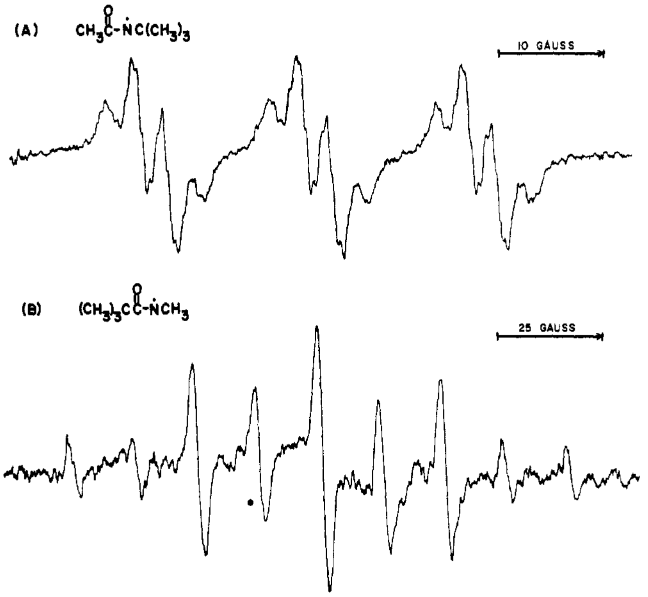

Figure 1. Esr spectra of (A) $CH_3CO\dot{N}C(CH_3)_3$ and (B) $(CH_3)_3C$-$CO\dot{N}CH_3$ in cyclopropane solution at −40 and −100°, respectively. The partially resolved splittings in (A) result from interaction with the hydrogens of the *tert*-butyl substituent.

has been reported but the literature is confusing and frequent misassignments of spectra have occurred. The most reliable evidence suggests that the nitrogen-centered radical derived from urea,[2] $H_2N\text{-}CO\text{-}\dot{N}H$, is best described as a π radical but the electron-donating NH_2 must interact strongly with the carbonyl group to effectively dampen its electron-withdrawing capability and this species cannot be considered truly representative of simple amido radicals. Likewise, *N-tert*-butoxyamido radicals, $R\text{-}CO\text{-}\dot{N}\text{-}O\text{-}t\text{-}Bu$, have been investigated[4] but the alkoxy substituent attached directly to nitrogen could conceivably bias these species in favor of a π structure.

In Table I are listed the esr spectral parameters for two simple amido radicals generated by photolysis of the corresponding *N*-chloramides in cyclopropane directly in the cavity of the esr spectrometer.[11] The esr spectra are shown in Figure 1. The derived data are typical of those for a π electronic ground state **1** rather than a σ structure **2**. The magnitudes of a^N and $a^H{}_{CH_3}$ are consistent with other nitrogen-centered π radicals[2,4,12–14] and suggest that there is not extensive delocalization of the unpaired electron onto the carbonyl group.[15] A σ radical such as **2** would be expected to exhibit a much greater a^N since the unpaired electron would reside in an orbital of appreciable s character. For example, σ-iminoxyl radicals have a^N values of about 30 G even though the spin density at nitrogen is only about 0.5 .[16,17]

Table I. Hyperfine Splitting Constants and *g* Values for Amido Radicals and Related Nitroxides[a]

Radical	a^N	a^H	*g* value[b]	Temp, °C
$(CH_3)_3C\overset{\overset{O}{\|}}{C}\dot{N}CH_3$	15.00	29.30[c]	2.0053	−100
$CH_3\overset{\overset{O}{\|}}{C}\dot{N}C(CH_3)_3$	15.70	2.71[c]	2.0044	−40
$CH_3\overset{\overset{O}{\|}}{C}\text{—}\overset{\overset{O\cdot}{\mid}}{N}C(CH_3)_3$	7.57		2.0066	−90
$CH_3\overset{\overset{O}{\|}}{C}\text{—}\overset{\overset{O\cdot}{\mid}}{N}CH_3$	7.20	8.53[c]	2.0065	−90

[a] Spectra of the amido radicals were recorded in cyclopropane solution; the nitroxides were generated in air-saturated toluene solution. Estimated accuracy of coupling constants is ±0.7%. [b] Corrected for second-order effects; estimated accuracy is ±0.0001. [c] Interaction with 3 H.

By photolyzing *N*-chloramides in air-saturated toluene solutions, spectra of the corresponding nitroxides are observed. The identity of these radicals is evidenced by the mode of generation, the relatively small a^N and $a^H{}_{NCH_3}$ coupling constants, the *g* values characteristic of nitroxides, the enhanced stability as compared to the transient amido radicals, and comparison to reported acyl nitroxides.[18,19] The present results indicate quite clearly that the paramagnetic species recently reported by Tordo, *et al.*,[3] and interpreted as amido radicals are instead the corresponding acyl nitroxides. We are presently investigating other amido radicals and will report additional results in the full publication of this work.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant No. PRF 5579-AC4), and the Kansas State University Bureau of General Research for support of this work.

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(11) A PEK AH6-2B, 2000-W high-pressure mercury capillary lamp was utilized in conjunction with a suitable lens system.

(12) W. C. Danen and T. T. Kensler, *J. Amer. Chem. Soc.*, **92**, 5235 (1970).

(13) W. C. Danen and C. T. West, *ibid.*, **93**, 5582 (1971).

(14) W. C. Danen and T. T. Kensler, *Tetrahedron Lett.*, 2447 (1971).

(15) G. A. Russell and J. Lokensgard, *J. Amer. Chem. Soc.*, **89**, 5059 (1967).

(16) R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967).

(17) The *g* values for the amido radicals are also reasonable for a π electronic structure although the reason(s) for the difference in *g* values between the first two entries in Table I is not immediately apparent.

(18) J. W. Hartgerink, J. B. F. N. Engberts, and Th. J. de Boer, *Tetrahedron Lett.*, 2709 (1971).

(19) A. Mackor, Th. A. J. W. Wajer, and Th. J. de Boer, *Tetrahedron*, **24**, 1623 (1968).

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Generation of Boron-Stabilized Carbanions

Sir:

The electronic configuration of trivalent boron is similar to that of carbon in a carbonyl grouping and many of the reactions of aldehydes or ketones have counterparts in the reactions of organoboranes.[1] Treatment of an aldehyde or a ketone possessing α hydrogens with base furnishes a carbonyl-stabilized anion (eq 1). Subsequent reactions of these enolate anions provide some of the most useful and versatile

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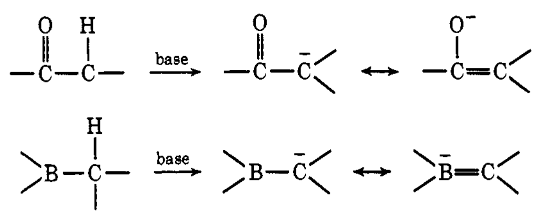
(1) For example, the Baeyer–Villiger oxidation and the Beckmann rearrangement of ketones are strikingly similar to the peroxide oxidation[2] and amination[3] reactions of organoboranes.

(2) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962, p 69.

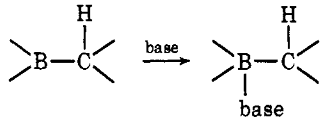
(3) M. W. Rathke, N. Inone, K. R. Varma, and H. C. Brown, *J. Amer. Chem. Soc.*, **88**, 2870 (1966).


(1)

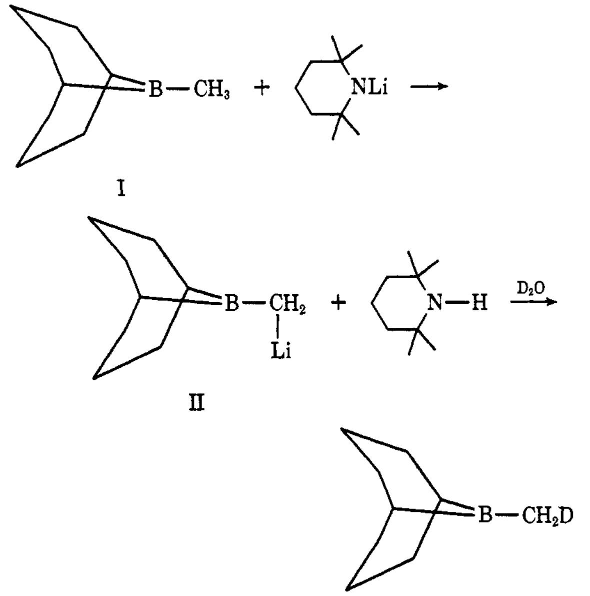
(2)

synthetic procedures available to the organic chemist. A similar removal of an α hydrogen from an organoborane to furnish a boron-stabilized carbanion appears feasible (eq 2), though to our knowledge such a reaction has never been reported.[4]

Addition of base to an organoborane normally results in coordination of the base to the boron atom (eq 3). In some cases, organoboranes can even be


(3)

titrated quantitatively with alkoxide bases. This effective neutralization reaction must represent a major obstacle to the formation of boron-stabilized carbanions.


I

II

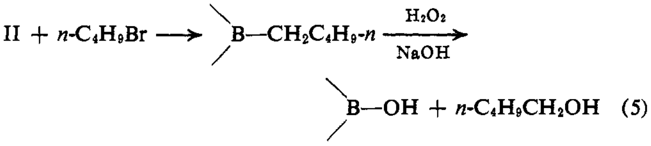
(4)

It seemed likely that this difficulty might be overcome by utilizing a base of such large steric requirements that coordination to boron becomes impossible. Accordingly, we prepared a series of lithium amide bases (by reaction of the corresponding secondary amines with n-butyllithium) and studied their reactions with the boron compound, B-methyl-9-borabicyclononane[6] (I). In each case, the boron compound was added to 1 equiv of the base suspended in benzene. The reaction mixtures were stirred for 12 hr at room temperature and then quenched with deuterium oxide. The boron compound was recovered by preparative glpc and analyzed for deuterium content by mass spectral analysis. The results (Table I) indicate that bases of smaller steric requirements, such as lithium diethyl- or diisopropylamide, are without effect. However, the highly hindered bases, lithium 2,2,6,6-tetramethylpiperidine or *tert*-butylneopentylamide,[8] furnish I which is 40–50% monodeuterated. We interpret these results to represent the first example of base-promoted α proton removal from an organoborane (eq 4). In support of this, we have successfully alkylated the intermediate anion with n-butyl bromide, as demonstrated by subsequent peroxide oxidation and isolation of 1-pentanol in 42% yield based on I (eq 5).

Table I. Reaction of B-Methyl-9-borabicyclononane with Lithium Amides in Benzene[a]

Lithium amide	Reaction time, hr	% deuterium incorporation[b]
Lithiodiethylamine	12	0
Lithiodiisopropylamine	12	0
Lithio-2,2,6,6-tetramethylpiperidine	12	50
	24	60
	48	65
	7 days	62
Lithio-*tert*-butylneopentylamine	12	40
	4 days	50

[a] Reaction mixtures are 1 M in boron compound. Equivalent amounts of base and boron compound were utilized. [b] From mass spectral analysis of recovered boron compound.



$$\text{II} + n\text{-C}_4\text{H}_9\text{Br} \longrightarrow \;>\!\text{B—CH}_2\text{C}_4\text{H}_9\text{-}n \xrightarrow[\text{NaOH}]{\text{H}_2\text{O}_2} \;>\!\text{B—OH} + n\text{-C}_4\text{H}_9\text{CH}_2\text{OH} \qquad (5)$$

Reaction of I with lithio-2,2,6,6-tetramethylpiperidine for longer periods of time increases the deuterium incorporation to 60% (Table I). However, times longer than 24 hr have no additional effect. Increasing the ratio of base to I likewise results in increased deuterium incorporation until a maximum of 75% is obtained with a twofold excess of base (Table II). The boron compound is recovered quantitatively in these room temperature experiments; however, refluxing causes extensive decomposition.

Table II. Reaction of B-Methyl-9-borabicyclononane with Varying Amounts of Lithio-2,2,6,6-tetramethylpiperidine in Benzene[a]

Base/boron compound	% deuterium incorporation
0.5	36
0.75	49
1.0	60
2.0	75
4.0	73

[a] Reaction times are 24 hr.

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[4] Boron-stabilized anions have previously been generated by cleavage of geminal diboron compounds with base,[5a–c] a reaction which is analogous to the base-promoted cleavage of β diketones. The removal of a γ proton from 1-phenyl-1,4-dihydroborabenzene to furnish an anion stabilized by aromatic resonance was recently reported.[5d]

[5] (a) G. Cainelli, G. Dal Bello, and G. Zubiana, *Tetrahedron Lett.*, **38**, 3429 (1965); (b) G. Zweifel and H. Avzoumanian, *ibid.*, **25**, 2535 (1966); (c) D. S. Matteson and J. R. Thomas, *J. Organometal. Chem.*, **24**, 263 (1970); (d) A. J. Ashe, III, and P. Shu, *J. Amer. Chem. Soc.*, **93**, 1804 (1971).

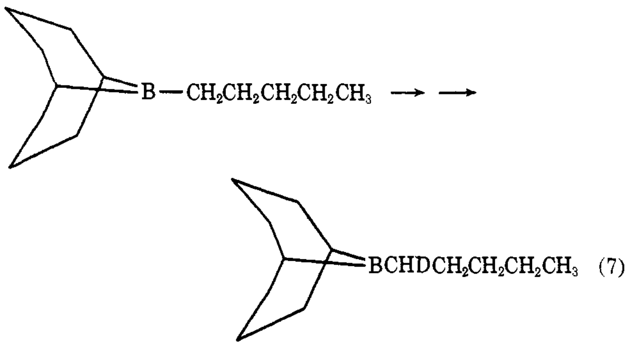
[6] I was chosen because it is readily prepared[7] and has only one type of acidic hydrogen, and the boron atom may be substituted with a wide variety of alkyl groups.

[7] H. C. Brown and M. Rogić, *J. Amer. Chem. Soc.*, **82**, 4908 (1960).

[8] G. F. Hennion and R. S. Hanyel, *ibid.*, 82, 4908 (1960).

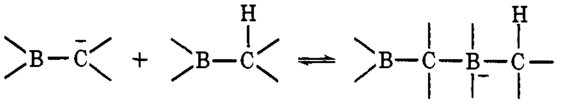
Using similar procedures we have obtained evidence for the formation of anions from a number of other simple trialkylboranes, although in lower conversions (eq 6 and 7).

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



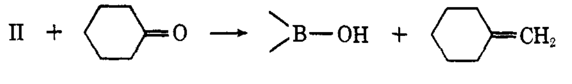
(7)

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.



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

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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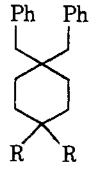
Ring Inversion in 1,1-Dibenzylcyclohexanes[1]

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).