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ORGANIC SYNTHESIS USING HALOBORATION REACTION, II. A STEREO- AND REGIOSELECTIVE SYNTHESIS OF [Z]-1-ALKYNYL-2-HALO-1-ALKENES

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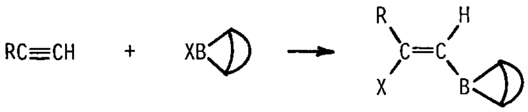
Summary: [Z]-1-Alkynyl-2-halo-1-alkenes can be stereo- and regioselectively synthesized in relatively good yields from 1-alkynes by the haloboration with B-halo-9-borabicyclo[3.3.1]nonane and subsequent treatment with lithium acetylides and iodine.

In the preceding paper, we reported that B-bromo- or B-iodo-9-borabicyclo[3.3.1]nonane (B-Br- or B-I-9-BBN; , X = Br or I) adds to 1-alkynes stereo-, regio- and chemoselectively (eq. 1).

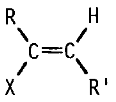


X = Br, I

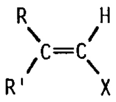
I

(1)

The substitution of the boron group of I with other groups provides an interesting synthetic methodology of trisubstituted alkenyl halides (II). Although the synthesis of trisubstituted alkenyl halides (III) were achieved by the carbometallation of 1-alkynes followed by metal-halogen exchange sequence,[1] the method is not applicable to the synthesis of such a type of alkenyl halides (II).

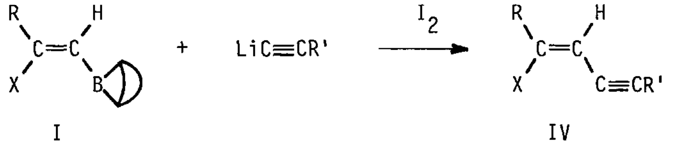


II



III

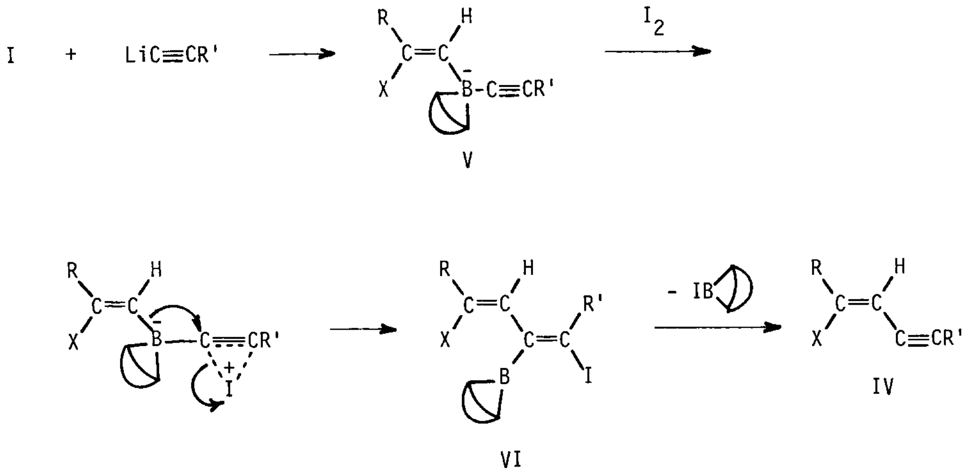
We wish to report here that the sequential treatment of I with lithium acetylides and iodine gives 1-alkynyl-2-halo-1-alkenes (IV) in relatively good yields. As the stereochemistry of the alkenylboranes (I) is completely retained during the reaction, the present reaction provides a convenient stereodefined synthesis of [Z]-1-alkynyl-2-halo-1-alkenes (IV) (eq. 2).



(2)

The following procedure for the preparation of [Z]-1-hexynyl-2-bromo-1-octene (IV: R=hexyl, R'=butyl) is representative. A dry 50-ml flask equipped with a magnetic stirring bar and a septum inlet was flushed with nitrogen. The flask was charged under nitrogen atmosphere with 0.267 g of B-Br-9-BBN[2] (1.33 mmol) and 5 ml of dry pentane, and cooled to 0 °C. To the well-stirred solution, 0.16 ml of 1-octyne (1.11 mmol) was added dropwise, and the solution was stirred for 2 h at 0 °C. The reaction mixture was cooled to -78 °C and 1-lithio-1-hexyne (1.60 mmol)[3] was introduced gradually to give a pale yellow solution. After stirring for 10 min at the temperature, 0.47 g of iodine (1.9 mmol) in 3 ml of THF was added and the resulting dark orange suspension was stirred at -78 °C for 30 min, and then at room temperature for 30 min. Finally, the mixture was oxidized with 3 ml of 3M NaOH and 3 ml of 30% hydrogen peroxide at 0 °C for 1 h, and the product thus obtained was extracted with hexane three times. The combined organic layers were washed with water and aqueous sodium chloride solution, dried over magnesium sulfate, and finally concentrated under vacuum and purified by column chromatography (silica gel, hexane) to give 0.193 g of IV (R=hexyl, R'=butyl; 64% yield). The representative results are summarized in Table 1.

The reaction seems to proceed through the following pathways. Lithium acetylide attacks the boron atom of I to form the alkynylborate intermediate (V), and then the alkenyl group migrates selectively from boron to the neighboring carbon by the attack of iodine cation to the triple bond to yield VI.[4] Finally, the B-I moiety is eliminated to give the product (IV), as depicted in eq. 3. The reaction mechanism appears to be similar to that of the reaction between trialkylalkynylborates and iodine.[6] However, it is noteworthy that although the borate (V) seems to be unstable because of having a good leaving group, halogen atom, at the β-position with respect to



(3)

the boron group, such an elimination reaction to make C≡C bond was not observed significantly by the addition of lithium acetylides to I. After the migration of the alkenyl group, the elimination of B-I moiety occurs.

Further applications of haloboration to organic synthesis are now under investigation.

REFERENCES AND NOTES

(1) J. F. Normant and A. Alexakis, Synthesis, 841 (1981), and the references cited therein.

(2) a) H. C. Brown and S. U. Kulkarni, J. Organomet. Chem., 168, 281 (1979). b) Idem, J. Org. Chem., 44, 2422 (1979).

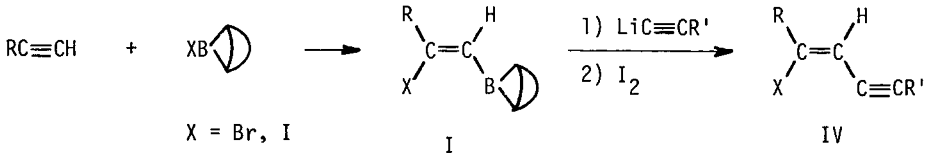
(3) 1-Lithio-1-hexyne was prepared as follows. To 0.18 ml of 1-hexyne (1.6 mmol) in 5 ml of THF was added at 0 °C, 0.8 ml of a butyllithium solution in ether (a 2 M solution, 1.6 mmol) and the mixture was stirred for 30 min at the temperature.

(4) In the reaction of alkynylborates with iodine, 9-BBN derivatives cannot be usually used because migration of the C-B bond of the cyclooctane ring occurs predominantly.[5] However, in the present reaction, the by-products derived from the cyclooctane ring-carbon migration were obtained only in 5-10% yields, which were readily removed by column chromatography.

(5) (a) S. W. Slayden, J. Org. Chem., 46, 2311 (1981). b) A. B. Levy, R. Angelastro and E. R. Marinelli, Synthesis, 945 (1980).

(6) A. Suzuki, N. Miyaura, S. Abiko, M. Itoh, H. C. Brown, J. A. Sinclair and M. M. Midland, J. Am. Chem. Soc., 95, 3080 (1973).

Table 1. The Synthesis of [Z]-1-Alkynyl-2-halo-1-alkenes from 1-Alkynes



R	R'	X	Yield (%)^{a} of IV^{b}	Selectivity (%)^{c}
Hexyl	Butyl	Br	64 (77)	98
"	"	I	74	99
	"	Br	62	98
Butyl	Hexyl	Br	66	98
"	Butyl	Br	66	98
"	"	I	72 (83)	98
Hexyl	Ethyl	Br	65	99
"	"	I	70	98
Ethyl	Hexyl	Br	63	98
"	"	I	67	98
Phenyl	Butyl	Br	53	99
Hexyl	PhOCH$_2$	Br	62	98
"	"	I	(73)	98
Cyclohexyl	Butyl	I	72	98

a) Isolated yields based on the 1-alkyne employed. The numbers in parentheses are glc yields.

b) The isolated products were adequately characterized by IR, ^{1}H NMR and mass spectra and the elemental analyses.

c) Determined from the ^{1}H NMR data of vinylic protons.

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