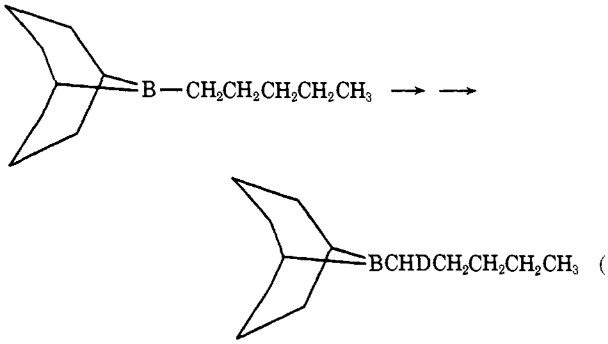
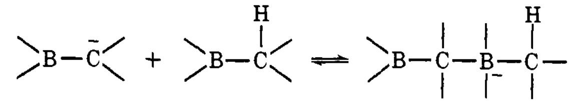
Using similar procedures we have obtained evidence for the formation of anions from a number of other simple trialkylboranes, although in lower conversions (eq 6 and 7).

$$(CH_3CH_2)B \longrightarrow \longrightarrow (CH_3CH_2)_2BCHDCH_3\ (10\%) \qquad (6)$$



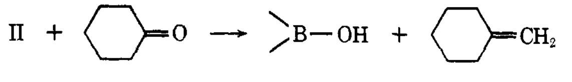
(7)

Interpretation of our results in terms of the equilibrium acidity of the organoboranes may be complicated by the possible occurrence of equilibria of the type shown in eq 8. In addition, in some of the reactions a boron-containing precipitate is formed.



$$>B-\bar{C}< \; + \; >B-\overset{H}{C}< \;\rightleftharpoons\; >B-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|^-}{B}}-\overset{H}{\underset{|}{C}}- \qquad (8)$$

Presumably, careful spectral analyses of these reactions will provide useful information concerning the precise nature of the boron species present. However, for the present, we prefer to concentrate on the synthetic utility of these conversions. Some of the potential in this regard is indicated by the following conversion of cyclohexanone into methylenecyclohexane, realized in overall yields of 55–65% from the starting boron compound, I (eq 9).



(9)

Currently, our efforts are directed toward obtaining higher conversions of boron compounds to the corresponding anions by utilizing stronger generating bases and by utilizing (presumably) more acidic boron compounds such as geminal diboraalkanes or diphenylalkylboranes. Our results in these areas will be reported shortly.

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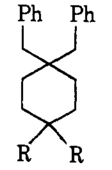
Ring Inversion in 1,1-Dibenzylcyclohexanes[1]

Sir:

In a recent communication, the barrier to chair–chair interconversion in 1,1-dimethyl-4,4-dibenzylcyclohexane (**1a**) was reported from studies of carbon and proton magnetic resonance spectroscopy to be at least 20 kcal/mol.[2] This observation was surprising in terms of what is known about inversion barriers in cyclohexane[3] and was rationalized in terms of hindered rotation of the benzyl groups. Because it would be expected to behave similarly, we have prepared 1,1-dibenzylcyclohexane,[4] **1b**, by reduction of the known α,α-dibenzylcyclohexanone.[5] The 60- and 220-MHz pmr spectra of **1b** at room temperature exhibited a sharp singlet at δ 2.61. On cooling at 60 MHz, this resonance gradually broadened and finally yielded two broadened singlets centered on δ 2.87 and 2.45. The coalescence temperature was $-58°$ in dichloromethane. The cmr data from **1b** (Table I) support both the gross structure and the time-averaged C_{2v} symmetry of the compound. These observations clearly indicate that the barrier energetics of **1b** are those of a normal cyclohexane derivative. Because introduction of geminal methyl groups at the 4 position of the ring of **1b** would not be expected to grossly affect the inversion rate, we have reinvestigated the behavior of **1a**.



1a, $R = CH_3$
1b, $R = H$

Table I. Cmr Spectral Data from **1a** and **1b**

	Chemical shift[a]	SFOR result	No. of protons attached
1a	50.7	Singlet	0
	63.2	Doublet	1
	64.2	Doublet	1
	67.7	Doublet	1
	146.1	Doublet	1
	147.6	Triplet	2
	151.0	Doublet	1
	151.6	Singlet or triplet	0 or 2
	153.7	Singlet or triplet	0 or 2
	154.5	Singlet or triplet	0 or 2
	162.1	Quartet	3
	163.1	Quartet	3
1b	53.5	Singlet	0
	61.4	Doublet	1
	64.8	Doublet	1
	66.7	Doublet	1
	147.8	Triplet	2
	154.8	Singlet	0
	159.4	Triplet	2
	166.5	Triplet	2
	170.5	Triplet	2

[a] In ppm upfield from CS_2; solvent was $CDCl_3$.

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[1] Supported by the National Science Foundation and the Public Health Service, Research Grant No. GM-11072 from the Division of General Medical Sciences.

[2] H. Kwart, M. C. Rock, R. Sánchez-Obregón, and F. Walls, *J. Amer. Chem. Soc.*, **94**, 1759 (1972).

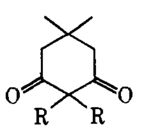
[3] *Cf.* D. Doddrell, C. Charrier, B. L. Hawkins, W. O. Crain, Jr., L. Harris, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **67**, 1588 (1970), and D. K. Dalling, D. M. Grant, and L. F. Johnson, *J. Amer. Chem. Soc.*, **93**, 3678 (1971), for examples, references, and discussion.

[4] A satisfactory elemental analysis was obtained.

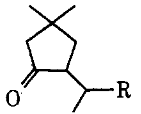
[5] P. Granger and M. M. Claudon, *Bull. Soc. Chim. Fr.*, 753 (1966).

The SFOR[6,7] cmr spectrum of the previously prepared **1a** showed two doublets, two quartets, and four singlets or triplets derived from the eight reported[2] saturated carbon absorptions (Table I). The two doublets must arise from CH groups; hence, the compound cannot be **1a**. Furthermore, the benzylic methylene protons which gave a broadened asymmetric doublet at 60 MHz turned into well-resolved multiplets consisting of at least ten lines at 220 MHz (Figure 1) in which the smallest splittings were 6 Hz. This part of the spectrum corresponds to expectations for a (C$_6$H$_5$-CH$_2$)$_2$CH– grouping where the benzyl groups are magnetically nonequivalent.

The literature has several examples of anomalous reductions of β-diketones.[8,9] Clemmensen reduction of dimedone (**2a**) yields **3a**;[8] in an analogous manner, reduction of **2b** might produce **3b**. This compound could subsequently be converted to **4** upon further reaction, as described earlier.[2]

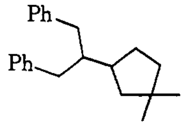


2



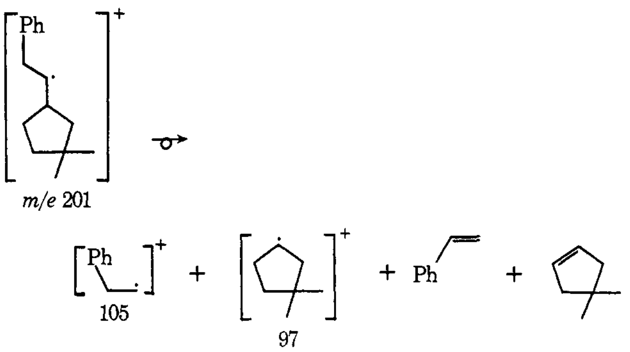
3

a, R = H
b, R = C$_6$H$_5$CH$_2$



4

Structure **4** is consistent with the cmr and pmr data previously assigned to **1a**.[2] The two methyl groups and the pair of benzylic methylenes are both diastereotopic and their resonances are not expected to coalesce upon heating or cooling. Because there are ten different carbon atoms in **4**, but only eight cmr signals were observed, some signals must be overlapping. On the basis of the SFOR data from Table I, the accidental degeneracies appear to involve the five different methylene moieties and/or the two quaternary carbons.



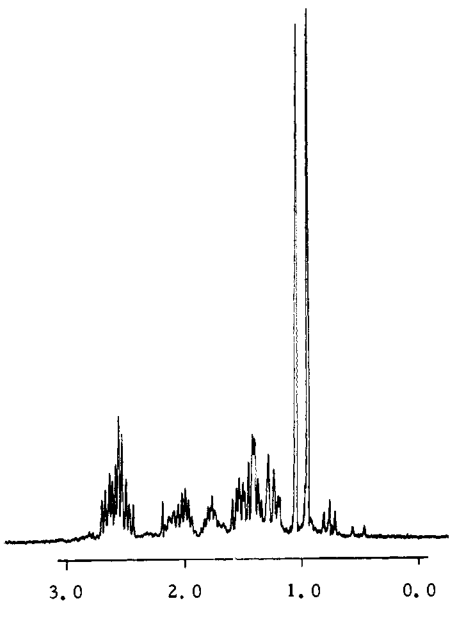


Figure 1. Aliphatic region of 220-MHz pmr spectrum of **4**.

The previously reported mass spectral data[2] are completely in accord with **4**. While both **1a** and **4** can produce ions at *m/e* 91 and 201 by benzyl cleavage, only the *m/e* 201 fragment derived from **4** can undergo straightforward decomposition to yield the observed ions at *m/e* 105 and 97.

We conclude that there is no experimental evidence at this time that dibenzylcyclohexanes exhibit other than normal inversion barriers.

Acknowledgment. We are pleased to acknowledge helpful discussions with Professor G. Stork of Columbia University.

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[6] H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 7445 (1969); SFOR, single frequency off resonance.

[7] M. Jautelat, J. B. Grutzner, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **65**, 288 (1970).

[8] N. J. Cusack and B. R. Davis, *J. Org. Chem.*, **30**, 2062 (1965).

[9] W. Reusch and D. B. Priddy, *J. Amer. Chem. Soc.*, **91**, 3677 (1969).

[10] National Institutes of Health Postdoctoral Fellow, 1971–1972.

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Ring Nonrigidity in the Chair Conformation of 1,1-Dibenzyl-4,4-dimethylcyclohexane

Sir:

It was recently reported[1] that the presence of geminal benzyl groups in 1,1-dibenzyl-4,4-dimethylcyclohexane (**4**) gives rise to an unprecedented increase in the magnitude of the cyclohexane ring inversion barrier (>20 kcal/mol), providing "direct evidence of the greater mobility of the boat as compared to the chair form."[1] We now wish to report that the properties described

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[1] H. Kwart, M. C. Rock, R. Sánchez-Obregón, and F. Walls, *J. Amer. Chem. Soc.*, **94**, 1759 (1972).