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1,4-Bromoboration of Nitroalkenes

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The selective 1,4-bromoboration of nitroalkenes occurs under mild conditions with a bromoborane featuring two 1-methyl-*ortho*-carborane substituents, $BrB^{Me}oCb_2$. The bromide is introduced on the β-carbon and the boryl moiety on the nitro group that is bound to boron in a κ^2 manner. Screening a variety of other haloboranes gave either no reaction or indiscernible mixtures indicating the necessity for the $BrB^{Me}oCb_2$ reagent. The haloboration reaction tolerates a variety of aryl functional groups on the β-carbon as well as a hydrogen or methyl group on the α-carbon that all proceed with excellent regioselectivity and high isolated yields.

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Boron addition reactions are powerful synthetic tools to introduce a boryl unit and additional functional group on an unsaturated substrate.[1, 2] The most prevalent boron addition reactions are hydroboration and carboboration that introduce a B–H and B–C bond as the second functional group, respectively.[3-11] Despite the first haloboration reaction being reported over 80 years ago, examples of haloboration reactions are considerably more scarce than hydroboration and carboboration.[12, 13] The haloboration reaction installs a C–halogen bond that can be an effective synthetic handle to diversify the products.[14]

The most common haloboration reactions have been with alkynes to furnish boryl-vinyl-halides (**I**) with terminal alkynes being more reactive than internal alkynes (Figure 1a).[14] Pioneering work by Lappert and Eisch revealed that bromoboranes are much more effective than chloroboranes.[12, 15-18] This is due to the substrate interacting more favorably with electrophilic boron reagents as well as the increased lability of the boron-halogen bond with the heavier halogens.[19, 20] Recently, Ingleson, Pei, and Yuan revisited this historical reaction on alkyne substrates cleverly designed for cascade cyclizations to furnish polycyclic frameworks.[21-23] From these efforts, biologically active compounds as well as B,N and B,O-containing analogues of polycyclic aromatic hydrocarbons have been accessed.[23-26]

The haloboration of alkenes has been investigated but advancements have been hindered by the saturated products bearing a vicinal halide and boryl group being thermodynamically uphill thus reverting to starting materials, other products, or polyolefins.[27-30] The first attempt was reported by Lappert on the haloboration of cycloalkenes with BBr_3 that did not give any haloboration product.[16] For example, the reaction with cyclohexene only gave CyBr, $CyBBr_2$, and cyclohexenyl-BBr_2.

In 1966, Lappert reported a haloboration with BCl_3 on the unconjugated diene, norbornadiene, which furnished a 1,4-choroboration product with a C–C bond formed to give the cyclopropane containing product **II** (Figure 1b).[15, 16] Allene haloboration has been more successful, however, the vinyl-BBr_2/BCl_2 products are susceptible to degradation, thus alkoxy groups have been used to isolate the haloboration products as boronic esters (Figure 1c).[31, 32] In 2019, Chang reported the chloroboration of allenylsilanes with BCl_3 and quenched with pinacol to furnish the 1,3-chloroboration product through an isomerization that was isolated as the Bpin species **IV** (Figure 1d).[33] In 2005, Bubov reported the reaction of allyl(dichloro)borane with alkynes to give the *cis*-allylboration intermediate **V** that underwent isomerization by an intramolecular chloroboration to give the cyclized product **VI** (Figure 1e).[34] Like alkenes, heteroatom multiple bonds are also rare with the minimal examples being with selected isocyanates, isothiocyanates, nitriles, isonitriles, and imines.[35-42]

In nitroalkenes, the C=C bond is activated by the NO_2 group that enhances electrophilicity at the β-carbon. We believed that the nitro group could also modulate the reactivity by coordination to boron to enable a haloboration reaction. In this work, we investigate if haloboranes react with nitroalkenes to furnish 1,4-haloboration products.

We first screened the reactions of haloboranes that had been successful in literature reports for alkyne haloboration, specifically BCl_3, BBr_3, $PhBCl_2$, $PhBBr_2$, and Ph_2BBr. The reactions with trans-β-nitrostyrene in benzene at 23 °C for 30 minutes were assessed by ^1H NMR spectroscopy that revealed all five gave indiscernible mixtures (Table 1, entries 1-5). The reaction with the more Lewis acidic bromoborane featuring electron withdrawing perfluorophenyl groups, $BrB(C_6F_5)_2$,[43] also gave multiple products that we were unable to isolate (entry 6).

Recently, it has been demonstrated that *ortho*-carboranes are highly effective substituents to enhance the Lewis acidity at boron.[44-55] Regarding boron addition reactions, the *ortho*-carborane substituted secondary borane, $HB^{Me}oCb_2$ (^{Me}oCb = 1-methyl-*ortho*-carborane) and related carborane borenium

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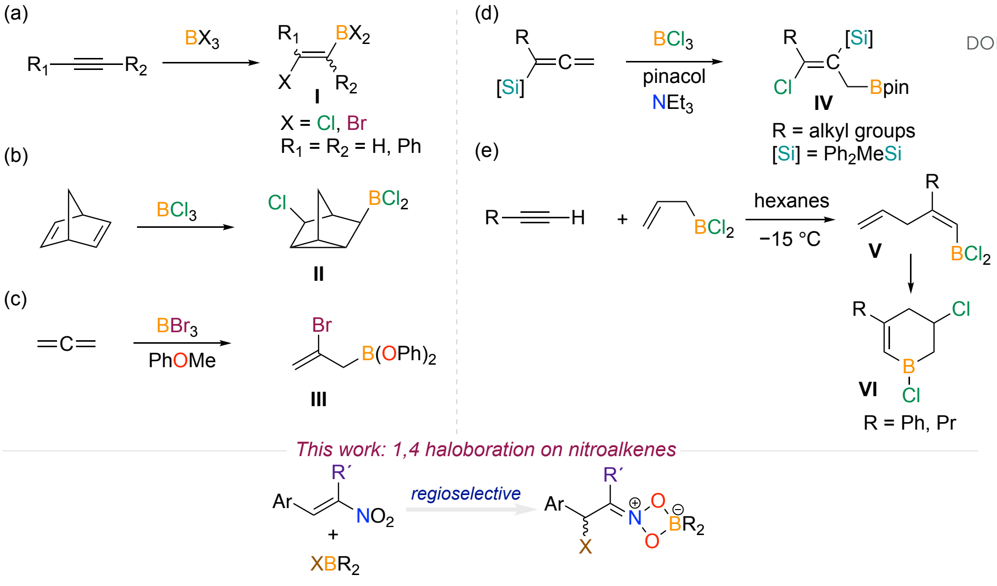
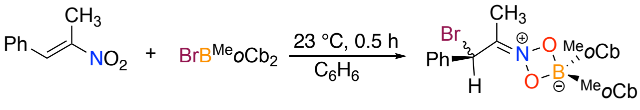


Figure 1: Representative haloboration reactions of unsaturated organic molecules.

compounds are extremely potent hydroboration reagents.[45, 54, 55] We surmised the tremendous bulk and Lewis acidity of *ortho*-carborane substituted haloboranes could enable selective haloboration. Bis(*ortho*-carboranyl)boranes with a halogen on boron that feature methyl and trimethylsilyl (TMS) groups on the *ortho*-carbons have been reported, specifically ClB^{Me}*o*Cb$_2$, BrB^{Me}*o*Cb$_2$, and BrB^{TMS}*o*Cb$_2$ (^{Me}*o*Cb = 1-methyl-*ortho*-carborane, ^{TMS}*o*Cb = 1-trimethylsilyl-*ortho*-carborane).[45, 56] The chloroborane with ^{TMS}*o*Cb substituents, ClB^{TMS}*o*Cb$_2$, was accessed by deprotonation of two equivalents of ^{TMS}*o*Cb and reaction with BCl$_3$ to complete the series. Reactions of both chloro species (ClB^{Me}*o*Cb$_2$ and ClB^{TMS}*o*Cb$_2$) and BrB^{TMS}*o*Cb$_2$ did not result in any reaction, only unreacted starting material was detected by ^{1}H NMR spectroscopy (Entries 7-9).

The reaction of trans-β-nitrostyrene with BrB^{Me}*o*Cb$_2$ led to a light-yellow solution that showed a dominant new species by ^{1}H NMR spectroscopy with consumption of both starting materials (Entry 10). The ^{11}B{^{1}H} NMR spectrum features a new peak in the tetracoordinate region at 8.8 ppm along with the disappearance of the peak corresponding to BrB^{Me}*o*Cb$_2$ at 64 ppm. The ^{1}H NMR spectrum has doublets at 5.57 and 5.12 ppm with matching coupling constants (J = 8 Hz). The product was isolated in 83% yield and the identity was determined by a single X-ray diffraction study as the 1,4-bromoboration product with the nitro group bound to boron in a κ^2 fashion with an iminium center and the bromine introduced on the α-carbon (**1**). The product bears a chiral center but crystallizes in the P2$_1$/c centrosymmetric space group indicating it is a racemate. The solid-state structure matches the solution NMR data with the tetracoordinate signal in the ^{11}B{^{1}H} NMR spectrum and the two doublets in the ^{1}H NMR spectrum at 5.57 and 5.12 ppm are assigned to the protons on the iminium carbon (H^a) and halogen substituted tertiary carbon (H^b). To determine if there is a solvent effect in the haloboration of trans-β-nitrostyrene with BrB^{Me}*o*Cb$_2$, we screened CH$_2$Cl$_2$, toluene, and fluorobenzene (Entries 11-13). Dichloromethane and toluene resulted in a decrease in isolated yield of **1** compared to benzene (63% and 68% *c.f.* 83%) while fluorobenzene gave a comparable yield (81%). Hence, we moved forward with BrB^{Me}*o*Cb$_2$ in benzene to investigate the breadth of the bromoboration reactions as the yield is the highest and enables monitoring reactions *in situ* in benzene-d^6.

The reaction between (*E*)-1-fluoro-4-(2-nitrovinyl)benzene and BrB^{Me}*o*Cb$_2$ led to a dark yellow solution which became colorless after stirring for 30 minutes at 23 °C (Entry 14). The product (**2**) was isolated in 75% yield. Growing single crystals enabled determination of the solid-state structure as the iminium haloboration product akin to **1**. The reaction tolerated alkoxy substitution with a methoxy group in the 4-position as well as a 3,4-methylenedioxy group that gave the iminium products in 79% (**3**) and 98% (**4**) isolated yields, respectively (Entries 15 and 16). The structure of **3** was confirmed by single crystal X-ray diffraction. A naphthyl group was investigated to determine the impact of aryl fusion to the styrene. The reaction of BrB^{Me}*o*Cb$_2$ with 1-(*E*)-2-nitroethenyl]naphthalene afforded iminium product **5** in 95% isolated yield (Entry 17). The reaction is tolerant to a heteroarene with a thiophene as the aryl group with (*E*)-2-(2-nitroethenyl)thiophene generating iminium **6** in 94% yield (Entry 18). To determine if substitution on the β-carbon could be tolerated, trans-β-methyl-β-nitrostyrene was reacted with BrB^{Me}*o*Cb$_2$ that smoothly generated the haloboration product **7** in 78% yield (Scheme 1).



7, 78%

Scheme 1: Reaction of trans-β-methyl-β-nitrostyrene with BrB^{Me}*o*Cb$_2$.

The ^{11}B NMR signals in **1**-**7** for the tetracoordinate boron all fit in the narrow region of 8.2-9.2 ppm (Table 2). The di-substituted alkene products (**1**-**6**) featured doublets from 5.02-5.92 ppm

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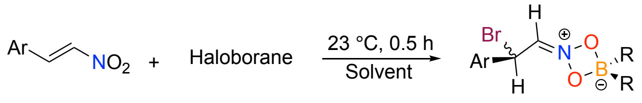
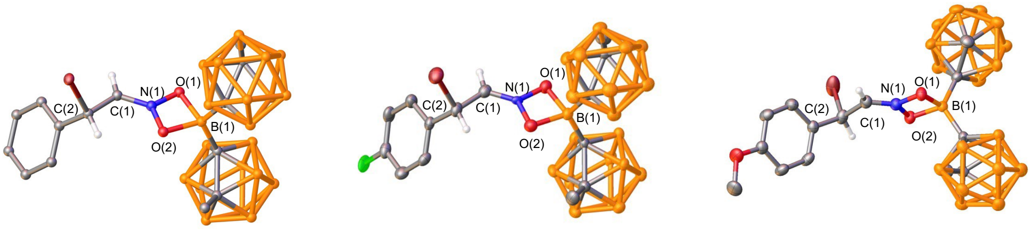
Table 1: Haloboration reactions of trans-β-nitrostyrenes and related species (NR = No reaction).



1-6

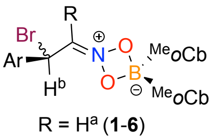
Entry	Ar	Haloborane	R	Solvent	Isolated Yield
1	Ph	BCl_3	Cl	C_6D_6	Complex mixture
2	Ph	BBr_3	Br	C_6D_6	Complex mixture
3	Ph	$PhBCl_2$	Ph/Cl	C_6D_6	Complex mixture
4	Ph	$PhBBr_2$	Ph/Br	C_6D_6	Complex mixture
5	Ph	Ph_2BBr	Ph	C_6D_6	Complex mixture
6	Ph	$(C_6F_5)_2BBr$	C_6F_5	C_6D_6	Complex mixture
7	Ph	ClB^{Me}*o*Cb$_2$	^{Me}*o*Cb	C_6D_6	NR
8	Ph	ClB^{TMS}*o*Cb$_2$	^{TMS}*o*Cb	C_6D_6	NR
9	Ph	BrB^{TMS}*o*Cb$_2$	^{TMS}*o*Cb	C_6D_6	NR
10	Ph	BrB^{Me}*o*Cb$_2$	^{Me}*o*Cb	C_6H_6	**1** (83%)
11	Ph	BrB^{Me}*o*Cb$_2$	^{Me}*o*Cb	C_7H_8	**1** (68%)
12	Ph	BrB^{Me}*o*Cb$_2$	^{Me}*o*Cb	CH_2Cl_2	**1** (61%)
13	Ph	BrB^{Me}*o*Cb$_2$	^{Me}*o*Cb	C_6H_5F	**1** (81%)
14	4-F-Ph	BrB^{Me}*o*Cb$_2$	^{Me}*o*Cb	C_6H_6	**2** (74%)
15	4-MeO-Ph	BrB^{Me}*o*Cb$_2$	^{Me}*o*Cb	C_6H_6	**3** (79%)
16	3,4-OCH$_2$O-Ph	BrB^{Me}*o*Cb$_2$	^{Me}*o*Cb	C_6H_6	**4** (98%)
17	1-Np	BrB^{Me}*o*Cb$_2$	^{Me}*o*Cb	C_6H_6	**5** (95%)
18	2-thiophene	BrB^{Me}*o*Cb$_2$	^{Me}*o*Cb	C_6H_6	**6** (94%)



1 **2** **3**

Figure 2: Solid state structures of **1**-**3**. Ellipsoids depicted at the 50% probability level and hydrogen atoms omitted for clarity except the two on the formerly alkenyl carbons.

with coupling constants of 8 Hz. The proton on the iminium carbon of **7** at 5.56 ppm lies in this chemical shift window. In **2**, the $^{19}F\{^1H\}$ NMR spectrum features an upfield shift for the *para*-fluorine from the starting material (–109.0 *c.f.* –105.7 ppm).



R = H^a (**1**-**6**)
= Me (**7**)

Table 2: Notable ^1H and ^{11}B NMR shifts for **1**-**7**

Compound	H^a	H^b	^{11}B
1	5.57	5.12	8.9
2	5.48	5.02	9.2
3	5.70	5.22	9.0
4	5.92	5.46	8.9
5	5.67	5.11	9.0
6	5.55	5.40	9.1
7	N/A	5.56	8.2

Examining the solid-state structures of **1**-**3** reveal short C(1)–N(1) bond distances consistent with the iminium structures with **2** and **3** having shorter bonds attributed to the electron withdrawing fluoro and methoxy substituents [Table 3, **1**: 1.323(5) Å, **2**: 1.291(3) Å, **3**: 1.278(3) Å]. The C(1)–C(2) bonds in the three compounds range 1.472(3) to 1.493(6) Å that validate the elongation of the alkenes to single bonds. The N–O bond distances all range 1.331(2) to 1.347(4) Å revealing that the two nitrogen-oxygen bonds are within the error of measurement in the three compounds. The B–O bond lengths are consistent with both oxygen atoms binding boron in an equivalent manner [range = 1.557(6) to 1.573(5) Å]. The geometry at nitrogen is trigonal planar [$\Sigma_{\angle N}$ range = 360.0(4)° to 360.1(3)°] but with a compressed O(1)–N(1)–O(2) bond angle due to the four membered ring [102.9(3) to 103.55(16)°].

To verify that nitro groups interact with BrB^{Me}*o*Cb$_2$, the reaction of BrB^{Me}*o*Cb$_2$ with nitrobenzene was carried out in C_6D_6 at 23 °C. After 20 min, slight shifts were observed in the aryl peaks of nitrobenzene (up to 0.13 ppm) that indicates a coordinative interaction. The

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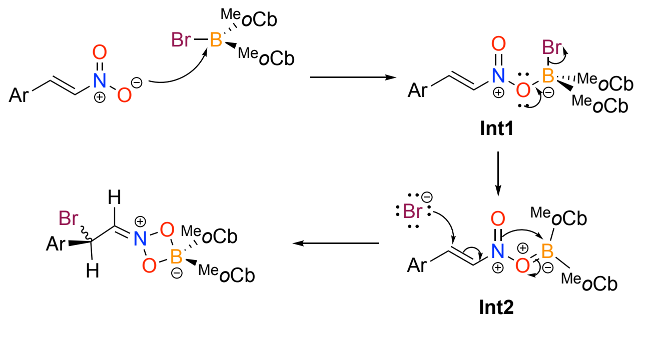
reaction of **1** with pyridine did not show any evidence of a retro-1,4-bromoboration, but rather a complex reaction mixture after stirring for 24 h at 23 °C in C_6D_6. To further determine if a retro-1,4-bromoboration occurs, the product with the electron withdrawing fluoride, **2**, was reacted with trans-β-nitrostyrene in C_6D_6 at 23 °C that did not result in any change based on *in situ* ^{1}H and ^{11}B NMR spectroscopy.

Table 3: Salient bond lengths (Å) and angles (°) in **1**-**3**.

	1	**2**	**3**
C(1)–N(1)	1.285(5)	1.291(3)	1.279(6)
C(1)–C(2)	1.493(6)	1.472(3)	1.489(7)
C(2)–C(1)–N(1)	121.0(3)	121.3(2)	119.5(4)
B(1)–O(1)	1.569(5)	1.570(3)	1.562(6)
B(1)–O(2)	1.573(5)	1.562(3)	1.557(6)
N(1)–O(1)	1.334(4)	1.331(2)	1.345(5)
N(1)–O(2)	1.347(4)	1.339(2)	1.343(5)
O(1)–N(1)–O(2)	103.0(3)	103.55(16)	102.9(3)
$\Sigma_{\angle N}$	360.1(3)	360.0(2)	360.0(4)

A proposed mechanism for the haloboration reaction is described in Scheme 2. The first step is coordination of the nitro oxygen to the haloborane to generate **Int1** where the molecule is neutral with positive charge on nitrogen and negative on the boron center. Next, the oxygen delocalizes electron density to make a π bond with boron to facilitate the displacement of the bromide to furnish **Int2**. Finally, the bromide attacks the Michael acceptor carbon to access the 1,4-bromoboration iminium product.



Scheme 2: Proposed mechanism for the bromoboration of trans-β-nitrostyrenes.

In this work, we shed light on rare haloboration reactions by demonstrating the 1,4-bromoboration of nitroalkenes in high isolated yields under mild reaction conditions. In haloborane screening, only $BrB^{Me}oCb_2$ was effective indicating that carboranyl substituted boranes can be leveraged to access unique reactivity. The products feature a chelated borate with an iminium nitrogen and bromide on the β-carbon as confirmed by single crystal X-ray diffraction and NMR spectroscopy. The reaction tolerates a variety of aryl groups on the β-carbon and a methyl group or hydrogen on the α-carbon. These findings greatly advance the miniscule amount of haloboration reactions in the literature that are potentially valuable tools for the synthetic chemist's arsenal.

Author contributions

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The following files are available free of charge. Supplementary information contains the experimental details, NMR spectra and the X-ray crystallographic details. CCDC No's 2523539-2523541 have been assigned for compounds **1**-**3**.

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Data availability

The following files are available free of charge. Supplementary information contains the experimental details, NMR spectra and the X-ray crystallographic details. CCDC No's 2523539-2523541 have been assigned for compounds **1-3**.

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