Synthesis of Pentaalkyl-6-bromo-2,3,4,5-tetracarba-nido-hexaboranes(6)

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Z. Naturforsch. 51b, 859 – 864 (1996); received November 22, 1995
2,3,4,5-Tetracarba-nido-hexaboranes(6). Exchange Reactions, NMR Spectra

Peralkylated 2,3,4,5-tetracarba-nido-hexaboranes(6) 1 react with boron tribromide, BBr₃, via selective exchange of the alkyl substituent in 6-position to give the corresponding new 6-bromo derivatives 2 in quantitative yield. The 6-iodo derivatives 2(1) can be prepared in the same way using BI₃. Treatment of the carbaboranes 2 with Et₃BH leads to the 1,2,3,4,5-pentaalkyl-2,3,4,5-tetracarba-nido-hexaboranes(6) 3. 1,3,4,6-Tetraethyl-2,3,4,5-tetracarba-nido-hexaborane(6) 4 reacts with BBr₃ via degradation of the carbaborane cage to give Et₂B₂Br² and (Z)-1,4-bis[bis(dibromoboryl)-3-hexene 5. A new bis(diethylboryl)-substituted dialkenyl(bromo)borane 8 was prepared, but attempts failed to convert it into a 1-bromo- or 6-bromo-nido-C₄H₆-carbaborane. Treatment of 1,1-dialkyldiethylboryl-4-ethylstannoles 9 with a large excess of BBr₃ also affords 5, whereas 6-bromo-1,3,4-triethyl-2,3,4,5-tetracarba-nido-hexaborane(6) 11 was isolated in low yield (<5%) from the reaction between 9 and BBr₃ (slight excess).

Introduction

Peralkylated 2,3,4,5-tetracarba-nido-hexaboranes(6) A are known since the mid-sixties [1]. Although they are readily accessible and surprisingly stable (in contrast to the parent compound nido-C₄B₆H₆ [2]) towards many reactive species, a systematic chemistry of the compounds A has not been developed as yet. Claims for the successful synthesis [3] of their classical counterparts, the peralkylated 1,4-dibora-2,5-cyclohexadienes B, could not be confirmed [4]. Subsequently, it was shown that compounds of type B can be prepared from the exchange reaction between the corresponding spiro-tin derivatives and organoboron dihalides under mild reaction conditions [5], and that compounds B start to undergo rearrangement already at temperatures > -20 °C to give the carbaboranes of type A via a complex route (the direct interconversion B → A is forbidden by symmetry [6]). The new route possibly involves cleavage of the six-membered rings B into two bori­renes which then recombine to give A [5]. Recent calculations [7] suggest that halogen substituents at the boron atom(s) in A lead to a preference of the classical structure, as was found in the case of 1,4-difluoro-1,4-dibora-2,5-cyclohexadiene [8]. However, we have found recently that tetraalkyl-1,6-dihalogeno-2,3,4,5-tetracarba-nido-hexaboranes(6) C are perfectly stable and do not show any tendency to undergo valence isomerization [9]. In this work, we report on attempts to prepare the carbaboranes D or E by the reaction of peralkylated carbaboranes A with boron tribromide. We have also included a partially alkyalted carbaborane F [10b] in this study in order to probe the limitation of the stability of the carbaborane cage. Furthermore, we report on attempts to prepare 6-bromo-1,3,4-triethyl-2,3,4,5-tetracarba-nido-hexaboranes(6), starting from 1,1-dialkyl-3-diethylboryl-4-ethylstannoles [10] or (E)-1-trimethylstannyl-2-diethylboryl-1-butene [11] and BBr₃.

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Results and Discussion

Synthesis

Treatment of the peralkylated carbaboranes 1 (corresponding to type A) with an excess of boron tribromide (or boron triiodide) leads selectively to compounds 2 (or 2(1)), carbaboranes of type E, via exchange of the B(6)-alkyl group against bromine (or iodine) [eq. (1)] (see also Fig. 1). There is no indication of the formation of carbaboranes C (even in the presence of a large excess of BBr₃ and on prolonged heating) or D. Interestingly, carbaboranes of type D are readily accessible, again via a selective reaction, by treating the 1,6-dibromo-carbaboranes C with alkyl lithium or Grignard reagents [12]. We note that interconversion between the carbaboranes D and E does not occur.

\[ \text{RnX} + \frac{\text{BBr₃}}{\Delta} \rightarrow \text{EtBBr₂} \]

The compounds 2 are obtained as colourless, oily, moisture-sensitive liquids after distillation under reduced pressure. As shown in eq. (2), the substitution of the B(6)-Br by a B(6)-H function is straightforward and affords the compounds 3, again without isomerization. This is promising for the chemistry of the carbaboranes 2, since (i) their precursors 1 are readily available [1], and (ii) it appears that the substitution of the B(6)-Br function in 2 by reaction with various nucleophiles works very well. The carbaboranes 3 are much more sensitive, e.g. towards oxygen and moisture, than the peralkylated compounds 1.

The selective formation of 2, together with the observation that carbaboranes E cannot be converted into compounds D, strongly suggests an exocyclic alkyl/Br exchange for the reaction shown in eq. (1). Otherwise one would expect either a mixture of 2 and carbaboranes of type D, or at least partial degradation of the carbaborane cage. Work is in progress on ¹⁰B isotopic labelling in order to prove this assumption.

In analogy to the reaction shown in eq. (1), we have studied the reaction between the partially alkylated carbaborane 4 [10] with BBr₃ in a 1:1 ratio and also with an excess of BBr₃. The 1:1 reaction affords a complex mixture of compounds, indicating the decomposition of the carbaborane system. In the presence of an excess of BBr₃, the carbaborane 4 reacts more cleanly to give EtBBr₂ and the product 5 shown in eq. (3). In the tetraborylated compound 5, the C₄-chain of the carbaborane is retained, but the carbaborane cage is absent. This means that it will be difficult to establish reaction conditions for a successful high-yield synthesis of B(6)-halogeno-substituted 2,3,4,5-tetracarba-*nido*-hexaboranes(6) bearing less than four C-alkyl substituents.
The synthesis of classical boranes in which the boron atoms bear the desired functions could open a route towards 2-bromo-1,3,4-triethyl-2,3,4,5-tetracarba-nido-hexaborane avoiding an excess of BBr₃. In principle, it should be possible to convert such a borane into a carbaborane by elimination of Et₃B. The synthesis of borane 8, fulfilling at least some of these conditions, is readily achieved as shown in eq. (4). However, various attempts to eliminate Et₃B either by heating 8 or by BH-catalysed exchange [13] failed. A dialkyl(chloro)borane, [Et₂B(Et)C=C(Et)]₂BCl, similar to 8, was prepared by other methods; it was converted into the EtB-derivative via treatment with Et₃Al, and, after elimination of Et₃B, hexaethyl-1,4-dibora-2,5-cyclohexadiene was trapped as a ligand in transition metal complexes [14].

The reaction of 1,1-dialkyl-3-diethylboryl-4-ethyl-stannoles with organoboron dihalides affords carbaboranes of type F in moderate yields [10]. Therefore we have also studied the reaction of these stannoles with BBr₃. With an excess of BBr₃ [eq. (5c)], EtBBR₂ and compound 5 [see also eq. (3)] were identified as the sole products (according to ¹H, ¹¹B and ¹³C NMR data) and only weak signals for traces of nido-C₄B₂-carbaboranes were detected in the ¹¹B NMR spectra.

If only a slight excess of BBr₃ is used in the reaction with the stannole, a small amount (< 5%) of a volatile material can be separated from the reaction mixture by fractional distillation and identified as the pure carbaborane 11. 3-Borolenes of the type 10 [eq. (5a)] are likely intermediates since they have been detected previously in the reactions of 1,1'-spirobistannoles with BBr₃ [9], and also in the course of the 1:1 reaction between 9 and PhBCl₂ [10b, 12]. The final intramolecular elimination of Me₂SnBr₃ requires rather harsh reaction conditions (≥ 150 °C), and is accompanied by many side reactions.

NMR spectroscopic results

The reactions according to eqs. (1)–(5) are readily monitored by ¹¹B NMR (see Fig. 1). ¹¹B and ¹³C NMR data of the carbaboranes 1–3 are listed in Table I. The data for 1 agree with those measured previously [4, 15]. The influence of the bromine substituent in 2 on the δ¹¹B data is analogous to that observed for carbaboranes C [9]. Similarly, the presence of the B(6)–H group in 3 affects the δ¹¹B values in the expected way [9, 16]. The δ¹¹B data of the pentaalkyl derivatives 2 and the 1,3,4-triaryl derivative 11 are almost identical. Surprisingly, the δ¹³C(2,3,4,5) values are hardly affected by the B(6)–Br group when compared with those for 1. In contrast, the B(6)–H group takes a noticeable influence in particular on δ¹³C(2,5) in the direction opposite to the effect usually ascribed to the replacement of a carbon atom in β-position by hydrogen; thus the δ¹³C(2,5) nuclei in 3 become deshielded with respect to 1, and there is also a slight deshielding of the ¹³C(3,4) nuclei.

The structure of 5 in solution is supported by the ¹³C NMR spectra which show one signal for the olefinic carbon atoms (δ¹³C 142.9) and a typi-
Table I. $^{11}$B and $^{13}$C NMR data of 2,3,4,5-tetracarba-nido-hexaboranes(6) 1, 2 and 3.

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$^a$ The compounds 1c, d, 2c, d and 3c, d are mixtures of isomers; $^b$ 6-Iodo-carbaboranes 2c, d(I); $^c$ $\delta^{11}$B(6) 5.9; $^d$ $\nu$(11B-1H) = 137.6 Hz; $^e$ $\nu$(11B-1H) = 131.9 Hz; $^f$ $\nu$(11B-1H) = 133.4 Hz; $^g$ broad signals owing to partially relaxed $^{13}$C-$^{11}$B spin-spin coupling; $^h$ $\nu$(13CnB) = 74.2 Hz; $^i$ $\nu$(13CnB) = 79.5 Hz; $^j$ $\nu$(13CnB) = 75.2 Hz; $^k$ $\nu$(13CnB) = 77.1 Hz; $^l$ $\nu$(13CnB) = 76.1 Hz; $^m$ $\nu$(13CnB) = 75.9 Hz; $^n$ $\nu$(13CnB) = 76.0 Hz; $^o$ $\nu$(13CnB) = 75.5 Hz; $^p$ $\nu$(13CnB) = 77.3 Hz.

Boron tribromide (40 g, 160 mmol) is added to the peralkylated carbaboranes 1 and the mixtures are stirred at room temperature for 12 h (1a), heated to 120 °C for 24 h (1b) or heated to 100 °C for 12 h (1c, d). Fractional distillation gives 2a (b.p. 60 °C/0.005 Torr), 2b (b.p. 69 °C/0.005 Torr) and 2c, d (b.p. 64 °C/0.005 Torr) in 90% yield each as yellowish liquids.

**Experimental**

All reactions were carried out in an inert atmosphere of Ar or N₂, observing all precautions to exclude moisture and oxygen. The carbaboranes 1 and 4, the alkenylboranes 6 and 7, and the stannole 9 were prepared following literature procedures. $^1$H, $^{11}$B and $^{13}$C NMR spectra were recorded using Bruker AC 300 and ARX 250 instruments equipped with multinuclear probeheads (samples ca. 10–20% in C₆D₆ at 25 ± 1 °C in 5 mm o.d. tubes were measured, if not mentioned otherwise). Chemical shifts are given with respect to internal Me₄Si (δ₁H = -0.63, s, 3H) and external Et₂O–BF₃ [δ₁₁B = 0 for $\varepsilon(^{11}B) = 32.083971$ MHz].

Pentaalkyl-6-bromo-2,3,4,5-tetracarba-nido-hexaboranes(6) (2)

Pentaalkyl-2,3,4,5-tetracarba-nido-hexaboranes(6) (3)

A solution of Li[Et₃BH] in THF (1 M; 20 ml) is added slowly to a stirred solution of 2 (19 mmol) in 20 ml of THF at 0 °C. After stirring for 1 h (3a), 6 h (3b) or 4 h (3c, d) at room temperature, the
solvent is removed, and 20 ml of hexane are added to the residue, LiBr is filtered off and fractional distillation gives 3b (b.p. 45 °C/0.005 Torr) and 3c, d (b.p. 39 °C/0.005 Torr) in ≈50% yield as colourless, mobile self-inflammable (on contact with air) liquids. Compound 3a was prepared only on a small scale for NMR measurements.

3a: $^1$H NMR: $\delta^1$H = -0.60 (s, 3H, B(1)-Me); 1.71, 1.42 (s, s, 12H, C(2,5)-Me and C(3,4)-Me); 3.98 (1:1:1:1 q, $^1$J(B,1H) = 137.6 Hz, B(4)-H).

3b: $^1$H NMR: 0.1, 0.54 (q, q, 5H, B(1)′-Et); 2.04, 1.15, 0.99 (m, t, 20H, C(2,5)-Et and C(3,4)-Et); 4.05 (1:1:1:1q, $^1$J(B,1H) = 132.0 Hz, B(6)-H).

Reaction of 1,3,4,6-tetraethyl-2,3,4,5-tetracarba-nido-hexaborane(6) (4) with BBr₃

A solution of 0.94 g (0.5 mmol) of 4 in 1 ml of [D₆]toluene is cooled to −78 °C in an NMR tube, and 0.5 g (2 mmol) of BBr₃ are added through a syringe. The mixture is slowly warmed to room temperature. $^1$H, $^{11}$B and $^{13}$C NMR data indicate the formation of (Z)-3,4-bis[bis(dibromoboryl)]-1,3-bismethyl-3-hexene 5.

5 in [D₆]toluene: $^1$H NMR: $\delta^1$H = 4.09 (s, 2H, HC(BBr₂)₂); 2.03, 0.90 (q, q, 10H, C(3,4)-Et).−$^{13}$C NMR: $\delta^{13}$C = 142.9, 68.9, 23.9, 13.6.−$^{11}$B NMR: $\delta^{11}$B = 60.0.

(E, E)-3,7-Bis(diethylboryl)-5-bromo-5-bora-3,6-nonadiene (8)

A solution of 1.47 g (5 mmol) of 7 in 30 ml of hexane is cooled to −78 °C, and a solution of 1.43 g (5 mmol) of 6 in 20 ml of hexane is added dropwise during 30 min. After warming to room temperature, the solvent is removed in a vacuum and fractional distillation of the residue gives 0.9 g of Me₂SnBr and 1.25 g (74%) of 8 as a colourless, oily, air- and moisture-sensitive liquid (b.p. 87 °C/8·10⁻³ Torr).−$^1$H NMR: $\delta^1$H = 6.37 (t, 2H, H-⁵-C=); 1.94, 0.96 (dq, t, 10H, Et-C=); 1.27, 1.02 (q, t 20H).−$^{11}$B NMR: $\delta^{11}$B = 55.7 (BBr, 76.6 (BE₂), 195.6 (C(3)), 130.6 (C(4)), 20.0 (Br), 10.2 (BE₂).

6-Bromo-1,3,4-triethyl-2,3,4,5-tetracarba-nido-hexaborane(6) (11)

After cooling a solution of 4.74 g (16 mmol) of freshly prepared [10a] 3-diethylboryl-4-ethyl-1,1-dimethylstannane in 60 ml of pentane to −78 °C, a solution of 5.0 g (20 mmol) of BBr₃ in 20 ml of pentane is added slowly (2 h). A vigorous reaction takes place, indicated by a colour change from light yellow to dark red and brown. The mixture is warmed to room temperature and stirred for 2 h. Then it is kept for 24 h at −78 °C, and a small amount of insoluble material (identified to consist mainly of Me₂SnBr₂) is filtered off, keeping the solution at −78 °C. Pentane is removed in a vacuum at room temperature. The temperature in the oil bath is raised to ca. 150 °C, keeping the pressure at 0.01 Torr, and all volatile material is collected in a cold (−78 °C) trap (Me₂SnBr₂, traces of pentane and the carbaborane 11). Fractional distillation of this material gives 0.15 g (4%) of pure 11 (b.p. 35 °C/0.01 Torr) as a colourless, air- and moisture-sensitive liquid.

Acknowledgment

Support of this work by the Deutsche Forschungsgemeinschaft, Volkswagen-Stiftung and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Prof. Dr. R. Köster (Mülheim a. d. Ruhr) for a generous gift of triethylborane and some of the carbaboranes 1.

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