C–C Borylation

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Mild Ring-Opening 1,3-Hydroborations of Non-Activated Cyclopropanes

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Abstract: *The Brown hydroboration reaction, first reported in 1957, is the addition of B–H across an olefin in an anti-Markovnikov fashion. Here, we solved a long-standing problem on mild 1,3-hydroborations of non-activated cyclopropanes. A three-component system including cyclopropanes, boron halides, and hydrosilanes has been developed for borylative ring-opening of cyclopropanes following the anti-Markovnikov rule, under mild reaction conditions. Density functional theory (M06-2X) calculations show that the preferred pathway involves a cationic boron intermediate which is quenched by hydride transfer from the silane.*

Cyclopropanes are a fundamentally important class of compounds not only because such small rings are found in many biologically active compounds but also because a broad range of pharmaceutical and agrochemical agents are synthesized from cyclopropanes, as they can serve as useful synthetic building blocks.[1] The inherent ring strain present in small rings is frequently used for ring-opening reactions, many of which are not readily accessible by other conventional methods.[2] Most of the existing cyclopropane ring-opening approaches have relied on the specific functional group assistance, including 1) polarizing one of the C–C bonds through the attachment of an activated donor–acceptor cyclopropane,[3] and 2) the attachment of directing groups that favor oxidative addition by a transition metal to form metallacyclobutane intermediates (Figure 1 a).[4] Although non-activated cyclopropanes are the most common three-membered ring systems found in nature, methods for their selective ring-opening remain scarce.[5] Some elegant research works have recently demonstrated that they could undergo 1,3-addition of $B(C_6F_5)_3$/^{t}Bu$_3$P,[6] 1,3-aminofluorination,[7] 1,3-difluorination,[8] 1,3-deoxygenation,[9] and elimination[10] reactions. Nevertheless, the development of new systems for efficient opening and functionalization of these compounds under mild and environmentally friendly conditions is still in high demand.

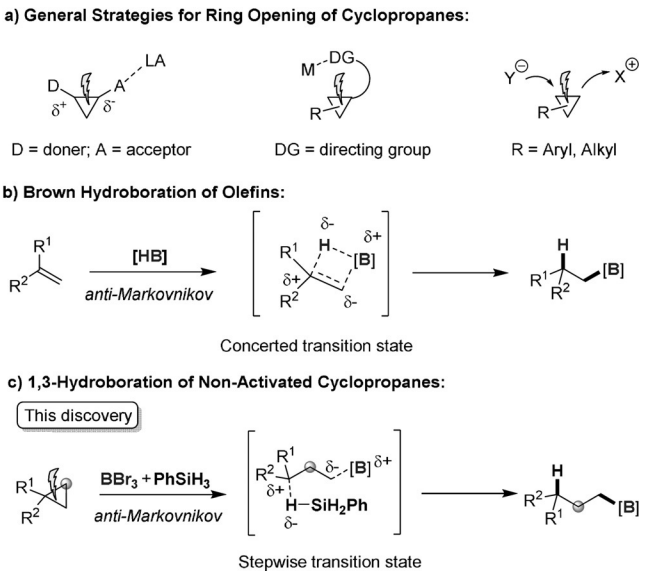

Figure 1. Ring-opening reactions of cyclopropanes.

Alkylboronic esters play important roles in a variety of fields ranging from material science to drug discovery and organic synthesis.[11] The well-known Brown hydroboration of olefins is a classic transformation used for their synthesize.[12] Hydroboration with HBR_2 (R = H, alkyl etc.) typically occurs in an anti-Markovnikov manner. It proceeds via a four-membered concerted transition state: the hydrogen and the boron atoms added on the same face of the double bond (Figure 1 b).[13] However, such a pathway for the hydroboration of cyclopropanes is very sluggish.[14] High reaction temperatures and poor functional group compatibility make this transformation less practical. Because boron halides were known to be applied in electrophilic borylation reactions with arenes, heteroarenes,[15] alkynes[16] and alkenes,[17] we envisioned that the alkene-like π-donating properties of non-activated cyclopropanes could facilitate similar electrophilic ring-opening and borylation. Herein, we describe the discovery of a mild three-component system for the ring-opening 1,3-hydroboration of non-activated cyclopropanes and the simplest cyclopropane gas, using BBr_3 as a boron source, and $PhSiH_3$ as an external hydride source (Figure 1 c). Through mechanistic experiments and density functional theory (DFT) calculations, we identified a stepwise pathway for this transformation, which allows high reactivity at room temperature.

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We began our investigation by monitoring the reactivity of 2-(1-methylcyclopropyl)naphthalene (**1a**) in the presence of boron Lewis acids (Table 1). The reaction was found to be facile with 1.2 equivalents of BBr_3 as a boron source in the presence of $PhSiH_3$ as a hydride source. In DCM at room temperature for 1 hour, 4,4,5,5-tetramethyl-2-(3-(naphthalen-2-yl)butyl)-1,3,2-dioxaborolane (**2a**) is formed in 92% GC yield after pinacol protection. $PhSiH_3$ is crucial for high conversion (entry 2). Inorganic reducing agents such as $NaBH_4$ and $LiAlH_4$ and other hydrosilanes such as Et_3SiH and Ph_2MeSiH were also effective and afforded boronate **2a** in 48–63% yields as the only ring-opened product (entries 3–6). The addition of BCl_3 also gave the desired product **2a** in 80% yield (entry 7), but BF_3 did not work in this reaction (entry 8). Further exploration showed that the common reagents applied in Brown hydroborations (BH_3·THF and $HBBr_2$·Me_2S) were completely ineffective in our reaction, suggesting that **2a** is formed by a different pathway (entries 9 and 10).

Table 1: Reaction optimization.[a]

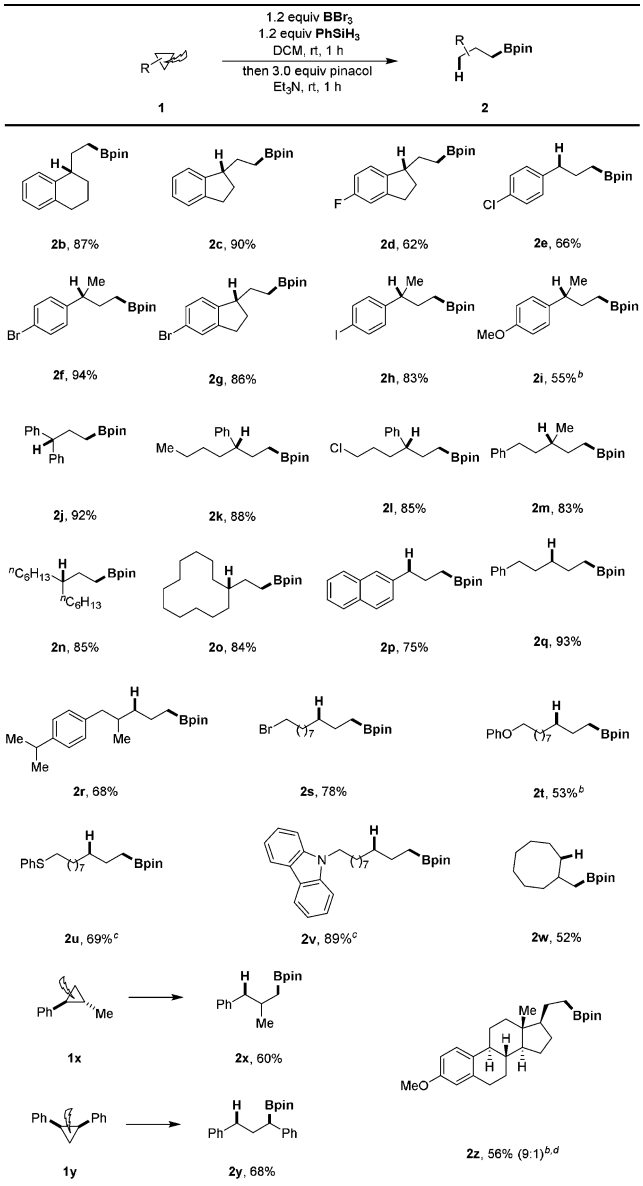
1a **2a**

Entry	Variation from the "standard conditions"	Yield of **2a** [%][b]
1	none	92 (81)[c]
2	without $PhSiH_3$	trace
3	$NaBH_4$ instead of $PhSiH_3$	48
4	$LiAlH_4$ instead of $PhSiH_3$	55
5	Et_3SiH instead of $PhSiH_3$	52
6	Ph_2MeSiH instead of $PhSiH_3$	63
7	BCl_3 instead of BBr_3	80
8	BF_3·Et_2O instead of BBr_3	0
9	BH_3·THF instead of BBr_3 + $PhSiH_3$	0
10	$HBBr_2$·Me_2S instead of BBr_3 + $PhSiH_3$	0

[a] Conditions: all reactions were run at a 0.20-mmol scale in 1.0 mL of DCM at room temperature for 1 hour, and then pinacol (0.6 mmol) in Et_3N was added, and the mixture was stirred for another 1 hour. [b] Yield determined by GC. [c] Yield of isolated product.

With the optimal conditions in hand, we examined the scope of this 1,3-hydroboration reaction (Table 2). Substrates containing spiro cyclopropanes with an indane or tetralin scaffold (**2b**,**c**) were all rapidly ring-opened, and the corresponding pinacol boronate esters were isolated in excellent yields. Halogen substituents (F, Cl, Br and I) worked well under the reaction conditions (**2d**–**h**), highlighting the potential of this process in combination with further conventional cross-coupling transformations. While the *O*-demethylation process with BBr_3 is well documented, substrate **1i** bearing a methoxy group is compatible with this process, affording desired product **2i** in 55% yield. The reaction of 1,1-diphenylcyclopropane (**1j**) in our system afforded desired product **2j** in 92% yield. Boronates **2k** and **2l** were obtained in good yields from 1,1-arylalkylcyclopropanes after the ring-opening reactions. 1,1-Dialkylcyclopropanes **1m**–**o** could also be subjected to our reaction conditions and desired products **2m**–**o** were obtained in good yields after the ring-opening–hydroboration reaction. Notably, this reaction is not limited to cyclopropanes with a quaternary carbon center. Monosubstituted cyclopropanes **1p**–**v** bearing aryl, benzyl, and alkyl groups worked well in this protocol and gave corresponding products **2p**–**v** with good yields and excellent regioselectivity. Among these substrates, those containing Br (**2s**), OPh (**2t**), SPh (**2u**), and carbazole (**2v**) functionalities were well tolerated. Ring-opening and borylation of fused 1,2-disubstituted cyclopropane **1w** occurred most favourably at the secondary methylene position, and ring expansion products were not observed. *Trans*-1,2-alkylarylcyclopropane **1x** was

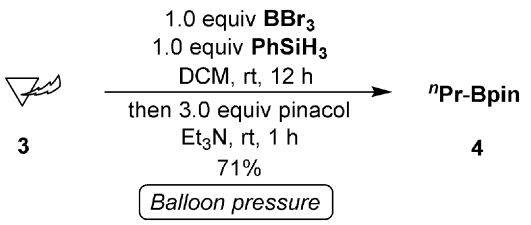
Table 2: Substrate scope.[a]



[a] Reaction conditions: **1** (0.50 mmol), BBr_3 (0.60 mmol), $PhSiH_3$ (0.60 mmol) in DCM (2.5 mL) at room temperature, 1 hour; then pinacol (1.5 mmol) in Et_3N was added, and the reaction was stirred for an additional 1 hour. [b] Using **1** (0.55 mmol), BBr_3 (0.50 mmol). [c] Using **1** (0.50 mmol), BBr_3 (1.10 mmol). [d] Determined by crude ^1H NMR.

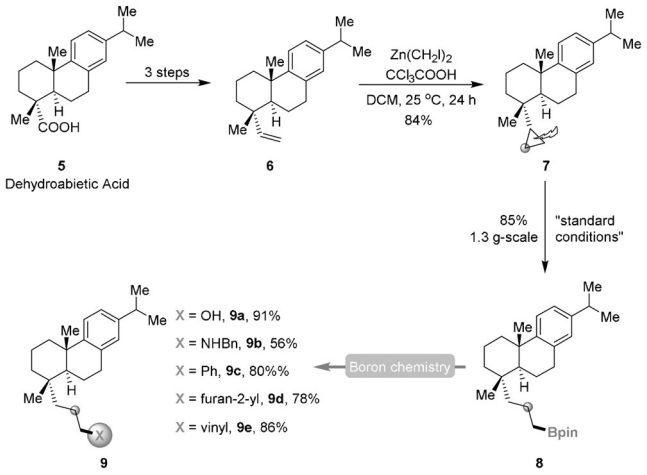
regioselectively converted into **2x** in 60% yield. However, *cis*-1,2-diphenylcyclopropane (**1y**) was transformed into product **2y** by cleavage of the most sterically hindered σ bond. This mild hydroboration procedure can also be utilized in late-stage functionalization of complexed biologically active molecules. The investigation was initiated with the preparation of cyclopropane **1z** from estrone. Then, **1z** was subjected to this developed method to produce **2z** in 56% isolated yields with good diastereoselectivity.

The activation of small molecules has been an increasingly popular area of research in recent years[18] and the C–H borylation of small molecules such as methane,[19] ethane,[19a] and cyclopropanes[20] have been recently developed. However, C–C bond cleavage–borylation of small molecules remains a major challenge.[21] Having established optimal reaction conditions, we found that the 1,3-hydroboration of cyclopropane gas (**3**) under the pressure generated by a balloon could produce ^{n}PrBpin (**4**) in 71% yield (Scheme 1).



Scheme 1. 1,3-Hydroboration of cyclopropane.

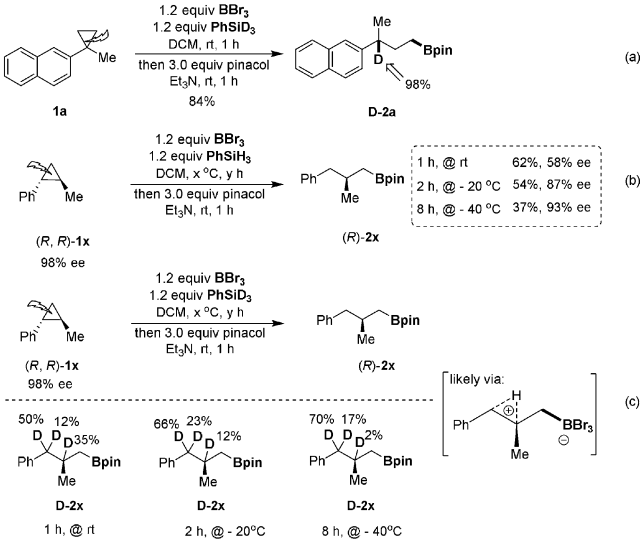
Compared to traditional Brown hydroborations of olefins, the value of a 1,3-hydroboration of cyclopropanes is highlighted by the fact that the corresponding product contains an additional methylene substituent. As shown in Scheme 2, dehydroabietic acid (**5**) with a carboxylic acid group readily produce olefin **6** and cyclopropane **7** in good yields. Not surprisingly, ring-opening of compound **7** on a gram-scale results in boronate **8** with excellent yield. As noted at the outset, the boronate group is an extremely versatile intermediate in organic synthesis because it can be converted into



Scheme 2. Derivatization of 1,3-hydroboration products.

other important compounds by reactions such as Brown oxidation (**9a**), amination (**9b**), arylation (**9c**), heteroarylation (**9d**), and vinylation (**9e**) reactions (For details, see the Supporting Information).

Several experiments were conducted to provide insight into the potential mechanism of this transformation (Scheme 3). When the reaction of **1a** is conducted with



Scheme 3. Mechanistic experiments.

$PhSiD_3$ under standard reaction conditions, the D label is nearly fully incorporated into **2a** (84% yield, 98% D). This observation confirmed that the hydrosilane is the sole source of the hydrogen atom in the product (Scheme 3a). We further employed (*R*,*R*)-**1x** under the standard reaction conditions, and desired product (*R*)-**2x** was formed in 62% yield with 58% *ee*. As the reaction temperature was gradually reduced, the enantioselectivity of the product increased to 93% (Scheme 3b). To further explore this process, $PhSiD_3$ was added to the above mentioned reaction, and the hydrogen on the chiral carbon was deuterated. Moreover, the ratio of deuteration is consistent with the racemization product. These results suggest that in situ-formed benzylic carbon cations should be intermediates in these reactions and that 1,2-H migration is likely to occur during the C–C cleavage process (Scheme 3c).

To better understand the mechanism of the 1,3-hydroboration of cyclopropanes, DFT calculations were performed on the model reaction of cyclopropylbenzene and BBr_3.[22] As shown in Figure 2, the C–C cleavage of cyclopropylbenzene promoted by BBr_3 to give benzylic cation **IN1** via **TS1** requires a barrier of 19.8 kcal mol^{-1}. The benzylic carbon abstracts a hydride from $PhSiH_3$ through **TS2** with a barrier of 9.1 kcal mol^{-1} relative to **IN1**. Such a barrier would allow the benzylic carbon to undergo 1,2-H migration, which has a barrier of only 6.3 kcal mol^{-1}. This is in line with the experimental observation of the racemized hydroboration product in the hydroboration of chiral cyclopropane **1x**. Based on the computed energy profile of the overall reaction pathway, the C–C cleavage is the rate-determining step, with

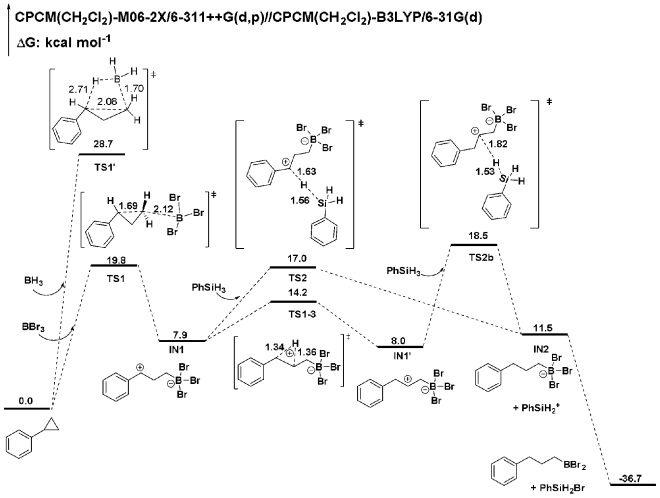


Figure 2. DFT-computed potential energy profile for the model reaction between cyclopropylbenzene and BBr_3 (standard state, 1 mol L^{-1}).

an overall activation energy of 19.8 kcal mol^{-1}. This is consistent with the relatively mild conditions required for the reaction. Notably, the calculated free energy of activation for the hydroboration of cyclopropylbenzene by BH_3 through a concerted process is as high as 28.7 kcal mol^{-1} (**TS1′**).[12]

In conclusion, we have discovered a direct, catalyst-free method for the 1,3-hydroboration of non-activated cyclopropanes under mild reaction conditions. With the developed system in hand, the first conversion of cyclopropane to *n*-propyl boronic esters has been achieved. The reaction proceeds through a stepwise pathway via energetically favourable transition states instead of a concerted four-membered transition state. As a practical method, the reaction cleanly and regioselectively produces widely used alkyl boronic esters in good to excellent yields. Owing to these advantages, this reaction should be of high synthetic value.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: C–C activation · cyclopropanes · DFT calculations · hydroboration · metal-free synthesis

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