

2013  $\text{s cm}^{-1}$ ) characteristic of *trans*-bis(organotin)tetra-carbonylosmium compounds.<sup>1,29,30</sup>

Cleavage of most of the trimetalide was accomplished with anhydrous HCl in  $\text{CH}_2\text{Cl}_2$  ( $-15^\circ$ , 30 min). The infrared spectrum of a hexane solution of the pale yellow residue, after removal of the solvent and excess HCl under vacuum, was essentially identical with that of **1** and indicated a yield of 35%.<sup>31</sup> Removal of the solvent and volatile by-products under vacuum at  $40^\circ$  and recrystallization from methanol gave pure **1** (18 mg, 17%) identified by infrared spectroscopy, melting point, and undepressed mixture melting point with an authentic sample.<sup>1</sup>

In a similar fashion, the coupling scheme was carried two steps beyond **7** to synthesize the analogous pentametalide. The residue from HCl cleavage contained two major high molecular weight components by GPC analysis.<sup>32</sup> The smaller of these was collected and identified as **1** by retention volume and ir spectrum. The larger (also collected) gave a mass spectrum with the highest observable multiplet peak centered at  $m/e$   $1316 \pm 2$  which probably arises from loss of a butyl group from the molecular ion of  $[\text{ClSnBu}_2\text{Os}(\text{CO})_4]_2\text{SnBu}_2$ .<sup>33</sup> Further characterization of this component is in progress. The presence of **1** in this mixture suggests that some of the resino-trimetalides may be doubly attached and/or physically inaccessible. The sharp drop in the level of substitution from **5** to **7** favors the latter. Experiments in progress are designed to eliminate both potential problems and to extend the method to other multifunctional organometallics.

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- (18) The  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$  for 1 gram of resin was prepared in situ from  $\text{HgO}$  (0.05 mmol),  $\text{CF}_3\text{COOH}$  (0.25 ml), and  $\text{CH}_2\text{Cl}_2$  (22.5 ml).
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- (24) More vigorous conditions produced a narrow annulus of mercury with a colorless center after reduction, indicating less than optimum distribution of resino-phenylmercuric chloride sites.
- (25) Neutron activation analysis of **3** gave 0.83% Hg and 0.15% Cl, i.e., 0.04 mequiv/g for each.
- (26) The large excess of  $(n\text{-Bu})_2\text{SnCl}_2$  also quenched intercalated or adsorbed  $n$ -butyllithium known to be present in **4** from other experiments.
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- (30) The spectral changes associated with the conversion of **6** to **7** argue against double attachment of the trimetalide in **6**.
- (31) The yield calculation is based on the osmium content of **7**, 0.0176 mg-atom per gram.
- (32) Gel permeation chromatographic analyses were performed using Waters Associates' 100 Å  $\mu$ -Styragel columns.
- (33) We observed that the base peak in the mass spectrum of **1** is ( $M - 57$ ) corresponding to loss of one butyl group.

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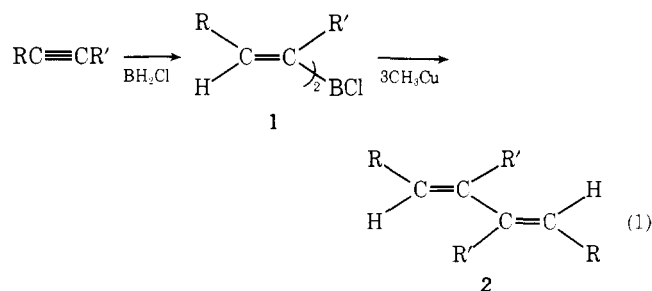
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## Methylcopper Induced Coupling of Dialkenylchloroboranes. A New Procedure for the Stereoselective Synthesis of (*E,E*)-1,3-Dienes

Sir:

Dialkenylchloroboranes (**1**), readily available through the reaction of acetylenes with chloroborane-ethyl etherate,<sup>1</sup> react rapidly at  $0^\circ$  with 3 molar equiv of methylcopper to produce (*E,E*)-1,3-dienes (**2**) in excellent yields (eq 1).




The stereochemical purity of the product is >99%. The present reaction, therefore, provides a facile and stereoselective transformation of acetylenes into the corresponding (*E,E*)-1,3-dienes and can even be extended to the accommodation of a functional group.

A number of metal salts react with organoboranes,<sup>2</sup> and such transmetalation reactions appear to hold promise for a noncarbanionic route to organo transition metallics.<sup>3</sup> During these investigations, we have discovered that methylcopper is a highly efficient coupling agent for dialkenylchloroboranes. The results are summarized in Table I.

To achieve the nearly quantitative conversion of borane into diene it was essential to utilize 3 molar equivalents of  $\text{CH}_3\text{Cu}$  as shown in Table II. Further increase of  $\text{CH}_3\text{Cu}$  did not exercise a significant influence on the yield. The reaction was quite rapid at  $0^\circ$ ; the addition of the borane to  $\text{CH}_3\text{Cu}$  in ether caused an instantaneous change of color from yellow to black. The GLPC analysis after 5 min revealed formation of the diene in 70% yield. In contrast to alkenylboranes, trialkylboranes and dialkylchloroboranes

Table I. Reactions of Dialkenylchloroboranes with  $\text{CH}_3\text{Cu}^a$ 

Entry	Acetylene	Product <sup>b</sup>	Yield, <sup>c</sup> % (by isoln)	Isomeric purity, %
1	$n\text{-C}_4\text{H}_9\text{C}\equiv\text{CH}$	(5 <i>E</i> ,7 <i>E</i> )-5,7-Dodecadiene	93 (72)	100 <sup>d</sup>
2	$n\text{-C}_4\text{H}_9\text{C}\equiv\text{CH}$	(5 <i>E</i> ,7 <i>E</i> )-5,7-Dodecadiene	60 <sup>e</sup>	100 <sup>d</sup>
3	$\text{C}_2\text{H}_5\text{C}\equiv\text{CC}_2\text{H}_5$	4,5-Diethyl-(3 <i>E</i> ,5 <i>E</i> )- 3,5-octadiene	100	100 <sup>d</sup>
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-(3 <i>E</i> ,5 <i>E</i> )-3,5- decadiene	64 <sup>f</sup>	99 <sup>g</sup>
5	$\text{PhC}\equiv\text{CPh}$	1,2,3,4-Tetraphenyl (1 <i>E</i> ,3 <i>E</i> )-1,3-butadiene	(32) <sup>h</sup>	100 <sup>h</sup>
6	$\text{CH}_3\text{CH}(\text{CH}_3)(\text{CH}_2)_2\text{C}\equiv\text{CH}$	2,11-Dimethyl-(5 <i>E</i> ,7 <i>E</i> )- 5,7-dodecadiene	94	99 <sup>g</sup>
7		1,4-Dicyclohexyl-(1 <i>E</i> ,3 <i>E</i> )- 1,3-butadiene	71 <sup>i</sup>	99 <sup>g</sup>
8	$\text{Cl}(\text{CH}_2)_3\text{C}\equiv\text{CH}$	1,10-Dichloro-(4 <i>E</i> ,6 <i>E</i> )- 4,6-decadiene	100 (70)	100 <sup>d</sup>
9	$\text{H}_3\text{CO}_2\text{C}(\text{CH}_2)_8\text{C}\equiv\text{CH}$	1,20-Dicarboxymethoxy-(9 <i>E</i> ,11 <i>E</i> )- 9,11-eicosadiene	(42) <sup>e</sup>	99 <sup>g</sup>

<sup>a</sup> Dialkenylchloroboranes (10 mmol), except where otherwise indicated, were added to  $\text{CH}_3\text{Cu}$  (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. <sup>b</sup> Satisfactory NMR, ir, and elemental analysis data were obtained for all new compounds. <sup>c</sup> By GLPC, based on the alkenyl group of the borane. <sup>d</sup> Determined by GLPC (SE-30) using authentic samples of (*E*,*Z*) and/or (*Z*,*Z*)-1,3-dienes. <sup>e</sup> Disiamylborane (10 mmol) was utilized. <sup>f</sup> The mixture of bis(1-hexenyl)chloroborane (6 mmol) and bis(3-hexenyl)chloroborane (5 mmol) was treated with  $\text{CH}_3\text{Cu}$  (33 mmol). The symmetrical dienes were also obtained. <sup>g</sup> By <sup>1</sup>H NMR spectra. <sup>h</sup> The yield is that of the recrystallized material. The purity was determined from its melting point and <sup>1</sup>H NMR spectrum. <sup>i</sup> The alkenylborane was utilized without purification directly after the hydroboration.<sup>1</sup>

Table II. Yield of 5,7-Dodecadiene vs. the Amount of  $\text{CH}_3\text{Cu}^a$ 

Bis(1-hexenyl)- chloroborane (mmol)	$\text{CH}_3\text{Cu}$ (mmol)	Yield, <sup>b</sup> %
10	10	0
10	20	44
10	30	93

<sup>a</sup> Conditions were the same as in Table I. <sup>b</sup> By GLPC.

were inert toward  $\text{CH}_3\text{Cu}$ .<sup>4</sup> The reaction of 1-hexenyldisiamylborane also proceeded smoothly, though considerable amounts of by-products such as Sia-Sia and  $n\text{-Bu-CH=CH-Sia}$  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.<sup>5</sup>

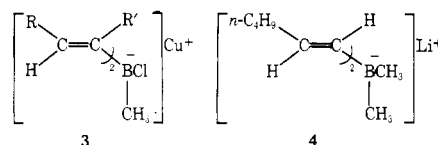
Two mechanisms are possible for the reaction: (i) a radical mechanism via an electron transfer,<sup>6</sup> and (ii) a transmetalation leading to formation of the alkenylcopper. The high degree of retention of configuration must exclude a "free" radical mechanism.<sup>7</sup> If simple transmetalation 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,<sup>8</sup> the high stereoselectivity, mildness, and high yields make the present reaction useful for the synthesis of isomerically pure (*E,E*)-1,3-dienes.<sup>9</sup> 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 (5*E*,7*E*)-5,7-dodecadiene is representative. In a 250-ml flask, equipped with a magnetic stirrer and maintained under  $\text{N}_2$ , was placed 11.4 g (60 mmol) of  $\text{CuI}$  and 20 ml of dry ether. Methylolithium 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)chloroborane<sup>1</sup> (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.<sup>10</sup> The aqueous layer was washed twice with  $n$ -hexane. The combined organic phase was dried over anhydrous  $\text{K}_2\text{CO}_3$ . The solvents were removed, and the

product, (5*E*,7*E*)-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.<sup>9a</sup> 1.4635).

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- (4) Although the color slowly changed from yellow to black, the alkaline hydrogen peroxide oxidation gave the corresponding alcohol in essentially quantitative yield.
- (5) 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,<sup>2a</sup> was also examined. However, the maximum yield of the diene attainable was only ~20%.
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- (8) We speculate that the boron ate complex (3) produced from the chloroborane and 1 molar equiv of  $\text{MeCu}$  may be involved as the key intermediate. Actually, the lithium borate (4) prepared from bis(1-hexenyl)chloroborane and 2 molar equiv of  $\text{MeLi}$  reacts with 2 molar equiv of  $\text{MeCu}$  at 0° to produce (5*E*,7*E*)-5,7-dodecadiene in 82% yield (cf. Table II).



- (9) 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  $\text{Ni(COD)}_2$ , M. F. Semmelhack, P. M. Helquist, and J. D. Gorzynski, *ibid.*, **94**, 9234 (1972); (d) via the ethylboranes, 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).
- (10) 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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