Tetrahedron Letters No. 24, pp 1961 - 1964, 1975. Pergamon Press. Printed in Great Britain.

THE REACTION OF IODINE WITH ATE-COMPLEXES OBTAINED FROM ORGANOBORANES AND LITHIUM CHLOROACETYLIDE. CONVENIENT SYNTHESES OF SYMMETRIC ALKYNES AND ALKENES

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(Received in Japan 10 April 1975; received in UK for publication 1 May 1975)

Recently, many reports have appeared dealing with new applications of alkali metal 1-alkynyltriorganoborates readily available from organoboranes for the synthesis of a wide variety of organic compounds.[1-11] We have previously published that treatment of such ate-complexes with iodine under mild conditions produces corresponding alkynes in essentially quantitative yields, and that the reaction is applicable to a wide variety of alkyl and aryl acetylenes and organoboranes (eq. 1).[3] We have also reported on the reaction of iodine with complexes formed from dilithium acetylide and organoboranes in an attempt to synthesize symmetric acetylenes (eq. 2).[4] However, it was found that the reaction does not proceed along the same type of reaction path which was considered in the reaction of lithium 1-alkynyltriorganoborates. Thus, symmetric alkynes were not obtained.

We wish to report here on the reaction of lithium 2-chloro-ethynyltrialkylborates with iodine to give corresponding symmetric alkynes (eq. 3).

$$R_3B + LiC{\equiv}CR' \longrightarrow [R_3\overset{-}{B}C{\equiv}CR']Li^+ \xrightarrow{+I_2} RC{\equiv}CR' \qquad (1)$$

$$2R_3B + LiC{\equiv}CLi \longrightarrow [R_3\overset{-}{B}C{\equiv}C\overset{-}{B}R_3]2Li^+ \xrightarrow{+I_2} RC{\equiv}CR \qquad (2)$$

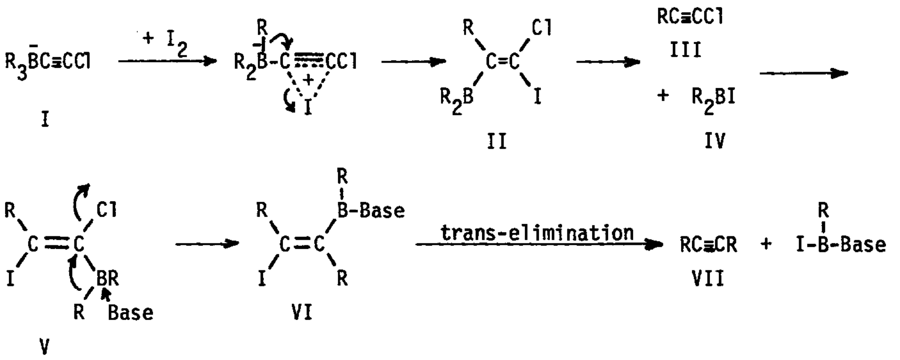
$$R_3B + LiC{\equiv}CCl \longrightarrow [R_3\overset{-}{B}C{\equiv}CCl]Li^+ \xrightarrow{+I_2} RC{\equiv}CR \qquad (3)$$

The following procedure for the preparation of 5-decyne is representative. A 25-ml flask equipped with a septum inlet, a reflux condenser and a magnetic stirring bar, was flushed with dry nitrogen. The flask was charged with 3.8 ml (4.5 mmol) of methyl lithium in ether and 0.27 ml (2.1 mmol) of trans-1,2-dichloroethylene at 0°C. After stirring for 1.5 hr, 0.65 ml (0.7 mmol) of tri-n-butylborane in THF was added to the solution at room temperature, followed by additional stirring for 3 hr. Then the reaction mixture was cooled down to -78°C in a dry ice-ethanol bath, and a solution of iodine (1.14 g, 4.5 mmol) in ether was added. After warming to room temperature, the mixture was oxidized with 2.0 ml of 3N-NaOH and 2.0 ml of 30%-H_2O_2 by the usual procedure. The organic layer separated by addition of K_2CO_3 was analyzed by glpc, and it was shown that 0.455 mmol (yield, 65%) of 5-decyne had been formed. The results of representative reactions are summarized in Table 1. The yield is calculated on the basis of the assumption that one mole of the ate-complex gives one mole of the corresponding alkyne, namely, the reaction proceeds intramolecularly as described in detail later.

Table 1. The Synthesis of Symmetric Alkynes <u>via</u> the Reaction of Iodine and Lithium 2-Chloro-1-ethynyltrialkylborates

Organoborane R_3B, R=	Reaction temp.	Reac. time hr	Molar ratio $ClC{\equiv}CLi/R_3B$	Product	Yield, %
n-Butyl	r.t.	3	3.0	5-Decyne	68
iso-Butyl	r.t.	18	2.0	2,7-Dimethyl-4-octyne	86
n-Pentyl	r.t.	3	3.0	6-Dodecyne	55
n-Pentyl	r.t.	24	2.0	6-Dodecyne	60
n-Hexyl	ether reflux	5	2.0	7-Tetradecyne	48

One possibility of the reaction path is as follows (eq. 4). By the same mode of reaction in the case of lithium 1-alkynyltrialkylborate with iodine,[3] lithium 2-chloro-ethynyltrialkylborate (I) appears to react with iodine to form the intermediate (II) which is converted into III and IV. The compound (III) reacts with IV to give V, which is changed into VI with a trans-relationship between the iodine atom and boron group. It was recently reported that such a boron compound(VI) gives the acetylene derivative (VII) by trans-elimination.[12] In order to clarify the possibility, we attempted a reaction of dibutylchloroborane and 1-chlorooctyne, but no formation of 5-dodecyne was observed. The first proposed mechanism, therefore, was ruled out.



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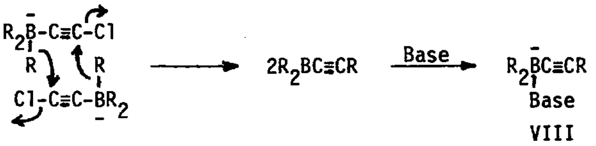
The second probable mechanism is that the reaction proceeds along an intermolecular reaction path, as shown in eqs. 5 and 6. We examined a crossover experiment by using an equivalent mixture



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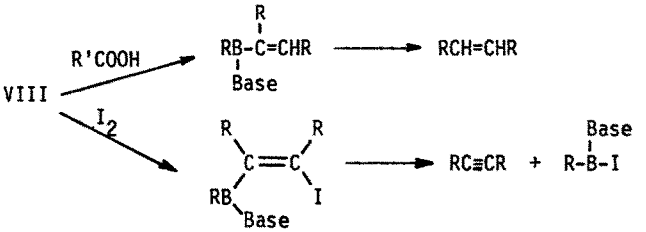
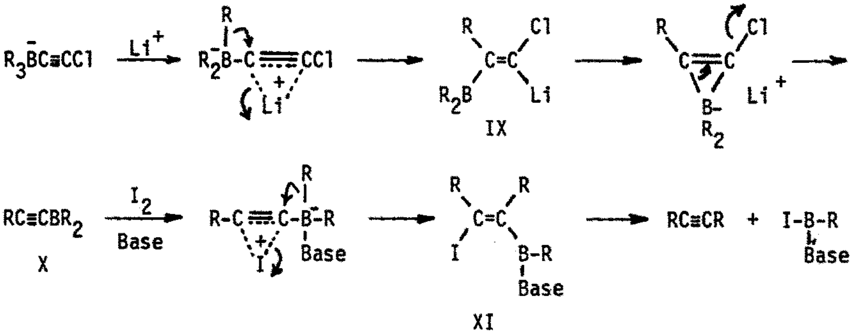


(6)

of tri-n-butylborane and tri-n-pentylborane to determine whether the rearrangement is intramolecular or intermolecular. The reaction products thus obtained were a mixture of 5-decyne, 5-undecyne and 6-dodecyne in a ratio of 10 : 1 : 10, demonstrating that this reaction proceeds partially through an intermolecular rearrangement, but mainly through an intramolecular rearrangement (eq. 7).

$$Bu_3B + Pen_3B \xrightarrow[I_2]{LiC\equiv CCl} BuC\equiv CBu\ (10) + BuC\equiv CPen\ (1) + PenC\equiv CPen\ (10) \qquad (7)$$

Although the reaction mechanism is not clear at present, the following path may be considered (eq. 8). The carbenoid (IX) formed from the ate-complex gives the borylacetylene derivative (X) by the rearrangement of Fritsch-Buttenberg-Wiechell reaction type.[13] The intermediate (X) is converted into the corresponding symmetric acetylene through the same reaction route which was postulated in the reaction of lithium 1-alkynyltriorganoborates.[3] If this mechanism is correct, one can expect to obtain the corresponding symmetric alkenes by treatment of the reaction mixture with a carboxylic acid via the reaction path as depicted in eq. 9. Actually, when propionic acid



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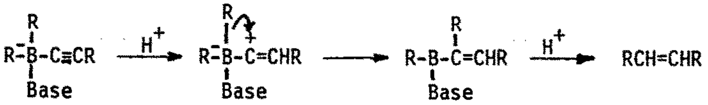

(9)

was added to the reaction mixture by the same procedure described above, followed by stirring overnight at room temperature, the expected alkene was produced. Some of the results are summarized in Table 2.

Table 2. The Synthesis of Symmetric Alkenes *via* the Reaction of Propionic Acid with Lithium 2-Chloro-1-ethynyltrialkylborates

Organoborane R_3B, R=	Reac. time hr	Molar ratio $ClC\equiv CLi/R_3B$	Product	Yield, %
n-Butyl	3	1.0	5-Decene	25
	3	2.0		46
	3	3.0		54
iso-Butyl	3	1.5	2,7-Dimethyl-4-octene	23
	5	1.5		39
	22	1.5		68

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