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Amphoteric α-Boryl Aldehydes

Zhi He and Andrei K. Yudin*

Davenport Research Laboratories, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6

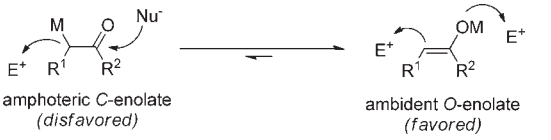
Supporting Information

ABSTRACT: A new class of stable molecules, α-boryl aldehydes, has been prepared from oxiranyl *N*-methyliminodiacetyl boronates by a 1,2-boryl migration with concomitant epoxide scission. A range of boryl imines, alkenes, alcohols, acids, enol ethers, enamides, and other functionalized boronic acid derivatives that are difficult or impossible to prepare using established protocols can be accessed from α-boryl aldehydes. The chemoselective transformations of these building blocks, including the facile synthesis of functionalized unnatural amino acids from silyloxy and amido vinyl boronates, attest to the potential of α-boryl aldehydes in chemical synthesis.

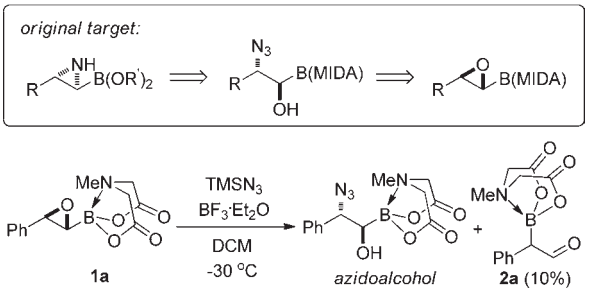
Enols and enolates are among the most widely used intermediates in chemical synthesis. In comparison with their ambident O-bound tautomers, the amphoteric C-bound metal and metalloid enolates are thermodynamically unstable (Scheme 1). Direct evidence in support of C-bound enolate species is sparse, despite the fact that α-boryl carbonyl compounds have been proposed as reactive intermediates in several transformations.[1,2] The well-known affinity of sp^2-hybridized boron to oxygen provides the driving force for the isomerization of the C-bound enolate into the corresponding O-bound isomer. Here we show that the quaternary nature of boron in *N*-methyliminodiacetyl (MIDA) boronates enables the isolation and structural characterization of stable α-boryl aldehydes. As part of this study, we report access to a range of densely functionalized organoboron derivatives and their chemoselective transformations.

As part of a program aimed at the discovery of new amphoteric molecules, we became interested in preparing aziridinyl boronic acid derivatives from oxiranyl MIDA boronates (Scheme 2). The latter molecules can be made by epoxidation of vinyl MIDA boronates,[3f] which were recently developed by Burke and coworkers.[3] During our initial attempts to make the azidoalcohol precursor to the target aziridinyl boronates, the starting oxiranyl MIDA boronate **1a** was charged with excess $TMSN_3$ in the presence of BF_3 etherate (Scheme 2). In addition to the expected azidoalcohol product, a white solid was isolated in 10% yield. This material exhibited an IR stretch at 1701 cm^{-1} and an ^1H NMR chemical shift of 9.73 ppm, consistent with rearranged α-boryl aldehyde **2a**. This unexpected result led us to explore further the rearrangement of oxiranyl MIDA boronates into α-boryl aldehydes. We found that exposure of oxiranyl MIDA boronate **1a** to BF_3 etherate in anhydrous CH_2Cl_2 (−30 to 0 °C) provided **2a** in nearly quantitative yield within 30 min. No ketone byproduct was detected during the reaction. The resulting α-boryl aldehyde **2a** proved to be stable during aqueous workup, silica gel chromatography, and storage in the solid form at room temperature under air.

Scheme 1. Equilibrium between *C*- and *O*-Enolates



Scheme 2



The preparation of other α-boryl aldehydes was tested in the same manner (Table 1). The reaction was found to work well not only with electron-neutral (**1a**) and electron-rich (**1b**) aryl substrates but also with electron-deficient (**1c**) aryl derivatives. Primary- and secondary-alkyl-substituted oxiranyl MIDA boronates (**1d** and **1e**) cleanly afforded the desired aldehyde products, but the *tert*-butyl substrate (**1f**) led to a complex mixture of intractable materials. The unsubstituted oxiranyl MIDA boronate **1g** was also tested in the reaction, and no rearrangement took place, even at an elevated temperature with a prolonged reaction time (40 °C, 24 h).

The regioselectivity of the reaction prompted us to investigate its mechanism. 1-Deuterated oxiranyl MIDA boronates **3a** and **3b**, which were prepared from the corresponding deuterated acetylenes, were thus subjected to the BF_3-promoted rearrangement (Scheme 3). We found that the deuterium label was exclusively incorporated at the carbonyl carbon of the resulting α-boryl aldehydes **4a** and **4b**. These results unambiguously prove that a 1,2-boryl migration took place. The MIDA-boryl group migrated not only in preference to the deuteride (hydride) but also to the alkyl or aryl substituents. While a similar rearrangement of silyl epoxides with migration of the silyl group is known,[4] the boron version of this process has remained elusive because

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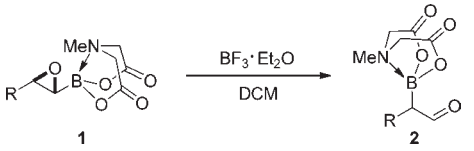
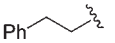
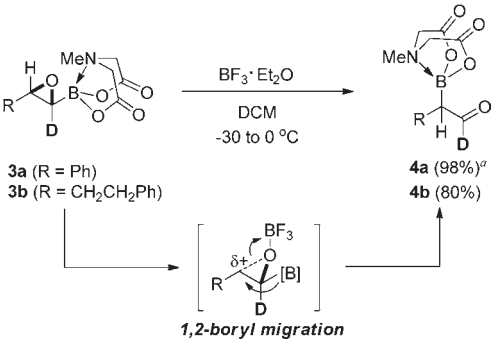
Table 1. Preparation of α-Boryl Aldehydes 2 via Rearrangement of Oxiranyl MIDA Boronates 1[a]



Starting material	R	product	yield[b]
1a	Ph	**2a**	98%
1b	*p*-Me-Ph	**2b**	97%
1c	*p*-F-Ph	**2c**	98%
1d		**2d**	76%
1e		**2e**	94%
1f	*t*-Bu	**2f**	mixture[c]
1g	H	**2g**	N.R.[d]

[a] Unless stated otherwise, the reactions were carried out using 1 equiv of epoxide and 1 equiv of $BF_3 \cdot Et_2O$ in anhydrous CH_2Cl_2 from −30 to 0 °C for 30 min. [b] Isolated yields after silica gel chromatography. [c] A complex mixture of intractable products. [d] The reaction was carried out at 40 °C for 24 h. N.R. = no reaction.

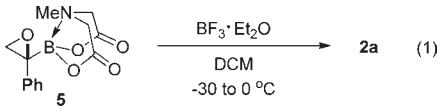
Scheme 3. Deuterium Labeling Experiments



[a] Isolated yields after silica gel chromatography.

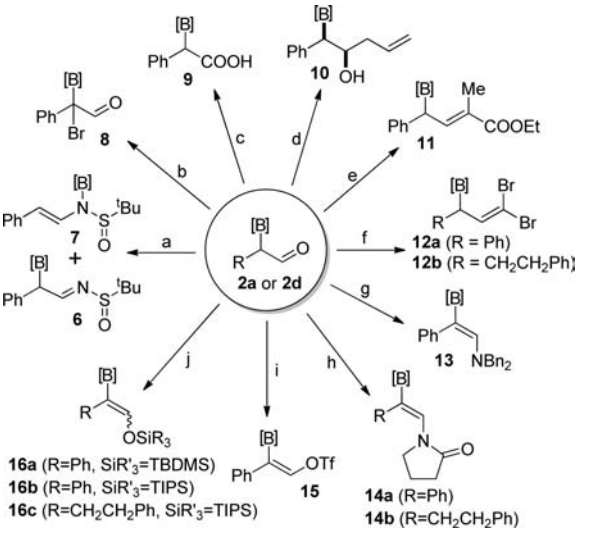
any attempt to enlist a tricoordinate boron-containing fragment has been met with rapid C-to-O transfer.[5] The unique feature of the trivalent MIDA ligand transforms the electron-deficient sp^2-hybridized boron center to an electron-rich sp^3-hybridized boron center, enabling the 1,2-boryl migration.[6]

In addition to 2-substituted oxiranyl MIDA boronates, a representative 1-substituted substrate **5** was also tested in the BF_3-promoted rearrangement. Interestingly, α-boryl aldehyde **2a** was isolated here also (eq 1). This result indicates that 1, 2-hydride migration instead of 1,2-boryl migration took place. Although it is likely that the rearrangement is concerted, the involvement of transient boryl-substituted cationic species during the rearrangement of **5** has not been ruled out.



In order to demonstrate the potential of amphoteric α-boryl aldehydes in synthesis, we evaluated their chemical reactivity

Scheme 4. Synthetic Transformations of α-Boryl Aldehydes[a,b]



[a] Reagents and conditions: (a) *t*-BuS(O)NH_2, $CuSO_4$, DCM, rt, 85% (**6**:**7** = 85:15). (b) Br_2, dioxane/DCM, rt, 77%. (c) $NaClO_2$, NaH_2PO_4, cyclohexene, *t*-BuOH/H_2O, rt, 73%. (d) Allylbromide, In(0), THF-H_2O (1:1), rt, 97% (syn:anti = 93:7). (e) $Ph_3P{=}C(Me)CO_2Et$, DCM, 60 °C, 72%. (f) CBr_4, PPh_3, DCM, rt; **12a** (60%), **12b** (65%). (g) Bn_2NH, 4 Å molecular sieves, $CHCl_3$, rt, 85%. (h) Pyrrolidin-2-one, TsOH, toluene, 120 °C; **14a** (50%), **14b** (43%). (i) $PhNTf_2$, KHMDS, THF, −78 °C, 41%. (j) Method A for TBDMS enol ether: TBDMSCl, Et_3N, MeCN, 80 °C, **16a** (55%, *E*:*Z* = 10:90). Method B for TIPS enol ether: TIPSOTf, DBU, THF, rt; **16b** (81%, *E*:*Z* = 20:80), **16c** (80%, *E*:*Z* < 5:95). [b] [B] = *N*-methyliminodiacetyl boronate.

under a variety of conditions. With **2a** and **2d** as model substrates, various novel boronic acid derivatives were obtained (Scheme 4). The stability of α-boryl aldehydes first encouraged us to investigate the synthesis of nitrogen-containing α-borylated species.[7] Different classes of amines and amides, including benzylamine, aniline, *p*-toluenesulfonamide, and *tert*-butanesulfinamide, were reacted with α-boryl aldehyde **2a** in the presence of dehydrating agents and/or Lewis acids.[8] The majority of amines and amides generated *N*-boryl enamines and enamides. *tert*-Butanesulfinamide led to the formation of α-boryl imine **6** along with a small amount of *N*-boryl enamide **7**.

α-Boryl aldehyde **2a** was also subjected to different oxidative conditions. The highly functionalized α-bromo-α-borylaldehyde **8** was obtained in good yield through α-bromination and characterized by X-ray crystallography.[9] On the other hand, oxidation with sodium chlorite generated the novel α-boryl carboxylic acid **9**. We also subjected **2a** to oxidation with sodium chlorite in ^{t}BuOH/D_2O, and no deuterium incorporation was observed at the α-position of the acid product (see the Supporting Information). This result attests to the configurational stability of the starting material during the course of the reaction as well as to the configurational stability of the acid product.

A highly diastereoselective preparation of boryl alcohol **10** from **2a** took place upon reaction with an allylindium species under mild conditions. Meanwhile, olefination of the aldehyde group afforded the novel (*E*)-γ-boryl-α,β-unsaturated derivative **11** equipped with an ester substituent at the terminal allylic carbon. *gem*-Dibromoallyl boronates **12a** and **12b** were also obtained. These allylboron reagents have not been reported to date. Since

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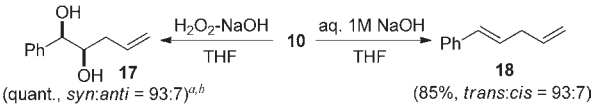
Scheme 5. Chemoselective Transformations of Allylated Boryl Alcohol 10



[a] Isolated yield after silica gel chromatography. [b] Diastereoisomeric ratios were determined by ^{1}H NMR analysis of the crude reaction mixtures.

the utility of *gem*-dihaloalkene intermediates in metal catalysis is well-documented,[10] one can anticipate interesting possibilities for these novel dibromoallyl boronates in tandem reactions. Finally, by taking further advantage of the enolizable aldehyde functionality, we synthesized a series of β-functionalized vinyl boronates, including enamine **13**, enamides **14a** and **14b**, and triflate enol ether **15** as well as silyl enol ethers **16a**−**c** with high chemo- and stereoselectivities.

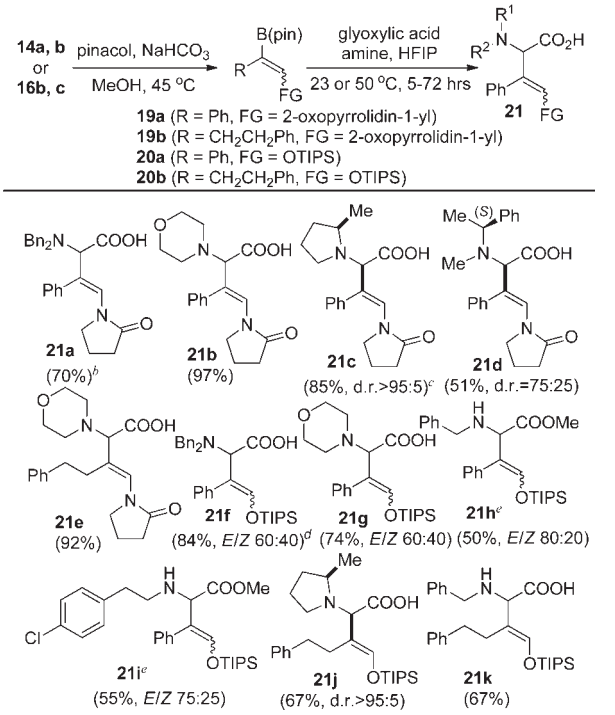
The densely functionalized building blocks accessible with this chemistry provide ample opportunities for synthesis. For example, allylated boryl alcohol **10** was directly converted to 1,2-diol **17** via oxidation in basic H_2O_2. In contrast, treatment of **10** with 1 M aqueous NaOH resulted in the stereospecific formation of 1,4-diene ("skipped" diene) **18**. This reaction likely proceeds via a Wittig-type syn-elimination process[11] promoted by NaOH (Scheme 5).

Ambident silyloxy and amido vinyl boronate molecules such as **14** and **16** obtained using our method aroused further curiosity. We recognized the bis-nucleophilic character of these species at the carbon equipped with the boryl group and opted to investigate the possibility of chemoselective transformations of nucleophilic C−B bonds. We chose the Petasis borono-Mannich reaction[12] as a testing ground. MIDA boronates **14a**, **14b**, **16b**, and **16c** were thus first transformed into the corresponding pinacolyl boronates **19a**, **19b**, **20a**, and **20b**. These pinacolyl boronates were subjected to the Petasis protocol with glyoxylic acid in the presence of different secondary or primary amines in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as the solvent.[13] To our delight, several novel unnatural amino acids **21a**−**k** with intact silyl enol ether or enamide functionalities were successfully obtained (Scheme 6). Importantly, no regular Mannich-type products were detected in the course of these reactions, even in the cases of silyl enol ether boronates **20a** and **20b**.

Generally, the alkyl-substituted boronates **19b** and **20b** were found to be more reactive than their aryl-substituted counterparts **19a** and **20a**. Electron-rich substrates **20a** and **20b** possessing silyl enol ether groups showed much higher reactivity than their corresponding enamide counterparts **19a** and **19b**. Thus, silyloxy vinyl boronates not only reacted more rapidly with secondary amines than did the amido ones but also worked very well with primary amines, with which amido vinyl boronates **19a** and **19b** showed no reactivity. In addition, we were able to glean insight into the diastereoselectivity of the Petasis reaction of these functionalized vinyl boronates. While (*S*)-*N*-methyl-1-phenylethanamine[14] gave inferior results (**21d**, d.r. = 75:25), the reaction of 2-methylpyrrolidine,[15] glyoxylic acid, and pinacolyl boronate **19a** or **20b** afforded alkenylglycine **21c** or **21j** with excellent diastereoselectivity (d.r. > 95:5).

In summary, we have reported the discovery of stable amphoteric α-boryl aldehydes arising from a 1,2-boryl migration. A range of boryl imines, alkenes, alcohols, enol ethers, enamides, and other poly functionalized boron derivatives that are difficult

Scheme 6. Preparation of Unnatural Amino Acids from Functionalized Boronates[a]



[a] Each Petasis reaction was carried out using 1 equiv of functionalized alkenyl pinacolyl boronic ester, 1.2 equiv of glyoxylic acid, and 1.2 equiv of amine (1° or 2°) in HFIP at 23 or 50 °C for 5−72 h. [b] Isolated yields after silica gel chromatography. [c] Diastereoisomeric ratios (d.r.) were determined by ^{1}H NMR analysis of the crude reaction mixtures. [d] *E*/*Z* ratios were determined by ^{1}H NMR analysis of purified product mixtures. [e] Stable methyl esters were generated by one-pot esterfication using $TMSCHN_2$.

to prepare using established methods can be accessed from α-boryl aldehydes. These molecules have enabled the facile and highly selective construction of densely functionalized molecules such as unnatural amino acids. In view of the facility with which amphoteric aziridine aldehydes orchestrate efficient bond-forming processes,[16] we expect that α-boryl aldehydes and their derivatives will find utility in synthesis and may open up interesting new opportunities for designing processes with high bond-forming efficiency.

■ ASSOCIATED CONTENT

Supporting Information. Complete experimental details, characterization data for new compounds, and crystallographic data (CIF) for **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
ayudin@chem.utoronto.ca

■ ACKNOWLEDGMENT

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