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

Bernd Wrackmeyer\textsuperscript{a}, Khadija Shahid\textsuperscript{a,b}, and Saqib Ali\textsuperscript{b}

\textsuperscript{a} Anorganische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany
\textsuperscript{b} Department of Chemistry, Quaid-I-Azam University, Islamabad, Pakistan

Reprint requests to Prof. Dr. B. Wrackmeyer. E-mail: b.wrack@uni-bayreuth.de

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The 1,1-ethylboration of dichloro(hexyn-1-yl)silane, Cl\textsubscript{2}Si(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\textsubscript{2}(H)Si-C≡C-SiMe\textsubscript{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

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\textsubscript{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-trichlorosilanes in triethylborane (BEt\textsubscript{3}) as the solvent at \(\geq 100 \, ^\circ\text{C}\) for several days leads to alkenes, in which diethylboryl and chlorosilyl groups [SiMe\textsubscript{2}(H)Cl or SiMe\textsubscript{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\textsubscript{3}.

The reaction of dichloro(hexyn-1-yl)silane \(1\text{a}\) with triethylborane BEt\textsubscript{3} as the solvent proceeded very slowly. After three weeks at 110 \(\, ^\circ\text{C}\) about 50\% of \(1\text{a}\) was converted selectively into the alkene \(2\text{a}\) (Scheme 1a). The 1,1-ethylboration of dichloro(trimethyl-silylethynyl)silane \(1\text{b}\) was complete already after three days under the same conditions to give a 4:1 mixture of the alkenes \(2\text{b}\) and \(3\text{b}\) (Scheme 1b). The greater reactivity of \(1\text{b}\) towards BEt\textsubscript{3}, when compared with \(1\text{a}\), can be explained by the presence of two silyl groups at the C≡C bond. However, it should be noted that Me\textsubscript{3}Si-C≡C-SiMe\textsubscript{3} does not react at all with BEt\textsubscript{3} under these conditions. The presence of the isomers \(2\text{b}\) and \(3\text{b}\) 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 \(2\text{a}\) could be purified by distillation, whereas the mixture of \(2\text{b}/3\text{b}\) could not be separated. Both \(2\text{a}\) and \(2\text{b}/3\text{b}\) are air- and moisture-sensitive, colourless liquids.

The alkenes \(2\text{a,b}\) and \(3\text{b}\) were characterized by their \(1\text{H}, 11\text{B}, 13\text{C}\) and \(29\text{Si}\) NMR data (Experimental Section). The typically broad \(13\text{C}\) NMR signals for carbon atoms bonded to boron [12] owing to unresolved one-bond \(13\text{C}-11\text{B}\) spin-spin coupling, and the observation of \(29\text{Si}\) satellites corresponding to \(^1J(29\text{Si},13\text{C})\) are useful for assignment purposes. In addition, the mutual positions of the substituents at the C≡C bond could be assigned unambiguously by selective \(^1\text{H}/^1\text{H}\) NOE difference experiments [13]. The NMR data of \(2\text{a,b}\) 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 triethyloxane 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 CDCl₃ solutions (ca. 5-10% V/V) in 5 mm tubes. Chemical shifts are given with respect to Me₄Si. δ²⁹Si = 0 for Me₂Si with Ξ(²⁹Si) = 19.867187 MHz, and δ¹¹B = 0 for BF₃·OEt₂ with Ξ(¹¹B) = 29.324371 MHz. ²⁹Si NMR spectra were recorded using the refocused INEPT pulse sequence with ¹H decoupling [15]. Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet (data for ¹¹B NMR; δ = 82.7. ²⁹Si[¹¹B] NMR (44.8 MHz); δ = -3.9. IR: ν(Si-H) = 2279 cm⁻¹. EI-MS: m/z (%) = 226 (100) [M⁻⁺]⁻, 198(22)[M⁻⁺⁺], 180 (8) [M⁻⁺⁻], 122 (22) [M⁻⁺⁻⁻]. ¹³C NMR: δ = 59.9 (Me₄Si); 73.2 (SiH₂Cl₂); 135.0 (si-C≡Si). ¹³C(¹³C) = 131.2 [68.2, 55.1] (Si-C≡Si), 191.3 (br, B-C≡Si), 29.7 [17.4, 9.6], 13.8 (Et), 21.5 (br), 9.3 (BEt₂). ¹¹B NMR (80.7 MHz); δ = 82.7. ²⁹Si[¹¹B] NMR (44.8 MHz); δ = -3.9 (SiHCl₂), -9.9 (SiMe₂), 2J(²⁹Si-²⁹Si) = 10.9 Hz. IR: ν(Si-H) = 2279 cm⁻¹. ²h : ¹H NMR (500 MHz): δ = 0.11 (s, 9H, SiMe₃), 2.28, 0.83 (q, t, 2H, 3H, =C-Et), 1.24 – 1.32, 0.89 (m, t, 4H, 6H, BEt₂), 5.95 (s, 1H, SiH, J=²⁹Si[H]) = 275.0 Hz. ¹³C[¹¹B] NMR (125.8 MHz); δ[J(¹¹B,¹³C)] = 131.2 [68.2, 55.1] (Si-C≡Si), 191.3 (br, B-C≡Si), 29.7 [17.4, 9.6], 13.8 (Et), 21.5 (br), 9.3 (BEt₂). ¹¹B NMR (80.7 MHz); δ = 82.7. ²⁹Si[¹¹B] NMR (44.8 MHz); δ = -3.9 (SiHCl₂), -10.7 (SiMe₃), 2J(²⁹Si-²⁹Si) = 13.1 Hz.

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Note


