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Cyclononatetraenyldipropylborane

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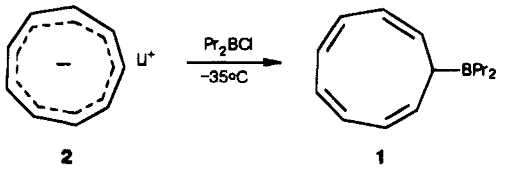
Summary: NMR investigations (including a low-temperature ^{13}C 2D NOESY experiment) demonstrated that [1,3]-boron shifts easily occur in the title compound ***1****, which therefore exhibits fluxional behavior. At room temperature, the unusual rearrangement* ***1*** *→* ***4*** *is the dominating reaction.*

Almost all known *β,γ*-unsaturated (allylic) triorganoboranes are fluxional molecules; *i.e.* fast [1,3]-boron shifts incessantly occurring in these compounds make them interconvert reversibly in either a degenerate or nondegenerate way.[1] Studies of this phenomenon in simple compounds of that type give unique information about the structure and reactivity of allylboranes.[1a] However, the most interesting objects in that respect are complex molecules (cyclic, polyunsaturated, or both) containing allylboron fragments because, in addition to multiple pathways for the sigmatropic boron shifts, some unexpected reactions are feasible in such compounds.[1b,c]

Cyclononatetraenylborane (**1**) seemed to be an interesting target molecule because a great variety of the possible thermal and photochemical rearrangements are known for substituted cyclononatetraenes,[2] which together with sigmatropic boron shifts could result in a unique dynamic behavior.

We have synthesized **1** by reaction of lithium cyclononatetraenide (**2**) with chlorodipropylborane in pentane at −35 °C (Scheme 1).[3]

Scheme 1. Synthesis of 1



Compound **1** was the only primary product of the reaction (Figure 1a); its structure was proved by ^1H–^1H COSY and XHCORR spectra recorded at −100 °C. Cyclononatetraenylborane (**1**) proved to be a fluxional molecule; *i.e.*, intense dynamics were found in both the ^1H and ^{13}C NMR spectra of **1** in the temperature range between −100 and 0 °C (Figure 1), while **1** undergoes a fast irreversible rearrangement at higher temperatures (Figure 1d,e).

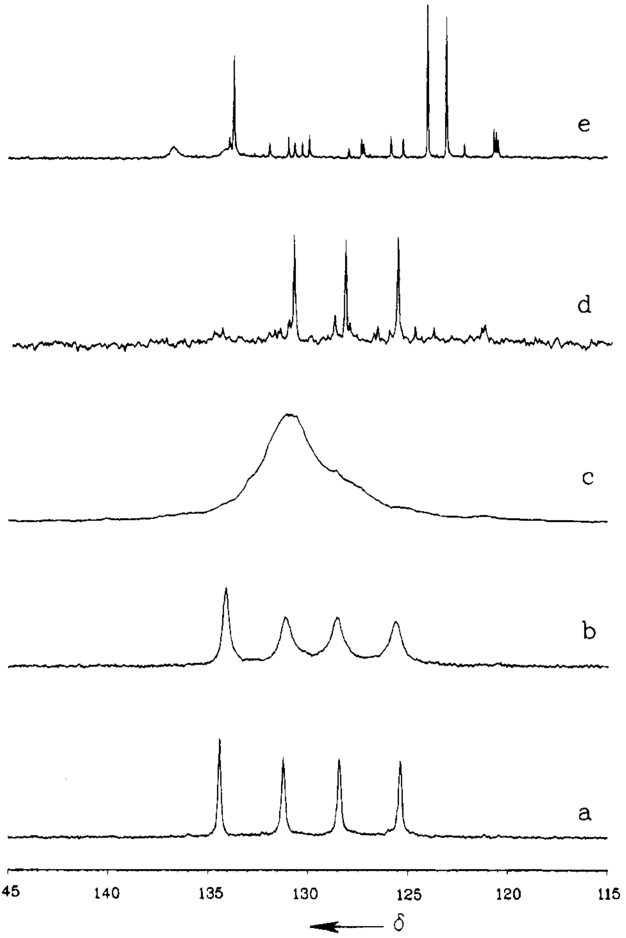


Figure 1. Section plots of ^{13}C NMR spectra (50 MHz, CD_2Cl_2) of **1** corresponding to olefinic carbon atoms of the borylation mixture (see experimental details in the text). (a) Initial spectrum at −100 °C. Four signals of the polyenic system of **1** indicate that **1** is the primary product. (b) Spectrum at −90 °C. Spectral lines are broadening due to reversible boron migration. (c) Spectrum at −60 °C. Only one broad signal is observed. (d) Spectrum of the same sample taken immediately after raising the probe temperature from −60 to +30 °C. Three signals correspond to the olefinic carbon atoms of the intermediate product **3b**; **1** is still present in the reaction mixture (about 50% by ^1H NMR), but its signals are not observed in the ^{13}C spectrum due to extensive broadening of the spectral lines. (e) Spectrum of the same sample after overnight storage at room temperature. It contains only signals of **4** (major product) and 15 low-intensity signals corresponding to olefinic carbon atoms of **3a**, **5a**, and **5b**.

Compound **1** is a unique example of a polyenic cyclic organoborane of the allylic type, and [1,3]-, [1,5]-, [1,7]-, and [1,9]-boron shifts could be expected in this compound. In order to distinguish between these processes, we have carried out a low-temperature 2D ^{13}C NOESY experiment. The spectrum shown in Figure 2 indicates that mutual exchange exists between every pair of carbon atoms of **1**. Nevertheless, analysis of the relative

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[1] (a) Bubnov, Yu. N.; Gurskii, M. E.; Gridnev, I. D.; Ignatenko, A. V.; Ustynyuk, Yu. A. Mstislavsky, V. I. *J. Organomet. Chem.* **1992**, *424*, 127–132. (b) Gurskii, M. E.; Gridnev, I. D.; Geiderikh, A. V.; Ignatenko, A. V.; Bubnov, Yu. N.; Mstislavsky, V. I.; Ustynyuk, Yu. A. *Organometallics* **1992**, *11*, 4056–4061. (c) Gridnev, I. D.; Gurskii, M. E.; Ignatenko, A. V.; Bubnov, Yu. N.; Il'ichev, Yu. V. *Organometallics* **1993**, *12*, 2487–2495.

[2] Scott, L. T.; Jones, M., Jr. *Chem. Rev.* **1972**, *72*, 181–202.

[3] Results of borylation were independent of the configuration of cyclononatetraenyl anion **2** used for the reaction; *all-cis*-**2**, *cis,cis,cis,-trans*-**2**, or their mixture gave only **1** as a primary product; see: Boche, G.; Bieberbach, A. *Chem. Ber.* **1978**, *111*, 2850–2858.

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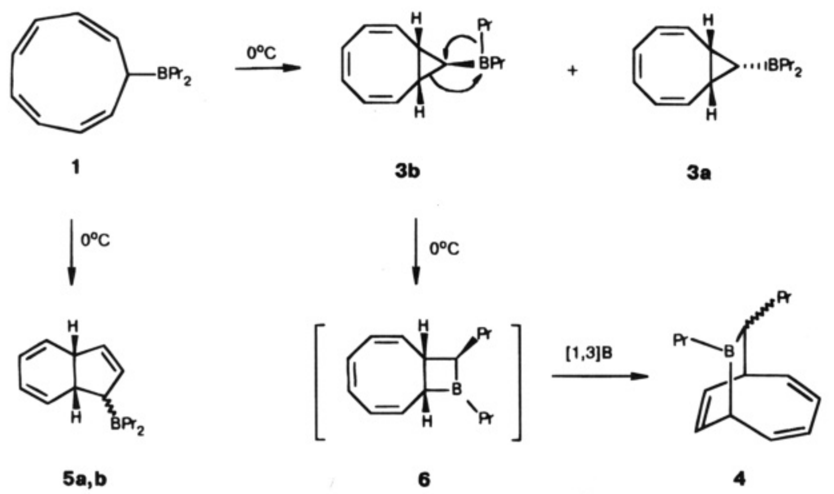
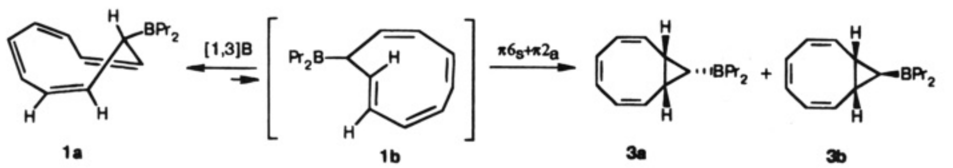
Scheme 2. Rearrangements Occurring in 1



Scheme 3. Possible Route of the Formation of 3a,b



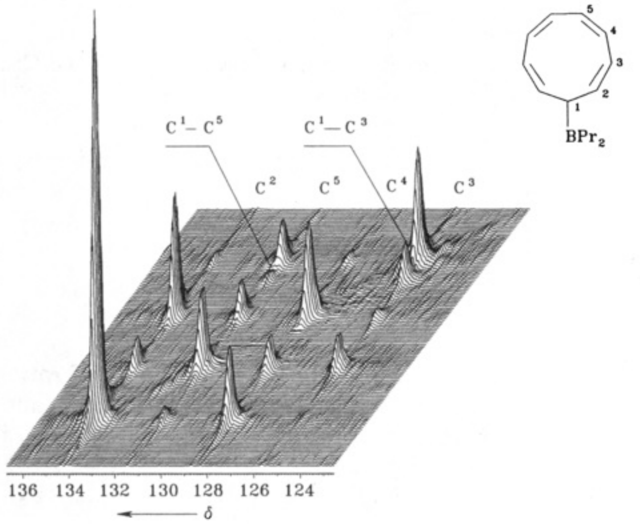


Figure 2. Stacked plot of the ^{13}C NOESY spectrum of **1** (50 MHz, −100 °C, CD_2Cl_2; spectrum size 1024 × 128; mixing time 0.1 s). The most intense cross-peak corresponds to the exchange between C-2 and C-4. C-3 gives an intense cross-peak with C-1 (it was folded in the F1 field). These two facts together with the relative intensities of other cross-peaks prove the scheme of consecutive [1,3]-boron shifts.

intensities of cross-peaks allowed us to conclude that the only dynamic process occurring in **1** is a series of consecutive [1,3]-boron shifts, resulting in a completely averaged ^{1}H spectrum of **1** at room temperature. Our previous studies of sigmatropic boron shifts in 2,4-pentadienyldipropylborane[1b] and 2,4,6-heptatrienyldipropylborane[1c] also indicated that [1,3]-boron shifts are usually the fastest ones.

It is well-known that all derivatives of cyclononatetraene,[4a] including Si, Ge, Sn, and As cyclononatetraenyls[4b] rearrange rapidly to the corresponding dihydroindenes at room temperature. However, we have found that the main primary products of the rearrangement of **1** are the isomeric bicyclo[6.1.0]-nonatrienes **3a,b**, which were identified by their ^{1}H, ^{13}C, and ^{1}H−^{1}H COSY spectra. The *exo* configuration of **3b** and *endo* configuration of **3a** were established on the basis of the size of the coupling constants $^{3}J(H^1,H^9)$, which are 6.3 and 10.1 Hz, respectively.[5] Compound **3a** remains in the resulting reaction mixture as a coproduct, while **3b** undergoes rearrangement into 9,10-dipropyl-9-borabicyclo[4.2.2]deca-2,4,7-triene (**4**).

Compound **4** is the main reaction product after distillation (see Figure 3), compounds **3a** and **5a,b** being coproducts (the ratio **4**:**5**:**3a** is 10:2:1).[6] We failed to observe any other intermediates between **3b** and **4**. Therefore, it can be assumed that a direct transformation of **3b** into **6** is possible, the latter being an allylic isomer of **4**; *i.e.*, the less strained **4** is formed rapidly from **6** as a result of a [1,3]-boron shift (Scheme 2). The very unusual transformation of **3b** to give **6** resembles rearrangements observed for cyclopropylcarbenes.[7]

Formation of **3a,b** from **1** is formally a thermal 8π-process, and it should therefore be antarafacial. Apparently, this process occurs through formation of the *cis,cis,cis,trans* isomers **1b**,[8] which can easily and reversibly interconvert to the *all-cis* isomer **1** through [1,3]-boron shifts out of the *endo* conformation of **1a** (Scheme 3).

Compound **4** is a fluxional molecule as well (Figure 3); two of its isomers differing in the orientation of the propyl group at C-9 and interconverting rapidly and

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[4] (a) Boche, G.; Heidenhain, F.; Thiel, W.; Eiben, R. *Chem. Ber.* **1982**, *115*, 3167−3190. (b) Boche, G.; Heidenhain, F. *J. Organomet. Chem.* **1976**, *121*, C49−C51.

[5] In corresponding chlorides the same couplings are known to be 4.2 Hz for the *exo* isomer and 8.6 Hz for the *endo* isomer.[10b]

[6] Structures of the compounds **4a** and **5a,b** were elucidated from 2D COSY and XHCORR spectra of their mixture with **3**.

[7] Grimme, W.; Riebel, H. J.; Vogel, E. *Angew. Chem.* **1968**, *80*, 803−804; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 823−824.

[8] (a) Neuenschwander, M.; Rutsch, W.; Engel, P. *Tetrahedron Lett.* **1979**, 233−236. (b) Boche, G.; Bernheim, D. *Lewaldt*, D.; Ruisinger, B. *Tetrahedron Lett.* **1979**, 4285−4286.

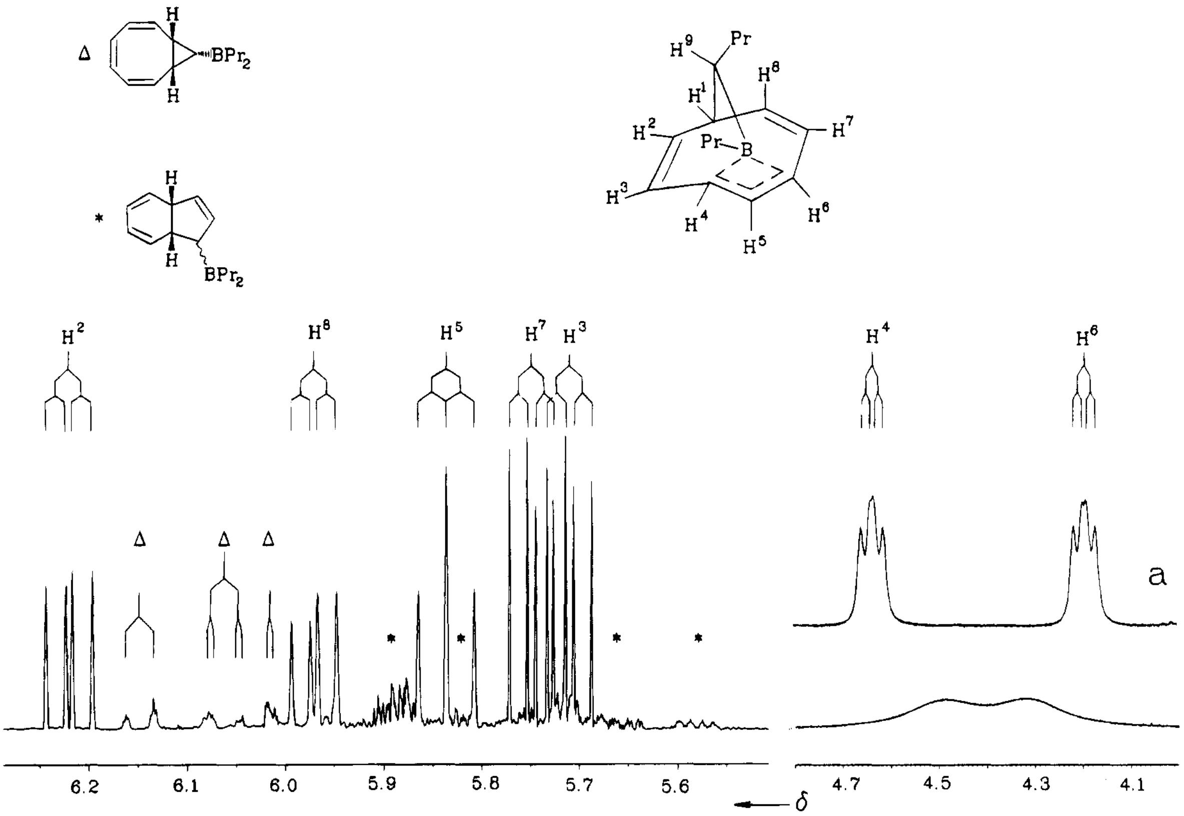
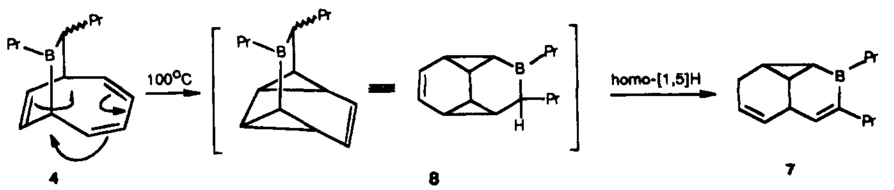


Figure 3. Section of the ^{1}H NMR spectrum of the mixture of compounds **4** (main product), **3a**, and **5a,b** (400 MHz, $CDCl_3$, 30 °C, TMS). Inset: coalescence pattern of the spectrum between 4.0 and 4.8 ppm at 80 °C.

Scheme 4. Thermolysis of 4



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reversibly result in an averaged ^{1}H spectrum at 80 °C (Figure 3, inset). Therefore, **4** is a peculiar heteroanalog of the $(CH)_{10}$ family of hydrocarbons, which are characterized by a great variety of sigmatropic and electrocyclic rearrangements.[9] Introducing boron in such molecules can even multiply the number of allowed processes due to the elimination of orbital prohibitions caused by the unoccupied 2p AO of boron. That statement is well illustrated by quantitative irreversible thermal rearrangement of **4** into compound **7** (Scheme 4).

It is known that the carbon analogue of compound **4** can be transformed into the carbon analog of compound **8**.[9] In the case of compound **4**, the reaction proceeds further, giving compound **7** by a [1,5]-homodienyl hydrogen shift due to the high stability of the vinyl–boron fragment.

Further studies of the dynamic behavior of **1** and **4** as well as the unusual chemical properties of **4** are in progress.

Experimental Procedure. The spectral data were obtained on Bruker AC-200P and AMX-400 (NMR) and UR-20 (IR) spectrometers.

A mixture of compounds **3a**, **4**, and **5** (in a 1:10:2 ratio) was prepared from cyclononatetraenyllithium[10] and chlorodipropylborane in hexane: yield 76%; bp 73–75 °C (0.08 Torr); $n_D^{20} = 1.5072$. IR (CCl_4): ν 1590, 1620, 1655, 3020, 3050 cm^{-1}. ^{11}B NMR (128 MHz, [D$_8$]-toluene, 25 °C, $BF_3 \cdot Et_2O$): δ 70.8 (**3**), 83.8 (**4**), 85.5 (**5**). Anal. Found: C, 83.91; H, 10.60; B, 5.11. Calcd for $C_{15}H_{23}B$: C, 84.12; H, 10.82; B, 5.05.

To obtain **7**, **4** was heated in a sealed tube for 2 h at 100 °C (water bath). Compound **7** was obtained quantitatively. IR (CCl_4): ν 1600, 3010, 3030 cm^{-1}. ^{11}B NMR (64 MHz, CD_2Cl_2, 25 °C, $BF_3 \cdot Et_2O$): δ 71.3.

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Supplementary Material Available: A table giving ^{1}H and ^{13}C NMR data for **1**, **3–5**, and **7** (1 page). Ordering information is given on any current masthead page.

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[9] (a) Jones, M., Jr.; Reich, S. D.; Scott, L. T. *J. Am. Chem. Soc.* **1970**, *92*, 3118–3126. (b) Jones, M., Jr.; Reich, S. D.; Scott, L. T.; Sullivan, L. E. *Angew. Chem.* **1968**, *80*, 631–623; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 644–645.

[10] (a) Katz, T. J.; Garrat, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 5194–5202. (b) LaLancette, E. A.; Benson, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 1941–1942.