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An Improved Synthesis Route to Functionalized 2-Alkyn-1-ylboronates: Useful Intermediates for the Preparation of α-Allenic Alcohols†

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Summary. Functionalized 2-alkyn-1-ylboronates were successfully prepared in good yields by reacting various acyclic and cyclic (iodomethyl)boronates with various alkynyllithium salts. Amongst various (iodomethyl)boronates studied, 2-(iodomethyl)-1,3,2-dioxa-4,4,5,5-tetramethylborolane provided improved chemical yields of 2-alkyn-1-ylboronates with pyran- and triisopropylsilyl-substituted alkynyllithium salts. 2-Alkyn-1-ylboronate bearing an acid sensitive structure (pyran) was successfully synthesized which would be very difficult to achieve under previously reported reaction conditions. The exceptionally rapid rearrangement of the "ate" complex derived from the pinacol (iodomethyl)boronate, suppression of the side product formation, and the stability of the pinacol 2-alkyn-1-ylboronate are some of the notable merits of this protocol. This new procedure offers a simple and convenient alternative route to the existing methodologies, in terms of the milder reaction conditions, functional group compatibility, and the ease of the operation. The synthesis scope of this class of 2-alkyn-1-ylboronates was demonstrated by reacting the pinacol 2-alkyn-1-ylboronate with benzaldehyde, which yielded the α-allenic alcohol in good yield and regioselectivity.

Keywords. 2-Alkyn-1-ylboronates; (Iodomethyl)boronates; Alkynyllithium salts; α-Allenic alcohol.

Introduction

The synthetic applications of allyl-, allenyl-, and propargylboranes are well recognized [1]. Allenyl and propargylic alcohols have been utilized extensively not only as building blocks for the synthesis of biologically active molecules such as (±)-9-deoxygoniopypyrone [2], 3-deoxy-D-glycero-D-galacto-2-ulosonic acids (*KDN*) [3], mono-*THF* acetogenins [4], and an immunosuppressant discodermolide [5], but also in coupling reactions [6] and in ene-yne metathesis [7]. Conceptually, the most attractive method appears to be the regiospecific addition of allenyl and propargyl nucleophiles to carbonyls, but these metal-mediated propargylation/allenylation suffer from regioselectivity due to the metallotropic rearrangement of these species and nonregiospecific addition to electrophiles [8]. A highly efficient transformation of an organotin intermediate into propargylboron reagent in excellent isomeric purity was reported by *Corey* and co-workers [9]. An insertion of a CH_2 group between the carbon and boron atom of the C–B bond, *via in situ* generation and capture of (halomethyl)lithiums, $LiCH_2X$, has proven to be a very important methodology for a variety of synthetic transformations [10]. One of the salient features of this one-carbon homologation is that the rearrangement of the initially formed "ate" complex takes place with absolute stereochemical integrity, which makes it a highly valuable reaction for general asymmetric syntheses utilizing organoboranes.

Matteson et al. found that the $LiCH_2Br$ was a much superior reagent compared to that of $LiCH_2Cl$, which suffers from certain problems, such as low reactivity and occasional β-elimination and oxygen

†Dedicated to my mentor, Professor *Herbert C. Brown*, who passed away on December 19, 2004 (1912–2004). The work described herein was carried out at Purdue University during my stay as a post-doctoral research associate (1995–2001)

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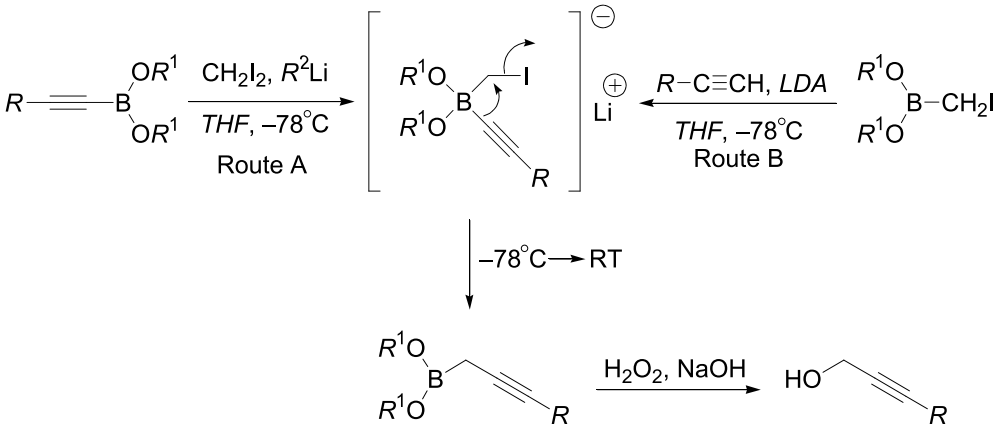

Fig. 1. Generation of a common "ate" complex

migration [11]. *Wallace* and *Zong* were able to improve the chemical yield of homologated boronic ester derived from Δ^2-isoxazolines when $LiCH_2I$ was generated from CH_2I_2 and *Me*Li, instead of *n-Bu*Li [12]. Encouraged by this unique behavior of $LiCH_2I$ carbenoid, a systematic study was undertaken to compare the relative reactivities of all the three (halomethyl)lithium reagents ($LiCH_2X$; $X = Cl$, Br, and I) with a wide variety of boronic esters in this laboratory [13]. This study revealed significant differences in reactivities, especially with alkenyl- and alkynylboronates. Alkynylboronates reacted much faster with $LiCH_2I$ while the alkenylboronates exhibited little difference in rates among all three (halomethyl)lithiums. This unique reactivity of alkyn-1-ylboronates due to the nature of the alkynyl-boron bonds in the "ate" complex is quite contrast to other classes of boronates, such as, alkyl-, alken-1-yl-, and arylboronates [14]. Later, a new general procedure for the preparation of higher propargylboronates in excellent isomeric purity (Fig. 1, Route A) was developed [15]. This successful synthesis of 2-alkyn-1-ylboronates was based on one-carbon homologation strategy. This method has certain limitations, such as, preparation of an individual starting alkynylboronates [16], avoidance of alkynylboronates bearing acid-sensitive functionalities (due to HCl treatment), significant formation of side products, and the instability of the acyclic propargylboronates. In view of the importance of propargylboronates in organic synthesis, it was of considerable interest to develop a practical, convenient, and general procedure. We reported a highly general procedure for the preparation of 2-alkyn-1-ylboronates in our preliminary communication (Fig. 1, Route B) [17] and herein present a detailed study of reactions of acyclic and cyclic (iodomethyl)boronates with various functionalized alkynyllithium salts.

Results and Discussion

Selection of Various (Iodomethyl)boronates ***1–4***

Reactions of alkynyllithium salts (generated *in situ* from the corresponding alkynes and *LDA*) with diisopropyl (iodomethyl)boronate would essentially produce an "ate" complex identical to the one formed in the previously reported procedure, which eventually would be expected to rearrange to the corresponding propargylboronates (Fig. 1). This strategy avoids the synthesis of an individual functionalized alkynylboronate (starting substrate). The commercially available functionalized alkynes can be used directly to generate alkynyllithium salts *in situ* in a

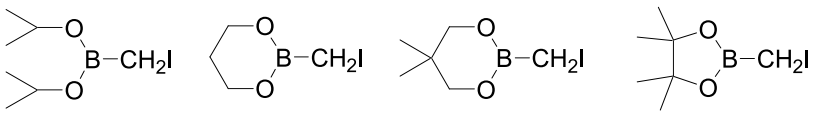

Fig. 2. Various (iodomethyl)boronates **1–4**

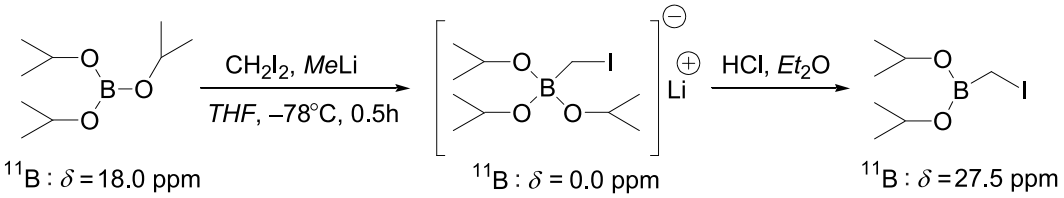

Fig. 3. Reaction of triisopropyl borate with carbenoid, $LiCH_2I$

single pot. Considering the stability of cyclic boronic esters, it was desirable to examine both acyclic and cyclic boronates (Fig. 2) [18]. Also, the selection of (iodomethyl)boronates was based on the literature report because the ''ate'' complex derived from alkynylboronate and $LiCH_2I$ provided results superior to those achieved with $LiCH_2Br$ and $LiCH_2Cl$ [13].

*Preparation of Diisopropyl (Iodomethyl)boronate (**1**)*

Previously, diisopropyl (iodomethyl)boronate (**1**) was prepared from triisopropyl borate and *in situ* generated $LiCH_2I$ using *n-Bu*Li in only 70% chemical yield [19]. The use of *Me*Li significantly improved the chemical yield of diisopropyl (iodomethyl)boronate (>92.4% based on ^{11}B NMR after dry HCl treatment). The isolated yield was >80% after distillation under reduced pressure (Fig. 3). Formation of side product *n-Bu*I (bp = 130–131°C) and unreacted starting borate always contaminated the product during fractional distillation. The use of *Me*Li in place of *n-Bu*Li not only improves the chemical yield (>90%) of the diisopropyl (iodomethyl)boronate but also makes the purification step easier. The *Me*Li procedure produces *Me*I which being a very low boiling liquid (bp = 41–43°C) makes the fractional distillation simpler.

*Reactions of Diisopropyl (Iodomethyl)boronate (**1**) with Various Alkynyllithium Salts*

Diisopropyl (iodomethyl)boronate (**1**) (^{11}B NMR at $\delta = 7.5$ ppm) was treated with *in situ* generated alkynyllithium salt at −78°C in *THF* (Fig. 4). The capture of alkynyllithium salt was almost instantaneous leading to the formation of the intermediate ''ate'' complex (^{11}B NMR at $\delta = -2.0$ to $+2.0$ ppm), which then slowly rearranged to the propargylboronate. The progress of the reaction was easily monitored by ^{11}B NMR with the disappearance of the ''ate'' complex peak and the appearance of the product propargylboronate peak ($\delta = +27.0$ ppm). These higher propargylboronates could not be isolated and characterized due to their inherent labile nature. Therefore, these propargylboronates were oxidized to propargylic alcohols with alkaline H_2O_2 and characterized spectroscopically (Fig. 5). The results obtained with representative alkynyllithium salts are summarized in Table 1.

This methodology appeared to be highly general accommodating alkynes bearing representative functional groups. It was important to note that the generation of the ''ate'' complex at 0°C, instead of, at −78°C, had little or no effect on the chemical yields of the propargylboronates, while greatly simplifying the experimental procedure. Formation of the ''ate'' complex was quantitative, with the moderately lower yields of the products due to the parallel formation

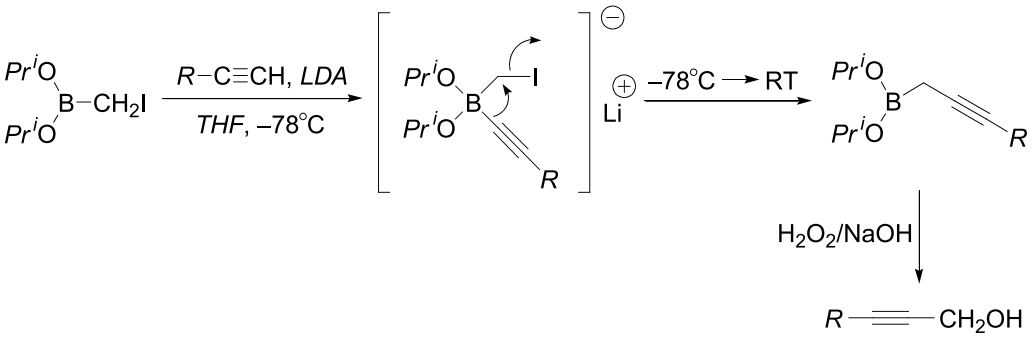

Fig. 4. Reactions of diisopropyl (iodomethyl)boronate (**1**) with various alkynyllithium salts

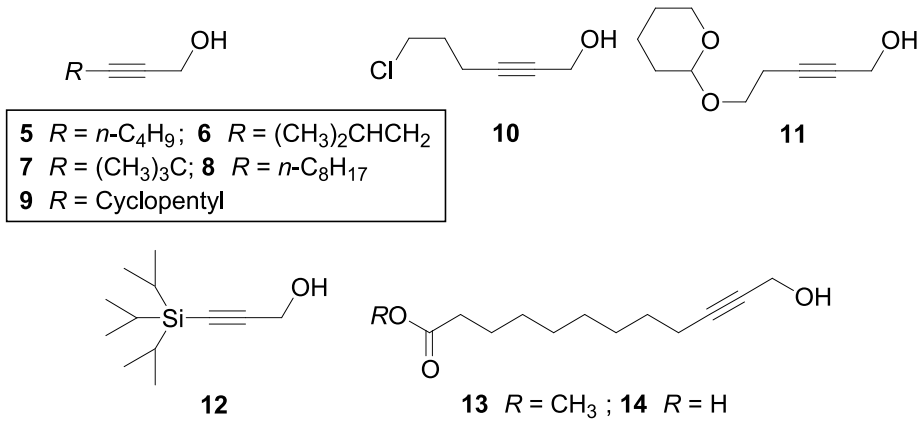

Fig. 5. Various propargylic alcohols **5**–**14**

Table 1. Reactions of diisopropyl (iodomethyl)boronate (**1**) with various alkynyllithium salts[a] *via* reactions shown in Fig. 4

Entry	$RC{\equiv}CCH_2B(O^iPr)_2$ (*R*)	Time/ h	Yield of $RC{\equiv}CCH_2OH$ after oxidation/%[b–c]
1	n-C_4H_9	2.0	65
2	$(CH_3)_2CHCH_2$	2.0	63
3	$(CH_3)_3C$[c]	2.5	80
4	n-C_8H_{17}	3.0	66
5	C_5H_9	1.5	64
6	$Cl(CH_2)_3$	3.5	80
7	2-(CH_2CH_2O)pyran	3.0	62
8	$[(CH_3)_2CH]_3Si$	22.0	53
9	$CH_3O_2C(CH_2)_8$	1.75	45

[a] 1.10 Equiv. of the reagent used
[b] Yields based on the ^{1}H NMR analyses of the alcohols produced by the oxidation of the propargylboronates with alkaline hydrogen peroxide using biphenyl as the internal standard
[c] Isolated yields were 3–5% lower than their NMR yields

of a side product (^{11}B NMR at $\delta = 17.5$ ppm). Earlier, we had made few attempts to characterize the side product, but without success [15]. The persistence of such impurity even after hydrolysis clearly ruled out the possibility of any tricoordinated borate species. The absence of a carbonyl stretching frequency ($\bar{\nu}_{C=O} \approx 1720\,cm^{-1}$) and an allenic frequency ($\bar{\nu}_{C=C=C} \approx 1930\,cm^{-1}$) in IR spectrum of the crude propargylic alcohol also eliminated the presence of any allenic intermediate possibly formed by the 1,3-rearrangement of the initially formed 2-alkyn-1-ylboronates (IR absorptions for propargylboronates: $\bar{\nu}_{C\equiv C} \approx 2220\,cm^{-1}$ and allenylboronates: $\bar{\nu}_{C=C=C} \approx 1925\,cm^{-1}$). The product undergoes complete decomposition in <2 days at room temperature. A sample kept at 0°C for several days showed little decomposition of the product, propargylboronate. On the other hand, the pure 2-alkyl-1-ylboronate completely transformed to the undesired side product ($\delta = 17.5$ ppm) when heated to 65°C for few hours. The completely converted undesired side product upon alkaline hydrogen peroxide oxidation yielded an unidentified sticky polymeric material that did not show any carbonyl or hydroxyl frequencies in IR spectrum. In the case of (triisopropylsilyl)-acetylene, the rearrangement of the ''ate'' complex was observed to be much slower than other acetylenes, which contributed to the formation of more undesired side product. The side product appeared to build up by the destruction of main product, propargylboronates. In another experiment, an alkynyllithium salt was generated separately at −78°C and was added to the (iodomethyl)boronic ester to form the ''ate'' complex, hoping to avoid any parallel reactions, such as, the possible coordination of *LDA* with boronate. Unfortunately, the experimental result showed no improvement in the chemical yield.

Table 2. Reactions of 2-(iodomethyl)-1,3,2-dioxaborinane (**2**) with various alkynyllithium salts[a]

Entry	$RC{\equiv}CCH_2B$-$[(OCH_2)_2CH_2]$ (*R*)	Time/ h	Yield of $RC{\equiv}CCH_2OH$ after oxidation/%[b,c]
1	n-C_8H_{17}	2.5	53
2	2-(CH_2CH_2O)pyran	3.5	45
3	$[(CH_3)_2CH]_3Si$	3.5	65

[a] 1.10 Equiv. of the reagent used
[b] Yields based on the ^{1}H NMR analyses of the alcohols produced by the oxidation of the propargylboronates with alkaline hydrogen peroxide using biphenyl as the internal standard
[c] Isolated yields were 3–5% lower than their NMR yields

Our next objective was essentially to improve the chemical yields of the various propargylboronates and simultaneously suppress the formation of the undesired side products. Our detailed study on the relative stability of various boronic esters employing transesterification suggested that a library of relatively more stable (iodomethyl)boronates could be synthesized from acyclic diisopropyl (iodomethyl)-boronate (**1**) by simple transesterification with the desired diols [20]. Three cyclic (iodomethyl)boronates, 2-(iodomethyl)-1,3,2-dioxaborinane (**2**), 2-(iodomethyl)-1,3,2-dioxa-5,5-dimethylborinane (**3**), and 2-(iodomethyl)-1,3,2-dioxa-4,4,5,5-tetramethylborolane (**4**), were prepared by transesterification of diisopropyl (iodomethyl)boronate (**1**) with the corresponding diols in dry *n*-pentane in almost quantitative yields and identified by ^{11}B, ^{1}H, and ^{13}C NMR spectroscopy.

The ''ate'' complexes derived from 2-(iodomethyl)-1,3,2-dioxaborinane (**2**) and alkynyllithium salts rearranged to propargylboronates at 0°C much faster than the corresponding acyclic diisopropyl (iodomethyl)boronate (**1**) (Table 2). In the case of 1-decyne, more than 60% rearrangement of the ''ate'' complex ($\delta = -2$ to $+2$ ppm) to propargylboronate ($\delta = +28.5$ ppm) was complete in <5 min in the probe of NMR spectrometer whereas the ''ate'' complex derived from diisopropyl (iodomethyl)boronate did not show any appreciable amount of rearranged product in 5 min (~25% in 20 min). The ''ate'' complex derived from (triisopropylsilyl)acetylene rearranged relatively slowly (50% in 0.5 h). The ''ate'' complex derived from 2-(3-butynyloxy)tetrahydro-2*H*-pyran rearranged 50% in <5 min. Interestingly, the formation of side product was suppressed considerably, but not completely. Only 5–6% of the side product (^{11}B NMR at $\delta = 17.5$ ppm) could be observed after 1.5 h. To ensure the quantitative capture of boronate with alkynyllithium salt, *LDA* was added at −78°C and the ^{11}B NMR spectrum was recorded immediately. After 0.5 h, ^{11}B NMR spectrum showed the complete absence of the starting boronate (^{11}B NMR at $\delta = 28.5$ ppm). Surprisingly, the chemical yields of the desired products did not improve substantially. We had observed the drop in chemical yield by 10% when the ''ate'' complex derived from 1,3-propanediol heptyn-1-ylboronate (81%) was used in place of diisopropyl heptyn-1-ylboronate (91%) with $LiCH_2I$. 2-(Iodomethyl)-1,3,2-dioxa-5,5-dimethylborinane (**3**) also provided results (comparable chemical yields) similar to those obtained from 2-(iodomethyl)-1,3,2-dioxaborolane (**2**) with representative alkynyllithium salt. Although the rearrangement of the ''ate'' complex was slightly faster than its unsubstituted analog, the formation of the side product (5–6%) could not be completely suppressed in this case also.

*Reactions of 2-(Iodomethyl)-1,3,2-dioxa-4,4,5,5-tetramethylborolane (**4**) with Various Functionalized Alkynyllithium Salts*

The ''ate'' complex derived from the pinacol (iodomethyl)boronate (**4**) rearranged slightly faster than the ''ate'' complexes derived from cyclic (iodomethyl)boronates **2** and **3**. More than 70–75% rearrangement was complete in 0.5 h in almost all the cases (Fig. 6). Even the ''ate'' complex derived from the (triisopropylsilyl)acetylene rearranged rapidly to the desired propargylboronate (>60% in <5 min). We

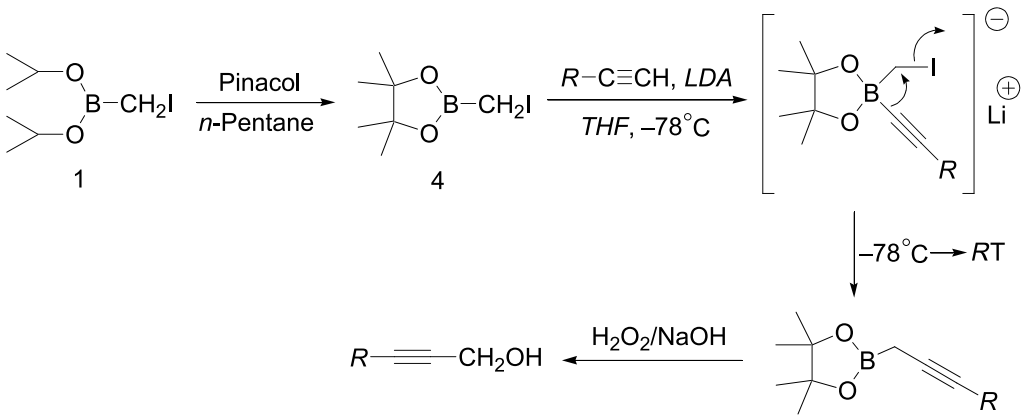

Fig. 6. Reactions of 2-(iodomethyl)-1,3,2-dioxa-4,4,5,5-tetramethylborolane (**4**) with various alkynyllithium salts

Table 3. Reactions of 2-(iodomethyl)-1,3,2-dioxa-4,4,5,5-tetramethylborolane (**4**) with various alkynyllithium salts[a] *via* reactions shown in Fig. 6

Entry	$RC{\equiv}CCH_2B$-$[OCH_2C(CH_3)_2{-}]_2$ (*R*)	Time/h	Yield of $RC{\equiv}CCH_2OH$ after oxidation/%[b]
1	n-C_8H_{17}	1.5	72
2	$Cl(CH_2)_3$	2.0	74
3	2-(CH_2CH_2O)pyran	2.5	76
4	$[(CH_3)_2CH]_3Si$	2.5	71
5	$CH_3O_2C(CH_2)_8$	1.0	61

[a] 1.25 Equiv. of the reagent used
[b] Yields based on the ^{1}H NMR analyses of the alcohols produced by the oxidation of the propargylboronates with alkaline hydrogen peroxide using biphenyl as the internal standard

were pleased to note that the formation of side product was completely suppressed. It was interesting to note that the pinacol propargylboronate derived from *n*-decynyllithium salt showed no significant deterioration (<2%) even after 24 h at room temperature. Significant improvements in chemical yields were also noticed with pyran- and triisopropylsilylalkynyllithium salts. Gratifyingly, pinacol (iodomethyl)-boronate (**4**) reacted rapidly with alkynyllithium salt derived from undec-10-ynoic acid methyl ester. The results of this study are summarized in Table 3.

Reaction of Pinacol Propargylboronate with Benzaldehyde

After successful preparation of reasonably stable propargylboronates, we were interested in synthesizing both achiral and chiral propargylboronates using our new methodology and study the diastereo- and enantioselective addition of carbonyl compounds. Unlike alken-1-yl- and allenylboronates, the propargylboronates appear to be much less reactive. Benzaldehyde, being an active aldehyde, did not react with the propargylboronate derived from 2-(iodomethyl)-1,3,2-dioxa-4,4,5,5-tetramethylborolane and *n*-decynyllithium salt, at −78°C (monitored by ^{11}B NMR). The reaction was found to be slow even at 0°C. The reaction took 14–18 h for completion at room temperature which upon oxidative workup afforded an α-allenic alcohol, 2-octyl-1-phenyl-2,3-butadien-1-ol (**15**) in 60% chemical yield (Fig. 7). The ^{1}H NMR spectrum of the oxidized crude product did not show any detectible amount of propargylic alcohol.

Conclusions

To conclude, we developed a simple, convenient, and general method for the preparation of a variety of functionalized propargylboronates in good chemical yields with excellent isomeric purity. The present procedure has several advantages over the first one. The second new methodology utilizes mild reagent, *LDA* (as compared to that of *n-Bu*Li) that is more beneficial for the functionalized boronic esters. This procedure also avoids the necessity of making individual cyclic and acyclic boronates. Various propargylboronates can simply be synthesized by just using different alkynes. The mildness of the procedure and the ability to run the reaction at ambient

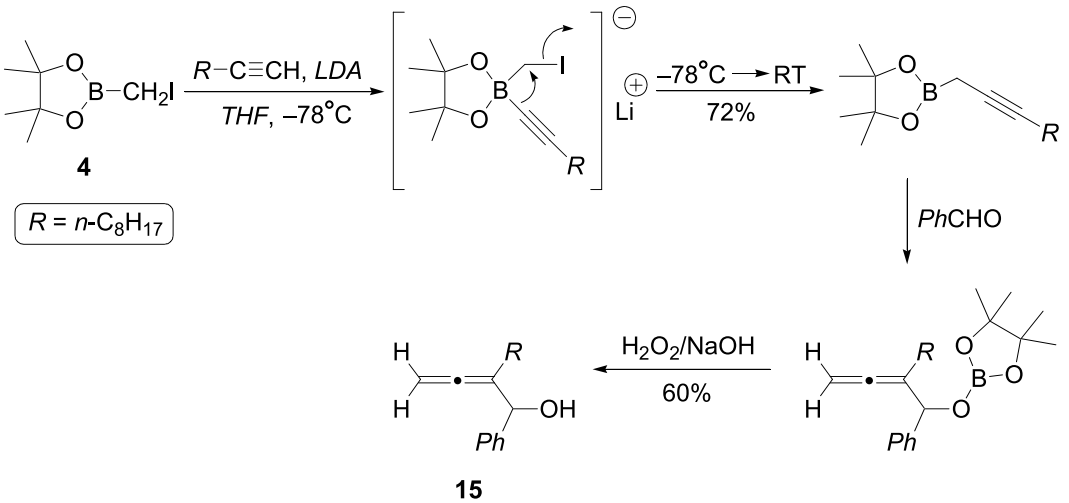

Fig. 7. Reaction of pinacol propargylboronic ester with benzaldehyde

conditions make it a simple and convenient alternative route for the large-scale reactions. Even an acid sensitive group, *e.g.*, acetal, which would be difficult to accommodate using previously developed methodology (due to the utilization of dry HCl in the preparation of starting alkyn-1-ylboronates), has been accommodated. The formation of the undesired side product, which could not be completely avoided in the first procedure, has been suppressed. Pinacol propargylboronates have been found to be the most stable ones amongst cyclic and acyclic analogs. The pinacol propargylboronate reacts with benzaldehyde with excellent regioselectivity yielding the α-allenic alcohol. This class of α-allenic alcohols is very useful as intermediates in organic synthesis.

Experimental

All air and moisture sensitive reactions were carried out under nitrogen using oven-dried glassware. The ^{11}B (96 MHz), ^{1}H (300 MHz), and ^{13}C (75 MHz) NMR spectra were recorded on a Varian Gemini NMR instrument, and the chemical shifts (δ) are given in ppm relative to external standard BF_3–*Et*$_2$O and internal standards *TMS* and $CDCl_3$ respectively. IR and Mass spectra were recorded on Perkin Elmer 137 IR and Finnegan mass spectrometers. *THF* was freshly distilled from sodium benzophenone ketyl. *Me*Li, and *LDA* were purchased from the Aldrich Chemical Co. All alkynes were purchased from the Farchan Laboratories (except 4-methyl-1-pentyne which was purchased from the Wiley Chemical Co.) and were used without further purification. Higher propargyl alcohols were purified by column chromatography on silica gel except pyranyl alcohol that was purified on neutral alumina.

Diisopropyl (iodomethyl)boronate (**1**, $C_7H_{16}BIO_2$)
A solution of *Me*Li (1.40 M) in ethyl ether (100 cm^3, 140 mmol) was slowly added to a mixture of triisopropylborate (32.3 cm^3, 140 mmol) and diiodomethane (11.2 cm^3, 140 mmol) in *THF* (75 cm^3) at −78°C while stirring. After addition, the mixture was stirred at −78°C for additional 0.5 h, followed by quenching with anhydrous HCl in *Et*$_2$O (150 cm^3, 150 mmol). The cold bath was removed and the mixture was allowed to warm up to room temperature for 1.25 h. The ^{11}B NMR spectrum showed 92% diisopropyl (iodomethyl)boronate. Volatiles were removed using aspirator and the residue was dissolved in *n*-pentane (100 cm^3). The pentane soluble part was transferred through cannula and the solid washed with dry *n*-pentane (20 cm^3). The combined pentane solution was concentrated and the residue was distilled under reduced pressure in the presence of copper wires (0.2 cm long) to afford a colorless liquid (30.2 g, 112 mmol) in 80% yield. ^{11}B NMR ($CDCl_3$): $\delta = 27.6$ ppm; ^{1}H NMR ($CDCl_3$): $\delta =$ 4.39 (septet, $J = 6$ Hz, 2H, $-OCH(CH_3)_2$), 2.12 (s, $-CH_2I$), 1.19 (d, $J = 6$ Hz, 12H, $-OCH(CH_3)_2$) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 66.06$ ($-OCH(CH_3)_2$, 24.23 ($-OCH(CH_3)_2$) ppm (It is usually difficult to observe the carbon atom α to boron in a ^{13}C NMR spectrum due to rapid quadruple-induced relaxation).

Preparation of Cyclic (Iodomethyl)boronates ***2–4***
Diisopropyl (iodomethyl)boronate (**1**) (5 mmol) was mixed with the corresponding diols (6.0–7.5 mmol) in dry *n*-pentane and the mixtures were stirred at room temperature for 4–6 h. Removal of *n*-pentane and 2-propanol under vacuum gave crude products which was further dissolved in *n*-pentane and excess of diols was removed by filtration under nitrogen atmosphere. Evaporation of solvent gave quantitative yields of corresponding cyclic boronates. Products were purified by distillation *in vacuo*. In the case of pinacol (iodomethyl)boronate, excess pinacol was just removed by washing the reaction mixture with water, because pinacol (iodomethyl)boronate was found to be an unusually stable boronate to water.

2-(Iodomethyl)-1,3,2-dioxaborinane (**2**, $C_4H_8BIO_2$)
^{11}B NMR ($CDCl_3$): $\delta = 28.30$ ppm; ^{1}H NMR ($CDCl_3$): $\delta =$ 4.05 (t, 4H, $-OCH_2-$), 2.09 (s, $-CH_2I$), 1.96 (q, $-CH_2-$) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 62.30$ ($-OCH_2-$), 20.97 ($-CH_2-$) ppm.

2-(Iodomethyl)-1,3,2-dioxa-5,5-dimethylborinane
(**3**, $C_6H_{12}BIO_2$)
^{11}B NMR ($CDCl_3$): $\delta = 27.99$ ppm; ^{1}H NMR ($CDCl_3$): $\delta = 3.65$ (s, 4H, $-OCH_2-$), 2.12 (s, $-CH_2I$), 1.00 (s, 6H, $-CH_3$) ppm.

2-(Iodomethy)-1,3,2-dioxa-4,4,5,5-tetramethylborolane
(**4**, $C_7H_{14}BIO_2$)
^{11}B NMR ($CDCl_3$): $\delta = 31.70$ ppm; ^{1}H NMR ($CDCl_3$): $\delta =$ 2.16 (s, $-CH_2I$), 1.27 (s, 12H, $-CH_3$) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 84.17$($-OCMe_2-$), 24.40 ($-CH_3$) ppm.

Reactions of (Iodomethyl)boronates ***1–4*** *with Various Alkynyllithium Salts*
A representative procedure for the reaction of diisopropyl (iodomethyl)boronate (***1***) *with alkynyllithium salt. LDA* (2.2 cm^3, 3.3 mmol) was added slowly to a stirring solution of diisopropyl (iodomethyl)boronate (**1**) (0.812 g, 3 mmol), and *n*-decyne (0.60 cm^3, 3.3 mmol) in *THF* (5 cm^3), cooled to 0°C under nitrogen atmosphere. The mixture was stirred at 0°C for 0.5–1.0 h, the cold bath was then removed and the contents were allowed to warm to room temperature without stirring for 3 h. The boronate was then oxidized with alkaline hydrogen peroxide according to the usual procedure [21]. After adding biphenyl (0.0385 g, 0.25 mmol) and saturating the aqueous layer with anhydrous K_2CO_3, the propargylic alcohol was extracted with *Et*$_2$O (3×30 cm^3), dried, and concentrated. The crude product was analyzed by ^{1}H NMR spectroscopy. The alcohol was purified by column chromatography on silica gel (using 5–20% ethyl acetate/*n*-hexanes mixture) and the chemical yield of the isolated product was also determined.

A representative procedure for the reaction of 2-(iodomethyl)-1,3,2-dioxa-4,4,5,5-tetramethylborolane (***4***) *with alky-*

nyllithium salt: LDA (1.7 cm^3, 2.5 mmol) was added slowly to a stirring solution of pinacol (iodomethyl)boronate **4** (0.536 g, 2 mmol), and *n*-decyne (0.45 cm^3, 2.5 mmol) in THF (5 cm^3), cooled to 0°C under nitrogen atmosphere. The mixture was stirred at 0°C for 0.5–1.0 h, the cold bath was then removed and the contents were allowed to warm to room temperature without stirring for 1.5 h. The boronate was then oxidized with alkaline hydrogen peroxide according to the usual procedure [21]. After adding biphenyl (0.0385 g, 0.25 mmol) and saturating the aqueous layer with anhydrous K_2CO_3, the propargylic alcohol was extracted with Et_2O (3×30 cm^3), dried, and concentrated. The crude product was analyzed by ^{1}H NMR spectroscopy. The alcohol was purified by column chromatography on silica gel (eluted with 5–20% ethyl acetate/*n*-hexanes mixture) and the chemical yield of the isolated product was also determined.

Spectral Data for Various Alkyn-2-yl-1-ols

Spectroscopic properties of hept-2-yl-1-ol **5** [22], 5-methylhex-2-yl-1-ol [23], 4,4-dimethylpent-2-yn-1-ol [24], undec-2-yn-1-ol [25], 6-chlorohex-2-yn-1-ol [26], 3-triisopropylsilanylprop-2-yn-1-ol [27], 12-hydroxydodec-10-ynoic acid methyl ester [28], and 12-hydroxydodec-10-ynoic acid [29] are in accordance with those published in literature.

3-(Cyclopentyl)prop-2-yn-1-ol (**9**, $C_8H_{12}O$)

Colorless liquid; IR (cm^{-1}, thin film): $\bar{\nu} = 3300$ (br, −OH), 2230 (C≡C) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 4.25$ (d, $-CH_2OH$), 2.60 (m, $-CH-C\equiv C-$), 2.15 (br, s, −O*H*), 1.90 (m, $-CH_2-$) 1.75–1.40 (m, 6H, $-CH_2-$) ppm; ^{13}C NMR ($CDCl_3$): $\delta =$ 90.61, 77.89, 51.32, 33.72, 30.14, 24.96 ppm; MS (EI): $m/z =$ 124 (M^+), 67 (base); HRMS: m/z found 124.0892, calcd. $C_8H_{12}O$ 124.0888.

2-(5-Hydroxy-3-butynyloxy)tetrahydro-2H-pyran (**11**, $C_{10}H_{16}O_3$)

Colorless liquid; IR (cm^{-1}, thin film): $\bar{\nu} = 3400$ (br, −OH), 2260 (C≡C) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 4.61$ (m, $-OCHO-$), 4.20 (m, $-CH_2OH$), 3.77 (m, $-OCH_2-$), 3.5 (m, $-OCH_2-$), 2.5 (m, 3H, $-CH_2-C\equiv C-$, −O*H*), 1.80–1.40 (m, 6H, $-CH_2-$) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 98.82$, 82.89, 79.56, 65.70, 62.35, 51.09, 30.52, 25.36, 20.21, 19.43 ppm; MS (EI): $m/z = 153$ (M^+-CH_2OH), 85 (base); HRMS: m/z found 184.1095, calcd. $C_{10}H_{16}O_3$ 184.1099.

3-Octyl-1-phenyl-2,3-butadien-1-ol (**15**, $C_{18}H_{26}O$)

A typical procedure for the reaction of the pinacol propargylboronate with benzaldehyde: LDA (1.7 cm^3, 2.5 mmol) was added slowly to a stirring solution of pinacol iodomethylboronate (0.536 g, 2 mmol) and *n*-decyne (0.45 cm^3, 2.5 mmol) in *THF* (5 cm^3), cooled to 0°C under nitrogen atmosphere. The mixture was stirred at 0°C for 0.5–1.0 h, the cold bath was then removed, and the contents were allowed to warm to room temperature without stirring for 1.5 h. The reaction mixture was cooled to −78°C, benzaldehyde (0.15 cm^3, 1.5 mmol) was added, and stirred for 1 h. ^{11}B NMR spectrum did not show any borate peak ($\delta = 22.0$ ppm). The reaction was found to be slow even at 0°C. Then the reaction mixture was allowed to warm up to room temperature. After 6 h, 50% boronate peak ($\delta = 31.93$ ppm) was converted to borate peak ($\delta = 22.0$ ppm). The reaction mixture was allowed to stir overnight, during which almost all the boronate was transformed to the borate. The borate was then oxidized with alkaline hydrogen peroxide according to the usual procedure. The α-allenic alcohol was extracted with Et_2O (3×30 cm^3), dried, and concentrated. The crude product was analyzed by ^{1}H NMR spectroscopy. The α-allenic alcohol, 3-octyl-1-phenyl-2,3-butadien-1-ol was purified by column chromatography on silica gel (eluted with 5–20% ethyl acetate/*n*-hexanes mixture) and the chemical yield (60%) of the isolated product was determined.

Colorless liquid; ^{1}H NMR ($CDCl_3$): $\delta = 7.50$–7.20 (m, 5H, *ArH*), 5.08 (m, *Ph*–C*H*(OH)−), 5.00 (m, $-C=C=CH_2$), 2.30–1.10 (m, $CH_2=C=C-(CH_2)_7-$), 0.85 (t, $-CH_3$) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 203.97$, 142.10, 128.33, 127.78, 126.72, 108.31, 79.90, 74.08, 31.83, 29.37, 29.24, 28.88, 27.92, 27.45, 22.65, 14.11 ppm (^{1}H and ^{13}C NMR spectra were compared with 2-butyl-1-phenyl-2,3-butadien-1-ol [8h]).

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