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# ORGANIC SYNTHESIS USING HALOBORATION REACTION VIII. STEREO- AND REGIOSELECTIVE SYNTHESIS OF [Z]-1,2-DIHALO-1-ALKENES

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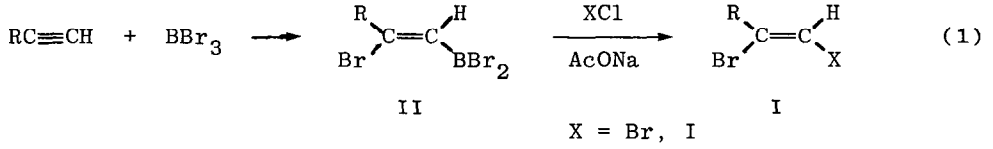
Summary: [Z]-1,2-Dihalo-1-alkenes can be prepared stereo- and regioselectively in good yields from 1-alkynes by the bromoboration with tribromoborane, followed by the treatment with iodine chloride or bromine chloride in the presence of sodium acetate.

Recently, we reported[1] that either [E]- or [Z]-1,2-dihalo-1-alkenes can be prepared by the haloboration reaction of 1-halo-1-alkynes. However, the stereoselectivity of the reaction was not satisfactory, which led us to continue the effort to improve it. Herein, we wish to report a new stereo- and regioselective synthesis of [Z]-1,2-dihalo-1-alkenes (I) from 1-alkynes.

Since the haloboration of 1-alkynes proceeds stereo- and regioselectively to give [Z]-2-halo-1-alkenylboranes (II),[2] the stereospecific displacement of the boron moiety to halogens would afford [Z]-1,2-dihalo-1-alkenes (I). In this approach, however, serious difficulty could interfere the reaction, that is, the halogenolysis of alkenylboranes requires basic conditions,[3] whereas II is unstable under such basic conditions.

When B-halo-9-borabicyclo[3,3,1]nonanes (B-X-9-BBNs)[2a,2b] were used as the haloboration agents, all attempts for the subsequent halogenolysis were unsuccessful. Next, we tried the haloboration of 1-alkynes by using tribromoborane instead of B-X-9-BBNs. The expected [Z]-1,2-dihalo-1-alkenes (I) were obtained selectively (>98%) in good yields by the bromoboration of 1-alkynes with tribromoborane, followed by the halogenolysis with iodine chloride or bromine chloride in the presence of sodium acetate (eq. 1).




II I X = Br, I (1)

The following procedure for the preparation of [Z]-1,2-dibromo-1-octene is representative. To a well-stirring solution of tribromoborane (0.25 g, 1 mmol) in 3 ml of dichloromethane, 1-octyne (0.11 g, 1 mmol) was added at -78 °C and the mixture was stirred for 2 h at the temperature. Then the solution was warmed up to 0 °C and 6 ml of THF, sodium bromide (0.20 g, 2 mmol) in water, chloramine-T trihydrate (0.56 g, 2 mmol) in methanol, and sodium acetate (0.12 g, 1.5 mmol) in methanol were added successively. The reaction solution was stirred at 0 °C for 1 h and then extracted with hexane three times. The combined organic layer was washed with an aqueous sodium bicarbonate solution and water, dried over magnesium sulfate and concentrated under vacuum. The purification of the residue by column chromatography (silica gel, hexane) gave [Z]-1,2-dibromo-1-octene (0.23 g, 84% yield). The representative results are summarized in Table 1.

Table 1. The Synthesis of [Z]-1,2-Dihalo-1-alkenes (I)

| RC≡CH, R= | XCl[a] | Product (I), X= | yield,[b](%) | Isomeric purity[c] (%) |
|---|---|---|---|---|
| n-Butyl | BrCl | Br | 80 | 98 |
| " | ICl | I | 74 | 99 |
| n-Hexyl | BrCl | Br | 84 | 99 |
| " | ICl | I | 76 | 99 |
| n-Octyl | BrCl | Br | 84 | 98 |
| " | ICl | I | 77 | 99 |
| Cyclohexyl | BrCl | Br | 72 | 98 |
| " | ICl | I | 61 | 98 |
| Phenyl | BrCl | Br | 70 | 95 |
| " | ICl | I | 62 | 95 |

a) BrCl and ICl were prepared in situ by the successive addition of chloramine-T, sodium bromide or sodium iodide, and sodium acetate. See the text.
b) Isolated yield by column chromatography.
c) Determined by glpc.

For the halogenolysis of alkenylboranes under the influence of base, Brown et al. postulated the addition-elimination mechanism.[3b] Thus, in the case of bromonolysis, the reaction proceeds with inversion of configuration through the usual trans addition of bromine to the double bond of [E]-1-alkenylboranes, followed by the base-induced trans elimination of boron and bromine to give the corresponding [Z]-1-alkenyl bromides. On the other hand, the iodine reaction of [E]-1-alkenylboranes was proposed to take place in the presence of sodium hydroxide by a trans addition of the elements of hypoiodous acid via an iodonium ion intermediates, followed by a cis elimination to yield [E]-1-alkenyl iodides which are products obtained by such a retention of configuration process.

However, in our reaction, both the bromonolysis and iodonolysis in the presence of base proceed with retention of the stereochemistry.[4] Moreover, as the alkenylboranes possess a bromo group at the β-carbon, the addition of halogen to the double bond under the reaction conditions would give the intermediates with two leaving groups, bromo and methoxy, acetoxy or chloro groups, at the β-carbon. It is unplausible that under basic conditions, the original bromo group survives and another leaving group is eliminated with boron selectively via a cis-manner.[6] These results may suggest that the present reaction proceeds through different mechanisms,[7] although it is preferable to defer more detailed consideration until such a time as more mechanistic data become available.

In spite of the precise mechanism involved, it is evident that we are now in a position to convert 1-alkynes into [Z]-1,2-dihalo-1-alkenes with two different halogen atoms, highly stereoselectively and very conveniently via haloboration. These halogen derivatives are readily converted into the corresponding Grignard[8] and lithium compounds[9] selectively with retention of their stereochemistry. Consequently, the present developments open up highly practical routes from the readily available 1-alkynes to these valuable vinylic metallics of known stereochemistry.

## References and Notes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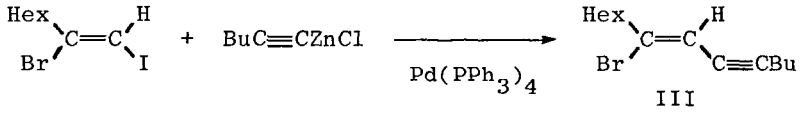
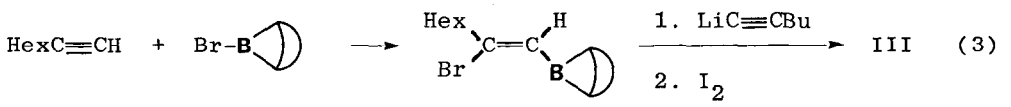
4. The stereochemistry of [Z]-1,2-dibromo-1-alkenes was confirmed by comparing them with the authentic samples prepared by known methods and haloboration of 1-bromo-1-alkynes.[1] [Z]-1-Iodo-2-bromo-1-alkenes were converted to the corresponding 1-alkynyl-2-bromo-1-alkenes by Negishi's procedure (eq. 2),[5] which were directly compared with the samples obtained by our previous method (eq. 3).[2a]




(2)




(3)

5. E. Negishi, N. Okukado, S. F. Lovich, and F. T. Luo, J. Org. Chem., 49, 2629 (1984).

6. In the product mixture, any ketone, acetoxy or methoxy vinyl ether, or chloroalkene derivatives which should be formed if the elimination of the bromo group occured, could not be detected.
7. Our preliminary study showed that the double bond with bromo group in alkenylboranes is hardly attacked by iodine. This evidence may also support that the present reaction does not proceed through the usual addition-elimination mechanism.

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