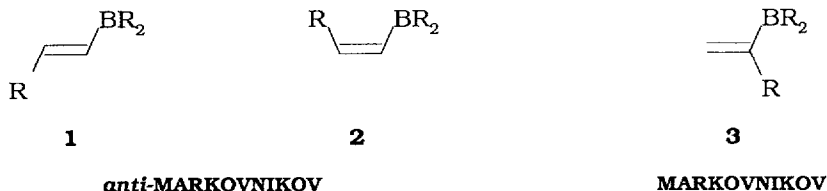


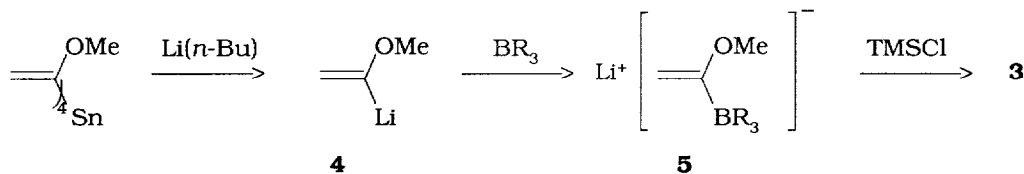
### MARKOVNIKOV VINYLBORANES VIA $\alpha$ -METHOXYVINYL LITHIUM

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**Abstract:** Pure  $\alpha$ -methoxyvinyl lithium, prepared from Sn/Li exchange, reacts cleanly with representative trialkylboranes, to form the corresponding "ate" complexes. These complexes rearrange in the presence of chlorotrimethylsilane (TMSCl) to provide an efficient route to Markovnikov vinylboranes which are isolable in 70-90% yields.



Vinylboranes are highly useful synthetic intermediates for both functional group conversions and carbon-carbon bond formation.<sup>2</sup> Hydroboration provides an efficient direct route to *anti*-Markovnikov *trans*-vinylboranes (**1**) from terminal acetylenes.<sup>3</sup> Their *cis* counterparts (**2**) are available from 1-haloacetylenes.<sup>4</sup> While inaccessible from the hydroboration of terminal acetylenes, the corresponding Markovnikov vinylboranes (**3**) can be generated *in situ* by two methods,<sup>5,6</sup> both based upon Negishi's "ate" chemistry.<sup>7</sup> Thus, either alkynyl- or  $\alpha$ -methoxyvinyl- borate complexes give **3** under the proper conditions. However, neither of the methods has been developed to provide **3** as an isolable compound. The first approach suffers both from the fact that it is operationally difficult and also, that aqueous base is required to prevent further reactions of **3** from occurring. The second method appeared very promising, but unfortunately relied upon the generation of  $\alpha$ -methoxyvinyl lithium (**4**) from the deprotonation of methyl vinyl ether, a reaction which is neither clean nor stoichiometric. Thus, this methodology could only implicate **3** as an intermediate from the subsequent chemistry that was observed. Fortunately, **4** can now be prepared as a pure solid from Sn/Li exchange.<sup>8</sup> This development has resulted in our now being able to carry out the reaction of **4** with trialkylboranes under conditions which give the corresponding borate complex, **5**, cleanly. This complex rearranges with TMSCl to give **3**, the volatile TMSOMe, and LiCl. The reaction is quite general for the examples examined and provides, for the first time, a convenient route to the pure organoboranes, **3**. These data are summarized in Table 1.



**Table 1.** Representative Markovnikov Vinylboranes from  $\alpha$ -Methoxyvinylolithium.

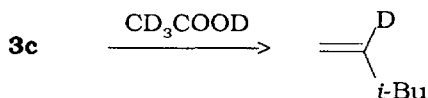
Series	R <sub>3</sub> B <sup>a</sup>	<b>3</b> : <sup>11</sup> B NMR <sup>b</sup> ( $\delta$ ppm)	Yield <sup>c</sup> (%)	bp ( $^{\circ}$ C, Torr)
<b>a</b>	B( <i>n</i> -Pr) <sub>3</sub>	80.4	90	37-40, 0.10
<b>b</b>	B( <i>n</i> -Bu) <sub>3</sub>	76.4	83	70-73, 0.15
<b>c</b>	B( <i>t</i> -Bu) <sub>3</sub>	77.3	87	57-58, 0.05
<b>d</b>	B( <i>s</i> -Bu) <sub>3</sub>	77.2	83	56-61, 0.10
<b>e</b>	B(CH <sub>2</sub> TMS) <sub>3</sub>	75.9	70	94-96, 0.05
<b>f</b>	<i>B</i> -Me-9-BBN	73.2	70	41-42, 0.15
<b>g</b>	<i>B</i> -( <i>n</i> -Bu)-9-BBN	73.1	75	78-81, 0.05

<sup>a</sup> Prepared by standard methods (cf. ref 3). <sup>b</sup> Recorded on a GN-300 NMR instrument in CDCl<sub>3</sub> solution (BF<sub>3</sub>·OEt<sub>2</sub>,  $\delta$  0.00 ppm). <sup>c</sup> Isolated.

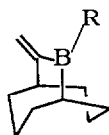
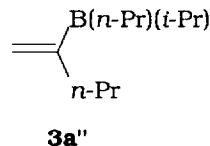
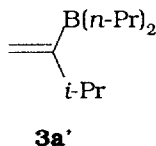
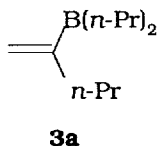
The following procedure is representative:

To a cold (0 $^{\circ}$ C), stirred solution of *tetrakis- $\alpha$ -methoxyvinyltin* (1.31 g, 3.8 mmol)<sup>8</sup> in dry pentane (8 mL), under a nitrogen atmosphere, was added Li(*n*-Bu) (5.1 mL 2.55 M, 13 mmol), dropwise *via* syringe. After the addition, the cold bath was removed and stirring was continued for 1 h. The solid **4** (*Caution!* Extremely pyrophoric!) was allowed to settle, and the clear supernatant was decanted, under a positive pressure of nitrogen, with a double-ended needle. The solid was washed with pentane (4 x 20 mL) and pentane (8 mL) was added, and the stirred slurry was cooled to -78 $^{\circ}$ C. To this, THF (8 mL) was added, followed by triisobutylborane (1.50 g, 8.2 mmol) *via* syringe. The mixture was allowed to warm to 25 $^{\circ}$ C over 1 h, recooled to -78 $^{\circ}$ C, and TMSCl (1.40 g, 13.0 mmol) was added dropwise. After warming to 25 $^{\circ}$ C over 1 h, the supernatant was transferred to a second flask, and the LiCl was washed with dry pentane (2 x 15 mL). The solvents were removed *in vacuo* (ca. 50 Torr), and the residue was distilled to give 1.49 g (87%) of **3c** (bp 57-8 $^{\circ}$ C, 0.05 Torr). (*Caution!* Pyrophoric!)<sup>9</sup>

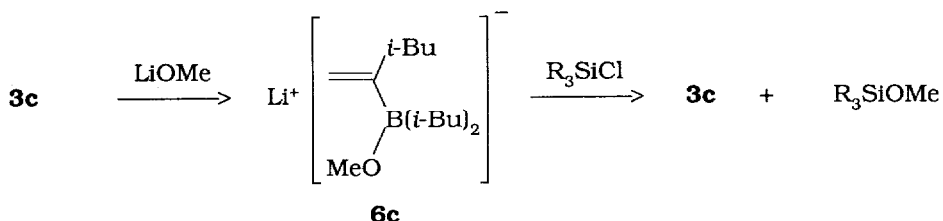
The most informative feature observed in the <sup>1</sup>H NMR spectra for **3** was the presence of the characteristic terminal vinylic proton absorbances {*e.g.* **3c** 5.38 (d, 1H, *J* = 3.5 Hz) and 5.43 (d, 1H, *J* = 3.5 Hz) ppm}. In the <sup>13</sup>C NMR spectra, as expected, the C-1 carbon was found consistently upfield from the more substituted C-2 carbon, which was very broad owing to the  $\alpha$ -boron atom {*e.g.* **3c**: 124.5 (CH<sub>2</sub>); 158.9 (C(BR<sub>2</sub>)R) ppm}. For **3c**, the addition of deuterated acetic acid gave 2-deuterio-1-hexene, cleanly, further proof for the 2-boryl configuration.<sup>10</sup>



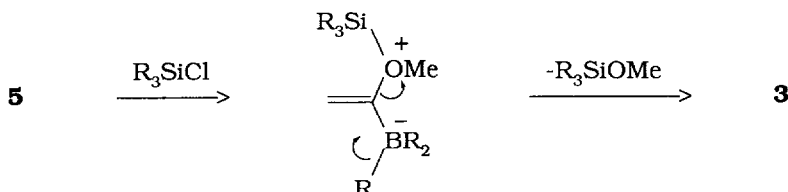
It should be pointed out that the combination of  $^{13}\text{C}$  NMR and capillary GC, proved to be highly effective for the analysis of these vinylboranes and their precursors. Thus, whereas triisobutylborane is produced as an essentially pure isomer, tri-*n*-propylborane is formed from the hydroboration of propene as an 88:12 mixture of the tri-*n*-propyl- and the isopropyl(di-*n*-propyl)-boranes, respectively. Similarly, 1-butene gives tri-*n*-butyl-, di-(*n*-butyl)(*sec*-butyl)- and *n*-butyl(di-*sec*-butyl)-boranes in an 85:13.5:1.5 ratio.<sup>3</sup> The first two of these gave rise to three observable products, namely **3a** (88%), **3a'** (6%) and **3a''** (6%). For, **3b**, we observed the related butyl isomers in an 87:8:5 ratio. Reminiscent of our previous studies on the selective oxidation of organoboranes,<sup>11</sup> the present migratory aptitude appears to be  $2^\circ > 1^\circ$ . To determine if a selective process could be realized for a more rigid system, we turned to the 9-BBN derivatives and found the reaction to be highly chemoselective, producing the 9-alkyl-10-methylene-9-borabicyclo[3.3.2]decane products (*i.e.* **3f** and **3g**) in >95% isomeric purity.



In an effort to better understand these results as well as to answer some of the questions which were raised by early studies,<sup>6</sup> we chose to examine this process in greater detail. To this end, the complex, **5c**, was prepared which was observed as a single resonance at -19.9 ppm by  $^{11}\text{B}$  NMR. *It was stable for at least 2 days at room temperature.* Reaction with  $\text{TMSCl}$  was exothermic and complete conversion to **3c** (77.3 ppm) occurred in less than 20 min. With less than 1 equiv of  $\text{TMSCl}$ , both **3c** and **5c** were observed. With chlorotriethylsilane ( $\text{TESCl}$ ), the reaction proceeded, but at a slower rate (*i.e.* 84% in 30 min). Addition of **3c** to  $\text{LiOMe}$  effects the dissolution of the latter and gives rise to two  $^{11}\text{B}$  NMR signals, one for uncomplexed **3c** (77.3 ppm) and one for its methoxyborate complex, **6c** (-2.4 ppm), in *ca.* 1:9 ratio. Both  $\text{TMSCl}$  and  $\text{TESCl}$  reacted instantaneously with this mixture to give the corresponding methoxysilane and regenerate **3c**, cleanly. Additionally, both silyl chlorides also reacted instantaneously with  $\text{LiOMe}$  to produce the corresponding methoxysilanes.



We interpret these findings as follows: The reaction of trialkylboranes with **4** gives **5** as a stable complex. Rearrangement does not take place prior to the addition of the silyl chloride which silylates at oxygen. Loss of the methoxysilane with concomitant migration of the *antiperiplanar group*<sup>11</sup> occurs to give **3**. The alternative, namely silylation at the terminal position of the carbon-carbon double bond, reactivity which has been observed with some electrophiles and vinyl- or alkynyl- borates, while possible, appears less likely since reaction at this position would give a  $\beta$ -methoxysilane which would not be expected to eliminate under these conditions.<sup>12</sup>



With their availability in pure form, the chemistry of Markovnikov vinylboranes can be further developed and compared to the known reactivities of other vinylboranes.<sup>2</sup>

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9. For **3c**, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.83 (d, 6H); 0.86 (d, 12H); 1.26 (d, 4H); 1.46 (m, 1H); 1.99 (m, 2H); 2.14 (d, 2H); 5.38 (d, 1H, J = 3.5 Hz); 5.43 (d, 1H, J = 3.5 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  22.8; 26.1; 26.3; 28.6; 37.9; 46.5; 124.5; 158.9 ppm.
10. For 2-deuterio-4-methyl-1-pentene: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.87 (d, 6H); 1.60 (m, 1H); 1.92 (d, 2H); 4.95 (bs, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  22.2; 28.1; 43.2; 115.1; 137.5 (t, J = 23 Hz) ppm.
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