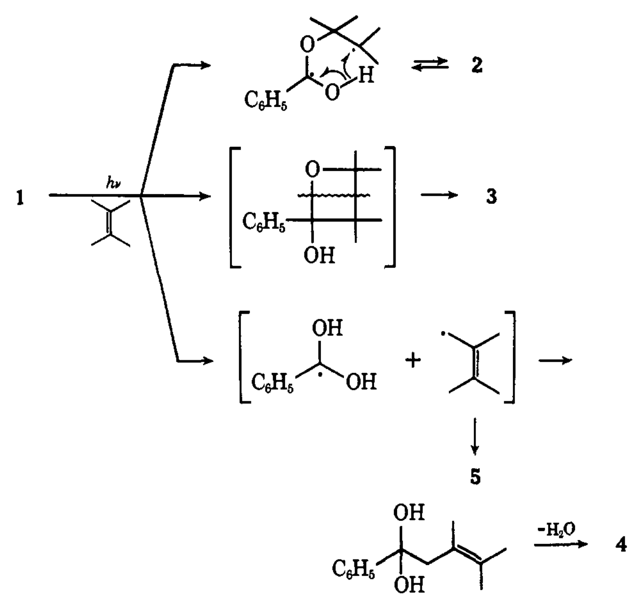

Irradiation of **1** in excess 2-methyl-2-butene until 50% of **1** was consumed gave a single ester, 3-methyl-2-butyl benzoate (**6**, 37%), the ketones isobutyrophenone (**3**) and propiophenone (**7**) (14 and 20%, respectively), a ketone believed to be 1-benzoyl-2-methyl-2-butene (**8**, 5%), as well as a mixture of C_{10} hydrocarbons derived from the olefin. Irradiation of mixtures of **1** and excess cyclohexene gave cyclohexyl benzoate (**9**, 55% based on unrecovered **1**), 3,3′-bicyclohexenyl (**10**, 20%), and 3-cyclohexylcyclohexene (**11**, 29%), as well as a complex mixture of C_{18} hydrocarbons derived from cyclohexenyl radicals. The quantum yields measured at 2537 Å[13] for the formation of **2** and **3** are 0.22 and 0.05, respectively. Those for **6**, **3**, and **7**, the products from 2-methyl-2-butene, are 0.12, 0.04, and 0.06.

The high triplet energy of **1** (78 kcal)[14] made meaningful sensitization experiments impractical. However, added 1,3-pentadiene at concentrations up to 0.5 *M* caused no reduction in the rate of formation of **2** and **3**; these results imply that the reactions of **1** with olefin occur *via* excited singlet states of **1**, or perhaps *via* very short-lived triplets. The high reactivity of **1** at the carbonyl group would imply that the reactive excited state is of predominantly n → π* character. This behavior is similar to that which we recently observed with benzonitrile, which reacts with electron-rich olefins at the nitrile group, apparently *via* an excited singlet state.[15] We hope to resolve this matter by fluorescence studies of benzoic acid and its derivatives. We have not thus far observed products of photochemical reaction of **1** at the benzene ring. Our study of the photochemical behavior of this and related compounds with lowest π → π* triplet excited states is continuing.

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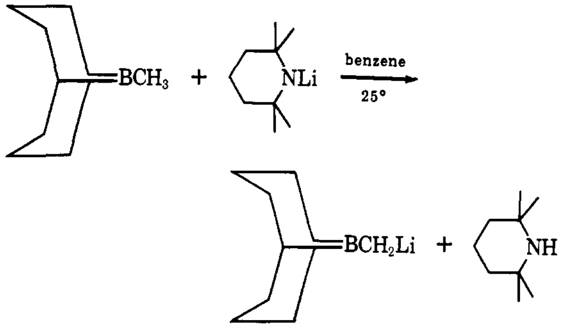
Formation and Reactions of Boron-Stabilized Carbanions Derived from Vinylboranes

Sir:

We recently reported that reaction of *B*-methyl-9-borabicyclononane with the hindered base lithium 2,2,6,6-tetramethylpiperidide (LiTMP) produces a boron-stabilized carbanion (I, eq 1).[1] With stoichiometric quantities of base, the conversion to I is approximately 65%; however, other trialkylboranes give much smaller conversions to the corresponding anions.



(1)

I

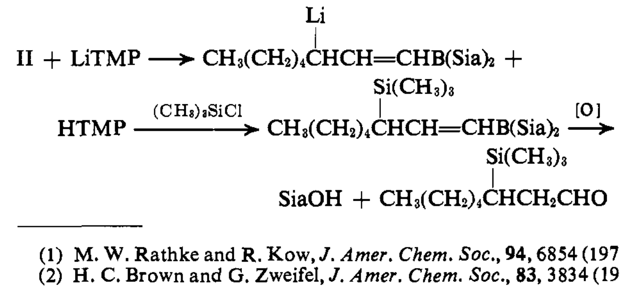
We now report results obtained with vinylboron compounds, prepared by the monohydroboration of alkynes with disiamylborane (eq 2).[2]

$$(Sia)_2BH + 1\text{-octyne} \xrightarrow[25°]{THF} CH_3(CH_2)_5CH{=}CHB(Sia)_2 \qquad (2)$$

II

Addition of vinylborane II to tetrahydrofuran solutions of a base of moderate steric requirements, such as lithium diisopropylamide or lithium *N*-isopropylcyclohexylamide, followed sequentially by treatment with trimethylchlorosilane and alkaline hydrogen peroxide gives only siamyl alcohol and octanal (60–85% yields), the normal oxidation products of II.[2] No silylated derivatives of the alkyl groupings were detected.

Addition of II to equivalent amounts of LiTMP in tetrahydrofuran produces a light red solution. Addition of trimethylchlorosilane to the reaction mixture gives an immediate precipitate of lithium chloride and subsequent peroxide oxidation furnishes 3-trimethylsilyloctanal in overall yields (from 1-octyne) of 75%. This result is rationalized by the formation of a boron-stabilized carbanion as shown in eq 3.



$$\text{II} + \text{LiTMP} \longrightarrow CH_3(CH_2)_4\overset{Li}{C}HCH{=}CHB(Sia)_2 + \text{HTMP} \xrightarrow{(CH_3)_3SiCl} CH_3(CH_2)_4\underset{Si(CH_3)_3}{C}HCH{=}CHB(Sia)_2 \xrightarrow{[O]} \text{SiaOH} + CH_3(CH_2)_4\underset{Si(CH_3)_3}{C}HCH_2CHO \qquad (3)$$

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[13] These experiments were performed on solutions flushed with argon in runs carried to 6–10% conversion; a correction was made for light absorbed by the products.

[14] Y. Kanda, R. Shimada, and Y. Takenoshita, *Spectrochim. Acta*, **19**, 1249 (1963).

[15] T. S. Cantrell, *J. Amer. Chem. Soc.*, **94**, 5929 (1972).

[1] M. W. Rathke and R. Kow, *J. Amer. Chem. Soc.*, **94**, 6854 (1972).

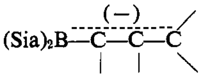
[2] H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 3834 (1961).

Using the same procedure, we obtained β-trimethylsilyl carbonyl compounds from a variety of vinylboranes in yields summarized in Table I. The results indicate that vinylboranes are metalated by LiTMP in conversions of 66–90%. These higher conversions, compared to those obtained with saturated organoboranes,[1] are presumably due to a greater delocalization of charge in the metalated vinylborane, as indicated by structure III. It is evident that reactions of

Table I. Conversion of Disiamylvinylboranes to β-Trimethylsilyl Carbonyl Compounds

Alkyne	Silylated product	% yield[a]
1-Pentyne	$CH_3CH_2CHSi(CH_3)_3CH_2CHO$	72
1-Hexyne	$CH_3(CH_2)_2CHSi(CH_3)_3CH_2CHO$	66
1-Octyne	$CH_3(CH_2)_4CHSi(CH_3)_3CH_2CHO$	75
3-Hexyne	$CH_3CHSi(CH_3)_3CH_2COCH_2CH_3$	90

[a] Glpc, based on starting alkyne.



III

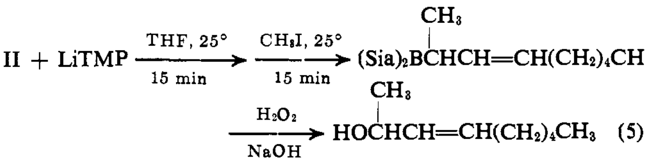
such an anion may occur at positions α or γ to the boron atom, and we explored this possibility with several reactions of disiamyl-1-octenylborane (II).

Quenching a reaction mixture of II and LiTMP with water followed by oxidation with alkaline hydrogen peroxide produces 2-octen-1-ol in 72% yield (eq 4).

$$\text{II} + \text{LiTMP} \xrightarrow[15\text{ min}]{\text{THF, }25^\circ} \xrightarrow{H_2O} \underset{\text{IV}}{(\text{Sia})_2BCH_2CH{=}CH(CH_2)_4CH_3} \xrightarrow[\text{NaOH}]{H_2O_2} HOCH_2CH{=}CH(CH_2)_4CH_3 \quad (4)$$

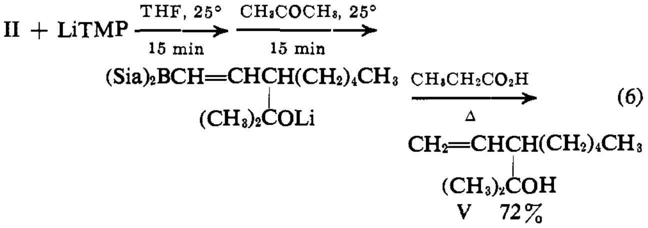
Other products present in the final mixture include 1-octene (5%), apparently formed by hydrolysis of the allylborane IV,[3] and octanal (10%).

Addition of methyl iodide to a reaction mixture of II and LiTMP followed by peroxide oxidation produces 3-nonen-2-ol in 70% yield (eq 5). Small amounts of 2-nonene (10%) and an aldehyde assumed to be 3-methyloctanal (6%) are also present.



$$\text{II} + \text{LiTMP} \xrightarrow[15\text{ min}]{\text{THF, }25^\circ} \xrightarrow[15\text{ min}]{CH_3I,\ 25^\circ} (\text{Sia})_2B\overset{CH_3}{\overset{|}{C}}HCH{=}CH(CH_2)_4CH \xrightarrow[\text{NaOH}]{H_2O_2} HO\overset{CH_3}{\overset{|}{C}}HCH{=}CH(CH_2)_4CH_3 \quad (5)$$

Treatment of a reaction mixture of II and LiTMP with acetone followed by protonation with propionic acid[2] produces the unsaturated alcohol V in 72% yield (eq 6).



$$\text{II} + \text{LiTMP} \xrightarrow[15\text{ min}]{\text{THF, }25^\circ} \xrightarrow[15\text{ min}]{CH_3COCH_3,\ 25^\circ} (\text{Sia})_2BCH{=}CH\underset{(CH_3)_2COLi}{\underset{|}{C}}H(CH_2)_4CH_3 \xrightarrow[\Delta]{CH_3CH_2CO_2H} \underset{\text{V}\quad 72\%}{CH_2{=}CH\underset{(CH_3)_2COH}{\underset{|}{C}}H(CH_2)_4CH_3} \quad (6)$$

These results show that the vinylborane anion, I, reacts with acetone or trimethylchlorosilane predominantly at the γ carbon, and with methyl iodide or water predominantly at the α carbon. To some extent, these results may be due to steric factors, with the larger reagents attacking at a position remote from the bulky siamyl groupings. It is interesting to note that enolate anions derived from α,β unsaturated ketones[4] or esters[5] undergo reaction almost exclusively at the carbon α to the carbonyl.

The following procedure for the conversion of 1-octyne into 2-octen-1-ol is representative of the general technique. A dry 50-ml round-bottomed flask equipped with septum inlet, magnetic stirring, and mercury relief valve was flushed with nitrogen and immersed in an ice–water bath. A solution of *n*-butyllithium (5 mmol, 2 ml) in hexane was injected followed by dropwise addition of 2,2,6,6-tetramethylpiperidine. The hexane was removed by vacuum distillation and the residue of LiTMP was treated with 10 ml of a tetrahydrofuran solution of disiamyl-1-octenylborane (10 mmol), prepared from 1-octyne according to a published procedure.[2] The reaction mixture was stirred at 25° for 15 min. The flask was then immersed in an ice–water bath and 2 ml of water was injected. Oxidation was achieved by the addition of 0.4 ml of 3 *N* sodium hydroxide followed by dropwise addition of 3.4 ml of 30% hydrogen peroxide. Glpc analysis of the reaction mixture using an internal standard established the presence of 2-octen-1-ol, 7.2 mmol, 72% yield.

The ready metalation of vinylboranes with hindered amide bases seems likely to have numerous synthetic applications. We note that these anions possess a reactivity of the type associated with metal enolate anions while maintaining the synthetic versatility associated with organoboron compounds.[6]

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (GP34384).

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(3) *Cf.* B. M. Mikhailov and F. B. Tutorskaya, *Dokl. Akad. Nauk SSSR*, **123**, 479 (1958).

(4) *Cf.* H. E. Zimmerman, *Mol. Rearrangements*, **1**, 345 (1963), and references cited therein.

(5) M. W. Rathke and D. Sullivan, *Tetrahedron Lett.*, 4249 (1972).

(6) *Cf.* H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972.

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Photodissociation Spectroscopy of Gaseous $C_7H_8^+$ Cations

Sir:

Since the original observation of extensive hydrogen randomization in the mass spectra of isotopically labeled toluenes,[1] there has been frequent speculation and experimental investigation of the possible isomerization of $C_7H_8^+$ cations derived from toluene and other C_7H_8 neutral precursors. The results of mass spectrometric experiments with labeled compounds have re-

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(1) R. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Amer. Chem. Soc.*, **79**, 842 (1957); H. M. Grubb and S. Meyerson in "Mass Spectroscopy of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 10.