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Determination of the activation parameters of permanent allylic rearrangement in allyl- and methallylboranes and in 1,1-bis(dipropylborylmethyl)ethylene by dynamic NMR spectroscopy

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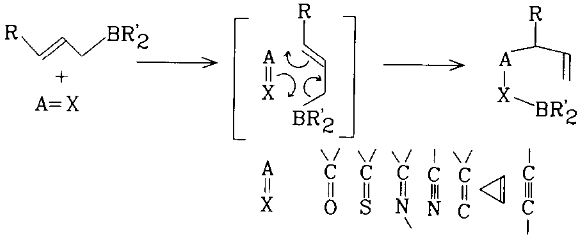
Abstract

The activation parameters were determined for the permanent allylic rearrangement (PAR) in five organoboranes of allylic type by means of complete line shape analysis for the dynamic NMR spectra The introduction of the second boron atom into the allylborane molecule leads to a significant decrease in the activation barrier of the PAR

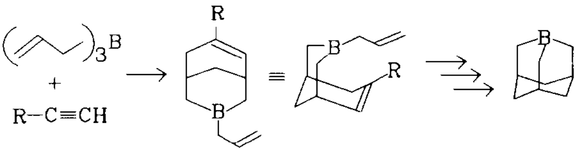
Introduction

β,γ-Unsaturated (allylic) boron derivatives possess unusual features among organoboron compounds. Their specific structure results in a dramatic distinction in chemical properties and reactivity. For more than two decades allylic organoboranes have been widely used in organic synthesis [1–4] and the scope of their synthetic application is continuously broadening. It became evident that allylboranes are a useful and in some cases a unique tool for the creation of new C–C and C–X bonds as well as for the cyclisation, functionalisation and homologisation of various classes of organic compounds [1–4].

One of the most interesting and important reactions of β,γ-unsaturated boron derivatives is allylboration, addition to organic compounds with multiple bonds C=O, C=S, C=N, C≡N, C=C and C≡C [2,3]. Allylboration reactions always proceed with rearrangement (via a six-membered transition state, see below); the more strained or polarised the multiple bond is, the easier addition occurs [3]. These reactions proceed chemo-, regio- and stereoselectively as well as enantioselectively if the chiral allylboranes are used, the asymmetric induction in some cases (RCHO) being near 100% [5–8].

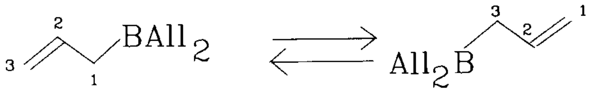


Another synthetically promising reaction of allylboranes is allylboron-acetylenic condensation [2,3,9,10], which led to the elaboration of convenient preparative methods for the construction of different types of polyunsaturated, cyclic, bicyclic and cage compounds [2,9,10], including 1-boraadamantanes [11] and 1-azaadamantane [12].



The broadening of the synthetic use of allylboranes has generated interest in more detailed study of their structure and reactivity as well as in the permanent allylic rearrangement, which is one of the most interesting features of this class of organoboron compounds.

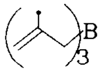
It was shown in 1965 that the ^1H NMR spectrum of triallylborane is temperature dependent. At temperatures below −40°C triallylborane gives the A_2BX_2 spectrum. An increase in the temperature leads to broadening of the signals (CH_2B and $CH_2=$) and at temperatures higher than 90°C the AX_4-spectrum is observed [13]. The character of the spectra temperature dependence as well as the absence of the concentration effect indicated the existence of the degenerated intramolecular 1,3-migration of the boron atom (1), which is sufficiently fast in the NMR time-scale.



(1)

The analysis of the spectra of triallylborane at different temperatures allowed an approximate evaluation of the activation energy for this process ($E_A \approx 10 \pm 1$ kcal mol^{-1}) [13].

Later the permanent allylic rearrangement (PAR) was established by NMR spectroscopy for the allylboranes **2**–**13**.



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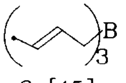

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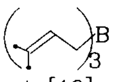

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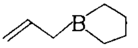

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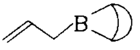

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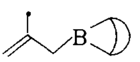

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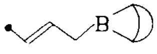

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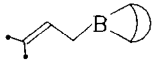

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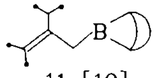

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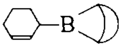

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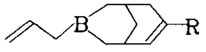


13 [20]

1,3-Sigmatropic rearrangements [21–23] similar to the PAR are prohibited by symmetry and consequently proceed usually with high activation barriers. For example, the activation barriers for the 1,3-shifts in the allylic derivatives of silicon and germanium are greater than 30 kcal mol^{-1} [24,25]; for the derivatives of aluminium, cadmium and zinc the rearrangement proceeds under mild conditions, but intermolecularly [26–29], and for the tin and mercury allylic compounds the intermolecular rearrangement occurs only in the presence of Lewis acids [30–32]. The facile intramolecular allylic rearrangement was found for the magnesium allylic compounds [33], but in this case interpretation of the experimental data is difficult owing to the Shlenk equilibrium and ionisation.

Woodword–Hoffman's rules for the sigmatropic rearrangements are known to be reversed when the migrating atom has a vacant AO [21,22]. The vacant $2p$-AO of the boron atom really is of major importance for process (1). It has been shown that the introduction into the allylborane molecule of oxygen or nitrogen containing groups, which are able to donate the electron pairs to the vacant $2p$-AO of boron, completely stops the rearrangement [34]. The same effect is observed in complexes of allylboranes with pyridine [35].

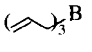
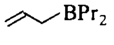
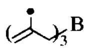
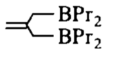
In unsymmetrically substituted allylboranes the PARs (eq. 1) become undegenerated and the result of the reactions of these compounds is dependent on the rates of allylic rearrangement and on the position of the borothropic tautomeric equilibrium, so exact knowledge of these parameters is essential for prediction of the results of allylboration reactions. With the great variety of structurally different allylic boron derivatives [3,36], we have begun detailed kinetic investigation of the PAR by means of NMR spectroscopy. In the present work we have determined the activation parameters of PAR for the two simple triallylboranes **1** and **2**, their dipropyl derivatives **14** and **15** as well as for the allylic diborane **16**, which can be regarded as dipropylallylborane **14** substituted by the CH_2BPr_2 group, or as dipropylmethallylborane **15** containing the BPr_2 group in position 2 (see Table 1).

Experimental

The exact determination of the activation parameters of the permanent allylic rearrangment in organoboranes encounters two experimental problems. The ^1H NMR spectra are in most cases too sophisticated owing to the existence of the fairly complex multiplet structure; thus complete line shape analysis cannot be carried out. In this work we used ^{13}C NMR spectroscopy because in the full decoupling mode the signals in ^{13}C NMR spectra are singlets. The second problem is the large quadrupole moment of the ^{10}B and ^{11}B atoms resulting in fast relaxation of the adjacent carbon atoms and broadening of their signals. To account for this relaxation effect we used the special procedure from an earlier elaborated program complex DISPARD NMR [37]. In this program the lineshape calculation for the dynamic NMR spectra is performed according to the universal algorithm for simultaneous analysis of the whole spectra set. The activation parameters as well as the temperature coefficients for the values of chemical shifts and line widths can be regarded as the varying parameters. The iteration process in DISPARD is carried out up to the best correlation of the whole set of the experimental and theoretical spectra.

Table 1

Low temperature NMR data [a] and activation parameters [b] for the permanent allylic rearrangement (PAR) in compounds **1**, **2** and **14–16**

Compound	δH (ppm)	δC (ppm)	Nucleus observed	No. of temperature points	Temperature range (K)	$\Delta G^{\ddagger}_{298}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})
 **1**	1 81(H^1), 6 10(H^2), 4 62, 4 83(H^3)	34.53(C^1), 134.93(C^2), 114.55(C^3)	^{13}C	13	210– 335	61.65 (0 09) [c]	-42 (3)
 **14**	1 75(H^1), 6.15(H^2), 4.58, 4 75(H^3)	33 48(C^1), 133 97(C^2), 112.56(C^3)	^{13}C	8	278– 335	66 2 (0 2)	-54 (10)
 **2**	2.25(H^1), 4 48, 4.80(H^3)	37 30(C^1), 142 60(C^2), 109.42(C^3)	^{1}H	11	212– 323	62 43 (0.09) [d]	-49 (5)
 **15**	2 20(H^1) 4 73, 4.52(H^3)	37 17(C^1), 141 56(C^2), 108.46(C^3),	^{1}H	11	223– 344	63 8 (0.1)	-68 (2)
 **16**	2 20(H^1) 4 46(H^3)	40 45(C^1), 146 87(C^2), 108 56(C^3)	^{1}H	14	213– 392	54.5 (0.1)	-8 (3)

[a] For the temperature -60°C [b] Confidence limits 95%. [c] 61(5) [13]. [d] 63(4) [14].

It is known that the rate of the quadrupole relaxation decreases with an increase in the absolute temperature. Accordingly, we have used the following dependence of the line width on the temperature for the signals of the carbons adjacent to the boron atom:

$$W = W_0 - W_1(1 - T/T_0)$$

The quadrupole broadening of the signal of C_1 is distinct at -60–20°C, i.e. in the temperature interval where the dynamic process is slow and does not affect the line width, which is evident as the C_3 signal is not broadened. This makes it possible to obtain the values W_0 and W_1 using low-temperature spectra only and then to correct them during the iteration cycle.

For the signal of C_1, which is adjacent to the boron atom, the values W_1 obtained by the procedure described are -1.0–1.2 Hz K^{-1}. For comparison, the values W_1 for the other carbon atoms are in the interval 0–0.05 Hz K^{-1}. Thus, essentially greater values of line widths for C_1 compared with C_3 in the temperature interval investigated, indicate the conservation of the C–B bond during the PAR, i.e. its intramolecular character.

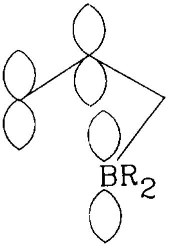
All the compounds studied were synthesised according to the procedures described earlier [2,18,38]. The samples sealed under argon containing neat liquids or 20–50% solutions in $CDCl_3$ or toluene-d_8 were used for the experiments. NMR spectra were recorded on a Jeol-FX 100 spectrometer. The temperature control was developed with the help of standard samples, methanol (for temperatures below 35°C) and ethylene glycol (for temperatures above 35°C). About 150 points were used for digitising each spectrum.

Results and discussion

Table 1 presents the values of chemical shifts ^1H and ^{13}C at -60°C, the conditions of the kinetic measurements and the activation parameters of PAR obtained for compounds **1**, **2** and **14–16**.

The values of the free activation energy obtained in this work for compounds **1** and **2** are in good agreement with the data of refs. 13 and 14, but we have improved the accuracy by more than one order of magnitude. Moreover, we have obtained reliable values of the activation entropy. For all the compounds investigated we have found the absence of the solvation effect which is in accordance with literature data [13,14] and indicates the intramolecular character of PAR in allylic boranes **1**, **2** and **14–16**.

Essentially negative values of the activation entropies for the compounds **1**, **2**, **14–16** point at the more regular structure of the transition state compared to the ground state of this process. Apparently the transition state would be similar to the conformation **17**, which is convenient for the homoallylic interaction of the π-MO of the double bond and the vacant $2p$-AO, analogous to homoallylic cations [23]. Some decrease of $\Delta S^{\ddagger}$ for **14** and **15** compared to **1** and **2** presumably indicates the higher steric requirements for the propyl groups compared to allyl radicals.



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The preference for this conformation in allylboranes was recently shown by developed quantum mechanics calculations [39]. Evidently, in allylic diborane **16** such a homoallylic interaction can be achieved for two $2p$-AO of both boron atoms. This fact, according to our point of view, is responsible for the essential decrease of the activation barrier of PAR in compound **16**.

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