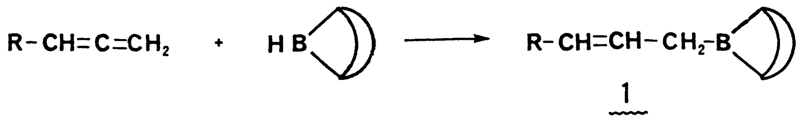
CHEMISTRY LETTERS, pp. 345 - 348, 1984.

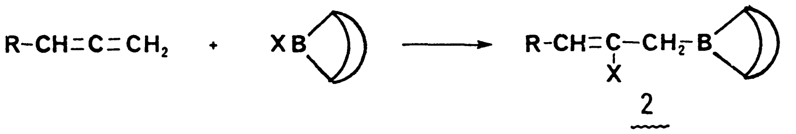
ORGANIC SYNTHESIS USING HALOBORATION REACTION. IV.
IODOBORATION REACTION OF TERMINAL ALLENES

Shoji HARA, Satoru TAKINAMI, Satoshi HYUGA, and Akira SUZUKI*
Department of Applied Chemistry, Faculty of Engineering,
Hokkaido University, Sapporo 060

Terminal allenes react smoothly with B-iodo-9-borabicyclo-[3.3.1]nonane (B-iodo-9-BBN), and the subsequent protonolysis with acetic acid gives the corresponding 2-iodoalkenes.

It is known that the hydroboration of terminal allenes with 9-borabicyclo-[3.3.1]nonane (9-BBN) provides synthetically useful B-allyl-9-BBN derivatives (1) directly (Eq. 1).1) Although the haloboration of allenes can potentially lead to the formation of more interesting allylic borane derivatives (2), no detailed work has been previously reported (Eq. 2).2)


(1)


(2)

Recently we have reported that B-bromo- and B-iodo-9-BBNs react with 1-alkynes stereo-, regio- and chemoselectively, and the resulting B-haloalkenylboranes provide stereospecific syntheses of alkenyl halides.3,4) In the course of our study on haloboration, the haloboration of allenes with B-halo-9-BBNs was examined. The reaction of B-bromo-9-BBN with 1,2-nonadiene was very slow, and even after 24 h at room temperature or 1 h at 69 °C, significant amounts of the allene remained unaltered. On the other hand, B-iodo-9-BBN reacted readily under the same reaction conditions, and the subsequent protonolysis with acetic acid gave 2-iodononenes. When straight chain terminal allenes are used, the corresponding 2-iodo-1-alkenes are obtained predominantly (entries 1-3, in Table 1). However, in the cases of allenes with secondary alkyl group or two substituents, the product selectivity decreases and considerable amounts of 2-iodo-2-alkenes are also produced (entries 4 and 5). As double bonds were found to be inert for the iodoboration with B-iodo-9-BBN,3) an allene with an isolated double bond in the molecule reacts at the allenic part selectively (entry 6).

The following procedure for the reaction of B-iodo-9-BBN with 1,2-nonadiene is representative. To a stirring solution of B-iodo-9-BBN (0.298 g, 1.2 mmol) in 8 mL of dry hexane was added 1,2-nonadiene (0.124 g, 1.0 mmol) at room temperature. The reaction mixture was refluxed with stirring for 1 h, and then 1 mL of acetic acid was added at the same temperature. After stirring for 1 h, the mixture was extracted with 20 mL of hexane, and the organic layer was washed with an aqueous sodium bicarbonate solution and then with water, dried over magnesium sulfate, and finally concentrated under vacuum. The purification by column chromatography (silica gel, hexane) gave 2-iodononenes (0.164 g, 65% yield). Glpc analysis showed that 2-iodo-1-nonene and 2-iodo-2-nonene were present in a ratio of 90 : 10. The representative results are summarized in Table 1.

In any cases, 1-iodo- or 3-iodoalkenes were not observed in the protonation products. This results may support the fact that the possible iodoboration adducts are 3 and/or 4. Fast interconversion between them was known and the isomers (3) were reported to exist preferentially.5) Especially, in the case of sterically hindered allenes (entries 4 and 5), 3 may be only possible intermediates. From such evidence, the protonation products (5 and 6) appear to be prepared as follows. The iodoboration occurs at the terminal double bonds of allenes to give the adducts (3). In the case of straight chain allenes, the selective protonation at the γ-carbon with respect to boron takes place to yield 5 predominantly (Eq. 3). On the other hand, in the cases of cyclohexyl allene and disubstituted allenes (entries 4 and 5), the steric hindrance around the γ-position increases the ratio of protonation at the α-position to give 6 (Eq. 4).

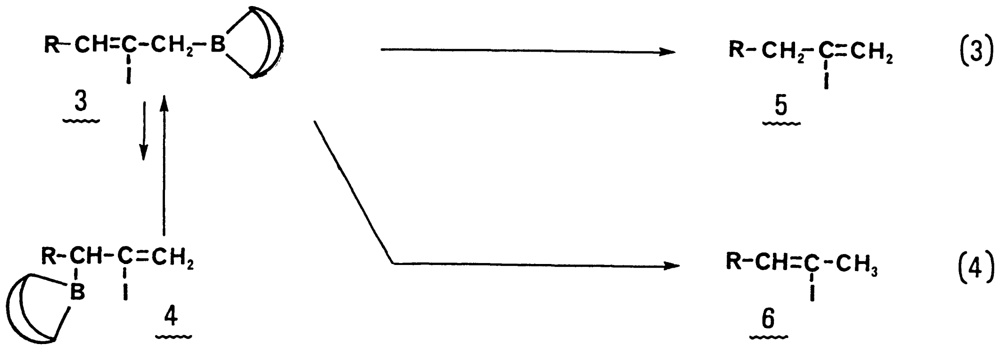
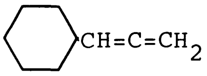
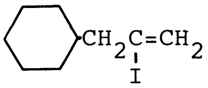
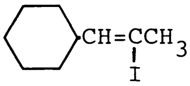
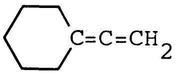
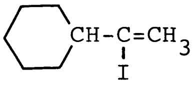
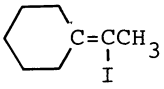
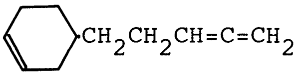
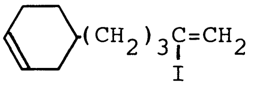
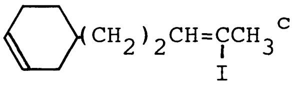


Table 1. The Synthesis of 2-Iodoalkenes from Terminal Allenes

Entry	Allene	Yield / %[a]	Product distribution / %[b]			
1	1,2-Heptadiene	(76)	$\mathrm{BuCH_2\underset{I}{C}=CH_2}$	94	$\mathrm{BuCH=\underset{I}{C}CH_3}$[c]	6
2	1,2-Nonadiene	65	$\mathrm{HexCH_2\underset{I}{C}=CH_2}$	90	$\mathrm{HexCH=\underset{I}{C}CH_3}$[c]	10
3	1,2-Undecadiene	65	$\mathrm{OctCH_2\underset{I}{C}=CH_2}$	90	$\mathrm{OctCH=\underset{I}{C}CH_3}$[c]	10
4		68		56	 [c]	44
5		55		79		21
6		73		94	 [c]	6

a) Isolated yield by column chromatography and in parenthesis, GLPC yield.

b) Determined by GLPC.

c) Mixture of E- and Z-isomers.

References

1) H. C. Brown, R. Liotta, and G. W. Kramer, J. Am. Chem. Soc., 101, 2966 (1979).

2) On the haloboration of allenes, the bromoboration of allene itself with BBr_3 was only briefly reported previously: F. Joy, M. F. Lappert, and B. Prokai, J. Organomet. Chem., 5, 506 (1966).

3) S. Hara, H. Dojo, S. Takinami, and A. Suzuki, Tetrahedron Lett., 1983, 731.

4) S. Hara, Y. Satoh, H. Ishiguro, and A. Suzuki, Tetrahedron Lett., 1983, 735.

5) G. W. Kramer and H. C. Brown, J. Organomet. Chem., 132, 9 (1977).

(Received November 24, 1983)