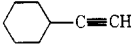


Table I. Reactions of Dialkenylchloroboranes with CH_3Cu^a

Entry	Acetylene	Product ^b	Yield, ^c % (by isoln)	Isomeric purity, %
1	$n\text{-C}_4\text{H}_9\text{C}\equiv\text{CH}$	(<i>SE,7E</i>)-5,7-Dodecadiene	93 (72)	100 ^d
2	$n\text{-C}_4\text{H}_9\text{C}\equiv\text{CH}$	(<i>SE,7E</i>)-5,7-Dodecadiene	60 ^e	100 ^d
3	$\text{C}_2\text{H}_5\text{C}\equiv\text{CC}_2\text{H}_5$	4,5-Diethyl-(<i>3E,5E</i>)- 3,5-octadiene	100	100 ^d
4	$n\text{-C}_4\text{H}_9\text{C}\equiv\text{CH}$ $\text{C}_2\text{H}_5\text{C}\equiv\text{CC}_2\text{H}_5$	4-Ethyl-(<i>3E,5E</i>)-3,5- decadiene	64 ^f	99 ^g
5	$\text{PhC}\equiv\text{CPh}$	1,2,3,4-Tetraphenyl (<i>1E,3E</i>)-1,3-butadiene	(32) ^h	100 ^h
6	$\text{CH}_3\text{CH}(\text{CH}_3)(\text{CH}_2)_2\text{C}\equiv\text{CH}$	2,11-Dimethyl-(<i>5E,7E</i>)- 5,7-dodecadiene	94	99 ^g
7		1,4-Dicyclohexyl-(<i>1E,3E</i>)- 1,3-butadiene	71 ⁱ	99 ^g
8	$\text{Cl}(\text{CH}_2)_3\text{C}\equiv\text{CH}$	1,10-Dichloro-(<i>4E,6E</i>)- 4,6-decadiene	100 (70)	100 ^d
9	$\text{H}_3\text{CO}_2\text{C}(\text{CH}_2)_6\text{C}\equiv\text{CH}$	1,20-Dicarbomethoxy-(<i>9E,11E</i>)- 9,11-eicosadiene	(42) ^e	99 ^g

^aDialkenylchloroboranes (10 mmol), except where otherwise indicated, were added to CH_3Cu (30 mmol) in ether at 0°, and the resultant mixture was kept at 0° for 1 hr. An excess (40%) of the 1-alkyne was required to achieve a high yield of the dialkenylborane. ^bSatisfactory NMR, ir, and elemental analysis data were obtained for all new compounds. ^cBy GLPC, based on the alkenyl group of the borane. ^dDetermined by GLPC (SE-30) using authentic samples of (*E,Z*) and/or (*Z,Z*)-1,3-dienes. ^eDisiamylborane (10 mmol) was utilized. ^fThe mixture of bis(1-hexenyl)chloroborane (6 mmol) and bis(3-hexenyl)chloroborane (5 mmol) was treated with CH_3Cu (33 mmol). The symmetrical dienes were also obtained. ^gBy ¹H NMR spectra. ^hThe yield is that of the recrystallized material. The purity was determined from its melting point and ¹H NMR spectrum. ⁱThe alkenylborane was utilized without purification directly after the hydroboration.¹

Table II. Yield of 5,7-Dodecadiene vs. the Amount of CH_3Cu^a

Bis(1-hexenyl)- chloroborane (mmol)	CH_3Cu (mmol)	Yield, ^b %
10	10	0
10	20	44
10	30	93

^aConditions were the same as in Table I. ^bBy GLPC.

were inert toward CH_3Cu .⁴ The reaction of 1-hexenyldisiamylborane also proceeded smoothly, though considerable amounts of by-products such as Sia-Sia and *n*-Bu-CH=CH-Sia were produced, causing decreased formation of the diene (Table I, entry 2). When the reaction was attempted by treating bis(1-hexenyl)chloroborane with other copper derivatives such as lithium dimethylcuprate, cupric salts, or cuprous salts at 0°, small amounts of coupling product were detected.⁵

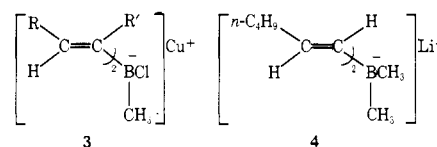
Two mechanisms are possible for the reaction: (i) a radical mechanism via an electron transfer,⁶ and (ii) a transmetalation leading to formation of the alkenylcopper. The high degree of retention of configuration must exclude a "free" radical mechanism.⁷ If simple transmetalation were involved, methanol should be produced via the hydrogen peroxide oxidation of the reaction mixture. None, however, was detected. Although the mechanism is not clear at present,⁸ the high stereoselectivity, mildness, and high yields make the present reaction useful for the synthesis of isomerically pure (*E,E*)-1,3-dienes.⁹ Further work is under way to delineate the mechanism and to explore potential applications of the present reaction system in organic synthesis.

The following procedure for the synthesis of (*SE,7E*)-5,7-dodecadiene is representative. In a 250-ml flask, equipped with a magnetic stirrer and maintained under N_2 , was placed 11.4 g (60 mmol) of CuI and 20 ml of dry ether. Methyl lithium in ether (51 ml, 60 mmol) was slowly added at 0°, and the resultant mixture (yellow suspension) was stirred at 0° for 10 min. Bis(1-hexenyl)chloroborane¹ (4.8 ml, 20 mmol) was then added at 0°, and the mixture was stirred 1 hr at 0°. Water (20 ml) was added, and the organic layer was separated.¹⁰ The aqueous layer was washed twice with *n*-hexane. The combined organic phase was dried over anhydrous K_2CO_3 . The solvents were removed, and the

product, (*SE,7E*)-5,7-dodecadiene, was obtained by distillation under reduced pressure: 2.4 g, 72% yield, bp 75–76° (3 mm), n_D^{25} 1.4640 (lit.^{9a} 1.4635).

References and Notes

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- (a) H. C. Brown, N. C. Hebert, and C. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1001 (1961); H. C. Brown and C. H. Snyder, *ibid.*, **83**, 1001 (1961); (b) R. C. Larock and H. C. Brown, *ibid.*, **92**, 2467 (1970); R. C. Larock, S. K. Gupta, and H. C. Brown, *ibid.*, **94**, 4371 (1972); (c) M. F. Lappert, "The Chemistry of Boron and Its Compounds", E. L. Muetterties, Ed., Wiley, New York, N.Y., 1967, p 443.
- D. E. Bergbreiter and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 4937 (1974); it seems to us that diastereomeric or enantiomeric organometallics may be preparable via organoboranes.
- Although the color slowly changed from yellow to black, the alkaline hydrogen peroxide oxidation gave the corresponding alcohol in essentially quantitative yield.
- With some Cu halides, the corresponding hexenyl halides were produced. The reaction of the hexenylborane with $\text{AgNO}_3\text{-OH}$, which is an effective coupling reagent for trialkylboranes,^{2a} was also examined. However, the maximum yield of the diene attainable was only ~20%.
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- G. M. Whitesides and C. P. Casey, *J. Am. Chem. Soc.*, **88**, 4541 (1966); G. M. Whitesides, C. P. Casey, and J. K. Krieger, *ibid.*, **93**, 1379 (1971).
- We speculate that the boron ate complex (3) produced from the chloroborane and 1 molar equiv of MeCu may be involved as the key intermediate. Actually, the lithium borate (4) prepared from bis(1-hexenyl)chloroborane and 2 molar equiv of MeLi reacts with 2 molar equiv of MeCu at 0° to produce (*SE,7E*)-5,7-dodecadiene in 82% yield (cf. Table II).



- The presently available methods are as follows: (a) via vinylalanes, G. Zweifel and R. L. Miller, *J. Am. Chem. Soc.*, **92**, 6678 (1970); (b) via vinyl halides and Cu, T. Cohen and T. Poeth, *ibid.*, **94**, 4363 (1972); (c) via vinyl halides and $\text{Ni}(\text{COD})_2$, M. F. Semmelhack, P. M. Helquist, and J. D. Gorzynski, *ibid.*, **94**, 9234 (1972); (d) via thexyboranes, E. Negishi Yoshida, *J. Chem. Soc., Chem. Commun.*, 606 (1973); (e) J. F. Normant, G. Cahiez, and C. Chuit, *J. Organomet. Chem.*, **77**, 269 (1974).
- During this operation, muddy material appeared between the organic and aqueous layers. This caused the relatively low isolated yield in comparison with the GLPC yield. It is recommended to filter the organic layer and muddy material through the column of alumina before distillation.

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