

# Reaction of Alkenylboranes with Methylcopper. A Convenient New Procedure for the Synthesis of Symmetrical (*E,E*)-1,3-Dienes<sup>1a</sup>

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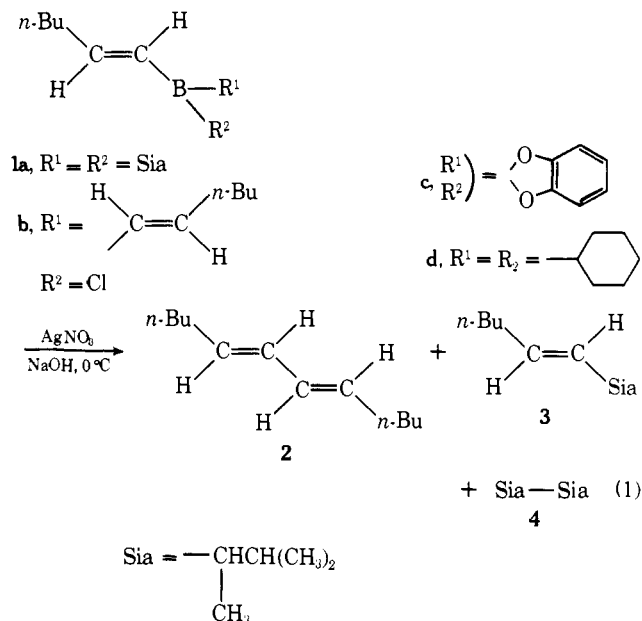
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**Abstract:** Dialkenylchloroboranes (**5**), readily available through the reaction of acetylenes with chloroborane-ethyl etherate, react with 3 molar equiv of methylcopper to produce symmetrical (*E,E*)-1,3-dienes (**6**) in high yields. The stereochemical purity of the product is >99%. The similar reaction with alkenyldisiamylboranes or alkenyldicyclohexylboranes produces (*E,E*)-1,3-dienes in moderate yields along with a considerable amount of by-products. In these reactions, it is essential to utilize 3 molar equiv of methylcopper in order to achieve the effective conversion of the boranes into the dienes. The reaction mechanism is described, and it is demonstrated that the formation of an ate complex, such as  $R_2\bar{B}(CH_3)_2Cu^+$  or  $R\bar{B}(CH_3)_3Cu^+$  ( $R$  = alkenyl), is the key step in the reaction of **5** with methylcopper.

Recently a number of new procedures for the preparation of conjugated dienes have appeared utilizing organoaluminum,<sup>2</sup> -boron,<sup>2b,3</sup> -cobalt,<sup>4</sup> -copper,<sup>5</sup> -lithium,<sup>4,5a-d,f,6</sup> -magnesium,<sup>5e</sup> -nickel,<sup>7</sup> -silver,<sup>5b,6</sup> -palladium,<sup>9</sup> and -mercury<sup>9</sup> reagents. Alkenyl halides are often employed as the starting materials in these reactions. However, the synthesis of the requisite stereodefined alkenyl halides is sometimes cumbersome. To alleviate this difficulty the direct use of alkenylboranes stereoselectively obtainable via hydroboration of acetylenes appeared to be highly promising. The procedure utilizing alkenylaluminum derivatives readily obtainable via hydroalumination of acetylenes is a similar approach to this problem.<sup>2b,c</sup> Unfortunately, the incorporation of various functional groups is difficult in such a reaction. A preliminary communication from this laboratory reported a reaction of dialkenylchloroboranes (**5**) with methylcopper to produce symmetrical (*E,E*)-1,3-dienes<sup>1</sup> (eq 2). We report herein the full details of this study.

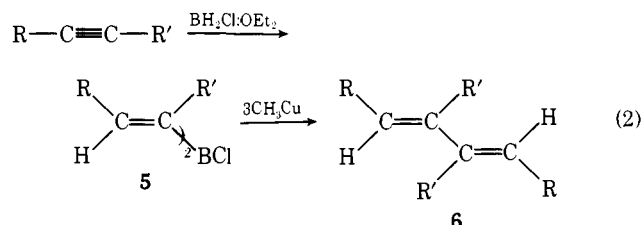
## Results and Discussion

**Synthetic Studies.** We initially investigated the reaction of *trans*-1-hexenyldisiamylborane (**1a**) with aqueous alkaline silver nitrate which is an effective coupling reagent for



trialkylboranes<sup>10</sup> (eq 1). Contrary to expectation, trace amounts of the desired diene (**2**) were detected by GLC analysis. Instead, 1-hexene (32%), 2,3-dimethyl-*trans*-4-nonene (**3**) (2%), and 2,3,4,5-tetramethylhexane (**4**) (20%) were produced. We also examined similar reactions using bis-(*trans*-1-hexenyl)chloroborane (**1b**) and *trans*-1-hexenylcatecholborane (**1c**). The former produced **2** at a maximum yield of 25%, but the latter gave only trace amounts of **2**.

During these investigations we discovered that methylcopper is a highly efficient coupling agent for dialkenylchloroboranes (**5**) (eq 2). The boranes (**5**) are readily prepared through the



reaction of acetylenes with chloroborane-ethyl etherate,<sup>11</sup> and the stereochemical purity of the product (**6**) is >99%. Therefore, this reaction provides a facile and stereoselective transformation of acetylenes into the corresponding (*E,E*)-1,3-dienes. The results are summarized in Table I.

Interestingly, utilization of 3 molar equiv of methylcopper was essential to achieve the nearly quantitative conversion of borane into diene (Table II). Additional methylcopper had no significant influence on the yield.

The reaction was quite rapid at 0 °C; the addition of the borane to methylcopper in ether caused an instantaneous change of color from yellow to black. The yields of dienes were sensitive to the reaction temperature. The olefin, alkenyl-CH<sub>3</sub>, derived from coupling of the alkenyl group with the CH<sub>3</sub> group, was produced as the by-product. For example, the rapid addition of **1b** to an ether solution of methylcopper at 0 °C afforded **14** in 10% yield. Fortunately, this by-product was

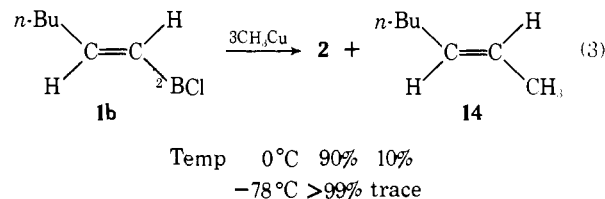
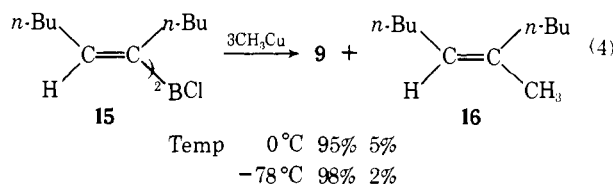


Table I. Reaction of **5** with Methylcopper<sup>a</sup>

Entry	Acetylene	Product	Yield, % <sup>b</sup> (by isoln)
1	<i>n</i> -C <sub>4</sub> H <sub>9</sub> C≡CH	( <i>5E,7E</i> )-5,7-Dodecadiene ( <b>2</b> )	93 (72)
2	C <sub>2</sub> H <sub>5</sub> C≡CC <sub>2</sub> H <sub>5</sub>	4,5-Diethyl-( <i>3E,5E</i> )-3,5-octadiene ( <b>7</b> )	99
3 <sup>c</sup>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> C≡CH	4-Ethyl-( <i>3E,5E</i> )-3,5-decadiene ( <b>8</b> )	64
	C <sub>2</sub> H <sub>5</sub> C≡CC <sub>2</sub> H <sub>5</sub>	<b>2</b>	23
		<b>7</b>	17
4	<i>n</i> -C <sub>4</sub> H <sub>9</sub> C≡C- <i>n</i> -C <sub>4</sub> H <sub>9</sub>	6,7-Di- <i>n</i> -butyl-( <i>5E,7E</i> )-5,7-dodecadiene ( <b>9</b> )	95
5	C <sub>6</sub> H <sub>5</sub> C≡CC <sub>6</sub> H <sub>5</sub>	1,2,3,4-Tetraphenyl-( <i>1E,3E</i> )-1,3-butadiene ( <b>10</b> )	(45) <sup>d,e</sup>
6	CH <sub>3</sub> CH(CH <sub>3</sub> )-CH <sub>2</sub> CH <sub>2</sub> C≡CH	2,11-Dimethyl-( <i>5E,7E</i> )-5,7-dodecadiene ( <b>11</b> )	94
7	<i>c</i> -C <sub>6</sub> H <sub>11</sub> C≡CH	1,4-Dicyclohexyl-( <i>1E,3E</i> )-1,3-butadiene ( <b>12</b> )	71 <sup>e</sup>
8	Cl(CH <sub>2</sub> ) <sub>3</sub> C≡CH	1,10-Dichloro-( <i>4E,6E</i> )-4,6-dodecadiene ( <b>13</b> )	99 (70)

<sup>a</sup> Dialkenylchloroboranes (10 mmol), except where otherwise indicated, were slowly added to methylcopper (30 mmol) in ether at 0 to -10 °C. <sup>b</sup> By GLC, based on the alkenyl group of the borane. Isomeric purity of the product was determined by a combination of GLC and <sup>1</sup>H NMR. <sup>c</sup> The mixture of **1b** (6 mmol) and bis(*trans*-3-hexenyl)chloroborane (5 mmol) was treated with CH<sub>3</sub>Cu (33 mmol). <sup>d</sup> Yield of the recrystallized material. <sup>e</sup> The alkenylboranes were used without purification directly after the hydroboration, and the yields were based on the acetylenes used (20 mmol) in the hydroboration.

suppressed by adding **1b** at -78 °C (eq 3). A similar result was obtained in the reaction of **15** (eq 4).



Some other features of the data in Table I deserve comment. In the case of 1-alkyne an excess of the acetylene is required to achieve a high yield of **5**,<sup>11</sup> though the internal acetylene reacts smoothly with stoichiometric amounts of chloroborane-ethyl etherate. The distilled dialkenylchloroboranes were used to obtain the dienes in high yields (entries 1-4, 6, and 8). The low yield in entry 5 was presumably due to the incomplete hydroboration of tolan with BH<sub>2</sub>Cl:OEt<sub>2</sub>, since considerable amounts of tolan were recovered after the reaction. Although the synthesis of unsymmetrical (*E,E*)-1,3-dienes was also attempted (entry 3), the coupling was approximately statistical as would be expected.

Of interest was the question whether other copper agents, such as lithium dimethylcuprate, cupric chloride, and cuprous chloride, would permit to induce the coupling of **1b**, since it was reported that cuprous chloride is an effective coupling agent for alkenylalanes.<sup>2c</sup> However, the attempts resulted in failure, with trace amounts of **2** being produced.

Since it had become clear that methylcopper is a highly effective coupling agent for **5**, we used this reagent with *trans*-1-hexenyldisiamylborane (**1a**). When 3 molar equiv of methylcopper was added to **1a** at 0 °C, the color of solution changed slowly from yellow to black. This suggested that the reaction of alkenyldisiamylboranes was more slower than that of **5**. The results are summarized in Table III. Here also, utilization of 3 molar equiv of methylcopper was required to achieve the

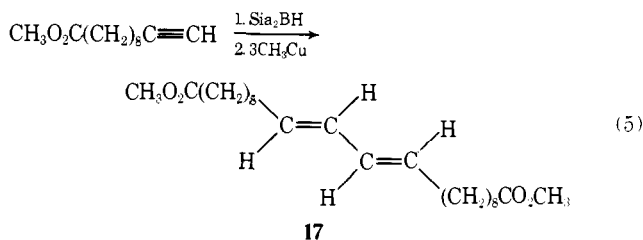
Table II. Yield of **2** vs. the Amount of Methylcopper

<b>1b</b> , mmol	CH <sub>3</sub> Cu, mmol	Yield, % <sup>a</sup>
10	10	0
10	20	44
10	30	93
10	40	92

<sup>a</sup> By GLPC, based on the alkenyl group of the borane.

effective conversion of the borane into the diene (60%), and the yield was not essentially influenced by the further increase of methylcopper. The formation of Sia-Me was not observed, and SiaH (or its olefin derivatives) could not be analyzed by GLC (SE-30) owing to the overlapping of its peak with that of the solvent.

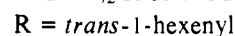
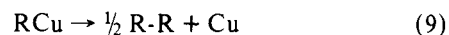
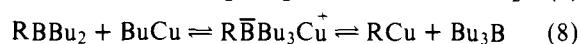
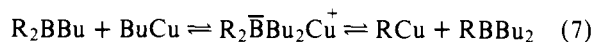
The result of Table III indicates that the preparative method via the reaction of alkenyldisiamylboranes with methylcopper is inferior to that via **5** with respect to yield. In one case, however, it was required to replace the procedure through **5** by that via the alkenyldisiamylborane. Hydroboration of methyl 10-undecynoate with BH<sub>2</sub>Cl:OEt<sub>2</sub> did not proceed smoothly, and the corresponding diene was not obtained satisfactorily via eq 2. This difficulty was overcome by use of the alkenyl-



disiamylborane (45% isolated yield based on the alkyne) (eq 5).

The reaction of *trans*-1-hexenyldicyclohexylborane (**1d**) with methylcopper was also examined. The results were essentially identical with those of **1a** (Table IV). Since cyclohexane (or cyclohexene) was formed in 1-2% yield, it was anticipated that the yield of SiaH (or its olefin derivatives) from the reaction of **1a** was approximately 1-2%. In contrast to these alkenylboranes (**1a** and **1d**), the similar reaction of **1c** with methylcopper did not proceed smoothly, producing trace amounts of **2**.

**The Course of the Reaction.** In order to understand the reaction mechanism of eq 2, we undertook to clarify the material balance of the CH<sub>3</sub> group. However, it was rather difficult to analyze such a small alkyl group. Instead, we investigated the reaction of **1b** with butylcopper (Table V). From these results, the following sequence of reactions is proposed (eq 6-9) (R = *trans*-1-hexenyl).



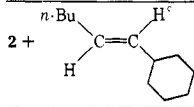

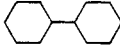

If the reaction proceeds as shown in eq 6-9, the trialkylborane is obtained. Actually, tri-*n*-butylborane was detected when the reaction mixture was analyzed before oxidation (0.85 mmol of Bu<sub>3</sub>B in run 3 and 0.55 mmol in run 2, by GLC). When 2 molar equiv of butylcopper was used (run 2), RBBu<sub>2</sub> was detected along with Bu<sub>3</sub>B. Consequently, eq 7 and 8 proceed competitively in run 2 and the formation of the ate complex, R<sub>2</sub>B<sup>+</sup>BBu<sub>2</sub>Cu<sup>-</sup>, is relatively slow.<sup>12</sup> Furthermore, the re-

Table III. Reaction of **1a** with Methylcopper<sup>a</sup>

CH <sub>3</sub> Cu, mmol	Products <sup>b</sup> (yields, mmol)					
	<b>2</b>	<b>3</b>	1-Hexene	<b>14</b>	<b>4</b>	Sial
1	0.08	<i>c</i>	0.11	<i>c</i>	<i>c</i>	0.18
2	0.24	0.03	0.11	0.02	0.03	0.12
3	0.30	0.06	Trace	0.02	0.05	0.15
4	0.29	0.04	0.03	0.10	0.04	0.28
6	0.32	0.06	<i>c</i>	0.14	0.03	0.28
7	0.30	0.08	<i>c</i>	0.16	0.02	0.26

<sup>a</sup> **1a** (1 mmol) was treated with methylcopper in ether at 0 °C. The reaction mixture was directly analyzed by GLC after the usual oxidation. <sup>b</sup> Yields refer to millimoles of the products. The yields of other products, such as SiaOH and capronaldehyde, were not determined. <sup>c</sup> Not detected.

Table IV. Reaction of **1d** with Methylcopper<sup>a</sup>

CH <sub>3</sub> Cu mmol		Products <sup>b</sup> (yield, mmol)				
		1-Hexene	<b>14</b>			
1	0.44	0.04	Trace	0.03	0.1	<i>d</i>
2	0.54	0.03	0.07	0.02	<i>d</i>	0.14
3	0.47	0.02	0.10	0.01	<i>d</i>	0.40

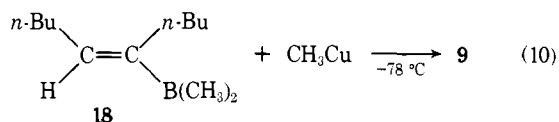
<sup>a</sup> **1d** (1 mmol) was treated with methylcopper in ether at 0 °C. The reaction was directly analyzed by GLC after the usual oxidation. The yields of other products, such as cyclohexanol and capronaldehyde, were not determined. <sup>b,d</sup> See footnotes to Table III (*b* and *c*). <sup>c</sup> These two products appeared with the same retention times (SE-30) and could not be separated by GLC. The yield was determined by assuming that the correction factor of 1-cyclohexyl-1-hexene was identical with that of **2**.

Table V. Reaction of **1b** with Butylcopper<sup>a</sup>

Run	<b>1b</b> , mmol	<i>n</i> -BuCu, mmol	Products, mmol <sup>b</sup>		
			<b>2</b>	<i>n</i> -BuCH=CH- <i>n</i> -Bu	<i>n</i> -BuOH
1	1.0	1.0	0.05	<i>c</i>	1.0
2	1.0	2.0	0.56	<i>c</i>	2.0
3	1.0	3.0	0.69	0.44	2.55

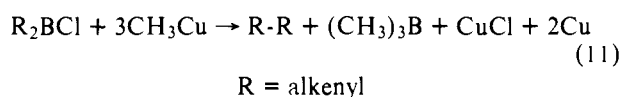
<sup>a</sup> **1b** was added to an ether solution of butylcopper at -78 °C. The resultant mixture was analyzed by GLC after an usual oxidation. <sup>b</sup> Yield of capronaldehyde was not determined. <sup>c</sup> Not detected.

action of 5-decenyldimethylborane (**18**) with an equivalent amount of methylcopper produced the diene (**9**) in ca. 100% yield (eq 10). These results are all consistent with the proposed



mechanism. The direct formation of diene (R-R) from the ate complexes may be proposed as an alternative mechanism. However, the approximately statistical coupling from the mixture of two different dialkenylchloroboranes (Table I, entry 3) supports the presence of alkenylcopper (RCu).

It should be noticed that considerable amounts of 5-decene are produced even at -78 °C (run 3). Alkenylcopper might react more readily with butylcopper than with methylcopper, or the equilibrium position in eq 7 or 8 might be shifted to the right in the case of methylcopper. Regardless of the precise reason, the reaction with methylcopper proceeds more cleanly than that with butylcopper. Consequently, the reaction with methylcopper is presumably obeying the following stoichiometry (eq 11).



With the above results in mind, it appears that the important step in the reaction of alkenylboranes with methylcopper is the formation of ate complex. The results of Tables III and IV suggest that the formation of ate complexes from **1a** or **1d** is sluggish owing to the steric crowding of the boron atom. Moreover, the secondary alkyl groups, such as Sia and cyclohexyl, seem to be removed more readily from the ate complexes than the CH<sub>3</sub> group. The origin of significant amounts of SiaI and cyclohexyl iodide is not clear. These products must arise from the copper iodide used for the preparation of CH<sub>3</sub>Cu. A similar product, such as hexenyl iodide, is not obtained in eq 2.

The present studies suggest that if (CH<sub>3</sub>)<sub>2</sub>BH was readily available and if alkenyldimethylboranes were easily obtained via the hydroboration of acetylenes with this reagent, the reaction of such alkenylboranes with an equivalent amount of methylcopper at -78 °C would give the (*E,E*)-1,3-dienes in excellent yields. Certainly, such a work should be attempted in the future. Facile and stereoselective displacement of the alkenyl groups from copper trimethylalkenylborates ensures that the present reaction system becomes a valuable new route to alkenylcopper intermediates.

## Experimental Section

NMR spectra were recorded on a JEOL JNM-MH-60 instrument; chemical shifts ( $\delta$  in CCl<sub>4</sub>) are expressed in parts per million relative to Me<sub>4</sub>Si. IR spectra were recorded on a Hitachi 215 spectrophotometer. GLC analyses were performed on a Yanaco GCG-550T or JEOL-JGC-20K instrument, using a 2-m 10% SE-30 column. Elemental analyses were performed by Mr. Y. Harada at our Department. All temperatures were uncorrected.

**Reagents.** Reagent grade solvents were purified by standard techniques and kept over a drying agent. B<sub>2</sub>H<sub>6</sub>:THF, BH<sub>2</sub>Cl:OEt<sub>2</sub>, and catecholborane were prepared according to the known methods.<sup>13</sup> Methylolithium in ether was prepared by standard procedure,<sup>14</sup> and butyllithium in hexane was a commercial product. The titrations were performed by Gilman's<sup>15</sup> or Eastham's<sup>16</sup> method. Cuprous iodide was purchased and purified.<sup>17</sup> Butylacetylene, diethylacetylene, di-*n*-butylacetylene, isoamylacetylene, and tolan were purchased, and cyclohexylacetylene,<sup>18</sup> 5-chloro-1-pentyne,<sup>19</sup> and methyl 10-undecynoate<sup>20</sup> were prepared according to the reported procedures.

Table VI. Properties of (*E,E*)-1,3-Dienes

Compd	Bp, °C (mm) or mp	$n_{D}^{25}$	NMR data (CCl <sub>4</sub> , 60 MHz)	IR, cm <sup>-1</sup> (neat)	Anal.
<b>2</b>	75–76 (3)	1.4640 1.4635 <sup>2c</sup>	6.40–5.17 (m, 4 H), 2.30–1.90 (m, 4 H) 1.53–1.20 (m, 8 H), 0.90 (t, 6 H, $J = 7$ Hz)	985	<i>a</i>
<b>7</b>	60–63 (7)	1.4623	5.23 (t, 2 H, $J = 7$ Hz), 2.33–1.83 (m, 8 H) 0.97 (t, 6 H, $J = 7$ Hz), 0.90 (t, 6 H, $J = 7$ Hz)	840	<i>a</i>
<b>8</b>	62–64 (7)	1.4732 <sup>b</sup>	6.03–5.12 (m, 3 H), 2.40–1.97 (m, 6 H) 1.63–1.23 (m, 4 H), 0.97 (t, 6 H, $J = 7$ Hz) 0.90 (t, 3 H, $J = 7$ Hz)	965	Calcd for C <sub>12</sub> H <sub>22</sub> : C, 86.66; H, 13.34. Found: C, 86.44; H, 13.44.
<b>9</b>	83–84 (0.005)	1.4650 <sup>b</sup>	5.37 (t, 2 H, $J = 7$ Hz), 2.30–1.87 (m, 8 H) 1.53–1.10 (m, 16 H), 0.93 (t, 6 H, $J = 7$ Hz) 0.90 (t, 6 H, $J = 7$ Hz)	840	Calcd for C <sub>20</sub> H <sub>38</sub> : C, 86.25; H, 13.75. Found: C, 86.05; H, 13.92.
<b>10</b>	182–183 <sup>c</sup> (183) <sup>d</sup>		7.62–6.62 (m, 20 H), 6.30 (s, 2 H)	1600	<i>e</i>
<b>11</b>	69–70 (8)	1.4646	6.10–5.17 (m, 4 H), 2.30–1.83 (m, 4 H) 1.77–1.13 (m, 6 H), 0.90 (d, 12 H, $J = 8$ Hz)	985	Calcd for C <sub>14</sub> H <sub>26</sub> : C, 86.51; H, 13.49. Found: C, 86.33; H, 13.60.
<b>12</b>	75–80 (2) or mp 25–26	1.5121 <sup>f</sup>	6.10–5.17 (m, 4 H), 2.00–0.98 (m, 22 H)	985	Calcd for C <sub>16</sub> H <sub>26</sub> : C, 88.00; H, 12.00. Found C, 87.82; H, 11.87.
<b>13</b>	107–109 (1)	1.5080 <sup>b</sup>	6.17–5.23 (m, 4 H), 3.47 (t, 4 H, $J = 6$ Hz) 2.43–1.73 (m, 8 H)	985	Calcd for C <sub>10</sub> H <sub>16</sub> Cl <sub>2</sub> : C, 57.98; H, 7.78; Cl, 34.23. Found: C, 57.97; H, 7.71; Cl, 34.66.
<b>17</b>	mp 54.5–55		6.05–5.08 (m, 4 H), 3.75 (s, 6 H) 2.45–1.83 (m, 8 H), 1.30 (broad s, 24 H)	1740 985	Calcd for C <sub>24</sub> H <sub>42</sub> O <sub>4</sub> : C, 73.05; H, 10.73. Found: C, 72.79; H, 10.79.

<sup>a</sup> The authentic samples were prepared by Zweifel's procedure.<sup>2c</sup> <sup>b</sup>  $n_{D}^{20}$ . <sup>c</sup> Recrystallized from petroleum ether–benzene. The NMR spectrum was taken in CDCl<sub>3</sub>. <sup>d</sup> H. H. Freedom, G. A. Doorakian, and V. R. Sandel, *J. Am. Chem. Soc.*, **87**, 3019 (1965). <sup>e</sup> The authentic sample was given by Dr. Toshima. <sup>f</sup>  $n_{D}^{30}$ . <sup>g</sup> Recrystallized from pentane–methanol.

**Reaction of Dialkenylchloroboranes (5) with Methylcopper. General Procedure.** Dialkenylchloroboranes (**5**) were prepared via hydroboration of acetylenes with BH<sub>2</sub>Cl:OEt<sub>2</sub>.<sup>11</sup> The following dialkenylchloroboranes were distilled under reduced pressure: bis(*trans*-1-hexenyl)chloroborane (**1b**),<sup>11</sup> bp 70–72 °C (0.05 mm), NMR  $\delta$  6.98 (d-t, 2 H,  $J_d = 16$ ,  $J_t = 6.0$  Hz), 6.08 (d, 2 H,  $J = 16$  Hz), 2.48–1.85 (m, 4 H), 1.68–1.08 (m, 8 H), 0.91 (t, 6 H,  $J = 6.8$  Hz); bis(*trans*-3-hexenyl)chloroborane,<sup>11</sup> bp 45–47 °C (0.05 mm), NMR  $\delta$  6.16 (t, 2 H,  $J = 6.8$  Hz), 2.60–1.95 (m, 8 H), 1.03 (t, 6 H,  $J = 6.8$  Hz), 0.90 (t, 6 H,  $J = 6.8$  Hz); bis(*trans*-5-decenyl)chloroborane (**15**), bp 110–115 °C (0.005 mm), NMR  $\delta$  6.16 (t, 2 H,  $J = 6.8$  Hz), 3.25–1.83 (m, 8 H), 1.83–1.08 (m, 16 H), 1.08–0.68 (broad s, 12 H); bis(5-methyl-*trans*-1-hexenyl)chloroborane, bp 86–88 °C (0.05 mm), NMR  $\delta$  7.01 (d-t, 2 H,  $J_d = 16$ ,  $J_t = 6.0$  Hz), 6.11 (d, 2 H,  $J = 16$  Hz), 2.50–2.05 (m, 4 H), 1.75–1.13 (m, 6 H), 0.90 (d, 12 H,  $J = 8.0$  Hz); bis(5-chloro-*trans*-1-pentenyl)chloroborane, bp 110–112 °C (0.01 mm), NMR  $\delta$  7.02 (d-t, 2 H,  $J_d = 16$ ,  $J_t = 6.0$  Hz), 6.20 (d, 2 H,  $J = 16$  Hz), 3.51 (t, 4 H,  $J = 6$  Hz), 2.75–2.20 (m, 4 H), 2.20–1.75 (m, 4 H).

In a 200-mL flask, maintained under N<sub>2</sub> and fitted with a septum inlet and magnetic stirrer, were placed CuI (5.7 g, 30 mmol) and dry ether (10 mL). The mixture was cooled to 0 °C and an ethereal solution of MeLi (1.5 M, 30 mmol) was added dropwise. The resultant mixture (yellow suspension) was stirred at 0 °C for 10 min, and then cooled to 0 to 10 °C with an ice–salt bath. Use of a dry ice–acetone bath is desirable to suppress the by-product (eq 3 and 4). Dialkenylchloroboranes (neat or ethereal solution, 10 mmol) were slowly added, and the resultant mixture was allowed to warm slowly to room temperature. Although the addition of the borane at 0 to 10 °C caused an instantaneous change of color from yellow to black, the yellow color did not change at –78 °C, and it slowly changed to black around –50 °C. The mixture was again cooled to 0 °C and oxidation was accomplished by the addition of aqueous NaOH (3 M, 3.3 mL)–H<sub>2</sub>O<sub>2</sub> (30%, 3.3 mL). Hydrogen peroxide should be slowly added to avoid vigorous reaction. The aqueous layer was saturated with NaCl and the organic layer was separated. The aqueous layer was again extracted with ether (10 mL). The combined organic phase was dried with anhydrous K<sub>2</sub>CO<sub>3</sub>. The solvent was removed and the product was obtained by distillation under reduced pressure. The solid products (**10** and **17**) were isolated by using TLC, silica gel 60F<sub>254</sub> Merck, where petroleum ether eluted **10** and benzene eluted **17**. 4-Ethyl-(3*E*,5*E*)-3,5-decadiene

(**8**) was isolated via preparative GLC. GLC yields were determined by the use of correction factors with appropriate hydrocarbons as an internal standard. All new products exhibited the expected spectral characteristics and provided satisfactory elemental analyses (Table VI).

**Isomeric Purity.** Authentic samples of (*Z,Z*)-,<sup>3a</sup> (*E,Z*)-,<sup>3d</sup> and (*E,E*)-5,7-dodecadiene<sup>2c</sup> were prepared according to the reported procedures. In general, the retention times on SE-30 increased along the series (*Z,Z*) < (*E,Z*) < (*E,E*). GLC examination of the reaction mixture revealed the presence of a sharp single peak, except for trace amounts of **14**, in the region expected for **2**, and the absence of the other isomers. The same procedure was used for **11** and **12**.

Authentic samples of (*E,Z*)-<sup>3d</sup> and (*E,E*)-4,5-diethyl-3,5-octadiene<sup>2c</sup> were prepared. Here also, the *E,Z* diene had shorter retention times than the *E,E* isomer. It was anticipated that the *Z,Z* isomer would appear with the shortest retention times among the three isomers. GLC examination revealed that the desired product (**7**) appeared as a sharp single peak in the expected region, and its <sup>1</sup>H NMR spectrum was completely identical with that of the authentic sample. The same examination was performed for **9** and **13**.

Although an authentic sample of **8** was not prepared, the *trans* geometry was indicated by the IR (965 cm<sup>-1</sup>) and <sup>1</sup>H NMR spectrum ( $J_{trans} = 16$  Hz). GLC examination of the reaction mixture revealed that the three sharp peaks (**7**, **8**, and **2**) appeared and the retention times increased along the series **7** < **8** < **2**.

It is known that the olefinic proton of each isomer of tetraphenyl-1,3-butadienes has a different chemical shift (Table VI, ref *d*). The product (**10**) exhibited the expected melting point and <sup>1</sup>H NMR spectrum. The *trans* geometry of **17** was indicated by the IR (985 cm<sup>-1</sup>) and <sup>1</sup>H NMR spectrum ( $J_{trans} = 16$  Hz). However, the absence of *cis* isomers in the reaction mixture cannot be completely ruled out in the latter two cases.

**Effect of the Reaction Temperature.** GLC examination of the reaction mixture of **1b** revealed the presence of a minor amount of **14**. Use of a dry ice–acetone bath was required to minimize this by-product. The same phenomenon was observed for **15**. The other reactions (Table I, entries 2, 3, and 5–8) were carried out at 0 to –10 °C. An authentic sample of **14** was purchased and that of **16** was prepared according to the reported procedure.<sup>21</sup>

**Reaction of Alkenylboranes with Aqueous Alkaline AgNO<sub>3</sub>.** Alkenylboranes (**1a**, **1b**, and **1c**), which were prepared by standard pro-

cedures, were treated with aqueous alkaline  $\text{AgNO}_3$  as previously reported.<sup>10,13</sup> Authentic samples of **3**<sup>22</sup> and **4**<sup>23</sup> were prepared according to the reported procedures.

**Reaction of Alkenylboranes with Methylcopper.** Alkenylboranes (**1a** and **1d**) were prepared by the hydroboration of 1-hexyne with disiamylborane and dicyclohexylborane,<sup>13</sup> respectively. Hydroboration of methyl 10-undecynoate was carried out in a similar fashion. These boranes were treated with methylcopper at 0 °C. Authentic samples of Sia1,<sup>24</sup> 1-cyclohexyl-1-hexene,<sup>22</sup> and dicyclohexyl<sup>23</sup> were prepared according to the known procedures. SiaH and its olefin derivatives appeared with the same retention times, and cyclohexane and cyclohexene could not be separated (SE-30).

**Mechanistic Studies.** The reaction of **1b** with butylcopper was carried out as described in the general procedure. Butylcopper was prepared from the reaction of CuI with butyllithium at -45 °C.<sup>17</sup> GLC analysis of the boranes was performed using a 1-m 5% SE-30 column. An authentic sample of *trans*-1-hexenyldi-*n*-butylborane was prepared by the reaction of *trans*-1-hexenyldichloroborane<sup>25</sup> with 2 equiv of *n*-butyllithium at -78 °C. This borane was not isolated. GLC examination of the reaction mixture of run 2 indicated the presence of *trans*-1-hexenyldi-*n*-butylborane. 5-Decenyldimethylborane (**18**) was prepared by the reaction of 5-decenyldichloroborane<sup>25</sup> with 2 equiv of methylolithium at -78 °C; bp 43–45 °C (1 mm); NMR  $\delta$  6.42 (t, 1 H,  $J = 8$  Hz), 2.50–1.88 (m, 4 H), 1.63–1.13 (m, 8 H), 0.98 (t, 6 H,  $J = 7$  Hz), 0.79 (s, 6 H).

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## The Structure of Trimethylphosphine Selenide by Electron Diffraction. Systematic Differences in Structure Patterns of Trimethyl and Trihalo Derivatives of Phosphorus and Arsenic

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**Abstract:** As determined by electron diffraction from a gaseous sample at a nozzle-tip temperature of 132–135 °C,  $(\text{CH}_3)_3\text{PSe}$  has the following structure parameters ( $r_a$  basis, distances in angstroms) with estimated uncertainties,  $2\sigma$ , in parentheses:  $r(\text{PSe}) = 2.091$  (0.003),  $r(\text{PC}) = 1.816$  (0.003),  $r(\text{CH}) = 1.100$  (0.009),  $\angle\text{SePC} = 113.8$  (0.3)°,  $\angle\text{PCH} = 109.9$  (1.7)°. Diffraction data support a finite barrier to methyl torsion, though no quantitative measure of it comes from the analysis. Valence force constants and vibrational amplitudes were calculated to fit reported fundamental frequencies. Diffraction and spectroscopic results suggest a high degree of similarity between  $(\text{CH}_3)_3\text{PSe}$  and  $(\text{CH}_3)_3\text{PS}$ . Structures for all pertinent  $(\text{CH}_3)_3\text{M}$  and  $(\text{CH}_3)_3\text{MY}$  molecules of group 5a M are examined in the light of previously established structure trends for trihalo analogues. Possible sources of the several differences found to distinguish the two classes of ligands are examined.

Simple tetracoordinate compounds, formed by coordination of the lone pair on tricoordinate phosphorus or arsenic with either a chalcogen (O, S, or Se) or an electron-deficient group such as  $\text{BH}_3$ , have received a flurry of attention from both structural and theoretical chemists in recent years. Related tricoordinate phosphorus, arsenic, and antimony derivatives have also been studied extensively. Even if one restricts con-

sideration to molecules of  $C_3$  or  $C_{3v}$  symmetry (i.e., with unmixed ligands), this class of compounds provides an excellent basis for testing various bonding models used by chemists. Trends in geometric parameters are well established by the large number and variety of these compounds for which high-precision structural data are known. In most cases, ancillary force field calculations are also available. One of the