Investigation of the Dynamic Equilibrium between 2-(Dialkylboryl)-1-methylenecyclobutane and 1-((dialkylboryl)methyl)-1-cyclobutene

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Received November 6, 1995[⊗]

The reaction of potassium methylenecyclobutanide with dibutylboron chloride and 9-bromo-9-borabicyclo[3.3.1]nonane yields the corresponding allylic type triorganoboranes **1** and **2**. Compounds **1** and **2** exhibit a facile [1,3]-B sigmatropic shift, which results in the reversible coexistence of isomeric 2-(dialkylboryl)-1-methylenecyclobutanes **1a** and **2a** with 1-((dialkylboryl)methyl)-1-cyclobutenes **1b** and **2b**. For both compounds **1** and **2**, the 2-(dialkylboryl)-1-methylenecyclobutane form (**1a**, **2a**) is predominant at low temperatures, while raising the temperature leads to a shift of the equilibrium in favor of the 1-((dialkylboryl)methyl)-1-cyclobutene form (**1b**, **2b**). Activation parameters for the equilibrium in **1** were found from the 2D $^{13}C-^{13}C$ spectra (for the transformation **1a** → **1b** $E_{act} = 35.5 \pm 2.5$ kJ mol^{-1}, $\Delta G^{\ddagger}_{298} = 53.8 \pm 0.5$ kJ mol^{-1}; for the transformation **1b** → **1a** $E_{act} = 33.8 \pm 2.5$ kJ mol^{-1}, $\Delta G^{\ddagger}_{298} = 52.8 \pm 0.5$ kJ mol^{-1}). For the equilibrium in **2**, the rate constants of the direct and reverse reaction were determined at 180 K ($k_{\mathbf{2a\rightarrow 2b}} = 0.30 \pm 0.03$ s^{-1}, $k_{\mathbf{2b\rightarrow 2a}} = 6.3 \pm 0.3$ s^{-1}).

Introduction

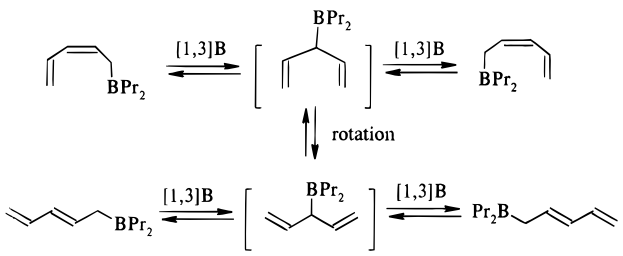
The sigmatropic [1,3]-shift of boron is a general phenomenon for triorganoboranes of the allylic type.[1] Usually, this process can be observed by NMR spectroscopy under conditions that result either in degenerate rearrangements (see for example Scheme 1)[1a,e] or in interconversion of geometrical isomers, which occur *via* a combination of several [1,3] boron shifts and conformational rotations (*e.g.* Scheme 2).[1b,c]

In a continuation of our investigations of the [1,3]-shift of boron in triorganoboranes of the allylic type with various structures, we synthesized the boron derivatives of methylenecyclobutane **1** and **2**. It was found that in these compounds one can observe a reversible equilibrium between 2-(dialkylboryl)-1-methylenecyclobutane and 1-((dialkylboryl)methyl)-1-cyclobutene forms. The present work deals with investigation of the dynamic properties and kinetics of the [1,3]-boron shift in triorganoboranes **1** and **2**.

Scheme 1

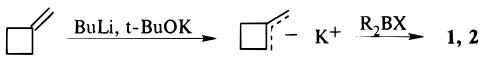
R = All, $\Delta G^{\neq}_{298} = 61.6$ kJ mol^{-1}
R = Pr, $\Delta G^{\neq}_{298} = 66.2$ kJ mol^{-1}

Scheme 2



$\Delta G^{\neq}_{tt} = 82.3$ kJ mol^{-1}; $\Delta G^{\neq}_{tc} = 85.5$ kJ mol^{-1}; $\Delta G^{\neq}_{cc} = 91.5$ kJ mol^{-1}

Scheme 3



1: R = Bu, X = Cl
2: R = 9-BBN, X = Br

Results

Compounds **1** and **2** were synthesized by the metalation of methylenecyclobutane[3] followed by the treatment of potassium methylenecyclobutanide with the corresponding dialkyl borohalide (Scheme 3).[2]

Figure 1 shows the temperature dependence of the ^{1}H NMR spectrum of compound **1**. At 203 K there are two sets of signals indicative of the presence of both 2-(dibutylboryl)-1-methylenecyclobutane (**1a**) and 1-((dibutylboryl)methyl)-1-cyclobutene (**1b**) in a 4:3 ratio. At 373 K the spectrum of the same sample is completely averaged (Figure 1).

The signals of the ^{1}H NMR spectrum of compound **1** at 203 K were assigned using the ^{1}H−^{1}H COSY spec-

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1996.

(1) (a) Bubnov, Y. N.; Gurskii, M. E.; Gridnev, I. D.; Ignatenko, A. V.; Ustynyuk, Y. A.; Mstislavsky, V. I. *J. Organomet. Chem.* **1992**, *424*, 127−132. (b) Gurskii, M. E.; Gridnev, I. D.; Geiderich, A. V.; Ignatenko, A. V.; Mstislavsky, V. I.; Ustynyuk, Y. A. *Organometallics* **1992**, *11*, 4056−4061. (c) Gridnev, I. D.; Gurskii, M. E.; Ignatenko, A. V.; Bubnov, Y. N.; Il'ichev, Y. V. *Organometallics* **1993**, *12*, 2487−2495. (d) Gridnev, I. D.; Gurskii, M. E.; Bubnov, Y. N. In *Current Topics in the Chemistry of Boron*; Royal Society of Chemistry: Cambridge, U.K., 1994; pp 56−59. (e) Gurskii, M. E.; Gridnev, I. D.; Buevich, A. V.; Bubnov, Y. N. *Organometallics* **1994**, *13*, 4658−4660.

(2) (a) Bubnov, Y. N.; Gurskii, M. E.; Lavrinovich, L. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 1918−1919. (b) Bubnov, Yu. N. *Pure Appl. Chem.* **1987**, *59*, 895.

(3) Wilson, R. S.; Phillips, L. P.; Natalie, K. J. *J. Am. Chem. Soc.* **1979**, *101*, 3340−3343.

S0276-7333(95)00863-6 CCC: $12.00

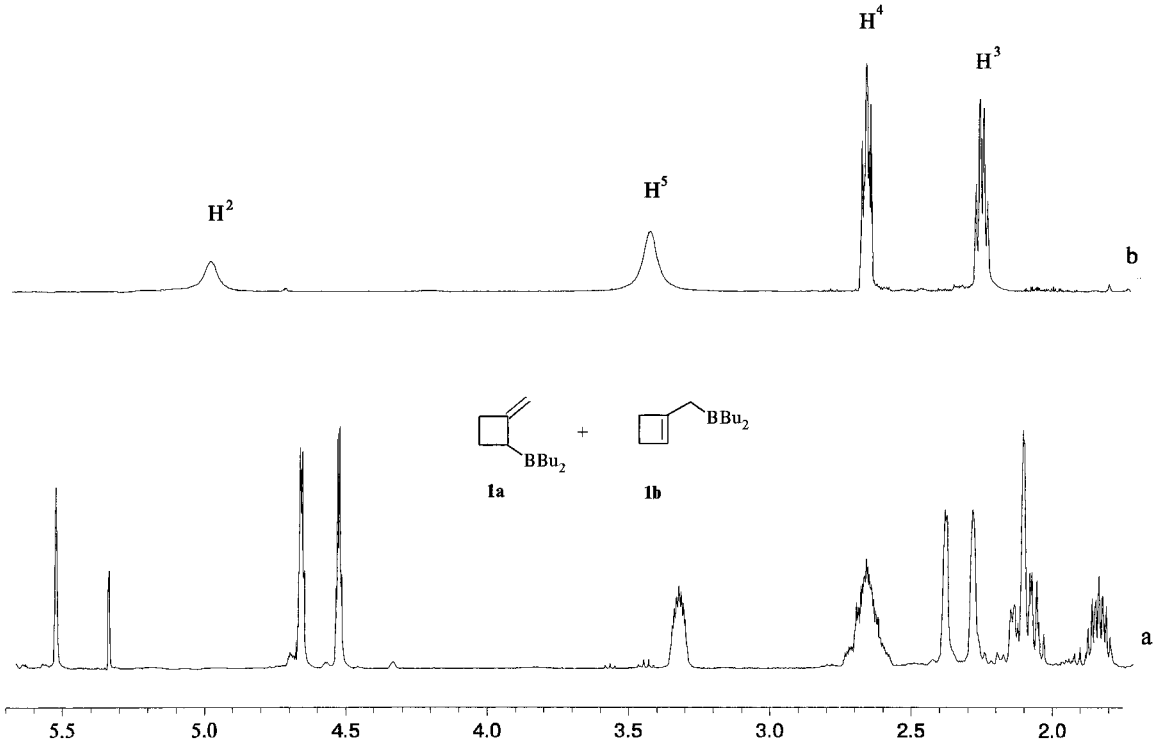
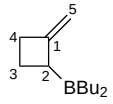
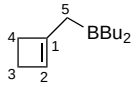


Figure 1. Section plots (without the signals of butyl groups) of the ^{1}H NMR spectra of compound **1** (400 MHz, neat liquid, internal standard TMS): (a) at 203 K (external lock CD_2Cl_2); (b) at 373 K (external lock DMSO-d_6).

Table 1. Parameters of ^{1}H and ^{13}C NMR spectra of Compounds 1a,[a] and 1b[a] and the Averaged Spectrum[b]

	 1a		 1b		averaged spectrum	
atom No.	δ(^{1}H)	δ(^{13}C)	δ(^{1}H)	δ(^{13}C)	δ(^{1}H)	δ(^{13}C)
1		150.07		147.04		148.66
2	3.37	45.22	5.56	127.29	4.59	*c*
3	1.88, 2.10	18.18	2.31	26.95	2.21	22.44
4	2.68	31.02	2.41	33.45	2.57	32.42
5	4.57, 4.69	106.21	2.15	32.10	3.23	*c*
Bu	0.89, 1.19−1.45	14.63, 26.40, 26.00, 27.34	0.89, 1.19−1.45	14.63, 25.87, 26.26, 27.18	0.92, 1.47, 1.31, 1.37	13.82, 26.03, 26.91, 27.29

[a] At 203 K. [b] At 373 K. [c] Signals were too broad to be observed.

trum (see Table 1). The phase-sensitive ^{1}H−^{1}H EXSY spectrum recorded at the same temperature is shown in Figure 2. The cross peaks detected in this spectrum unequivocally support the conclusion about the reversible interconversion of **1a** and **1b** observed in the system (see Scheme 4). The ^{13}C−^{13}C EXSY spectrum obtained at 203 K (Figure 3) is also completely in agreement with the proposed scheme of tautomerism.

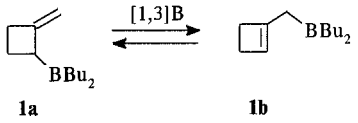
It is known that, in the case of two-positional exchange with unequal populations, the ratio between the rate constant and the intensities of cross and diagonal peaks in a two-dimensional exchange spectrum (which has a matrix form in general)[4] may be simplified as follows:[5]

$$k = \frac{1}{t_m} \ln \frac{r+1}{r-1}$$

$$r = 4X_A X_B \frac{I_{AA} + I_{BB}}{(I_{AB} + I_{BA}) - (X_A - X_B)^2} \qquad (1)$$

where t_m is the mixing time, X_A and X_B are mole proportions of the isomers, I_{AA} and I_{BB} are the intensities of the corresponding diagonal peaks, and I_{AB} and I_{BA} are the intensities of the corresponding cross peaks.

Scheme 4



We recorded the 2D ^{13}C−^{13}C EXSY spectra for compound **1** at five different temperatures and calculated the rate constants with eq 1 using the integral intensities of the diagonal and cross peaks that corresponded to the quaternary C^2 carbon atoms in **1a** and **1b**. The equilibrium constants at each temperature were measured by integration of the signals of quaternary carbon atoms in one-dimensional ^{13}C NMR spectra. The results of the kinetic analysis are given in Table 2.

(4) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon: New York, 1987.
(5) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935−967.

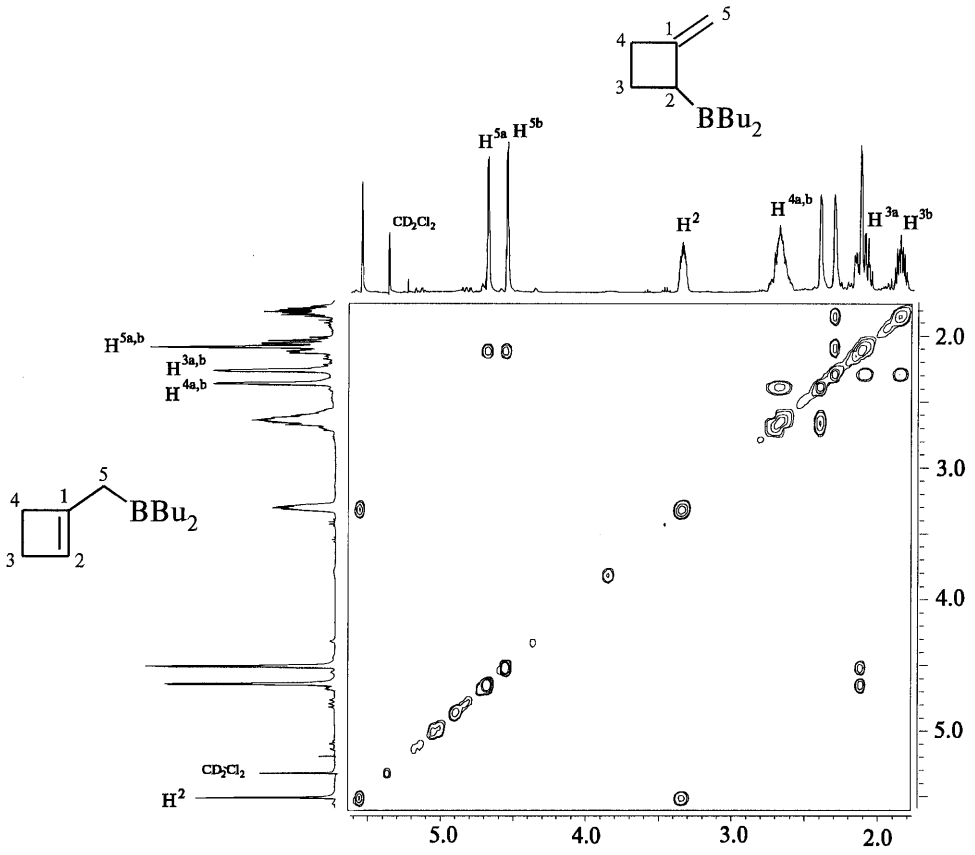


Figure 2. $^1H-^1H$ EXSY spectrum of compound **1** at 203 K (400 MHz, neat liquid, internal standard TMS, external lock CD_2Cl_2): spectrum size 1024 × 512, mixing time 1 s, delay 2 s.

Table 2. Rate Data and Activation Parameters for Rearrangement of 1a to 1b and of the Back-Reaction[a]

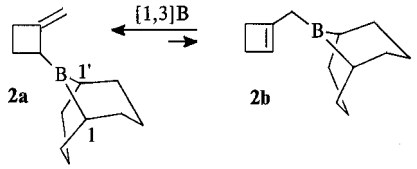
T, K	*K*	$k + k_{-1}$, s^{-1}	k(**1a** → **1b**)	k_{-1}(**1b** → **1a**)
180	1.98	0.48	0.16	0.32
187	1.92	1.55	0.53	1.02
193	1.84	2.48	0.87	1.61
198	1.77	5.19	1.87	3.32
207	1.68	9.76	3.66	6.40

[a] For the transformation **1a** → **1b**: $E_{act} = 35.5 \pm 2.5$ kJ mol^{-1}, ln $A = 22.0 \pm 1.6$, $\Delta G^{\ddagger}_{298} = 53.8 \pm 0.5$ kJ mol^{-1}. For the transformation **1b** → **1a**: $E_{act} = 33.8 \pm 2.5$ kJ mol^{-1}, ln $A = 21.6 \pm 1.5$, $\Delta G^{\ddagger}_{298} = 52.8 \pm 0.5$ kJ mol^{-1}.

The values of $\Delta G^{\ddagger}_{298}$ for the interconversion of **1a** and **1b** obtained in the present work coincide, within the limits of experimental accuracy, with the values that we obtained previously by the line shape analysis of the C^2 signals of **1**.[1d] Nevertheless, an attempt of the Eyring treatment gave a significantly different value for the activation entropy (−3 J mol^{-1} K^{-1},[1d] compared to −70 J mol^{-1} K^{-1} calculated from the data of Table 2), which supports the opinion that the free energies are the most reliable values obtained from the dynamic NMR data.

Figure 4 shows the temperature dependence of the ^{13}C NMR spectrum of compound **2**. Analogously to compound **1**, at high temperature (323 K) we observed the spectrum that corresponds to rapid exchange between methylenecyclobutane form **2a** and methylcyclobutene form **2b**. However, the spectrum at 163 K shows that the concentrations of **2a** and **2b** differ considerably. Integration of the signals of quaternary carbon atoms of **2a** and **2b** at 163 K gave a 24:1 ratio. Thus, the intensities of the signals of **2b** are comparable

Scheme 5



to those of impurities and the positions of some signals of **2b** could be barely detected in a one-dimensional ^{13}C spectrum. Nevertheless, the ^{13}C chemical shifts of compound **2b** (see Table 3) were easily determined from the $^{13}C-^{13}C$ 2D EXSY spectrum (Figure 5), which unequivocally confirms the reversible interconversion of **2a** and **2b** (see Scheme 5). The signals in the ^1H NMR spectrum (see Table 3) were assigned on the basis of the two-dimensional $^1H-^1H$ COSY, $^1H-^1H$ EXSY, and $^1H-^{13}C$ XHCORR spectra of compound **2b** obtained at 163 K.

Due to the existence of an asymmetric center at position 2 of compound **2a**, carbon atoms C^1 and $C^{1'}$ in the bicyclononane fragment become nonequivalent, which results in splitting of the corresponding signals in both the ^1H and ^{13}C NMR spectra (see, for example, Figure 4; the C and C′ signals). There is no asymmetric center in compound **2b**; therefore, the **2a** → **2b** → **2a** conversion results in the reversible inversion of the asymmetric center. This process accounts for the presence of a cross peak between the C and C′ signals in Figure 5.

At 323 K the ^{13}C NMR spectrum of compound **2** is averaged (Figure 4b). The chemical shifts of the C^2 and C^5 atoms found from this spectrum together with those of the C^2 and C^5 atoms of compounds **2a** and **2b**

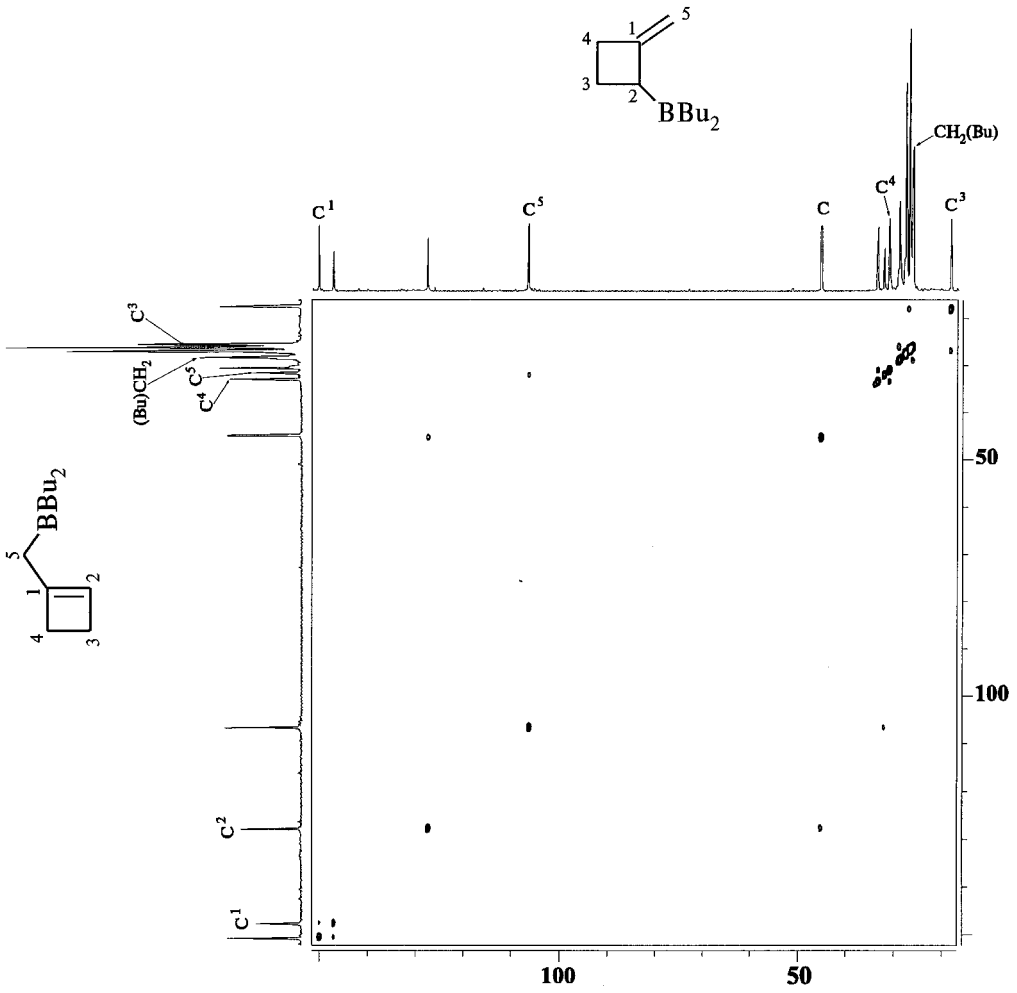


Figure 3. $^{13}C-^{13}C$ EXSY spectrum of compound **1** (100 MHz, neat liquid, 203 K): spectrum size 1024 × 512, mixing time 0.1 s, delay 1 s.

Table 3. Parameters of ^1H and ^{13}C NMR Spectra of Compounds 2a and 2b[a] and the Averaged Spectrum[b]

atom no.	2a $\delta(^1H)$	2a $\delta(^{13}C)$	2b $\delta(^1H)$	2b $\delta(^{13}C)$	averaged spectrum $\delta(^1H)$	averaged spectrum $\delta(^{13}C)$
1		150.12		149.73		150.79
2	3.23	45.91	5.50	126.61	4.00	72.3
3	1.82, 2.21	18.11	2.20, 2.52	27.07	2.61	22.17
4	2.60	31.35	2.41	33.51	2.12	33.55
5	4.57, 4.69	106.21	2.15	32.10	3.91	81.2
BBN	1.08, 1.49, 1.60	34.45, 32.91, 30.87, 24,62	1.08, 1.49, 1.60	*c*	1.22, 1,69, 1.83	34.71, 31.87, 26.54

[a] At 163 K. [b] At 353 K. [c] Low-intensity peaks overlap with these of **2a**.

(obtained from the ^{13}C NMR spectrum at 163 K) allowed us to calculate the **2a:2b** ratio at 323 K, which was found to be 65:35. Thus, the equilibrium constant of two forms of compound **2** is strongly dependent on temperature, which significantly complicates the investigation of the kinetics of interconversion between **2a** and **2b**.

We managed to measure the rate constant of the transformation of **2a** to **2b** by 2D $^{13}C-^{13}C$ EXSY spectroscopy. It is known[5] that, at different mixing times, a rate constant at a certain temperature can be obtained as a slope of the linear dependence of the cross peak integral intensity on the diagonal peak intensity multiplied by the mixing time. The results of establishing such a dependence for the cross peak between the C^3 signals in **2a** and **2b** are given in Table 4 and Figure 6. The rate constant for the reverse process could not be determined directly from the experimental data due to the low intensity of the C^3 diagonal peak in **2b**. The value of the rate constant for the reverse process was

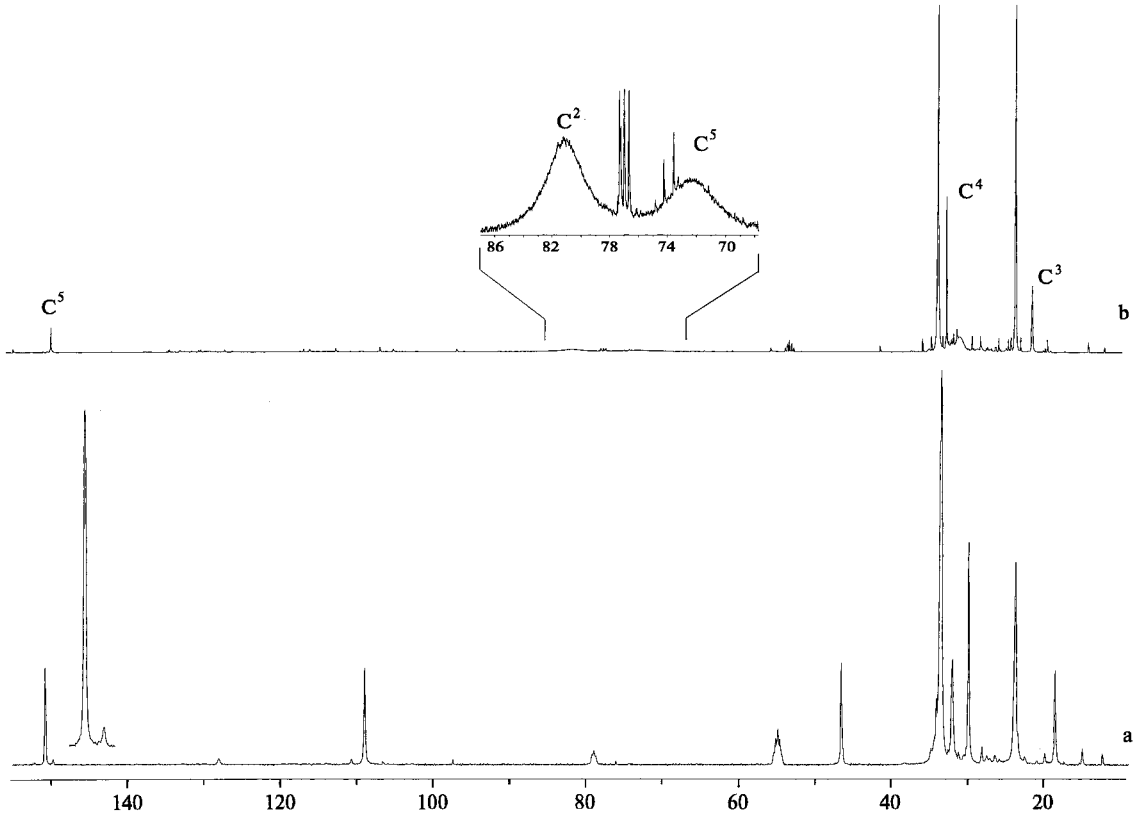


Figure 4. ^{13}C NMR spectrum of compound **2** (100 MHz, mixture $CD_2Cl_2-CDCl_3-CCl_4$ 60:27:13): (a) at 163 K; (b) at 323 K.

Table 4. Normalized Volumes of the Cross Peak between C^3 Carbons in 2a and 2b and of the Diagonal Peak of C^3 in 2a in $^{13}C-^{13}C$ 2D EXSY Spectra of 2 at 180 K[a]

t_m, s	vol of the cross peak	vol of the diagonal peak
0.050	5.2	100
0.075	6.5	100
0.100	6.9	100
0.125	7.5	100

[a] Rate constant for the transformation, **2a** → **2b**: 0.30 ± 0.03 s^{-1}. Rate constant for the transformation **2b** → **2a**: 6.3 ± 0.3 s^{-1}.

calculated using the equilibrium constant at 180 K ($K = 20.9$), which was obtained from the dependence of K on temperature determined on the basis of two values (at 163 and 323 K). Thus, the rate constant for the rearrangement at 180 K is 0.30 ± 0.03 s^{-1}, while the rate constant for the reverse process is 6.3 ± 0.3 s^{-1}.

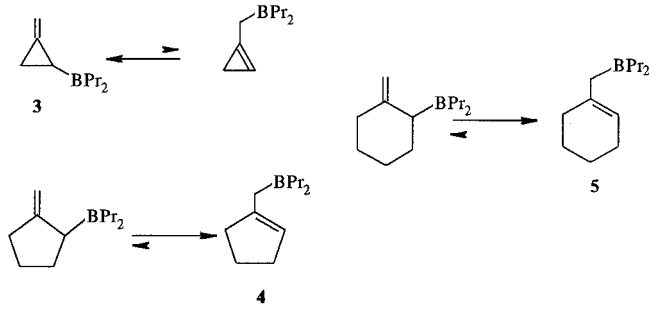
Discussion

As regards the series of the allylic type triorganoboranes **1**−**5**, the equilibrium between exo- and endocyclic structures was detected only for the cyclobutane derivatives **1** and **2**. The cyclopropane derivative **3** exists exclusively as 2-(dibutylboryl)-1-methylenecyclopropane **3**,[6] whereas only the endocyclic forms are observed in the NMR spectra of the corresponding allylboranes with five- and six-membered rings[7] (see Scheme 6).

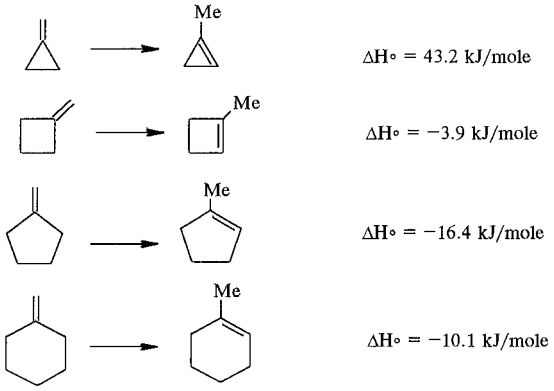
It is interesting to note that this order of the relative thermodynamic stability of the endo- and exocyclic forms of allylic type triorganoboranes **1**−**5** is in perfect correlation with the known order of the relative thermodynamic stability of the cyclic hydrocarbons[8] (see Scheme 7).

The activation barrier of the [1,3]-B shift in compound **1** is somewhat lower than those for the linear triorganoboranes of allylic type studied earlier[1a,d] (compare the

Scheme 6



Scheme 7



(6) Bubnov, Y. N.; Gurskii, M. E.; Ignatenko, A. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 2184.
(7) Bubnov, Y. N.; Lavrinovich, L. I. *Tetrahedron Lett.* **1985**, 4551−4554.

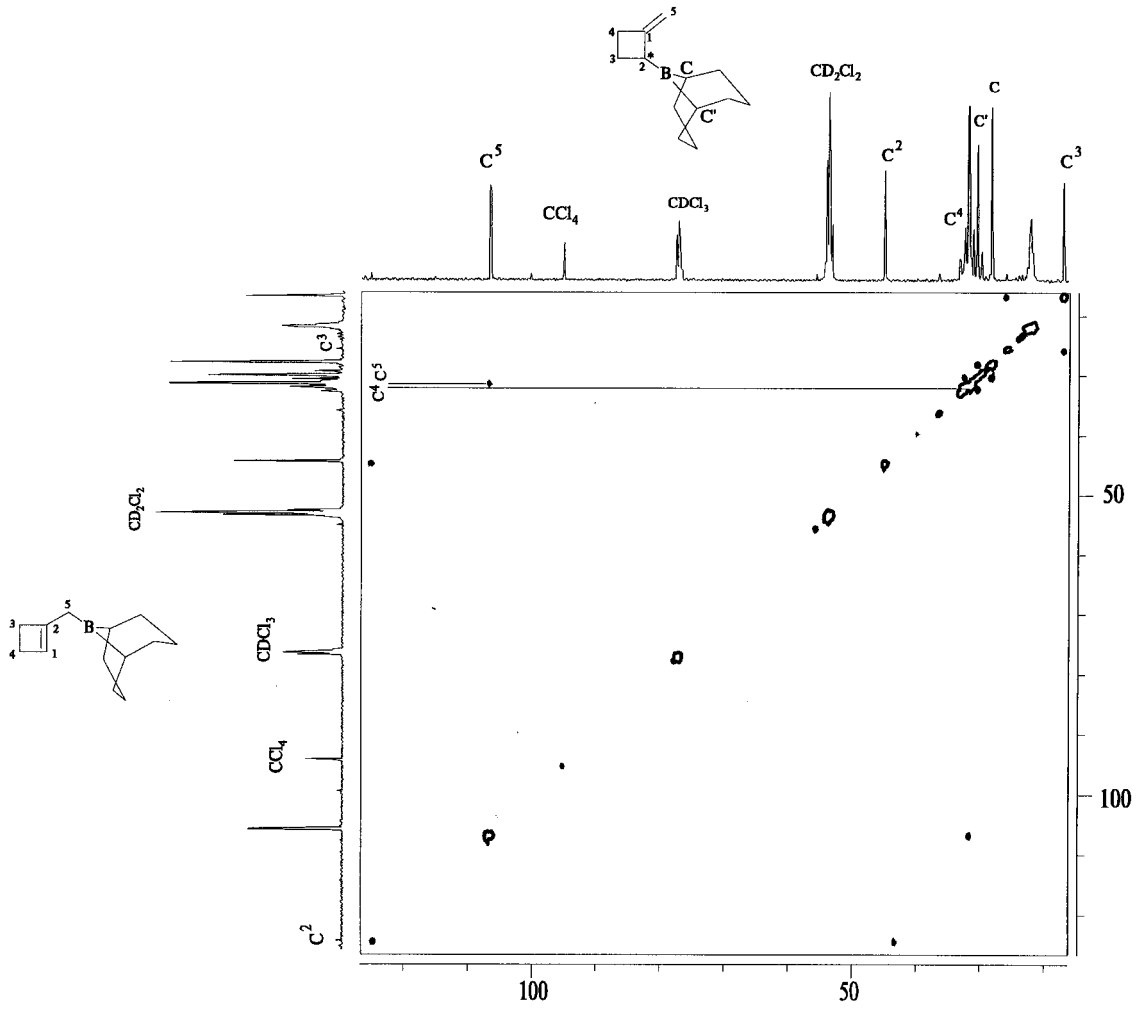


Figure 5. $^{13}C-^{13}C$ EXSY spectrum of compound **2** (100 MHz, mixture $CD_2Cl_2-CDCl_3-CCl_4$ 60:27:13, 163 K): spectrum size 1024 × 512, mixing time 0.1 s, delay 1 s.

data from Scheme 1 with the data of Table 2). The activation barrier in **1** is close to that in tris(1,3-dimethylallyl)borane ($\Delta G^{\ddagger}_{298} = 54.6$ kJ mol^{-1}),[1d] which supports the conclusion about the relatively high rate of the [1,3]-boron shift in 1-alkyl-substituted allylic type triorganoboranes.[1d]

Of interest is the higher rate of the rearrangement in compound **2** compared to compound **1** (compare the rate constants at 180 K in Tables 2 and 4). Apparently this effect can be accounted for by the unusual geometry of the boron atom present in the bicyclic framework. Similar effects of the acceleration of the [1,3]-boron shift were previously observed for 9-BBN[9] and 3-borabicyclononene[10] derivatives of allylboranes.

For both compounds **1** and **2**, the 2-(dialkylboryl)-1-methylenecyclobutane form (**1a**, **2a**) is predominant at low temperatures, while raising the temperature leads to a shift of the equilibrium in favor of the 1-((dialkylboryl)methyl)-1-cyclobutene form (**1b**, **2b**). This phenomenon can be considered as the representation of the thermodynamic properties of the cyclobutene skeleton. However, significantly different ratios of the two forms

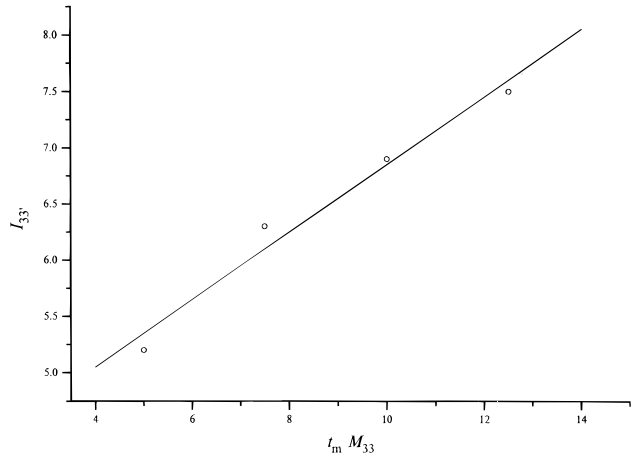


Figure 6. Plot of the intensity of the cross peak (between C^3 in **2a** and **2b**) *vs* the intensity of the diagonal peak (of C^3 in **2a**) multiplied by the mixing time.

in compounds **1** and **2** indicate a notable influence of the nature of the substituents on the boron atom on the state of the equilibrium.

The data on the kinetic and thermodynamic parameters of rearrangements occurring in **1** and **2**, obtained in the present work, will be used in research on the chemoselective introduction of the cyclobutene fragment into organic molecules by allylboration of the polar multiple bonds by allylboranes **1** and **2**.

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Experimental Section

All operations with organoboranes were performed under an atmosphere of dry argon. ^{1}H, ^{13}C, and ^{11}B NMR spectra were obtained on a Bruker AMX-400 spectrometer (400 MHz for protons, 100 MHz for carbon, and 128 MHz for boron).

Synthesis of an Equilibrium Mixture of 2-(Dibutylboryl)-1-methylenecyclobutane (1a) and 1-((dibutylboryl)-methyl)-1-cyclobutene (1b). An 82 mL amount (0.143 mol) of 1.75 M BuLi in hexane was added dropwise at 0−10 °C to a mixture of 16.08 g (0.143 mol) of *t*-BuOK and 26 mL (0.28 mol) of methylenecyclobutane. The reaction mixture was stirred at room temperature for 3 h. Then, it was cooled to −50 °C and 23.04 g (0.143 mol) of Bu_2BCl was added dropwise. The mixture was stirred for 1 h at −50 °C. The temperature was then raised slowly to room temperature, and the mixture was stored overnight. The precipitate was filtered off, and the solvent was removed in vacuo. Double distillation of the residue gave 13.85 g (51%) of **1**: bp 57−58 °C (1 mmHg); n_D^{20} = 1.4525. Anal. Found: C, 80.90; H, 13.15; B, 5.54. Calcd for $C_{13}H_{25}B$: C, 81.26; H, 13.11; B, 5.63. ^{11}B NMR (neat liquid, external standard $BF_3{\cdot}Et_2O$): δ 83.5.

Synthesis of an Equilibrium Mixture of 9-(2-Methylenecyclobutyl)-9-borabicyclo[3.3.1]nonane (2a) and 9-(1-cyclobutenylmethyl)-9-borabicyclo[3.3.1]nonane (2b). A 62.2 mL amount (0.121 mol) of 1.945 M BuLi in hexane was added dropwise at 0−10 °C to a mixture of 13.6 g (0.121 mol) of *t*-BuOK and 16.46 mL (0.24 mol) of methylenecyclobutane. The reaction mixture was then stirred at room temperature for 3 h. Then, it was cooled to −50 °C and 22.29 g (0.12 mol) of 9-bromo-9-borabicyclononane was added dropwise. The mixture was stirred for 1 h at −50 °C. The temperature was then raised slowly to room temperature, and the mixture was stored overnight. The precipitate was filtered off, and the solvent was removed in vacuo. Double distillation of the residue gave 5.85 g (25%) of **2**: bp 73−75 °C (1 mmHg); n_D^{20} = 1.5104. Anal. Found: C, 83.00; H, 11.43; B, 5.84. Calcd for $C_{13}H_{21}B$: C, 83.00; H, 11.25; B, 5.75. ^{11}B NMR (neat liquid, external standard $BF_3{\cdot}Et_2O$): δ 84.3.

Dynamic NMR Studies. All 2D NMR spectra were obtained on a Bruker AMX-400 spectrometer. ^{13}C 2D EXSY spectra were acquired with a NOESYTP pulse program slightly modified to allow the decoupling from protons during the aquisition. Areas of cross peaks and diagonal peaks were obtained by volume integration of appropriate voxels surrounding the peaks.

Acknowledgment. This work was partially supported by the International Science Foundation (Grant No. M3Y300) and by the Russian Fundamental Research Foundation (Grant No. 94-03-08857).

OM950863E