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Boroalkyl Group Migration Provides a Versatile Entry into α-Aminoboronic Acid Derivatives

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Supporting Information

ABSTRACT: A reaction exemplifying migration of boron-substituted carbon is described. We show that α-boroalkyl groups of transient boroalkyl acyl azide intermediates readily migrate from carbon to nitrogen. This process allows access to a new class of stable molecules, α-boryl isocyanates, from α-borylcarboxylic acid precursors. The methodology facilitates synthesis of a wide range of α-aminoboronic acid derivatives, including α,α-disubstituted analogues.

Organoboron compounds are widely used in material science and medicinal chemistry,[1] but their efficient preparation remains a long-term challenge. Over the past decade, the use of boronic acids containing a unique *gem*-aminoboron motif has drawn attention both in academia and in the pharmaceutical industry. A number of studies have documented the utility of aminoboronic acid derivatives as biochemical probes of protein function.[2] These studies hinge on reversible covalent interactions that are possible between boron and nucleophilic protein residues. The realization of *gem*-aminoboronic acids as promising drug candidates culminated in the recent success of Bortezomib (Velcade), an FDA-approved boropeptide used for the treatment of multiple myeloma.[3] Such studies have resulted in increased interest in the design of boron-containing peptides. The emergence of biotechnology companies that are focused on the boropeptide platform further underscores the growing interest in this area.[4]

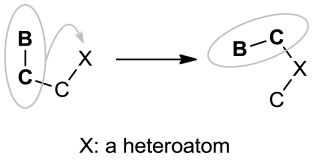

Figure 1. Migration of an α-boroalkyl group.

Despite the significance of the *gem*-aminoboron functionality, the application of these molecules in chemical biology and drug discovery programs is made difficult by the lack of methods adaptable to synthesis under mild reaction conditions.[5] The vast majority of established synthetic routes to organoboron reagents involve late-stage installation of a new carbon−boron σ-bond, which presents chemoselectivity challenges. We have been interested in developing reactions that *transpose* carbon−boron bonds under mild conditions (Figure 1). If successful, reactions of this type can be used in skeletal rearrangement of boron-containing precursors. To the best of our knowledge, reactions accompanied by migration of boron-substituted carbon are presently unknown. Here we show that the migration of an α-boroalkyl group from carbon to nitrogen occurs under mild conditions, allowing access to a class of hitherto unknown bench-stable α-boryl isocyanates.[6] α-Boryl isocyanates were found to afford new opportunities to efficiently prepare a range of α-amino boronic acid derivatives, including urea-containing boronic acids, boropeptides, and α,α-disubstituted variants.

Recent reports from our laboratory and from that of Martin Burke disclosed the synthesis of α-boryl aldehydes.[7] As part of our efforts aimed at demonstrating synthetic applications of these molecules, we showcased their oxidative conversion into configurationally stable α-borylcarboxylic acids. With these molecules in hand, we questioned the possibility of α-boroalkyl migration as a general means of assembling *gem*-aminoboron compounds. When **1a** was subjected to one-pot diphenylphosphoryl azide (DPPA)/Et_3N-mediated Curtius rearrangement conditions (50 °C, 1 h),[8,9] we detected a clean conversion of the starting material to α-boryl isocyanate **2a**, which exhibited an IR stretch of 2244 cm^{-1} and a ^{13}C NMR chemical shift of 122.9 ppm, consistent with the presence of isocyanate functionality. **2a** was isolated in 71% yield as a white powder after silica gel chromatography and was found to be stable to storage at ambient temperature. This result prompted us to test the generality of the preparation of stable α-boryl isocyanates. A range of monosubstituted α-borylcarboxylic acids **1a**−**i** were subjected to one-pot Curtius rearrangement conditions (Table 1). The reaction worked well with aryl substrates **1a**,**b**. Primary and secondary alkyl-substituted α-borylcarboxylic acids **1d**−**h** also afforded the desired isocyanates in good to excellent yields.

To obtain stereochemical insight into this novel migratory process, α-borylcarboxylic acids **3a**,**b** were prepared as single diastereomers (dr > 95:5) using diastereoselective epoxidation of vinyl boronates[7b] followed by stereospecific rearrangement and oxidation (see Supporting Information). **3a**,**b** were subjected to one-pot Curtius rearrangement conditions (Scheme 1). ^1H NMR analysis revealed that α-boryl isocyanate **4b** was produced from alkyl-substituted acid **3b** with complete retention of stereochemistry (dr > 95:5). The rearrangement of phenyl-substituted acid **3a** resulted in the isocyanate product **4a** with a slightly eroded diastereomeric ratio (dr = 85:15). This

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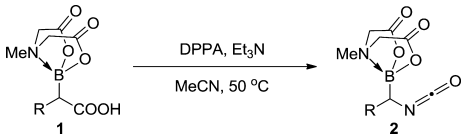
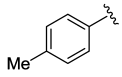
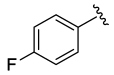
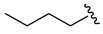
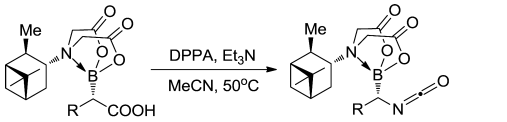
Table 1. Preparation of α-Boryl Isocyanates via Curtius Rearrangement[a]



Starting material	R	product	yield[b]
1a		**2a**	71%
1b		**2b**	57%
1c		**2c**	62%
1d		**2d**	91%
1e		**2e**	84%
1f		**2f**	86%
1g		**2g**	71%
1h		**2h**	73%

[a]The reactions were carried out using 1.0 equiv of α-boryl acid, 1.1 equiv of DPPA, and 1.1 equiv of Et_3N in anhydrous MeCN at 50 °C for 1 h. [b]Isolated yields after silica gel chromatography.

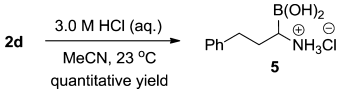
Scheme 1. Stereochemical Investigation of the α-Boroalkyl Migration[a]



[a]Diastereomeric ratios (dr) were determined by ^1H NMR analysis of crude reaction mixtures.

could be attributed to the vulnerability of the acidic α-proton in either the acid starting material or the isocyanate product to the basic reaction conditions.

The facile preparation of α-boryl isocyanates encouraged us to investigate their downstream transformations to generate α-aminoboronic acid derivatives. To explore this possibility, we first tried to generate the free amino group from α-boryl isocyanates by direct acid hydrolysis. Treatment of α-boryl isocyanate **2d** with 3.0 M HCl aqueous solution in MeCN afforded α-aminoboronic acid **5** (eq 1). The hydrolysis not only

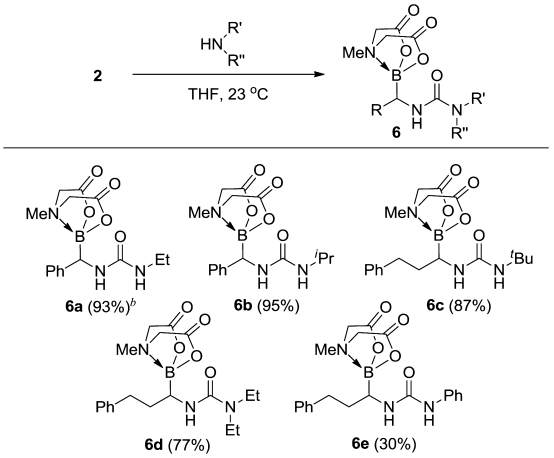


(1)

resulted in the formation of an amine from the isocyanate functional group but also converted the *N*-methyliminodiacetyl boronate (MIDA boronate) to the free boronic acid.

We then explored the reactivity of boryl isocyanates toward amines and alcohols with the ultimate goal of preparing α-boryl ureas and carbamates, respectively. We had initially suspected that conditions required for nucleophilic attack at the isocyanate would be incompatible with the adjacent boronate functionality. Interestingly, reactions between α-boryl isocyanates and different types of amines were found to occur smoothly at room temperature in THF with retention of the boronate groups. A series of α-boryl urea products **6** (α-ureido MIDA boronates) were obtained in good to excellent yields (Scheme 2). All aliphatic amines afforded the desired products

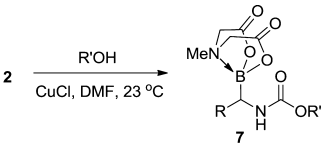
Scheme 2. Preparation of α-Boryl Ureas[a]

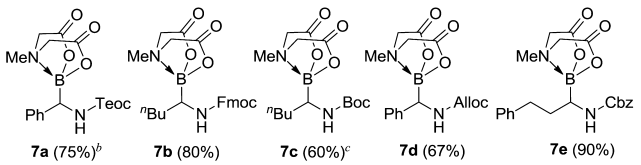


[a]The reactions were carried out using 1.0 equiv of α-boryl isocyanate and 1.5 equiv of amine in anhydrous THF at 23 °C for 1−12 h. [b]All yields in parentheses are isolated yields after silica gel chromatography.

in full conversion within 1−5 h, although reactions with aromatic amines, such as aniline, reached 50% completion only after 12 h (Scheme 2, **6e**). In contrast to the facile reactions between amines and α-boryl isocyanates, alcohols were found to be reactive only in the presence of CuCl in DMF.[10] By choosing different alkoxy nucleophiles, a series of α-amino MIDA boronates **7** with representative amino-protecting groups were obtained (Scheme 3). In view of the wide use of

Scheme 3. Preparation of α-Boryl Carbamates[a]





[a]Unless specified otherwise, reactions were carried out using 1.0 equiv of α-boryl isocyanate, 3.0 equiv of alcohol, and 1.0 equiv of CuCl in anhydrous DMF at 23 °C for 3 h. [b]All yields in parentheses are isolated yields after silica gel chromatography. [c]The reaction was carried out using 10.0 equiv of *t*-BuOH at 70 °C for 24 h.

ureas and carbamates in medicinal chemistry and material science, these borylated analogues are expected to find utility in solid-phase peptide synthesis. The orthogonality of protecting groups in these building blocks will be useful in the synthesis of complex boron-containing compounds.

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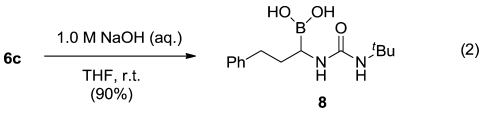
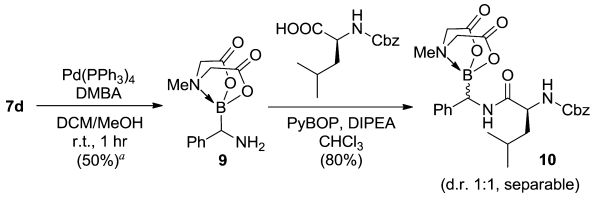
A range of deprotection conditions were tested in the hopes of chemoselective release of the free boronic acid or amino group. For instance, treating **6c** with 1.0 M aqueous NaOH in THF at room temperature selectively removed the MIDA protecting group to afford the α-ureidoboronic acid **8** (eq 2).



The combination of boronic acid and urea functionality in the same molecule has potential for applications in organocatalysis and molecular recognition.[11−14] A $Pd(PPh_3)_4$-catalyzed deallylation of carbamate **7d** gave stable α-amino boronate **9**, leaving the (MIDA)boryl group intact (Scheme 4).[15] To the best of our knowledge, stable α-aminoboronic acid derivatives containing an unsubstituted primary α-amino group are presently unknown.[16] Subsequent coupling of **9** with *N*-Cbz-leucine successfully afforded the MIDA-protected boro-dipepetide **10** as a mixture of two diastereomers, which were easily separated by flash silica gel chromatography in good yields.

Scheme 4. Preparation of Boro-dipeptide 10

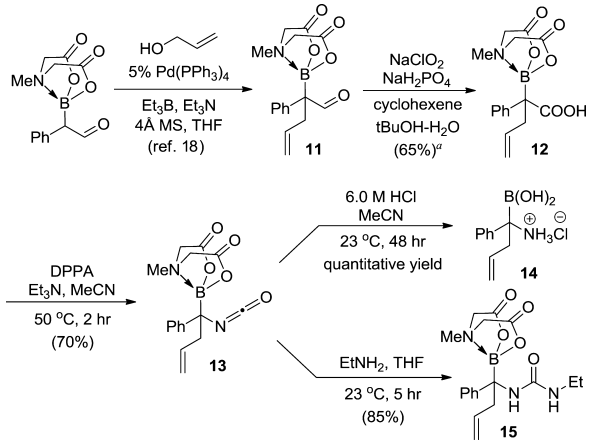


[a]All yields in parentheses are isolated yields after silica gel chromatography.

The successful preparation of monosubstituted α-aminoboronic acids via boryl isocyanates encouraged us to further pursue the synthesis of α,α-disubstituted derivatives. This type of α-aminoboronic acid analogue is not easy to obtain due to the difficulties in installing a quaternary α-carbon center using known methodologies.[17] To evaluate the feasibility of α-boroalkyl migration for the synthesis of α,α-disubstituted aminoboronic acids, we chose α-borylcarboxylic acid **12** as a testing ground (Scheme 5). **12** can be prepared from the corresponding monosubstituted α-boryl aldehyde by a sequence of transformations involving palladium-catalyzed α-allylation and oxidation.[18] Gratifyingly, the Curtius rearrangement of **12** occurred smoothly at 50 °C in MeCN. Although a longer reaction time was required for full conversion, α-boryl isocyanate product **13** was afforded in good yield. Further transformations of **13**, such as acidic hydrolysis and nucleophilic attack, were conducted. The final α,α-disubstituted aminoboronic acid products **14** and **15** were thus successfully obtained.

In summary, we have realized the first example of an α-boroalkyl group migration and accessed a range of α-boryl isocyanates. These novel bench-stable molecules have enabled mild and convenient access to a wide range of α-aminoboronic acid derivatives, including carbamates, ureas, and peptides. Additionally, this methodology allows for the facile preparation of α,α-disubstituted analogues. Given the advances in isocyanate chemistry[19,20] and the recent developments in cross-coupling applications of organoboron compounds,[21] we expect that our discovery will find utility in synthesis and medicinal chemistry.

Scheme 5. Preparation of α,α-Disubstituted α-Aminoboronic Acid Derivatives



[a]All yields in parentheses are isolated yields after silica gel chromatography.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete experimental details and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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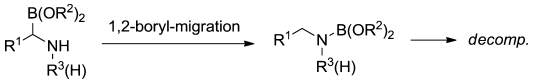

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