1,1-Ethylboration of Alkyn-1-yl-(dichloro)silanes: Alkenes Bearing Dichlorosilyl and Diethylboryl Groups

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The 1,1-ethylboration of dichloro(hexyn-1-yl)silane, Cl_2Si(H)-C≡C-Bu, affords selectively an alkene which is the first example with dialkylboryl and dichlorosilyl groups in *cis*–positions at the C=C bond. The analogous reaction of dichloro(trimethylsilylethynyl)silane, Cl_2(H)Si-C≡C-Si Me_3, leads to a 4:1 mixture of alkenes, in one of which the boryl and dichlorosilyl groups are in *trans*–positions. The alkenes were characterized by a consistent set of NMR data.

Key words: Alkynes, Alkenes, Boranes, Silanes, Organoboration, NMR

Scheme 1.

Various methods have been reported for the preparation of alkenes bearing both boryl and silyl groups [1 – 5]. Although alkenes with silyl and boryl groups in *cis*-positions together with functional groups at silicon would be highly welcome synthons, straightforward routes to such compounds are not known. The clean reaction of trialkyl(alkyn-1-yl)borates with chlorosilanes [6 – 8] appears to be restricted to Me_2(R)SiCl (R = Me, Et, Ph). Similarly, the 1,1-organoboration of alkyn-1-ylsilanes [8, 9] has been reported to work well only with alkyn-1-ylsilanes with methyl groups and/or hydrogen atoms bonded to silicon [8 – 10]. However, recent studies have shown that heating of alkyn-1-yl-monochlorosilanes in triethylborane (BEt$_3$) as the solvent at $\geq$ 100 °C for several days leads to alkenes, in which diethylboryl and chlorosilyl groups [SiMe)(H)Cl or SiMe$_2$Cl] are in *cis*-positions [11]. The presence of chloro and hydrido functions at the silicon atom invites for numerous further transformations. In the light of these results [11] it seemed worthwhile to investigate alkyn-1-yl-dichlorosilanes, although the
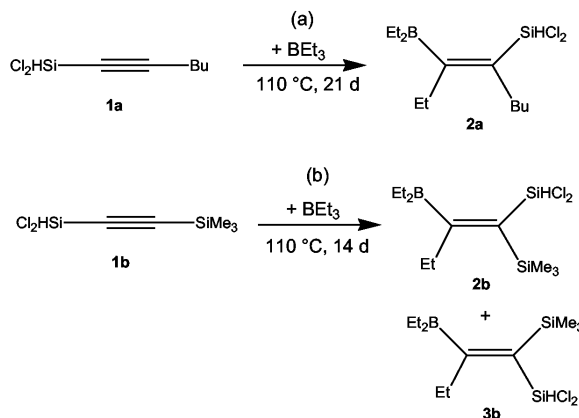
dichlorosilyl group may further reduce the reactivity of the alkyne towards BEt$_3$.

The reaction of dichloro(hexyn-1-yl)silane **1a** with triethylborane BEt$_3$ as the solvent proceeded very slowly. After three weeks at 110 °C about 50% of **1a** was converted selectively into the alkene **2a** (Scheme 1a). The 1,1-ethylboration of dichloro(trimethyl-silylethynyl)silane **1b** was complete already after three days under the same conditions to give a 4:1 mixture of the alkenes **2b** and **3b** (Scheme 1b). The greater reactivity of **1b** towards BEt$_3$, when compared with **1a**, can be explained by the presence of two silyl groups at the C≡C bond. However, it should be noted that Me_3Si-C≡C-SiMe$_3$ does not react at all with BEt$_3$ under these conditions. The presence of the isomers **2b** and **3b** is typical of 1,1-organoboration reactions if two organometallic groups are linked to the C≡C bond in the starting alkyne [8]. The alkene **2a** could be purified by distillation, whereas the mixture of **2b/3b** could not be separated. Both **2a** and **2b/3b** are air- and moisture-sensitive, colourless liquids.

The alkenes **2a,b** and **3b** were characterized by their ^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR data (Experimental Section). The typically broad ^{13}C NMR signals for carbon atoms bonded to boron [12] owing to unresolved one-bond [13]C-[11]B spin-spin coupling, and the observation of [29]Si satellites corresponding to $^1J(^{29}Si,^{13}C)$ are useful for assignment purposes. In addition, the mutual positions of the substituents at the C=C bond could be assigned unambiguously by selective ^{1}H/^{1}H NOE difference experiments [13]. The NMR data of **2a,b** do not indicate the presence of Si-H-B [14] or Si-Cl-B bridges [11].

Experimental Section

All preparative work was carried out by observing necessary precautions to exclude traces of oxygen and moisture. Trichlorosilane, 1-hexyne, ethynyl(trimethyl)silane, butyllithium in hexane (1.6 M) and triethylborane were used as commercial products without further purification.

NMR spectra were recorded at 23 °C on Bruker ARX 250, DRX 500 or Varian Inova 400 spectrometers, all equipped with multinuclear units, using C_6D_6 solutions (*ca.* 5 – 10% V/V) in 5 mm tubes. Chemical shifts are given with respect to Me_4Si $[\delta^1H$ (C_6D_5H) = 7.15, $\delta^{13}C$ (C_6D_6) = 128.0, $d^{29}Si$ = 0 for Me_4Si with $\Xi(^{29}Si)$ = 19.867187 MHz], and $\delta^{11}B$ = 0 for BF_3-OEt_2 with $\Xi(^{11}B)$ = 32.083971 MHz. ^{29}Si NMR spectra were recorded using the refocused IN-EPT pulse sequence with ^1H decoupling [15]. Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet (data for $(^{12}C, ^1H, ^{11}B, ^{35}Cl, ^{28}Si)$. IR spectra: Perkin-Elmer Spectrum 2000 FTIR.

Dichloro(hexyn-1-yl)silane **1a** *and dichloro(trimethylsilylethynyl)silane* **1b**

A freshly prepared suspension of of the respective lithium alkynide (hexyne-1-yllithium: 0.15 mol; trimethylsilylethynyllithium; 0.1 mol) in pentane (110 and 75 ml) was cooled to −196 °C, and trichlorosilane (0.45 mol, 45 ml; 0.3 mol, 30.3 ml) was added under nitrogen gas within 10 min. The mixture was allowed to reach room temperature, and stirring was continued for 12 h. Insoluble materials were filtered off, all volatiles were removed in a vucuum, and the residue containing **1a** or **1b** along with the corresponding dialkyn-1-yl(chloro)silane and trialkyn-1-ylsilane (in the ratio 1 : 0.2 : 1.4 for **1a**, and 1 : 0.5 : 0.8 for **1b**) was separated by fractional distillation to give **1a** (b. p. 59 °C/10^{-2} Torr; yield 19%) and **1b** (b. p. 45 – 47 °C/10^{-2} Torr; yield 20%) as colourless liquids.

1a: ^1H NMR (250 MHz): δ = 1.82, 1.10 – 1.16, 0.67 (t, m, t, 2H, 4H, 3H, Bu), 5.38 (s, 1H, SiH, $^1J(^{29}Si,^1H)$ = 317.1 Hz). $^{13}C\{^1H\}$ NMR (62.9 MHz): $\delta[J(^{19}Si,^{13}C)]$ = 77.3 [136.9] (Si*C*≡), 114.5 [28.3] (≡*C*-Bu), 22.0, 29.7, 19.5, 13.5 (Bu). $^{29}Si\{^1H\}$ NMR (44.8 MHz): δ = −30.7. IR: ν(Si-H) = 2179, ν(C≡C) = 2281 cm^{-1}. **1b**: ^1H NMR (250 MHz): δ = 0.0 (s, 9H, SiMe_3), 5.31 (s, 1H, SiH, $^1J(^{29}Si,^1H)$ = 318.4 Hz). $^{13}C\{^1H\}$ NMR (62.9 MHz): $\delta[J(^{19}Si,^{13}C)]$ = 102.9 [122.9, 11.1] (Cl_2HSi*C*≡), 121.4 [69.3, 21.8] (≡*C*-SiMe_3), −0.9 [56.9] (Si*Me*_3). $^{29}Si\{^1H\}$ NMR (44.8 MHz): δ = −32.2 (*Si*HCl_2); −15.4 (*Si*Me_3). IR: ν(Si-H) = 2116.5, ν(C≡C) = 2277 cm^{-1}.

(E)-3-Diethylboryl-4-(dichlorosilyl)-3-hexene **2a**

Dichloro(hexyn-1-yl)silane **1a** (2.9 g, 10.4 mmol) was dissolved in triethylborane (4 ml, 31.2 mmol), and the mixture was heated to 110 °C (oil bath) for 21 d until ^{29}Si NMR spectra showed that about 50% of the alkyne had been consumed. The excess of BEt_3 and **1a** were distilled off, and fractional distillation of the residue gave pure **2a** (b. p. 85 °C/5 · 10^{-3} Torr; yield 30%).

The 4:1 mixture of the alkenes **2b/3b** was obtained in the same way, when ^{29}Si NMR spectra showed that the reaction was complete after heating for 3 d. Fractional distillation gave the mixture of **2b/3b** (b.p. 69 – 71 °C/5 · 10^{-3} Torr; yield 60%), and the product distribution was the same, within experimental error, as in the reaction mixture.

2a: ^1H NMR (400 MHz): δ = 2.30, 1.26 – 1.58, 0.94 (t, m, t, 2H, 4H, 3H, Bu), 1.94, 0.87 (q, t, 2H, 3H, =C-Et), 1.18, 0.94 (q, t, 4H, 6H, BEt_2), 5.24 (s, 1H, SiH, $^1J(^{29}Si$-$^1H)$ = 269.7 Hz). $^{13}C\{^1H\}$ NMR (62.9 MHz): $\delta[J(^{19}Si,^{13}C)]$ = 130.5 [94.2] (Si*C*=), 173.4 (br, B-*C*=), 32.8, 28.5, 23.4, 12.8 (Bu), 23.1, 14.1 (Et), 21.5 (br), 9.5 (BEt_2). ^{11}B NMR (80.7 MHz); δ = 82.8. $^{29}Si\{^1H\}$ NMR (44.8 MHz): δ = −3.9. IR: ν(Si-H) = 2267 cm^{-1}. EI-MS: m/z (%) = 226 (100) [M$^+$-53], 198(22)[M$^+$-81], 180 (8) [M$^+$-99], 122 (22) [M$^+$-157]. **2b**; ^1H NMR: δ (500 MHz) = 0.29 (s, 9H, SiMe_3), 2.18, 0.79 (q, t, 2H, 3H, =C-Et), 1.04 – 1.18, 0.93 (m, t, 4H, 6H, BEt_2), 5.26 (s, 1H, SiH, $^1J(^{29}Si$-$^1H)$ = 261.4 Hz). $^{13}C\{^1H\}$ NMR (125.8 MHz): $\delta[J(^{19}Si,^{13}C)]$ = 132.7 [71.0, 55.6] (Si_2*C*=), 196.2 (br, B-*C*=), 39.6, 13.1 (Et), 21.5 (br), 9.5 (BEt_2), 1.8 [51.2] (Si*Me*_3). ^{11}B NMR (80.7 MHz); δ = 82.7. $^{29}Si\{^1H\}$ NMR (44.8 MHz): δ = −2.9 (*Si*HCl_2), −9.9 (*Si*Me_3, $^2J(^{29}Si,^{29}Si)$ = 10.9 Hz). IR: ν(Si-H) = 2279 cm^{-1}. **3b**: ^1H NMR (500 MHz): δ = 0.11 (s, 9H, SiMe_3), 2.28, 0.83 (q, t, 2H, 3H, =C-Et), 1.24 – 1.32, 0.89 (m, t, 4H, 6H, BEt_2), 5.95 (s, 1H, SiH, $^1J(^{29}Si$-$^1H)$ = 275.0 Hz). $^{13}C\{^1H\}$ NMR (125.8 MHz): $\delta[J(^{19}Si,^{13}C)]$ = 131.2 [68.2, 55.1] (Si_2*C*=), 193.1 (br, B-*C*=), 29.7 [17.4, 9.6], 13.8 (Et), 21.5 (br), 9.3 (BEt_2), 1.7 [51.4] (Si*Me*_3). ^{11}B NMR; δ = 82.7. $^{29}Si\{^1H\}$ NMR (44.8 MHz): δ = −3.9 (*Si*HCl_2), −10.7 (*Si*Me_3, $^2J(^{29}Si,^{29}Si)$ = 13.1 Hz).

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