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Selective Cascade Reaction of Bisallenes via Pd-Catalyzed Aerobic Oxidative Carbocyclization-Borylation and Aldehyde Trapping

Veluru Ramesh Naidu, Daniels Posevins, Chandra M. R. Volla, and Jan-E. Bäckvall*

Abstract: A cascade reaction, consisting of a palladium-catalyzed regioselective aerobic oxidative carbocyclization-borylation of bisallenes and a final aldehyde trapping, afforded triene alcohols with high diastereoselectivity. The cascade reaction occurs under mild reaction conditions and proceeds via an allylboron intermediate that is trapped by the aldehyde in a stereoselective manner.

In synthetic organic chemistry, cyclization of allenes is an important class of reactions that can be applied for the synthesis of a variety of carbocyclic and heterocyclic compounds.^[1,2] In particular, transition metal-catalyzed cyclizations of conjugated and non-conjugated bisallenes provide efficient and atom-economical routes to polyunsaturated molecules.^[3] In the synthesis of carbocyclic molecules, metal-catalyzed cascade reactions with C-C bond formation are of great interest for obtaining complex structures with high stereoselectivity.^[4-5]

Organoboron compounds can be obtained through different routes such as Brown hydroboration and the palladium-catalyzed Miyaura borylation etc., and they are versatile building blocks in the synthesis of natural products and bioactive compounds.^[6-8] In recent years, metal-catalyzed non-oxidative or oxidative carbocyclization studies with unsaturated systems have been well explored.^[9,10,11] There are recent reports on non-oxidative palladium-catalyzed borylative cyclization of enynes and enallenes employing bis(pinacolato)diboron (B_2pin_2) as the borylating agent.^[9]

In the past decade, our group has focused on the understanding of the mechanistic pathways in palladium-catalyzed oxidative carbocyclization reactions of enallenes, and allenynes (Scheme 1a).^[3b,3c,10] These studies include palladium-catalyzed oxidative carbocyclization-borylation and carbocyclization-arylation of enallenes by the use of B_2pin_2 and arylboronic acids, respectively.^[10b,10c] In a similar fashion we have studied the palladium-catalyzed oxidative carbocyclization-borylation of allenynes in a regioselective manner.^[10d] There is a demand of exploring these allene-based carbocyclizations towards new applications. Recently, we have developed a carbocyclization-arylation of bisallenes.^[3c] It would be highly interesting to use a diboronate (e.g. B_2pin_2) instead of an arylboronic acid in the

latter reaction of bisallene **1** leading to allylborane **2**, since the latter may undergo an additional C-C bond formation with an aldehyde (Scheme 1b). It is expected that the reaction of the cyclic allylboron intermediate **2** with an aldehyde is highly stereoselective.^[12] In this communication we report on a one-pot domino-cascade reaction of bisallenes involving oxidative carbocyclization-borylation and final trapping with an aldehyde (Scheme 1b).

Previous reports

Scheme 1. Previous work and proposal for this work.

In palladium-catalyzed oxidative carbocyclizations, the use of an aerobic biomimetic oxidation system is an environmentally benign procedure associated with high atom economy.^[10a,11] We have applied an aerobic oxidation process via multistep electron transfer involving three redox systems: Pd^{II}/Pd⁰-benzoquinone (BQ)/hydroquinone (HQ)-Co(salophen)^{ox}/Co(salophen). In the carbocyclization reaction the substrate is oxidized to the desired product by the substrate-selective catalyst^[11a] Pd(OAc)₂, which becomes reduced to Pd⁰. The Pd⁰ is subsequently reoxidized to Pd^{II} by catalytic amounts of BQ, which is reduced to HQ. The HQ is reoxidized to BQ by the catalytic electron transfer mediator (i.e. Co(salophen)) with molecular oxygen as the oxidant.^[10a,11,13,14,15]

Bisallenes **1a** – **1g** were prepared according to literature procedures.^[16] In an initial investigation to optimize the reaction, we employed bisallene **1a** (Table 1) as a model substrate, and a series of experiments were performed in combination with B_2pin_2 to examine the oxidative palladium-catalyzed reactions for carbocyclization and borylation using Pd(OAc)₂ (5 mol%) and BQ. Different amounts of BQ and B_2pin_2 were employed in the Pd-catalyzed carbocyclization of **1a**. The use of 1.5 equiv of BQ in the absence of B_2pin_2 at 50 °C for 7 h in DCE (1,2-dichloroethane), afforded product **A** in 72% yield (Table 1, entry 1) most likely via isomerization of **Int-3** (Scheme 1b) to the secondary σ -allyl-Pd complex followed by β -hydride elimination. Surprisingly, with an increased amount of BQ (2.5 to 3 equiv) in

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the presence of B_2pin_2 (1.5 to 1 equiv), BQ derivative **B** was obtained in 62 to 75% yield (Table 1, entries 2 and 3). Interestingly, when B_2pin_2 was reduced to 0.1 equiv in the presence of BQ (3 equiv), compound **A** (60%) was formed as the main product together with small amounts of secondary boronic ester triene derivative **3a** (5%) and quinone derivative **B** (10%) (Table 1, entry 4). In this initial study, we were not able to obtain the desired carbocyclic primary boron compound **2a**, probably because of its reaction with BQ.

Table 1. Results of initial study.^[a]

Entry	BQ (equiv)	B_2pin_2 (equiv)	Yield [%] ^[b,c]		
			A	3a	B
1	1.5	-	72(70)	-	-
2	2.5	1.5	Traces	25	62
3	3	1.0	Traces	Traces	75(71)
4	3	0.1	60	5	10

[a] Reaction conditions: **1a** (1.0 equiv) (0.2 mmol), 5 mol% of $Pd(OAc)_2$, anhydrous DCE (2.0 mL). [b] Yield determined by 1H NMR using mesitylene as an internal standard. [c] Isolated yield in parenthesis.

We therefore decided to carry out the carbocyclization/borylation reaction with different oxidants with the aim of isolating **2a**. After trying various oxidants, it was finally found that tetrafluoro-1,4-benzoquinone (F_4 -BQ) (1.5 equiv) with bisallene **1a** using catalytic amount of $Pd(OAc)_2$ (5 mol%) in the presence of B_2pin_2 (2 equiv) at room temperature in DCE provided allylic primary and secondary carbocyclic boronic esters **2a** (74%) and **3a** (26%) as major and minor products, respectively (Table 2, entry 1).

Table 2. Optimization of the reaction conditions.

Entry	Additives	Ratio of 2a:3a	Yield [%] ^[a]
1	-	74:26	99
2	PTSA	NR	0
3	Et_3B	Decompose	0
4	AcOH	70:30	44
5	$BF_3 \cdot Et_2O$	100:0	34
6	$LiOAc \cdot H_2O$	79:21	97
7	NaOAc	74:26	99
8	Na_2CO_3	84:16	99
9 ^[b]	Na_2CO_3	79:21	99

[a] Yield determined by 1H NMR analysis using mesitylene as an internal standard. [b] 50 mol% of additive. NR - no reaction

We then turned our attention towards optimizing the yield of the primary boronic ester **2a** by addition of various additives. It was found that addition of base substantially improved the yield of allylic primary carbocyclic boronic ester **2a**. The employment of *p*-toluenesulphonic acid (PTSA) or Et_3B additives was ineffective as well as the addition of catalytic amounts of AcOH (Table 2, entries 2-4). Addition of $BF_3 \cdot Et_2O$ gave a high selectivity (100:0) but the yield was low. With, $LiOAc \cdot H_2O$ the yield was high and the selectivity **2a:3a** was 79:26 (Table 2, entry 6). NaOAc decreased the ratio **2a:3a** (entry 7). Finally, with 20 mol% of Na_2CO_3 , **2a** was formed with good selectivity (84/16 ratio) and yield (entry 8). Increasing the amount of Na_2CO_3 to 50 mol% decreased the selectivity (79/21 ratio, entry 9). Moreover, the use of various Pd(II) catalysts did not improve the regioselectivity (see Supporting Information).

With these improved reaction conditions for obtaining **2a** as the major isomer, we studied various substrates **1a** – **1g** for the borylative carbocyclization (Table 3). The corresponding allylboryl compounds **2a** – **2g** were obtained in good yields (64 – 84%). It was desirable to apply an aerobic oxidative carbocyclization-borylation process. Pd-catalyzed reaction of **1a** with B_2pin_2 (2 equiv) at room temperature using catalytic amounts of F_4 -BQ (20 mol%) and Co(salophen) (5 mol%) as electron transfer mediators (ETMs) under 1 atm of molecular oxygen (O_2) in DCE (Table 3, entry 1, method B) afforded **2a** in 83% yield. A similar yield (Table 3, entry 1, method A, 84%) was obtained in the non-aerobic oxidative reaction.

Table 3. Scope of substrates.

Entry	Substrate (E = CO_2Me)	Product	Yield of 2 (%) ^[a] (method A/B)
1	1a	2a	A:84 B:83
2	1b	2b	A:84 B:82
3	1c	2c	A:81
4	1d	2d	A:80
5	1e	2e	A:85

[a] Isolated yield after column chromatography. **Method A:** Pd(OAc)₂ (5 mol%), F₄-BQ (1.5 equiv), B₂pin₂ (2 equiv), Na₂CO₃ (20 mol%), DCE, rt, 7 h. **Method B:** Pd(OAc)₂ (5 mol%), F₄-BQ (20 mol%), Co(salophen) (5 mol%), B₂pin₂ (2 equiv), Na₂CO₃ (20 mol%), DCE, rt, O₂ balloon, 7 h.

In the aerobic oxidative carbocyclization-borylation reaction, Co(salophen) was the best ETM for obtaining product **2a** in high yield. Similar results were obtained for substrates **1a** and **1b**, with either stoichiometric amounts of F₄-BQ (method A) or under aerobic conditions (method B) affording products **2a** and **2b**, respectively, in good yields (Table 1, entries 1 and 2).

With the results in Table 3, we now can provide an explanation for the formation of carbocyclic benzoquinone derivative **B** (Table 1, entry 3). In this case the allylboron compound **2a** generated will react with the carbonyl group of the quinone followed by a [3,3'] rearrangement (Scheme 2).^[17] Subsequent tautomerization and oxidation lead to derivative **B**. This cascade reaction inspired us to develop a cascade reaction where the generated allylboron compound is continuously trapped by a carbonyl compound (such as an aldehyde) present in the reaction mixture.

Scheme 2. Reaction of allylboron derivative **2a** with BQ.

In the planned cascade reaction, an allyl-Bpin intermediate **2a** is generated via an *in situ* carbocyclization-borylation and this intermediate can continuously be trapped by an aldehyde present in solution. Normally, it is difficult to control the relative configuration at two adjacent stereocenters in a single reaction but the cascade reaction sequence proceeded in a highly stereoselective manner. This high stereoselectivity is due to the fact that the reaction between the allylboron intermediate and the aldehyde involves a Zimmerman-Traxler (ZT) transition state^[12a,12b,18] (see Supporting Information). The cascade reaction of **1a** with benzaldehyde by method A or B afforded **4aa** (Table 4) as the major product in a mixture with small amounts of regioisomers **5**.

Table 4. Palladium-catalyzed cascade reaction.^[a,b]

[a] Isolated yield after column chromatography. [b] The ratio in parenthesis is the ratio **4:5**. **Method A:** Same as in Table 3 but with 1.5 equiv of an aldehyde. **Method B:** Same as in Table 3 but with 1.5 equiv of an aldehyde.

In the one-pot reaction using method A or B, **1b** was allowed to react with various substituted benzaldehydes with electron-rich or electron-deficient substituents to give of **4bb** - **4bf**, in good yields (79–89%) with minor amounts of regioisomer **5**. Under biomimetic oxidative conditions (method B), aliphatic aldehydes such as phenylpropionaldehyde and cyclohexyl-carboxaldehyde with **1b** gave the corresponding derivatives **4bg** and **4bh** in 71% and 66% yields, respectively. Similarly, heterocyclic aldehydes, for example 2-thiophenecarboxaldehyde and furfural, were also allowed to react under aerobic conditions (method B) producing the corresponding derivatives **4bi** and **4bj** in 70% and 80% yields, respectively, with small amounts of regioisomers **5bi** and **5bj** (**4bi:5bi** = 93:7 and **4bj:5bj** = 92:8). In all these cases two stereocenters were created in the reaction that gave isomer **4** but only one diastereomer of **4** was observed (>99% dr).

In the cascade reaction described in Table 4, we noticed that triene alcohol derivatives **4** undergo lactone formation on prolonged reaction times. This lactonization was faster when dimethyl malonate derivative **1a** was used. When **1a** was used together with 4-(trifluoromethyl)benzaldehyde a crystalline bicyclic lactone adduct was obtained on prolonged reaction time. The bicyclic lactone product was submitted to X-ray crystallography analysis, which allowed stereochemical assignment of the trienol product **4** from the cascade reaction.^[19]

Scheme 3. Proposed mechanism for the formation of **4** and **5**.

A possible mechanism for the carbocyclization-borylation-aldehyde trapping is given in Scheme 3. Previous studies in our group have shown that carbocyclization involving 1,1-dimethyl allenes is initiated by an allene attack on Pd^{II} .^[10] Formation of chelate complex **Int-1** from bisallene **1** and subsequent allene attack on the Pd^{II} would generate vinyl-palladium intermediate (**Int-2**). The latter complex reacts via insertion of allene into the Pd -vinyl bond affording $(\sigma\text{-allyl})\text{Pd}^{\text{II}}$ species **Int-3**, which can rearrange to **Int-5** via the more stable π -allyl complex (not shown). The σ -allyl intermediates with primary or secondary carbon-Pd bonds can undergo transmetalation with B_2pin_2 to produce complexes **Int-4** or **Int-6**, respectively. Subsequent reductive elimination from **Int-4** and **Int-6** results in the formation of boron compounds **2** and **3**, respectively, with concomitant formation of Pd^0 . The latter species is reoxidized to Pd^{II} by either BQ or by the O_2/ETM system. Subsequent reaction of the allylboron compound **2** with the aldehyde present in the mixture gives product **4**. Similarly, reaction of **3** with the aldehyde gives the minor product **5**.^[16] In the absence of B_2pin_2 , β -hydride elimination from **Int-5** occurs to furnish **A** as the sole product.

In conclusion, we have developed a Pd^{II} -catalyzed aerobic oxidative carbocyclization-borylation-aldehyde trapping cascade reaction of bisallenes to give triene alcohols with high diastereoselectivity. A wide range of bisallenes having different functionality and aldehydes with various functional groups are tolerated under biomimetic or nonaerobic conditions. The efficient construction of stereoselective complex structures via cyclic allylboronates and their applications in a one-pot reaction should be useful in natural product synthesis. Further investigations directed towards synthetic applications and asymmetric variants of this one-pot cascade reaction are underway in our laboratory.

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Keywords: • palladium • catalysis • biomimetic oxidation • bisallene • cascade reaction

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- [19] Lactone formation of **4af** gives a crystalline lactone **6**. (CCDC: 1486074)

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COMMUNICATION

Veluru Ramesh Naidu, Daniels Posevins, Chandra M. R. Volla, and Jan-E. Bäckvall*

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Selective Cascade Reaction of Bisallenenes via Pd-Catalyzed Aerobic Oxidative Carbocyclization-Borylation and Aldehyde Trapping

Efficient cascade reaction. A palladium-catalyzed regioselective aerobic oxidative carbocyclization-borylation of bisallenenes generates a reactive allylboron intermediate that is trapped by aldehyde present in the reaction mixture. The cascade reaction proceeds with high diastereoselectivity.