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REACTION OF LITHIUM ALKYNYLTRIALKYLBORATES WITH PROPIONIC ACID.
GENERAL AND CONVENIENT SYNTHESES OF INTERNAL AND TERMINAL OLEFINS USING ORGANOBORANES

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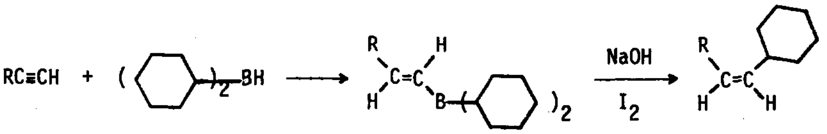
Many reports have appeared recently dealing with a new application of organoboranes to the synthesis of a wide variety of organic compounds.$^{1)}$ The synthesis of alkenes by hydroboration or by using the resulting organoboranes have also been reported. Such procedures may be classified into the following three categories. The first is based on the hydroboration-isomerization-displacement sequence of reactions$^{1b)}$ as a method of shifting a double bond from a thermodynamically stable internal position to the less stable terminal position. The second is a method formed on the basis of hydroboration of alkynes, followed by protonolysis with carboxylic acid to give corresponding cis-alkenes.$^{2)}$ The third procedure involves a reaction in which the B-alkyl group of organoboranes migrates from boron to the acetylenic carbon. The majority of such intermediates organoboranes are prepared by monohydroboration of alkynes with selective hydroborating agents such as disiamyl-, and dicyclohexyl-boranes. The organoboranes thus obtained are treated with iodine in the presence of sodium hydroxide resulting in a transfer of an alkyl group from boron to the adjacent carbon atom to give the corresponding alkenes.$^{3,4)}$ A typical example is shown in eq. 1. This procedure has also been applied to diene synthesis$^{5,6,7)}$ and modified procedures have also been reported.$^{8.9)}$



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Although the last alkene synthesis mentioned above is of some interest, there is a limitation. Namely, the alkyl groups such as 3-methyl-2-butyl, cyclohexyl, cyclopentyl and 2,3-dimethyl-2-butyl which are contained in selective hydroborating agents, are only available for the reaction.

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We wish to report here on a synthetic procedure of internal and terminal alkenes by the reaction of carboxylic acid with lithium alkynyltrialkylborates readily obtainable from all types of organoboranes and metal acetylides. Although Binger et al[10] suggested that such an ate-complex gives a mixture of the corresponding cis- and trans-alkenes by treatment with hydrogen chloride, the experiment was not described in detail. We used propionic acid as a protonolyzing agent.

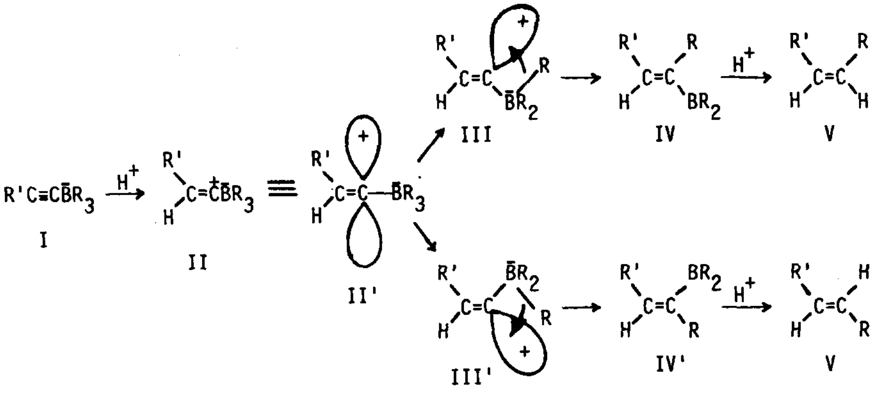
The following procedure for the preparation of 1-phenyl-1-hexene is representative. A dry 25-ml flask, fitted with an inlet equipped with a rubber septum cap, a magnetic stirring bar and a condenser, was flushed with nitrogen. In the flask was placed 0.282 ml (2.56 mmol) of phenylacetylene and 1 ml of anhydrous ether. Then, 2.56 mmol (1.42 ml of a 1.8M solution in ether) of methyl lithium was added at 0°C, and the reaction mixture was stirred for 30 min. To the ether solution was added 2 ml (2.32 mmol) of n-butylborane in THF. The mixture was stirred at 0°C for 2 hr to form lithium 1-hexynyltributylborate. Then 1.73 ml (23.2 mmol) of propionic acid was added, followed by stirring overnight at room temperature. Finally, the reaction mixture was oxidized with alkaline hydrogen peroxide under the usual conditions. Analysis of the organic layer by glpc indicated that 1.69 mmol (73%) of the expected olefin had formed. Representative results are summarized in Table 1.

Table 1. The Reaction of Propionic Acid with Lithium 1-Alkynyltrialkylborates[a)]

R_3B	Acetylene	Product	Yield,[b)] %	cis:trans
n-Butyl	PhC≡CH	n-BuCH=CHPh	73	74:26
sec-Butyl	PhC≡CH	sec-BuCH=CHPh	75	81:19
iso-Butyl	PhC≡CH	iso-BuCH=CHPh	78	54:46
n-Butyl	$CH_3C≡CH$	n-BuCH=$CHCH_3$	77	72:28
n-Pentyl	$CH_3C≡CH$	n-PenCH=$CHCH_3$	74	72:28

a) Acetylene/R_3B=1.1. At 0°C. b) Based on organoborane used.

Since our effort were mainly directed toward the practical application of the reaction, we have not undertaken a mechanistic investigation of the reaction. However, the reaction should be considered to proceed through the following reaction path (eq. 2). It has been recently reported that ate-complexes (I) are attacked at the β-carbon relative to the boron atom with various electrophiles to give products which may be considered to be formed through intermediates (II).[11)] In the other kinds of organic compounds, reactions which appear to proceed through vinylic cations as the intermediates have been reported.[12)] On the other hand, in spite of the recent growing theoretical interest in the vinyl cation, the structure has not been established as yet.[13)] If the vinylic cation would have a linear structure (II'), the empty p-orbital on the positive center is coplanar with the terminal hydrogen and alkyl group (R'). Consequently, an alkyl group (R) migration should predominantly occur through the bent form (III), because it is a more preferred structure stereochemically. The vinyldialkylborane (IV) thus formed gives a cis-olefin (V) by protonolysis with carboxylic acid. This appears to be the cause that cis-olefins were



(2)

produced predominantly in the reaction. If the consideration is right, one can expect to obtain cis-alkenes more selectively by using organoboranes having bulky alkyl groups on boron. We next examined this possibility by using dialkylthexylboranes which are readily prepared by hydroboration of olefins with thexylborane (eq. 3). The reaction was found to run smoothly to yield corresponding olefins with high cis-isomer ratios, as expected. The results are summarized in Table 2. In these cases, the thexyl group migration does not seem to occur remarkably.

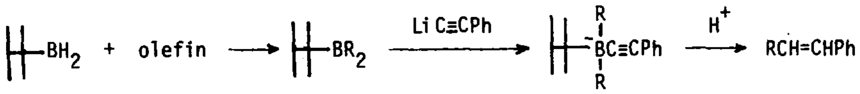


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Table 2. The Reaction of Propionic Acid with Lithium 2-Phenyl-1-ethynylthexyldialkylborates

R_3B	Product	Temp., °C	Yield,[a] %	cis:trans
iso-Butyl	iso-BuCH=CHPh	0	56	86:14
iso-Butyl	iso-BuCH=CHPh	-30	68	92: 8
iso-Butyl	iso-BuCH=CHPh	-70	74	97: 3
n-Butyl	n-BuCH=CHPh	-70	81	98: 2
Ethyl	EtCH=CHPh	-70	82	95: 5

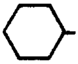
a) Based on organoborane used.

Finally, we attempted to extend this synthesis to the preparation of terminal olefins. Lithium ethynyltrialkylborates formed from monolithium acetylide and trialkylboranes are not used for the purpose, because such complexes are known to be subjected to disproportionation into acetylene and dilithium ethynylbistrialkylborate (eq. 4).[11b] However, this difficulty was recently overcome by using monolithium acetylide-ethylenediamine complex instead of lithium acetylide itself.[14] We employed this reagent for the present reaction. Treatment of the resulting complexes with propionic acid under the same reaction conditions described above, gave corresponding terminal alkenes in relatively good yields (eq. 5). Some of the results are shown in Table 3.

$$2R_3B + 2NaC\equiv CH \longrightarrow 2[R_3\bar{B}C\equiv CH]Na^+ \longrightarrow CH\equiv CH + [R_3\bar{B}C\equiv C\bar{B}R_3]2Na^+ \qquad (4)$$

$$CH\equiv CLi\cdot EDA + R_3B \longrightarrow [CH\equiv C\bar{B}R_3]Li^+\cdot EDA \xrightarrow{CH_3CH_2COOH} RCH{=}CH_2 \qquad (5)$$

Table 3. Terminal Olefin Synthesis[a)]

R_3B	Acetylene	Product	Yield,[b)] %
n-Hexyl	CH≡CLi·EDA	n-Hex-CH=CH_2	64
n-Octyl	CH≡CLi·EDA	n-Oct-CH=CH_2	65
Cyclohexyl	CH≡CLi·EDA	-CH=CH_2	56

a) CH≡CLi·EDA/R_3B=1.1. b) Based on organoborane used.

Although Pelter and his co-workers[11c)] recently pointed out that the same kind of olefin synthesis is possible from alkynyltrialkylborates by protonation with methane sulfonic acid, followed by hydrolysis with acetic acid, the present procedure also provides a general synthesis of internal and terminal olefins under mild conditions.

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