Tetrahedron Letters Vol. 21, pp 537 - 540
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0040-4039/80/0201-0537$02.00/0

THE SYNTHESIS OF METHOXYCYCLOPROPANES VIA THE TREATMENT OF ATE-COMPLEXES OBTAINED FROM B-ALKYL-9-BORABICYCLO[3,3,1]NONANES AND LITHIUM METHOXYALLENE WITH ACETIC ACID

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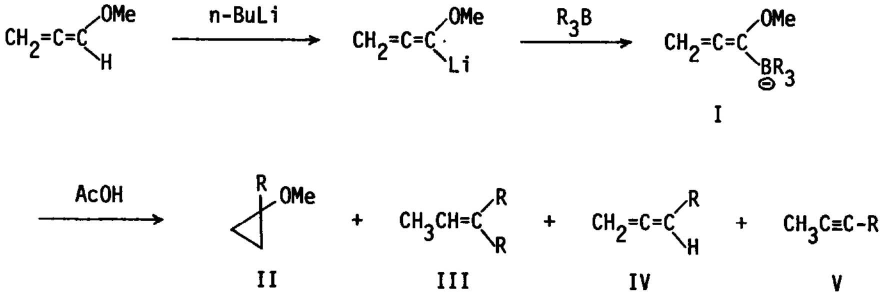
Summary: The reaction of acetic acid with ate-complexes prepared from B-alkyl-9-borabicyclo-[3,3,1]nonanes and 1-lithio-1-methoxyallene gives corresponding 1-alkyl-1-methoxycyclopropanes in good yields.

Recently, many reports have appeared dealing with new applications of alkali metal organoborates for the synthesis of various kinds of organic compounds. We previously reported such reactions using lithium 1-alkynyltrialkylborates$^{1-5)}$ and lithium 1-alkenyltrialkylborates$^{6)}$ for the syntheses of internal alkynes and alkenes. In an attempt to develop the reaction of such borates, we explored the possibility of achieving a related synthesis based on lithium methoxyallene and B-alkyl-borabicyclo[3,3,1]nonanes (B-alkyl-9-BBN).

To a solution of the ate-complex (I) obtained from trialkylborane and lithium methoxyallene,$^{7)}$ acetic acid was added at -30°C. After the reaction was complete, the residual organoborane was oxidized under the usual conditions. Glpc analysis showed the formation of the methoxycyclopropane derivative (II) and olefin (III) with a small amount of allene (IV) and acetylene (V).

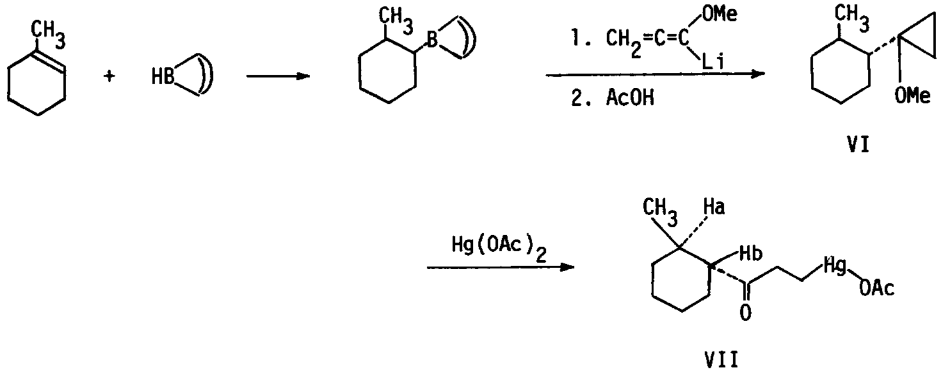


(1)

However, when we used the B-alkyl-9-BBN, available by hydroboration of an olefin with 9-BBN,$^{8)}$ the reaction was found to be more favorable. Addition of acetic acid to a solution of the ate-complex obtained from B-hexyl-9-BBN and lithium methoxyallene at -30°C followed by warming to room temperature gave 1-hexyl-1-methoxycyclopropane in a yield of 81%. In this case we can prevent the formation of undesirable by-products, III, IV and V. The reaction was then applied to representative organoboranes. Good yields, in the range of 73-83%, were obtained with the majority of organoboranes. The results were summarized in Table 1.

The following procedure for the preparation of 1-(2-methylcyclohexyl)-1-methoxycyclopropane (VI) is representative. A dry 200 ml flask equipped with a septum inlet and a magnetic stirring bar was flushed with nitrogen. The flask was charged with 1.53 ml (20 mmol) of 1-methoxy-1,2-butadiene[7] and 10 ml of anhydrous ether. Buthyllithium (15 ml, 1.2 M in ether) was added to the solution at -30°C, and the reaction mixture was stirred for 1 h. To the solution was added 30 ml (15 mmol) of B-(2-methylcyclohexyl)-9-BBN in THF at -30°C. The reaction was continued for an additional hour. Finally, acetic acid (3 ml) was added to the solution with vigorous stirring. After 30 min at -30°C, the solution was brought to room temperature and oxidized with alkaline hydrogen peroxide under the usual conditions. The extract was dried, and then distilled in vacuum to give VI (1.84 g, 79%); bp 96°C/15 mmHg.

The stereochemistry of the present reaction was established by the following experiment. The cyclopropane derivative obtained from B-(2-methylcyclohexyl)-9-BBN was indicated to be a single isomer, presumably E-isomer by glpc analysis. Ring opening with mercury acetate[9] produced the crystalline compound (VII). The assignment of trans-geometry was confirmed by a coupling constant between Ha and Hb, Jab=7.5 Hz.[10]



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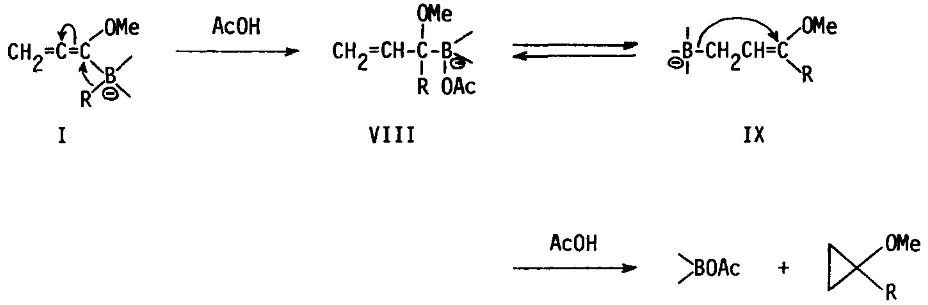
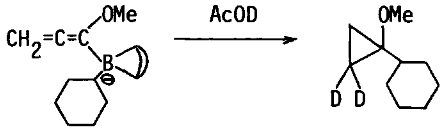
We have not undertaken a mechanistic investigation of the reaction. However, the reaction may be considered to proceed through the following reaction path.



(3)

It has been recently reported that ate-complexes are attacked with various electrophiles at the β-carbon relative to the boron atom.[11] This mode of reaction may give the intermediate (VIII), which is then isomerized to IX through allylic rearrangement. The allylborane (IX) thus formed gives methoxycyclopropane by protonation with acetic acid.

The formation of 2,2-d_2-1-cyclohexyl-1-methoxycyclopropane by protonolysis of the ate-complex obtained from B-cyclohexyl-9-BBN with deutero acetic acid supported this mechanism.



m/e 156

(4)

Although Brown and his co-workers reported the synthesis of various cyclopropanes via hydroboration of allylhalides,[12] the present procedure also provides a new synthetic method for alkoxycyclopropanes.

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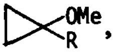
Table 1. Synthesis of Methoxycyclopropanes from the Ate-complexes Obtained from B-Alkyl-9-BBNs and Lithium Methoxyallene.

B-R-9-BBN from olefin	Product  OMe, R, R=	Yield (%)[a)]
1-Octene	n-Octyl	81
1-Hexene	n-Hexyl	73
Cyclohexene	Cyclohexyl	80
Cyclopentene	Cyclopentyl	76 (63)
Norbornene	exo-Norbornyl	83 (78)
1-Methylcyclohexene	trans-2-Methylcyclohexyl	— (79)
1-Trimethylsilyloxycyclohexene	trans-2-Trimethylsilyloxycyclohexyl	81

a) Analyzed by glpc, based on the olefin used, and the isolated yield was showed in parenthesis.

(Received in Japan 16 November 1979)