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Letter

Allylboronic Esters as Acceptors in Radical Addition, Boron 1,2-Migration, and Trapping Cascades

Kalipada Jana and Armido Studer*

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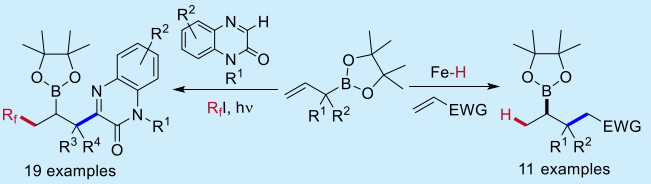
ABSTRACT: Radical 1,3-carboheteroarylation and 1,3-hydroalkylation of allylboronic esters comprising a 1,2-boron shift is reported. Allylboronic esters are generally used in synthesis as allylation reagents, where the boronic ester moiety gets lost. In the introduced cascades, alkylboronic esters are obtained with the boron entity remaining in the product. The carboheteroarylation of the allylboronic esters are conducted without a metal catalyst, and the 1,3-hydroalkylation is achieved using iron catalysis. Both reactions work efficiently under mild conditions.

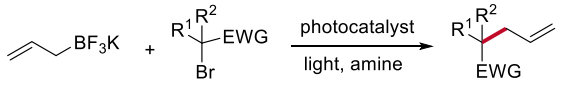


Boronic esters have been intensively used as alkyl, alkynyl, aryl, and allyl donors in various C−C bond forming reactions, rendering such compounds highly important building blocks in organic synthesis.[1] Most of these transformations either are catalyzed/mediated by a transition metal or are ionic in nature.[1] In comparison, radical chemistry using boron-based reagents is far less well developed but has recently received increased attention.[2] For example, allylboronic esters have been intensely used in ionic chemistry,[3] but their radical chemistry is nearly unexplored. The Leonori group successfully used allyl trifluoroborates as reagents for C-radical allylation (Scheme 1a).[4] However, as in the ionic allylations, the valuable boron moiety no longer appears in the final product. Addressing that issue, we recently showed that allylboronic esters can engage as acceptors in two-component radical 1,3-difunctionalization reactions. These cascades comprise a 1,2-boron migration and the important boronic ester moiety remains in the product.[5a] This was shown for the 1-trifluoromethyl-3-alkynylation and also for the 1-trifluoromethyl-3-azidation of allylboronic acid pinacol esters (Scheme 1b). It is worth noting that radical 1,2-boron migration was first reported by Batey[6] and was more recently applied by Aggarwal[7] to the selective functionalization of 1,2-bis-boronic esters. More recently, we also found that radical 1,2-boron shifts from boron to carbon are highly efficient processes.[8] To further explore the potential of allylboronic esters as radical acceptors for boron-retaining functionalizations, we decided to utilize such boron compounds for three-component[5b] 1,3-carboheteroarylations and iron-catalyzed 1,3-hydroalkylations (Scheme 1c).

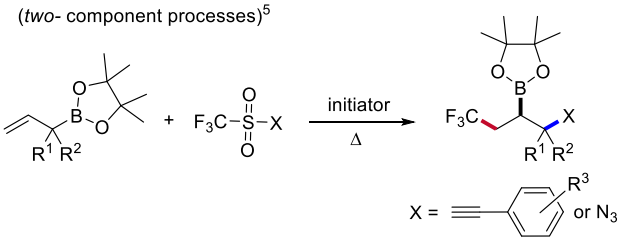
Different strategies have been developed for the radical heteroarene alkylation where the C-radical directly reacts with the heteroarene acceptor.[9] However, a three-component carboheteroarylation of alkenes in which the initial C-radical is first intercepted by the alkene and the adduct radical thus generated then engages in a heteroarylation has been less well

Scheme 1. Allylboronic Compounds as Radical Acceptors

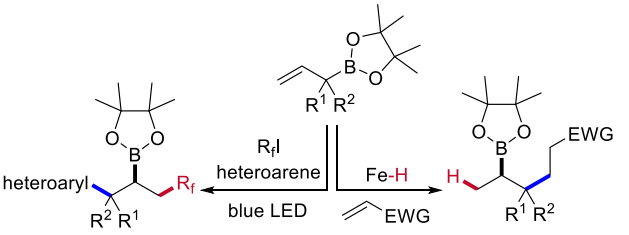
a) C-Radical allylation with allyl trifluoroborates[4]



b) 1,3-Carboalkenylation and carboazidation of allylboronic esters (*two*- component processes)[5]



c) 1,3-Carboheteroarylation and formal hydroalkylation of allylboronic esters (*three*- component reactions, *this work*)



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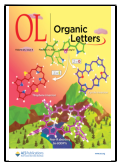

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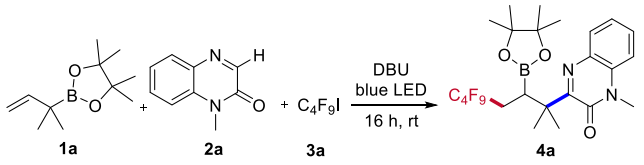
investigated.[10] To realize such a goal, we decided to use perfluoroalkyl iodides as C-radical precursors along with quinoxalin-2(1*H*)-ones[10b,e] as heteroarene acceptors, applying electron catalysis[11] for the 1,3-difunctionalization[12] of allylboronic esters.

Notably, heteroarenes containing fluorine atoms or perfluoroalkyl groups are important in the agrochemical industry and also in medicinal chemistry.[13] We therefore selected perfluoroalkyl iodides as C-radical precursors, and initiation of the chain reaction should be easily achieved by simple light irradiation.[10b] The initial perfluoroalkyl radical addition at the terminal position of the allylboronic ester will lead to the corresponding secondary alkyl radical, which in turn should engage in a thermodynamically driven 1,2-boron shift.[5a] The translocated C-radical thus generated will then regioselectively add at the 3-position to the quinoxalin-2(1*H*)-one. Deprotonation and oxidation by the starting perfluoroalkyl iodide[10b] will eventually lead to the targeted 1,3-difunctionalization product with the valuable boron entity at the 2-position.

Reaction optimization was started using the heteroarene **2a** as a model substrate in combination with the allylboronic ester **1a** and nonafluoro-1-iodobutane (Table 1). Blue light

Table 1. Reaction Optimization[a]



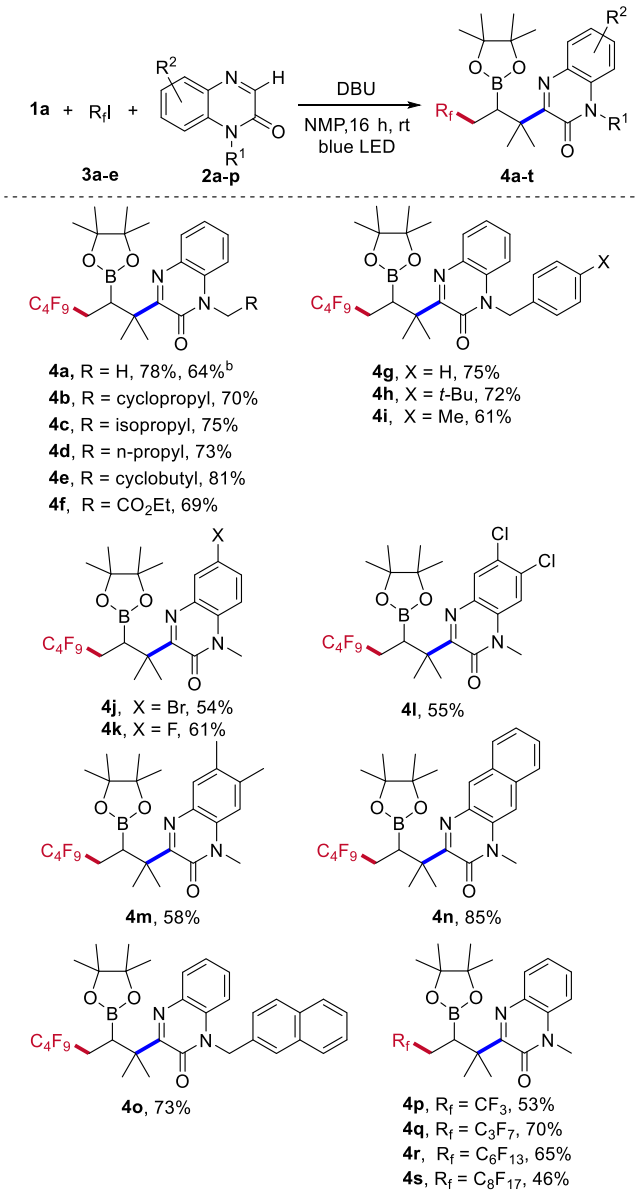
entry	solvent	DBU (equiv)	3a (equiv)	1a (equiv)	yield (%)[b]
1	DMF (0.2 M)	2	1.2	1	28
2	DMF (0.2 M)	2	1	2	36
3	DMF (0.2 M)	3	2	2.5	42
4	DMF (0.1 M)	3	2	2.5	35
5	DMF (0.4 M)	3	2	2.5	73
6	DMF (0.4 M)	2	2	2	52
7	**NMP (0.4 M)**	**3**	**2**	**2.5**	**83**

[a]Reaction conditions: **2a** (0.1 mmol, 1 equiv), rt, Ar, 16 h. [b]Yields were determined by NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

irradiation (LED) of a DMF solution (0.2 M) of **2a** (1 equiv), **3a** (1.2 equiv), **1a** (1 equiv), and DBU (2 equiv) as base for 16 h provided the desired product **4a** in an encouraging 28% yield (Table 1, entry 1). When the amount of **3a** was reduced in combination with a 2-fold excess of **1a**, the yield of **4a** increased to 36% (Table 1, entry 2). A slightly better result was achieved by increasing the excess of DBU (3 equiv) and the allylboronic ester **1a** (2.5 equiv) (42%, Table 1, entry 3), but decreasing the concentration (0.1 M) led to a worse result (Table 1, entry 4). Pleasingly, the yield significantly increased to 73% upon further increasing the reaction concentration (0.4 M, Table 1, entry 5). Keeping that concentration and using equal amounts of **1a** and **3a** (2 equiv each) led to a worse result (Table 1, entry 6). The best yield was achieved upon changing the solvent to *N*-methyl-2-pyrrolidone (NMP) (83%; Table 1, entry 7).

Under the optimized conditions, we then explored the substrate scope by first varying the quinoxalin-2(1*H*)-one component using **1a** and **3a** as reaction partners. The starting quinoxaline derivatives **2a**–**p** were easily prepared (see the Supporting Information). First, the robustness of the protocol was documented by running the cascade with the heteroarene **2a** on a 1 mmol scale and **4a** could be isolated in 64% yield (Scheme 2). Various alkyl groups such as methyl, cyclo-

Scheme 2. 1,3-Carboheteroarylation of Allylboronic Ester 1a[a]



[a]Reaction conditions unless specified otherwise: **2** (0.1 mmol, 1 equiv), NMP (0.25 mL), **1** (0.25 mmol, 2.5 equiv), DBU (45 μL, 3 equiv), rt, Ar, 16 h. [b]Reaction conducted on a 1 mmol scale.

propylmethyl, isobutyl, *n*-butyl, cylclobutylmethyl, and methoxycarbonylmethyl were tolerated as N-substituents of the quinoxalin-2(1*H*)-one, and the alkylboronic esters **4a**–**f** were obtained in 69–81% yields. *N*-Benzyl-substituted quinoxalin-2(1*H*)-ones also worked well, and the corresponding products **4g**–**i**,**o** were obtained in moderate to good yields (54–75%).

Next, quinoxalin-2(1*H*)-ones bearing substituents at the arene moiety were tested. The 6-fluoro-substituted quinoxaline **2k** afforded **4k** in 61% yield. 6,7-Disubstituted congeners bearing electron-withdrawing chloro (**2l**) and also electron-

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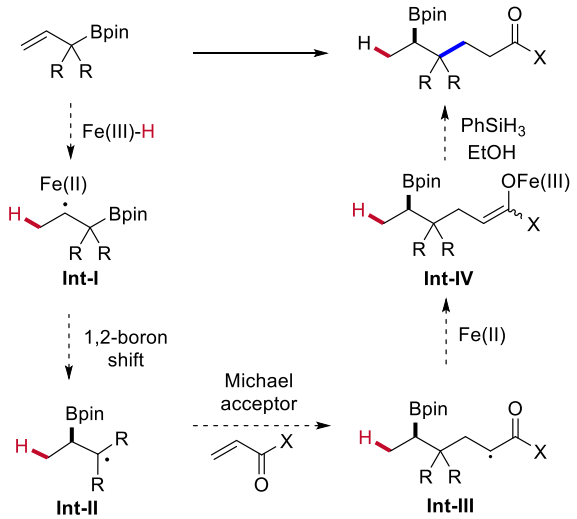
donating methyl groups (**2m**) were eligible acceptors for this transformation (**4l**, 55%; **4m**, 58%). Extending the π-conjugation of the heteroarene (see **2n**) improved the reaction efficiency, and **4n** was isolated in an excellent 85% yield.

We then continued the studies by varying the C-radical precursor. For example, the reaction of **1a** and **2a** with trifluoromethyl iodide provided **4p** in 53% yield. As expected, longer perfluoroalkyl iodides also worked well and the C_3F_7, C_6F_{13} and C_8F_{17} congeners **4q**–**s** were obtained in satisfactory yield (46–70%). We also tested other heterocyclic compounds such as benzothiazole and protonated quinoline (triflate salt) as radical acceptors in combination with C_4F_9I under the optimized reaction conditions. Unfortunately, the corresponding targeted 1,3-carboheteroarylation products were not formed (see the Supporting Information).

To further document the generality of allylboronic esters as valuable radical acceptors for boron-retaining transformations, we decided to also study iron hydride mediated hydrofunctionalizations (see Scheme 1c). Guided by the seminal work of Mukayama,[14] the Baran group developed an iron-catalyzed alkene cross-coupling reaction, where initial metal hydride hydrogen atom transfer (MHAT) was followed by a radical C–C bond forming step.[15] More generally, radical-based hydrofunctionalizations of alkenes mediated or catalyzed by *in situ* generated metal hydride complexes have been intensively investigated by various groups in the past.[16] Encouraged by these reports, we envisaged that allylboronic esters could be used as radical acceptors for reductive alkene cross-coupling reactions in combination with electron-poor alkenes, where couplings proceed with a concomitant 1,2-boron shift.

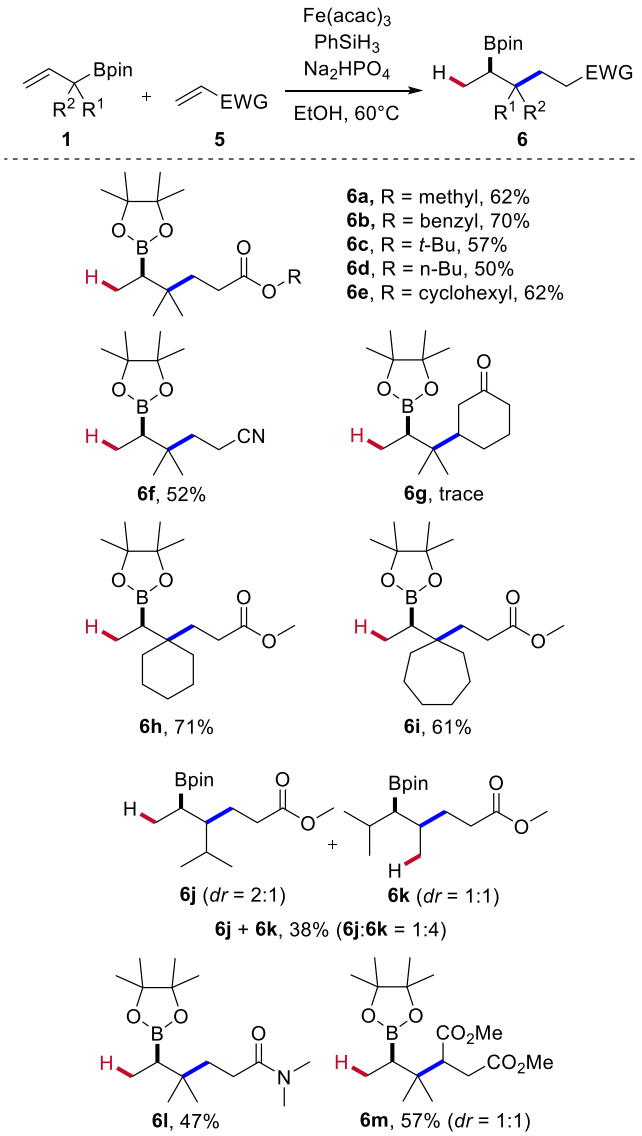
The underlying mechanism is depicted in Scheme 3. First, an iron hydride will be generated *in situ* from $Fe(acac)_3$ in the presence of phenylsilane and ethanol.[17] The Fe(III)-H complex will then react with the more nucleophilic double bond of the allylboronic ester to give the intermediate **Int-I**. Reaction of Fe(III)-H with the Michael acceptor is slower due to electronic effects.[18] **Int-I** will then undergo a 1,2-boron shift to provide the more stable C-radical intermediate **Int-II**.[5a,7] This nucleophilic C-radical **Int-II** will be efficiently trapped by the Michael acceptor to give the electrophilic adduct C-radical **Int-III**. Trapping with the initially generated Fe(II) complex should lead to the Fe(III)-enolate **Int-IV**, which upon reaction with $PhSiH_3$ in EtOH will finally give the product, thereby regenerating the Fe(III)-H complex.[16]

Scheme 3. Suggested Mechanism



The suggested cascade could be realized using the allylboronic ester **1a** (1 equiv), methyl acrylate (3 equiv), Na_2HPO_4 (1 equiv), phenylsilane (3 equiv), and $Fe(acac)_3$ (5 mol %) in EtOH to afford the desired 1,3-hydroalkylation product **6a** in 62% yield (Scheme 4). When these conditions were applied, various acrylates such as benzyl acrylate (**5b**), *tert*-butyl acrylate (**5c**), *n*-butyl acrylate (**5d**), and cyclohexyl acrylate (**5e**) were successfully reacted with allylboronic ester **1a** to afford the corresponding hydrofunctionalization products **6b**–**e** in moderate to good yields (50–70%). Acrylonitrile **5f** was found to be an eligible Michael-type acceptor, and **6f** was isolated in 52% yield. However, in a reaction with cyclohex-2-en-1-one as an acceptor, the targeted product **6g** was formed in

Scheme 4. Formal 1,3-Hydroalkylation of Allylboronic Esters with Different Michael Acceptors[a]



[a]Reaction conditions: **1** (0.2 mmol, 1 equiv), **5** (0.3 mmol, 3 eqiuv), $Fe(acac)_3$ (5 mol %), $PhSiH_3$ (0.3 mmol, 3 equiv), Na_2HPO_4 (0.2 mmol, 1 equiv), EtOH (1 mL), 60 °C, Ar, 1 h.

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only traces. Moreover, *N*,*N*-dimethylacrylamide (**5h**) and dimethyl fumarate (**5i**) afforded the targeted products **6l**,**m** in 47−57% yield. Next, the allylboronic ester moiety was varied using methyl acrylate as the electrophilic alkene component. 1,3-Hydroalkylation products **6h**,**I** were isolated in good yields (61−71%).

Finally, we explored the α-isopropyl-substituted allylboronic pinacol ester in combination with methyl acrylate (**5a**). The cascade provided the B-migrated **6j** and the nonmigrated product **6k** in 38% combined yield in a ratio of 1:4. The targeted **6j** (minor regioisomer) was formed with 2:1 diastereoselectivity (the relative configuration could not be assigned), whereas **6k** showed no diastereoselectivity. Due to the lower thermodynamic driving force, B-migration is, as expected, less efficient when monoalkylsubstituted allylboronic esters are used as the H-atom acceptors. The two regioisomers could be assigned after oxidation of the C−B bond and subsequent lactonization by comparison with the corresponding compounds known in the literature (see the Supporting Information).

In summary, we have presented radical 1,3-carboheteroarylation and 1,3-hydroalkylation of allylboronic esters that proceed with concomitant 1,2-boron migration. The synthetically valuable boron moiety is retained in the products. These results together with the few existing examples convincingly show that allylboronic esters are valuable radical acceptors to realize 1,3-difunctionalization reactions. The 3-substituted quinoxalin-2(1*H*)-ones obtained are useful compounds bearing a perfluoroalkyl group as well as a boron moiety. The latter functionality can be readily used for follow-up transformations. Further, it has also been shown that iron-catalyzed reductive alkene cross-couplings can be achieved with allylboronic esters as coupling partners. The two methods introduced further extend the emerging field of boron-based radical chemistry.[2]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.2c00039.

Experimental details and characterization data and NMR spectra of new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Armido Studer − *Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, 48149 Münster, Germany;* orcid.org/0000-0002-1706-513X; Email: studer@uni-muenster.de

Author

Kalipada Jana − *Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, 48149 Münster, Germany*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.2c00039

Notes

The authors declare no competing financial interest.

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