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Reaction of Bis(*trans*-1-hexenyl)methylborane with Two Molar Equivalents of Methylcopper(I). Evidence for the Presence of *trans*-1-Hexenylcopper(I) as an Intermediate

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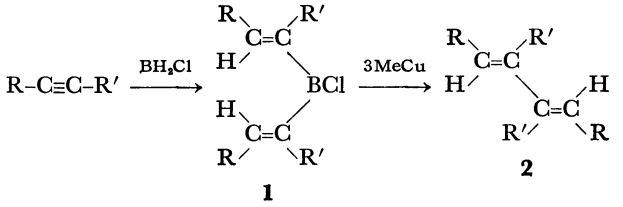
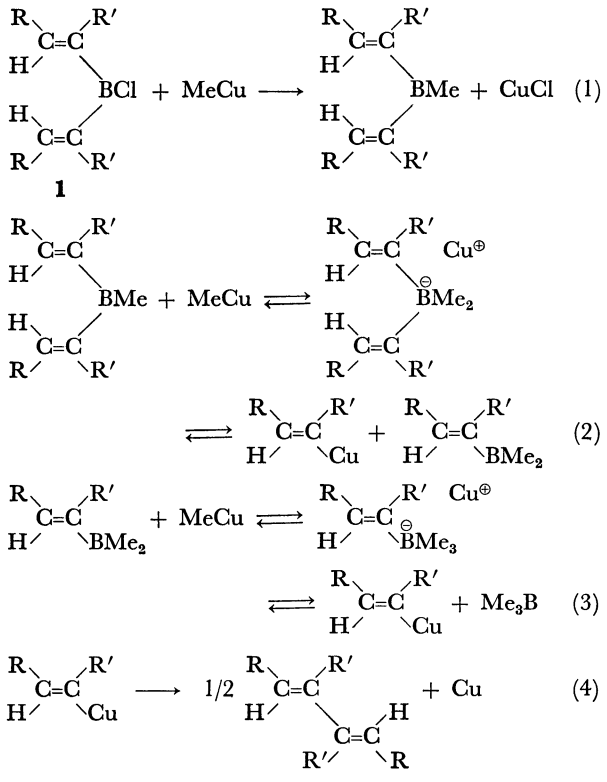
Synopsis. Bis(*trans*-1-hexenyl)methylborane, prepared by the reaction of bis(*trans*-1-hexenyl)chloroborane with methyllithium, was treated with 2 molar equivalents of methylcopper(I) at −78 °C to give (5*E*,7*E*)-5,7-dodecadiene quantitatively. The result indicates the presence of *trans*-1-hexenylcopper(I) intermediate.

It was reported that dialkenylchloroboranes (**1**) react with 3 molar equivalents of methylcopper(I) to give (*E*,*E*)-1,3-dienes (**2**) in a high yield.[1]



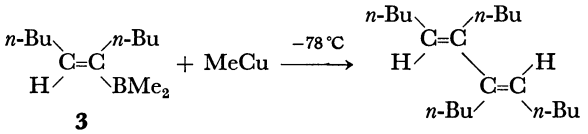
1 **2**

The transformation from **1** to **2** appears to involve the following sequence of reactions (Scheme 1), proceeding through an alkenylcopper(I) intermediate.[2] Actually, the reaction of (1-butyl-1-hexenyl)dimethylborane (**3**) with an equivalent amount of methylcopper(I) gave



Scheme 1. Proposed mechanism.

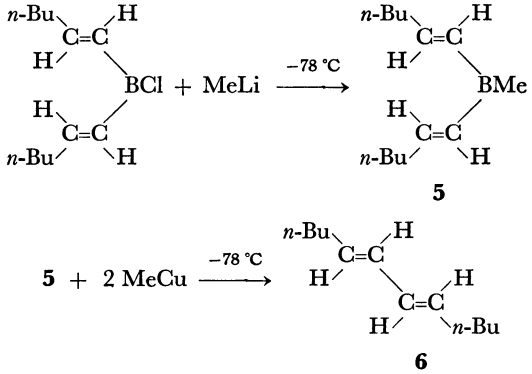
(5*E*,7*E*)-6,7-dibutyl-5,7-dodecadiene (**4**) in *ca.* 100% yield.[2] The result strongly supports the process shown by Eq. 3. However, no verification of Eq. 2 was obtained.[2] We wish to report an experimental evidence, establishing the proposed mechanism in Scheme 1.



3 **4**

Results and Discussion

Bis(*trans*-1-hexenyl)methylborane (**5**) was prepared by the reaction of bis(*trans*-1-hexenyl)chloroborane with an equivalent amount of methyllithium at −78 °C. An ether solution of **5** was slowly added to an ether suspension of 2 molar equivalents of methylcopper(I) at −78 °C. The color immediately changed from yellow to black. GLPC analysis revealed the approximately quantitative formation of (5*E*,7*E*)-5,7-dodecadiene (**6**).



5 **6**

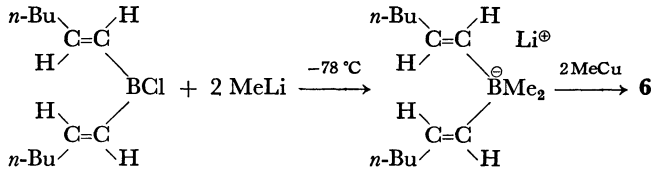
The result indicates that process (2) is involved in the transformation from **1** to **2**. Since an alkenylcopper(I) is far more unstable than methylcopper(I), it dimerizes even at low temperature (probably>−30 °C) (Eq. 4). Consequently, the equilibrium in Eqs. 2 and 3 lies to the right, two molar equivalents of methylcopper(I) being necessary for **5** to complete the reaction.

Process (1) was confirmed by GLPC examination of the borane product; the direct GLPC analysis (SE-30) of the reaction product from bis(*trans*-1-hexenyl)-chloroborane with an equivalent amount of methylcopper(I) at −78 °C revealed the quantitative formation of **5**.

As regards the copper(I) borates in Scheme 1, direct transmetalation from the alkenylboranes to the alkenyl-

copper(I) without passing through the copper(I) borates can be proposed as an alternative mechanism. So far we have no unambiguous evidence for such copper species. Copper(I) tetraarylborates were prepared by cation exchange reaction.[4] Recently copper(I) tetraalkylborates have been used for organic synthesis.[5] By analogy to these results, it is reasonable to assume the presence of copper(I) dialkenyldimethylborate and copper(I) alkenyltrimethylborate. The present results provide an evidence for the formation of alkenylcopper(I) species, confirming the mechanism in Scheme 1.

The lithium borates (**7**) prepared from bis(*trans*-1-hexenyl)chloroborane and 2 molar equivalents of methyllithium react with 2 molar equivalents of methylcopper(I) to give **6** in 82% yield.[1]



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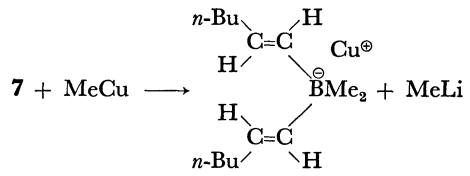
The result can be explained according to Scheme 1 by an equilibrium between the lithium borate (**7**) and the copper(I) borate (**8**).[6]



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Experimental

All temperatures were uncorrected. The NMR spectra were obtained on a Jeol JNM-MH-60 spectrometer, TMS being chosen as an internal standard. GLPC analyses were carried out on a Yanagimoto GCG 550T using a 2 m column packed with SE-30 10 wt% on Celite 545 AW.

Materials. The reagent grade solvent and copper(I) iodide were purified by standard techniques. Commercial 1-hexene was used. $BH_2Cl:OEt_2$[7] and methyllithium[8] were prepared according to the known procedures. The titration of methyllithium was performed according to the method of Watson and Eastham.[9]

Preparation of **5**. To an ether solution of bis(*trans*-1-hexenyl) chloroborane, prepared from the reaction of 1-hexyne with $BH_2Cl:OEt_2$,[7] was added an equivalent amount of methyllithium ether solution at −78 °C. The temperature was regulated to reach room temperature in 1—2 h. Bis(*trans*-1-hexenyl)methylborane was then distilled under reduced pressure; 80—90% yield; bp 65—70 °C/0.5 mmHg NMR(δ in CCl_4, J=Hz) 6.73 (d—t, 2H, J_d=16, J_t=6), 6.16 (d, 2H, J_d=16) 2.44—1.80 (m, 4H), 1.80—1.20 (m, 8H), 0.90 (t, 6H, J_t=6), 0.70 (s, 3H).

Reaction of **5** *with Methyl Copper(I).* The reaction was carried out as described previously.[2] The reaction mixture was analyzed by GLPC with an appropriate internal standard (dodecane). The structure of **6** was assigned by comparison with an authentic sample.[1] Methanol should be produced according to Scheme 1. The peak corresponding to methanol was observed, but its precise yield could not be determined under the present analytical conditions.

*Reaction of the Lithium Borate (***7***).* To an ether solution of bis(*trans*-1-hexenyl) chloroborane was added 2 molar equivalents of methyllithium ether solution at −78 °C. The temperature was regulated to reach 0 °C in 1—2 h. In this case, lithium borate (**7**) was not isolated but directly reacted with methylcopper(I) as described above. The product was analyzed by GLPC with dodecane as an internal standard.

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6) The complex (**7**) is stable and does not give the diene if it is not treated with methylcopper(I).

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