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UNUSUAL THERMAL ISOMERIZATION OF B-ALKYLBORACYCLANES; EVIDENCE FOR LOW STERIC REQUIREMENTS OF BORACYCLANES IN THERMAL ISOMERIZATION[‡]

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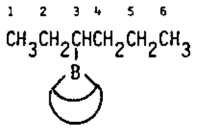
Abstract - The thermal isomerizations of B-3-hexylborolane (5), B-3-hexylborinane (6) and B-3-hexylborepane (7) were compared under identical conditions: 150°C in diglyme. The rates of isomerization decreased with decreasing steric requirements of the boracyclane. For example, the rate of thermal isomerization of B-3-hexylborepane (7) is 2 times greater than that of B-3-hexylborinane (6) and 5 times greater than that of B-3-hexylborolane (5). Moreover, the least sterically crowded B-3-hexylborolane (5) yielded an equilibrium mixture which contained more boron distributed on the terminal primary carbon atom compared to the equilibrium mixtures derived from B-3-hexylborinane (6) and B-3-hexylborepane (7).

It was recently reported[1] that B-3-hexylbis(2,5-dimethylcyclohexyl)borane undergoes thermal isomerization approximately 100 times faster than B-3-hexyldicyclohexylborane (3), 500 times faster than trihexylborane (2) and 4,000 times faster than B-3-hexyl-9-borabicyclo[3.3.1]nonane (1). Further, the organoborane (4) also yields a synthetically highly useful equilibrium mixture containing only one component, with 100% boron on the terminal carbon atom. These results were rationalized in terms of progressively increasing steric crowding, which becomes maximum in 4.

[‡] Dedicated to Professor Herbert C. Brown, an inspiring teacher, on the occasion of his 70th birthday.



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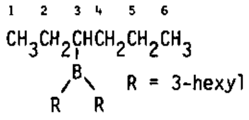

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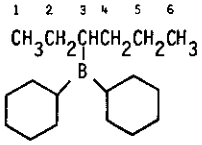

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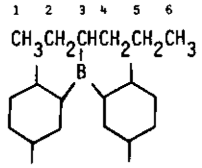

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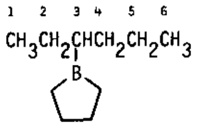
$\xrightarrow[\text{increasing rate of isomerization}]{\text{increasing steric crowding}}$

In this series, the thermal isomerization of B-3-hexyl-9-BBN (1) is exceptionally slow[2] and reaches equilibrium in 264 h (11 days), a discovery that made possible a number of synthetic applications.[2,3,4] This unusually slow thermal isomerization behavior of B-3-hexyl-9-BBN (1) prompted us to explore the thermal isomerization of other similar B-alkylboracycles in order to precisely understand the factors controlling the rate and equilibrium of isomerization.

In the recent past, simple methods have been developed for the preparation of various boracycles.[5,6,7] Accordingly we prepared B-3-hexylborolane (5), B-3-hexylborinane (6) and B-3-hexylborepane (7) and compared their thermal isomerizations under identical conditions (150°C ∿ 1 M solution in diglyme).



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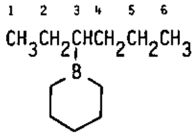

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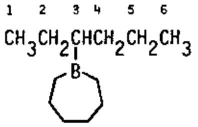

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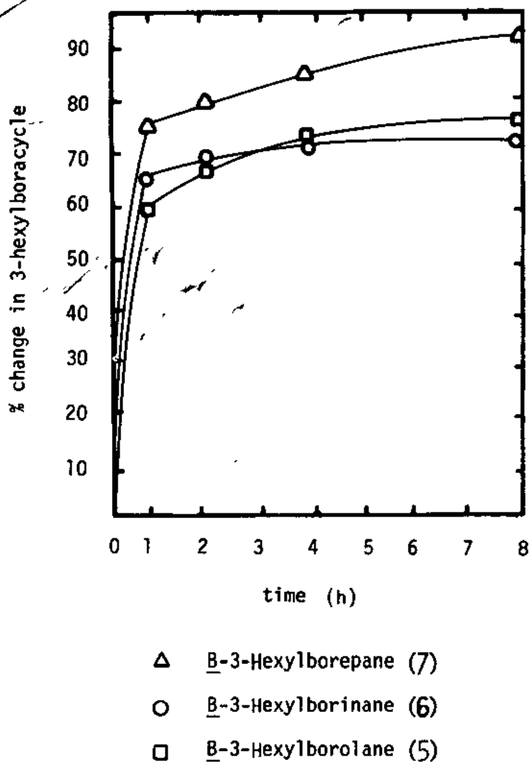
In view of the recent findings,[1] we hoped that by gradually increasing the ring size of the boracycle, we could progressively enhance the steric crowding in the B-alkylboracycle and thereby observe an increase in the rate of isomerization.

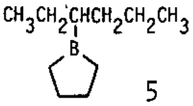
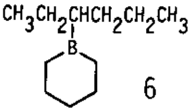
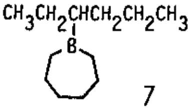
Indeed, we were gratified to find that B-3-hexylborepane (7) isomerizes approximately 2 times faster than B-3-hexylborinane (6) which in turn isomerizes approximately 2.5 times faster than B-3-hexylborolane (5, Fig. 1).

Figure 1. The Comparison of the Rates of Isomerization



More interestingly, however, we discovered an unusual trend in the equilibrium distribution of boron atom on the hexyl chain. Thus the least sterically crowded B-3-hexylborolane (5) yielded an equilibrium mixture which contained more boron distributed on the terminal carbon atom compared to the equilibrium mixtures derived from B-3-hexylborinane (6) and B-3-hexylborepane (7, Table I). This is counter to the trend previously observed for boron moieties of increasing steric requirements. The precise cause of this reversal is still under investigation.

Table I. Thermal Isomerization of B-Alkylboracycles[a]

Organoborane	$t_{1/2}$(min)	Time to Reach Equilibrium (h)	%Composition of Alcohols[b]		
			1-ol	2-ol	3-ol
 5	22	120	80	15	5
 6	10	48	61	23	16
 7	5	24	75	20	5

[a]All thermal isomerizations were done at 150 ± 2°C in diglyme using 0% hydride excess. [b]Equilibrium distribution.

B-3-Hexylborolane (5) was prepared by the general method[5] reported in the literature and purified by distillation (bp 40°/2 mm). B-3-Hexylborinane (6) was prepared by the hydroboration of cis-3-hexene with borinane[6] in THF at 25°C. B-3-Hexylborepane (7) was prepared by reducing B-chloroborepane[7,8] with $LiAlH_4$ in THF at 0°C in the presence of cis-3-hexene and purified by distillation under high vacuum (0.01 mm) and low temperature (40°C) to prevent any possible thermal isomerization. The purity of B-alkylboracycle was determined in each case by ^{11}B, ^{13}C nmr and oxidation followed by gc analysis.

Thermal isomerization was conducted in all cases by dissolving 10 mmol of B-3-alkylboracycle in 10 ml of dry diglyme; the resulting mixture (∿ 1 M solution) was maintained accurately at 150 ± 2°C by using a thermowatch. The progress of the isomerization was checked by withdrawing aliquots at regular intervals of time, oxidizing them with alkaline hydrogen peroxide and analyzing them by gc. The standard conditions used for the gas chromatographic separation of alcohols were: 10% Carbowax 1540 on Chromosorb W (100/120) column (12 ft x 1/8 in), isothermal analysis at 70°C, Varian 1200 FID gas chromatograph. Until oxidation of the product, all of the manipulations were done under N_2 atmosphere using standard techniques.[9]

The present exploratory study on the thermal isomerization of B-3-hexylboracycle shows that the rate of isomerization is in fact controlled by the steric crowding in the organoborane. However, it is not clear what factors govern the equilibrium distribution of boron atom on the hexyl chain. More detailed studies are currently in progress in order to clearly establish the factors controlling the equilibrium of the isomerization of B-alkylboracycle.

Acknowledgements

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