Homogeneous Catalysis

Catalytic Borylative Opening of Propargyl Cyclopropane, Epoxide, Aziridine, and Oxetane Substrates: Ligand Controlled Synthesis of Allenyl Boronates and Alkenyl Diboronates

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Abstract: A new copper-catalyzed reaction for the stereo- and regioselective synthesis of alkenyl diboronates and allenyl boronates is presented. In this process propargyl derivatives of strained three/four-membered rings were employed as substrates and B(pin)2 was used as the boronate source. Selective formation of the alkenyl diboronate versus the allenyl boronate products was controlled by the choice of phosphine ligand.

Allyl, allenyl, and alkenyl boronates are very useful reagents in stereoselective synthesis, in particular for synthesis of natural products. However, selective synthesis of these organoboron compounds is still a very challenging task in organic synthesis because of the specific properties of the carbon–boron bonds conjugated with carbon–carbon double bonds. Synthesis of functionalized allyl boronates and boronic acids is probably the most developed area in the field of preparation of unsaturated boronates. Recently, the synthesis and application of alkenyl diboronates, in which one of the carbon–boron bonds is in the vinylic position and the other is in the allylic position, has attracted a lot of attention. The reason for the attraction is that the two types of carbon–boron bonds may undergo either orthogonal functionalization or consecutive functionalization, thus creating molecular complexity in a single reaction step with high stereoselectivity. Another emerging area is allenylboration of carbonyl compounds. This powerful synthetic transformation requires a diversity of allenyl boronates. However, synthesis of stereodefined functionalized allenylboronates is still a major challenge in organic synthesis.

The first platinum catalyzed diboration of allenes for the preparation of alkenyl diboronates was reported by Miyaura and co-workers. Subsequently, a series of studies based on palladium-catalyzed reactions was published by the groups of Cheng and Morken. Recently, transition-metal-free diboration of allenes was also reported. The groups of Hoveyda, Tsuji, Ma, and others published several studies on the efficient synthesis of allenyl boronates by copper-catalyzed hydroboration of allenes using diboronates. However, copper-catalyzed hydroboration of allenyl boronates is an unexplored area in organic synthesis.

Opening of a strained ring bearing a propargylic moiety is an efficient approach for the synthesis of functionalized allenes. Recently, we reported a new method for the synthesis of allenyl boronates based on catalytic borylation of propargyl carbonates and related compounds. We also attempted to prepare allenyl boronates by borylative ring opening of propargylic epoxides. These efforts remained fruitless, as the reaction led to formation of bis(borodiene)s, probably via allenyl boronate intermediates.

We have now found that by appropriate choice of the catalytic system, in particular the employed phosphine ligand, the outcome of the borylation reaction can be fully controlled. When the reaction with a propargylic cyclopropane (1; or other strained rings) and B(pin)2 (2) was carried out with a copper catalyst in the presence of PCy3 (Cy = cyclohexyl) the reaction resulted in allenyl diboronates [Eq. (1)]. However, when the same reaction conditions were used in the presence of the bulky P(1-nap), (1-nap = 1-naphthyl) ligand, the reaction led to an allenyl boronate product.

First we optimized the reaction of the borylative opening of the propargylic cyclopropane derivative 1a (Table 1). When 1a was reacted with 3 equivalents of B(pin)2 (2) in the presence of iBuOK and a catalytic amount of CuCl, the allenyl diborionate 3a and allenyloboronate 4a were formed in 3:97 ratio with 61 % yield (entry 1). The reaction could be carried out at room temperature, and is beneficial as the borylated product may undergo protodeborylation or other undesired transformations at elevated temperatures. Use of CuI instead of CuCl led to exclusive formation of 4a, albeit with a lower yield (entry 2). In this case a large amount of unreacted starting material, 1a, remained. We found that addition of alcohols substantially improved the yield. By using
Table 1: Development of copper-catalyzed mono- and diboration of 1a.\[a\]

| Entry | [Cu]cat | Ligand | M Additive | (E)-3a/ (Z)-3a/4a | Yield [%][f] |
|-------|---------|--------|------------|-------------------|-------------|
| 1     | CuCl    | PCy3   | K          | 3.0:97            | 61          |
| 2     | CuI     | PCy3   | K          | 0.0:100           | 47          |
| 3     | CuI     | PCy3   | MeOH       | 32.3:65           | 93          |
| 4     | CuI     | PCy3   | tBuOH      | 96.4:0            | (88)        |
| 5     | CuI     | PPh3   | K          | 80.9:11           | 94          |
| 6     | CuI     | P( C\(_6\)H\(_5\)-p-OMe\(_3\)\)) | K | tBuOH | 33.3:64 | 91 |
| 7     | CuI     | P(1-nap) | K | tBuOH | 18.0:82 | 83 |
| 8     | CuI     | P(2,4,6-trimethylphenyl) | K | tBuOH | 5.0:95 | 67 |
| 9     | CuI     | P(1-nap) | Li | tBuOH | 0.0: > 99 | (76) |
| 10(h) | CuI     | P(1-nap) | Li | tBuOH | 0.0: > 99 | (74) |
| 11(g) | CuI     | P(1-nap) | Li | tBuOH | 0.0: > 99 | (68) |

[a] Reaction conditions: 1a (0.10 mmol), Bu_3P, (2, 3.0 equiv), Cu catalyst (10 mol %), ligand (20 mol %), tBuOM (30 mol %), and additive (3.0 equiv) in toluene (0.2 mL) were reacted at RT for 24 h under Ar. [b] The ratio was determined from \(^1\)H NMR analysis of the crude reaction mixture. [c] Combined yield as determined by \(^1\)H NMR spectroscopy using naphthalene as an internal standard. The yields of the isolated products are shown within parentheses. [d] Without any additive. [e] Bu_3P, (1.3 equiv) and tBuOH (2.0 equiv) were used. [f] The reaction was carried out for 72 h.

MeOH the yield was indeed improved, but lowered the 3a/4a selectivity (entry 3). However, application of tBuOH (instead of MeOH) maintained the high yield and gave an excellent 3a/4a selectivity and E/Z ratio (entry 4). Application of PCy3 was very important for the selectivity of the reaction. The 3a/4a selectivity decreased when PCy3 was replaced with either PPh3 or P( C\(_6\)H\(_5\)-p-OMe\(_3\)\)) (entries 5 and 6). When PCy3 was replaced with a more bulky ligand, such as P(1-nap) or P(2,4,6-trimethylphenyl), the 3a/4a selectivity was shifted toward formation of 4a (entries 7 and 8). Noticeably, by using P(2,4,6-trimethylphenyl), 4a was formed with high selectivity, but the yield was reduced (entry 8). The high yield and high selectivity could also be achieved when P(1-nap), was used and tBuOK was replaced by tBuOLi (see entries 7 and 9). Apparently, a slight change in basicity was beneficial for the allenyl selectivity. In the above optimization studies, we used 3 equivalents of 1 to allow either disubstitution (3a) or monosubstitution (4a). However, the amount of Bu_3P, can be reduced to 1.3 equiv without significant change in the yield of 4a (entry 10). The very high allenyl selectivity could be maintained, even if the reaction time was extended to 72 hours with using 3 equivalents Bu_3P, (entry 11). In the absence of the copper salt and the ligand, the borylated products 3a/4a were not observed.

With the optimal reaction conditions in hand, we studied the synthetic scope of the reaction. Similar to 1a, either 1b or 1c reacted with 2 in the presence of catalytic amounts of Cu and PCy3 (Method A) to give the diborylated products 3b and 3c, respectively, at room temperature with excellent E/Z ratios (Table 2, entries 1 and 3). By changing the ligand to PCy3 or P(C\(_6\)H\(_5\)-OMe\(_3\)\)) the synthetic scope of the reaction. Similar to 1a, either 1b or 1c reacted with 2 in the presence of catalytic amounts of Cu and PCy3 (Method A) to give the diborylated products 3b and 3c, respectively, at room temperature with excellent E/Z ratios (Table 2, entries 1 and 3). By changing the ligand to PCy3 or P(C\(_6\)H\(_5\)-OMe\(_3\)\)) the synthetic scope of the reaction.

Table 2: Borylative opening of propargyl cyclopropanes.

| Entry | Substrate | Method | Product | Yield [%][h] |
|-------|-----------|--------|---------|--------------|
| 1     | outset    | A      | A       | 87 \(E/Z\) 21:1 |
| 2     | outset    | B      | B       | 73            |
| 3     | outset    | A      | A       | 61 \(E/Z\) 21:1 |
| 4     | outset    | A      | A       | 93 \(E/Z\) 21:1 |
| 5     | outset    | A      | A       | 67 \(E/Z\) 21:1 |
| 6     | outset    | A      | A       | 93 \(E/Z\) 21:1 |
| 7     | outset    | A      | A       | 56            |
| 8     | outset    | A      | A       | 93 \(E/Z\) 21:1 |
| 9     | outset    | A      | A       | 56            |
| 10    | outset    | A      | A       | 85 \(E/Z\) 21:1 |
| 11    | outset    | A      | A       | 86            |
| 12    | outset    | A      | A       | 15           |
| 13    | outset    | A      | A       | 15           |
| 14    | outset    | A      | A       | 15           |
| 15    | outset    | A      | A       | 15           |

[a] Method A: a mixture of 1 (0.10 mmol), 2 (0.30 mmol), Cu (10 mol %), PCy3 (20 mol %), tBuOK (30 mol %), and tBuOH (3.0 equiv) in toluene (0.2 mL) was reacted at RT for 24–48 h under Ar. Method B: 1 (0.10 mmol), 2 (0.13 mmol), Cu (10 mol %), P(1-nap) (20 mol %), tBuOLi (30 mol %), and tBuOH (2.0 equiv) in toluene (0.2 mL) was reacted at RT for 24–48 h under Ar. [b] Yield of isolated product. The E/Z ratio was determined by \(^1\)H NMR analysis of the crude reaction mixture. [c] The reaction was performed at 15 \(\pm\) 5 \(\circ\)C for 48 h. [d] The reaction was performed for 36 h. [e] The reaction was performed for 48 h. [f] The reaction was performed at 15–20 \(\circ\)C for 48 h. [g] CuCl (10 mol %), PCy3 (20 mol %), tBuOK (30 mol %) were used. TBS = tert-butylimidethylsilyl.

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P(1-nap), (Method B) the outcome of the reaction was different (entries 2 and 4), and resulted in the allenyl boronates 4b and 4c, with no formation of either 3b or 3c. A bulky alkynyl substituent, such as in 1d, led to slower borylation, and therefore the reaction was either conducted at 35 °C (entry 5) or the reaction time was extended (entry 6). By using PCy₃ (Method A) 3d was formed with a high diastereoselectivity (E/Z = 25:1), while with P(1-nap), (Method B) the reaction resulted in a high yields of the allenyl boronate 4d. The reaction tolerated several functional groups, such as chloro, ether, ester groups (entries 9–14). Gratifyingly, the outcome and the selectivities of the reactions using 1f–h as substrates were similar to those for 1b–e. In most cases, we used disubstituted methy-propargyl-type cyclopropane derivatives to obtain tetrasubstituted allenyl boronates. However, trisubstituted allenyl boronates (such as 4i) or less-substituted alkynyl diboronates (such as 3i) can also be obtained by using the propargyl cyclopropane 1i (entries 15 and 16). In the case of the synthesis of 4i the reaction conditions were slightly changed. By using CuI and P(1-nap), (Method B) a protodeborylation of 4i occurred, therefore we used catalytic amounts of CuCl and PCy₃ (Method C) to improve the yield of 4i.

We found that the borylative opening of the propargyl cyclopropanes 1a–i can be extended to propargyl substrates with other strained rings (Table 3), such as the epoxide 5, oxetane 6, and aziridine 7. The ligand effects on the outcome of the reaction were identical to those of the reactions for 1. By using bulky P(1-nap), (Method B) the reaction resulted in allenyl boronate products, such as 4j (entry 1), 4k (entry 3), and 4l (entry 4). However, by using PCy₃ (Method A), the reaction led to formation of the diborylated product 3j (entry 2). It is interesting to point out that according to our previous studies, the epoxy 5 gave the diborylated product when PCy₃ (or PPh₃) was employed under similar reaction conditions. The solution for stopping the reaction at the formation of the allenyl boronate product was to use the bulky P(1-nap) ligand (entry 1). In the above reactions (Tables 2 and 3), we observed full ligand control. Except for formation of 4i (Table 2, entry 16) and 4j (Table 3, entry 1), the reaction resulted in a single borylated product.

We briefly studied the mechanistic aspects of the process. The reactions proceeded with high yields and selectivities required tBuOH as an additive. Our isotopic-labelling studies showed that tBuOH served as proton source of the process [Eqs. (2)–(4)]. When we added tBuOD and PCy₃ to the reaction of 1a and the allenyl diboronic product [D₃]-3a was formed [Eq. (2)]. In this compound we observed deuterium uptake at two positions: at the position α to the COOME groups and at the allylic positions. In case of using P(1-nap), as the ligand under similar reaction conditions the allenyl boronate [D₃]-4a was obtained with deuterium uptake only at the position α to the COOME groups [Eq. (3)]. The isolated 4a with 2 in the presence of PCy₃ resulted in [D₃]-3a [Eq. (4)]. In this case the deuterium uptake is somewhat lower than for the reaction of 1a [Eq. (2)]. A possible reason is that 4a contains an exchangeable proton (α-position to the carbon-bond).

Based on the deuterium-labelling studies [Eqs. (2)–(4)] and the above results in Tables 1 and 2, we constructed plausible catalytic cycles, using 1a as an example, and tBuOH as the additive (Figure 1). We suggest that CuI in the presence of tBuOM (M = K, Li) and either P(1-nap), or PCy₃ undergoes transmetallation[10] with 2 to give the complex 8. The complex 8 is selectively inserted[9,11] into the triple bond of 1a to give

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Table 3: Extension of the scope of the reaction to propargyl epoxide, oxetane, and aziridine substrates.

| Entry | Substrates | Method[a] | Product | Yield [%][b] |
|-------|------------|-----------|---------|-------------|
| 1     | ![](image) | A         | 4j      | 74          |
| 2     | ![](image) | A         | 3j      | 64          |
| 3     | ![](image) | A         | 4k      | 56          |
| 4     | ![](image) | A         | 4l      | 55          |

[a] Method A: a mixture of 1 (0.10 mmol), 2 (0.30 mmol), CuI (10 mol %), PCy₃ (20 mol %), tBuOK (30 mol %), and tBuOH (3.0 equiv) in toluene (0.2 mL) was reacted under Ar at RT for 24 h. Method B: 1 (0.10 mmol), 2 (0.13 mmol), CuI (10 mol %), P(1-nap) (20 mol %), tBuOli (30 mol %), and tBuOH (2.0 equiv) in toluene (0.2 mL) was reacted at RT for 24 h under Ar. [b] Yield of isolated product. The E/Z ratio was determined by ¹H NMR analysis. [c] In this reaction about 7% of the bis(borodiene) product was also formed. [d] tBuOK (30 mol %), MeOH (2.0 equiv) was used instead of tBuOli (30 mol %) with tBuOH (2.0 equiv). [e] tBuOK (30 mol %) was used instead of tBuOli (30 mol %) and tBuOH (2.0 equiv). [f] The reaction was performed for 48 h. Ts = 4-toluensulfonyle.
are useful reagents in functionalization of carbonyl compounds for stereoselective synthesis of homoallyl and homopropargylic alcohols,[1a, b, c, d, 15] and useful precursors for allenyl derivatives by Suzuki–Miyaura coupling.[10]

**Experimental Section**

In a typical procedure (Method A): Boronate source Bpin$_3$ (2; 0.30 mmol), CuI (10 mol %), PCy$_3$ (20 mol %), tBuOK (30 mol %) were mixed in toluene (0.4 mL) and the resulting slurry was stirred for 10 minutes at room temperature under Ar. Then a toluene solution (0.1 mL) of the mixture of the propargylic cyclopropane 1a (0.1 mmol) and tBuOH (500 mol %) was added by syringe. The reaction mixture was stirred at room temperature for 24 hours, and then diluted by n-pentane (1.5 mL). The precipitate was filtered off by a silica pad using and washed with EtOAc/hexane (1:2 v/v) as an eluent. The solvent was removed and the alkenyl diborate product 3a was purified by silica chromatography. The synthesis of the allenyl boronate 4a was performed in a similar way (Method B), except that P(1-nap) (20 mol %), tBuOLi (30 mol %), and tBuOH (200 mol %) were used.

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