1,1-Ethylboration of ethynyl(trimethyl)tin. (E)-1-Trimethylstannyl-2-diethylboryl-but-1-ene, isomerization and conversion into hydridoborates

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Dedicated to Rosalinda Contreras

Abstract
1,1-Ethylboration of ethynyl(trimethyl)tin affords quantitatively and selectively (E)-1-trimethylstannyl-2-diethylboryl-but-1-ene 1a, which isomerizes fast at room temperature into the (Z)-isomer 2a, followed by slow isomerization into the (E/Z)-1-diethylboryl-2-trimethylstannyl-but-1-enes 3a and 4a. These rearrangements are independent of the solvent (hexane, benzene, or benzene/THF) and take place at comparable rates at daylight or in the dark. A mechanism is proposed invoking hyperconjugation and three-membered cyclic structures, for which three-coordinate boron atoms as in 1a - 2a are a prerequisite. In order to prove this point, hydridoborates were prepared. The reaction of a mixture (80:20) of 1a and 2a with sodium hydride gives the corresponding hydridoborates 5a and 6a, respectively, which in contrast to the boranes do not undergo further rearrangements. An extended NMR data set of the compounds 1a – 6a was measured (1H, 11B, 13C, 119Sn NMR) and discussed. In addition, the synthesis of a mixture of the silicon analogues 1a(Si) and 2a(Si) was reproduced, the corresponding NMR data were obtained, the molecular structures were optimized by DFT methods [B3LYP/6-311+G(d,p)], and relevant chemical shifts were calculated at the same level of theory.

Keywords: Triethylborane, alkynes, alkenes, organotin, isomerization, multinuclear NMR, DFT calculations

Introduction

Organometallic-substituted alkenylboranes are useful synthons for further transformations.1-3 In this context, 1,1-organoboration of alkyn-1-ylmetal compounds has opened a convenient route to such alkenes.4 Thus, triethylborane, BEt₃, reacts readily with numerous alkyn-1-yltin compounds below 0 °C in inert solvents by cleavage of the Sn-C≡ bond via a short-lived zwitterionic alkyn-
1-ylborate-like intermediate A to give alkenes of type 1. In most cases, these organometallic-substituted alkenes are formed quantitatively and stereoselectively, bearing the boryl and the stanny1 groups in cis positions at the C=C bond (Scheme 1). The analogous reaction with alkyn-1-ylsilanes, although under much more severe reaction conditions (in boiling BEt3 at ca. 100 °C), affords the corresponding alkenylsilanes 1(Si). The mechanism is well established, and after removing of readily volatile materials (solvent and the excess of BEt3), the alkenes 1 can be used without further purification.

Scheme 1

For R1 = alkyl or phenyl, the pure alkenes 1 are stable under Ar or N2 atmosphere for several days at room temperature. However, in the case of R1 = H (1a), it has been noted that (E/Z)-isomerization starts within minutes at room temperature (2a), followed more slowly by further rearrangements (3a, 4a). Since 1a is one of the most simple 1,1-organoboration products of alkyn-1-yltin compounds, we have studied the formation of 1a and its isomerization in greater detail, aiming for a more complete set of NMR data. It was also of interest to find out whether the three-coordinate boron atom in 1a is a prerequisite for the isomerization. Furthermore, for comparison we have measured a complete NMR data set for the analogous isomers 1a(Si) and 2a(Si) which result from 1,1-ethylboration of ethynyl(trimethyl)silane.

Results and Discussion

1,1-Ethylboration, isomerization, proposed mechanism and formation of hydridoborates

In the original report, the 1,1-ethylboration of ethynyl(trimethyl)tin was carried out in THF, since this particular ethynyltin compound is most readily available as a THF solution. In all other cases of 1,1-ethylboration of alkyn-1-yl(triorgano)tin derivatives, the solvents have been hexane, toluene, benzene or dichloromethane. This includes triethyl- and tributyl(ethynyl)tin, for which the 1,1-ethylboration products were found to be stable towards isomerization. Therefore, a priori it could not be excluded that traces of THF catalyze the isomerization.

We have now prepared ethynyl(trimethyl)tin as a solution in hexane, using the reaction of freshly prepared Li2C2 in hexane with trimethyltin chloride in the presence of ethyne in excess. Although this leads mainly to bis(trimethylstanny1)ethyne, the desired ethynyl(trimethyl)tin (about 15-20 % yield) was found (δ119Sn -68.3) in the hexane fraction which was removed from the reaction mixture in a vacuum and collected in a cold trap at -196 °C. The compound 1a was then prepared by addition of BEt3 at -78 °C to this hexane solution, warming to room
temperature, and isolated. It was dissolved in C₆D₆, and the isomerization of 1a was studied without or with addition of a small amount of THF. The results were virtually identical (see Fig. 1). A sample of 1a in hexane gave the same $^{119}$Sn NMR spectra. Therefore, a significant influence of THF on the isomerization process can be excluded. There was also no appreciable difference in the type of products and rate of isomerization, when the samples were kept in the dark or at day light.

**Figure 1.** 149.2 MHz $^{119}$Sn{¹H} NMR spectra of 1a, dissolved in C₆D₆ (left) and C₆D₆/THF (1:1) (right) measured at room temperature at the times indicated. After 7 d, decomposition becomes apparent, and the product distribution is affected by the presence of THF.

The slow isomerization of other non-cyclic or cyclic alkenyltin compounds with a boryl group present at the C=C bond has been discussed,¹² and the general idea is lined out here for the isomerization of 1a (Scheme 2). The contribution of the canonic structure B to the ground state is most likely negligible, although this type of structure is often invoked for vinylboranes. Clearly, B would in principle account for (E/Z)-isomerization (dashed arrows in Scheme 2). However, alkenylboranes, in general, do not exhibit such a pronounced tendency for (E/Z)-
isomerization and further rearrangements. In the case of 1a, it is also necessary to consider the preferred perpendicular orientation of the Et₂B group with respect to the C=CB plane, preventing efficient CB(pp)π interactions (see however 2a, where this may play a role). On the other hand, this particular conformation around the boryl group of 1a favors hyperconjugative C-B interactions represented in the structure C, where the stannyl group in β-position relative to the positively charged carbon atom exerts a stabilising effect. Structure C helps to explain the observed fast isomerization of 1a into 2a. Migration of the stannyl group transforms C into D, which is of comparable energy or even more stable because of the additional ethyl group in β-position to the positive charge. The intermediacy of D explains the observed concomitant formation of 3a and 4a, of which 4a appears to be preferred, most likely for steric reasons. It should be noted that other isomers bearing the boryl and the stannyl groups at the same olefinic carbon atom were not observed, and, indeed, neither C nor D provide an obvious route to such isomers. This also rules out 1,2-dehydroboration, conceivable at a first glance for 2a, which should give rise to the formation of such alkenes.

![Diagram](image)

**Scheme 2**

If the arguments for C and D (Scheme 2) are relevant, the isomerization of 1a as well as further rearrangements of 2a will be suppressed when the boron atom becomes tetra-coordinate as in borates. Therefore, the reaction of 1a with sodium hydride (NaH) was studied. Since the heterogeneous reaction with NaH was slow and isomerization of 1a occurred before significant amounts of hydridoborates were formed, NaH was activated in boiling hexane with BEt₃ prior to its reaction with 1a. By this, a mixture of 1a/2a (80:20) was converted completely into the hydridoborates 5a and 6a (Scheme 3). The isolated materials were redissolved in C₆D₆, and NMR spectra indicated the presence of the desired hydridoborates in an unchanged 80:20 ratio. The C₆D₆ solution was monitored over several weeks by ¹H, ¹¹B and ¹¹⁹Sn NMR spectroscopy, and further isomerization was not detected.
Scheme 3

NMR spectroscopic results

The consistent set of NMR data leaves no doubt on the proposed solution state structures of the compounds 1a – 6a, and their $^{11}$B, $^{13}$C and $^{119}$Sn NMR parameters are given in Table 1 (see the Experimental Section for $^1$H NMR data), together with data for the silicon analogues 1a(Si) and 2a(Si).

The chemical shifts $\delta^{11}$B for 1a – 4a are in the typical range for three-coordinate boron atoms bearing three organyl groups without or with weak BC(pp)$\pi$ interactions, whereas those for 5a and 6a are characteristic for borates.\textsuperscript{22} The slight increase in $^{11}$B nuclear shielding observed for 2a ($\delta^{11}$B 78.9) relative to that for 1a, 3a and 4a indicates that the mean angle formed between the C$_2$B plane of the Et$_2$B group and the C=CB plane in 2a deviates markedly from 90° and allows for CB(pp)$\pi$ interactions. The reduced line width of the $^{11}$B NMR signal of 2a indicates longer relaxation times T$_Q$($^{11}$B), most likely as a result of a more freely rotating Et$_2$B group in 2a when compared with the situation in 1a. CB(pp)$\pi$ interactions in 2a and 2a(Si) are supported by the $\delta^{13}$C(SnC=) and $\delta^{13}$C(SiC=) data for the pairs 1a/2a and 1a(Si)/2a(Si). Typically, the possibility for extended $\pi$ interactions between the C=C bond and an appropriate $\pi$ acceptor orbital at a neighbored atom induces deshielding of the olefinic $^{13}$C nucleus in $\beta$-position relative to the $\pi$ acceptor\textsuperscript{23} (here by 12.5 and 10.2 ppm). Such a difference in the $\delta^{13}$C(SnC=) values is absent for the pair 3a/4a, and one can conclude that the preferred conformation of the Et$_2$B group is similar in these isomers. The enforced absence of an extended $\pi$ system in the borates 5a and 6a is mirrored by the shielding of the $^{13}$C(SnC=) nuclei, which is very similar to that in 1a, for which the arrangement of the Et$_2$B group is unfavorable for CB(pp)$\pi$ interactions.

The assignment of all $^{13}$C NMR signals is straightforward, using the information from $^{117/119}$Sn and $^{29}$Si satellites [$J$(Sn$^{13}$C) (Fig. 2) or $J$(Si$^{29}$, $^{13}$C)], the typically broad lines for $^{13}$C nuclei linked directly to boron (scalar relaxation of the second kind owing to $^{13}$C-$^{11}$B spin-spin coupling\textsuperscript{24,25}). The mutual positions of substituents at the C=C bond are further confirmed by $^1$H/$^1$H NOE difference spectra.\textsuperscript{26}
Table 1. $^{11}$B, $^{13}$C, $^{29}$Si and $^{119}$Sn NMR parameters $[^{[a]}$ of the alkenes 1 – 6

<table>
<thead>
<tr>
<th></th>
<th>$\delta^{13}$C</th>
<th>$\delta^{119}$Sn (h/2) [Hz]</th>
<th>$\delta^{11}$B (h/2) [Hz]</th>
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<td>Sn-C=</td>
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<td>1a(Si)</td>
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<td>171.4</td>
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<td>{51.2}</td>
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<td>[336.1]</td>
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$[^{[a]}$ Samples (5-10 %) in C$_6$D$_6$ at 296 K; coupling constants $J(^{119}$Sn,$^{13}$C) are given in brackets [± 0.5 Hz], and $J(^{29}$Si,$^{13}$C) in braces {± 0.5 Hz}; (br) denotes $^{13}$C NMR signals broadened by partially relaxed scalar $^{13}$C-$^{11}$B spin-spin coupling; $^{25}$h$_{1/2}$ means full line width at half height.

$[^{[b]}$ n.m. = not measured, because of overlapping $^{11}$B NMR signals.

The $^{119}$Sn NMR parameters $^{27}$ of 1a – 6a are instructive in several respects. $^{119}$Sn nuclear shielding increases in the borates 5a and 6a by 11.5 and 9.0 ppm, when compared with the boranes 1a and 2a, respectively. This fairly constant change means that CB(pp)$\pi$ interactions in 2a have little influence on $\delta^{119}$Sn. It appears that the $\delta^{119}$Sn data of 1a – 6a depend on substituent effects exerted by the proximity and the respective nature of the substituent rather than on small changes in the bonding situation of the C=C bond. There are also changes in the magnitude of $J(^{119}$Sn,$^{13}$C$_{(SnC=)}$) depending on the other substituents. This parameter may change readily with the bond angle at the olefinic carbon SnC= as a function of the bulkiness of other substituents in geminal or cis positions relative to the stannyl group. In contrast to changes in $J(^{119}$Sn,$^{13}$C$_{(SnC=)}$), the magnitude of $J(^{119}$Sn,$^{13}$C$_{(SnMe)}$) remains fairly constant throughout the series of compounds 1a – 6a. The magnitude of the coupling constants $^{3}J(^{119}$Sn,$^{13}$C$_{(E)}$) across the C=C bond is expectedly greater for the trans (1a) than for the cis coupling-pathway (2a).$^{27,28}$ A similar behavior is expected for $^{119}$Sn-$^{11}$B spin-spin coupling.$^{8}$ Although splitting due to this coupling is not resolved, the comparison of the line widths (Fig. 3) of the $^{119}$Sn NMR signals shows that
\[ |J(\text{Sn}^{119}, \text{B})_{\text{trans}}| > |J(\text{Sn}^{119}, \text{B})_{\text{cis}}| \]. In the borates 5a and 6a, the times \( T^0(\text{B}) \) are longer than in the boranes. Therefore, the lifetime of the \( \text{B} \) nuclear spin states increases, and the residual broadening of the \( \text{Sn}^{119} \) NMR signals as a result of scalar \( \text{Sn}^{119}-\text{B} \) coupling is larger in 5a and 6a when compared with the boranes 1a and 2a, respectively.

Figure 2. Parts of the 100 MHz \( ^{13}\text{C}\{^{1}\text{H}\} \) NMR spectrum of the mixture of isomers 1a – 4a in C\(_6\)D\(_6\) (10 % v/v; at 296 K) showing the \( ^{13}\text{C}(\text{Sn-C}-) \) NMR signals with the \( ^{117}/^{119}\text{Sn} \) satellites (marked by asterisks) corresponding to \( J(\text{Sn},^{13}\text{C}) \), and the data \( J(\text{Sn}^{119},^{13}\text{C}) \) are given.

Figure 3. 149.2 MHz \( ^{119}\text{Sn}\{^{1}\text{H}\} \) NMR spectrum of the mixture of isomers 1a – 4a showing the different line widths owing to partially relaxed scalar \( ^{119}\text{Sn}-^{11}\text{B} \) spin-spin coupling for \( |J(\text{Sn}^{119},^{11}\text{B})_{\text{trans}}| > |J(\text{Sn}^{119},^{11}\text{B})_{\text{cis}}| \).
In the case of the silanes 1a(Si) and 2a(Si), the residual broadening of the 29Si NMR signals is much less pronounced (Fig. 4), since the magnitude of \(^3J(29Si,^{11}B)\) is expectedly markedly smaller than that of \(^3J(119Sn,^{11}B)\) and, at the same time, the quadrupolar relaxation of the \(^{11}B\) nuclei is similarly efficient in the stannanes and silanes, as can be seen from the line widths of the \(^{11}B\) NMR signals (Table 1). However, the 29Si NMR spectra, if measured by using the refocused INEPT pulse sequence with \(^1H\) decoupling,\(^{29}\) serve for measuring \(^{13}C\) satellites corresponding to coupling constants \(J(29Si,^{13}C)\), some of which may be difficult to obtain from \(^{13}C\) NMR spectra.

**Figure 4.** 99.4 MHz 29Si{\(^1H\)} NMR spectrum of the mixture of the silanes 1a(Si) and 2a(Si) refocused INEPT \(^{29}\) showing the \(^{13}C\) satellites (marked by filled circles) in agreement with the information from \(^{13}C\) NMR spectra.

**DFT Calculations**

The assumption of a significant conformational difference between 1a and 2a concerning the Et₂B-group is supported by optimizing the geometry of the silicon analogues 1a(Si) and 2a(Si) using DFT methods [B3LYP/6-311G(d,p)],\(^{30}\) and the result is shown in Fig. 5. Relevant chemical shifts, calculated (GIAO \(^{31}\)) at the same level of theory, show reasonable agreement with the experimental data. The calculated orientation of the ethyl groups may not represent exactly the preferred structures in solution. This appears to affect in particular some of the calculated \(\delta^{13}C\) values. The experimental trend, however, is correctly reproduced.
Figure 5. Optimized molecular structures of 1a(Si) and 2a(Si), and comparison of calculated (GIAO 31) and experimental chemical shifts [B3LYP/6-311+G(d,p)]. It shows the almost perpendicular arrangement of the BC2 plane of the BEt2 group relative to the BC=C plane in 1a(Si) (mean angle 85°), in contrast to the analogous much less twisted conformation in 2a(Si) (mean angle 38°).

Conclusions

The fast (E/Z)-isomerization of the title compound 1a into 2a was found to be independent of the solvent or day light. Isomerization was not observed when the boron atom became tetra-coordiante in the case of the hydridoborate 5a. Therefore, the electron-deficient character of the boron atom in the Et2B group plays a decisive role. The selective further rearrangement of 2a into the isomers 3a and 4a, again not observed for the hydridoborate 6a, points towards a three-membered cyclic transition state, in which the stannyl- and the boryl groups can readily migrate from one olefinic carbon to the other. Application of multinuclear NMR serves for the unambiguous structural assignment of the compounds studied and 119Sn NMR spectroscopy, in particular, allows for monitoring of the isomerization process.

Experimental Section

General Procedures. The preparations and all handling of samples were carried out under an inert atmosphere (Ar), and carefully oven-dried glassware and dry solvents were used throughout. BuLi in hexane (1.6 M), trimethyltin chloride, ethynyl(trimethyl)silane, triethylborane, sodium hydride in mineral oil (Aldrich), and ethyne (purified by passing it through a trap at -78 °C, followed by washing it with concentrated H2SO4) were commercial products. NMR measurements in C6D6 (concentration ca. 5 – 15 %) were carried out with samples in 5 mm tubes at 23 ± 1 °C, using a Bruker DRX 500 and Varian Inova 300 and 400 spectrometers for 1H, 11B, 13C, 29Si and 119Sn NMR; chemical shifts are given with respect to SiMe4 [δ1H (C6D5H) = 7.15; δ13C (C6D6) = 128.0; δ29Si = 0 for Ξ(29Si) = 19.867184 MHz];
Ethynyl(trimethyl)tin as a hexane solution. Under an Ar atmosphere butyllithium (1.6 M in hexane; 85.5 mL, 136.8 mmol) was further diluted with hexane (100 mL) and cooled at 0 °C. Purified ethyne was slowly bubbled into the stirred solution for 90 min. Immediately, a white precipitate was formed. Then trimethyltin chloride (27.2 g, 136.55 mmol) was added as a solid, when the suspension was cooled at -78 °C. The cooling bath was taken away, and the reaction precipitate was formed. Then trimethyltin chloride (27.2 g, 136.55 mmol) was added as a solid, and in a mixture of C \(_6\)D\(_6\) and in a mixture of C \(_6\)D\(_6\)/THF (1:1), and the time-dependent isomerization was studied by \(^{119}\)Sn NMR spectroscopy (Fig. 1). Daylight does neither affect the rate of isomerization nor the product distribution. 1a: \(^1\)H NMR (300 MHz): \(\delta^1\)H \([J(\text{\textsuperscript{119}Sn},\text{\textsuperscript{1}H})] = 0.09 [52.5] (s, 9H, Me\(_3\)Sn), 1.27, 0.99 (q, t, \(J = 7.5\) Hz, 10H, Et\(_2\)B), 2.12, 0.99 (q, t, \(J = 7.3\) Hz, 5H, Et-C=). 2a: \(^1\)H NMR (300 MHz): \(\delta^1\)H \([J(\text{\textsuperscript{119}Sn},\text{\textsuperscript{1}H})] = 0.19 [53.0] (s, 9H, Me\(_3\)Sn), 1.27, 0.99 (q, t, \(J = 7.5\) Hz, Et\(_2\)B), 2.32, 0.90 (q, t, \(J = 7.3\) Hz, 5H, Et-C=), 6.34 [98.6] (s, 1H, H-C=). 3a: \(^1\)H NMR (300 MHz): \(\delta^1\)H \([J(\text{\textsuperscript{119}Sn},\text{\textsuperscript{1}H})] = 0.13 [52.5] (s, 9H, Me\(_3\)Sn), 1.27, 0.99 (q, t, \(J = 7.5\) Hz, Et\(_2\)B), 2.32, 0.98 (q, t, \(J = 7.3\) Hz, 5H, Et-C=), 6.86 [190.6] (s, 1H, H-C=). 4a: \(^1\)H NMR (300 MHz): \(\delta^1\)H \([J(\text{\textsuperscript{119}Sn},\text{\textsuperscript{1}H})] = 0.16 [52.5] (s, 9H, Me\(_3\)Sn), 1.27, 0.99 (q, t, \(J = 7.6\) Hz, Et\(_2\)B), 2.32, 0.97 (q, t, \(J = 7.3\) Hz, Et-C=), 6.26 [109.4] (s, 1H, H-C=).
29 mmol) were heated in a closed Schlenk tube under Ar at 120 °C (oil bath) for 100 h. The reaction was monitored by $^{29}$Si NMR (see Table 1 and Fig. 4) until about 40% conversion of the alkyne was achieved. The excess of BEt$_3$ and unreacted alkyne were removed in a vacuum, and the products were left as air-sensitive colorless oil. In one of these experiments, the mixture contained a small amount (< 10%) of a third compound (δ$^{29}$Si -7.4), most likely a hydroboration product,$^{32}$ not mentioned in the first report.$^5$ 1a(Si): $^1$H NMR (400 MHz): δ$^1$H = 0.00 (s, 9H, Me$_3$Si), 1.21, 0.93 (q, t, $J$ = 7.5 Hz 10H, Et$_2$B), 1.91, 0.90 (dq, t, $J$ = 0.8 Hz, $J$ = 7.3 Hz, 5H, Et-C=). 5.67 (t, $J$ = 0.8 Hz, 1H, H-C=). 2a(Si): $^1$H NMR (300 MHz): δ$^1$H = 0.13 (s, 9H, Me$_3$Si), 1.21, 0.93 (q, t, $J$ = 7.3 Hz. 10H, Et$_2$B), 2.36, 0.92 (q, t, 5H, Et-C=), 5.85 (s, 1H, H-C=).

Sodium 2-[(E)-1-trimethylstannyl-but-1-enyl]diethylhydridoborate 5a and the (Z)-isomer 6a. Sodium hydride was filtered off from a suspension in mineral oil, washed repeatedly with pentane and dried in a vacuum. Then the powder of NaH (2.5 g) was given into a Schlenk tube, suspended in hexane, BEt$_3$ (0.5 mL) was added, and the mixture was heated to reflux for 90 min. At room temperature, a small amount of an 80:20 mixture of 1a and 2a (0.86 g, 3 mmol) was added, and the mixture was kept stirring for 90 min. The supernatant solution was decanted, and volatiles were removed in a vacuum, leaving a colorless oily material which was dissolved in C$_6$D$_6$ and characterized by NMR spectroscopy (Table 1). 5a: $^1$H NMR (300 MHz): δ$^1$H $[^2$J($^{119}$Sn,$^1$H)] = 0.22 [51.2] (s, 9H, Me$_3$Sn), 0.17, 0.95 (q, t, $J$ = 7.6 Hz, 10H, Et$_2$B), 2.25, 0.84 (q, t, $J$ = 7.3 Hz, Et-C=), 6.02 [110.3] (s, 1H, H-C=). 6a: $^1$H NMR (300 MHz): δ$^1$H $[^2$J($^{119}$Sn,$^1$H)] = 0.24 [51.2] (s, 9H, Me$_3$Sn), 0.17, 0.95 (q, t, $J$ = 7.6 Hz, Et$_2$B), 2.19, 1.09 (q, t, $J$ = 7.3 Hz, Et-=), 5.76 [115.9] (s, 1H, H-C=).

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