Study of the rearrangement of cyclononatetraenyl(dipropyl)borane to 7,8-dipropyl-7-borabicyclo[4.2.2]deca-2,4,9-triene by NMR spectroscopy*

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Using NMR spectroscopy it was found that at ambient temperature 9-cyclononatetraenyl(dipropyl)borane (**1**) rapidly rearranges to give 7,8-dipropyl-7-borabicyclo[4.2.2]deca-2,4,9-triene (**2**), *cis-endo*-9-dipropylborylbicyclo[6.1.0]nona-2,4,6-triene (**3a**), and two isomeric boranes with dihydroindene skeletons (**4a,b**) (the ratio **2** : **3a** : **4a,b** is 10 : 1 : 2). *cis-exo*-9-Dipropylborylbicyclo[6.1.0]nona-2,4,6-triene (**3b**) is an intermediate product of the rearrangement; it is formed as a result of 8π-electrocyclization in *E,Z,Z,Z*-cyclononatetraenyl(dipropyl)borane **1a**. The transformation of bicycle **3b** to final product **2** occurs apparently *via* a synchronous exchange of the groups at the B atom (the transformation of the cyclopropane ring to the boracyclobutane ring accompanied by simultaneous migration of the propyl group from the B atom to the α-C atom). Borane **6** formed in this rearrangement rapidly isomerizes to **2** *via* a [1,3]-B shift.

Key words: 9-cyclononatetraenyl(dipropyl)borane, 7,8-dipropyl-7-borabicyclo[4.2.2]deca-2,4,9-triene, 9-dipropylborylbicyclo[6.1.0]nona-2,4,6-trienes; electrocyclic reactions, [1,3]-B shift; NMR spectroscopy.

NMR spectroscopy is virtually the only method for investigating compounds with dynamic properties and, in particular, their intramolecular degenerate rearrangements.[2,3]

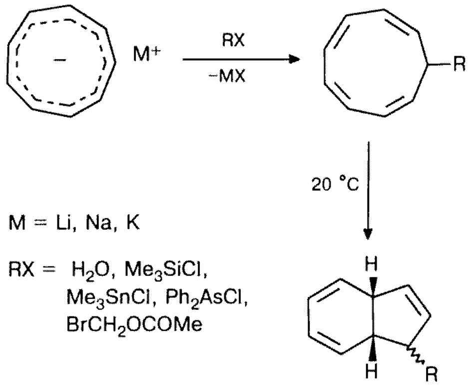
Triorganoboranes of allylic type are fascinating examples of fluxional compounds.[4] The sigmatropic [1,3]-B shift that is observed in almost all such compounds has been the subject of intensive experimental investigations[4—9] and quantum chemical calculations[10—12] for the three last decades.

Continuing the investigations of the [1,3]-B shift in cyclic and polyunsaturated allylic type triorganoboranes,[4—9] we have synthesized 9-cyclononatetraenyl(dipropyl)borane (**1**).[11] Using two-dimensional chemical exchange NMR spectroscopy, it was shown that the main process occurring in borane **1** in the −100 to −20 °C temperature interval is a series of subsequent [1,3]-B shifts.[1] However, it turns out that the fluxional behavior of compound **1** is not restricted to borotropy only. Here we report the results of a study of irreversible thermal rearrangements that occur in cyclononatetraenyldipropylborane **1** at ambient temperature.

Results and Discussion

Determination of the structures of the products of rearrangement of 1. It is well-known that cyclononatetraene derivatives formed upon treatment of the cyclononatetraenide anion with electrophilic reagents readily rearrange to the corresponding dihydroindenes within a period of 30—60 min (Scheme 1).[14—17]

Scheme 1



It was natural to propose, that the product of the borylation of cyclononatetraenyl anion, 9-cyclononatetraenyl(dipropyl)borane **1**, would behave similarly. However, it was found that the chemical properties of borane **1** considerably differ from those of the known compounds of this type, and the classic transformation of **1** to the corresponding borylated dihydroindene is a minor

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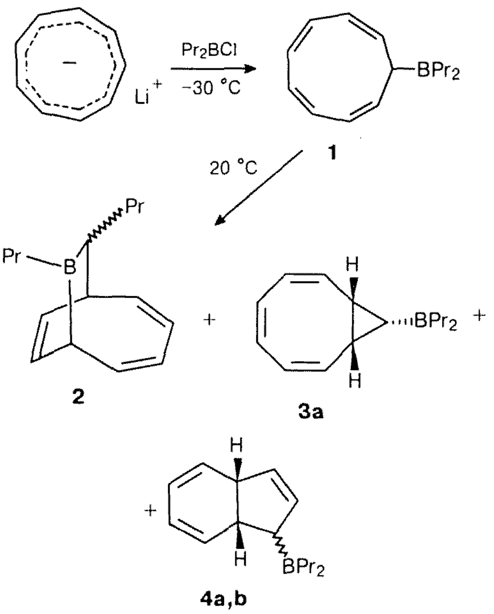
process only. Thus, the reaction of chlorodipropylborane with lithium cyclononatetraenide at −30 °C followed by vacuum distillation (b.p. 73—75 °C, 0.8 Torr) gave a mixture of products **2**, **3a**, and **4a,b** in a 10 : 1 : 2 ratio (Scheme 2). Corresponding dihydroindenylboranes **4a,b** were easily identified by ^{1}H—^{1}H NMR COSY spectrum of the reaction mixture. Detailed analysis of this spectrum showed that the low-intensity peaks in the ^{1}H NMR spectrum (the triplet at 0.64 ppm, the doublet at 1.89 ppm, and the group of three signals at 6.1—6.2 ppm) can be assigned to *endo*-9-dipropylborylbicyclo[6.1.0]nona-2,4,6-triene **3a**.

Scheme 2



The main product of the obtained mixture (**2**) had a completely unexpected structure, and its determination by NMR spectroscopy required considerable efforts.

The ^{1}H NMR spectrum of compound **2** recorded at room temperature contains two broad signals in the 4—5 ppm region (Fig. 1, *b*), which is indicative of dynamic processes. At lower temperatures, these two signals undergo a further broadening (Fig. 1, *a*), and the other signals in the spectrum of **2** also become broader. *Vice versa,* increasing the temperature resulted in a sharpening of all of the signals of **2** (Fig. 1, *c*).

The ^{1}H—^{1}H COSY spectrum of compound **2** recorded at 70 °C (Fig. 2) allowed us to determine the structure of the carbon ring in the molecule of **2**. As can be seen from Fig. 2, compound **2** contains an eight-membered ring. A multiplet at 2.83 ppm has a weak cross-peak with a signal at 1.55 ppm. However, the latter signal is overlapped with the intensive signals of the propyl groups and has no cross-peaks with the other low-field signals, which complicates the further analysis of the structure of **2** by the COSY spectrum. Nevertheless, based on the ^{1}H—^{13}C heteronuclear correlation NMR spectrum, it was found that the proton with the signal at 1.55 ppm is attached to the carbon atom which has a chemical shift at 49.5 ppm. The latter, in turn, is adjacent to the boron atom, as follows from the characteristic broadening of this signal in the ^{13}C NMR spectrum caused by a quartet splitting on the B atom. The further analysis of the COSY and XHCORR spectra showed that one of the two propyl groups in the molecule is attached not to the B atom, but to the C atom. All of the above-mentioned facts allowed us to conclude that the main product of rearrangement of **1** is 7,8-dipropyl-7-borabicyclo[2.2.4]deca-2,4,9-triene (**2**).

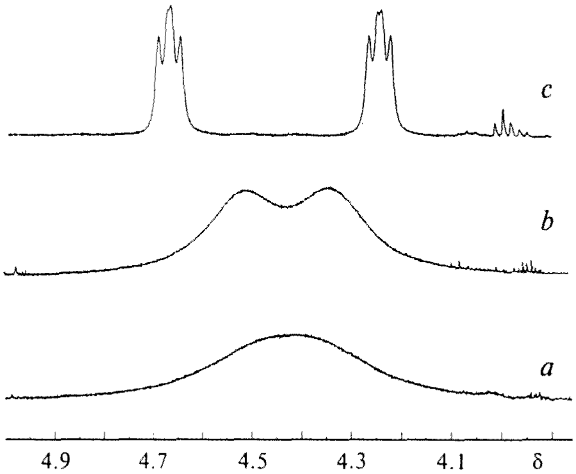
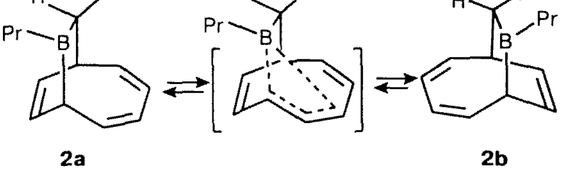


Fig. 1. Signals of the H(4) and H(6) atoms in the ^{1}H NMR spectrum of compound **2** (400 MHz, toluene-d_8) at 0 °C (*a*), 25 °C (*b*), and 70 °C (*c*).

Dynamic effects in the ^{1}H and ^{13}C NMR spectra of compound **2** are explained by the reversible interconversion of two geometric isomers **2a** and **2b**, which occurs *via* the 1,3-migration of the boryl fragment (from the C(4) to C(6) atom, Scheme 3). This conclusion was confirmed by a detailed study of the temperature dependence of NMR spectra of **2**, which will be discussed in a separate paper.

Scheme 3



Mechanism of formation of compound 2. When the reaction was carried out in a NMR tube, a series of signals were observed to arise and than dissapear in the

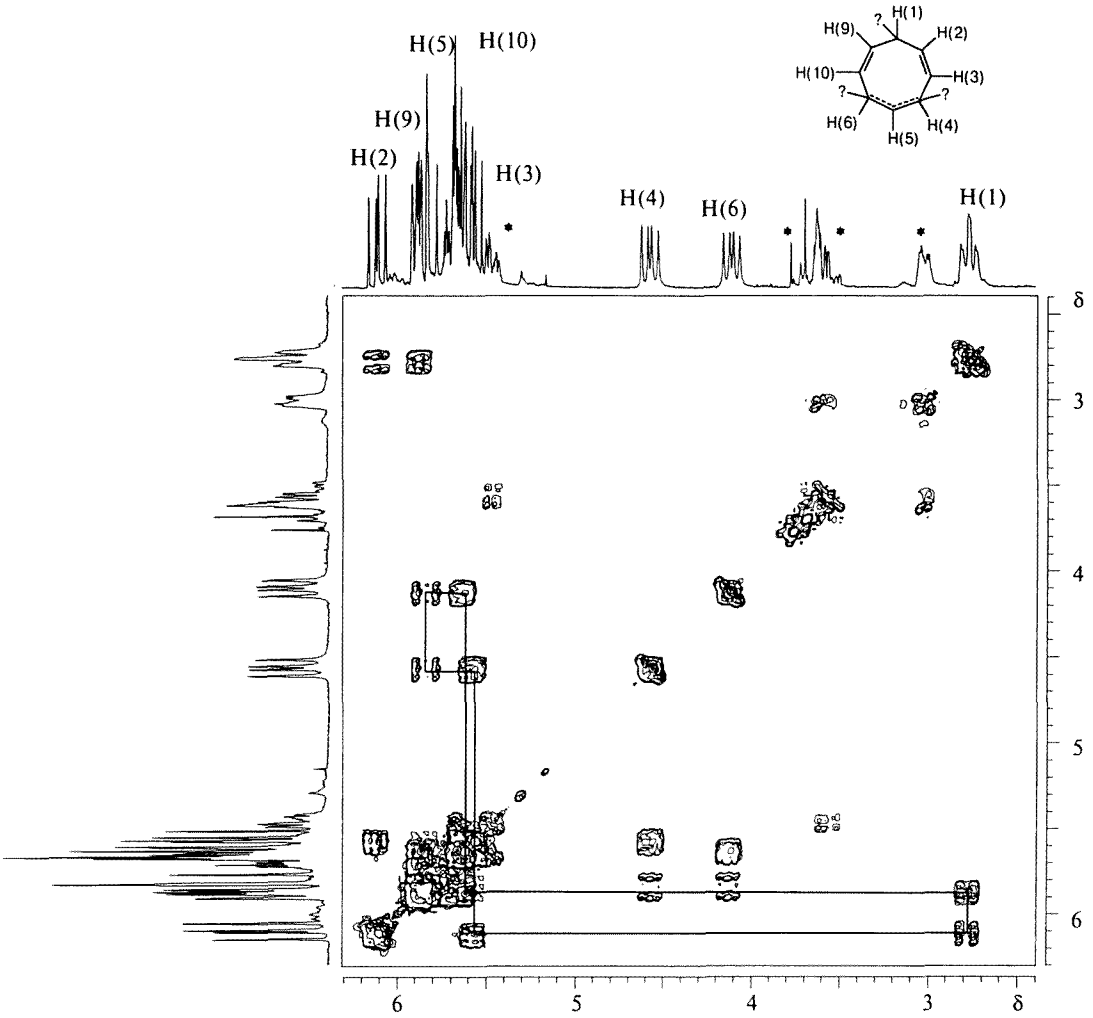


Fig. 2. $^1H-^1H$ NMR COSY spectrum of the mixture of rearrangement products **2**, **3a**, and **4a,b** (200 MHz, toluene-d_8, 70 °C). Straight lines show how the presence of the eight-membered carbon ring in the main product of borylation **2** can be elucidated.

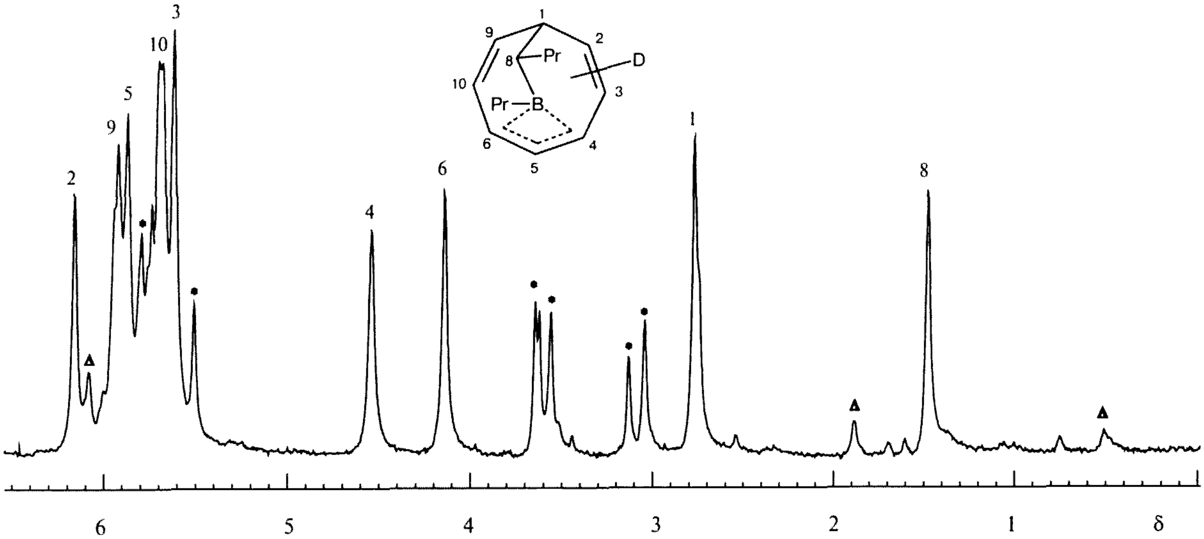


Fig. 3. ^2H NMR spectrum (62 MHz, toluene-d_8, 25 °C) of the mixture of products of the rearrengement of monodeuterated lithium cyclononatetraenide **5(D)**. Asterisks point out the signals of isomeric dihydroindenylboranes **4a,b(D)**, and the Δ sign marks the signals of compound **3a(D)**.

^{1}H NMR spectra. This is caused by possible intermediate products of the **1** → **2** transformation. However, these signals overlapped the intense signals of propyl groups in the upfield area. To observe the above-mentioned intermediates, ^{2}H NMR spectroscopy was used.

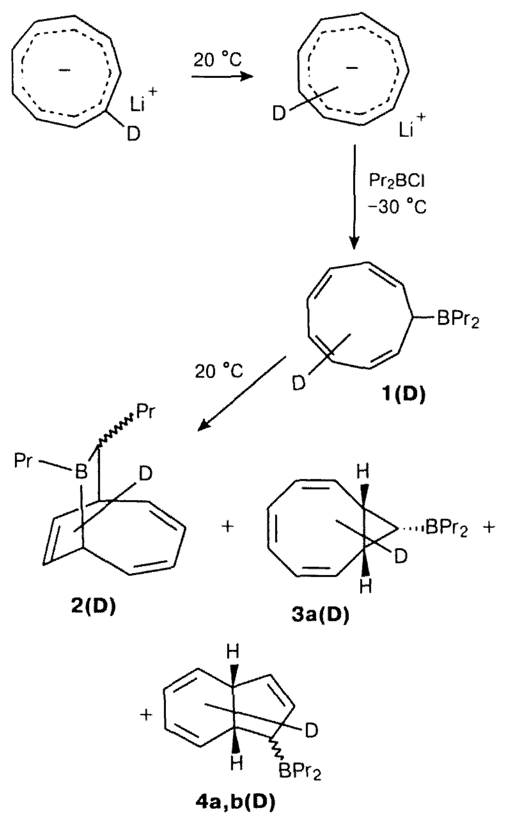
We have prepared monodeuterated cyclononatetraenyl anion **5(D)** by the procedure described earlier.[18,19] This anion was treated with chlorodipropylborane at −30 °C.

It is known that, in the monodeuterated cyclononatetraenyl anion, deuterium is statistically distributed between all nine atoms of the cyclononatetraene ring.[19] The same situation should occur in the molecule of monodeuterated compound **1(D)**, and, as a result, each product of the thermal rearrangement **2(D)**—**4(D)** would exist as a mixture of nine isomers with different positions of the deuterium atom (Scheme 4). The validity of this proposal is illustrated by Fig. 3 which shows the ^{2}H NMR spectrum of the mixture of rearrangement products after distillation.

Figure 4 demonstrates the evolution of the ^{2}H NMR spectrum (30.7 MHz) of monodeuterated cyclononatetraenyl(dipropyl)borane **1(D)** at 25 °C. A comparative analysis (see Fig. 4, *a* and *b*) indicates the existence of an intermediate product, which is characterized by the three signals in the ^{2}H NMR spectrum at 6.2, 2.55, and 1.75 ppm (the ratio of integral intensities is 6 : 2 : 1, respectively). According to Fig. 4, this intermediate product is formed directly from initial cyclononatetraenylborane **1(D)** (besides the three signals of the intermediate product, only a signal of initial **1(D)** at 5.8 ppm is observed in Fig. 4, *a*). First, it accumulates in the reaction mixture (in Fig. 4, *b* the signals of the intermediate product predominate). Then it begins to be consumed (see Fig. 4, *c* and *d*), and when the rearrangement is finished after 3 h, there are no signals of this product in the spectrum of the reaction mixture (see Fig. 4, *e*).

The structure of the intermediate product was elucidated from analogous NMR experiments using not deuterated cyclononatetraenyl(dipropyl)borane **1**. Figure 5 shows ^{13}C NMR spectra that illustrate an experiment on low-temperature generation of **1** and investigation of its evolution after raising the temperature. The spectrum shown in Fig. 5, *a* was recorded immediately after heating the sample of **1** from −60 to 25 °C (under the

Scheme 4



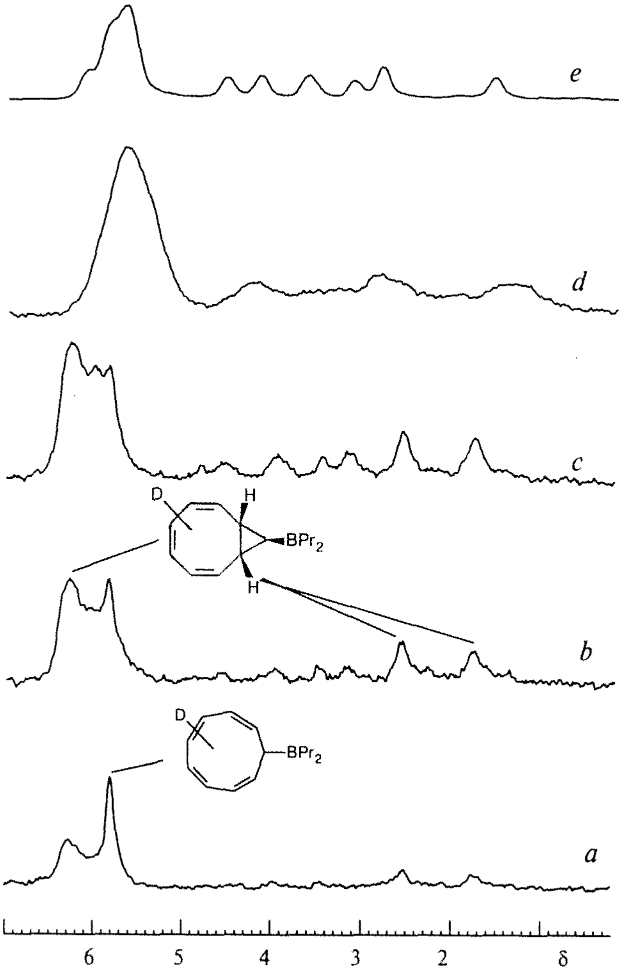


Fig. 4. ^{2}H NMR spectra of sample that initially contained monodeuterated cyclononatetraenyl(dipropyl)borane **1(D)** (31 MHz, pentane, 25 °C): *a*, spectrum obtained immediately after placing a sample previously cooled to −30 °C into the spectrometer probe with a fixed temperature of 25 °C; *b*, spectrum of the same sample after 10 min; *c*, after 20 min; *d*, after 30 min; *e*, after 3 h (spectrum of the final reaction mixture heated to 80 °C), *cf.* Fig. 3.

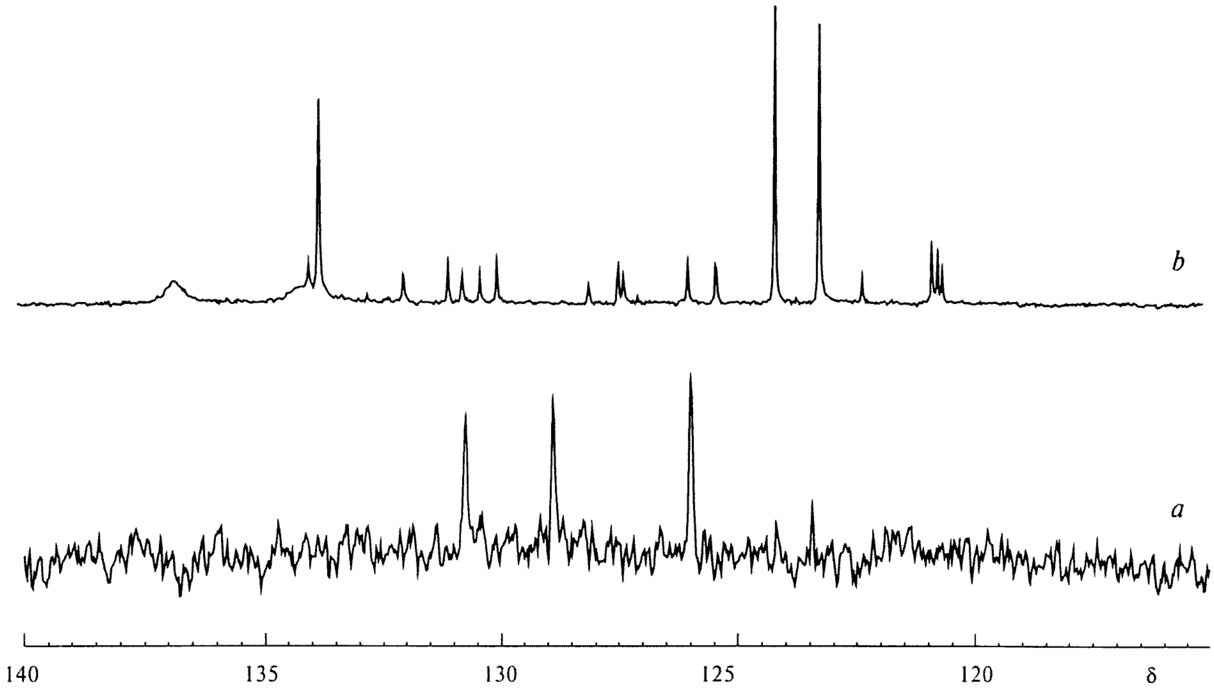


Fig. 5. Olefinic region of the ^{13}C NMR spectra (50 MHz, $CDCl_3$, 25 °C) of a sample that initially contained cyclononatetraenyl(dipropyl)borane **1**: *a*, spectrum obtained immediately after placing a sample previously cooled to −30 °C into the spectrometer probe with a fixed temperature of 25 °C; *b*, spectrum of the same sample after 3 h (spectrum of the final reaction mixture).

same conditions as the ^2H NMR spectrum in Fig. 4, *a*). In this spectrum, only three ^{13}C signals were observed in the low-field region, and these signals completely dissapeared after 3 h. Therefore, they are related to the intermediate product of the reaction.

Additional experiments (with repeated cooling of the sample to −100 °C, ^1H NMR spectral data) showed that, under the conditions of recording the spectrum shown in Fig. 5, *a*, about 50 % of the initial cyclononatetraenyl(dipropyl)borane **1** is still present in the reaction mixture However, the signals of **1** are not observed in the ^{13}C NMR spectrum at room temperature due to an extensive broadening of spectral lines caused by fast reversible [1,3]-boron shifts. Thus, the ^{13}C NMR spectra also indicate that the intermediate reaction product is formed directly from borane **1**.

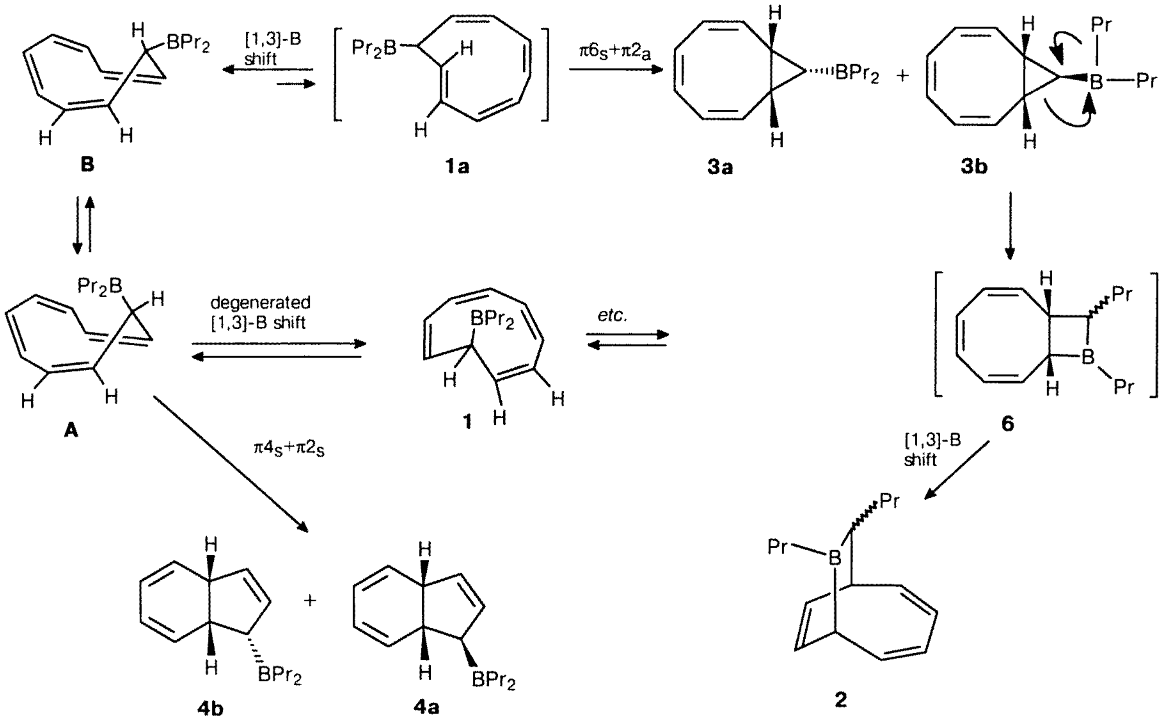
The ^1H—^1H COSY and ^1H—^{13}C XHCORR experiments performed under the same conditions as those for the spectra shown in Figs. 4, *a* and 5, *a* allowed us to establish the structure of the intermediate product. In the ^1H NMR spectrum, the signal at 2.16 ppm is a doublet with coupling constant of 10.2 Hz. This signal had a distinct cross-peak with the triplet at 1.72 ppm, which was not observable in the one-dimensional ^1H NMR spectrum due to overlapping with intensive signals of propyl groups. Two downfield signals at 5.8 and 5.9 ppm also have weak cross-peaks with a doublet at 2.16 ppm and correleate with three downfield ^{13}C signals in the two-dimensional spectrum of heteronuclear correlation. All of the data obtained by the NMR experiments allowed us to assign the structure of *exo*-9-dipropylborylbicyclo[6.1.0]nona-2,4,6-triene **3b** to the intermediate product of the rearrangement.

Apparently, isomers **3a** and **3b** are the primary products of the rearrangement of 9-cyclononatetraenyl(dipropyl)borane **1**, but only **3b** is irreversibly transformed to compound **2**, whereas *endo*-isomer **3a** is thermally stable and does not exhibit dynamic properties. No other intermediates were found during the transformation of **3b** to **2**. A general view of the rearrangements of compound **1** is shown by Scheme 5.

We believe that direct conversion of cyclopropanic compound **3b** to cyclobutanic compound **6** occurs as a result of migration of the propyl group from the boron atom to the α-C-atom, and the ring is simultaneously enlarged (see Scheme 5). In turn, compound **6**, which is a borane of allylic type, immediately rearranges to its thermodynamically more stable allylic isomer **2** *via* a [1,3]-boron shift. The rearrangement of the **3b** → **6** type has been observed in the chemistry of boron for the first time. Similar transformations were earlier described for cyclopropylmethylcarbenes,[20,21] which have a close structure, and for phospharenes.[22]

Thus, unlike the other substituted cyclononatetraenes, the formation of the corresponding dihydroindenyl boranes **4a,b** is only a side process for borane **1**, *i.e.*, the

Scheme 5



cyclization of **1** to **3b** is the main reaction. It appears that the reaction readily occurs in such an unusual way due to a [1,3]-boron shift, which proceeds in **1**, as was mentioned above, at a high rate. In fact, the rearrangement of borane **1** to **3b** is a thermal 8π-process and, therefore, should be antarafacial. For an antarafacial rearrangement to be occur, the formation of the intermediate *Z,Z,Z,E*-isomer **1a** is necessary (see Scheme 5). The latter can be formed as the result of the [1,3]-boron shift in conformation **B**, whereas the [1,3]-boron shift in conformation **A** is degenerate. Obviously, the interconversion of conformations **A** and **B** is a reversible process. Therefore, the fact that the overall equilibrium is strongly shifted towards the formation of **2** (*via* intermediate compound **3b**) indicates the relative thermodynamic stability of compound **2**. However, the reasons for this stability are not apparent. Relatively high thermodynamic stability is characteristic of the vinylic type organoboranes, which is associated with the overlapping of the unoccupied 2p-AO of the boron atom and the π-system of the neighboring double bond.[4] It is worth noting that similar orbital overlapping (though, *via* space) seems to occur in molecule **2**. This is confirmed by the ^{11}B chemical shift in compound **2** (70.2 ppm, the value characteristic of the vinylic type triorganoboranes[23]). Similar effects of the p—π homoconjugative interaction were recently observed for a series of bicyclic organoboranes.[24]

Thus, it can be concluded that the driving force for the rearrangement of **1** to **2** is a relative thermodynamic stability of the latter due to the homoconjugation of the unoccupied 2p-AO of the boron atom with the π-system of double bonds.

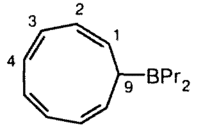
Experimental

All experiments were performed in an atmosphere of dry argon using absolute solvents. NMR spectra were recorded on Bruker AC-200 and AMX-400 spectrometers. IR spectra were registered on a UR-20 spectrophotometer in CCl_4. Parameters of the ^1H and ^{13}C NMR spectra of compounds **1—4** are given in Table 1.

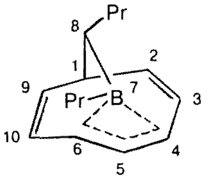
Preparation of samples of 9-cyclononatetraenyl(dipropyl)borane (1) and monodeuterated cyclononatetraenyl(dipropyl)borane (1(D)) for NMR studies. A suspension of lithium cyclononatetraenide[13] or lithium monodeuterated cyclononatetraenide[18,19] was treated with an equivalent amount of chlorodipropylborane with vigorous stirring at −30 °C. When the reaction was finished, a crystalline residue of LiCl was allowed to precipitate, and a transparent pentane solution of **1** was removed in a small two-neck flask. Pentane was eliminated *in vacuo* (0.1 Torr) at −20 °C, and the residue was dissolved in cooled CD_2Cl_2 and transfered into a NMR tube.

Borylation of lithium cyclononatetraenide. A solution of 2.8 g (0.1 mol) of chlorodipropylborane in 20 mL of hexane was added dropwise with vigorous stirring at room temperature to a suspension of lithium cyclononatetraenide prepared from 15.3 g (0.1 mol) of 9-chlorobicyclo[6.1.0]nonane in absolute hexane. The precipitate of LiCl formed was filtered off, hexane was removed *in vacuo*, and the residue was distilled *in vacuo* to obtain the fraction with b.p. 73—75 °C (0.08 Torr). The latter was a mixture of compounds **2**, **3a**, and **4a,b** in a 10 : 1 : 2

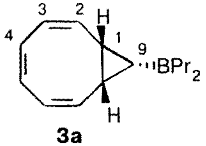
Table 1. Chemical shifts and coupling constants ($J_{H,H}$/Hz) in the ^1H and ^{13}C NMR spectra of compounds **1**,[a] **2**,[b] **3**, and **4** (excluding BPr_2 groups)



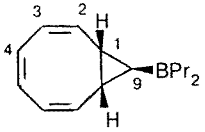
1



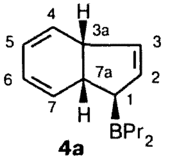
2



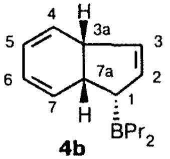
3a



3b



4a



4b

Atom	Compound **1**		Compound **2**		Compound **3a**		Compound **3b**		Compound **4a**		Compound **4b**	
	δ ^1H ($J_{H,H}$)	δ ^{13}C	δ ^1H ($J_{H,H}$)	δ ^{13}C	δ ^1H ($J_{H,H}$)	δ ^{13}C	δ ^1H ($J_{H,H}$)	δ ^{13}C	δ ^1H ($J_{H,H}$)	δ ^{13}C	δ ^1H ($J_{H,H}$)	δ ^{13}C
H(1), C(1)	5.68 (2×9.4)	135.8	2.83 (7.8, 8.2, 2.4)	38.1	1.89 (6.5)	27.3	2.16 (10.2)	28.6	2.80 (2.5, 4.2)	54.5	3.07	50.2 (10.0, 3×2.0)
H(2), C(2)	4.79 c	125.0	6.22 (8.2, 10.8)	137.6	6.15 (11.2)	129.9	5.94 c	130.9	5.71 c	131.9	5.87	130.3 c
H(3), C(3)	4.88 c	130.6	5.72 (7.2, 10.8)	125.3	6.10 (11.2)	127.4	5.91 c	128.3	5.58 (9.6, 4.5)	128.0	5.66	127.3 (9.2, 5.5)
H(4), C(4)	4.45 c	128.7	4.15 (7.2, 11.4)	78.9	6.03 c	125.9	5.83 c	125.7	d d	133.9[e] 120.5[e]	d d	131.0[e] 120.6[e]
H(5), C(5)			5.81 (11.4, 11.4)	134.3								
H(6), C(6)			4.53 (7.5, 11.3)	90.5					d	130.7[e]	d	127.3[e]
H(7), C(7)									d	122.2[e]	d	120.8[e]
H(8), C(8)			1.55 c	41.5								
H(9), C(9)	3.33 (2×9.4)	27.2	5.97 (7.8, 10.8)	134.9	0.64	25.0 (2×6.5)	1.32	30.4 (2×10.2)				
H(10), C(10)			5.68	124.3 (7.4, 10.8)								
H(3a), C(3a)									3.67	45.9 c	3.71	45.8 c
H(7a), C(7a)									3.16	40.79 (12.6, 5.9, 4.2, 1.4)	3.56	39.28 (13.3, 10.0, 4.5, 1.6)

[a] NMR spectra of compound **1** were recorded at −100 °C in CD_2Cl_2. [b] Data are given for the averaged structure of compound **2**. [c] Spectral parameters are not determined, due to overlapping of the signals and/or effects of strong binding. [d] The values of chemical shifts fall within the 5.7—6.0 ppm interval. [e] An alternative assignment is possible.

ratio, n_D^{20} 1.5072. IR (CCl_4), ν/cm^{-1}: 1590, 1620, 1655, 3020, 3050. Found (%): C, 83.91; H, 10.60; B, 5.11. $C_{15}H_{23}B$. Calculated (%): C, 84.12; H, 10.82; B, 5.05.

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