

via the symmetrical intermediate. In order to obtain the same isotope effect^{15b} for deprotonation of **2** during the solvolysis of **4ZZ** as was obtained from **4EZ**, it is necessary for the remainder of the elimination reaction to proceed with an isotope effect of 2.6 instead of the 2.0 as used for **4EZ**. Since E₂ elimination is a commonly observed pathway for vinyl halide solvolysis when hydrogen is trans to the leaving group, we assume that a small contribution from this process is present. It is this contribution which results in the higher isotope effect for the nonchlorolium portion of the elimination. Analyzing the yields and deuterium distribution for **4ZZ** according to Scheme II, we find that 20% of the reaction proceeds via the chlorolium ion **2**, of which 14% appears as acetylene, and, tentatively, 6% as acetate.

An important feature of the solvolysis mechanism may be that the vinyl cation is present in cisoid and transoid conformations, which do not readily interconvert. Thus, the amount of chlorolium ion formed is a function of the fraction of cisoid ion generated and not one of thermodynamic stability or vinyl cation lifetime. Such a hypothesis explains the lack of solvent sensitivity to the amount of chlorolium ion formed. It is also consistent with the smaller than usual amount of elimination product (**6Z**) formed from the open ion since in the transoid ion attack of base on the proton at C₂ is hindered.

The product distribution observed rules out cyclization of **1** to give cyclobutenyl cations, since this would result in the formation of a tertiary benzylic chloride which would rapidly solvolyze further. No halogen-containing products would be expected. Halogen-substituted cyclobutenyl cations apparently do not open to chlorolium or bromolium ions under conditions where cation lifetime is short.¹⁶

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(16) (a) T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, **86**, 1600 (1964); (b) H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962).

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Stereochemical Course in the Photochemistry of the 1,2,3-Trisilacycloheptane System

Sir:

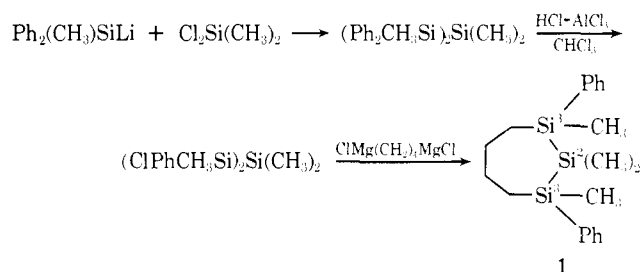
In a recent communication¹ we have reported that 1,2,3-trisilacycloheptane derivatives release a central silicon atom as a silylene on irradiation and that this system can be used generally as a precursor for a tailor-made organosilylene. The unique photochemical reaction in cyclic organopolysilicon compounds may be a cheletropic reaction in the system composed of only a "σ" electron framework.² This possibility prompted

(1) H. Sakurai, Y. Kobayashi, and Y. Nakadaira, *J. Amer. Chem. Soc.*, **93**, 5292 (1971).

(2) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

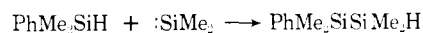
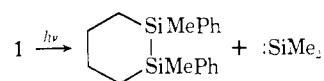
us to prepare *cis*- and *trans*-1,2,2,3-tetramethyl-1,3-diphenyl-1,2,3-trisilacycloheptane (**1a** and **1b**), in an attempt to study stereochemistry of photochemical generation of dimethylsilylene from the 1,2,3-trisilacycloheptane system.

The synthesis of **1** was accomplished by procedures depicted in the following reactions.



A mixture of *cis*- and *trans*-1,2,2,3-tetramethyl-1,3-diphenyl-1,2,3-trisilacycloheptane (**1**) was obtained as an oil in 48.1% yield: bp 159–161° (0.38 mm); mass spectral, M⁺, *m/e* 354.³ Since the *cis*-*trans* mixture showed a single peak on vpc under various conditions and also gave one spot on silica gel tlc, the separation of these two isomers was rather tedious and proceeded as follows. The single spot on a preparative silica gel tlc plate developed with *n*-hexane was divided into lower and upper parts. Each portion was crystallized several times from ethanol at –78°. The *cis* isomer **1a** was obtained from the lower portion as a crystal: mp 45°; uv (*n*-hexane) 251 nm (20,400); nmr (CCl₄, δ) three singlets at –0.41 (6 H, Si¹-CH₃ and Si³-CH₃), –0.09 (3 H, Si²-CH₃), and 0.23 (3 H, Si²-CH₃) and three multiplets at 1.12 (4 H, Si-CH₂–), 1.82 (4 H, C-CH₂–), and 7.37 (10 H, C₆H₅). Similarly the *trans* isomer **1b** was afforded from the upper portion of the spot: mp 33.5–34.5°; uv (*n*-hexane) 247.5 nm (23,400); nmr (CCl₄, δ) two singlets at 0.16 (6 H, Si²-CH₃) and 0.45 (6 H, Si¹-CH₃ and Si³-CH₃) and three multiplets at 1.18 (4 H, Si-CH₂–), 1.90 (4 H, C-CH₂–), and 7.37 (10 H, C₆H₅). Stereochemical assignments of these isomers, **1a** and **1b**, were established unequivocally by inspection of their nmr spectra, especially of the signals due to the Si²-CH₃ groups. Thus, in the case of *cis* isomer **1a**, two Si²-CH₃ groups are magnetically nonequivalent and appear as two separate singlets. On the other hand, in *trans* isomer **1b**, these groups are magnetically equivalent so that they give a single absorption at δ 0.16.

On irradiation externally through a Vycor filter with a 160-W low-pressure mercury arc lamp for 3 hr, **1** (*cis/trans* = 1/1.4) in *n*-hexane yielded 1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane (**2**) in 99.8% yield at 11.5% conversion with accompanying evolution of dimethylsilylene. The latter was trapped by dimethylphenylsilane.



Stereochemistry of the 1,2-disilacyclohexane (**2**) formed from pure **1a** and **1b** was determined by comparing spectral and vpc properties with those of

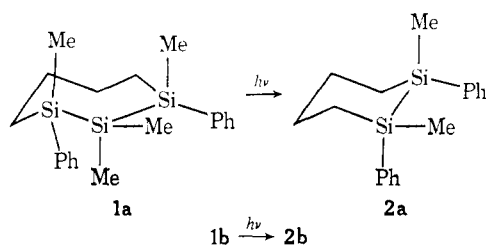
(3) Satisfactory elemental analyses were obtained.

Table I. Stereochemical Consequence in the Photochemical Conversion of **1** to **2**

Composition of 1 (%)		Irradiation time (hr)	Solvent	Composition of 2 (%)	
Cis	Trans			Cis	Trans
95.0	5.0	1.0	Benzene	95.3	4.7
99.4	0.6	0.75	<i>n</i> -Hexane	95.2	4.8
8.6	91.4	1.5	<i>n</i> -Hexane	8.0	92.0
5.2	94.8	1.0	<i>n</i> -Hexane	5.4	94.6

authentic samples,⁴ the results being summarized in Table I. The composition of the trisilane **1** was determined from integrated intensities of the corresponding Si²-CH₃ nmr signals.⁵ The stereochemical assignment of **2** was performed by vpc analysis, and the results were corrected by the factor calculated from analysis of **2** with known composition by vpc and nmr at the same time.

The results in Table I clearly indicate that the photochemical ring contraction of 1,2,3-trisilacycloheptane proceeds in a highly stereospecific manner with retention of configurations at both Si¹ and Si³ centers as shown in the following scheme.



(4) K. Tamao, M. Kumada, and M. Ishikawa, *J. Organometal. Chem.*, **31**, 17 (1971).

(5) Spectra were integrated at 100 Hz/250-sec sweeps, on a Varian HA-100.

The photochemically generated dimethylsilylenes undergo insertion into an Si-H bond with retention of configuration,⁶ and their relative rates of insertion into XC₆H₄SiMe₂H indicate nucleophilic character of the species.⁷ These results together with the present finding suggest a concerted elimination of the singlet silylene in the irradiated 1,2,3-trisilacycloheptane systems. However, due to the known configurational stability of chiral silyl radicals,⁸ the possibility of homolytic fission of an Si-Si bond followed by SH₂ type attack of the silyl radical⁹ on the residual Si-Si bond cannot necessarily be eliminated at the present moment.

Related work is in progress.

(6) H. Sakurai and M. Murakami, *J. Amer. Chem. Soc.*, **94**, 5080 (1972).

(7) H. Sakurai, S. Komiya, and Y. Nakadaira, 28th Annual Meeting of the Chemical Society of Japan, April 2, 1973, Abstracts, III-1226, reported log (relative rate) = 0.84σ^o in the reaction with the photochemically generated :SiMe₂ from **1**.

(8) (a) H. Sakurai, M. Murakami, and M. Kumada, *J. Amer. Chem. Soc.*, **91**, 519 (1969); (b) A. G. Brook and J. M. Duff, *ibid.*, **91**, 2118 (1969).

(9) (a) A. Hosomi and H. Sakurai, *J. Amer. Chem. Soc.*, **94**, 1384 (1972); (b) *Chem. Lett.*, 193 (1972); (c) Y. Nakadaira and H. Sakurai, *J. Organometal. Chem.*, **47**, 61 (1973).

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Book Reviews*

Carbenes. Volume I. Edited by MAITLAND JONES, Jr. (Princeton University), and ROBERT A. MOSS (Rutgers University). Wiley-Interscience, New York, N. Y. 1973. 356 pp. \$24.95.

"The past decade has seen carbene chemistry change from a compendium of novelties to a discipline requiring close attention to the intricate details of mechanism," the editors state in their preface. They have accordingly initiated a series of "critical surveys of topical areas," of which this volume is the first collection.

There are three chapters: Carbenes from Diazo Compounds; The Application of Relative Reactivity Studies to the Carbene Olefin Addition Reaction; and Generation of Carbenes by Photochemical Cycloelimination Reactions. Although these chapters are not meant to be encyclopedic, the fact that the references cited total 908 indicates coverage of the topics with substantial degree of thoroughness. It is, however, particularly unfortunate in such a rapidly advancing field that the authors do not state the dates after which they ceased covering the literature. The preface is dated May, 1972, and references later than 1971 are not apparent to casual examination.

The emphasis is on carbenes themselves—their formation, properties, and reactions. Accordingly, the effects of spin multiplicity, coordination, method of generation, etc., are examined in detail, and the evidence is critically weighed. It becomes evident

in reading these chapters that the number of unanswered questions and incompletely understood phenomena is large. One aspect of this situation is that tabulation of comparative data (rates, yields, etc.) are commonly spotty, out of necessity. This can lead to a feeling of frustration that is in no way the fault of the authors. One set of tables, however, is really impressive in extent; the chapter on the carbene-olefin addition contains nearly 100 pages of them.

This volume is an indispensable reference to chemists concerned with carbenes, not only because of the depth of its treatment but also because of the competence of the contributors in presenting critical discussions of the sometimes bewildering mass of data available.

The Chemistry of Synthetic Dyes. Volume VI. Reactive Dyes. Edited by K. VENKATARAMAN (National Chemical Laboratory, Poona, India). Academic Press, New York, N. Y. 1972. xix + 463 pp. \$32.00

This series is designed to cover new developments since 1950, and is "intended primarily for chemists and technologists who are concerned with the synthesis of dyes and their applications," but there is much of general organic interest. The reactive dyes covered in this volume are entirely a new development since 1950, and are thus not discussed in Volumes I and II. The term is used to describe dyes with a capability for reaction with a hydroxyl group, which

* Unsigned book reviews are by the Book Review Editor.