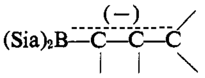
Using the same procedure, we obtained β-trimethylsilyl carbonyl compounds from a variety of vinylboranes in yields summarized in Table I. The results indicate that vinylboranes are metalated by LiTMP in conversions of 66–90%. These higher conversions, compared to those obtained with saturated organoboranes,[1]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

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.



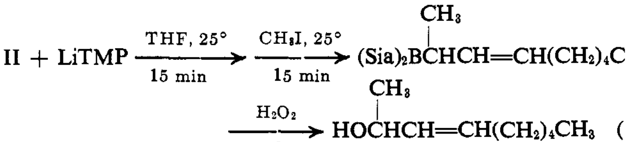
III

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).

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

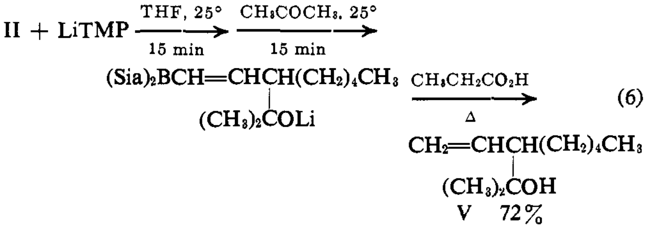
Other products present in the final mixture include 1-octene (5%), apparently formed by hydrolysis of the allylborane IV,[3] and octanal (10%).

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.



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

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).



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

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.

peatedly been interpreted as showing isomerization of the parent cations to a common intermediate for toluene, cycloheptatriene, norbornadiene, and other C_7H_8 systems.[1-8] Recent photodissociation results for toluene cations confirmed that hydrogen randomization prior to dissociation is essentially complete even at energies near threshold.[9] However, Bursey and Hoffman,[10] using ion cyclotron resonance (icr) spectroscopy as a means of identifying characteristic chemical reactions of isomeric $C_7H_8^+$ cations, have recently shown that nondissociating $C_7H_8^+$ cations from toluene and from cycloheptatriene are noninterconverting on a time scale of milliseconds, indicating that interconversion of these cations, if it occurs at all, is slow unless the ions are highly excited.

We report here the application of the technique of photodissociation spectroscopy to the investigation of the structures of isomeric $C_7H_8^+$ cations, with the hope of obtaining, in a direct and unambiguous manner, information about their isomerization on a time scale of seconds. The investigation of photoexcitation processes in gaseous cations has recently been facilitated by the recognition of the ion-trapping and detection capabilities of the icr spectrometer, which has been exploited to follow photodissociation,[9,11-13] photodetachment,[14-16] and photon-induced reaction[17] processes of gaseous cations.

The reaction observed was

$$C_7H_8^+ \xrightarrow{h\nu} C_7H_7^+ + H$$

$C_7H_8^+$ cations were obtained from toluene, cycloheptatriene, and norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) near 11 eV ionizing voltage at pressures ranging from 3×10^{-8} to 3×10^{-7} Torr. Table I summarizes the known thermochemistry for these ions.[9,18] The photodissociation spectra could be followed as previously described[9] by following either the disappearance of $C_7H_8^+$ or the appearance of $C_7H_7^+$ as a function of wavelength. Monitoring the formation of product ion ($C_7H_7^+$) can lead to underestimation of photodissociation rates because (a) some product ions may be lost by recoil,[12] and (b) product ions often undergo subsequent chemical reactions, as is known to be the case for toluene.[9] Accordingly, the results reported here are based entirely on monitoring the disappearance of the parent $C_7H_8^+$ ions. The disappearance spectra of $C_7H_8^+$ for the three systems are shown in Figure 1. The instrumental method was similar to that used in ref 9 and 13.

Table I. Thermochemistry of $C_7H_8^+$ Cations[a]

	$C_7H_8^+$			$C_7H_7^+$		
	Toluene	CHT	Norbornadiene	Toluene	CHT	Norbornadiene
ΔH_f, kcal/mol	215	240	267	216	209	236
AP, eV	8.82	8.52	8.67	11.8	10.4	9.6

[a] Reference 18.

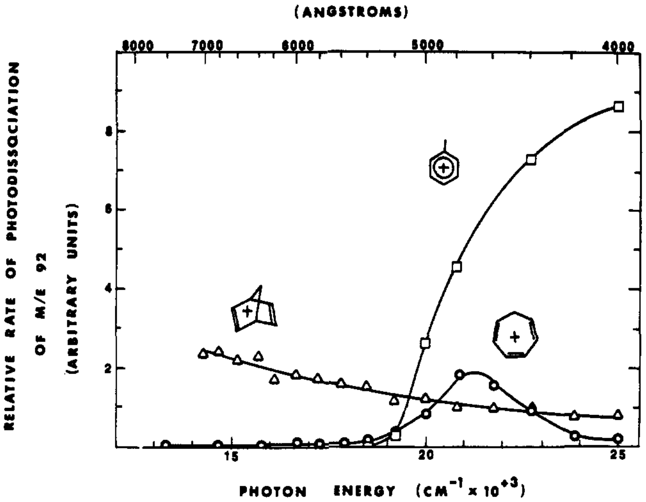

Figure 1. Relative photodissociation rates of $C_7H_8^+$ ions as a function of wavelength for toluene (□), cycloheptatriene (○), and norbornadiene (△). As described in the text, the three curves were normalized to a common (arbitrary) vertical scale and may be compared directly.

The three curves in Figure 1 were normalized to a common sensitivity by comparing the extent of dissociation under identical instrumental conditions. The ion lifetimes were measured (ranging from 3 to 10 sec), and a linear correction for ion lifetime was made to the extent-of-dissociation data.[11] As in ref 9 the data are presented in the form of relative dissociation rates, with a correction for light intensity.

Both toluene and norbornadiene (but not cycloheptatriene) showed icr peaks above *m/e* 100 corresponding to ion-molecule reaction products. It was verified by resonance ejection of the various product ions[9,11] that these ions did not affect the photodissociation spectra. As has been discussed in previous publications,[9,13,17] vibrational excitation of the parent ion, either at the electron beam or from a rearrangement process, can in principle lead to serious errors in photodissociation spectra. Under the conditions of these experiments a typical ion undergoes tens of collisions with neutral molecules during its residence time in the cell so that a very high degree of vibrational excitation would probably not be retained. To test this question further, the experiments were repeated with addition of inert gases to provide increased collisional relaxation. No significant change in the spectra was found for addition of 3×10^{-6} Torr of methane to toluene, 8×10^{-7} Torr of ethane to cycloheptatriene, and 2×10^{-6} Torr of ethane to norbornadiene. At these pressures the ions

(2) S. Meyerson, *J. Amer. Chem. Soc.*, **85**, 3340 (1963).

(3) P. N. Rylander, S. Meyerson, and H. M. Grubb, *ibid.*, **79**, 842 (1957).

(4) K. L. Rinehart, Jr., A. C. Buchholz, G. E. Van Lear, and H. L. Cantrill, *ibid.*, **90**, 2983 (1968).

(5) A. S. Siegel, *ibid.*, **92**, 5277 (1970).

(6) S. Meyerson, *Rec. Chem. Progr.*, **26**, 257 (1965).

(7) F. Meyer and A. G. Harrison, *J. Amer. Chem. Soc.*, **86**, 4757 (1964).

(8) I. Howe and F. W. McLafferty, *ibid.*, **93**, 99 (1971).

(9) R. C. Dunbar, *ibid.*, **95**, 472 (1973).

(10) M. K. Hoffman and M. M. Bursey, *Tetrahedron Lett.*, 2539 (1971).

(11) R. C. Dunbar, *J. Amer. Chem. Soc.*, **93**, 4354 (1971).

(12) R. C. Dunbar and J. M. Kramer, *J. Chem. Phys.*, **58**, 1266 (1973).

(13) J. M. Kramer and R. C. Dunbar, *J. Chem. Phys.*, in press.

(14) J. I. Brauman and K. C. Smyth, *J. Amer. Chem. Soc.*, **91**, 7778 (1969).

(15) K. C. Smyth, R. T. McIver, J. I. Brauman, and R. W. Wallace, *J. Chem. Phys.*, **54**, 2758 (1971).

(16) K. C. Smyth and J. I. Brauman, *ibid.*, **56**, 1132, 4620, 5993 (1972).

(17) J. M. Kramer and R. C. Dunbar, *J. Amer. Chem. Soc.*, **94**, 4346 (1972).

(18) J. L. Franklin, *et al.*, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 26 (1969).

undergo several hundred collisions during their residence times. There is no indication of reaction of any observed ions with these alkanes. Cycloheptatriene and norbornadiene showed no change in their photodissociation spectra in going from 11 to 15 eV ionizing energy.

The strikingly different photodissociation curves for these three isomeric ions make it obvious that there is no important degree of interconversion or conversion to a common structure on a time scale of seconds. The curves of Figure 1 rule out the possibility that any one of the ions converts on this time scale to one of the other two observed structures to the extent of more than a few per cent, except that conversion of about half the norbornadiene cations to the cycloheptatriene structure would not be inconsistent with the data (although this does not appear very likely). Conversion of either of the other cations to the most stable toluene structure does not occur to more than 10% (2% for cycloheptatriene).

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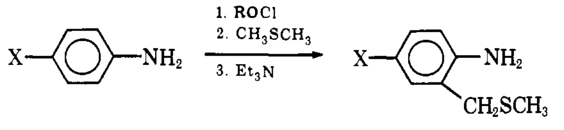
A General Method for the Synthesis of Oxindoles

Sir:

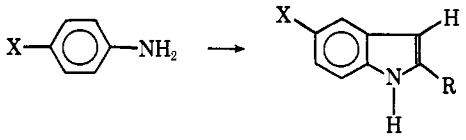
We wish to report a general method for the synthesis of oxindole and its derivatives.[1]

Recent reports from our laboratory have provided the details of a simple, stereospecific method for the ortho alkylation of aromatic amines.[2] This procedure involved the addition of dialkyl sulfides to the mono-N-chlorinated amine to give an azasulfonium salt, followed by ylide formation and intramolecular attack of the ylide at the ortho position. In this way, **1** could be converted into **2** in good to excellent yields.



1 2

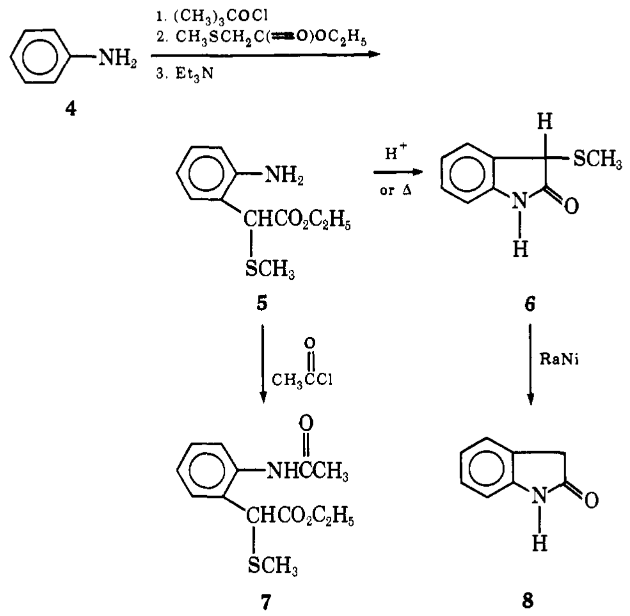
Raney nickel desulfurization then produced the desired alkyl side chain. We have also found that use of a β-keto sulfide in place of a dialkyl sulfide provided a simple process for the conversion of aniline **1** to the 2-substituted indole **3**.[3] We have now discovered that the use of certain sulfur-containing esters in place of the dialkyl sulfides provides a valuable modification of our method, which leads directly to oxindoles.



1 3

In a typical procedure, 1 equiv of aniline (**4**) in methylene chloride at −65° was treated with 1 equiv of *tert*-butyl hypochlorite (see Scheme I). After 5–10 min, 1 equiv of the appropriate ethyl methylthioacetate was added (slight exotherm) and stirring was continued for 1 hr. One equivalent of triethylamine was then added and the reaction mixture was allowed to warm to room temperature. Careful workup of the reaction mixture at this stage gave a 62% yield of the very unstable amino ester **5**. Acetylation of the crude reaction mixture gave a 60% yield of **7**.[4] Treatment of **5** with dilute acid gave the oxindole **6** in 84% yield.[5] When the crude reaction mixture derived from **4** was treated directly with acid, the overall yield of **6** was 63%. Raney nickel reduction of **6** resulted in the formation of oxindole (**8**) in 76% yield.

Scheme I



The conversions described above were found to be quite general when applied to substituted anilines. As shown in Scheme II, a variety of functional groups, which differ considerably in electronic character, can be tolerated. Raney nickel reduction of **10a**, **10b**, **10c**, and **10f** gave the corresponding desulfurized oxindole in 55, 72, 77, and 67% yields, respectively. The formation of **10e** from **9e** represents an interesting case. In principle, either a 4- or 6-substituted oxindole could be formed. In practice, the 4-nitrooxindole derivative **10e** was the overwhelming product.

When the nature of the sulfide was changed by substituting the active methylene, a route to 3-substituted oxindoles was provided. When **4** was treated first with *tert*-butyl hypochlorite, then with ester **11**, and subsequently with base we observed base-catalyzed re-

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(1) For detailed discussions of the presently known methods of oxindole synthesis see: R. J. Sundberg, "The Chemistry of Indoles," Academic Press, New York, N. Y., 1970.

(2) P. G. Gassman, G. Gruetzmacher, and R. H. Smith, *Tetrahedron Lett.*, 497 (1972); P. G. Gassman and G. Gruetzmacher, *J. Amer. Chem. Soc.*, **95**, 588 (1973).

(3) P. G. Gassman and T. J. van Bergen, *ibid.*, **95**, 590, 591 (1973).

(4) Satisfactory elemental analyses have been obtained on all new compounds except **5**.

(5) The conversion of **5** into **6** could also be accomplished by heating **5** or by allowing **5** to stand at room temperature.