conditions.[22] We were pleased to observe that the B-C-C-N and B-C-N linkages in these aminoboronic acid derivatives remained intact as evidenced by high-resolution mass spectrometry (HRMS) and NMR spectroscopy.

While the basic and acidic deprotections of MIDA were successful, we realized that the Lewis-acidic nature of boron might facilitate the epimerization of the α-center(s) in boron-containing peptides. We proceeded to determine the extent of deuteration of **6c** and **6d** under both acidic and basic conditions by using ^1H NMR spectroscopy (Scheme 2). Upon complete MIDA removal, deuteration of the α-centers in **7d** and **7e** did not occur (see the Supporting Information). Therefore, both basic and acidic protocols were found to be compatible with boron-containing peptides.

To further gauge the stability of β-aminoboronic acids in aqueous acid and alkaline solutions, a pH/NMR study between pH values of 3.0 and 13.6 was conducted for a β-aminoboronic acid (see the Supporting Information). By using ^1H and ^{11}B NMR spectroscopy, a boronic acid pK_a value of 8.6 was found, and is approximately two orders of magnitude lower than expected for an sp^3 boronic acid such as methylboronic acid ($pK_a = 10.4$).[4h] In addition, no decomposition was observed 24 hours after pH analysis. The markedly lowered boronic acid pK_a value and observed pH stability speaks to the potential utility of β-aminoboronic acids in applications which depend on the discovery of hydrolytically stable compounds for enzymatic inhibition.

In the course of our study, we have characterized the fundamentally significant and previously unknown boron-containing iminium ions. This work has allowed us to develop a novel approach to α- and β-aminoboronic acid derivatives. Apart from providing access to novel building blocks which contain boron and nitrogen centers, our chemistry offers a straightforward way to modify various amines, including linear and cyclic peptides, with boron-containing groups. Our mild method of making derivatives of α- and β-aminoboronic acids would be useful not only in the design of reversible covalent inhibitors of proteases, but also in studies which seek enhanced permeability, cellular internalization,[23] and ^{18}F-radiolabelled peptide conjugates.[24] Considering the utility of peptides in nonbiological applications such as catalysis, one can envisage straightforward modification of peptide catalysts with electrophilic boron functionalities.[25] The fundamental reactivity of boron-substituted iminium ions, which has emerged as the main focus of this work, should enable a wealth of additional synthetic applications.

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