anol, 111-27-3; cyclohexene, 110-83-8; ethyl dicyclohexylborinate, 81340-09-2; ethyl dicyclopentylborinate, 81340-10-5; cyclopentene, 142-29-0; triethylcarbinol, 597-49-9; dicyclopentyl ketone, 17610-48-9; 2-methyl-1-pentene, 763-29-1; 4,8-dimethylundecan-6-one, 40238-04-8; ethyl benzoate, 93-89-0; benzyl alcohol, 100-51-6; ethyl pivalate, 3938-95-2; neopentyl alcohol, 75-84-3; 1-hexene, 592-41-6; 2-hexanol, 626-93-7; 2-methyl-1-pentanol, 105-30-6; cyclopentanol, 96-41-3; cyclohexanol, 108-93-0; norbornene, 498-66-8; *exo*-norbornanol, 497-37-0; *endo*-norbornanol, 497-36-9; 1-pentene, 109-67-1; 1-methylcyclohexene, 591-49-1; limonene, 138-86-3; $LiBH_4$, 16949-15-8.

Thermal Isomerization of 3-Hexyldicycloalkylboranes: Evidence for an Important Steric Factor on the Rate of Isomerization and Equilibrium Distribution

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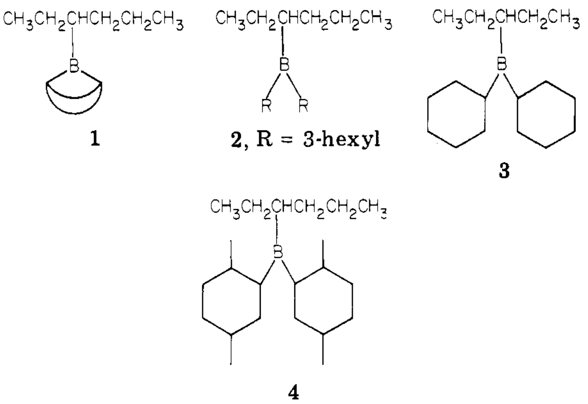
Summary: The thermal isomerizations of 3-hexyldicycloalkylboranes were compared under identical conditions. The rate of thermal isomerization of 3-hexyldicyclooctylborane (**7**) is approximately 7 times greater than that of 3-hexyldicycloheptylborane (**6**), about 33 times more than that of 3-hexyldicyclohexylborane (**3**), and nearly 100 times greater than the rate of 3-hexyldicyclopentylborane (**5**), a discovery of great importance in understanding the high dependence of the rate and equilibrium of isomerization on the size of the cycloalkyl substituents present on the boron atom.

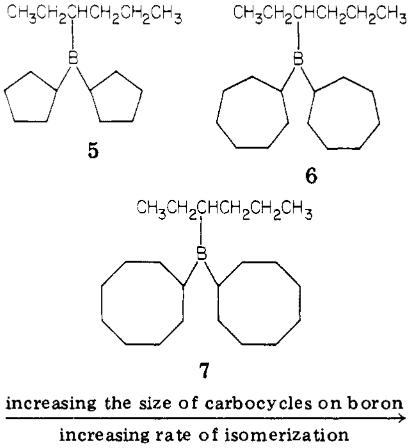
We recently reported[2] that *B*-(3-hexyl)bis(2,5-dimethylcyclohexyl)borane (**4**) isomerizes at an exceptionally rapid rate compared to 3-hexyldicyclohexylborane (**3**), tri-3-hexylborane (**2**), and *B*-(3-hexyl)-9-borabicyclo-[3.3.1]nonane (**1**, Chart I). We rationalized these results in terms of increasing steric crowding in the organoboranes.

Chart I



It then occurred to us that it might be possible to achieve significant enhancement in the rate of isomerization above that of 3-hexyldicyclohexylborane in yet another way by gradually increasing the size of the carbocyclic substituents present on the boron atom (as in Chart II) instead of introducing methyl substituents onto the cyclohexyl ring (as shown in Chart I). Therefore, we decided to study the thermal isomerization of 3-hexyldicycloalkylboranes.

Chart II



Accordingly, we prepared 3-hexyldicyclopentylborane (**5**), 3-hexyldicycloheptylborane (**6**), and 3-hexyldicyclooctylborane (**7**) and compared their rates of isomerization with that of 3-hexyldicyclohexylborane (**3**) under identical conditions: 150 °C in diglyme using 0% hydride excess (Chart II).

It is indeed gratifying to observe that 3-hexyldicyclooctylborane (**7**) isomerizes approximately 7 times more rapidly than 3-hexyldicycloheptylborane (**6**), about 33 times faster than 3-hexyldicyclohexylborane (**3**), and nearly 100 times faster than 3-hexyldicyclopentylborane (**5**, Figure 1). This is in nice agreement with our prediction that increasing the ring size of the substituent cycloalkyl groups on the boron atom could significantly increase the steric crowding in the resulting organoboranes so as to increase the rate of isomerization.

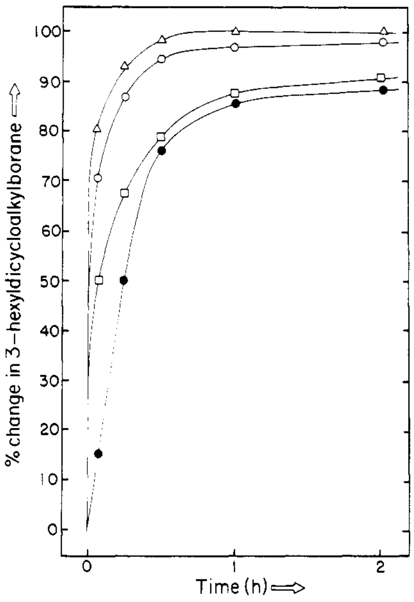


Figure 1. A comparison of the rates of isomerization of 3-hexyldicycloalkylboranes: △, 3-hexyldicyclooctylborane; ○, 3-hexyldicycloheptylborane; □, 3-hexyldicyclohexylborane; ●, 3-hexyldicyclopentylborane.

More interestingly, we also found that 3-hexyldicyclooctylborane (**7**) yields an equilibrium mixture containing more boron distribution on C-1 compared to that derived from 3-hexyldicycloheptylborane (**6**), which in turn is better than the boron distribution on C-1 observed in the equilibrium mixtures of 3-hexyldicyclohexylborane (**3**) and 3-hexyldicyclopentylborane (**5**, Table I). This shows that

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[1] Graduate research assistant on grants from the Exxon Research and Engineering Corp. and the National Science Foundation.

[2] Brown, H. C.; Racherla, U. S.; Taniguchi, H. *J. Org. Chem.* 1981, *46*, 4313.

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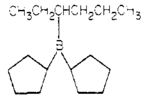
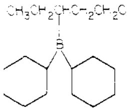
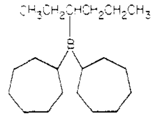
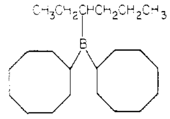
Table I. Thermal Isomerization[a] of *B*-(3-Hexyl)dicycloalkylboranes

organoborane	$t_{1/2}$,[b] s	time to reach equilibrium, h	% composition of hexanols of equilibrium: 1-ol	2-ol	3-ol
	900	48	93	5	2
	300	48	97	2	1
	60	2	98	1	1
	9	1	99	1	0

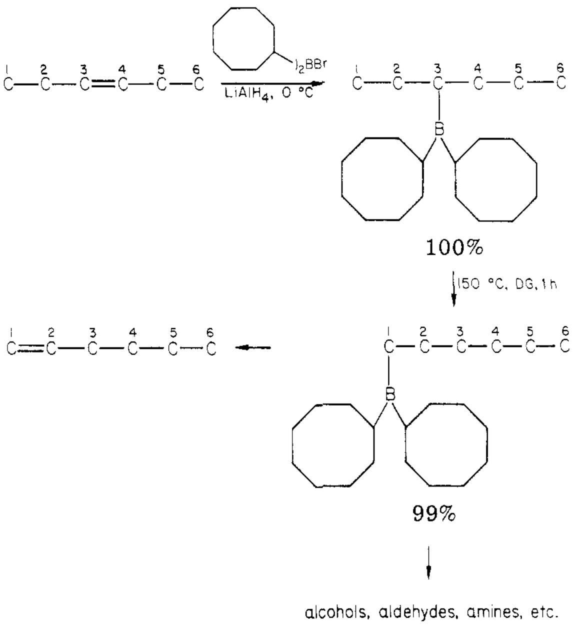
[a] All thermal isomerizations were done at 150 ± 2 °C in diglyme with 0% hydride excess. [b] $t_{1/2}$ was determined graphically from kinetic data obtained in each case.

the rate of isomerization and the equilibrium distribution increase in the same direction, consistent with the importance of a steric factor in both phenomena.

The following procedure is representative for the preparation of 3-hexyldicycloalkylboranes. Dicycloheptylbromoborane was first prepared by adding 1.2 mL of 8.3 M $BH_2Br{\cdot}SMe_2$ (neat liquid, 10 mmol) to 2.115 g of cycloheptene (22 mmol) in 5 mL of dry CH_2Cl_2 at 0 °C and then stirring the solution at 25 °C for 5 h. The completion of the reaction was checked by ^{11}B NMR. The solvent CH_2Cl_2 and excess olefin were then pumped off under vacuum, and the reaction mixture was dissolved in 5 mL of anhydrous ether. Next, 1.5 mL of *cis*-3-hexene (12 mmol) was added, followed by 2.6 mL of 0.98 M $LiAlH_4$ solution[3] in ether 2.5 mmol), and the reaction mixture was stirred at 0 °C for 12 h. The excess olefin and solvent ether were then pumped off under vacuum, and 10 mL of anhydrous pentane was added. Next, 2.6 mL of 3.9 M NaOMe (10 mmol) in methanol was added to precipitate aluminum bromide as aluminum methoxide, and then the supernatant liquid was carefully transferred into another flask. The precipitate was washed twice with 2 mL of pentane, and the washings were added to the already collected pentane solution. The pentane was subsequently evaporated, and the trialkylborane was distilled under very high vacuum (0.005-mmHg pressure). The pure 3-hexyldicycloheptylborane was then dissolved in 10 mL of dry diglyme, and the resulting mixture was isomerized at 150 ± 2 °C by using a thermowatch. The progress of the isomerization was checked at regular intervals of time by oxidizing 1-mL aliquots with alkaline hydrogen peroxide and analyzing the alcohols (extracted into ether) by GC. The standard conditions used for GC analysis were 10% Carbowax 1540 on Chromosorb W ($^1/_8$ in. × 12 ft) and isothermal analysis at 70 °C (Varian 1200 FID GC). A nitrogen atmosphere was maintained until the completion of oxidation.

Thus, the present exploratory study clearly brings out the influence of an important steric factor, namely, the ring size of the cycloalkyl substituents on the boron atom, on the rate and equilibrium of thermal isomerization of 3-hexyldicycloalkylboranes. It also enhances the scope of thermal isomerization for synthetic purposes (Scheme I).

Scheme I



We continue to explore the steric influences on the rate and equilibrium of thermal isomerization. Efforts are currently underway to develop dicycloalkylboranes from still higher membered rings, which we hope to be of utmost synthetic importance.

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[3] Brown, H. C.; Kulkarni, S. U. *J. Organomet. Chem.* **1981**, *218*, 309.

Coupling of Methylidyne and Carbonyl Ligands on Tungsten. Crystal Structure of $W(\eta^2\text{-}HC{\equiv}COAlCl_3)(CO)(PMe_3)_3Cl$

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Summary: $W(CH)(PMe_3)_4Cl$ reacts with carbon monoxide in the presence of AlX_3 (X = Me or Cl) to give complexes of the type $W(\eta^2\text{-}HC{\equiv}COAlX_3)(CO)(PMe_3)_3Cl$. Single crystals of $W(\eta^2\text{-}CH{\equiv}COAlCl_3)(CO)(PMe_3)_3Cl$ are monoclinic, space group $P2_1/c$, with a = 10.4197 (17) Å, b = 12.8965 (25) Å, c = 19.3194 (45) Å, β = 105.88 (2)°, V = 2497 (1) Å^3, and ρ(calcd) = 1.73 g cm^{-3} for Z = 4 and molecular weight 650.

Carbon–carbon bond formation via the reaction of surface-bound methylene or methylidyne groups with carbon monoxide might play a significant role in heterogeneous metal-catalyzed reductions of carbon monoxide with molecular hydrogen,[1] even though the latest theory

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