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Structure and Derivatization of the Product from Carbonylation of Lithium Triethylborohydride

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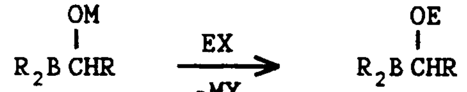
ABSTRACT

Treatment of the reactive product from carbonylation of lithium triethylborohydride with the electrophilic reagent chlorotrimethylsilane does not produce the expected α-hydroxyborane derivative. Instead, a borinate arising through migration of a second ethyl group from boron to carbon is obtained. This result is rationalized in terms of the initial product being a borate having two possible constitutions. The borate nature of this initial product is confirmed by ^{11}B *NMR.*

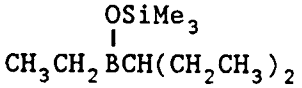
The initial product from hydride-induced carbonylation of organoboranes is readily converted to aldehydes [1], alkylmethanols [1], dialkylmethanols [2], or homologated organoboranes [3]. This versatile material was previously postulated to have the structure **1** [4–6]. However, neither isolation nor establishment of constitution has been attempted heretofore.



$$R_2\overset{\overset{\displaystyle OM}{|}}{B}CHR \xrightarrow[-MX]{EX} R_2\overset{\overset{\displaystyle OE}{|}}{B}CHR \qquad (1)$$

1 **2**

It was predicted that a structure such as **1** (M = Li, Na, K) should react with an electrophile EX to form **2** (Eq. 1). To test this hypothesis, carbonylation of lithium triethylborohydride was chosen because of ready availability and relative simplicity. Chlorotrimethylsilane was chosen as the electrophile since it should give a virtually quantitative yield of a stable and reasonably volatile derivative.

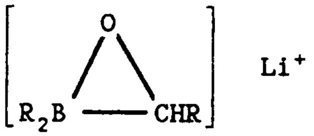


$$CH_3CH_2\overset{\overset{\displaystyle OSiMe_3}{|}}{B}CH(CH_2CH_3)_2$$

3

After allowing a tetrahydrofuran (THF) solution of lithium triethylborohydride to react with carbon monoxide at room temperature, one molar equivalent of chlorotrimethylsilane was added. This produced an exothermic reaction and formation of a white precipitate, presumably lithium chloride. Filtration and distillation resulted in a 68% yield of what was initially assumed to be **2** (R = Et, E = $SiMe_3$). Elemental analysis was in satisfactory agreement with the calculated composition. However, ^1H NMR did not show the 1H triplet near δ 4.0 expected for **2** [7]. Instead, the spectrum suggested the novel trimethylsilyl ethyl(1-ethylpropyl)borinate, **3.** ^{11}B NMR also supported structure **3**, the resonance at δ 55.2 (relative to boron trifluoride etherate) indicating a tricoordinate boron with one boron-oxygen bond.

There is no apparent way to explain this unexpected development using structure **1**. However, noting that **1** contains both an alkoxide (a Lewis base) and a tricoordinate boron (a Lewis acid), it is reasonable to propose that the borates **4** and/or **5** are more likely constitutions for the initial product.



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This paper is dedicated to Professor Herbert C. Brown on the occasion of his 80th birthday.

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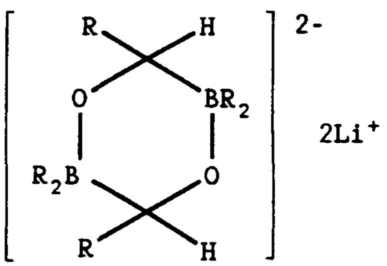

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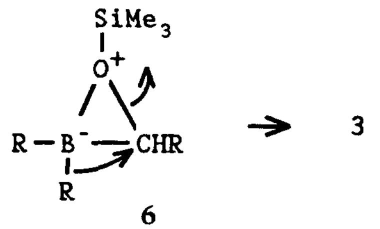
Examination of the THF solution resulting from carbonylation by ^{11}B NMR revealed a broad but intense resonance at δ −2.74. This is consistent with an "ate" complex incorporating an alkoxy group as one of the ligands.

Mechanisms of the reactions of **4** and/or **5** (R = Et) with chlorotrimethylsilane to yield **3** are postulated to be as shown (Eq. 2 and 3). Coordination of silicon with oxygen and concomitant precipitation of lithium chloride yields **6** and/or **7**. Removal of the consequent electron deficiency at oxygen might result from cleavage of the boron-oxygen or carbon-oxygen bond. Since the former is considerably stronger [8], the latter breaks, thus creating an electron deficiency at the α-carbon and inducing migration of a second alkyl group from boron to give product.

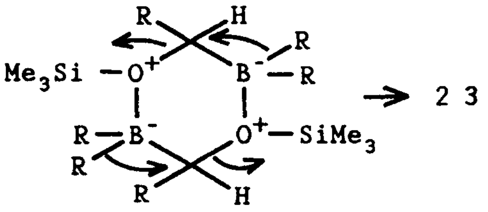
It was of interest to determine if oxidizing **3** results in formation of 3-pentanol, as is the case when **4/5** is treated with acid followed by oxidation [2]. Indeed, such a procedure produced an 85% yield of the expected alcohol. While this yield compares favorably with those obtained when concentrated hydrochloric acid and glacial acetic acid are used to induce migration of the second group [2], using these acids is far more economical.

Production of **3** reveals the potential to make derivatives having the general structure **8** using various electrophiles of the form EX. For example, when EX = HCl or HOAc it should be possible to isolate the corresponding borinic acid (**8:** E = H). There is no apparent access to (1–substitutedpropyl)diethylboranes (**2:** R = Et) or similar α-substituted compounds, although these are formed and rearrange after a brief time to **8** in certain situations [9].



(2)

6



(3)

7

$$\overset{OE}{\overset{|}{\mathrm{RBCHR_2}}}$$

8

Preliminary indications are that carbonylation of trialkylboranes using the soluble complex hydrides $LiAl(OMe)_3H$, $LiAl(OCMe_3)_3H$, or $KB(OCHMe_2)_3H$ does not result in structures exactly analogous to **4** or **5**. It is likely that this is due to the presence of the corresponding aluminates or borate, all of which coordinate competitively with oxygen.

EXPERIMENTAL

General

The techniques used for handling air- and water-sensitive materials are described elsewhere [10]. The automatic gasimeter [10, 11] was a commercial model obtained from Delmar Scientific Laboratories, Inc., Maywood, Illinois. All glassware was dried at 140°C for at least 4 hours, assembled hot, and cooled under a stream of prepurified nitrogen. The reaction flasks were fitted with sidearms capped with rubber septa.

Materials

All materials were kept under an atmosphere of prepurified nitrogen in Teflon stopcock-protected ampoules. THF was distilled from lithium aluminum hydride. Chlorotrimethylsilane (Aldrich) was distilled from calcium hydride. Lithium triethylborohydride was prepared as described previously [12].

Analyses

GC analyses were carried out on a Hewlett-Packard 5752B chromatograph using 0.25 in OD columns 6 ft long filled with 10% Carbowax 20M on 60/80 AW-DMCS Chromosorb W.

^{1}H NMR spectra were obtained using a Varian T-60 spectrometer.

^{11}B NMR spectra were recorded using a Varian XL-100-15 spectrometer (32.1 MHz) fitted with a Nicolet 1080 data acquisition system. All spectra were recorded in the CW mode and signals were averaged 4 to 25 scans. The spectra were referenced to boron trifluoride etherate (δ 0) using either ^{2}H or ^{19}F external locks.

Carbonylation of Lithium Triethylborohydride

A dry 200-mL flask with magnetic stirring bar and septum inlet was attached to an automatic gasimeter and the system was flushed with nitrogen. The flask was immersed in a water bath and the solution of lithium triethylborohydride in THF was introduced. After flushing the system with carbon monoxide, vigorous stirring was begun. After carbon monoxide absorption ceased, the system was flushed with nitrogen. The foregoing procedure was followed prior to (a)–(c) below.

(a) Trimethylsilyl Ethyl(1-ethylpropyl)borinate (**3**)

Carbonylation was carried out using 23.5 mL of 1.49 *M* lithium triethylborohydride (35 mmol). Then 4. 5 mL (35 mmol) chlorotrimethylsilane was added. There was an exothermic reaction and formation of a white precipitate, presumably lithium chloride. After the solution cooled to room temperature, it was passed through a small filter chamber into a dry 50-mL flask with magnetic stirring bar and septum inlet. The reaction flask and filter were each washed with 5 mL THF. The filter chamber was then replaced by a distilling head and a two-flask receiver. The THF was removed using a water aspirator. After a small forerun, the product **3** was distilled as a colorless liquid. Yield, 4.74 g, 68%; bp 68–75°C (18 mmHg); ^{11}B NMR δ 55.2; ^{1}H NMR δ 0.6–1.6 (m, 16H), 0.1 (s, 9H); *analysis*, calculated for $BC_{10}H_{23}OSi$: B, 5.40; C, 59.99; H, 12.87; Si, 14.03; found, B, 5.20; C, 60.09; H, 12.87; Si, 14.00.

(b) Formation of (**3**) *and Oxidation*

Carbonylation was carried out using 6.71 mL of 1.49 *M* lithium triethylborohydride (10 mmol). Then 1.29 mL (10 mmol) chlorotrimethylsilane was added and the mixture was stirred 8 hours (overnight). Oxidation was accomplished using 3.5 mL 3 *N* aqueous sodium hydroxide and 4 mL 30% aqueous hydrogen peroxide. (**Caution:** exothermic! An ice bath was necessary to moderate the temperature during the addition.) After 1 hour, 5.0 mmol (1.30 mL) *n*-tetradecane was added as an internal standard, then 7.5 g anhydrous potassium carbonate was added and dissolved. The THF layer was separated and dried over anhydrous magnesium sulfate, then powdered 3Å molecular sieves. GC analysis revealed 8.5 mmol (85%) 3-pentanol.

(c) ^{11}B NMR of the Initial Product (**4**/**5**)

Carbonylation and addition of chlorotrimethylsilane were carried out as in (b). After the reaction mixture cooled to room temperature, an aliquot of the supernatant liquid was transferred to an NMR tube. ^{11}B NMR δ −2.74 (s, br).

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