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MILD CONVERSION OF ALKENYL BORONIC ACIDS TO ALKENYL HALIDES WITH HALOSUCCINIMIDES

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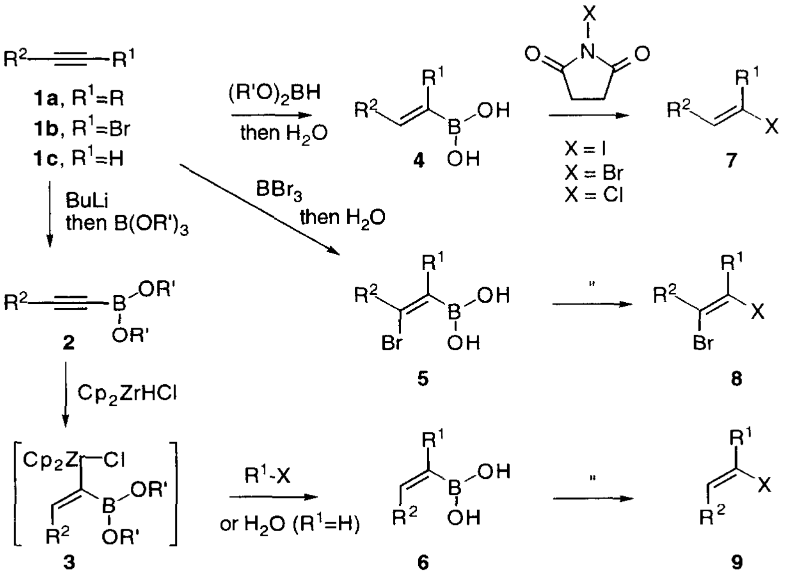
Abstract: Reaction of alkenyl boronic acids with halosuccinimides (NIS, NBS or NCS) gives the corresponding alkenyl halides with the same geometry. This method is suitable for the synthesis of geometrically pure (E) and (Z) alkenyl halides, as well as 1,1- and 1,2-dihaloalkenes.

Alkenyl boronic acids are readily available and synthetically useful intermediates that are configurationally stable and easy to handle.[1] They are usually prepared in geometrically pure form by several methods,[1] including the hydroboration or haloboration of alkynes (**1**) and via the hydrozirconation of alkynes[2] (**1c**) or alkynyl borates[3] (**2**). Since most reactions involving migration from boron to another atom proceed with complete retention of configuration, alkenyl boronic acids are useful for the preparation of several types of geometrically pure alkene derivatives.[1] Thus, we have recently shown that these intermediates can be used for the synthesis of geometrically pure allylamines.[4] Herein we report the mild conversion of several types of alkenyl boronic acids (**4**-**6**) to geometrically pure alkenyl halides (**7**-**9**), using N-iodo-, N-bromo- or N-chloro- succinimides.

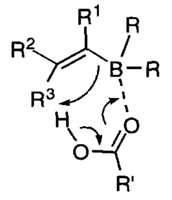


The conversion of alkenyl boronic acids[5] or boronates[5,6] to alkenyl iodides,[5,6] bromides[5] or chlorides[5,7] has been performed with the corresponding halogen (I_2, Br_2 or Cl_2) in the presence of a base. Other procedures include the initial conversion to alkenylmercury intermediates followed by a mercury-halogen exchange,[8] and the use of iodine monochloride for the conversion of alkenylboronic acids[9] or alkenyl boronates[10] to alkenyl iodides.

The procedure reported herein, involving the use of halosuccinimides, is complimentary to the above methods, and in some cases is milder, more convenient and more efficient. Table 1 shows some representative examples for the synthesis of (E) and (Z) alkenyl halides with various substitution patterns. The conversion of alkenyl boronic acids to chlorides was best carried out in chloroform in the presence of triethylamine.[11] The analogous conversion to alkenyl iodides or bromides can take place more efficiently in acetonitrile without an external base.[12] In addition to alkenyl boronic acids the corresponding boronates can also be used in this reaction (entry 12).

Unlike previous procedures,[5] this method allows the conversion of alkenyl boronic acids to alkenyl bromides with the same geometry (entries 2, 4 6). Also, some of the compounds prepared in this manner are not readily available with other methods. Noteworthy is the formation of geometrically pure alkenyl chlorides without the use of chlorine (entries 3, 7, 11), and the efficient synthesis of internal alkenyl halides (entries 5-7, 13) as well as mixed 1,2-dihaloalkenes[13] (entries 10,11) and 1,1-dihaloalkenes (entry 12).

In contrast to procedures involving halogens, that are believed to involve the electrophilic addition to the alkene followed by a base-promoted elimination,[5] the retention of configuration during the reaction with N-halosuccinimides suggests that it probably proceeds via a direct migration of the alkenyl moiety from boron to halogen. Similarly to the proposed mechanism for the protonation of alkenylboron derivatives by carboxylic acids[1] (**10**), this boron to halogen exchange may be assisted intramolecularly by the carbonyl group of the succinimide moiety (**11**). Alternatively, the conversion of boron to a borate species via the addition of an external nucleophile may lead to an intermolecular transfer of the alkenyl moiety to the electrophilic halogen (**12**).



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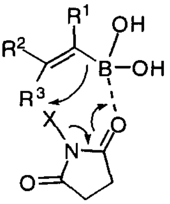

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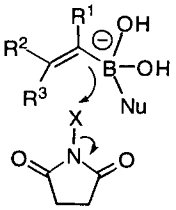

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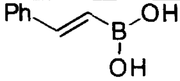
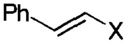
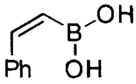
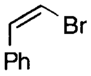
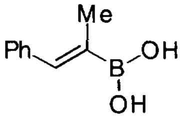
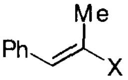
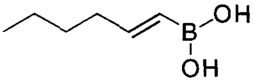
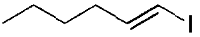
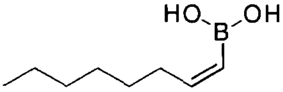
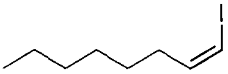
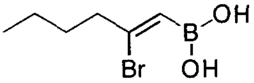
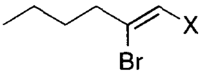
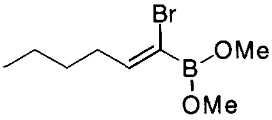
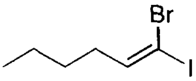
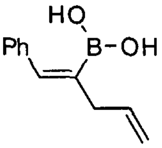
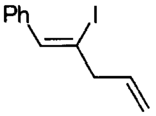
Overall, the reported procedure gives geometrically pure alkenyl halides without requiring the use of highly reactive halogens, strong bases, oxidizing agents or mercury salts and, therefore, it is experimentally convenient and practical.

Acknowledgments: Support by the Loker Hydrocarbon Research Institute and by a USC Merit Fellowship to IAZ is gratefully acknowledged.

Table 1

Entry	Boronic acid or boronate	Conditions (at 25°)	Product	Yield
1		NIS, MeCN	 X = I	86%
2		NBS, MeCN	X = Br	85%
3		NCS, $CHCl_3$, Et_3N	X = Cl	82%
4		NBS, MeCN		81%
5		NIS, MeCN	 X = I	83%
6		NBS, MeCN	X = Br	84%
7		NCS, $CHCl_3$, Et_3N	X = Cl	77%
8		NIS, MeCN		73 %
9		NIS, MeCN		68%
10		NIS, MeCN	 X = I	71 %
11		NCS, $CHCl_3$, Et_3N	X = Cl	76 %
12		NIS, MeCN		62%
13		NIS, MeCN		68%

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11. General procedure (entry 3): Triethylamine (0.111 g, 1.1 mmol) was added dropwise over 15 min to a suspension of (E)-2-phenylethenyl boronic acid (0.148 g, 1 mmol) and N-chlorosuccinimide (0.147 g, 1.1 mmol) in $CHCl_3$ (6 mL). After stirring for an additional 15 min, the product was extracted with pentane (3 X 30 mL), washed with water (2 X 40 mL) and dried ($MgSO_4$). Solvent evaporation *in vacuo* and purification by flash column chromatography (silica gel, pentane), afforded pure (E)-1-chloro-2-phenylethene (0.114 g, 82%). ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.24-7.31 (m, 5H), 6.85 (d, J=13.67 Hz, 1H), 6.65 (d, J=13.67 Hz, 1H); ^{13}C-NMR (90 MHz, $CDCl_3$) δ 134.89, 133.28, 128.78, 128.14, 126.11, 118.69.
12. General procedure (entry 5): To a solution of (E)-1-phenyl-2-propenyl boronic acid (0.160 g, 1 mmol) in MeCN (6 mL) protected from light was added N-iodosuccinimide (0.270 g, 1.2 mmol). After stirring for 2 h at rt the product was extracted with pentane (3X30 mL), washed with aqueous $Na_2S_2O_5$ (2X20 mL), water (2X20 mL), and dried ($MgSO_4$). Solvent evaporation *in vacuo* and purification by flash column chromatography (silica gel, pentane), afforded pure (E)-2-Iodo-1-phenylpropene (0.201 g, 83%): ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.1-7.4 (m, 6 H), 2.61 (d, J=1.9 Hz, 3H). ^{13}C-NMR (90 MHz, $CDCl_3$) δ 140.79, 137.47, 128.37, 128.25, 127.20, 98.50, 29.40. (E)-2-Bromo-1-phenylpropene (entry 6) was prepared similarly by using N-bromosuccinimide. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.20-7.42 (m, 5H), 6.95 (s, 1H), 2.45 (d, J=1.4 Hz, 1H); ^{13}C-NMR (90 MHz, CDCl3) δ 136.49, 132.28, 128.42, 128.32, 127.18, 123.63, 24.93.
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