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ORGANIC SYNTHESIS USING HALOBORATION REACTION. PART 9. A DIRECT AND SELECTIVE SYNTHESIS OF (Z,Z)-1-BROMO-1,3-DIENES AND (E,Z)-1,3-DIENES BY THE HYDROBORATION-BROMOBORATION SEQUENCE OF TWO ALKYNES

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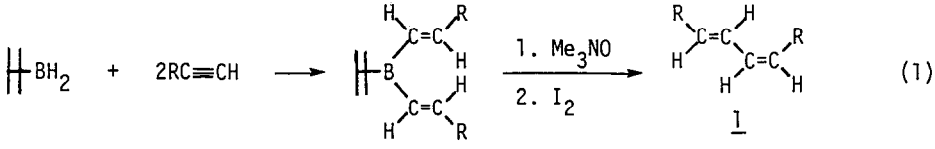
Summary: 1-Alkenyldibromoboranes readily obtainable by the hydroboration of first alkynes with dibromoborane-dimethyl sulfide followed by treatment with tribromoborane, react without any difficulty with second 1-alkynes as bromoborating agents to give (1-alkenyl)(2-bromo-1-alkeny)-bromoboranes (5). The reaction of 5 with iodine in the presence of potassium acetate provides (Z,Z)-1-bromo-1,3-dienes (6), specifically, which are readily converted into the corresponding (E,Z)-1,3-dienes (7) by treatment with t-butyllithium and methanol.

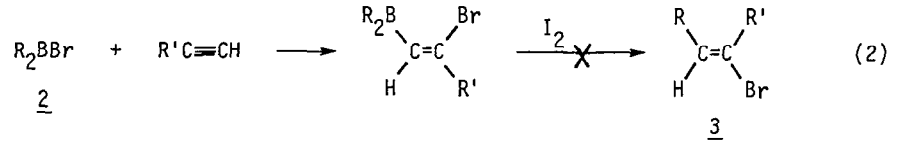
Recently, a stereo- and regiospecific synthesis of stereodefined 1,3-dienes by the Pd-catalyzed cross-coupling reaction between 1-alkenylboranes and 1-alkenyl halides has been reported,[1] but the stereospecific synthesis of 1-alkenyl halides is sometimes difficult. On the other hand, Zweifel and his coworkers[2] reported that the hydroboration of 1-alkyne with thexylborane, followed by the oxidation with trimethylamine oxide and the addition of iodine gives (E,Z)-1,3-diene (1) directly (eq. 1). However, the extension of this method for the unsymmetric diene synthesis is unsuccessful,[3] because in the reaction of dialkenylboranes with iodine, the attack of iodine cation to two alkenyl groups on boron occurs indistinguishably, thereby giving a mixture of (E,Z)- and (Z,E)-1,3-dienes.



(1)

1

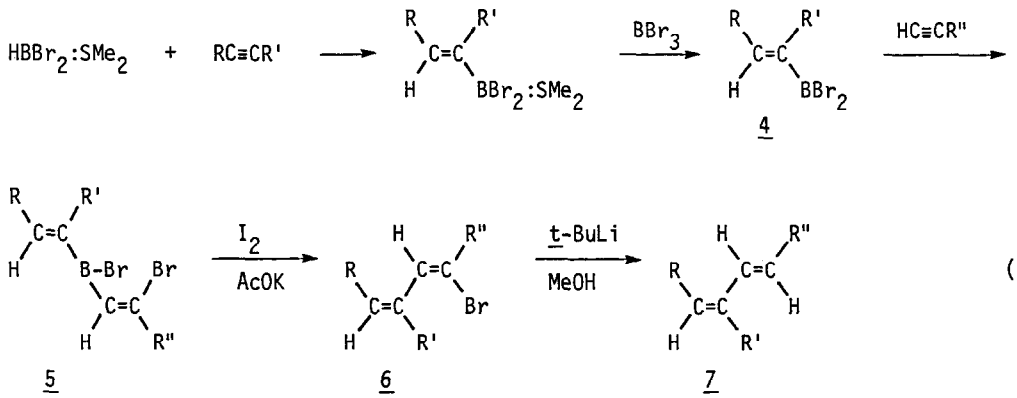
During the course of our study on the organic synthesis using haloboration reaction,[4] we attempted to prepare disubstituted bromoalkenes (3) by the bromoboration of 1-alkynes with dialkylbromoborane (2), followed by the addition of iodine. However, it was found that the reaction of iodine cannot cause the migration of alkyl group from boron to the neighboring carbon. Consequently, the expected bromoalkenes (3) were not obtained by such a reaction (eq. 2), whereas the migration of alkyl group takes place readily when the halo substituent is not at



(2)

the double bond.[5] This result suggested that a bromo substituent decreases the reactivity of the double bond toward iodine cation. Therefore, we considered that in the reaction of iodine with (1-alkenyl)(2-bromo-1-alkenyl)borane derivatives, the reaction may occur only at the 1-alkenyl group but not at the 2-bromo-1-alkenyl group. Such (1-alkenyl)(2-bromo-1-alkenyl)-boranes are easily prepared from alkynes by using hydroboration and haloboration reactions.

Thus, alkynes were first hydroborated with dibromoborane-dimethyl sulfide complex[6] to give (1-alkenyl)dibromoborane-dimethyl sulfide complexes, which were, however, found to be not effective as bromoborating agents for 1-alkynes. Fortunately, free (1-alkenyl)dibromoboranes (4), readily obtainable by treatment with tribromoborane, were ascertained to bromoborate 1-alkynes to yield the desired (1-alkenyl)(2-bromo-1-alkenyl)bromoboranes (5), which reacted with iodine in the presence of potassium acetate to give corresponding (Z,Z)-1-bromo-1,3-dienes (6) selectively (eq. 3).



(3)

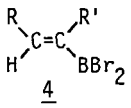
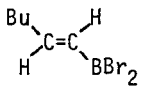
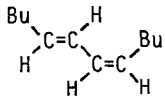
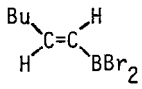
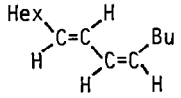
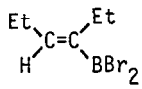
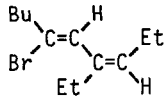
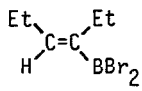
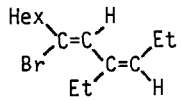
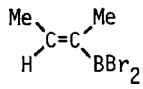
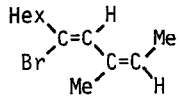
In order to determine the structure and isomeric purity of the products (6), bromodienes (6) were converted into the corresponding 1,3-dienes by the treatment with t-butyllithium in THF at -78 °C, followed by the quenching with methanol. In comparison of the 1,3-dienes thus obtained with the corresponding four possible isomers prepared by the known method,[1] it was shown that 1,3-dienes prepared by the procedure depicted in eq. 3 have (E,Z)-stereochemistry, and (Z,Z)-1-bromo-1,3-dienes (6) are synthesized specifically, more than 97% of isomeric purity, as exemplified in Table 1.

The following procedure for the preparation of (Z,Z)-6-bromo-4-ethyl-3,4-dodecadiene is representative. To dichloromethane solution (3 ml) of (Z)-3-dibromoboryl-3-hexene (0.245 g, 1 mmol),[6] prepared by the hydroboration of 3-hexyne with dibromoborane-dimethyl sulfide complex, followed by the reaction with tribromoborane, was added 1-octyne (0.11 g, 1 mmol) at -78 °C. The reaction mixture was stirred for 1 h at the temperature and for 30 min at room temperature. After cooling again to -78 °C, THF (5 ml), potassium acetate (0.588 g, 6 mmol) in methanol (6 ml) and iodine (0.305 g, 1.2 mmol) in THF (3 ml) were added successively. Then,

the cooling bath was removed, and the reaction mixture was stirred for 2 h at room temperature. Finally, the mixture was extracted with hexane (20 ml), and the organic layer was washed with an aqueous solution of sodium thiosulfate and water, dried with magnesium sulfate, concentrated under reduced pressure, and purified by column chromatography (silica gel, hexane) to give (Z,Z)-6-bromo-4-ethyl-3,5-dodecadiene (0.164 g, 60% yield), the isomeric purity of which was 99%.

When 1-alkynes were used for the preparation of alkenyldibromoboranes, the corresponding conjugated alkadienyl bromides thus obtained were unstable and decomposed soon. Consequently, these unstable bromodienes were protonated immediately by the treatment with t-butyllithium, followed by the reaction with methanol to be changed to (E,Z)-1,3-dienes as shown in Table 1. Some of the representative results are summarized in Table 1.

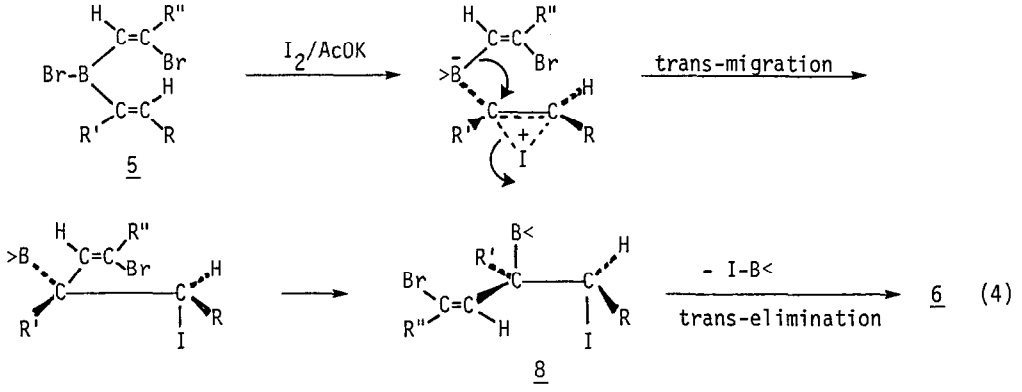
Table 1. The Synthesis of (Z,Z)-1-Bromo-1,3-dienes and (E,Z)-1,3-Dienes

 4	HC≡CR"	Product	Yield,[a] (%)	Purity,[b] (%)
	1-Hexyne		53	97
	1-Octyne		51	97
	1-Hexyne		63	98
	1-Octyne		60	99
	1-Octyne		56	99

a. Isolated yield based on the 1-alkyne HC≡CR" used.

b. Determined by glpc.

The high stereospecificity of this reaction can be explained as follows. In the reaction of (1-alkenyl)(2-bromo-1-alkenyl)bromoborane (5) with iodine, the iodine cation attacks specifically the 1-alkenyl group which is not deactivated by the bromo substituent. The 2-bromo-1-alkenyl group then migrates from boron to carbon with the retention of the stereochemistry to give the intermediate (8), from which trans-elimination of the iodoborane moiety provides the corresponding (Z,Z)-1-bromo-1,3-diene (6) specifically (eq. 4).[2]



5 8

Although vinylic halides are generally unreactive towards nucleophilic substitution, unless other activating groups are also present in the molecule, there have been appeared many reports for the utilization of vinylic halides.[7] The present development opens up a promising new route to the stereodefined synthesis of useful alkadienyl halides which are difficult to be prepared by conventional methods.

Our observations with the combination of hydroboration and haloboration to alkynes suggests that the reverse-combination sequence of the two reactions may provide interesting results. This reaction is currently under investigation.

References

1. N. Miyaura, K. Yamada, H. Suginome, and A. Suzuki, J. Am. Chem. Soc., 1985, 107, 972.
2. G. Zweifel, N. L. Polston, and C. C. Whitney, J. Am. Chem. Soc., 1968, 90, 6243.
3. For example, see: E. Negishi, in "Comprehensive Organometallic Chemistry," Vol. 7, G. Wilkinson, F. G. A. Stone, and E. W. Abel Ed., Pergamon Press, Oxford, 1982, p. 315.
4. (a) S. Hara, H. Dojo, S. Takinami, and A. Suzuki, Tetrahedron Lett., 1983, 24, 731. (b) S. Hara, Y. Satoh, H. Ishiguro, and A. Suzuki, ibid., 1983, 24, 735. (c) S. Hara, T. Kato, and A. Suzuki, Synthesis, 1983, 1005. (d) S. Hara, S. Takinami, S. Hyuga, and A. Suzuki, Chem. Lett., 1984, 345. (e) Y. Satoh, H. Serizawa, S. Hara, and A. Suzuki, Synth. Commun. 1984, 14, 313. (f) Y. Satoh, T. Tayano, H. Koshino, S. Hara, and A. Suzuki, J. Am. Chem. Soc., 1985, 107, 5225.
5. G. Zweifel, H. Arzoumanian, and C. C. Whitney, J. Am. Chem. Soc., 1967, 89, 3652.
6. H. C. Brown and J. B. Campbell, Jr., J. Org. Chem., 1980, 45, 389.
7. (a) A. Suzuki, Acc. Chem. Res., 1982, 15, 178. (b) A. Suzuki, "Topics in Current Chemistry," Vol. 112, Springer, Berlin, 1983, p. 67.

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