Hydroboration and Haloboration of Propyne and 1-Butyne

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Hydroboration, Haloboration, Boron

Hydroboration of propyne and 1-butyne with HBCl₂ obtained from BCl₃ and Me₃SiH in equimolar amounts leads to 1,1-bis(dichloroboryl)alkanes 1. When BCl₃ is used in excess, no 1,1-bis(dichloroboryl)alkanes 1 but E-1-dichloroborylalkene 2 besides E-1-dichloroboryl-2-chloro-alk-1-ene 3 are formed. Other by-products are tris(2-chloro-alk-1-ene-1-yl)boration 4 and bis(2-chloro-alk-1-ene-1-yl)chloroborane 5. The reaction of 3 with catechol and the formation of pyridine adducts of 4 and 5 lead to crystalline products. The composition of the products was determined by NMR spectroscopy, MS spectrometry and X-ray structure analyses of 6a, 6b, 7a and 8b.

Introduction
In 1976 the first double hydroboration of terminal alkynes with HBCl₂ was reported by H. C. Brown and N. Ravindran using HBCl₃ · OEt₂/BCl₃ [1] as hydroboration reagent [2]. Because hydroboration reactions with Me₃SiH/BCl₃ are more convenient [3], acetylene [4], 3,3-dimethyl-1-butyne [5, 6], phenylacetylene [7], and mesitylacetylene [7] have been hydroborated according to this method. Zhao et al. [8] observed that 1-octyne and 1-hexyne undergo both monohydroboration and chloroboration when the alkyne was reacted with HBCl₂ · SMet in a 1.4 : 1 ratio at –20 °C in the presence of BCl₃. At 0 °C double hydroboration took place preferentially [8]. The bromoboration of 1-hexyne, investigated by Blackborow [9], shows that Z- or E-bromo-hex-1-ene-1-ylidibromoborane (I), Z,E- and Z,Z-bis(2-bromo-hex-1-ene-1-yl)bromoborane (II) and Z,Z,Z-tris(2-bromo-hex-1-ene-1-yl)boration (III) can be prepared by addition of a stoichiometric amount of 1-hexyne to tribromoborane. The Z-I, Z,Z-II and Z,Z,Z-III isomers, respectively, are formed preferentially. In the case of chloroboration no definite results regarding the preferred configurations of chlorohexenylidichloroborane, bis(chlorohexenyl)chloroborane and tris(chlorohexenyl)boration were reported because of difficulties in determining the configuration of the hexenylboranes [9].

We report here on the hydroboration of propyne and 1-butyne with BCl₃ and Me₂SiH in equimolar amounts, which leads to the expected 1,1-bis(dichloroboryl)alkanes 1, whereas the reaction of propyne with BCl₃ and Me₂SiH in the molar ratio 1.25 : 1 forms a product mixture of monohydroborated and haloborated compounds. Furthermore the chloroboration products of propyne and 1-butyne were investigated. This included substitution reactions of the organo-chloroborane products to obtain crystalline derivatives, suitable for X-ray structure analyses.

Results and Discussion

Synthesis and reactivity of organo-chloroboranes

Hydroboration of propyne and 1-butyne with equimolar amounts of Me₂SiH and BCl₃ at –78 °C in pentane leads to the products 1a and 1b, respectively, in good yields. The NMR spectra of 1a are in agreement with the reported data [6]. The ¹H, ¹¹B and ¹³C NMR spectra of 1b exhibit the expected
Table 1. Crystal data and structure refinement for 6a, 7a, 6b, and 8b.

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<tr>
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<th>6a</th>
<th>7a</th>
<th>6b</th>
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signals (for details see experimental section). An EI mass spectrum of 1b shows the molecular ion peak [M⁺] at m/z = 218.

Both hydroboration 2 and chloroboration products 3 and 4 are obtained in the reaction of propyne and 1-butyne, respectively, with BCl₃ and Me₃SiH in the molar ratio 1.25:1. The isolation of the compounds 2 and 3 is difficult because of similar boiling points. Compounds 3 and 4 are also formed in absence of Me₃SiH in excellent yields. Depending on how long propyne or 1-butyne, respectively, is bubbled through the reaction solution, the product ratio of monoalkenylated to trisalkenylated borane varies. In the case of 1-butyne, the appearance of E,E-bis(2-chloro-but-1-ene-1yl)chloroborane (5b) is observed. It is surprising that no indication is found for the existence of bis(propenyl)-chloroborane (5a) which also should be formed as intermediate during the chloroboration of three molecules of propyne. Heating of compound 3 leads to the symmetrical product 4 with elimination of BCl₃.

In order to have evidence for the exact configuration the products 3, 4 and 5b were reacted with catechol or pyridine to obtain crystalline derivatives appropriate for X-ray structure analyses. Compounds 3a, b gave the substitution products 6a, b, while 4 and 5b yielded the donor-acceptor compounds 7a, 7b and 8b.

The crystal structure analyses reveal that the monoalkenylated 6a and 6b, the bisalkenylated 8b and the trisalkenylated compound 7a have E configuration. Most probably the kinetically preferred
Fig. 1. Structure of 6a in the crystal; selected bond lengths [Å] and angles [°]: B1-C1 1.532(2), C1-C2 1.320(2), C2-C1 1.760(2), C2-C3 1.483(3), B1-O1 1.392(2), B1-O2 1.396(2), C1-B1-O1 121.8(1), C1-B1-O2 127.7(2), O1-B1-O2 110.6(1).

Fig. 2. Structure of 6b in the crystal; selected bond lengths [Å] and angles [°]: B1-C7 1.534(2), C7-C8 1.317(2), C8-C1 1.757(1), B1-O1 1.395(1), B1-O2 1.395(1), C7-B1-O1 127.1(1), C7-B1-O2 121.8(1), O1-B1-O2 111.1(1).

Z-isomers are formed first at low temperature. Under distillation conditions the activation energy necessary for isomerisation is supplied, so that finally the thermodynamically most stable E-configurated products are formed. The olefinic protons of 3b, 4b, 5b, 6b, 7b and 8b would be expected to show a triplet pattern, however, the fine structures were not well resolved and therefore the resonances were treated as "singlets".

Crystal structures of 6a, 6b, 7a and 8b

To elucidate the structures, X-ray diffraction studies were carried out (crystal data and structure refinement parameters for 6a, 6b, 7a and 8b are presented in Table 1). The colorless crystals of 6a, grown at –30 °C from a solution in dichloromethane, belong to the monoclinic system, space group P21/n. The molecular structure is shown in Fig. 1. The coordination of the boron atom is trigonal planar.

A single crystal of 6b was grown from a solution in dichloromethane at 20 °C. 6b crystallizes in the monoclinic space group P21/n. The molecular structure is shown in Fig. 2. For all distances and bonding angles no significant differences in comparison to the structural data of 6a are observed.

Crystals of 7a and 8b were grown from toluene at –30 °C. 7a crystallizes in the orthorhombic space group P212121, while 8b belongs to the triclinic
Experimental Section

All experiments were performed under argon using the Schlenk technique. Solvents were dried, distilled and saturated with nitrogen. Glassware was dried with a heat gun under high vacuum. ¹H, ¹³C and ¹¹B NMR: Bruker DRX 200 spectrometer, Et₂O-BF₃ was used as the external standard for ¹¹B NMR. As internal references for ¹H and ¹³C NMR spectra the signals of the deuterated solvents were used and calculated for TMS. The mass spectra were measured on a ZAB-2F VH Micromass CTD spectrometer (EI and HR-EI techniques) and on a Jeol MS station JMS 700 (EI, and HR-EI techniques). – Melting points (uncorrected) were measured with a Büchi apparatus using capillaries which were filled under argon or nitrogen and sealed.

1,1-Bis(dichloroboryl)butane (1b)

Dried 1-butyne is bubbled at −78 °C through a solution of 76 g (0.65 mol) of BCl₃ in 250 ml of pentane. At the same time a solution of 67 g (0.55 mol) of BCl₃ in 150 ml of pentane. At the same time 2.93 q, 3 J = 17.2 Hz, 1 H, CH₂Cl₂), 7.10 - 7.29 (m, 1 H, CHCl₂). – ¹³C{¹H} NMR (50.32 MHz, CDCl₃): δ = 14.3 (CH₂Cl₂), 24.9 (CH₂Cl₂), 32.9 (Br₂CHCl₂), 49 (br., Br₂CHCl₂). – ¹¹B NMR (64.21 MHz, CDCl₃): δ = 60.3. – MS (EI, 70 eV): m/z (%): 236 (1) [M⁺], 196 (18) [M⁺ - C₂H₄Cl₂], 161 (33) [M⁺ - Cl₂C₂H₄Cl2; 102 (100) [M⁺ - Cl - BCl₃], 81 (89) [BCl₂⁺], 43 (66) [C₂H₄⁺], 29 (67) [CH₂⁺].

E-1-Dichloroboryl-prop-1-ene (2a), E-1-dichloroboryl-2-chloro-prop-1-ene (3a) and E,E,E-tris(2-chloro-prop-1-ene-1-yl)borane (4a)

Dried propyne is bubbled at −78 °C through a solution of 67 g (0.55 mol) of BCl₃ in 150 ml of pentane. At the same time a solution of 29.0 g (0.39 mol) of trimethylsilane in 50 ml of pentane is added slowly via a dropping funnel so that almost all propyne passing through the solution is absorbed. Then the reaction mixture is allowed to warm to 20 °C. After removal of the pentane at 50 mbar the residue is distilled to yield 38.4 g of 2a (55.1%), 12.3 g of 3a (13.7%) and 5.4 g of 4a (4.0%). 2a: B. p. 40 °C / 200 mbar. – ¹H NMR (200.13 MHz, CDCl₃): δ = 1.98 (dd, 3 J = 6.6 Hz, 2 J = 1.5 Hz, 3 H, CH₂Cl₂), 6.08 (dq, 3 J = 17.2 Hz, 2 J = 1.5 Hz, 1 H, BCl₃), 7.10 - 7.29 (m, 1 H, CHCl₂). – ¹³C{¹H} NMR (50.32 MHz, CDCl₃): δ = 22.0 (CH₂Cl₂), 132 (br., BCl₃), 160.8 (CHCl₂). – ¹¹B NMR (64.21 MHz, CDCl₃): δ = 52.5. – MS (EI, 70 eV): m/z (%): 122 (23) [M⁺], 86 (100) [C₂H₅BCl⁺].

Alternative synthesis of 3a and 4a

Dried propyne is bubbled at −78 °C through a solution of 47.3 g (0.4 mol) of BCl₃ in 250 ml of pentane for 1 h. Then the reaction mixture is allowed to warm to 20 °C. An ¹¹B NMR spectrum of the crude product shows that only 3a is formed. Then pentane is removed in a vacuum and the residue is purified by distillation to give 42.7 g of 3a (67.6%) and 5.7 g of 4a (6.0%).

E-1-Dichloro-2-chloro-but-1-ene (3b), E,E-bis(2-chloro-but-1-ene-1-yl)chloro-borane (5b) and E,E,E-tris(2-chloro-but-1-ene-1-yl)borane (4b)

Dried 1-butyne is bubbled at −78 °C through a solution of 47.3 g (0.4 mol) of BCl₃ in 250 ml of pentane for 3 h. Then the reaction mixture is allowed to warm to 20 °C. After removal of pentane at 50 mbar the residue is distilled to yield 54.8 g of 3b (79.1%), B. p. 88 °C / 160 mbar) and 4.3 g of 5b (4.7%). B. p. 52 °C / 0.05 mbar). A third fraction is obtained at 90 - 100 °C / 0.5 mbar consisting of 3.17 g of 5b (3.5%) and 2.2 g of 4b (2.0%). The separation of 4b from 5b was not possible (yield determined by ¹¹B NMR). 3b: B. p. 88 °C/160 mbar. – ¹H NMR (200.13 MHz, CDCl₃): δ = 1.23 (t, 3 J = 7.4 Hz, 3 H, CH₂CH₂), 2.93 (q, 3 J = 7.4 Hz, 2 H, CH₂CH₂), 6.24 (s, 1 H, BCl₃). – ¹³C{¹H} NMR (50.32 MHz, CDCl₃): δ = 13.0 (CH₂CH₂),
E-1-[1,3,2-Benzodioxaborol-2-yl]-2-chloro-prop-1-ene (6a)

Catechol (110 mg, 1 mmol) is dissolved in 20 ml of CH₂Cl₂ and 160 mg (1 mmol) of 3a is added dropwise at -60 °C. After the solution is allowed to warm to 20 °C, CH₂Cl₂ is removed in a vacuum to give 169 mg of colorless 6a (85.4%). - M. p. 48 °C. - 1H NMR (200.13 MHz, CDCl₃): δ = 2.52 (d, 3H), 7.3 Hz, 6 H, CH₂CH₂). 5.86 (q, 3J = 7.0 Hz, 1 H, BCH), 7.18-7.20 (m, 4 H, CH₆H), - 13C[¹ Hirrama (50.32 MHz, CDCl₃): δ = 26.5 (CCC₃H), 112.6, 123.1, 148.1 (C₆H₄), 153 (br. BCH), 156.0 (CCCl₃H). - 11B NMR (64.21 MHz, CDCl₃): δ = 30.0 - MS (EI, 70 eV): m/z (%) = 194 (28) [M⁺], 154 (100) [M⁺ - CH₆H₄ - HR-MS: m/z = 194.0304 (M⁺)], calcd. 12C12H11B13Cl15O: 194.0306 (Δ = 0.2 mmu).

E-1-[1,3,2-Benzodioxaborol-2-yl]-2-chloro-but-1-ene (6b)

Catechol (1.10 g, 10 mmol) is dissolved in 80 ml of CH₂Cl₂ and 1.71 g (10 mmol) of 3b is added dropwise at -60 °C. After the solution is allowed to warm to 20 °C, CH₂Cl₂ is removed in a vacuum to yield 1.90 g of colorless 6b (91.3%). - M. p. 28 °C. - 1H NMR (200.13 MHz, CDCl₃): δ = 1.24 (t, 3J = 7.4 Hz, 3 H, CH₃CH₂), 2.89 (q, 3J = 7.4 Hz, 2 H, CH₂CH₂), 5.86 (s, 1 H, BCH), 7.00 - 7.25 (m, 4 H, CH₆H₄), - 13C[¹ Hirrama (50.32 MHz, CDCl₃): δ = 13.2 (CH₂CH₂), 32.3 (CH₃CH₂), 112.5, 122.8, 147.8 (C₆H₄), 159 (br. BCH), 162.2 (CCCl₃H). - 11B NMR (64.21 MHz, CDCl₃): δ = 29.9 - MS (EI, 70 eV): m/z (%): 108.13 (13) [M⁺], 173 (2) [M⁺ - Cl], 154 (100) [M⁺ - CH₂CH₂], 144 (7) [M⁺ - Cl - CH₂CH₂], 119 (2) [C₆H₄O₂B⁺]. - HR-MS (EI): m/z = 208.0465 (M⁺), calcd. 12C10H10B13Cl15O: 208.0468 (Δ = 0.3 mmu).

E.E-Tris(2-chloro-prop-1-ene-1-yl)borane-pyridine adduct (7a)

The solution of 0.51 g (2.1 mmol) of 4a in 20 ml of pentane is cooled to -10 °C and 0.17 g (2.1 mmol) of pyridine is added dropwise. After the solution is allowed to warm to 20 °C, pentane is removed in a vacuum to yield 0.64 g of colorless 7a (94.1%). - M. p. 78 °C. - 1H NMR (200.13 MHz, CDCl₃): δ = 1.95 (d, 3J = 0.8 Hz, 9 H, C₆H₄Cl), 5.84 (q, 3J = 0.8 Hz, 3 H, BCH), 7.66 (m, 2 H, py-H), 8.07 (m, 1 H, py-H), 8.66 (m, 2 H, py-H). - 13C[¹ Hirrama (50.32 MHz, CDCl₃): δ = 24.4 (CCCl₃H), 138 (br. BCH), 145.7 (CCCl₃H), 126.1, 135.0, 140.9 (py-C). - 11B NMR (64.21 MHz, CDCl₃): δ = -3.3.

E.E-Bis(2-chloro-but-1-ene-1-yl)chloroborane-pyridine adduct (8b)

The solution of 1.03 g (4.6 mmol) of 5b in 30 ml of pentane is cooled to -10 °C and 0.36 g (4.6 mmol) of pyridine is added dropwise. After the solution is allowed to warm to 20 °C, pentane is removed in a vacuum to yield 1.27 g of colorless 8b (91.2%). - M. p. 72 °C. - 1H NMR (200.13 MHz, CDCl₃): δ = 1.03 (t, 3J = 7.3 Hz, 6 H, CH₂CH₂), 2.39 (q, 3J = 7.3 Hz, 4 H, CH₃CH₂), 5.87 (s, 2 H, BCH), 7.71 (m, 2 H, py-H), 8.13 (m, 1 H, py-H), 8.90 (m, 2 H, py-H). - 13C[¹ Hirrama (50.32 MHz, CDCl₃): δ = 12.3 (CH₂CH₂), 30.9 (CH₃CH₂), 135 (br. BCH), 144.7 (CCCl₃H), 126.0, 135.0, 142.0 (py-C). - 11B NMR (64.21 MHz, CDCl₃): δ = 2.5.
$^{13}$C($^1$H) NMR (50.32 MHz, CDCl$_3$): $\delta = 12.1$ (CH$_2$CH$_3$), 31.0 (CH$_2$CH$_3$), 141 (br., BCH), 144.7 (CCICH$_2$), 126.0, 141.5, 145.6 (py-C). $^{-11}$B NMR (64.21 MHz, CDCl$_3$): $\delta = -4.2$.

Crystal structure determinations of 6a, 6b, 7a, 8b

A summary of the crystal data and details of the structure determinations is given in Table 1. Data were collected on a Bruker AXS area detector Smart 1000 (Mo-K$_\alpha$-radiation, $\lambda = 0.71073$ Å, $\omega$-scans) at low temperature. Data were corrected for Lp- and absorption effects (semi-empirical, SADABS [12]). The structures were solved by direct methods and refined by full-matrix least-squares methods based on $F^2$ (SHELXTL) [13]. The crystals of 6a were twinned. A data set of non-overlapped and exactly overlapped reflections of both components was prepared using the program GEMINI [14]. The structure was refined using the TWIN option in SHELXL97 [15]. The ethyl group in 6b is disordered. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in difference Fourier synthesis and refined with isotropic displacement parameters (with exception for those of the disordered ethyl group in 6b, which were inserted in calculated positions and refined using a riding model). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-176330 (6a), -176331 (6b), -176332 (7a), -176333 (8b).

Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.)+44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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