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ORGANIC SYNTHESIS USING HALOBORATION REACTION. A DIRECT AND SELECTIVE SYNTHESIS OF (*Z*,*Z*)-1-BROMO-1,3-DIENES BY USING HALOBORATION-HYDROBORATION OF TWO ALKYNES1)

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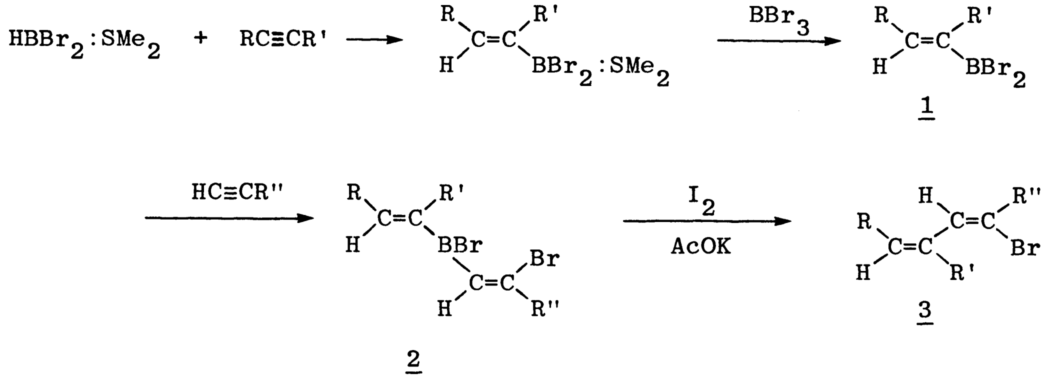
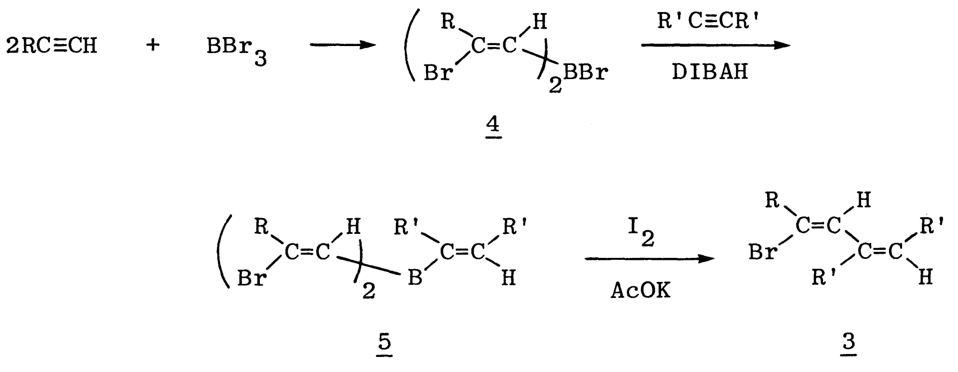
Bis(2-bromo-1-alkenyl)bromoboranes, readily obtainable by the bromoboration of 1-alkynes with tribromoborane, have been found to be converted *in situ* into the corresponding borohydrides by the reduction with diisobutylaluminum hydride. Such borohydrides are effective as hydroborating agents for internal alkynes to provide bis(bromoalkenyl)(alkenyl)boranes, which react with iodine in the presence of potassium acetate to give (*Z*,*Z*)-1-bromo-1,3-dienes, specifically.

It has been previously reported that dialkenylbromoboranes (**2**), readily prepared by the hydroboration-haloboration sequence of alkynes, react with iodine and potassium acetate to give (*Z*,*Z*)-1-bromo-1,3-dienes (**3**) selectively (Eq. 1).1) Although this method affords 1,3-diene functionality directly from alkynes without any difficulty, alkenyldibromoboranes (**1**) must be isolated after the hydroboration of alkynes, followed by the reaction with tribromoborane to make it free from dimethyl sulfide,2) because the sulfide complexes cannot be used for the haloboration reaction.3) In this Letter, we describe a more efficient and simple procedure for the synthesis of bromodienes (**3**), in which all reactions can be carried out without isolation of any intermediates.



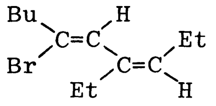
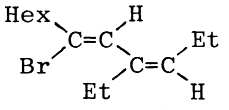
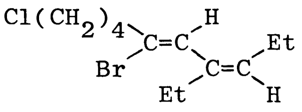
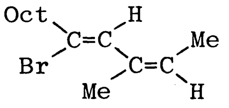
(1)

In this new method, the order of hydroboration and haloboration reactions was changed. Thus, the bromoboration of 1-alkynes with tribromoborane in dichloromethane was carried out at first,$^{4)}$ and then the resulting bis(2-bromo-1-alkenyl)-bromoboranes (4) were employed for the subsequent hydroboration$^{5)}$ after conversion into the corresponding borohydrides by the reduction with diisobutylaluminum hydride (DIBAH) in the presence of second internal alkynes.$^{6)}$ Finally, the selective migration of 2-bromo-1-alkenyl group was achieved by the addition of iodine and base to the reaction mixture.$^{7)}$ All the step-reactions can be accomplished only by the successive additions of reagents to the reaction vessel, and (*Z*,*Z*)-1-bromo-1,3-dienes (3) can be obtained in good yields with high isomeric purity (Eq. 2).$^{1)}$



(2)

Table 1. The Synthesis of (*Z*,*Z*)-1-Bromo-1,3-dienes (3)

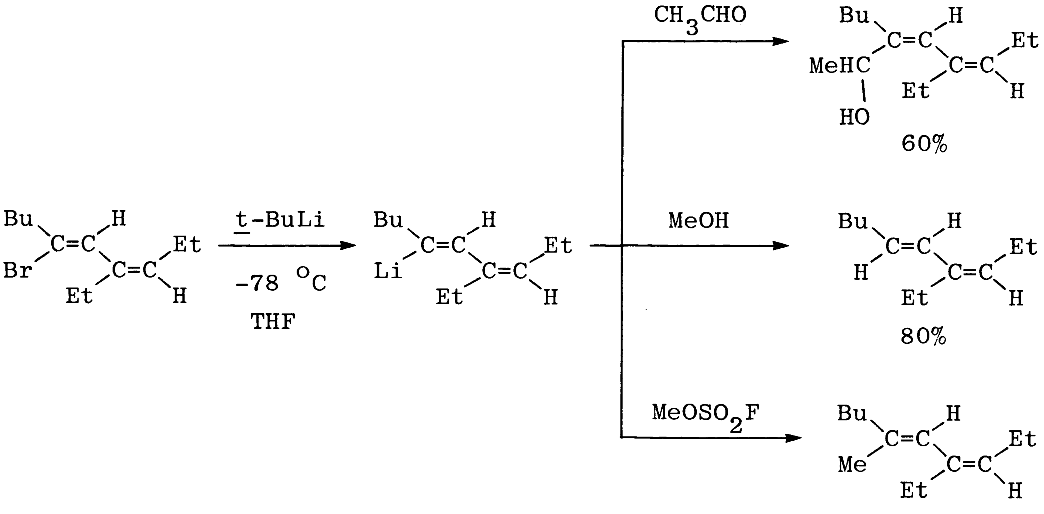
RC≡CH, R=	R'C≡CR', R'=	Product (3)	Yield$^{a)}$/%	Isomeric purity$^{b)}$/%
Butyl	Ethyl		74	99
Hexyl	Ethyl		73	99
$Cl(CH_2)_4$-	Ethyl		63	99
Octyl	Methyl		54	99

a) Isolated yield based on the alkyne used for hydroboration.

b) Determined by GLPC.

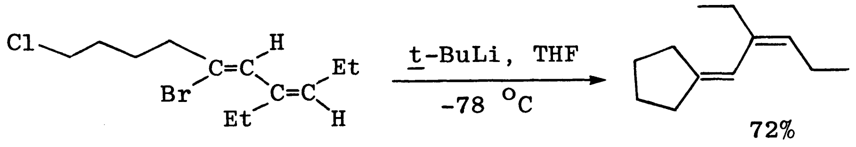
The following procedure for the preparation of (Z,Z)-6-bromo-4-ethyl-3,5-decadiene is representative. To a dichloromethane solution (3 ml) of tribromoborane (0.25 g, 1 mmol) was added 1-hexyne (0.164 g, 2 mmol) at -78 °C under argon atmosphere. The reaction mixture was stirred at the temperature for 30 min and at room temperature for 30 min, and then dimethyl sulfide (0.2 ml) was added at 0 °C. After stirring for 30 min at 0 °C, THF (8 ml), 3-hexyne (0.082 g, 1 mmol), and DIBAH (1.8 ml of 1 M solution of hexane, 1.8 mmol) were added at -78 °C successively. The resulting mixture was stirred at 0 °C for 3 h and at room temperature for 2 h, and finally potassium acetate (0.588 g, 6 mmol) in methanol and iodine (1.17 g, 4.6 mmol) in THF were added at -78 °C. After stirring for 2 h at room temperature, the reaction mixture was quenched with water and extracted with hexane. The organic layer thus obtained was washed with an aqueous solution of sodium thiosulfate and water, dried over magnesium sulfate, and concentrated under reduced pressure. The purification by column chromatography (silica gel, hexane) gave (Z,Z)-6-bromo-4-ethyl-3,5-decadiene (0.182 g, 74% yield), the isomeric purity of which was 99%. The representative results are summarized in Table 1.

The metal-halogen exchange reaction of vinylic halides with alkyllithium compounds leads readily to the corresponding vinylic lithium derivatives.[8)] Consequently the vinylic bromides prepared by the present procedure are convertible to the other functionalized dienes with the retention of stereochemistry by the reaction with various electrophiles. Some of such examples are exemplified in Eq. 3.



(3)

Furthermore, the intramolecular alkylation of bromodienes such as 6 prepared from 6-chloro-1-hexyne afforded five-membered cyclic dienes like 7 in good yields, as depicted in Eq. 4.[9)]



6 7 (4)

Although such alkadienyl halides are considered to be potentially valuable intermediates in organic synthesis, as revealed above, conventional synthetic methods of them, for instance, involving the dehalogenation or dehydrohalogenation of polyhaloalkanes may not provide stereodefined alkadienyl halide products. The present synthesis now opens up a new and convenient route to a wide variety of such useful intermediates.

References
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3) S. Hara, H. Dojo, S. Takinami, and A. Suzuki, Tetrahedron Lett., 24, 731 (1983)
4) In this reaction two equivalents of an alkyne were necessary for the haloboration reaction to obtain the product in a good yield.
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