

carbon was deposited on the walls of the cell, and the yield of acetylene fell correspondingly.

To further confirm the fact that acetylene was formed by reaction of the evaporated carbon,⁴ the experiment was carried out with carbon evaporated into deuterium, and the corresponding deuterated products were identified. When carbon was evaporated into an argon atmosphere *via* focused laser bursts, no volatile products were formed, and a black deposit of carbon coated the walls of the cell.

Evidence that butadiyne results from reaction of acetylene with carbon vapor was obtained from an experiment in which carbon was evaporated in an infrared cell containing acetylene at 10 cm pressure. Under these conditions, 1,3-butadiyne was produced in much larger quantity than in the above reactions of hydrogen with carbon vapor, but the yield was not quantitative since some of the carbon was deposited on the walls of the cell.

It has been found that carbon vaporized by laser pulses on graphite undergoes a variety of reactions with oxygen, hydrogen chloride, sulfur, nitric oxide, nitrous oxide, carbon tetrachloride, silane, and olefins. Further experimentation is continuing in these studies and details will be reported at a later date.

The generality of the technique has further been demonstrated by formation of boron trichloride from laser-evaporated boron in a hydrogen chloride atmosphere.

Acknowledgment. The authors wish to thank Dr. James Swain for making the laser facility at the Lawrence Radiation Laboratory available for this work.

(4) It has been shown that a laser pulse on coal produces a variety of hydrocarbon products: A. G. Sharkey, Jr., J. L. Shultz, and R. A. Friedel, "Gases from Flash and Laser Irradiation of Coal," *Advances in Chemistry Series*, No. 55, American Chemical Society, Washington, D. C., 1966, pp 643-649.

Riley Schaeffer

Department of Chemistry
Indiana University, Bloomington, Indiana

R. K. Pearson

Lawrence Radiation Laboratory
University of California, Livermore, California

Received January 17, 1969

A Novel Synthesis of Methyl Trimethylsilanecarboxylate. The $n \rightarrow \pi^*$ Transition of Silanecarboxylates

Sir:

We wish to report a novel synthesis of methyl trimethylsilanecarboxylate (**1**). Previously reported^{1,2} silanecarboxylates have been prepared *via* the silyllithium reagent and have had phenyl groups present to facilitate the formation of the lithium compound.^{3,4} As a result **1** is the first silanecarboxylate for which the electronic spectrum attributable to the $n \rightarrow \pi^*$ transition of the carbonyl

(1) A. G. Brook, *J. Amer. Chem. Soc.*, **77**, 4827 (1955); A. G. Brook and R. J. Mauris, *ibid.*, **79**, 971 (1957).

(2) H. Gilman and W. J. Trepka, *J. Org. Chem.*, **25**, 2201 (1957).

(3) D. Wittenberg and H. Gilman, *Quart. Rev.* (London), **13**, 116 (1959).

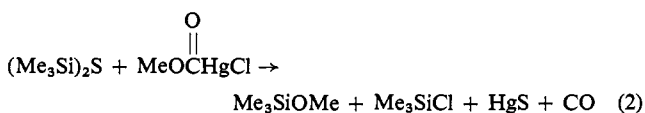
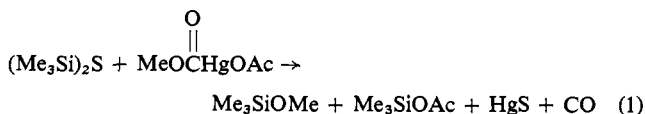
(4) The carbonation of triethylsilyllithium to give triethylsilanecarboxylic acid in low yield has been claimed, but no experimental details or properties of the acid have been reported.⁵

group has been observed. There is a great deal of current interest in the effect of the silicon on the $n \rightarrow \pi^*$ transition in the ultraviolet absorption spectra of the related acylsilanes,⁶⁻¹⁰ and it seemed of considerable interest to determine if a similar effect was present in **1**.

When hexamethyldisilthiane¹¹ (13.5 mmol) was slowly added to a mechanically stirred mixture of bis(carbomethoxy)mercury¹² (13.5 mmol) in 10 ml of ether effervescence of carbon monoxide occurred and a gray-white solid precipitated. Gas-liquid partition chromatography¹³ indicated that the only volatile components were ether, hexamethyldisilthiane, and a small amount of trimethylmethoxysilane. When the mixture was refluxed for 40 hr under a nitrogen atmosphere the solid slowly turned black. Filtration gave 3.1 g (98%) of mercuric sulfide. Glpc of the filtrate showed, in addition to solvent, trimethylmethoxysilane and **1** in a 1:2 molar ratio. Preparative-scale glpc¹⁴ gave 1.1 g (35%) of **1**.

Bis(trimethylsilyl)mercury,¹⁶ (**2**) reacted rapidly at room temperature with carbomethoxymercuric chloride¹² to give **1** (30%), trimethylmethoxysilane (60%), and trimethylchlorosilane (10%). Since **2** is considerably more difficult to prepare and handle than hexamethyldisilthiane, this preparation is less useful than the first one.

A number of unsuccessful attempts to prepare **1** are outlined below in eq 1-3. All of these reactions pro-



ceeded under mild conditions to give virtually quantitative yields of the products shown. No other products were detected by glpc or nmr in any of these systems.

Methyl trimethylsilanecarboxylate (**1**) was a volatile, sweet smelling liquid. Complete decarbonylation of **1** occurred within 0.5 hr at 200°. The infrared carbonyl



(5) N. S. Vyazankin, G. A. Razuvaev, E. N. Gladyshev, and S. P. Korneva, *J. Organometal. Chem.*, **7**, 353 (1967).

(6) A. G. Brook, *Advan. Organometal. Chem.*, **7**, in press.

(7) H. Bock, A. Alt, and H. Seidl, *J. Amer. Chem. Soc.*, **91**, 355 (1969).

(8) P. A. Jones and R. West, *ibid.*, **90**, 6978 (1968).

(9) G. J. D. Peddle, *J. Organometal. Chem.*, **14**, 139 (1968).

(10) F. Agolini, S. Kleimenko, J. G. Csizmadia, and K. Yates, *Spectrochim. Acta*, **24A**, 169 (1968).

(11) G. Champetier, Y. Etienne, and R. Kullman, *Compt. Rend.*, **234**, 1985 (1952).

(12) F. E. Paulik and R. E. Dessy, *Chem. Ind.* (London), **15**, 1650 (1962).

(13) All analytical glpc was done on an Aerograph A90-P3 instrument using a 20 ft \times $\frac{1}{8}$ in. i.d. stainless steel column packed with 5% SE-30 on 60-80 mesh Chromosorb W.

(14) Preparative-scale glpc was done on an Aerograph A90-P3 instrument using a 10 ft \times $\frac{3}{8}$ in. i.d. column packed with 30% SE30 on 60-80 mesh Chromosorb P. The retention volume of **1** was 1700 ml at a column temperature of 100°. *Anal.* Calcd for $\text{C}_5\text{H}_{12}\text{O}_2\text{Si}$: C, 45.4; H, 9.15; molecular ion: 132.0606. Found: C, 45.4; H, 9.03; molecular ion: 132.0606.¹⁵

(15) The mass spectrum was determined on an A.E.I. MS9 spectrometer at 70 eV.

(16) E. Wiberg, O. Stecher, H. J. Andrascheck, L. Kreuzbichler, and E. Staude, *Angew. Chem. Intern. Ed. Engl.*, **2**, 507 (1963).

group absorption of **1** was at 1680 cm^{-1} , the same position as in previously reported silanecarboxylates.²

The ultraviolet spectra of **1**, methyl pivalate, trimethylacetylsilane, and 3,3-dimethyl-2-butanone are shown in Table I. The position of the absorption for **1** shows a small shift to shorter wavelength in more polar solvents, and thus it is reasonable to assign it to the $n \rightarrow \pi^*$ transition.¹⁷ The absorption of both silicon compounds shows exaltation and large bathochromic shifts in position relative to that of their carbon analogs. In addition the absorption of the esters occurs at higher energy than that of the ketones. Previous workers^{18,19} have suggested that the $n \rightarrow \pi^*$ transition of the esters occurs at higher energy due to a lowering in the energy of the n orbital and an increase in the energy of the π^* orbital of the ester relative to those of the ketone. Calculations based upon the ionization potential²⁰ and the electronic spectra of a series of related esters and ketones such as methyl acetate, acetone, and ethyl acetate and methyl propanoate and 2-butanone indicate that the energy of the n orbitals of the esters is approximately 0.6 eV lower than those of the ketones while the π^* orbitals of the esters are approximately 0.9 eV higher in energy than those of the ketones. Since previous MO calculations¹⁰ have shown that the 3d orbitals of silicon are even higher in energy, there should be better matching in energy between the π^* orbital of the ester and the 3d orbitals of silicon than between the π^* orbital of the ketone and the 3d orbital of silicon.

Table I. The Electronic Spectra of Esters and Ketones

Compound	$n \rightarrow \pi^*$ transition		$\Delta\epsilon\text{V}$
	$m\mu$	eV	
$\text{Me}_3\text{SiCOOMe}$ (1) ^{a,c}	245 (330)	5.06	0.81
	250 (330)	4.96	
$\text{Me}_3\text{SiCOOMe}$ ^b	245 (320)	5.85	1.02
Me_3CCOOMe ^a	212 (100)	3.33	
Me_3SiCOMe ^{a,c,d}	372 (126)	4.35	
Me_3CCOMe ^a	285 (25)		

^a In cyclohexane. ^b In 95% ethanol. ^c Shows additional fine structure. ^d A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *J. Amer. Chem. Soc.*, **89**, 431 (1967).

As a result, if stabilization of the π^* orbital due to $d\pi\text{-}p\pi$ bonding were a major factor in producing the observed bathochromic shifts, a larger shift would be expected for silanecarboxylates than for silyl ketones. However, as shown in Table I, the effect of the silicon is actually less in **1** than in trimethylacetylsilane.

Acknowledgment. We are grateful to the National Research Council of Canada for partial support of this work.

(17) W. D. Closson and P. Haug, *J. Amer. Chem. Soc.*, **86**, 2384 (1964).

(18) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, pp 179-187.

(19) K. Higashi, H. Baba, and A. Rembaum, "Quantum Organic Chemistry," Interscience Publishers, New York, N. Y., 1965, pp 175-212.

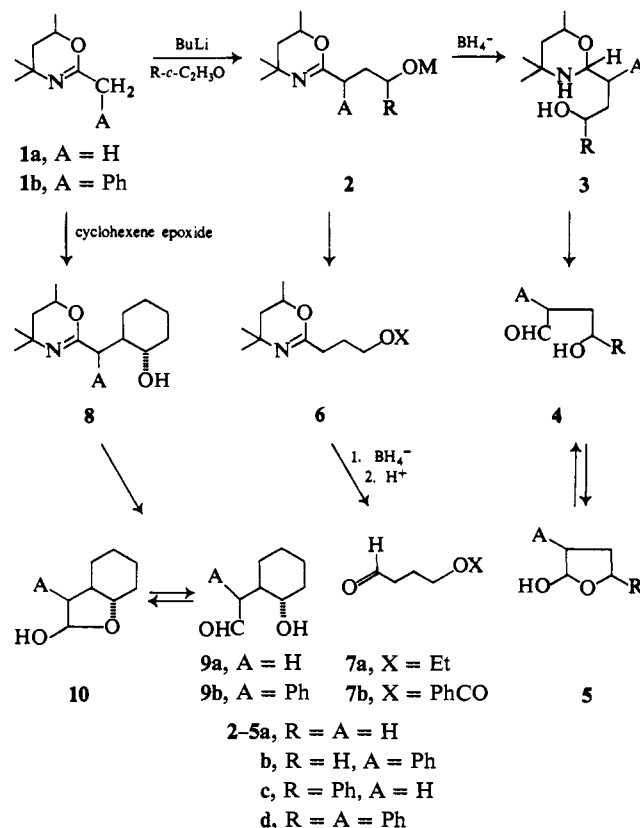
(20) R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, pp 162-203, 308-318.

G. J. D. Peddle, R. W. Walsingham
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada
Received December 23, 1968

Aldehydes from Dihydro-1,3-oxazines. IV. A New Synthesis of γ -Hydroxy Aldehydes and Their γ -Oxo Derivatives

Sir:

Recently, the lithio salt of **1a,b** was shown to be an excellent nucleophile in the reaction with alkyl halides and carbonyl compounds producing ultimately acyclic, alicyclic, and α,β -unsaturated aldehydes and their C-1 deuterated derivatives.¹ We now report that the reaction of **1a,b** with typical epoxides (ethylene, styrene, and cyclohexene) produces precursors to γ -hydroxy aldehydes and their γ -oxo derivatives.²



Addition of the epoxides to a THF solution of the lithio salt **1** (**a** or **b**) at -78° followed by hydrolytic work-up results in excellent yields (Table I) of the adducts **2** (M = H) and **8**. These oxazinylcarbinols were sufficiently pure (tlc, nmr, ir) to be utilized directly for reduction at -35° by sodium borohydride,¹ affording the corresponding tetrahydro-1,3-oxazines **3** in high yield (Table I). Cleavage of **3** or reduced **8** in aqueous oxalic acid and recovery of the aldehyde by extraction or steam distillation produced the γ -hydroxy derivatives **4** or **9** in 57-69% over-all yields (Table I). The hydroxy aldehydes were expected to exist primarily as the cyclic hemiacetals **5** and **10**, and their spectral characteristics (ir, nmr) confirmed this.³ The sequence is therefore a

(1) A. I. Meyers, A. Nabeya, H. W. Adickes, and I. R. Politzer, *J. Am. Chem. Soc.*, **91**, 763 (1969); A. I. Meyers, A. Nabeya, I. R. Politzer, H. W. Adickes, J. M. Fitzpatrick, and G. R. Malone, *ibid.*, **91**, 764 (1969); A. I. Meyers, H. W. Adickes, I. R. Politzer, and W. N. Beverung, *ibid.*, **91**, 765 (1969).

(2) The C-1 deuterated derivatives reported in ref 1 can also be obtained for this class of compounds, using sodium borodeuteride in place of borohydride. We did not attempt to prepare the deuterio derivative for the oxo aldehydes reported herein.