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Advance Publication on the web May 15, 2020
doi:10.1246/bcsj.20200122

Tertiary Alkylations of Aldehydes, Ketones or Imines Using Benzylic Organoboronates and a Base Catalyst

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Hirohisa Ohmiya

Hirohisa Ohmiya received his Ph.D. degree from Kyoto University in 2007 under the supervision of Professor Koichiro Oshima. He spent one year as a JSPS postdoctoral fellow in the group of Professor Timothy F. Jamison at MIT. In 2008, he became an Assistant Professor at Hokkaido University working with Professor Masaya Sawamura. He was promoted to Associate Professor in 2010. Since 2017, he has been a Full Professor at Kanazawa University. He is acting as JST PRESTO Researcher (2019–2023). He received The Chemical Society of Japan Award for Young Scientists (2014) and The Young Scientists' Prize, The Commendation for Science and Technology by MEXT (2015).

Abstract

The KHMDS-catalyzed tertiary alkylation of aldehydes, ketones or imines using tertiary benzylic organoboronates is reported. This protocol permitted the use of tertiary benzylic alkylboronates as the tertiary alkyl anion for construction of highly congested contiguous sp^3 carbon centers. The mild and transition-metal-free reaction conditions are attractive features of the protocol.

Keywords: Base catalyst, Organoboron, 1,2-Addition, Alkylation

1. Introduction

The demand for construction of sp^3-carbon-rich chemical scaffolds in pharmaceuticals and bioactive natural products has increased recently.[1] C(sp^3)–C(sp^3) bond formation using a tertiary alkyl organometallic nucleophile is a direct and reliable approach for realizing highly congested sp^3-carbon-rich chemical scaffolds. Tertiary alkylboron compounds are particularly attractive organometallic reagents because of their high chemical stability and widespread availability (Figure 1A).[2] Recent progress in the catalytic preparation of tertiary alkylborons from various simple organic molecules is remarkable.[3] Nevertheless, catalytic C(sp^3)–C(sp^3) bond formation using tertiary alkylborons is still in its infancy given the limited progress in recent years.[4] Specifically, 1,2-addition of tertiary alkylborons to carbon–heteroatom bonds is limited to the use of aldehydes with a rhodium catalyst and imines under an iridium-based photoredox catalyst as reported by Aggarwal[5a] and Molander[5b], respectively.

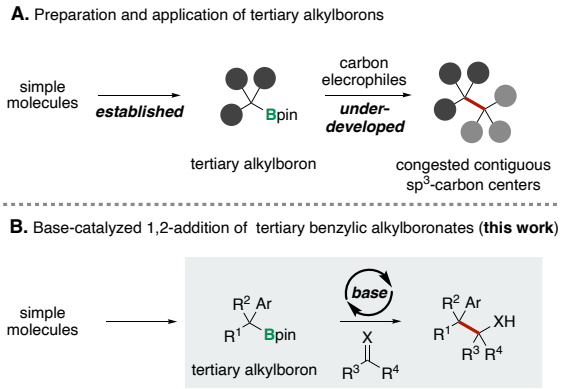


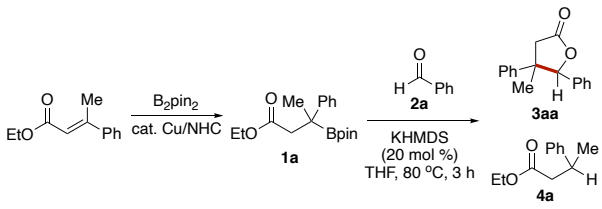
Figure 1. Preparation and application of tertiary alkylborons

In a study on new methodology based on the formation of a secondary α-alkoxyalkyl anion from the aldehyde,[6] our focus has been the generation of a tertiary alkyl anion and its application to C(sp^3)–C(sp^3) bond formation. We report here the tertiary alkylations of aldehydes, ketones, or imines using teriary benzylic organoboronates and a base catalyst (Figure 1B).[7] The reaction involves the generation of tertiary alkyl anions from organoboronates under mild and transition-metal-free reaction conditions. The protocol allows the construction of highly congested contiguous sp^3-carbon centers.

2. Results and Discussion

In numerous studies in this laboratory, we have found that the reaction between tertiary alkylboronate **1a** (0.2 mmol), easily prepared by copper-catalyzed conjugate addition with bis(pinacolato)diboron (B_2pin_2) and β,β-disubstituted α,β-unsaturated ester,[3b] and benzaldehyde (**2a**) (0.24 mmol) occurred in the presence of a catalytic amount of KHMDS (20 mol %) in THF at 80°C to provide the desired γ-lactone (**3aa**) with an 88% yield (Table 1, entry 1). Other alkali metal hexamethyldisilazides such as NaHMDS and LHMDS were less effective (entries 2 and 3). The use of a less nucleophilic alkoxide base gave only a moderate yield, although a significant amount of deborylprotonated product **4a** was observed (entries 4 and 5).

Table 1. Screening of conditions for allylation of **1a** with **2a**[a]



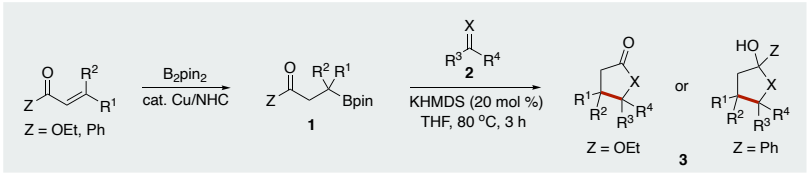
Entry	Change from standard conditions	Yield (%) of **3aa**[b, c]	Yield (%) of **4a**[b]
1	none	98 (88)	0
2	NaHMDS instead of KHMDS	29	0
3	LHMDS instead of KHMDS	0	0
4	KO^{t}Bu instead of KHMDS	54	46
5	KOMe instead of KHMDS	68	32

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), KHMDS (20

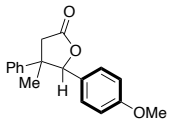
mol %), THF (1 mL), 80 °C, 3 h. [b]^{1}H NMR yield based on **1a**. Yield of the isolated product is in parentheses. [c]diastereomeric ratio (1:1). KHMDS: potassium hexamethyldisilazide. NaHMDS: sodium hexamethyldisilazide. LHMDS: lithium hexamethyldisilazide.

It should be noted that this overall process represents a reductive umpolung β-functionalization of β,β-disubstituted α,β-unsaturated carbonyls. The reductive umpolung β-functionalization of α,β-unsaturated carbonyls has been extensively studied. [8,9] For example, N-heterocyclic carbene (NHC) catalysis enabled the generation of a β-carbonylalkyl anion (homoenolate) from a α,β-unsaturated aldehyde and its application to carbon–carbon bond formation.[8] However, this process has not yet been applied to the formation of a tertiary β-carbonylalkyl anion from β,β-disubstituted α,β-unsaturated carbonyls.

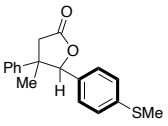
Table 2. Scope of substrates[a,b]



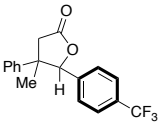
Aldehydes, Ketones & Imines with 1a



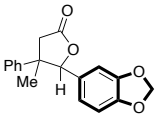
3ab, 73% (1:1.1)



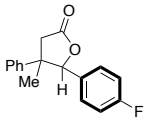
3ac, 85% (1:1)



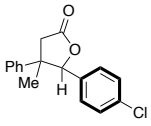
3ad[c], 54% (1:1.6)



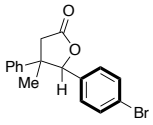
3ae, 81% (1:1.1)



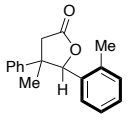
3af, 77% (1:1.1)



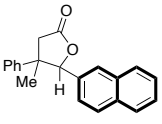
3ag, 54% (1:1.1)



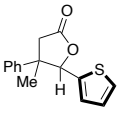
3ah, 76% (1:1)



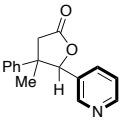
3ai, 66% (1:1.2)



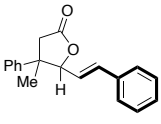
3aj, 75% (1:1.1)



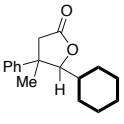
3ak, 80% (1:1.1)



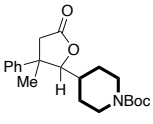
3al, 36% (1:1.5)



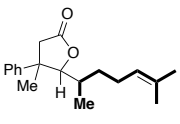
3am, 33% (1:1.1)



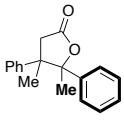
3an, 64% (1:1.1)



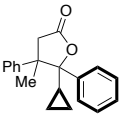
3ao, 52% (1:1.1)



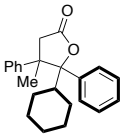
3ap, 47%[d]



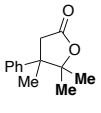
3aq, 93% (1:1.1)



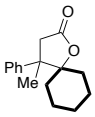
3ar, 93% (1:1.2)



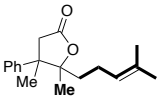
3as[e], 66% (1:1.7)



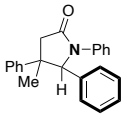
3at[f], 70%



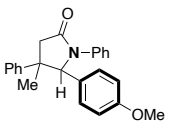
3au, 73%



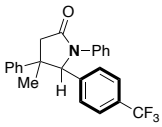
3av, 61% (1:1)



3aw, 83%[g] (1:1.2)

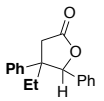


3ax, 89%[g] (1:1.4)

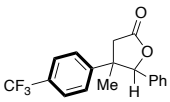


3ay, 74%[g] (1:1.3)

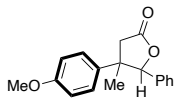
Alkylboronates with 2a



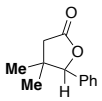
3ba, 77% (1:1)



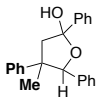
3ca, 67% (1:1.3)



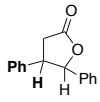
3da[e], 28% (1:1.1)



3ea, 0%



3fa[h], 50%[d]



from sec-alkylboronate
3ga[i], 58% (1:1.4)

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.24 mmol), KHMDS (20 mol %), THF (1 mL), 80°C, 3 h. [b]Number in parenthesis is diastereomeric ratio. [c]KHMDS (30 mol %) was used. [d]Diastereomeric ration was not determined. [e]The reaction was carried out at 100 °C. [f]Acetone (0.3 mmol) was used. [g]$ZnCl_2$ (20 mol %), KHMDS (80 mol %), THF (1 mL), 80°C, 3 h. [h]18-crown-6 (20 mol %) was added. [i]**2a** (0.4 mmol) was used.

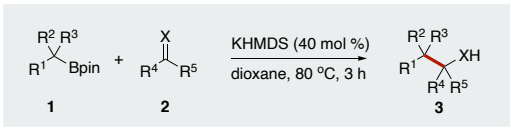
Under optimized reaction conditions, we next explored the scope of the substrate in the base-catalyzed 1,2-addition reaction (Table 2). A broad array of aryl aldehydes was found to act as suitable substrates (Table 2, top). Both electron-rich and electron-poor functional groups did not affect the product yield (**3ab**–**ah**). Halogen substituents were well tolerated (**3af**–**ah**). The aromatic aldehyde possessing an *o*-substituent was coupled with **1a** to give the corresponding γ-lactone product (**3ai**). Naphthalene and heteroaromatic rings such as thiophene and pyridine were also found to be good substrates (**3aj**–**al**). The reaction with cinnamyl aldehyde gave only the 1,2-adduct product (**3am**). In addition to aromatic aldehydes, aliphatic aldehydes participated in the reaction. For example, α-branched aldehydes underwent the reaction (**3an**–**ap**). However, the use of unbranched aliphatic aldehydes was not successful, possibly due to the occurrence of the self-aldol reactions (data not shown).

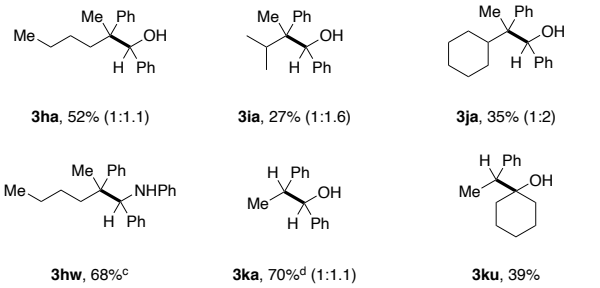
The protocol was also possible with ketones, allowing the construction of highly congested continuous quaternary carbon centers (Table 2). Acetophenone, which bears an acidic α-proton, underwent the 1,2-addition to give the desired product in excellent yield (**3aq**). The cyclopropyl or the cyclohexyl group participated in this reaction (**3ar**, **as**). The reaction with the simple molecule acetone gave the β,β-dimethyl-γ-lactone (**3at**) in high yield. Cyclohexanone was coupled with organoboron to give a spirolactone scaffold (**3au**), which is found in many bioactive compounds. The presence of an alkene moiety in the ketone substrate was tolerated (**3av**).

Imines were evaluated as coupling partners (Table 2). The addition of catalytic amounts of zinc salt was required to improve the product yield.[10] The reaction of electron-rich and electron-poor imines afforded the corresponding lactams (**3aw**–**ay**). The reactions with ketimine under several conditions resulted in no conversion of the substrate (data not shown).

Next, we investigated the scope of the β-carbonylalkylboronates, which are prepared through copper-catalyzed borylation of α,β-unsaturated carbonyls (Table 2). An ethyl group instead of the methyl substituent at the β-position was tolerated (**3ba**). A trifluoromethyl group on the aromatic ring at the β-position did not affect the product yield (**3ca**). However, a methoxy group drastically diminished the reaction efficiency (**3da**). The reaction with β,β-dialkyl borylacrylate resulted in no product being formed (**3ea**). Thus, the applicability of this protocol seems to be limited to benzylboronates, the results indicating that the reaction would proceed through the formation of the benzyl anion from the organoboronate (*vide infra*). The reaction with β-ketoalkylboronate proceeded to afford the corresponding hemiketal product in high yield (**3fa**). The protocol is not limited to cases with tertiary alkylboronates. The secondary alkylboronate derived from borylation of cinnamyl ester was also found to be a suitable substrate (**3ga**). Although the data was not shown, the ring-fused alkylboron compounds did not work at all.

Table 3. Scope of substrates[a, b]





[a]Reaction conditions: **1** (0.2 mmol), **2** (0.24 mmol), KHMDS (40 mol %), 1,4-dioxane (1 mL), 80°C, 3 h. [b]Number in parenthesis is diastereomeric ratio. [c]Diastereomeric ration was not determined. [d]KHMDS (20 mol %) was used.

The carbonyl group at the β-position of the alkylboronates is not necessary for promotion of the reaction (Table 3). For example, the reaction between tertiary alkylboronate **1h** and benzaldehyde **2a** gave the corresponding product in moderate yield (**3ha**). The alkylboronates having a bulky substituent participated in the reactions to construct the highly congested contiguous sp^3 carbon centers, although the product yields were low (**3ia** and **3ja**). The same substrate **1h** was also applicable to the reactions with imine (**3hw**). The secondary alkylboronate **1k** having a hydrocarbon backbone served as a substrate (**3ka** and **3ku**).

To gain insights into the mechanism of the base-catalyzed 1,2-addition of alkylboronates, the experiments using the chiral alkylboronates were conducted (Figures 2A–C). When the chiral β-borylacrylate (*S*)-**1a** was subjected to the optimal conditions, a complete loss of chiral information was observed (Figure 2A). The use of chiral alkylboronate (*R*)-**1h** having a hydrocarbon backbone resulted in some erosion of enantiomeric purity (Figure 2B). The reaction of (*S*)-**1l** and **2a** occurred with complete stereospecificity (Figure 2C). The derivatization of **3la** to (*R*)-**5la** by PCC oxidation indicated that the addition proceeded with retention of configuration. These are in contrast to the disappearance of the chirality in the reaction with (*S*)-**1a** (Figure 2A vs Figures 2B, 2C). We assumed that the 1,2-addition of the boron-ate derived from (*R*)-**1h** or (*S*)-**1l** would be faster than racemization of the chiral benzyl anion formed by a significant C–B bond cleavage.[11] The observed drop of stereospecificity in **3ha** bearing sterically hindered butyl group is consistent with this assumption.

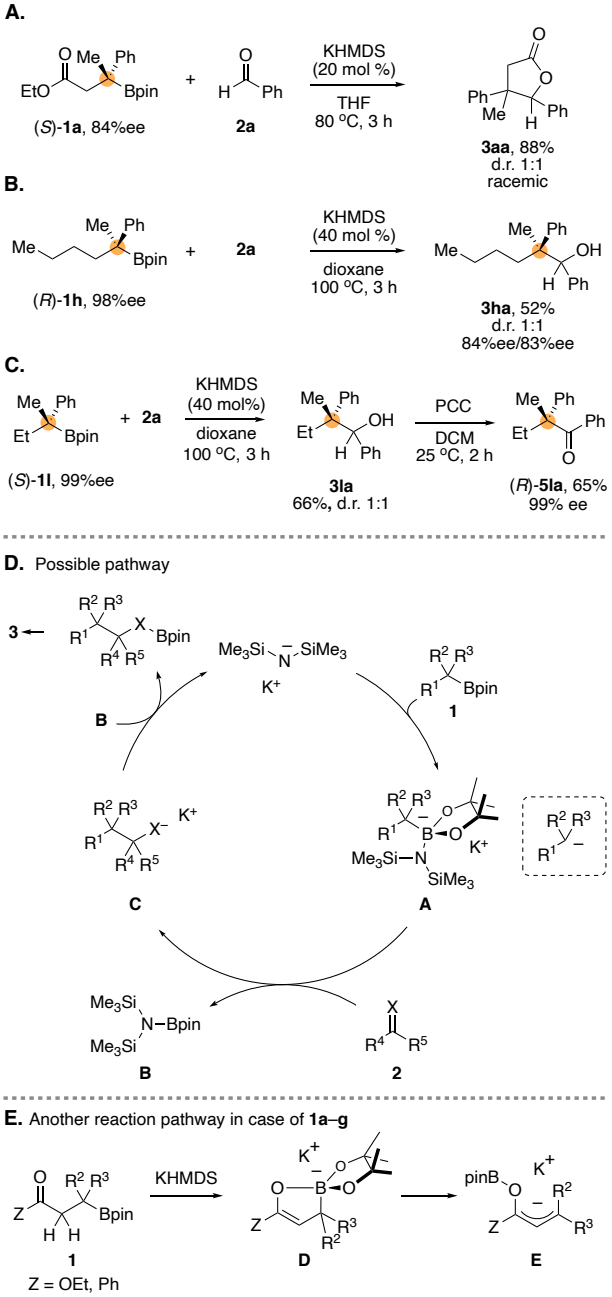


Figure 2. Mechanistic considerations

Based on the experiments outlined above, a reaction pathway for the KHMDS-catalyzed alkylation was proposed as shown in

Figure 2D. Initially, the reaction between KHMDS and the alkylboronate **1** produces the organoborate intermediate **A** as a tertiary alkyl anion equivalent.[7b, 12, 13] Then, the reaction of borate **A** with **2** forms the 1,2-adduct **C** with the formation of aminoboron **B**. Finally, **C** reacts with **B** to produce **3** with regeneration of KHMDS. When **1** has an ester group at the β-position, **C** undergoes an intramolecular substitution to give the γ-lactone and the alkoxide anion, which can act as a base catalyst for the next cycle. In the case of β-carbonylalkylboronates **1a–g**, α-deprotonation by KHMDS might cause the facile formation of the organoborate **D** due to the intramolecular coordination of the enolate to the boron center (**D→E**, Figure 2E). This borate would lead to the facile C–B bond cleavage causing the problematic racemization before 1,2-addition event. This mechanism provides the good explanation to the result of Figure 2A.

3. Conclusion

In summary, KHMDS-catalyzed tertiary alkylation of aldehydes, ketones or imines using tertiary benzylic organoboronates has been demonstrated. The protocol enabled the use of tertiary benzylic alkylboronates as tertiary alkyl anions for the construction of the highly congested contiguous sp^3 carbon centers. The mild and transition-metal-free reaction conditions are attractive features of the protocol. Extending the scope of the reaction to electrophiles and further mechanistic studies are in progress.

4. Experimental

Procedure for Lewis Base-Catalyzed Tertiary and Secondary Alkylations of Aldehydes and Ketones. β-Borylacrylate **1a** (63.6 mg, 0.2 mmol) was placed in a schlenk tube containing a magnetic stirring bar. The tube was sealed with a rubber septum, and then evacuated and filled with nitrogen. THF (1.0 mL), KHMDS (8.0 mg, 0.04 mmol) and benzaldehyde (**2a**) were sequentially added to the tube. After 3 h stirring at 80 ˚C, the reaction mixture was diluted with ethyl acetate (1 mL) then filtered through a short plug of silica gel with ethyl acetate as an eluent. After volatiles were removed under reduced pressure, flash column chromatography on silica gel (100:0–90:10, hexane/EtOAc) gave **3aa** (44.3 mg, 0.175 mmol) in 88% yield. 4-Methyl-4,5-diphenyldihydrofuran-2(3H)-one (**3aa**). The product **3aa** was purified by flash chromatography on silica gel (100:0–90:10, hexane/EtOAc) (Table 1, entry 1; 44.3 mg, 0.18 mmol, 88% isolated yield). The diastereomeric ratio is 1:1 determined by ^{1}H NMR.

Acknowledgement

This work was supported by JSPS KAKENHI Grant Number JP18H01971 to Scientific Research (B), JSPS KAKENHI Grant Number JP17H06449 (Hybrid Catalysis), and Kanazawa University SAKIGAKE project 2018 (to H.O.).

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