ORGANOMETALLICS

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A Series of Sigmatropic Rearrangements in 2,4,6-Heptatrienyldipropylborane. Kinetic Study of a 1,7-Hydrogen Shift Facilitated by 1,3-Boron Shifts

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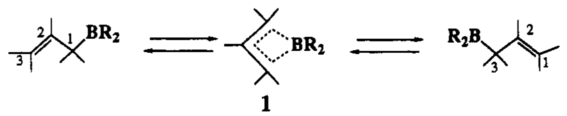
The dynamic behavior of a novel polyunsaturated allylic borane, 2,4,6-heptatrienyldipropylborane, **5**, was studied by NMR spectroscopy. It was found that four geometric isomers **5a–d** interconvert reversibly via successive 1,3 sigmatropic shifts of boron (BPr_2 group). Due to the thermal 1,7-hydrogen shift occurring in the minor *Z,Z*-isomer, **5d**, the allylic borane **5** is converted stereoselectively and reversibly into the vinylic (*E,Z,Z*)-1,3,5-heptatrienyldipropylborane, **8**. The final equilibrium mixture contains 92% **8** and 8% **5**. The effective activation energy of the conversion of **5** into **8** and the activation energy for the reverse reaction were found to be 79.8 and 87.1 kJ/mol, respectively; the preexponential factors proved to be the same, $4 \cdot 10^8$ s^{-1}. Reaction of **5** with cyclopentanone gives the trans-homoallylic alcohol **15a**, while **8** reacts with cyclopentanone yielding (*Z,Z*)-1,3,5-heptatriene, **18**.

Introduction

Allylic triorganoboranes are interesting compounds from several points of view. First, the chemistry of these compounds is rather rich because of the great synthetic power of the allylboration reaction[1] and especially due to its enantioselective variant.[2] Secondly, many cyclic, bicyclic, and cage compounds including 1-boraadamantanes and 1-azaadamantanes can be synthesized starting from triorganoboranes.[1a,c,3] And there is also a unique feature of allylboranes—permanent allylic rearrangement (PAR; 1,3 shift of boron) which occurs readily in compounds of this type.[4]

The intramolecular character of PAR[4] distinguishes it clearly from similar metallotropic rearrangements of allylic derivatives of tin,[5a] mercury,[5b] and zinc,[5c] which are intermolecular. The cyclic transition state **1** for the PAR was recently supported by advanced quantum mechanical calculations.[6] A vacant 2p-atomic orbital of the boron atom is believed to be the reason for the facile 1,3 shift of boron because this orbital decreases the energy of the four-centered transition state that normally is very high and makes it easily accessible.[6,7]

Scheme I



The permanent allylic rearrangement is a universal reaction. To date more than 20 examples of fluxional allylboranes have been described, the activation energy of PAR being in the wide range 30–80 kJ/mol.[4] Only one strictly established example of a nonfluxional allylic triorganoborane is known, (2-methylene-1-cyclopropyl)-dibutylborane.[8] In the case of unsymmetrical allylboranes the facile 1,3 shift of boron leads to the establishment of a thermodynamic equilibrium between the possible isomers. Thus, in the simplest case of tricrotylborane **2** only *Z*- and *E*-isomers **2a** and **2b** are detectable in the NMR spectra, their ratio of 1:3 being only slightly dependent on the temperature. The α-methylallylic form **2c** was not detected under any conditions.[4c]

The unusually facile 1,3 shift of boron is also responsible for the dramatic difference in the fluxional properties of

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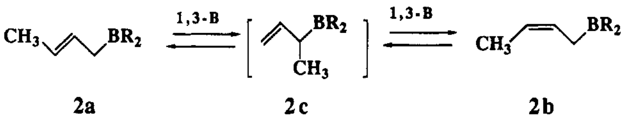
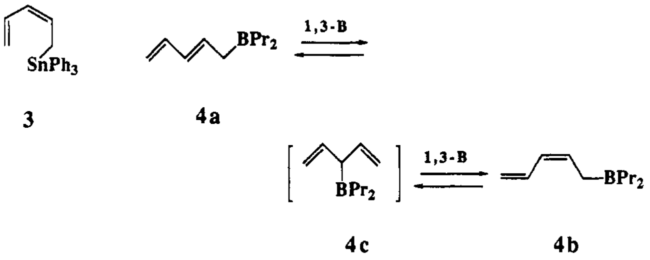
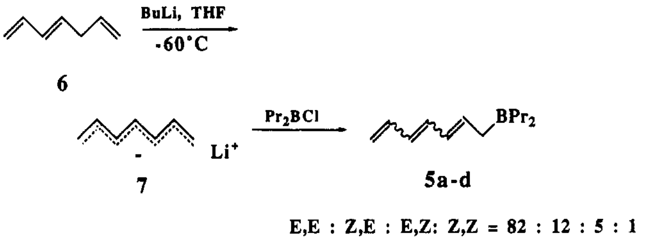
Scheme II



Scheme III



Scheme IV



pentadienyl derivatives of boron and tin. Though allyltin compounds do not undergo a 1,3 shift of tin, in the *Z*-isomer of 2,4-pentadienyltriphenyltin (3) a 1,5-Sn shift was observed, while the *E*-isomer is nonfluxional.[9] However, we have found that in 2,4-pentadienyldipropylborane (4) the interconversion of *E*- and *Z*-isomers **4a** and **4b** occurs through two consecutive 1,3-B shifts. The symmetrical compound **4c** which is formed as an intermediate could not be detected due to its relative thermodynamic instability.[10]

To continue our studies of novel allylic boron compounds[1c-d] and the PAR,[10,11] we decided to investigate the universal character of the 1,3-B shift in a more complex system, 2,4,6-heptatrienyldipropylborane (5).

Results and Discussion

2,4,6-Heptatrienyldipropylborane (5) was synthesized from 1,3,6-heptatriene (6).

Metalation of triene 6 was accomplished with *n*-butyllithium in hexane–THF.[12] Subsequent treatment of the lithium heptatrienyl 7 with chlorodipropylborane gave 5 in 70% yield.

In considering the structure of 5, one can see the multiplicity of possibilities for dynamic behavior. Theoretically, 1,3, 1,5, and 1,7 sigmatropic shifts of boron can be expected. Moreover, thermal 1,5-H and 1,7-H shifts are well documented for polyenic hydrocarbons and their derivatives with similar structures.[13] A variety of possible interconversion paths could result in complicated NMR spectra of 5. Fortunately, this was not the case.

NMR Spectral Assignment. According to the ^{1}H and ^{13}C NMR spectra (Figures 1 and 2), a major component of compound **5** is the *E,E*-isomer **5a**. Three other geometric isomers, **5b–d**, are also detectable, the ratio of **5a**:**5b**:**5c**:**5d** being 82:12:5:1 at room temperature (the relative amounts of the isomers were determined by comparison of intensities of the signals in the area of 115–116 ppm in the ^{13}C NMR spectrum; see Figure 2). The signal assignments in the ^{1}H and ^{13}C NMR spectra of **5a** were performed by two-dimensional NMR spectroscopy using standard procedures (COSY and XHCORR). The *E,E*-configuration of the major isomer **5a** was established on the basis of the coupling constant values $^3J(H^2,H^3)$ = 14.9 Hz and $^3J(H^4,H^5)$ = 14.7 Hz. Although some signals of the second isomer **5b** are not detectable in the ^{1}H NMR spectrum, the signals of H^2 and H^5 are clearly visible. That enabled us to obtain the coupling constant values $^3J(H^2,H^3)$ = 10.3 Hz and $^3J(H^4,H^5)$ = 15.3 Hz. Therefore, **5b** is 2,4-*Z,E*-isomer.

Thermal 1,7-Hydrogen Shift in Compound 5. The temperature dependences of the ^{1}H and ^{13}C NMR spectra of the mixture of the isomers **5a–d** proved to be most fascinating (see Figure 3). The temperature increase from 300 to 360 K led to the broadening of signals and the simultaneous appearance of new signals in the spectra (Figure 3b). After heating of 5 at 360 K (30 min), the NMR spectra were completely changed (Figure 3c). The ^{13}C spectrum of the same sample cooled to 300 K is given in Figure 3d. The signals of the four isomers **5a–d** are detectable, but their intensities are very low. The main component of the mixture is the vinylic borane 8.

The structure of 8 was assigned on the basis of spectral data. The strong absorption band at 1560 cm^{-1} in the IR spectrum, the chemical shift of the main signal in the ^{11}B spectrum (δ = 76.3), and the broad ($LW_{1/2}$ = 25 Hz) signal with δ = 137.21 in the ^{13}C NMR spectrum indicated the presence of the B–vinylic fragment in a product of the thermal rearrangement. The absence of the signals characteristic for the $=CH_2$ group and the appearance of the signals of the methyl group (δ = 12.39 in ^{13}C) in the spectra of 8 were in accordance with the above assumption. The complete signal assignment was achieved by 2D-correlation spectroscopy (COSY, XHCORR). Compound 8 was formed as a mixture of two isomers in a 95:5 ratio. The structure of the major isomer **8a** was elucidated from coupling constant values $^3J(H^1,H^2)$ = 16.7 Hz, $^3J(H^3,H^4)$ = 11.5 Hz, $^3J(H^5,H^6)$ = 10.3 Hz, which indicate the 1,3,5-*E,Z,Z*-structure of **8a**. The structure of the minor isomer **8b** could not be deduced directly from NMR spectra due to its low concentration, but its *Z,Z,Z*-structure could be elucidated according to literature data[14] (see also below).

The formation of vinylic borane 8 indicates clearly that the 1,7-hydrogen shift occurs in compound 5.

The thermal percyclic 1,7-hydrogen shift has been of great theoretical interest.[15] The conversion of provitamin D$_3$ to vitamin D taking place in Nature was the first

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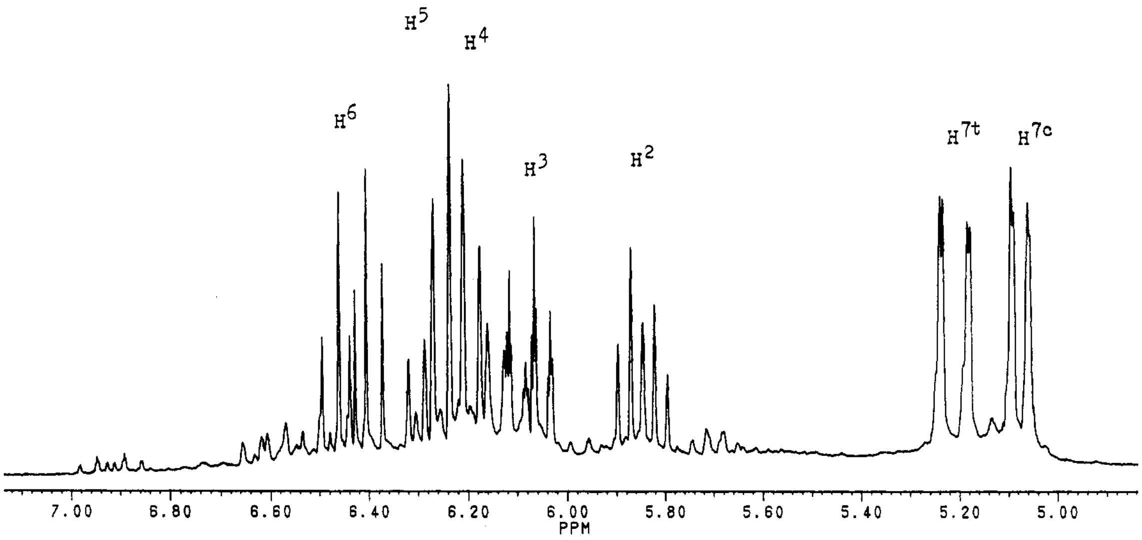


Figure 1. Section plot of the ^{1}H NMR spectrum (300 MHz, benzene-d_6, 300 K) of 2,4,6-heptatrienyldipropylborane (**5**) (olefin region).

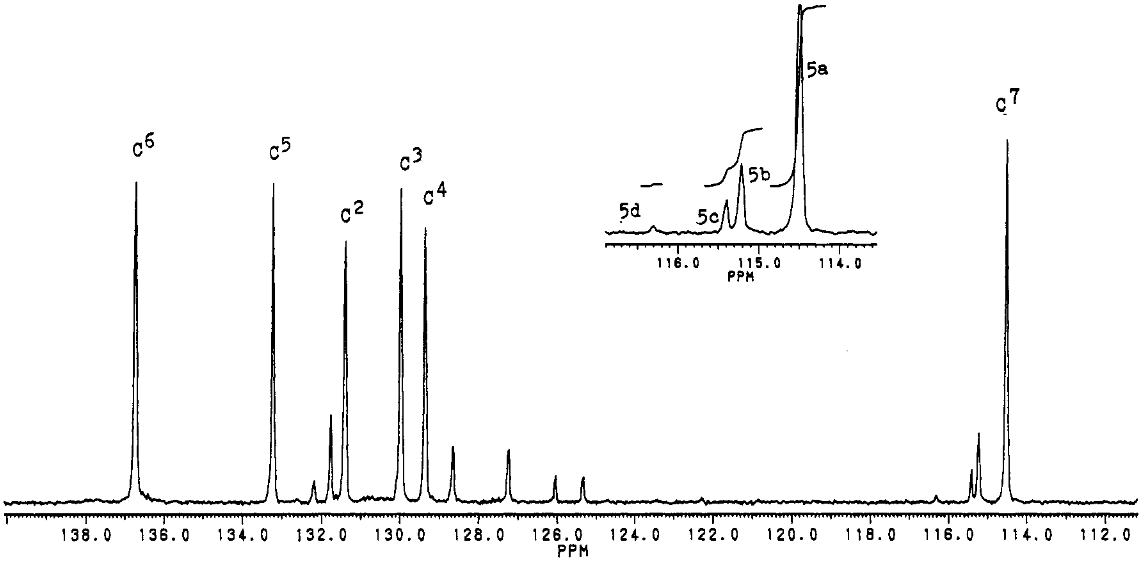
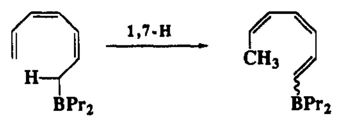


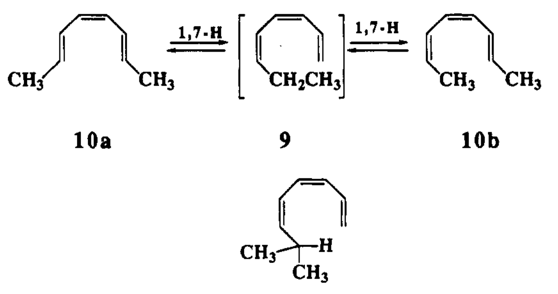
Figure 2. Section plot of the ^{13}C NMR spectrum (50 MHz, neat liquid, 300 K) of **5** (low-field region).

Scheme V



5d **8** E,Z,Z : Z,Z,Z = 95 : 5

Scheme VI



10a **9** **10b**

11

example of this reaction,[16] but only recently has its antrafacial character been proved experimentally.[17] Unfortunately, the examples described of the 1,7-hydrogen shift are rather limited due to the difficult accessibility of appropriate systems.[18] Thus, the *Z,Z*-1,3,5-octatriene (**9**), undergoes the 1,7-hydrogen shift, but it is very unstable and difficult to obtain.[13a] The interconversion of *E,E*- and *E,Z*-isomers of **10** was shown to proceed via intermediate formation of **9**.[13b] Similar processes were observed for compound **11**.[13c]

At ambient temperature the transformation of **5** into **8** proceeds in 3 weeks and at 100 °C within several minutes. Nevertheless, regardless of the temperature, 100% conversion cannot be achieved. This fact indicates the reversible character of the reaction. This statement is also supported by the temperature dependence of the line shape in the ^{13}C NMR spectrum of the final equilibrium mixture (see Figure 3c,d): with an increase in temperature, signals in the spectrum broaden distinctly. So in the case of borane **5** we have a reversible, highly stereo-

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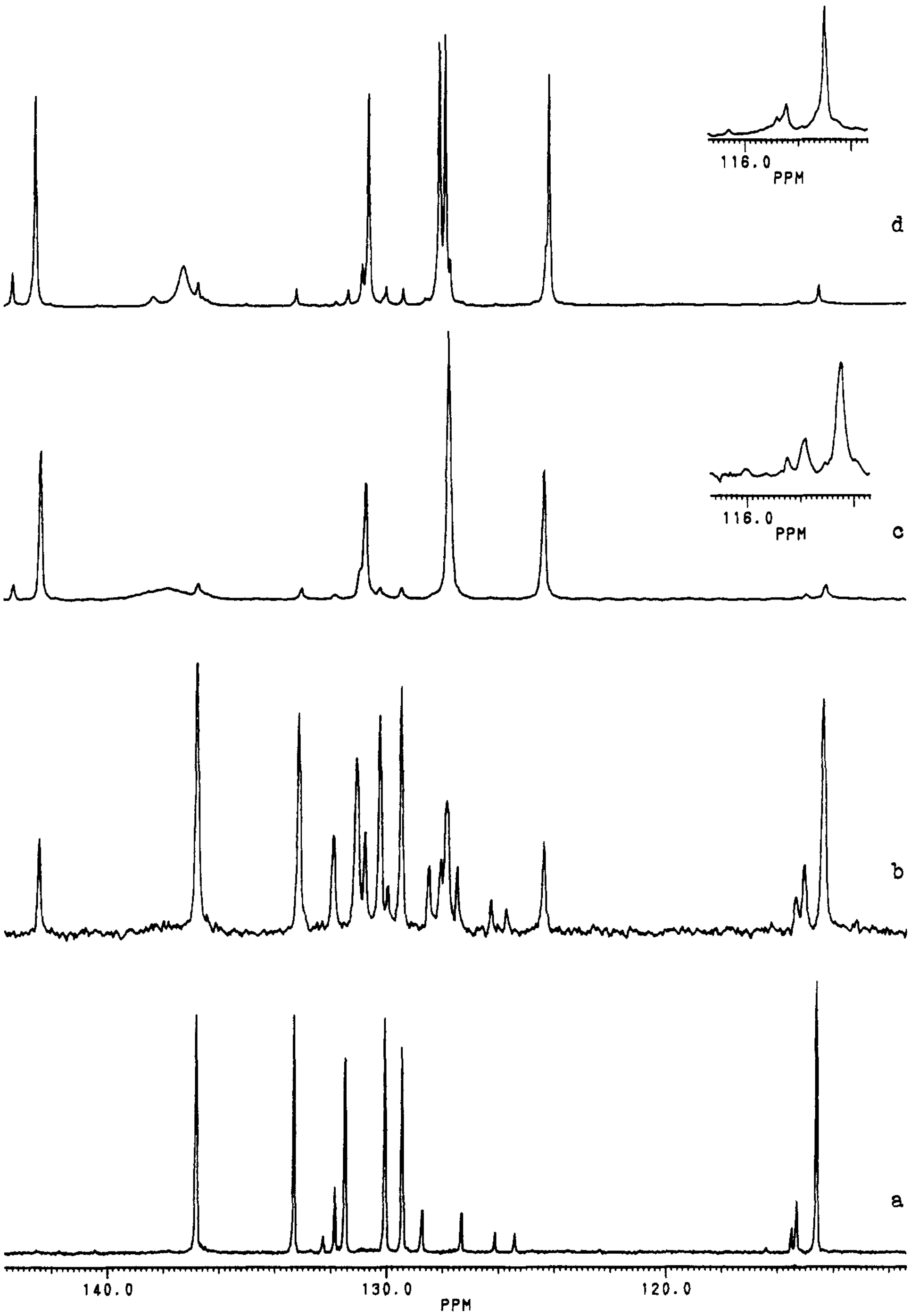


Figure 3. Changes in the ^{13}C NMR spectrum of **5** (low-field region) observed with the heating of the sample (50 MHz, neat liquid): (a) initial spectrum at 300 K; (b) spectrum obtained at 360 K just after heating (the signals of **5** are broad and the signals of **8** appear); (c) spectrum obtained after heating for 3 h at 360 K (compound **8** has become the main component of the mixture); (d) spectrum of the same sample after cooling to 300 K.

selective 1,7-hydrogen shift. An overall pattern of the reactions proceeding is given in Scheme VII.

As was mentioned above, the 2,4,6-heptatrienyldipropylborane (**5**) exists as a mixture of four geometric isomers **5a–d**. These isomers interconvert rapidly by consecutive 1,3-boron shifts via intermediate unstable isomers **5e** and **5f**. Compounds **5e** and **5f** are not detectable in the spectra due to their low concentrations, as in the case of α-methylallylic form **2c** in crotylborane **2** (see above).[4]

Apparently, a 1,7-H shift takes place in the *Z,Z*-isomer **5d**. Although it is a minor isomer in the equilibrium mixture (about 1%), the 1,7-H shift proceeds until the new equilibrium position is established due to rapid interconversion of the isomers. The final equilibrium mixture contains 92% **8a,b** in the ratio 95:5 and 8% **5a–d** in the ratio 82:12:5:1.

The high stereoselectivity of the 1,7-hydrogen shift can be rationalized by considering the geometry of the possible conformers of **5d**. Examination of the two alternative conformers **12a** and **12b** suitable for the formation of the transition state of the antrafacial 1,7-H shift, demonstrates an evident preference for the latter because of the considerable steric hindrance in **12a**.

Similar stereoselectivity was observed for the 1,5-hydrogen shift,[14a] but for the 1,7-H shift such stereoselectivity was not reported earlier.

Scheme VII

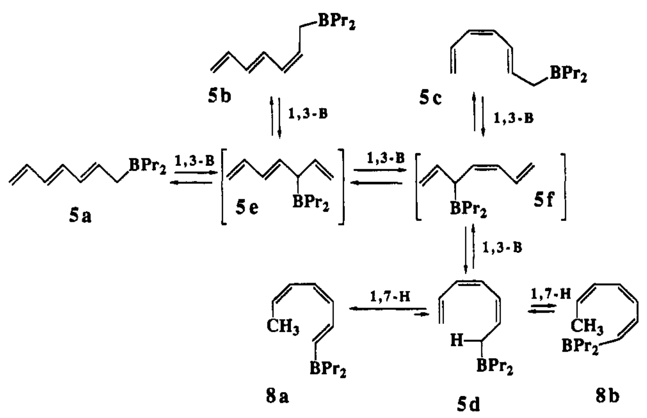


Chart I

12a **12b**

Kinetic Measurements. For the kinetic analysis it is convenient to perform Scheme VII in the following way:

$$\begin{tikzcd}
 & A_2 \arrow[d, shift left, "k_{-2}"] & A_3 \arrow[d, shift left, "k_{-3}"] & & \\
A_1 \arrow[r, shift left, "k_1"] & A_5 \arrow[u, shift left, "k_2"] \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_5"] & A_6 \arrow[u, shift left, "k_3"] \arrow[l, shift left, "k_{-5}"] \arrow[r, shift left, "k_4"] & A_4 \arrow[l, shift left, "k_{-4}"] \arrow[r, shift left, "k_+"] & V \arrow[l, shift left, "k_-"]
\end{tikzcd}$$

where A_1–A_4 denote four allylic isomers **5a–d**, A_5 and A_6 are nondetectable intermediate products **5e** and **5f**, V is vinylic isomer **8a** (because of the small concentration of the second isomer **8b** in the equilibrium mixture it was not taken into consideration in the kinetic study), k_i, k_{-i} are the rate constants of 1,3-B shifts, and k_+ and k_- are the rate constants of 1,7-H shifts.

As was mentioned above, at high temperatures (about 100 °C) the conversion of the allylic borane **5** into the vinylic borane 8 becomes rather fast and the line shape in the NMR spectra is very complex due to several simultaneous processes. Therefore in this case the rate of the permanent allylic rearrangement is very difficult to determine by means of the line shape analysis. Nevertheless, a rough estimation of the interconversion rate for the isomers of the allylic form is given by the known rate of the interconversion of *Z*- and *E*-isomers of crotylborane 2 (see above). The rate constant for the 1,3-B shift in 2 was found to be about 10 s^{-1} at 330 K and 10^2 s^{-1} at 380 K.[4c] Therefore, the characteristic time for the equilibrium establishment does not exeed 0.01–0.1 s. Comparing this value with the characteristic conversion time for the 1,7-H shift under examination, which is about 10^3–10^4 s at 330–380 K, one can conclude that the equilibrium for allylic isomers is established much faster than the 1,7-hydrogen shift occurs. In this case the concentrations of the allylic forms A_1–A_6 can be regarded as equilibrium ones and the system of differential equations corresponding to the kinetic scheme shown above can be reduced to two equations for the first order reversible reaction (see Appendix):

$$\frac{d[A]}{dt} = -k_+^{\text{eff}}[A] + k_-[V] \qquad (1)$$

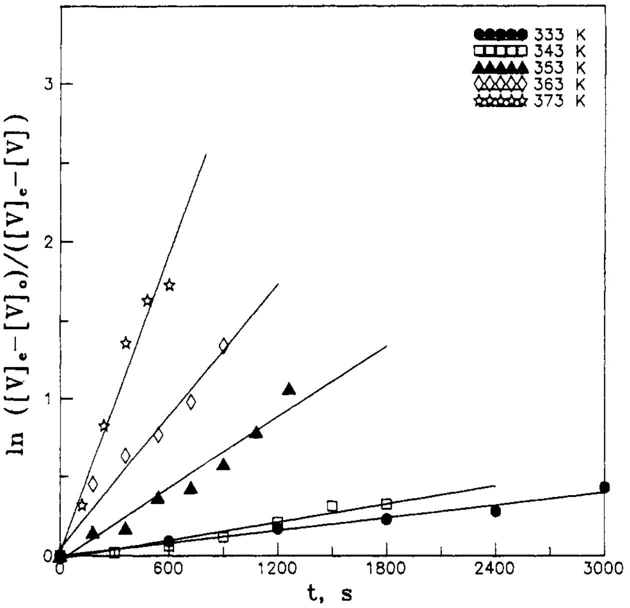


Figure 4. First-order plots of reversible formation of the vinylic borane 8 at various temperatures.

$$\frac{d[V]}{dt} = k_+^{\text{eff}}[A] - k_-[V] \qquad (2)$$

where [A] is the sum concentration of the allylic isomers, $k_+^{\text{eff}} = \alpha k_+$ is an effective rate constant of the conversion of the allylic isomer into a vinylic one (see Appendix), and k_- is the rate constant of the 1,7-H shift in 8. The solution of these equations is

$$[V](t) = [V]_e - ([V]_e - [V]_0)e^{-(k_+^{\text{eff}}+k_-)t} \qquad (3)$$

or in another form

$$\ln\frac{[V]_e - [V]_0}{[V]_e - [V]} = (k_+^{\text{eff}} + k_-)t \qquad (4)$$

where $[V]_0$ and $[V]_e$ are the initial and equilibrium concentrations of the vinylic borane 8.

Figure 4 presents kinetic kurves of the vinylic borane accumulation linearized according to eq 4. These data were obtained by ^{1}H NMR spectroscopy. Mole fractions of the vinylborane 8 were determined from the integrated ratio of olefin methylene signals of the allylic form and the integrated H^2 signal of the vinylic form (with an account of the number of protons).

The concentration of the vinylic borane determined in the first measurement at each temperature was taken as the initial concentration $[V]_0$. The equilibrium concentrations $[V]_e$ at each temperature were obtained from the equilibrium constants K_{eq} calculated on the basis of the effective value of the reaction free energy. The latter was found from three experimental values of K_{eq}. The equilibrium constants at temperatures of 300, 360, and 390 K were determined from the ratio of the integral intensities in ^{13}C NMR spectra after prolonged storage at each temperature. The effective reaction free energy $\Delta G°_{\text{eff}}$ was found to be −7.1 kJ/mol.

The values of the sum of the constants obtained from the kinetic curves as well as the calculated values of the rate constants are given in Table I. The part of A_4 in the equilibrium mixture is 1%; therefore the true k_+ value is of about 10^{-1}–10^{-2} s^{-1}.

The temperature dependences of the rate constants k_+^{eff} and k_- described by the Arrhenius equation $k(t) = A^{-E/RT}$

Table I. Rate Constants for the Conversion 5 → 8

T, K	K_{eq}	$10^4(k_+^{eff} + k_-)$, s^{-1}	$10^4k_+^{eff}$, s^{-1}	10^4k_-, s^{-1}
333	13.1	1.34	1.25	0.095
343	12.1	2.32	2.14	0.177
353	11.3	8.30	7.63	0.675
363	10.6	11.8	10.8	1.02
373	9.93	30.2	27.4	2.76

are given in Figure 5. The activation energies were found to be 79.8 kJ/mol ($A = 3.9 \times 10^8\ s^{-1}$) for the forward reaction (effective values) and 87.7 kJ/mol ($A = 4.0 \times 10^8\ s^{-1}$) for the reverse reaction.

The results of the kinetic investigation correspond exellently to the assumptions made above concerning the process scheme. Thus, the rate constants given in Table I are of the order 10^{-3}–$10^{-4}\ s^{-1}$, which is at least by 4 orders slower than the assumed rate constants of the interconversion of the geometric isomers **5a–d**. The values of the preexponential coefficients are indicative of the highly organized transition state and are in good agreement with the literature data for 1,7-hydrogen shifts.[13,14a]

Thus, we have discovered that allylic borane **5** and vinylic borane **8** interconvert reversibly due to a thermal 1,7-hydrogen shift. The equilibrium is strongly shifted to the vinylic borane **8** in accordance with the higher stability of the B–C bond in vinylic boranes in comparison with alkylboranes.[1a]

Reactions of 5 with Acetone and Cyclopentanone. It is well-known that allylboranes react rapidly with carbonyl compounds even at −100 °C.[1] So, as anticipated, allylic borane **5** reacted immediately with acetone and cyclopentanone at −30 °C with complete allylic rearrangement ($2\pi + 2\pi + 2\sigma$ process), yielding the borinic esters **13a** and **14a** which, after treatment with triethanolamine, gave trienic alcohols **15a** and **16a** in 70% and 74% yields, respectively.

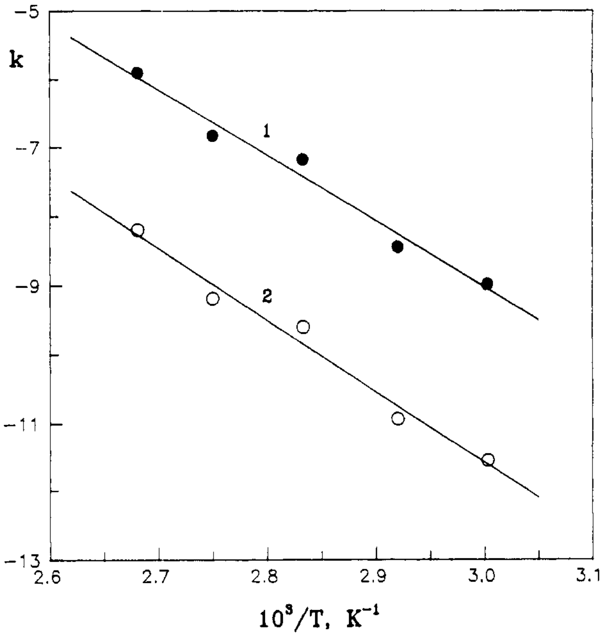
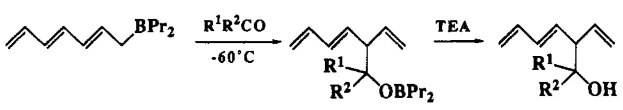


Figure 5. Arrhenius plots of the 1,7-H shift rate constants, k_+^{eff} (1) and k_- (2).

Scheme VIII



5a **13a, 14a** **15a, 16a**

13a, 15a $R^1=R^2=CH_3$
14a, 16a $R^1+R^2=(CH_2)_4$

^{1}H NMR spectra of **15a** and **16a** appeared to be of the first order, so we could easily obtain the values of coupling constants $^3J(H^4,H^5)$; they both appeared to be 15.3 Hz, which is consistent with the *E*-structures of **15a** and **16a**. Apparently, *Z*-isomers **15b** and **16b** can also be formed in the reaction of ketone with the equilibrium mixture **5a–d**, but their amounts should be very small; signals due to 3–5% **15b** and **16b** were detected in the ^{13}C NMR spectra of **15a** and **16a**. Thus, **5** readily reacts with ketones. Nevertheless, considering the existence of the equilibrium **5** ⇄ **8**, one could expect the possibility of the conversion of **8** into **15** or **16** by the reaction of **5** with ketones, the

Table II. ^{1}H NMR Chemical Shifts (δ, ppm) and Coupling Constants (J, Hz) for Compounds 5, 8, 13b, 15a, 16a, and 18

compd	$\delta(H^1)$ (J_{12})	$\delta(H^2)$ (J_{23})	$\delta(H^3)$ (J_{34})	$\delta(H^4)$ (J_{45})	$\delta(H^5)$ (J_{56})	$\delta(H^6)$ (J_{67c})	$\delta(H^{7c})$ (^2J)	$\delta(H^{7t})$ (J_{67t})	other data
5a	2.19 (8.4)	5.85 (14.9)	6.08 (9.8)	6.28 (14.7)	6.17 (9.8)	6.43 (9.8)	5.08 (1.9)	5.21 (17.0)	1.49 (m), 1.23 (t), 1.02 (t), $J_{13} = 1.2$
5b	2.29 (8.5)	5.70 (10.3)	*a* (11.5)	6.61 (15.3)	*a* (10.1)	6.92 (10.1)	*a*	*a* (16.8)	*a*
8a	6.68 (16.7)	7.87 (10.6)	6.31 (11.5)	6.55 (10.8)	6.81 (10.3)	5.63	1.81, $J_{67} = 7.2$		1.51 (m), 1.32 (t), 0.96 (t), $J_{57} = 1.6$, $J_{36} = J_{46} = 1.5$, $J_{35} = 2.0$, $J_{24} = 2.4$
13b	5.37[b]	6.14	3.40	5.91	6.42	6.55	5.37[b]	*b*	
15a	4.90[b] (14.8)	5.78 (8.3)	2.68 (8.3)	5.65 (15.3)	5.92 (15.3)	6.22 (10.0)	4.90[b]	*b* (6.6, 16.9)	2.00 (s)
16a	4.97[b] (16.9)	5.88 (7.8)	2.86 (7.8)	5.77 (15.3)	6.11 (10.3)	6.33 (10.3)	4.97[b]	*b* (10.6, 16.7)	1.4–1.8 (m), 0.9 (m), $J_{35} = 1.0$
18	5.21, 5.11 (10.6, 16.9)	6.85 (10.6)	6.03 (10.6)	6.31 (10.6)	6.52 (10.6)	5.55 (7.2)	1.70		$J_{57} = 1.6$, $J_{46} = 1.2$, $J_{35} = 0.6$, $J_{24} = 0.9$, $J_{31c} = 0.6$

[a] The signals are overlapped by the signals of the major isomer. [b] The signals of the four protons H^1 and H^7 give an unresolved multiplet.

Table III. Chemical Shifts ^{13}C (δ, ppm) for Compounds 5, 8, 13b, 15a, 16a, and 18

compd	C^1	C^2	C_3	C_4	C_5	C_6	C_7	other data
5a	33.06	131.42	130.01	129.41	133.27	136.76	114.55	16.79, 17.27, 30.38
8a	137.21	142.52	130.57	127.84	124.15	128.07	12.39	16.94, 17.95, 28.46
8b	138.32	143.35	130.82	127.68	124.28	128.50	13.40	16.86, 17.48, 30.25
13b	115.45	132.93	54.53	130.66	130.02	132.07	117.43	26.41, 54.53, 76.98
15a	115.04	137.48	59.81	133.60	132.40	136.94	117.42	26.89, 59.81, 77.14
16a	116.09	137.27	56.84	133.16	133.04	136.81	117.17	23.82, 37.81, 37.90, 56.84, 83.42
18	116.93	131.55	128.65	123.90	123.80	126.77	12.09	

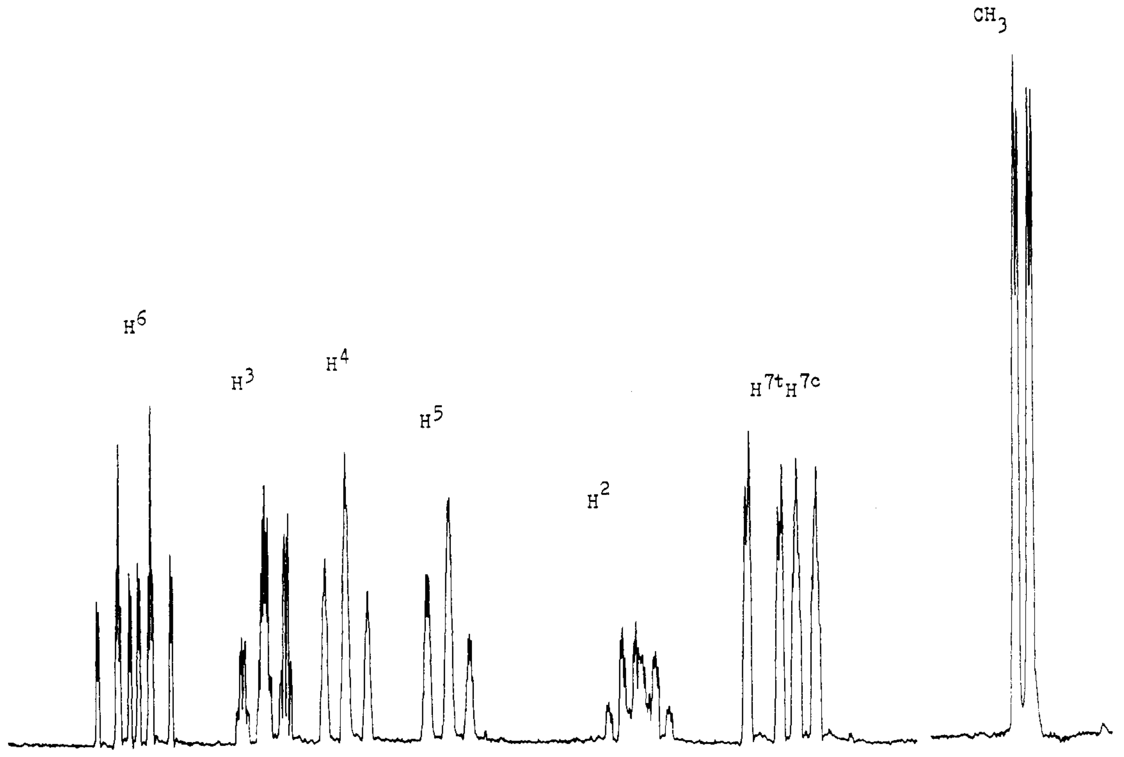
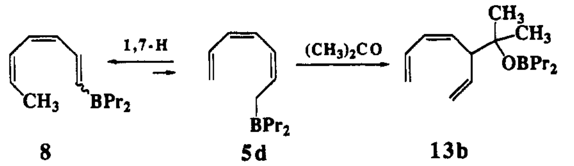
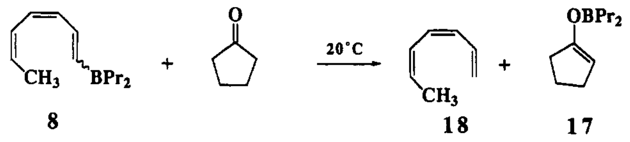


Figure 6. ^{1}H NMR spectrum of (*Z,Z*)-1,3,5-heptatriene (18) ($CDCl_3$, 200 MHz).

Scheme IX



Scheme X



rate constant being equal to k_-. So we have studied the reactions of an equilibrium mixture of 5 and 8 with acetone and cyclopentanone.

Reaction of the Equilibrium Mixture 5–8 with Acetone. The equilibrium mixture of vinylic and allylic boranes 5 and 8 (95:5) when treated with acetone (2 h at 100 °C) gives the homoallylic borinic ester **13b** with a *Z*-configuration of the double bond.

The *Z*-configuration of the reaction product is consistent with the following reaction scheme. The 1,7-hydrogen shift transforms 8 into the *Z,Z*-isomer **5d** which immediately reacts with acetone before the equilibrium between the isomers **5a–d** is established.

This fact makes possible the estimation of the relative rates of the permanent allylic rearrangement in 5 and of the reaction of 5 with acetone. We were not able to observe the presence of *E*-isomer **13a** in the reaction mixture (the sensitivity is about 1–2%); therefore, the reaction of 5 with acetone is at least 10^2 times faster than the permament allylic rearrangement in 5.

Reaction of the Equilibrium Mixture 5–8 with Cyclopentanone. We have found that the vinylic borane 8 reacts with cyclopentanone, giving borinic ester 17 and (*Z,Z*)-1,3,5-heptatriene (18) (a small amount of 5 present in the equilibrium mixture gives the ester **13a**). This reaction takes place due to the higher mobility of the α-protons of cyclopentanone (in comparison with acetone) and is similar to the protonolysis of vinylic boranes with carboxylic acids.[1a]

The *Z,Z*-configuration of the triene **18** was established on the basis of the coupling constant values $^3J(H^3,H^4)$ = 10.6 Hz and $^3J(H^5,H^6)$ = 10.6 Hz.

It should be noted that (*Z,Z*)-1,3,5-heptatriene (18) was not described earlier, while it can be obtained from 8 in high yield and in isomerically pure form. Triene **18** can be obtained more conveniently by the reaction of 8 with acetic acid.

Triene **18** is a parent compound for the study of 1,7 sigmatropic hydrogen shift.[13a] We have observed a degenerate 1,7-H shift in **18** by means of two-dimensional chemical exchange spectroscopy and performed kinetic measurements of 1,7-H shift in the parent compound using its monodeutero analog.[19] Therefore it is interesting to compare the kinetic data obtained for the several compounds of similar structure.

The rate constants given in Table IV were recalculated by considering the number of migrating hydrogen atoms and are therefore the rate constants for the single hydrogen atom transfer.

Comparison of the data given in Table IV indicates similar values for the activation energies of the 1,7-H shift in related compounds. Nevertheless, it should be noted that the rate constant of the 1,7-H shift in heptatrienyldipropylborane (5) is the highest (about 1–2 orders of magnitude higher than in other systems). This effect can be caused

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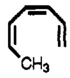
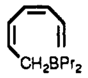
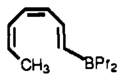
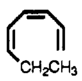
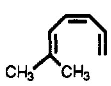
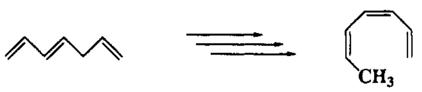
(19) Gurskii, M. E.; Gridnev, I. D.; Il'ichev, Yu. V.; Ignatenko, A. V.; Bubnov, Yu. N. *Angew. Chem.* **1992**, *104*, 762–764; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 781–783.

Table IV. Comparison of the Activation Parameters for 1,7-Hydrogen Shifts

compd	E_A, kJ/mol	A, s^{-1} (for one proton)	ref
	87	1.6×10^8	19
	80^a	$2 \times 10^{8\,a}$	this work
	87	1.3×10^8	this work
	89^b 85^c	1.3×10^9	13a
	90	5.9×10^9	13b

[a] Effective values. [b] For the conversion into (*Z*,*Z*,*Z*)-2,4,6-octatriene. [c] For the conversion into (*Z*,*Z*,*E*)-2,4,6-octatriene.

Scheme XI



by the vacant 2p-AO of the boron atom which is disposed near the migrating hydrogen atom in compound **5**.

Conclusion

2,4,6-Heptatrienyldipropylborane was synthesized, and its unusual dynamic behavior was investigated by means of NMR spectroscopy. It was shown that four isomers **5a–d** interconvert rapidly by consecutive reversible 1,3-boron sigmatropic shifts. The minor *Z*,*Z*-isomer **5d** undergoes reversible a 1,7-hydrogen sigmatropic shift, giving the vinylic borane **8**. Four isomers of **5** and two isomers of **8** coexist in the equilibrium mixture, permanently interconverting due to 1,3-B and 1,7-H sigmatropic shifts.

The *Z*,*Z*-configuration of the vinylic borane **8**, stipulated for its genesis from (*Z*,*Z*)-heptatrienylborane **5d**, allowed us to synthesize for the first time (*Z*,*Z*)-1,3,5-heptatriene, a parent compound for the study of the 1,7-hydrogen sigmatropic shift. Its synthesis can be considered as the conversion of the unconjugated (*E*)-heptatriene **4** into the conjugated (Z,Z)-heptatriene (**18**).

Experimental Section

All operations with organoboranes were performed in the atmosphere of dry argon. ^1H, ^{13}C, and ^{11}B spectra were obtained on a Bruker AC200P spectrometer (200.13 MHz for protons, 50.32 MHz for carbon, and 64.21 MHz for boron); the ^1H NMR spectrum of compound **5** was recorded on a Bruker AM-300 spectrometer.

2,4,6-Heptatrienyldipropylborane (5). To a solution of *n*-butyllithium in hexane (1 N, 40 mL) was added at −60 °C 15 mL of THF. Then at −60 °C was added dropwise 3.75 g (40 mmol) of 1,3,6-heptatriene (mixture of isomers), and the reaction mixture was stirred at −50 °C for 1 h. To the solution of heptatrienyllithium in hexane–THF thus obtained[12] (40 mmol) was added dropwise at −70 °C 6 mL (40 mmol) of dipropylchloroborane. Then the mixture was heated to room temperature, the precipitate was filtrated, and the solvent was removed. The residue was distilled in vacuo to give **5** (ratio **5a**:**5b**:**5c**:**5d** is 82:12:5:1). Yield: 4.65 g (70%). Bp: 75 °C (2 mmHg). n_D^{20} = 1.5115. IR (cm^{-1}): ν 1584, 1629, 3010, 3023, 3091. ^{11}B NMR (neat, 64 MHz): δ 85.1 (relative to $Et_2O{\cdot}BF_3$). Anal. Calcd for $C_{13}H_{23}B$: C, 82.11; H, 12.19; B, 5.69. Found: C, 82.00; H, 12.48; B, 5.63.

(*E*,*Z*,*Z*)-1,3,5-Heptatrienyldipropylborane (8). Compound **5** was heated in a sealed tube at 100 °C (water bath) for 1 h. According to NMR spectroscopy the equilibrium mixture of **8** (92%) and **5** (8%) was obtained: n_D^{20} = 1.5029. IR (cm^{-1}): ν 1556, 1598, 1729, 3017, 3045. ^{11}B NMR (neat, 64 MHz): δ 76.6 (**8**), 85.1 (**5**).

Reactions of 5 with Ketones. Ketone (2 mmol) was added dropwise at −40 °C to the solution of **5** (0.35 g, 2 mmol) in chloroform (10 mL). Then the reaction mixture was treated with an excess of triethanolamine, and the product was extracted with ether and purified on silica gel.

(*E*)-3-(Dimethylhydroxymethyl)-1,4,6-heptatriene (15a). Yield: 70%. IR (cm^{-1}): ν 1605, 1645, 1655, 3660. Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.22; H, 10.82.

(*E*)-3-(Tetramethylenehydroxymethyl)-1,4,6-heptatriene (16a). Yield: 74%. IR (cm^{-1}): ν 1600, 1638, 1648. Anal. Calcd for $C_{12}H_{18}O$: C, 80.84; H, 10.18. Found: C, 80.60; H, 9.99.

Reaction of the Equilibrium Mixture of 5 and 8 with Acetone. The equilibrium mixture of **5** and **8** (0.35 g, 2 mmol) was added to acetone (0.12 g, 2 mmol) and heated in a sealed tube for 2 h at 100 °C. According to NMR analysis (^1H, ^{13}C, ^{11}B) the borinic ester **13b** (^{11}B NMR: δ 56) was formed. However it was unstable and all attempts to obtain the corresponding alcohol or isolate **13b** in pure form were unsuccessful due to its polymerization.

Reaction of the Equilibrium Mixture of 5 and 8 with Cyclopentanone. Cyclopentanone (0.85 g, 10 mmol) was added to the equilibrium mixture of **5** and **8** (0.35 g, 2 mmol) at room temperature. The fraction collected in a trap (CO_2–acetone) at 2 mmHg contained a solution of **18** in cyclopentanone.

Reaction of the Equilibrium Mixture of 5 and 8 with Acetic Acid. Acetic acid (0.48 g, 8 mmol) was added at −30 °C with a syringe to 1.38 g (8 mmol) of the equilibrium mixture of **5** and **8**. Cooling was removed, and **18** was collected in vacuo in a cooled trap (CO_2–acetone). It was washed twice with water and dried with Na_2SO_4. Yield: 0.45 g (65%). n_D^{20} = 1.5199. IR (cm^{-1}): ν 1570, 1620, 3034, 3950, 3090. Exact mass calcd for C_7H_{10} 94.0782, found 94.0763.

Appendix

The following system of differential equations corresponds to Scheme VII:

$$\frac{d[A_1]}{dt} = -k_1[A_1] + k_{-1}[A_5] \qquad (A1)$$

$$\frac{d[A_2]}{dt} = -k_2[A_2] + k_{-2}[A_5] \qquad (A2)$$

$$\frac{d[A_3]}{dt} = -k_3[A_3] + k_{-3}[A_6] \qquad (A3)$$

$$\frac{d[A_4]}{dt} = -(k_4 + k_+)[A_4] + k_-[V] + k_{-4}[A_6] \qquad (A4)$$

$$\frac{d[A_5]}{dt} = k_1[A_1] + k_2[A_2] + k_{-5}[A_6] - (k_{-1} + k_{-2} + k_5)[A_5] \qquad (A5)$$

$$\frac{d[A_6]}{dt} = k_3[A_3] + k_4[A_4] + k_5[A_5] - (k_{-3} + k_{-4} + k_{-5})[A_6] \qquad (A6)$$

$$\frac{d[V]}{dt} = k_+[A_4] - k_-[V] \qquad (A7)$$

Summing up eqs A1–A6, the system can be reduced to the two equations:

$$\frac{d[A]}{dt} = -k_+[A_4] + k_-[V] \qquad (A8)$$

$$\frac{d[V]}{dt} = k_+[A_4] - k_-[V] \qquad (A9)$$

where $[A] = [A_1] + [A_2] + [A_3] + [A_4] + [A_5] + [A_6]$ is the total concentration of the allylic isomers. If it is considered that the equilibrium between the allylic isomers is established much faster than the equilibrium on the stage of the 1,7-H shift, then the concentration of $[A_4]$ can be expressed by

$$[A_4] = K_1K_2K_3K_5/(K_2K_3K_4 + K_1K_3K_4 + K_1K_2K_3K_4 + K_1K_2K_4K_5 + K_1K_2K_3K_5)[A] \qquad (A10)$$

where $K_i = k_i/k_{-i}$ is the equilibrium constant of the ith stage.

So the system of the seven equations is reduced to the two equations for the reversible reaction of the first order:

$$\frac{d[A]}{dt} = -k_+^{eff}[A] + k_-[V] \qquad (A11)$$

$$\frac{d[V]}{dt} = k_+^{eff}[A] - k_-[V] \qquad (A12)$$

where

$$k_+^{eff} = \alpha k_+ \qquad (A13)$$

and $\alpha = [A_4]/[A]$, a fraction of the $[A_4]$ in the equilibrium mixture of allylic isomers.

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