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Synthesis and dynamic behaviour of 1-(dipropylboryl)cyclohepta-2,4-diene

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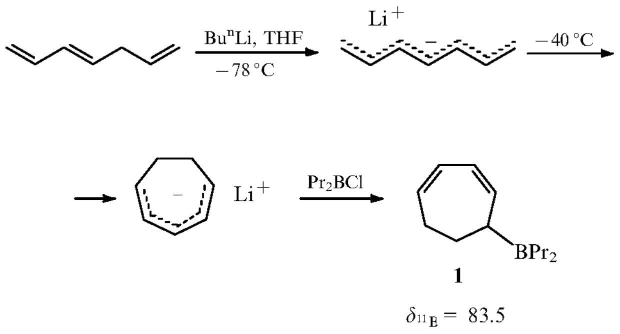
Two sequential [1,3] boron shifts in 1-(dipropylboryl)cyclohepta-2,4-diene 1 result in a degenerate rearrangement (E_A = 98.9±3.3 kJ mol^{-1}, ln A = 39.3±1.4, $\Delta G^{\neq}_{298}$ = 118.3±0.3 kJ mol^{-1}); reaction of 1 with acetone affords non-conjugated alcohol 2.

Reactions of [1,3] sigmatropic migration are prohibited by orbital symmetry and are usually characterised by high activation barriers.[1] Thus, the activation energy of [1,3] sigmatropic shifts of silicon and germanium is over 150 kJ mol^{-1} for the corresponding allylic compounds.[2] For the allylic derivatives of zinc and cadmium,[3,4] the second order of [1,3] migration was experimentally confirmed, while [1,3] sigmatropic shifts of tin and mercury are observed only in the presence of Lewis acids,[5,6] which indicates the intermolecular character of these processes. In a series of this type of reactions, one can clearly distinguish the intramolecular [1,3] boron shift in allylic boron derivatives, the so-called ‘permanent allylic rearrangement’, which is characterised by relatively low activation barriers (the activation energy is between 20 and 100 kJ mol^{-1}).[7]



Scheme 1

Continuing our investigations into the influence of structural factors on the regularities of [1,3] boron migration in allylic type triorganoboranes,[7] we synthesized a new cyclic compound of this type, 1-(dipropylboryl)cyclohepta-2,4-diene **1**, and using NMR spectroscopy investigated its dynamic properties and reaction with acetone.

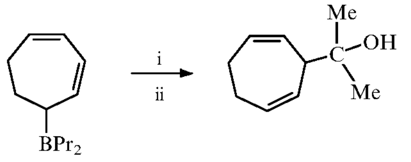
Compound **1** was prepared in 40% yield by the reaction of lithium cycloheptadienide[8] with chloro(dipropyl)borane (Scheme 1).[†]

Dienic borane **1** is a liquid which spontaneously ignites in the air. Its chemical shift ($\delta_{^{11}B}$ = 83.5) is characteristic of triorganoboranes. Similarly to other allylboranes,[9] compound **1** reacts with acetone with the allylic rearrangement to give a non-conjugated dienic alcohol **2** (Scheme 2).

It should be pointed out that this reaction has a remarkable feature, *i.e.*, the selective formation of 1,4-dienic compound **2** involves the destruction of the system of conjugated double bonds in the starting borane **1**. A similar phenomenon was observed in the reactions of linear penta-2,4-dienylboranes.[10]

[†] *Cycloheptadienyl(dipropyl)borane* **1** was obtained in 40% yield by borylation of lithium cycloheptadienide[8] at −30 to −20 °C. bp 58–59 °C (1 mmHg), n_D^{16} = 1.4895.

2-(Cyclohepta-1,4-dien-3-yl)propan-2-ol **2** was prepared by the reaction of **1** with acetone followed by oxidation with H_2O_2 and column chromatography on SiO_2. Yield 48%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): 1.24 (s, 6H, 2CH$_3$); 1.7–1.8 (br.s, 1H, OH); 2.05–2.45 (m, 4H, H-4); 3.25 (m, 1H, H-1); 5.68 (dd, 2H, ^3J = 11.5, ^3J = 4.2, H-2); 5.80 (dm, 2H, ^3J = 11.5, H-3). ^{13}C NMR (400 MHz, $CDCl_3$, 298 K): 26.24 (C-4); 27.12 (CH$_3$); 49.84 (C-1); 73.71 (C–OH); 130.04, 131.05 (C-2, C-3).



1 **2**

Scheme 2 *Reagents:* i, Me_2CO; ii, H_2O_2, OH^-.

The assignment of signals in the NMR spectra of compound **1** was performed using two-dimensional correlation NMR spectroscopy (see Table 1). On increasing the temperature to 100 °C, ^{1}H and ^{13}C NMR spectra exhibit a reversible broadening of the signals, which indicates the dynamic behaviour of borane **1**. Figure 1 shows the ^{13}C 2D EXSY spectrum of compound **1**. This spectrum contains three cross-peaks corresponding to the exchange between C^1 and C^5, C^2 and C^4, and between C^6 and C^7. The presence of these three cross-peaks attests to the degenerate rearrangement in **1** occurring as a migration of the boryl group from position 1 to position 5.

One can propose two mechanisms for the migration of the dipropylboryl group in **1**, and both are in agreement with all of the obtained experimental data, *viz.*, [1,5] sigmatropic boron shift (see Scheme 3) and two sequential [1,3] boron shifts involving the formation of a thermodynamically unstable isomer **1a** as an intermediate. We believe the mechanism of two sequential [1,3] boron migrations to be more valid, because we have previously shown that it is the [1,3] boron shift that is the most rapid process in linear penta-2,4-dienyl(dipropyl)borane **3**^{7b} (Scheme 4).

Table 1 Parameters for the ^{1}H and ^{13}C NMR spectra of **1**.

Atom	δ_H	J/Hz	δ_C
1	2.55	^{a}	44.11
2	5.91	5.9 (H^1,H^2), 11.8 (H^2,H^3)	136.45
3	5.82	^{a}	123.67
4	5.82	^{a}	125.63
5	5.82	^{a}	132.71
6	1.77, 1.98	13.4 (^2J), 9.0 (H^{6a},H^{7a}), 4.0 (H^{6a},H^{7b}), 3.0 (H^1,H^{6a}) 7.5 (H^1,H^{6b}), 7.5 (H^{6b},H^{7b}), 3.1 (H^{6b},H^{7a})	27.38
7	2.17, 2.28	17.4 (^2J) ^{a}	32.24
Pr	0.9, 1.2, 1.4	–	17.51, 17.71, 29.63

[a] Unresolved multiplet.

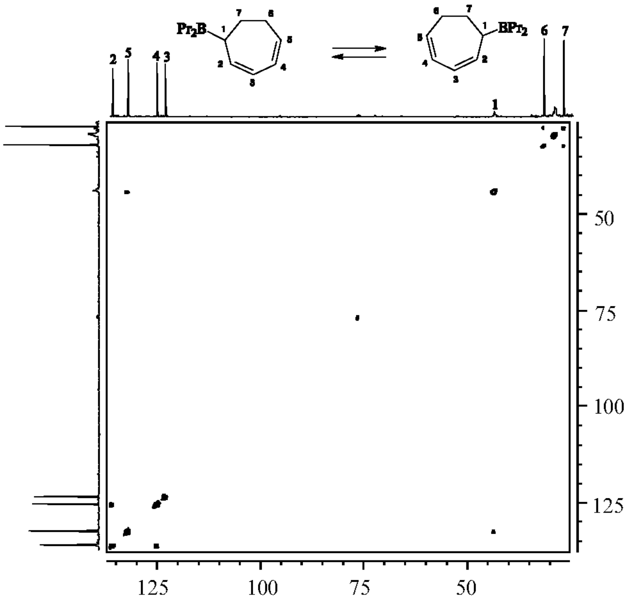
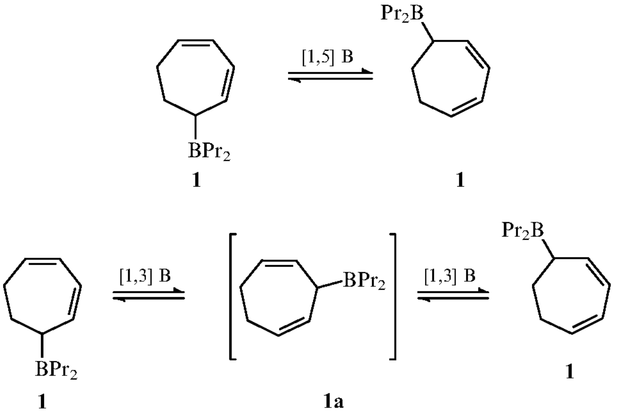
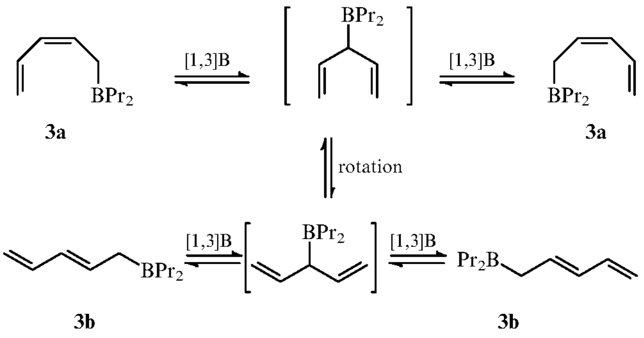


Figure 1 ^{13}C EXSY spectrum of **1** (100 MHz, 298 K, CDCl$_3$), matrix size 1024×1024, mixing time τ_m 1s.



Scheme 3



Scheme 4 $\Delta G^{\neq}$(**3a**→**3a**) = 91.5 kJ mol^{-1}; $\Delta G^{\neq}$(**3a**→**3b**) = 85.5 kJ mol^{-1}; $\Delta G^{\neq}$(**3b**→**3b**) = 82.3 kJ mol^{-1} (values at 366 K).

Kinetic analysis of the degenerate rearrangement in **1** (Figure 2) was carried out using a series of ^{1}H and ^{13}C EXSY spectra recorded at different temperatures. The rate constants were calculated by equation (1)^{11} using the intensities of diagonal and cross-peaks corresponding to the exchange between H^1 and H^5, H^6 and H^7, C^6 and C^7. The analysis gave the following values of activation parameters:

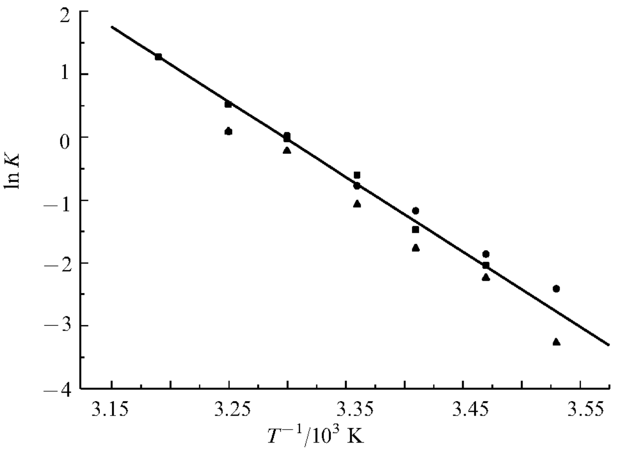


Figure 2 Arrhenius plot for the degenerate rearrangement in **1**. Squares correspond to rate constants obtained from ^{13}C EXSY spectra (exchange between C^6 and C^7), circles and triangles to the rate constants obtained from ^{1}H EXSY spectra (exchange between H^1 and H^5 and averaged data for the exchanges in two pairs of H^6 and H^7). Goodness of fit is 0.997.

$E_A = 98.9\pm3.3$ kJ mol^{-1}, $\ln A = 39.3\pm1.4$, $\Delta G^{\neq}_{298} = 118.3\pm0.3$ kJ mol^{-1}.

$$k = \frac{1}{t_m}\ln\frac{r+1}{r-1}, \qquad r = \frac{I_{AA} + I_{BB}}{I_{AB} + I_{BA}} \tag{1}$$

where I_{AA}, I_{BB} are the intensities of the diagonal peaks; I_{AB}, I_{BA} are intensities of the cross-peaks.

The activation barrier of the [1,3] boron shift obtained for compound **1** ($\Delta G^{\neq}_{298} = 118.3$ kJ mol^{-1}) is the highest of those measured for a series of allylic type organoboranes.[7] The most close values were obtained for *cis*,*cis*-penta-2,4-dienyl(dipropyl)borane **3a** (Scheme 4),[7b] which indicates that the system of conjugated double bonds in the molecule of allylic type triorganoborane retards the [1,3] boron shift.

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