

Figure 1. Variable-temperature 250-MHz ^1H NMR of $\text{Cp}(\text{CO})_2(\text{PEt}_3)\text{W}=\text{CH}_2^+$ in CD_2Cl_2 .

moiety adopts the "upright" conformation with the H_a -C- H_b plane aligned with the W-P bond. Using extended Hückel calculations for the similar system $\text{Cp}(\text{CO})_2(\text{PH}_3)\text{Mo}=\text{CH}_2^+$, Hoffmann²¹ has predicted such a ground-state conformation, with a calculated barrier to rotation around the Mo=C bond of 15 kcal/mol. The upright conformation is also that observed by X-ray crystallography for the structurally similar heteroatom carbenes, $\text{Cp}(\text{CO})_2(\text{Ph}_3\text{M})\text{M}=\text{CR}(\text{OR})$.⁹ The assignment of H_a resonances to the synclinal hydrogen is based on the close comparison of the chemical shifts and ^{31}P - ^1H coupling constants to those in the benzylidene complex **2c**. In **2c** the aryl ring is assumed to be in the sterically less crowded anticlinal position. Thus the benzylidene hydrogen occupies the synclinal position.

The ^1H NMR spectra of both tungsten methylene complexes **2a** and **2b** are temperature dependent and allow calculation of the barrier to rotation around the tungsten-carbon multiple bond (see Figure 1). As the temperature is raised above -110 °C, the two resonances for the nonequivalent methylene hydrogens begin to broaden. Coalescence for **2a** occurs at -85 °C (250 MHz) and for **2b** at -70 °C (250 MHz). Each spectrum sharpens to a doublet above -40 °C. Line-shape analysis yields free energies of activation, ΔG^\ddagger , for bond rotation of 8.3 ± 0.1 kcal/mol for **2a** and 9.0 ± 0.1 kcal/mol for **2b**. The higher barrier for **2b** is consistent with the better donor properties of Et_3P relative to PPh_3 .

For the molybdenum methylene complex, **3**, only a two-proton doublet (δ 15.4 ($J_{\text{P-H}} = 12.5$ Hz)) can be observed even at temperatures as low as -90 °C. The similarity of the chemical shift and $J_{\text{P-H}}$ to those observed for the high-temperature averaged spectra of **2a** (δ 15.1 ($J_{\text{P-H}} = 16.2$ Hz)) and **2b** (δ 14.8 ($J_{\text{P-H}} = 16.2$ Hz)) suggests that the molybdenum complex also adopts the upright conformation, but that the rotational barrier is quite low. With the use of the high-temperature approximation formula to obtain a minimum rate constant for the exchange, a conservative upper limit to the rotational barrier can be set at 6.7 kcal/mol.²² The observed values of $\Delta G^\ddagger_{\text{rot}}$ for the Mo and W methylene complexes are somewhat lower than those of the $\text{Cp}(\text{diphos})\text{Fe}=\text{CH}_2^+$ system ($\Delta G^\ddagger_{\text{rot}} = 10.4$ kcal/mol)^{3d} and considerably lower than the $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}=\text{CH}_2^+$ system whose nonequivalent methylene signals remain sharp to 10 °C ($\Delta G^\ddagger_{\text{rot}} \geq \text{ca. } 15$ kcal/mol).^{4a}

The high electrophilicity of these complexes is substantiated by their observed reactivity with olefins. Transfer of the methylene moiety of **2a**, **2b** and **3** to styrene in CH_2Cl_2 occurs within 10-15 min at -78 °C to produce phenylcyclopropane in $> 50\%$ yields. On the basis of these results, the readily generated and easily modified $\text{Cp}(\text{CO})_2\text{LM}=\text{CHR}^+$ systems appear to have potential as carbene-transfer reagents. Synthetic modifications of these complexes as well as reactions with other nucleophilic and unsaturated organic substrates are currently under investigation.

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(22) Line broadening of the methylene signal of **3** is ca. 8.8 Hz at half-height (ΔW) at -90 °C (broadening may be viscosity related). Assuming the chemical shift difference, $\nu_A - \nu_X$, in the static spectrum will be similar to that for the tungsten species **2a** (458 Hz) and applying the high-temperature approximation $k = (\nu_A - \nu_X)^2 / 2(\Delta W)$, we can estimate the minimum rate constant for exchange at -90 °C as $3.64 \times 10^4 \text{ s}^{-1}$ ($\Delta G_{\text{rot}} \leq 6.7$ kcal/mol).

Controlled Hydroboration of Alkenes by Lithium Borohydride Induced by the Reduction of Carboxylic Esters

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Summary: Alkenes, which are normally inert to lithium borohydride, are rapidly hydroborated in the presence of carboxylic esters in ether at 25 °C to dialkylborinates, valuable intermediates for various conversions. At the same time, catalytic amounts of alkenes markedly enhance the rate of reduction of esters of lithium borohydride.

Lithium borohydride is a valuable reagent for the selective reduction of carboxylic ester groups in the presence of many other reducible substituents.¹⁻³ In the course of

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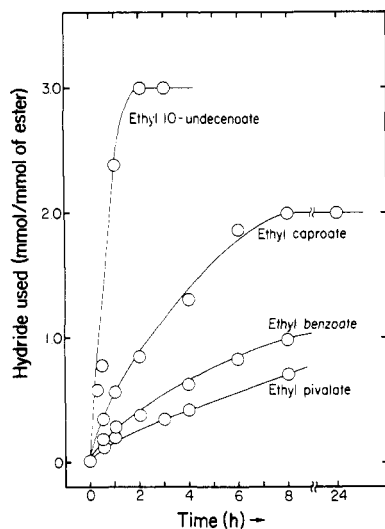


Figure 1. Reduction of esters by LiBH_4 in ether at 25°C : [ester] = 1.0 M; $[\text{LiBH}_4] = 1.0 \text{ M}$.

Table I. Reduction of Esters by Lithium Borohydride in Ether at 25°C ^a

ester	time, h, hydride used for reduction ^b					
	0.5	1.0	2.0	4.0	6.0	8.0
ethyl caproate	0.34	0.56	0.81	1.29	1.86	1.99
ethyl benzoate	0.18	0.27	0.37	0.61	0.82	0.98
ethyl pivalate	0.14	0.21	0.35 ^c	0.42		0.69
ethyl 10-undecenoate	0.77	2.38	d			

^a [ester] = $[\text{LiBH}_4] = 1.0 \text{ M}$. Reaction monitored by hydrolysis of LiBH_4 using glycerine- H_2O -THF (1:1:1) mixture and measuring the hydrogen evolved. ^b Mmol/mmol of ester. ^c 3.0 h. ^d White precipitate formed.

a study of the rate of reduction of esters by lithium borohydride in ethyl ether and tetrahydrofuran, we observed that under identical reaction conditions (1.0 M each in LiBH_4 and ester, 25°C) the uptake of hydride by the unsaturated ester, ethyl 10-undecenoate, was far faster than the uptake by the saturated ester, ethyl caproate (Figure 1, Table I). This unexpected result prompted us to investigate this phenomenon in detail.

Accordingly, ethyl 10-undecenoate (30 mmol) was treated with LiBH_4 (30 mmol) in ether at 25°C for 2.0 h. The reaction product was then hydrolyzed with 6 N HCl (5 mL, 30 mmol). A total of 31 mmol of hydrogen was evolved. This indicates that 3 mmol of hydride are utilized per mmol of ester, compared to 2 mmol of hydride utilized by ethyl caproate and similar saturated carboxylic esters. The solution was made alkaline with aqueous sodium hydroxide and oxidized with 10 mL of 30% hydrogen peroxide. The solution was saturated with potassium carbonate and extracted with tetrahydrofuran ($3 \times 10 \text{ mL}$). Distillation gave 5.08 g: bp $190\text{--}192^\circ\text{C}$ (20 mm); solidified, mp $54\text{--}57^\circ\text{C}$. GLC analysis (Carbowax 10%, 20 M on Chromosorb W, 6 ft \times $1/4$ in.) showed two peaks, corresponding to 1,10-undecanediol (15%) [lit.⁴ bp 168°C (8 mm); mp 48°C] and 1,11-undecanediol (85%) [lit.⁴ bp 178°C (12 mm); mp 62°C]. Thus the recovered yield is 90%.⁵

Table II. Stoichiometry of the 1-Decene Catalyzed Reduction of Ethyl Caproate by Lithium Borohydride in Ether at 25°C ^a

ester, mmol	LiBH_4 , mmol	olefin, mmol	residual reactants		
			ester, ^b mmol	LiBH_4 , ^c mmol	olefin, ^d mmol
1	1	6	0.18	0	3.63
1	1.25	6	0	0	3.04
1	2	6	0	0.75	3.02
1	6	6	0	4.76	3.05
1	1.25	3	0	0	0.06 ^e

^a Reaction time, 8 h. ^b Analyzed by GLC after oxidation using Carbowax 10% 20M on Chromosorb W, 6 ft \times $1/4$ in. ^c Estimated by hydrolysis method. ^d Determined by ^1H NMR using benzene as internal standard. ^e ^{11}B NMR showed two peaks: δ 8 and 2.6.

Table III. Hydroboration-Oxidation of Representative Alkenes by Lithium Borohydride in the Presence of Ethyl Acetate^a

alkene	product	% yield ^b
1-hexene	1-hexanol	92
	2-hexanol	8 (97)
1-decene	1-decanol	92
	2-decanol	8 (98)
2-methyl-1-pentene	2-methyl-1-pentanol	100 (96)
cyclopentene ^c	cyclopentanol	95
cyclohexene ^c	cyclohexanol	96
norbornene ^c	exo-norbornanol	98
	endo-norbornanol	2 (96)

^a Ethyl acetate = 5.0 mmol; alkene = 15 mmol; $\text{LiBH}_4 = 6.88 \text{ mmol}$. ^b GLC yields. Values in parentheses represent overall yield based on olefin reacted. The products were identified by coinjection with standard samples. ^c Alkene = 10 mmol; $\text{LiBH}_4 = 5.5 \text{ mmol}$.

Alkenes are normally inert to the action of lithium borohydride. Consequently, the reduction of the ester grouping in ethyl 10-undecenoate in some way activates the lithium borohydride reagent so that it concurrently hydroborates the carbon-carbon double bond in the molecule. It was of interest to examine whether the same phenomenon would be observed if the carbon-carbon double bond were contained in a separate molecule.

Accordingly, the rate of reduction of ethyl caproate by lithium borohydride in ethyl ether in the presence of an equimolar concentration of 1-decene was examined. Indeed, we observed a very fast uptake of 3 equiv of hydride (30 min) with complete reduction of the ester and complete hydroboration of the alkene. Oxidation of the reaction product and analysis by GLC indicated 92% 1-decanol and 8% 2-decanol, as well as 98% 1-hexanol (from the ester).

We then studied the stoichiometry of this reaction in order to provide a useful method for the hydroboration of alkenes. It is evident from Table II that a maximum of 3 mol of 1-decene are hydroborated by lithium borohydride for each mole of ester reduced. Similar results were obtained with ethyl acetate.⁶ Although the stoichiometry indicates the formation of trialkylborane, ^{11}B NMR analysis of the reaction mixture showed two peaks around δ 8 and 3. Hydrolysis of this mixture and analysis of the ether layer indicated two peaks: δ 87 (R_3B) and 54 ($\text{R}_2\text{BOR}'$). However, when the alkene present was decreased to two alkenes per ester, only the dialkylborinate was formed.⁷ Interestingly, in the case of cyclic olefins,

(6) Attempts to use methyl formate at 25 and 0°C resulted in incomplete hydroboration, probably due to its fast reduction by LiBH_4 (100%, 5 min).

(7) When equal concentrations of olefin and ester were used, ^{11}B NMR indicated again the formation of $\text{LiR}_2\text{B}(\text{OEt})_2$ and $\text{LiB}(\text{OEt})_4$.

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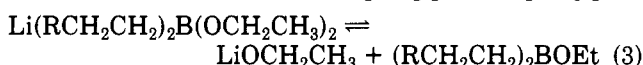
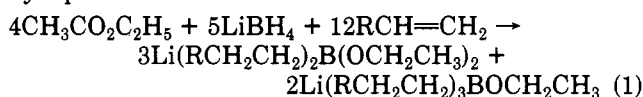
(5) Paul, R.; Joseph, N. *Bull. Soc. Chim. Fr.* 1952, 550. The authors reported the formation of unsaturated alcohol when reacted with KBH_4 in the presence of LiCl in THF. However, we found that even in THF the double bond was hydroborated with LiBH_4 .

Table IV. Alkene-Catalyzed Reduction of Esters by Lithium Borohydride in Ether at 25 °C^a

ester	alkene	[alkene], M	time, h, hydride used for reduction ^b							
			0.1	0.25	0.5	1.0	1.5	2	3	
ethyl caproate	1-decene	1.0	1.08	2.2	3.03	3.03				
		0.2		1.04	1.45	2.2	2.2			
		0.1		0.42	0.96	1.6	2.01	2.10	2.10	
	1-pentene	0.05	0.21	0.57	0.99	1.28	1.58	1.99		
		0.1	0.85	1.35	2.10	2.10				
		0.1	0.85	1.34	1.93	2.11	2.11			
		0.1	0.67	1.08	1.55	2.10	2.10			
		0.1	0.71	1.15	1.49	2.09	2.10			
		0.1	1.2	1.87	2.15	2.2	2.2			
ethyl benzoate	1-decene	0.1	0.11	0.32	0.68	0.79	0.99	1.71		
ethyl pivalate	1-decene	0.1	0.35	0.53	1.51	2.07	2.10			

^{a, b} See corresponding footnotes in Table I.

only 2 mol are hydroborated per ester reduced, even in the presence of excess olefin, producing both the dialkylborinate and its ate complex (¹¹B NMR spectrum δ 52 and 7.4). The formation of these products as well as the observed stoichiometry for the reaction could be expressed by eq 1–3.



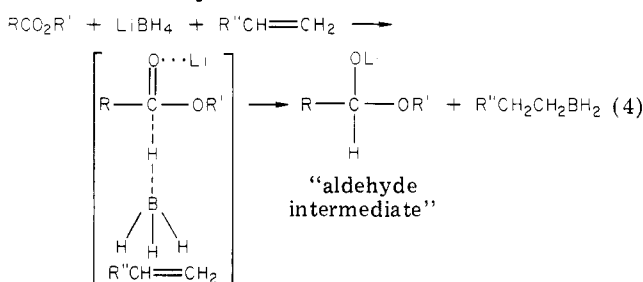
Dialkylborinates are synthetically valuable intermediates which are not accessible through direct hydroboration with borane.⁸ Currently, the best method for synthesizing such dialkylborinates utilizes hydroboration with haloboranes.⁹ However, the ester induced hydroboration of alkenes by lithium borohydride affords a simple alternate route to these intermediates. Thus, cyclohexene (10 mmol) was reacted with lithium borohydride (5 mmol) in the presence of ethyl acetate (5 mmol) in ether at 25 °C for 1 h. After the completion of the reaction, ether was removed. The solid was extracted with pentane (3 × 10 mL) and centrifuged and the clear pentane solution collected in a flask. Removal of pentane provided 1.04 g (94%) of ethyl dicyclohexylborinate [identified by ¹H NMR (CDCl₃) δ 0.6–1.4 (m, 25 H), 3.4 (q, 2 H, OCH₂); ¹¹B NMR (CDCl₃) 52 ppm; also by ¹³C NMR]. Ethyl dicyclopentylborinate was isolated similarly: yield 95%.

Further applications of this reaction are the synthesis of alcohols by a new hydroboration–oxidation procedure involving the activation of lithium borohydride by esters and the one-pot conversion of alkenes to symmetrical ketones utilizing dichloromethyl methyl ether (DCME).⁸ The alcohols are obtained in essentially quantitative yield with selectivities similar to those from borane⁸ (Table III). The ketones are obtained as follows: cyclopentene (10 mmol) is treated with lithium borohydride (5 mmol) and ethyl acetate (5 mmol) in ether at 25 °C for 1 h. To the reaction product is added 10 mmol of DCME followed by 5 mmol of lithium triethylcarboxide. After 15 min, the product is oxidized with alkaline hydrogen peroxide and extracted with pentane. Pentane is removed under reduced pressure, followed by triethylcarbinol, bp 54–56 °C (16 mm). Further distillation provided pure dicyclopentyl

ketone, bp 115–117 °C (15 mm) [lit.¹⁰ 86 °C (5 mm); 0.664 g (80%)]. The product is identified by ¹H NMR, IR, and ¹³C NMR spectra. Similarly, 2-methyl-1-pentene afforded 4,8-dimethylundecan-6-one in 79% yield; bp 124–126 °C (20 mm).

We have earlier reported that the reduction of esters is catalyzed by the presence of dialkylborinates, such as *B*-methoxy-9-borabicyclo[3.3.1]nonane.¹¹ The formation of dialkylborinates in the present reaction prompted us to study the catalytic effect of alkenes on the rate of reduction of esters. Indeed, we found 10 mol % of alkene markedly catalyzes the reduction of esters (Table IV).

We can account for the rate-enhancing effect of the alkene on the reduction of the ester grouping by postulating a coupled reaction. Accompanying the transfer of the hydride to the carbonyl group is a transfer of borane to the alkene (eq 4).



Since the second hydroboration is usually very fast, the alkylborane would form dialkylboranes.¹² The formation of trialkylborane should be kinetically slow compared to the reduction of the “aldehyde intermediate”. However, with high olefin concentration, the trialkylborane is formed.

Thus, the present study demonstrates the possibility of preparing dialkylborinates from simple reagents, the conversion of alkenes into ketones, and the rapid reduction of esters by lithium borohydride in the presence of catalytic amounts of alkenes. We are investigating further the synthetic utility of this ester-induced hydroboration of alkenes by lithium borohydride.

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Registry No. ethyl 10-undecenoate, 692-86-4; 1,10-undecanediol, 10596-05-1; 1,11-undecanediol, 765-04-8; ethyl caproate, 123-66-0; 1-decene, 872-05-9; 1-decanol, 112-30-1; 2-decanol, 1120-06-5; 1-hex-

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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 reported² 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.

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.

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

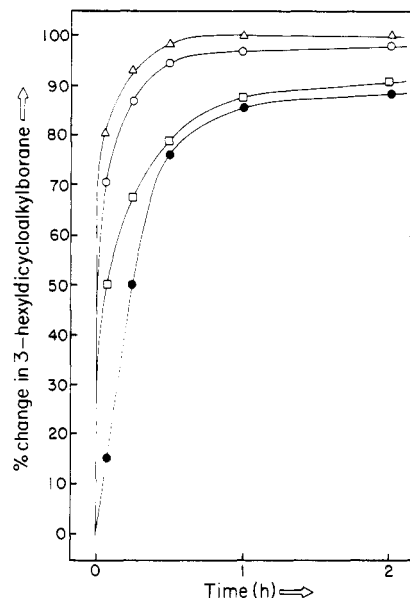
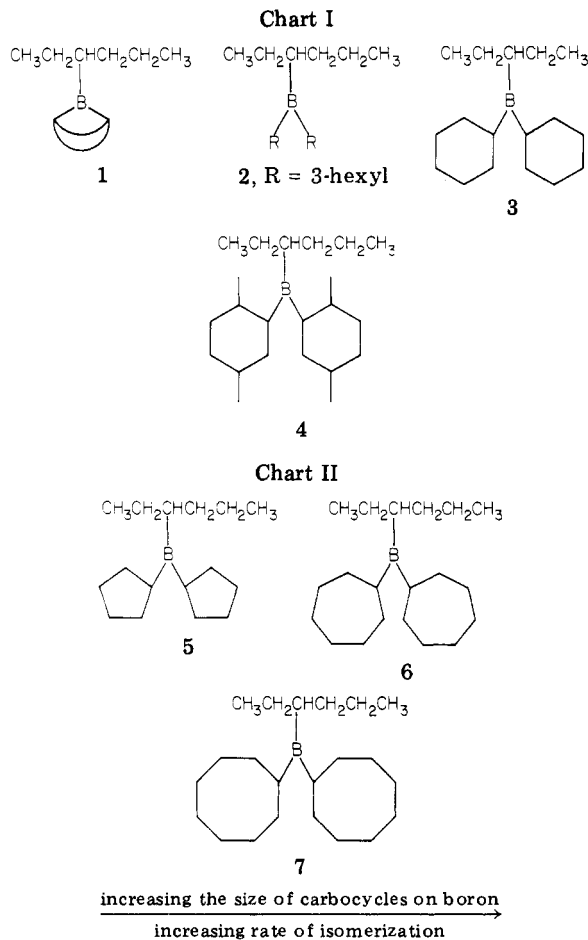


Figure 1. A comparison of the rates of isomerization of 3-hexyldicycloalkylboranes: Δ , 3-hexyldicyclooctylborane; \circ , 3-hexyldicycloheptylborane; \square , 3-hexyldicyclohexylborane; \bullet , 3-hexyldicyclopentylborane.

crowding in the resulting organoboranes so as to increase the rate of isomerization.

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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