1,2-Hydroboration of Alkyn-1-yl dichlorosilanes using Triethylborane

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Triethylborane, BEt₃, can act as a 1,2-hydroborating reagent towards alkyn-1-ylsilanes, depending on the nature of the silane. A mechanism is proposed invoking hydrogen transfer from the β-carbon of one ethyl group, quite different from the 1,2-hydroboration mechanism using tri-n-propylborane, BnPr₃. The structure of the products has been confirmed by comparison with that obtained using 9-borabicyclo[3.3.1]nonane, 9-BBN, as a well established 1,2-hydroboring reagent. All products have been characterized by a consistent set of NMR data (¹H, ¹¹B, ¹³C and ²⁹Si NMR). The molecular structure of (Z)-1-dichlorosilyl-1-[9-(9-borabicyclo[3.3.1]nonyl)]-2-phenylethene has been determined by single crystal X-ray diffraction.

Key words: Alkynes, Alkenes, Triethylborane, 9-BBN, Silanes, Hydroboration, NMR

Introduction

Triethylborane, BEt₃, has been considered for a long time as thermally robust [1–6], and 1,2-dehydroboration, common for many other trialkylboranes, to give ethene and Et₂BH via β-hydrogen elimination had not been observed [1, 5, 6]. This is in contrast with tri-n-propylborane, BnPr₃, which slowly forms propene and nPr₂BH at temperatures > 80 °C [4]. So far, we have used BEt₃ frequently for 1,1-ethylboration reactions of organometallic-substituted alkynes [7, 8]. In order to induce 1,1-ethylboration reactions of alkyn-1-ylsilanes, heating of a large excess of BEt₃ with the respective alkyn-1-ylsilane was required for prolonged periods of time at about 100 °C. Although this led to cleavage of the B–C(Et) bond, evidence for 1,2-dehydroboration and/or formation of ethene was missing [9–12]. Recently, however, we observed [13] that trichloro(hexyn-1-yl)silane, Cl₃Si–C≡C–nBu, and trichloro(phenylethynyl)silane, Cl₃Si–C≡C–Ph, react with BEt₃ by 1,2-hydroboration and elimination of ethene (Scheme 1a). In contrast, the reaction of dichloro(hexyn-1-yl)silane, Cl₂(H)Si–C≡C–nBu, with BEt₃ (Scheme 1b) affords the 1,1-ethylboration product in essentially quantitative yield [12].

The stereo- and regioselective 1,2-hydroboration (Scheme 1a) was readily confirmed, since the reaction of Cl₃Si–C≡C–nBu with BnPr₃ or 9-borabicyclo[3.3.1]nonane, 9-BBN, gave the analogous products [13]. In the present study, we have investigated the reactivity of alkyn-1-yl(dichlorosilanes

Results and Discussion

Alkyn-1-ylsilanes

The alkyn-1-yl(chloro)silanes 1–4 were prepared [12–14] from the reactions of RSiCl₃ with the alkynyl
Table 1. $^{11}$B, $^{13}$C and $^{29}$Si NMR data$^a$ of the alkenes 6–8.

<table>
<thead>
<tr>
<th></th>
<th>$\delta^{13}$C(BC=)</th>
<th>$\delta^{13}$C(C=)</th>
<th>$\delta^{13}$C(R1)</th>
<th>$\delta^{11}$B</th>
<th>$\delta^{29}$Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>145.1 (br) [88.2]</td>
<td>154.9</td>
<td>35.5, 31.3, 22.6, 14.3</td>
<td>21.7 (br), 8.9</td>
<td>82.8, -7.8</td>
</tr>
<tr>
<td>6a'</td>
<td>n. o. (br)</td>
<td>164.1</td>
<td>33.6, 31.0, 22.5, 14.1</td>
<td>n. o. (br), 9.0</td>
<td>82.8, -5.8</td>
</tr>
<tr>
<td>6c</td>
<td>147.0 (br) [90.5]</td>
<td>151.6</td>
<td>138.2 (i), 129.6 (o), 128.5 (m), 129.3 (p)</td>
<td>21.3 (br), 8.9</td>
<td>83.8, -0.5</td>
</tr>
<tr>
<td>6c'</td>
<td>147.8 (br)</td>
<td>161.1</td>
<td>137.9 (i), 129.6 (o), 128.7 (m) (p)</td>
<td>21.6 (br), 8.4</td>
<td>83.0, -6.9</td>
</tr>
<tr>
<td>7c</td>
<td>147.8 (br)</td>
<td>164.1</td>
<td>140.1 (i), 129.5 (o), 128.4 (m), 132.6 (p)</td>
<td>21.7 (br), 9.4</td>
<td>86.8, -7.7</td>
</tr>
<tr>
<td>8c</td>
<td>141.9 (br) [78.5]</td>
<td>160.8</td>
<td>138.0 (i), 129.6 (o), 130.3 (p), 128.7 (m)</td>
<td>34.5, 31.3 (br), 23.6 (BBN)</td>
<td>82.4, -6.4</td>
</tr>
</tbody>
</table>

*a Measured in C$_6$D$_6$ at 23 °C; (br) indicates a broad NMR signal owing to partially relaxed $^{13}$C-$^{11}$B scalar coupling [15]; some coupling constants $J(^{29}$Si,$^{13}$C) $\pm 0.4$ Hz are given in square brackets; $^b$ data from ref. [13].

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Fig. 1. 100.5 MHz $^{13}$C{$^1$H} NMR spectrum of 3,3-dimethylbutyn-1-yl(dichloro)(phenyl)silane 3b in C$_6$D$_6$; in expanded parts satellites are marked by asterisks and correspond to $^1J(^{29}$Si,$^{13}$C) and $^2J(^{29}$Si,$^{13}$C).

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Fig. 2. NMR spectra of the alkene 8c in C$_6$D$_6$ [expanded parts show satellite signals, marked by asterisks, corresponding to $J(^{29}$Si,$^{13}$C)]: Upper trace: Part of the 100.5 MHz $^{13}$C{$^1$H} NMR spectrum. Middle trace (inserted): 59.6 MHz $^1$H-coupled $^{29}$Si NMR spectrum (INEPT [20]). Lower trace: $^{29}$Si{$^1$H} NMR spectrum (INEPT [20]).

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lithium reagents Li–C≡C–nBu (a), Li–C≡C–tBu (b) or Li–C≡C–Ph (c) characterized by $^1$H, $^{13}$C and $^{29}$Si NMR spectroscopy (e. g. Fig. 1) and purified by fractional distillation.

Reaction of dichloro(phenylethynyl)silane 1c with triethylborane

According to Scheme 1b [12], it was expected that the reaction of 1c with BEt$_3$ proceeds via 1,1-ethylboration. However, it was found that the exchange of R$^1$ = nBu in 1a against R$^1$ = Ph in 1c caused a complete reversal of the reaction to give the 1,2-hydroboration product 7c instead in essentially quantitative yield. A small amount (< 10 %) of 7c', the (E)-isomer, was formed along with 7c. The structure of 7c follows conclusively from the consistent set of NMR data (Table 1). The analogous 1,2-hydroboration product 8c was obtained from 1c using 9-BBN as the 1,2-hydroborating reagent (Scheme 3). The NMR data of 8c (Ta-
Reactions of alkyn-1-yl(dichloro)(organosilanes 2 and 3 with triethyl- and tri-n-propylborane and with 9-BBN

From these reactions, the alkenes 9 and 12 are formed in high yield (Scheme 4, Fig. 3), accompanied by small amounts (< 10 %) of the corresponding (E)-isomers. The analogous reactions with BnPr3, under milder conditions, afford the alkenes 10 and 13 as mixtures with the respective (E)-isomers in variable amounts (up to 30 %), and a small amount of dialkenyl(n-propyl)boranes. The 1,2-hydroboration of 2 and 3 with 9-BBN gives the pure alkenes 11 and 14 in essentially quantitative yield. The NMR data (Tables 2 and 3) are in agreement with the proposed structures.

Reactions of dichloro(hexyn-1-yl)(phenyl)silane 4a and trichloro(hexyn-1-yl)silane 4a with 9-ethyl-9-borabicyclo[3.3.1]nonane

9-Ethyl-9-borabicyclo[3.3.1]nonane, 9-Et-9-BBN, usually does not undergo 1,2-dehydroboration or decomposition at temperatures < 150 °C even after pro-
reactions take place to give mixtures of three products, viz. 14a/ 16a/ 17a and 15a/ 18a/ 19a, respectively (Scheme 5). The different alkenes are readily identified by their consistent NMR data sets (Table 4, Fig. 4). Two alkenes are formed in major quantity by dehydroboration into propene and elimination of ethene.

Mechanism

There is no doubt in the case of B\textsubscript{8}Pr\textsubscript{3} that it slowly decomposes upon heating > 80 °C via 1,2-dehydroboration into propene and B\textsubscript{8}Pr\textsubscript{2}BH which then reacts with alkynes or alkenes in the usual way as a 1,2-dehydroboration reagent [3, 4]. In contrast, even under more harsh conditions, BE\textsubscript{3} or 9-Et-9-BBN do not undergo elimination of ethene to give dialkylboron hydrides Et\textsubscript{2}BH or 9-BBN. Nevertheless, BE\textsubscript{3} and 9-Et-9-BBN act as hydrobrotating reagents in the longed periods of heating without a solvent [5]. However, in the presence of the alkyne-1-ylsilanes 3a or 4a reactions take place to give mixtures of three products, viz. 14a/ 16a/ 17a and 15a/ 18a/ 19a, respectively (Scheme 5). The different alkenes are readily identified by their consistent NMR data sets (Table 4, Fig. 4). Two alkenes are formed in major quantity by dehydroboration into propene and elimination of ethene.

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Table 4. $^{11}$B, $^{13}$C and $^{29}$Si NMR data$^a$ of the alkenes 15 – 18.

<table>
<thead>
<tr>
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<th>$\delta^{11}$B(BC≡)</th>
<th>$\delta^{13}$C(BC≡)</th>
<th>$\delta^{13}$C(C=)</th>
<th>$\delta^{13}$C(R1)</th>
<th>$\delta^{13}$C(BEt₂/BBN)</th>
<th>$\delta^{11}$B</th>
<th>$\delta^{29}$Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>15a</td>
<td>144.1 (br)</td>
<td>162.2</td>
<td>35.9, 31.1, 22.6, 14.0</td>
<td>19.9 (br), 9.1</td>
<td>83.2</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>16a</td>
<td>n. a.</td>
<td>164.8</td>
<td>35.6, 31.0, 22.7, 14.0</td>
<td>20.2 (br), 8.9</td>
<td>82.2</td>
<td>−5.9</td>
<td></td>
</tr>
<tr>
<td>17a</td>
<td>145.5, 143.3</td>
<td>166.0, 152.6</td>
<td>36.2, 35.9, 31.4, 30.8, 22.8, 22.5, 14.2, 14.1</td>
<td>19.9 (br), 10.5</td>
<td>83.2</td>
<td>1.6, −0.6</td>
<td>−5.6</td>
</tr>
<tr>
<td>18a</td>
<td>n. a.</td>
<td>167.9, 154.9</td>
<td>35.9, 35.5, 31.3, 30.7, 22.8, 22.6, 14.1, 14.0</td>
<td>20.2 (br), 10.3</td>
<td>82.2</td>
<td>−7.8, −5.6</td>
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</tbody>
</table>

$^a$ Measured in C₆D₆ at 23 °C; n. a. denotes not assigned; (br) indicates a broad NMR signal owing to partially relaxed $^{13}$C-$^{11}$B scalar coupling [15].

Fig. 4. NMR spectra of the mixtures (in C₆D₆) obtained from the reactions shown in Scheme 5. Upper traces: Olefinic regions (=CH) of the 100.5 MHz, $^{13}$C{¹H} NMR spectra for the mixtures of 14a/16a/17a and 15a/18a/19a. Middle trace (right): 400 MHz $^1$H(=CH) NMR spectrum for the mixture of compounds 17a/18a/19a. Middle trace (left) and lower trace: 59.6 MHz $^{29}$Si{¹H} of the mixtures 14a/16a/17a and 15a/18a/19a solution in C₆D₆.

presence of certain alken-1-ylsilanes. An explanation is offered in Scheme 6, where the first interaction (A) between the borane and the alken-1-ylsilane is the same for 1,1-ethylboration and 1,2-hydroboration. Cleavage of the Si–C≡ bond leads to a borate-like zwitterionic intermediate B [7] and finally to 1,1-ethylboration [7 – 12]. If the Si–C≡ bond is particularly strong, cleavage of this bond does not occur, leaving alternative routes for the subsequent steps. In particular for substituents R¹ capable of delocalizing a positive charge (e.g., R¹ = Ph), an intermediate C is stabilized, and transfer of a hydrogen atom from the $\beta$-carbon atom is favored to give the 1,2-hydroboration product accompanied by elimination of ethene. Compelling evidence for the influence of R¹ is provided by comparison of the reaction of 1a (Scheme 1b, 1,1-ethylboration) and 1c with BEt₃ (Scheme 3, 1,2-hydroboration). The $\beta$-hydrogen transfer in Scheme 6 reminds of the processes proposed for limiting the chain lengths of polymers, in the chemistry of aluminum alkyls [17]. It may also be important in the catalyzed high-temperature alkane isomerization of alkanes caused by carbenium ions [18] which are isoelectronic with boranes.
X-Ray structural analysis of the alkene 8c

The molecular structure of the alkene 8c is shown in Fig. 5 together with selected structural parameters. The main structural features are similar to those already published for similar alkenes [16, 19]. The CBC plane of the 9-borabicyclo[3.3.1]nonyl group is twisted by 37°, and the Ph plane (C11–C16) by 41.9°, against the Si(B)C=C plane. The surroundings of the boron atom are trigonal planar within the experimental error. Thus, the structure of 8c does not indicate Si–Cl···B or Si–H···B interactions in the solid state in spite of the spatial proximity of the silyl and boryl groups. This has been observed previously [16, 19] and is consistent with the absence of such interactions in solution. As for other structural constraints, marked Si–H···B interactions have been observed both in the solid state and in solution [21].

Experimental Section

All preparative work was carried out by observing necessary precautions to exclude traces of oxygen and moisture. Tetrachlorosilane, trichlorosilane, trichloro(methyl)silane, trichloro(phenyl)silane, 1-hexyne, 3,3-dimethylbut-1-yne, ethynylbenzene, n-butyllithium in hexane (1.6 M), triethylborane (BEt3), and 9-borabicyclo[3.3.1]nonane (9-BBN) were used as commercial products without further purification. NMR spectra: Varian Inova 300 and 400 spectrometers (23 °C), both equipped with multinuclear units, using C6D6 solutions (ca. 5–10% v/v) in 5 mm tubes. Chemical shifts are given with respect to SiMe4 [δ1H(C6D5H) = 7.15, δ13C(C6D6) = 128.0, δ29Si = 0 for SiMe4 with Ξ(29Si) = 19.867187 MHz], and δ11B = 0 for BF3·OEt2 with Ξ(11B) = 32.083971 MHz. 29Si NMR spectra were recorded using the refocused INEPT pulse sequence with 1H decoupling [20], based either on J(29Si,1H) ≈ 280 Hz or J(29SiC=C1H) ≈ 25–35 Hz (after optimization of the refocusing delay). Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet (data for 1H, 11B, 12C, 35Cl, 28Si).

Synthesis of silanes 1, 2, 3 and 4

A suspension of R1C≡CLi (R1 = nBu, tBu, Ph; 25 mmol) in hexane (60 mL) was freshly prepared, and the solution was cooled to −78 °C. Then the respective chlorosilane was added (in 6–8 fold excess) slowly with constant stirring. The reaction mixture was warmed to r.t. and kept stirring for 3–4 h. Insoluble materials were filtered off, and volatiles were removed in a vacuum. The colorless oily residue was identified as a mixture of silanes, from which the pure desired silanes were obtained by fractional distillation. 3b: b.p. 74–76 °C (2 × 10−2 mbar). − 1H NMR (400 MHz): δ = 0.9 (s, 9H, tBu), 7.1. 7.4 (m, m, 5H, Si-Ph). − 13C NMR: δ [J(29Si,13C)] = 132.7 [80.2] (t-C), 133.3 (o-C), 132.2 (p-C), 128.6 (m-C) (Ph-Si); 121.8 [23.8] (≡C); 76.2 [138.3] (Si–C≡C); 30.0, 28.5 (t-Bu). − 29Si NMR: δ = −19.8. For the other silanes see refs. [12, 13].
Hydroboration of the dichloro(phenylethynyl)silane 1c with BEt3 and 9-BBN

An NMR tube was charged with dichloro(phenylethynyl)-silane 1c (0.37 g, 1.8 mmol) and BEt3 was added in excess. The tube was sealed and kept at 110 – 120 °C for 3 d. The reaction was monitored from time to time by 29Si NMR. After the reaction was complete, the NMR tube was cooled in liquid nitrogen and was opened carefully. All the volatiles were removed, and the oily compound left was identified as 7c (yield 80 %). – 1H NMR (400 MHz): δ = 0.9, 1.4 (t, q, 6H, 4H, BEt2), 5.6 (s, 1H, 1J(29Si,1H) = 292.4 Hz, SiH). – EI-MS: m/z (%) = 185 (29) [M]+, 316 (91) [M–H]+, 281 (5) [M+Cl]−, 274 (22) [M–C3H7]−, 260 (12) [M–Bu]+, 113 (60), 113 (60), 67 (100).

Hydroboration of the alkyne-1-yldichlorosilanes 2 with BEt3, BnPr2 and 9-BBN

Silane 2a (0.32 g, 1.6 mmol) was given into an NMR tube, and BEt3 (0.8 mL) as solvent was added, after which the NMR tube, was sealed. The reaction mixture was kept at 110 – 120 °C for 19 d. After the reaction was completed, the NMR tube was cooled in liquid N2, opened, warmed to r.t., and volatile materials were removed in a vacuum. The oily residue was identified as 9a (yield 85 % from 1H NMR spectroscopy). An analogous procedure was adopted for the synthesis of 9c, 10a and 10c (except for the reaction time): 9c (14 d), 10a (7 d) and 10c (10 d). In the case of hydroboration with 9-BBN, the reaction was complete after 4 – 8 h at r.t. in THF or after 15 min in C6D6 at 80 °C.

9a: 1H NMR (400 MHz): δ = 0.7 (s, 3H, Si-Me, 2J(29Si,1H) = 7.4 Hz), 1.2, 1.0 (m, t, 10H, BEt2), 2.2, 1.1, 0.8 (q, m, t, 9H, Bu). – EI-MS: 59 (t, 1H, =CH, 1J(29Si,1H) = 26.7 Hz), 250 (11) [M+Si(H)2]+, 229 (27) [M–Cl]+, 207 (15) [M–Bu]+, 196 (10) [M–BEt2]+, 151 (12) [M–Si(Me)Cl2]+, 43 (87) [C3H7]+, 41 (100) [C2H5]+.

9c: 1H NMR (400 MHz): δ = 0.3 (s, 3H, Si-Me, 2J(29Si,1H) = 8.6 Hz), 1.2, 0.8 (q, m, t, 10H, BEt2), 6.8 – 7.0 (m, 5H, Ph), 6.7 (s, 1H, =CH, 3J(29Si,1H) = 26.3 Hz). – EI-MS: m/z (%) = 185 (29) [M]+, 270 (35) [M–CH3]+, 257 (30) [M–C2H5]+, 216 (11) [M–BEt2]+, 207 (69), 171 (27) [M–MeSiCl2]+, 113 (82), 102 (32), 103 (47), 91 (100).

10a: 1H NMR (400 MHz): δ = 0.7 (s, 3H, 2J(29Si,1H) = 7.4 Hz, SiMe), 0.8, 1.3, 2.2 (t, m, q, 9H, Bu), 1.0, 1.3 (t, m, 14H, BnPr2), 6.0 (t, 1H, 3J(1H,1H) = 7.5 Hz, 3J(29Si,1H) = 34.7 Hz, =CH).

Hydroboration of the alkyne-1-yldichlorosilanes using Triethylborane 1273
13a: 1H NMR (400 MHz): δ = 2.0, 1.0 – 1.4, 0.5 (m, t, 9H, 6Bu), 1.0 – 1.4, 0.8 (m, t, 14H, BPr²), 6.9 – 7.6 (m, 5H, SiPh), 5.9 (t, 1H, =CH, 3J(1H,3H) = 7.4 Hz).

13b: 1H NMR (400 MHz): δ = 0.9 (s, 9H, 6Bu), 0.9, 1.3 – 1.4 (t, m, 14H, BPr²), 5.8 (s, 1H, =CH, 3J(29Si,1H) = 30.9 Hz), 7.1, 7.7 (m, m, 5H, Ph).

13c: 1H NMR (400 MHz): δ = 6.8 − 7.2, 7.4 (m, m, Ph, SiPh, =CH), 0.9, 1.5 (t, m, 14H, BPr²).

14b: 1H NMR (400 MHz): δ = 1.1 (s, 9H, 6Bu), 1.3 – 1.9 (m, 14H, BBN), 7.0 (s, 1H, =CH, 3J(29Si,1H) = 29.5 Hz), 7.1, 7.7 (m, m, 5H, SiPh).

Reaction of dichloro(hexyn-1-yl)(phenyl)silane 3a and trichloro(hexyn-1-yl)silane 4a with 9-Et-9-BBN

A mixture of the silane 3a and 9-Et-9-BBN was sealed in an NMR tube which was kept at 110–120 °C. After 30 d the NMR tube was opened, and volatile materials were removed in a vacuum. The components of the oily residue were identified as a mixture of compounds 14a, 15a and 16a (ratio 15:60:25). The same procedure was followed for the synthesis of 17a, 18a and 19a (ratio 60:30:10) except that 40 d of heating was necessary to achieve sufficient conversion of reactants into products.

16a: 1H NMR (400 MHz): δ = 6.63 (t, 2H, =CH).

17a: 1H NMR (400 MHz): δ = 6.91, 5.98 (t, t, 1H, 1H, =CH).

18a: 1H NMR (400 MHz): δ = 6.57 (t, 2H, =CH).

19a: 1H NMR (400 MHz): δ = 6.81, 5.98 (t, t, 1H, 1H, =CH).

X-Ray structural analysis of 8c

The X-ray crystal structural analysis of 8c was carried out for a single crystal fixed in a sealed capillary at 293(2) K using a Stoe IPDS I system; MoKα radiation, λ = 0.71073 Å, C16H20BCl2Si, M = 322.12, crystal size: 0.22 × 0.15 × 0.12 mm³, crystal system: triclinic, space group PІ, a = 7.5130(15), b = 9.7552(2), c = 12.508(3) Å, α = 92.44(3)°, β = 98.85(3)°, γ = 110.66(3)°, V = 842.9(3) Å³, Z = 2, Dcalc = 1.269 mg m⁻³, μ(MoKα) = 0.443 mm⁻¹, F(000) = 338 e, θmax = 1.010 (1000), area ranges: −9 < h < 9, −11 < k < 9, −15 ≤ l ≤ 14, 5126 collected reflections, 3039 independent reflections, R(int) = 0.041, completeness to θ = 26.08°: 91.0%, data/parameters: 3039/182, goodness-of-fit on F² = 0.844, final R indices [I > 2σ(I)] 3781: R1 = 0.0543, wR2 = 0.1502; R indices (all data): R1 = 0.0951, wR2 = 0.1345; largest difference peak and hole: 0.43 and −0.25 e Å⁻³.

Structure solution and refinement were accomplished using SHELXTL version 5.1 [22]. CCDC 576258 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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