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Transition-metal-Free Synthesis of 1,1-Diboronate Esters with a Fully Substituted Benzylic Center via Diborylation of Lithiated Carbamates

Accepted 00th January 20xx DOI: 10.1039/x0xx00000x

Received 00th January 20xx,

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Abstract: A transition-metal-free lithiation-borylation method has been developed to access a variety of 1,1-diboronate esters with a fully substituted benzylic center from readily available secondary benzylic *N*,*N*-diisopropyl carbamates. The method is applicable to scale-up synthesis of 1,1-diboron compounds. Furthermore, The current method is also applicable to synthesizing optically active 1,1-silylboronate esters.

1,1-Dimetallic organic compounds are valuable building blocks to streamline synthesis of molecules with structural diversity.¹ Particularly, 1,1-diboronate esters have gained great interest recently as they have advantages of unique stability, operational simplicity, and non-toxicity over other 1,1dimetallic organic reagents.² 1,1-diboronate esters can be served as nucleophilic partners in a variety of chemo-selective C-C bond forming reactions.³⁻⁶ Besides, 1,1-diboron compounds can also be used in boron-Wittig reaction to form multisubstituted olefins⁷ and employed as unconventional borylation reagents.⁸

Although recent years have witnessed that 1,1diboronate esters have engaged in promising application in organic synthesis, the methods to construct this kind of compounds are still limited. Most of current methods rely on transition-metal catalysis, including Rh(I),⁹ Cu(I),¹⁰ or Co¹¹catalyzed diboration of terminal alkynes, Cu(I)-catalyzed asymmetric boron addition to vinylboron derivatives,^{3b,12} platinum catalyzed insertion of diazo compounds into B-B bonds of Bis(pinacolato)diboron (B₂pin₂),¹³ and Ir(I)¹⁴ or Co¹⁵catalyzed diborylation of benzylic C-H bonds. Besides, transition-metal-free protocols have also been developed to synthesize 1,1-diboronate esters, examples including alkylation



of deprotonated diborylmethane^{2d,4a,6a} and insertions of in-situ

generated diazo compounds into B-B bonds of B₂Pin₂.¹⁶

$$R \xrightarrow{\text{Rh(I) or [Co]}} R \xrightarrow{\text{Bpin}} Bpin$$

b) boron addition to the vinyl boron derivatives (Hall, Yun):

c) diborylation of benzylic C-H bonds (Hartwig, Chirik):

$$R_{ll} \xrightarrow{\text{Ir(l) or [Co], B_2pin_2}} R_{ll} \xrightarrow{\text{Bpin}}$$

d) Insertion of diazo compounds into B-B bonds of B₂pin₂ (Srebnik, Kingsbury, and Wang):

e) Alkylation of deprotonated diborylmethane (Matteson, Morken, and Fu)

$$\begin{array}{c|c} B(OR)_2 & \underline{LiTMP, R'X} & R' & B(OR)_2 \\ B(OR)_2 & & B(OR)_2 \end{array}$$

This work: synthesis of 1,1-diboronate esters with a fully substituted benzylic center via Lithiation-borylation method.



Scheme 1 Synthesis of 1,1-diboronate esters.

However, methods to synthesize 1,1-diboronate esters with a fully substituted benzylic center are sporadic and limited to insertion of diazo compounds to B-B bonds of B_2Pin_2 ,^{13,16} which require high reaction temperature and have scope limitations. The operational mechanism of transition-

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⁺ Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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metal-free diboration of diazo compounds consists of two steps: addition of nucleophilic diazo carbon to one of the borons in B₂Pin₂ to form a boron "ate" complex and subsequent 1,2-metallate shift of the Bpin group from the tetrahedral boron to the adjacent carbon by expulsion of the dinitrogen molecule.¹⁶ Therefore, a carbon anion tethered with a proper leaving group could also be feasible to access 1,1-diboron. Pioneered by Matteson,¹⁷ reaction of 1-halo-1lithioalkanes with organoboron compounds has emerged as the powerful chain-extension method in which halogen is served as the leaving group along with 1,2-metalate shift.¹⁸ Recently, Aggarwal and co-workers developed numerous elegant lithiation-borylation methods of secondary alcohol derived carbamates to access a variety of transformations with key step of 1,2-metallate shift of boron "ate" complexes.¹⁹ To the best of our knowledge, the central atoms of migrating groups are limited to carbon,¹⁹ hydrogen,²⁰ and silicon²¹ exclusively. In addition, successful synthesis of 1,1diborylalkenes through reaction of 1-halo-1-lithioalkenes with B₂Pin₂ demonstrates that 1,2-metalate shift of Bpin group is feasible under lithiated conditions.²² Cognizant of these results, we envisioned that the 1,1-diboronate esters could be accessible from carbamates via lithiation-borylation procedure if boryl is served as the migrating group. We herein disclose a general method for the synthesis of the 1,1-diboronate esters with a fully substituted benzylic center through lithiationborylation of secondary benzylic alcohol derived N,Ndiisopropyl carbamates with B₂Pin₂ under transition-metal-free conditions. We also demonstrate the current method is applicable to synthesize optically active 1,1-silylboronate esters.

Table 1 Optimization of lithiation-borylation reaction conditions for the synthesis of 1,1-diboronate ester **2a**^{*a*}

O Ph Me 1a	(ⁱ Pr) ₂ <u>bas</u>	se (1.5 equiv), B₂ solvent, temp.	Pin ₂ ►	Bpin Ph ∕H Bpin Me 2a
entry	base	solvent	temp. (°C)	yield (%) ^b
1 ^{<i>d</i>}	LDA	Et ₂ O	-10	0
2 ^e	LDA	Et ₂ O	-10	0
3 ^e	LDA	CpOMe	-10	0
4	LITMP	Et ₂ O	-20	6
5	LITMP	СрОМе	-20	40
6	LITMP	THF	-20	43
7	sec-BuLi	Et ₂ O	-78	94(92) ^c

^aUnless otherwise noted, the reaction conditions were as follows: **1a** (0.5 mmol), base (0.75 mmol), B₂Pin₂ (0.75 mmol), and solvent (2.75 mL) under a N₂ atomsphere. ^bGC yield. ^cisolated yield. ^dCommercialized LDA. ^efreshly prepared.

The *N*,*N*-diisopropyl carbamates **1** can be easily prepared from the reaction of corresponding secondary benzylic alcohols with diisopropylcarbamoyl chloride.^{39j} They have been known to generate carbon anions upon treatment with strong bases. Our study commenced with diboration of the **1**-phenylethanol derived carbamate **1a**. Initial investigation was concentrated on the base candidates for the deprotonation of 1a. As show in table 1, neither commercialized nor freshly prepared lithium diisopropylamide (LDA) worked for the reaction in Et₂O or cyclopentyl methyl ether (CpOMe) (table 1, entries 1-3), although LDA has been known to generate lithiated carbamates efficiently towards synthesis of tertiary boronates.²³ Then we moved to stronger base lithium tetramethylpiperidide (LiTMP) that has also been used to form lithiated carbamates.^{19P} However, the corresponding product 1,1-diboron 2a was obtained in less than 50% GC yields (table 1, entries 4-6). The reaction could not complete even with 2.0 equiv of LiTMP. To facilitate the reaction, we turned to sec-BuLi. To our great delight, treatment of carbamate 1a with 1.5 equiv of sec-BuLi in Et₂O at -78 °C for 30 min followed by addition of 1.5 equiv of B₂pin₂ resulted in complete conversion (table 1, entry 7), affording corresponding 1,1-diboronate ester 2a in 94% GC yield and 92% isolated yield. The reaction was quite sensitive to the loading amount of sec-BuLi, it was found that the reaction could not complete when less than 1.5 equiv of sec-BuLi was used.²⁴

Table 2 Substrate scope of synthesis of 1,1-diboronate estersby lithiation-borylation method a



^aUnless otherwise noted, the reaction conditions were as follows: 1 (0.5 mmol), sec-BuLi (0.75 mmol), B₂Pin₂ (0.75 mmol), and Et₂O (2.75 mL) under a N₂ atomsphere. The products were isolated by column chromatography on silica gel.

With optimized reaction conditions in hand, a series of secondary benzylic carbamates were then surveyed as shown in table 2. For the substituted 1-phenylethanol derived carbamates, the reaction underwent smoothly to give the corresponding 1,1-diboronate esters in moderate to excellent

DOI: 10.1039/C7OB00654C

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yields (table 2, 2a-e). When the substituents in phenyl rings are electron-withdrawing groups, the isolated yields are inferior (table 2, 2d and 2e) due to their being more prone to protodeboronation.²⁵ Reactions of carbamates with benzylic position of 1-naphthyl and 2-naphthyl moieties also occurred, albeit with diminished yields (table 2, 2f and 2g). The similar tendency was also found in carbamates with R in 1 of extended or branched alkyl substituents that gave the corresponding 1,1-diboronate esters in moderate yields (table 2, 2h-l). Interestingly, the unprecedented 1,1-diboronate ester 2m bearing the *m*-tolyl group in benzylic position could also be obtained in 37% yield although it was found to undergo deprotoboronation readily. Unfortunately, reaction of primary benzylic carbamate 1n under standard conditions resulted in the mixture of inseparable diborylated and mono-borylated products.

The current method is also applicable to synthesizing chiral 1,1-silylboronate esters with a fully substituted benzylic center in one step. As shown in Scheme 2, reaction of the enantioriched carbamate (S)-1a (96% ee) under standard conditions afforded the optically active 1,1-silylboronate ester 3 in 95% isolated yield with 92% ee.²⁶



Scheme 2 Synthesis of enantioriched 1,1-silylboronate ester 3.

To demonstrate the practical utility, the reaction of model substrate in gram scales was performed. As shown in Scheme 3, the 1,1-diboronate ester **2a** was isolated in 88% yield when the reaction was carried out in 1.25-gram scale under standard conditions.



Scheme 3 Gram-scale synthesis of 1,1-diboron 2a

We are interested in synthetic utility of the 1-substituted-1,1-benzyldiboronate esters **2** obtained from the new reaction,





and Scheme 4 illustrates that ${\bf 2}$ is capable in engaging in subsequent C-H and C-C bonds forming reactions. For example,

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protodeboronation of **2i** in the presence of NaOMe afforded benzylboronate ester **4** in 75% yield (scheme 4, eq. 1).²⁷ Furthermore, **2a** can undergo deborylative allylic alkylation to furnish tertiary boronate ester **5** in 89% yield (scheme 4, eq. 2).^{13c} Finally, treatment of **2a** with MeLi followed by the addition of acetophenone furnished the *tetra*-substituted olefins **6** in 42% yield (Z/E = 2: 1) (scheme 4, eq. 3).

Conclusions

We have developed a lithiation-borylation method to access 1,1-diboronate esters with a fully substituted benzylic center from secondary benzylic *N*,*N*-diisopropyl carbamates. The reaction could proceed smoothly with *sec*-BuLi as the base, affording a series of 1,1-diboron compounds in moderate to excellent yields. The readily available starting materials and transition-metal-free process allow the scale-up synthesis of 1,1-diboronate esters. We also demonstrate the current method is applicable to synthesizing optically active 1,1silylboronate esters with a fully substituted benzylic center. Further application of the 1,1-dibronates are underway in our laboratory, and the results will be reported in due course.

Acknowledgement

This work was funded by the National Natural Science Foundation of China (21573262) and Natural Science Foundation of Jiangsu Province (BK20161259).

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Diborylation of lithiated carbamtes is reported for the first time to synthesize 1,1-diboronate esters with a fully substituted benzylic center.

