# Communications

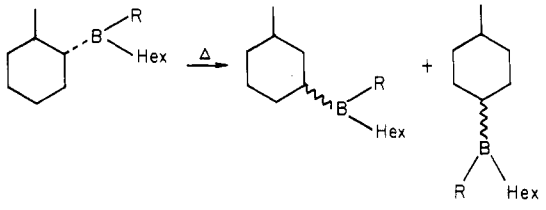
## Exceptionally Rapid Thermal Isomerization of *B*-(3-Hexyl)bis(2,5-dimethylcyclohexyl)borane. A Sterically Enhanced, Highly Efficient Synthetic Route for the Conversion of Internal Acyclic Olefins into Terminal Olefins and Their Derivatives

*Summary:* The thermal isomerization of *B*-(3-hexyl)bis-(2,5-dimethylcyclohexyl)borane (IV) is approximately 100 times faster than *B*-(3-hexyl)dicyclohexylborane (III), 500 times faster than tris(3-hexyl)borane (II), and about 4000 times faster than *B*-(3-Hex)-9-BBN (I), a discovery of great promise in utilizing the isomerization of organoboranes for synthetic purposes.

*Sir:* We previously reported that *B*-(3-hexyl)-9-borabicyclo[3.3.1]nonane (I) isomerizes at a rate significantly slower compared to that of $(3\text{-Hex})_3B$ (II) under similar thermal isomerization conditions. The reluctance of the 9-BBN moiety to move along the carbon skeleton was accounted for in terms of the smaller steric crowding in the *B*-(3-Hex)-9-BBN structure, as compared to the $(3\text{-Hex})_3B$ derivative. This discovery made possible a number of important synthetic applications.[1-3] It then occurred to us that it might be possible to go in the opposite direction, increasing the rate of thermal isomerization by increasing the steric bulk of the migrating boron moiety.

Accordingly, we hydroborated *cis*-3-hexene with both dicyclohexylborane and bis(2,5-dimethylcyclohexyl)borane, two borane moieties of evidently enhanced steric requirements. These reactions produced the organoboranes III and IV (Chart I).

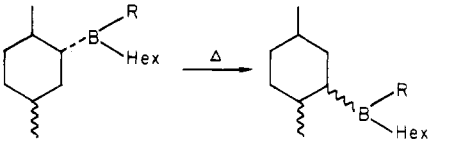
We selected bis(2,5-dimethylcyclohexyl)borane, rather than bis(2-methylcyclohexyl)borane, for our borane moiety of increased steric requirements in order to minimize the possibility that isomerization within the moiety might decrease its steric requirements during the reaction. Isomerization of bis(2-methylcyclohexyl)borane would produce moieties with steric requirements essentially identical with those of dicyclohexylborane (R will be 2-methylcyclohexyl or one of its isomers; eq 1). On the other




(1)

hand, such isomerization of bis(2,5-dimethylcyclohexyl)-borane (eq 2) would not alter the steric requirements significantly (under these conditions boron moves with great difficulty past a tertiary carbon atom).

We then compared the rates of the thermal isomerizations of the four organoboranes I–IV under identical conditions [150 °C, ~1 M solution in diglyme (DG)] in the hope of achieving enhanced rates of isomerization.




(2)

Indeed, we were gratified to observe that III isomerizes about 5 times faster than II and 40 times faster than I. The rate of isomerization of IV was far faster. IV isomerizes 100 times faster than III itself, 500 times faster than II, and 4000 times faster than I (Figure 1). In addition to this exceptionally rapid rate of thermal isomerization, organoboranes III and IV give far superior equilibrium distribution of the boron moiety on the hexyl chain, compared to II and I (Table I), achieving in IV 100% conversion to the terminal isomer.

A typical procedure for the preparation of *B*-(3-hexyl)dicyclohexylboranes III and IV is as follows. Dicyclohexylborane was prepared under nitrogen by the standard procedure[4] of adding 1.0 mL of 10 M borane–methyl sulfide (10 mmol) to a cold solution of 2.0 mL of cyclohexene (20 mmol) in 20 mL of THF at 0 °C and stirring the solution at 0 °C for 4 h. Then, 1.5 mL of the olefin, *cis*-3-hexene, was added in 20% excess (12 mmol) so as to ensure complete reaction and the absence of excess hydride.[5] The reaction mixture was permitted to stand overnight to ensure complete conversion. The completion of the reaction was checked by $^{11}B$ NMR. The excess olefin and THF were then pumped off under vacuum. Diglyme (10 mL) was added to make a ~1.0 M solution of the trialkylborane, and the mixture was maintained at 150 ± 2 °C to isomerize the borane. The progress of the reaction was checked by removing aliquots, oxidizing them with alkaline hydrogen peroxide, and analyzing the alcohols by GC. The standard conditions used for the gas chromatographic separation of the alcohols were 10% Carbowax 1540 on a Chromosorb W column (12 ft × $^1/_8$ in.) and isothermal analysis at 70 °C (Varian 1200 FID GC). A nitrogen atmosphere was maintained until the product was oxidized.

The exceptional thermal isomerization properties of *B*-(3-hexyl)bis(2,5-dimethylcyclohexyl)borane (IV) and *B*-(3-hexyl)dicyclohexylborane (III) clearly demonstrate that thermal isomerization of organoboranes is indeed a powerful and highly efficient synthetic route for the conversion of internal olefins into terminal olefins and their derivatives (Scheme I).

Thus, the present comparative study on the thermal isomerizations of organoboranes (I–IV) involving increasing steric crowding of the boron moiety clearly established the major effect of steric influences on the rate and equilibrium of the thermal isomerization. It is also clear that both dicyclohexylborane and bis(2,5-dimethylcyclohexyl)borane are exceptionally valuable hydroborating agents for organic syntheses proceeding via the isomerization of organoboranes.

(1) Taniguchi, H.; Brener, L.; Brown, H. C. *J. Am. Chem. Soc.* **1976**, *98*, 7107.
(2) Krishnamurthy, S.; Vogel, F.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 2534.
(3) (a) Midland, M. M.; Greer, S.; Tramontano, A.; Zderic, S. A. *J. Am. Chem. Soc.* **1979**, *101*, 2352. (b) Midland, M. M.; McDowell, D. C.; Hatch, R. L.; Tramontano, A. *Ibid.* **1980**, *102*, 867.
(4) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.
(5) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1966**, *88*, 1433.

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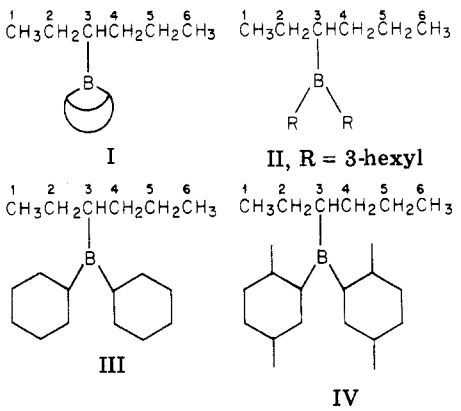
Chart I



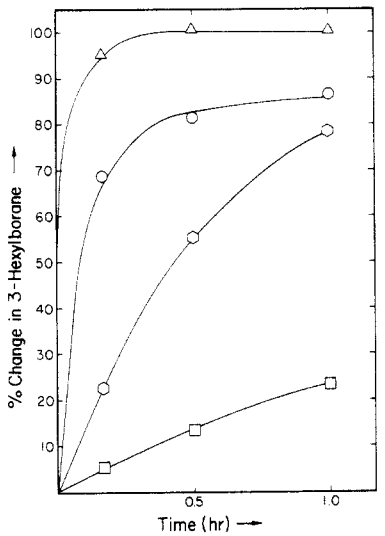
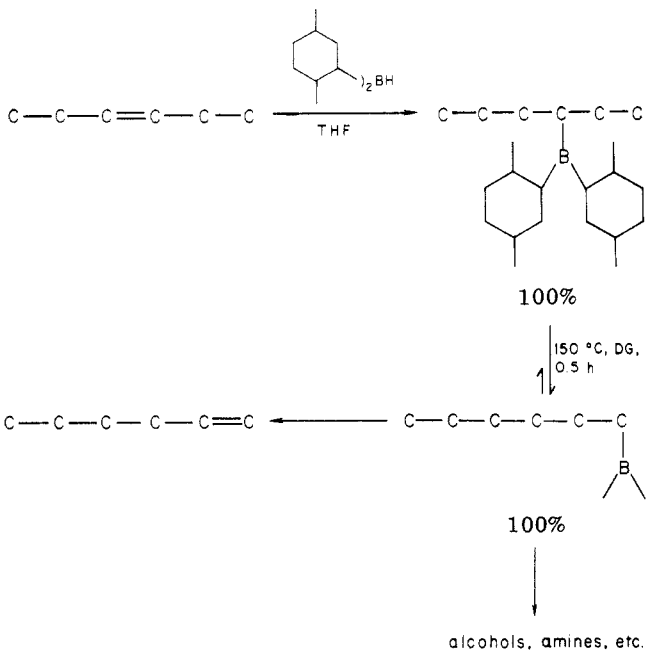



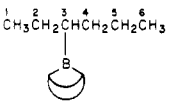
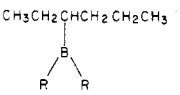
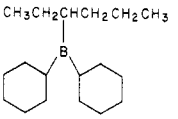
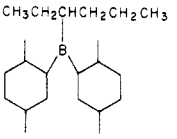

**Figure 1.** Rates of isomerization at 150 °C of *B*-(3-hexyl)dialkylboranes: □, *B*-R-9-BBN; hexagon, $RBR_2$; ○, RB-c-$Hex_2$; △, RB(2,5-$Me_2$-c-Hex)$_2$.

Scheme I




We continue to probe further into the steric influences on the rates and equilibrium involved in thermal isomerization and to explore the full scope of the isomerization of *B*-alkylbis(2,5-dimethylcyclohexyl)boranes.

Table I. Thermal Isomerization[a] of Organoboranes

| organoborane | $t_{1/2}$, s[b] | time to reach equilibrium, h | % composition of hexanols at equilibrium: 1-ol | 2-ol | 3-ol |
|---|---|---|---|---|---|
|  I | 12060 | 264 | 90 | 6 | 4 |
|  II[c] | 1500 | 72 | 90 | 6 | 4 |
|  III | 300 | 48 | 97 | 2 | 1 |
|  IV | 3 | 0.5 | 100 | 0 | 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 in each case. [c] R = 3-hexyl.

**Registry No. I**, 78964-99-5; **II**, 1883-34-7; **III**, 72487-19-5; **IV**, 78965-00-1; *cis*-3-hexene, 7642-09-3; dicyclohexylborane, 1568-65-6; bis(2,5-dimethylcyclohexyl)borane, 78965-01-2; 1-hexanol, 111-27-3; 2-hexanol, 626-93-7; 3-hexanol, 623-37-0.

(6) Graduate research assistant on grants from the Exxon Research and Engineering Corp. and the National Science Foundation.
(7) Visiting scholar, 1972–1973, on funds provided by the Maruzen Oil Co., Ltd., Osaka, Japan.

**Herbert C. Brown,* Uday S. Racherla[6] Hiroaki Taniguchi[7]**
*Richard B. Wetherill Laboratory*
*Purdue University*
*West Lafayette, Indiana 47907*
*Received June 29, 1981*

## Mechanism of the Backbone Rearrangement of Amino Steroids. A High-Field Proton, Deuterium, Carbon-13, and $^1$H Two-Dimensional Nuclear Magnetic Resonance Spectroscopic Study of Isoholamine and Polydeuterated Isoholamine

*Summary:* The determination of the label distribution in polydeuterated isoholamine resulting from $D_2SO_4$-catalyzed rearrangement of holamine has been carried out. A mechanism for the rearrangement is proposed.

*Sir:* Considerable effort has been directed in recent years toward the elucidation of the mechanism of the backbone rearrangement of steroids.[1] Deuterated reagents were used in a number of cases,[1] but no appropriate technique

(1) Ph.D. Thesis, J. Thierry, Université de Paris-Sud, Centre d'Orsay, France, 1976 and references cited therein.

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