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Photoinduced Fragmentation Borylation of Cyclic Alcohols and Hemiacetals

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Supporting Information Placeholder

ABSTRACT: A visible-light photoinduced fragmentation borylation of *O*-phthalimido cycloalkanols with bis(catecholato)diboron is described. Structurally diverse keto and formyloxy alkyl boronic esters are shown to be conveniently prepared by radical-mediated ring-opening of cyclic alcohols and hemiacetals, respectively. The reactions proceed under mild conditions in the absence of additives or photocatalysts, display excellent functional group tolerance, and are shown to allow cleavage of 4-, 5-, 6-, and 7-membered ring substrates. The mechanism proceeds via sequential homolytic N–O and C–C bond cleavages, the latter of which involves β -scission of an alkoxy radical, generating a carbonyl and an alkyl radical that is trapped by the diboron reagent. Spectroscopic studies suggest direct photoexcitation of either the phthalimide or diboron substrates with blue-light can initiate a radical chain mechanism.

Carbon–carbon single bond cleavage reactions provide a powerful platform for diversification of organic molecules. These methods allow non-traditional and often dramatic structural changes, which can be beneficial for accessing new chemical space in the search for compounds with novel bioactivities.¹ This is particularly attractive in carbocyclic and heterocyclic ring systems, where fragmentation provides structures vastly different to those of the parent substrates. However, the inertness of C–C bonds makes this challenging, especially for heterolytic cleavage pathways, which typically require multiple activating groups,² strained ring systems,³ or directing groups.⁴ By contrast, homolytic C–C bond cleavage can allow fragmentation of non-activated and unstrained cycloalkanes, for example, via β -scission of high energy heteroatom-centered radicals (Figure 1a).⁵ Recent developments in visible-light photocatalysis have provided valuable methods to achieve such deconstructive functionalizations of cyclic alcohols⁶ and oximes⁷ under mild conditions.^{1b,8}

We and others recently reported a range of radical-mediated borylation reactions that allow access to alkyl boronic esters by substitution of native functional groups, including carboxylic acids,⁹ amines,¹⁰ and alcohols.¹¹ While these are useful methods for transforming feedstock chemicals into highly versatile organoboron compounds,¹² the nature of

substitution reactions means they do not provide products of greater functional complexity than that of the substrate. We recognized the potential to expand on these radical borylations by taking advantage of homolytic C–C bond cleavage via β -scission of alkoxy radicals derived from readily available cycloalkanols. In comparison to deoxygenative borylations,¹¹ such a process would benefit from providing boronic ester products that retain the oxygen functionality (Figure 1b).

In our previously reported radical borylations, we demonstrated that these reactions proceed under catalyst- and additive-free conditions by taking advantage of photoinduced electron-transfer (PET) reactions of electron donor–acceptor (EDA) complexes formed between the substrate and bis(catecholato)diboron [B₂(cat)₂].^{9a,10a,13} Therefore, we reasoned that *O*-activated cycloalkanols could form EDA complexes with B₂(cat)₂ to initiate fragmentation borylations under similar conditions. Previous reports by the groups of Guo and Zuo demonstrated the feasibility of photoinduced fragmentation borylations of oxime esters,¹⁴ including under catalyst-free conditions; however, they were limited to ring-opening of strained cyclobutanes. To date, reports of fragmentation borylations of cycloalkanol derivatives have relied on the use of hazardous peroxide substrates under copper catalysis.¹⁵ To access alkoxy radicals under photoinduced, catalyst-free conditions, we selected *O*-

phthalimido cycloalkanols **1** as radical precursors (Figure 1c),¹⁶ as these species are easily prepared, stable, and we have previously shown that the phthalimide moiety forms complexes with $B_2(cat)_2$.^{9a} The use of these reagents as alkoxy radical precursors under visible-light photocatalysis was pioneered by the groups of Chen and Meggers in 2016, both of which involved 1,5-hydrogen atom transfer reactions and trapping of the resulting alkyl radicals with various alkenes.¹⁷ Their application was subsequently extended to β -scission reactions.¹⁸ Interestingly, all of these reports utilized the *O*-phthalimido substrates in overall reductive transformations that required super-stoichiometric quantities of Hantzsch ester as the reductant. To the best of our knowledge, there are no reports of their use in redox neutral photoinduced alkoxy radical-mediated reactions, nor are there examples of trapping the intermediate alkyl radicals with heteroatom-based reagents. Herein, we report that *O*-phthalimido cycloalkanols and hemiacetals undergo photoinduced fragmentation borylations with $B_2(cat)_2$ to provide acyclic keto and formyloxy alkyl boronic esters, without the need for catalysts or other additives.

Figure 1. Radical-mediated ring-opening functionalizations of cycloalkanes

We began our investigation by studying the reaction of *O*-phthalimido 1-methylcyclopentanol **1a** with $B_2(cat)_2$ (Table 1). Pleasingly, irradiation of an *N,N*-dimethylacetamide (DMAc) solution of **1a** and 1.5 equivalents of $B_2(cat)_2$ with blue LEDs at RT for 20 h yielded the desired δ -keto boronic ester **2** in 90% yield (entry 1). To facilitate isolation of the boronic ester product, the initially formed catechol boronic ester was converted to the stable pinacol boronic ester by in situ transesterification with pinacol. The amount of $B_2(cat)_2$ could

be lowered to 1.2 equivalents without reduction in efficiency (entries 2 and 3). The important role of the catechol ligand on the diboron reagent was highlighted through the unsuccessful reactions with bis(pinacolato)diboron (B_2pin_2) and $B_2(NMe_2)_4$ (entries 4 and 5). Interestingly, a moderate yield of **2** could also be obtained using tetrahydroxydiboron [$B_2(OH)_4$] (entry 6). Evaluation of various solvents indicated that higher yields were achieved with more Lewis basic solvents, such as DMAc and DMF (entries 7–10). The use of Lewis basic solvents has been reported to promote EDA complex formation with $B_2(cat)_2$,^{10c} facilitate homolytic substitution of $B_2(cat)_2$ by alkyl radicals, and stabilize chain propagating boryl radical intermediates.¹⁹ A control reaction performed in the dark showed that an inefficient thermal reaction was also operative (entry 11), which is in agreement with previously reported decarboxylative and deaminative borylations with $B_2(cat)_2$.^{9a,10} Finally, the reaction was found to be sensitive to oxygen, as no product formed if the reaction was run open to air (entry 12).

Table 1. Optimization Studies^a

entry	deviation from standard conditions	yield(%)
1	None	90
2	1.2 equiv of $B_2(cat)_2$	92
3	1.0 equiv of $B_2(cat)_2$	83
4	$B_2(pin)_2$ instead of $B_2(cat)_2$	0
5	$B_2(NMe_2)_2$ instead of $B_2(cat)_2$	0
6	$B_2(OH)_2$ instead of $B_2(cat)_2$	50
7	DMF as solvent	70
8	MeCN as solvent	38
9	EtOAc as solvent	45
10	THF as solvent	0
11	No light	19
12	Under air	0

^a Reactions were performed on a 0.10 mmol scale and irradiated with a 40 W Kessil lamp. Yields were determined by ¹H NMR using diethyl phthalate as an internal standard.

With the optimum conditions in hand, we first examined the scope of the fragmentation borylation of *O*-phthalimido cycloalkanols, which are easily prepared from readily available cyclic alcohols (Scheme 1).²⁰ A broad range of functionalized 1-alkyl cyclobutanols were efficiently borylated, providing acyclic δ -keto boronic esters **3–25**. The mild conditions tolerated aryl (**13–17**), heteroaryl (**18–20**) and alkyl carboxylate esters (**21–25**), as well as various useful synthetic handles, including alkyl tosylates (**11**), bromides (**12**, **23**), and aryl halides (**15**, **16**). Various cyclopentanol were also borylated in high yield (**26–31**), including those with additional substituents, which provided mixtures of regioisomers (**28**, **29**). This ring-opening strategy was also successfully applied to bridged bicycles, which regioselectively generated the secondary boronic esters **30** and **31** in good

Scheme 1. Cycloalkanol fragmentation borylation scope^a

^a Reactions were carried out on a 0.10-0.50 mmol scale. Yields are of isolated products after chromatographic purification. The regioisomeric ratios (r.r.) and diastereomer ratios (d.r.) were determined by ¹H NMR analysis of the purified product. ^b Yields in parentheses were obtained on a 3.5 mmol scale.

yields. Pleasingly, the 5,5-fused bicyclic product **31** was formed with complete diastereoselectivity, which highlights the potential utility of this method in the stereoselective synthesis of complex molecular architectures. Interestingly, a secondary cyclopentanol provided the corresponding aldehyde **32**, albeit in low yield. This example is notable given the lower thermodynamic driving force for fragmentation due to the formation of a weaker carbonyl bond, and also the known instability of aliphatic aldehydes in the presence of B₂(cat)₂.²¹ The borylation protocol was also suitable for ring-opening of *O*-phthalimido cyclohexanols (**33–36**) and cycloheptanols (**37**), although lower yields were obtained compared to the more strained 4- and 5-membered ring substrates. The successful borylation of these larger ring substrates contrasts the reactivity previously observed by Wang and co-workers, who reported them to be inert to their Hantzsch ester-mediated fragmentation alkynylation and alkenylation conditions.^{18b} Finally, the synthetic utility of this photoinduced fragmentation borylation reaction, was demonstrated by synthesizing boronic ester **6** in high yield on a preparative scale (3.5 mmol), and through successful derivatizations of the boronic ester group, including hydrolysis, fluorination, and arylation.²⁰

The scope of the fragmentation borylation was then extended to *O*-phthalimido cyclic hemiacetals (Scheme 2a).^{18b}

Both tetrahydrofuran and tetrahydropyran derivatives were successfully borylated to provide γ- and δ-formyloxy boronic esters, respectively, in moderate to good yields (**38–46**). Substitution adjacent to the oxygen of the cyclic ether was tolerated, including alkyl (**39**), aryl (**40**, **42**), and protected alcohol groups (**43–45**). In addition, a glucal derivative was successfully borylated in good yield to provide the densely functionalized boronic ester **46**, which bears three contiguous stereocenters and may serve as a versatile building block in synthetic chemistry. We also investigated a one-pot activation/fragmentation borylation sequence to enable direct access to formyloxy boronic esters from cyclic enol ethers (Scheme 2b). Sequential treatment of 3,4-dihydro-2*H*-pyran in acetonitrile with *N*-hydroxyphthalimide and triphenylphosphine hydrobromide, followed by B₂(cat)₂ and DMAc and subsequent blue-light irradiation provided boronic ester **41** in 44% yield, which is comparable to that obtained from the isolated *O*-phthalimido substrate (51%, Scheme 2a).

The success of this fragmentation borylation reaction is intriguing given the potential alternative mechanistic pathways of the postulated phthalimide radical anion intermediate **47** (Figure 2a). For formation of the desired alkoxy radical **48**, homolytic cleavage of the N–O bond of the *O*-phthalimido group in **47** must occur. However, in the case of

substrates derived from hemi-acetals ($X = O$), prior work by the group of Sammis has shown that radical anions **47** undergo preferential intramolecular elimination to form carbonyls **49** and phthalimide radical anion **50**.²² This pathway was also investigated by Chen,^{17a} who concluded that protonation of radical anion **47**, or coordination to tin, was required for successful alkoxy radical formation. As our fragmentation borylation reactions proceed under aprotic conditions, we postulate that a key boron-oxygen interaction prevents undesired elimination of **47**, thus favoring alkoxy radical formation. Another competing pathway is the direct *O*-borylation of alkoxy radicals **48** to form borate esters **51**, a process that has been widely exploited for the generation of alkyl radicals from catechol boronic esters.²³ As this process is facile, *O*-borylation becomes competitive if β -scission of **48** is slow. Indirect evidence for this was provided by the lower yields obtained when the reactions were performed at higher concentration,²⁰ and the observation of cycloalkanol side-products, formed after hydrolysis of borates **51** during workup.

Scheme 2. Cyclic hemiacetal fragmentation borylation^a

^a Reactions were carried out on a 0.10–0.50 mmol scale. Yields are of isolated products after chromatographic purification.

Based on these observations, and additional competition experiments, spectroscopic studies, and quantum yield measurements,²⁰ we propose the mechanism shown in Figure 2b. Surprisingly, UV/Vis analysis of DMAc solutions of **1a** and $B_2(cat)_2$ did not support the formation of an EDA complex. However, the absorbance spectra of both species extended to 450 nm; therefore, a radical chain process could be initiated by photoexcitation of either **1a** or $DMAc \cdot B_2(cat)_2$ complex **52**.^{9a} This initiation generates the DMAc-stabilized boryl radical **53** and *O*-borylated phthalimide radical **54**, both of which are chain propagating species. Subsequent homolytic N–O bond cleavage of **54** and rapid β -scission of alkoxy radical **56** forms the keto-substituted alkyl radical **57** and the phthalimide-B(cat) by-product **55**. Borylation of **57** with $B_2(cat)_2$ proceeds via a

two-step process involving initial formation of radical complex **58**, with subsequent B–B bond cleavage facilitated by complexation with DMAc to form **59**.¹⁹ This provides the boronic ester product **60** and DMAc-stabilized boryl radical **53**. Chain propagation to generate **54** could occur via SET and boron transfer,^{10c} or via boryl radical addition to phthalimide **1a**, analogous to tin radical-mediated reactions of *N*-alkoxyphthalimides.¹⁶

Figure 2. Potential competing pathways and proposed mechanism

In conclusion, we have developed the first photoinduced catalyst- and additive-free C–C bond cleavage/borylation of *O*-activated cyclic alcohols and hemiacetals. This was achieved using readily available *O*-phthalimido cycloalkanols, which efficiently reacted with $B_2(cat)_2$ in a photoinitiated radical chain mechanism. This borylation reaction benefits from providing distally difunctionalized products, wherein structural reorganization of cyclic alcohols enables retention of the oxygen functionality, therefore providing keto and formyloxy alkyl boronic esters. Given the mild conditions, and the ready availability of cyclic alcohols and hemiacetals from feedstock chemicals, this new radical borylation strategy could find wide application for the preparation of synthetically and biologically important boron-containing molecules.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and characterization data for new compounds (PDF).

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Notes

The authors declare no competing financial interests.

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