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UNSATURATED ORGANOSILICON HETEROCYCLES.(U)
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FINAL SCIENTIFIC REPORT

Period covered October 1, 1972 to September 30, 1976

Grant Number 73-2424

Air Force Office of Scientific Research

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UNSATURATED ORGANOSILICON HETEROCYCLES

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UNSATURATED ORGANOSILICON HETEROCYCLES

Period covered October 1, 1972 to September 30, 1976

Final Scientific Report

Personnel Employed at Various Times on This Grant.

The following people were employed as post-doctoral Research Associates:
Dr. Thomas Isami Ito, Dr. Il Nam Jung, and Dr. Michael Edward Dexheimer.

The following people were employed as Research Assistants on this project:
Raymond A. Felix, Phillip B. Valkovich, Karl E. Koenig, Michelle M. Radcliffe,
Michael E. Childs, H.N. Soysa, and Bruce I. Rosen.

Publications

1. Synthesis and Mass Spectral Behavior of Representative 1,1-Dichloro-2-phenylcyclopropanes and 1,1-Dichloro-2-ferrocenylcyclopropanes. G.W. Gokel, J.P. Shepherd, and Wm. P. Weber, H.G. Boettger, J.L. Holwick, and D.J. McAdoo, J. Org. Chem., 38, 1913 (1973).
2. The reaction of DCl with cis and trans- β -Trimethylsilyl Styrene. K.E. Koenig and Wm. P. Weber, J. Am. Chem. Soc., 95, 3416 (1973).
3. Mass Spectrometry of Organosilicon Compounds - Some Examples of Interaction of the Silyl Center with Remote Functional Groups. Wm. P. Weber and H.G. Boettger, Intra-Science Reports, 7, 107 (1973).
4. The Reaction of Bromine with cis and trans- β -Trimethylsilyl Styrene. K.E. Koenig and Wm. P. Weber, Tetrahedron Letters, 2533 (1973).
5. Addition of H S to α,ω -Dienes to Yield Medium Sized Heterocycles 1,1-Dimethyl-1-sila-5-thiacyclooctane, Wm. P. Weber and Karl E. Keonig, Tetrahedron Letters, 3151 (1973).
6. Reaction of 1,2-Glycols with Dichlorocarbene Produced by Phase Transfer Catalysis, Wm. P. Weber, P. Stromquist, and M. Radcliffe, Tetrahedron Letters, 4523 (1973).

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7. Unsaturated Organosilicon Heterocycles, K.E. Koenig, R.A. Felix, and W.P. Weber, J. Org. Chem., 39, 1539 (1974).
8. The Effect of a Neighboring Trimethylsilyl Group on the Photochemical and Mass Spectral Fragmentation Pathways of S-Alkyl Thioacetates, T.I. Ito and W.P. Weber, J. Org. Chem., 39, 1691 (1974).
9. Synthesis and Mass Spectra of ω -(Trimethylsilyl) Alkyl Methyl Sulfides and Sulfones, T.I. Ito and W.P. Weber, J. Org. Chem., 39, 1694 (1974).
10. Observations on the Mechanism of Reduction of Sulfones to Sulfides William P. Weber, Phillip Stromquist, and Thomas I. Ito, Tetrahedron Letters, 2595 (1974).
11. Pyrolytic and Photochemical Fragmentation of 1,1-Dimethyl-2-Phenyl-1-Silacyclobutane, Phillip B. Valkovich, Thomas I. Ito, and William P. Weber, J. Org. Chem., 39, 3543 (1974).
12. Competing (2+2) and (2+4) Cycloaddition Reactions of a Carbon-Silicon Double Bonded Intermediate with an α,β -Unsaturated Aldehyde. Copyrolysis of 1,1-Dimethyl-2-Phenyl-1-Silacyclobutane and Acrolein, Phillip B. Valkovich and William P. Weber, J. Org. Chem., 40, 229 (1975).
13. Synthesis of Unsaturated Organosilicon Heterocycle-Reaction of Silylene with Cyclic Dienes, Michael E. Childs and William P. Weber, Tetrahedron Letters, 4033 (1974).
14. A Convenient Synthesis of 1,2-Dimethyltetramethoxydisilane. Michael E. Childs and William P. Weber, J. Organometal. Chem., 86, 169 (1975).
15. Pyrolysis of 1-Phenyl-1,3-Butadienes, A New Synthesis of 1,2-Dihydronaphthalenes, Phillip B. Valkovich, James L. Conger, Frank A. Castiello, Todd D. Brodie, and William P. Weber, J. Am. Chem. Soc., 97, 901 (1975).
16. Synthesis and Pyrolysis of 1,1-Dimethyl-2-Phenyl-1-Silacyclobut-2-ene, Phillip B. Valkovich and William P. Weber, Tetrahedron Letters, 2153 (1975).
17. Copyrolysis of 1,1-Dimethyl-1-Silacyclobutane and Acrolein, Phillip B. Valkovich and William P. Weber, J. Organometal. Chem., 99, 231 (1975).
18. Radical Chain Reactions of Halomethyldimethylsilanes, Il nam Jung and W.P. Weber, J. Org. Chem., 41, 946 (1976).
19. Copyrolysis of Sym-Tetramethoxydimethyldisilane with 2,5-Dimethylfuran, M.E. Childs and W.P. Weber, J. Org. Chem., 41, 1799 (1976).
20. Mercury Sensitized Photolysis of Pentamethyldisilane and Sym-Tetramethyldisilane, Il nam Jung and William P. Weber, J. Organometal. Chem., 114, 257 (1976).

Seminars were presented on work supported by the AFOSR grant 73-2424

at the following institutions:

University of Buffalo, June 9, 1975.

Non-Metallic Materials Laboratory, Wright-Patterson Air Force Base,
June 11, 1975.

University of Indiana, June 12, 1975.

Dow-Corning Company, June 16, 1975.

Washington University, June 17, 1975.

Iowa State University, June 18, 1975.

University of Southern California, Los Angeles, March 16, 1976.

Tulane University, New Orleans, Louisiana, March 29, 1976.

University of Oklahoma, Norman, Oklahoma, April 1, 1976.

University of Houston, Houston, Texas, April 2, 1976.

Bowling Green University, Bowling Green, Ohio, May 19, 1976.

University of Akron, Akron, Ohio, July 15, 1976.

An invited talk on work supported by the AFOSR was presented at the
Gordon Research Conference on Organic Reactions and Processes, July 20, 1976.

Papers Presented

The Reaction of β -Trimethylsilyl Styrene with HX at the Dallas, American
Chemical Society meeting, April 1973, Kipping Award Symposium.

Three papers were delivered at West Coast regional ACS meeting, San
Diego, November 1973.

The Effect of Neighboring Trimethylsilyl Groups on the Photochemical
Fragmentation Patterning of S-Alkyl Thioacetate, American Chemical Society
meeting, Los Angeles, April 1974.

The Reaction of Methoxymethylsilylene with Cyclic Dienes, W.P. Weber and M.E. Childs, Fourth International Symposium on Organosilicon Chemistry, Moscow, July 1975.

Pyrolysis of 1,1-Dimethyl-2-Phenyl-1-Silacyclobutane, P.B. Valkovich and W.P. Weber, Fourth International Symposium on Organosilicon Chemistry, Moscow, July 1975. Neither of these papers were presented but they will appear in the Abstracts of the Meeting since both were accepted for presentation.

[2+2] and [2+4] Cycloaddition Reaction of Carbon Silicon Doubly Bonded Intermediates with Acrolein, W.P. Weber. This paper was presented at the Bartlett Symposium in Fort Worth, August 1975.

Copyrolysis of 1,1-Dimethyl-1-silacyclobutane and Acrolein, American Chemical Society Meeting, Mexico City, Mexico, November 1975.

Research Accomplishments

I shall attempt to summarize the scientific accomplishments of the past four years (October 1, 1972 to September 30, 1976) achieved by us while working on Air Force Office of Scientific Research grant number 73-2424 titled UNSATURATED ORGANOSILICON HETEROCYCLES.

Most of the work has been published (see publication list). Often results related to a single main goal or objective are the subject of more than one publication. For this reason, I will attempt to bring our work into clear focus.

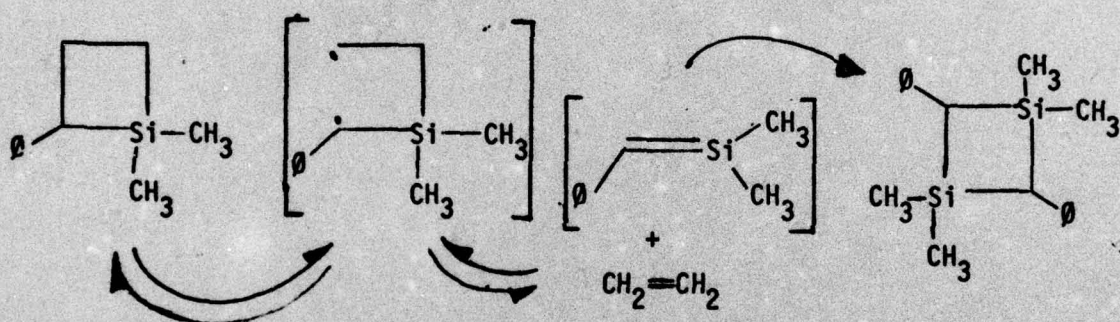
→ The generation of carbon-silicon double bonds as reactive intermediates and their cycloadditions with alpha, beta unsaturated aldehydes has been a primary goal.

To accomplish this objective 1,1-dimethyl-2-phenyl-1-silacyclobutane was prepared. Pyrolysis of this compound in the gas phase led to ethylene

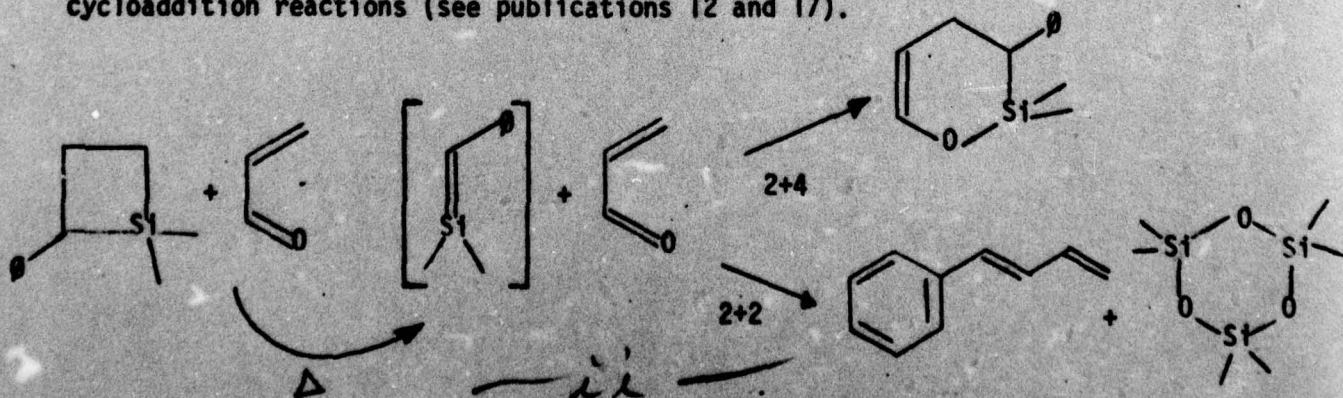
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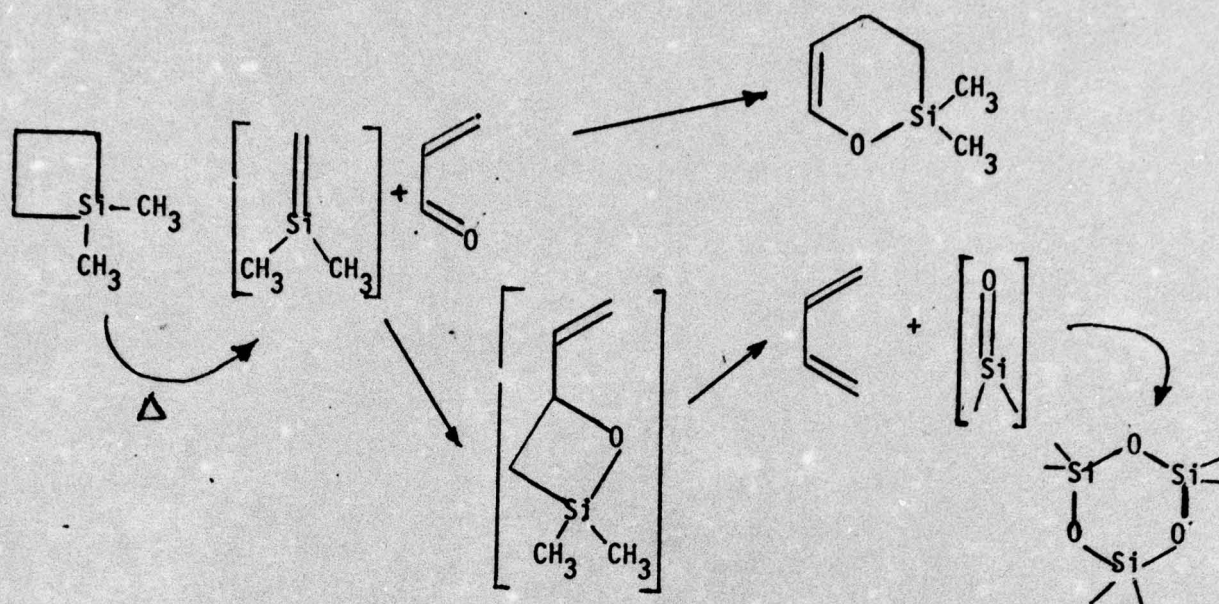
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and a reactive intermediate possessing a carbon-silicon double bond with a phenyl substituent on the carbon atom. Apparently, the phenyl group stabilizes the carbon-silicon double bond. Thus, 1,1-dimethyl-2-phenyl-1-silacyclobutane decomposes at 450° whereas 1,1-dimethylsilacyclobutane does not decompose until 600° under comparable conditions. The phenyl substituted carbon-silicon double bonded intermediate ultimately dimerizes to yield 1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane. These results support the conclusion that a carbon-carbon bond breaks first in preference to a carbon-silicon bond (see Publication 11).

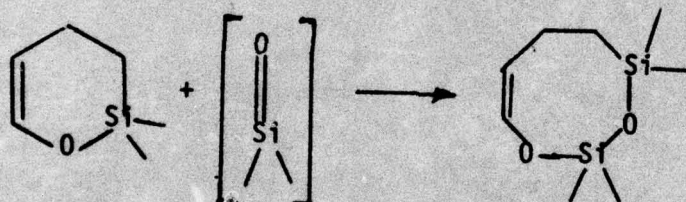


The cycloaddition reactions of carbon-silicon doubly bonded intermediates with alpha,beta unsaturated aldehydes such as acrolein were studied by carrying out co-pyrolysis reactions of acrolein with 1,1-dimethyl-2-phenyl-1-silacyclobutane and with 1,1-dimethyl-1-silacyclobutane. It was found that carbon silicon double bonded intermediates undergo both 2+2 and 2+4 cycloaddition reactions (see publications 12 and 17).

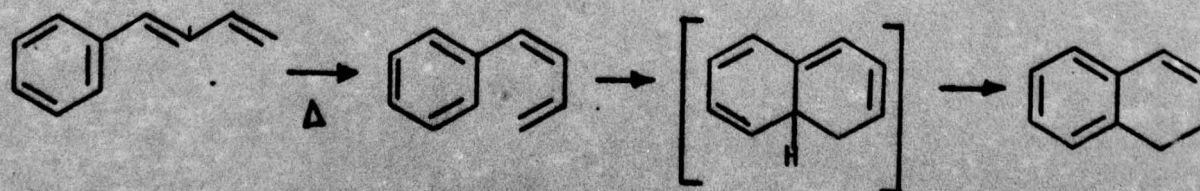




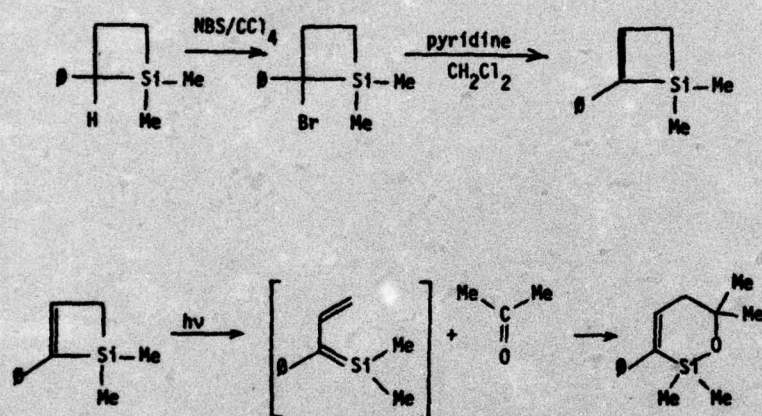
The insertion of silicon-oxygen doubly bonded intermediate was also observed. This is of great potential importance since it may permit chemistry on the backbone of silicon polymers (see publication 17).



An unexpected out-growth of this work was the finding that 1-phenyl-1,3-butadiene, a product of the 2+2 cycloaddition reaction of the phenyl substituted carbon-silicon doubly bonded intermediate with acrolein, undergoes a pyrolytic electrocyclic reaction to yield 1,2-dihydronaphthalene. The generality of this new synthesis and the mechanism of the reaction were explored (see publication 15).



While we now had high temperature thermal sources of reactive intermediates possessing carbon-silicon double bonds - we wanted a way to generate such intermediates at low temperature - preferably photochemically. With this objective, we prepared 1,1-dimethyl-2-phenyl-1-silacyclobut-2-ene and studied its photochemical ring opening to yield the first intermediate possessing a carbon-silicon double bond conjugated to a carbon-carbon double bond. The cycloaddition reactions of this new intermediate with acetone were studied. Both 2+2 and 2+4 cycloaddition reaction products were found (see publication 16).

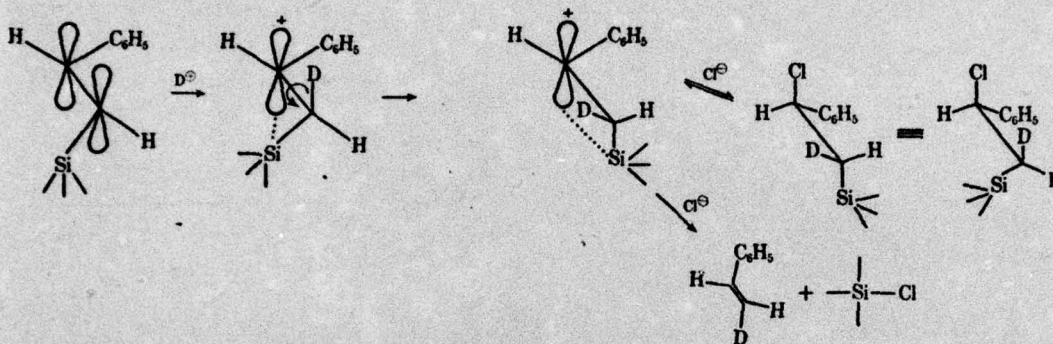


Another major goal was to prepare unsaturated organosilicon heterocycles possessing 6 π electrons and a silyl center to determine if conjugation through silicon would permit such compounds to possess aromatic or other unusual properties.

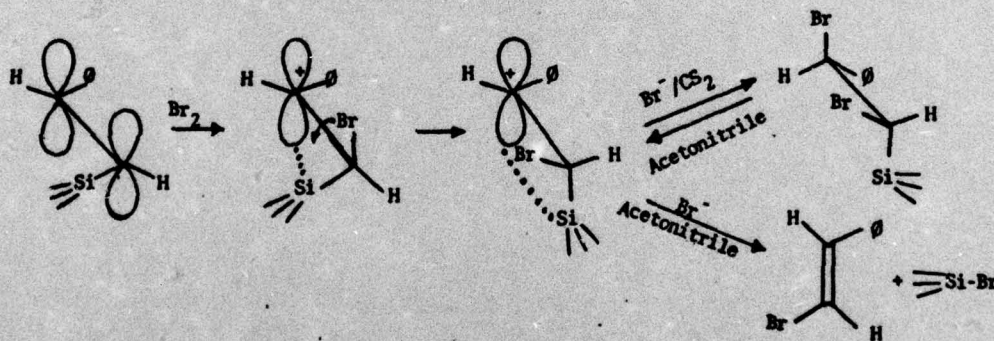
Preliminary work was done to determine the sensitivity of vinylic carbon-silicon bonds to electrophilic cleavage. The stereochemistry of such cleavage reactions provided insight into the mechanism by which vinylic carbon-silicon bonds are cleaved by electrophiles. Specifically,

it was found that trans-beta-trimethylsilylstyrene was cleaved by deuterium chloride to yield styrene in which the deuterium had replaced silicon.

Similar results were obtained with cis-beta-trimethylsilylstyrene.

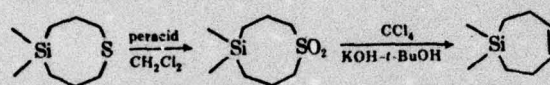
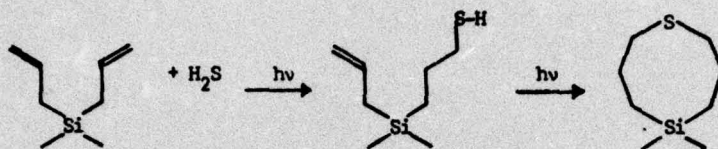


Cleavage of cis- and trans-beta-trimethylsilylstyrene with bromine likewise resulted in retention of stereochemistry. These results could be explained by a cis addition followed by a trans elimination mechanism (see publications 2 and 4).

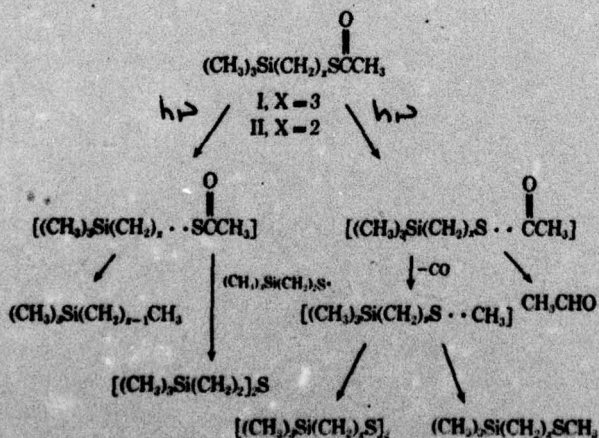


New ring closure reactions - which would permit facile introduction of a carbon-carbon double bond in an organosilicon heterocycles were developed. Thus the photocatalyzed addition of H_2S to dimethyldiallylsilane was shown to yield 1,1-dimethyl-1-sila-5-thiacyclooctane. Oxidation of this sulfide gave the corresponding sulfone which was directly converted

to 1,1-dimethyl-1-sila-4-cycloheptene via a Ramberg-Bäcklund reaction (see publications 5 and 7).

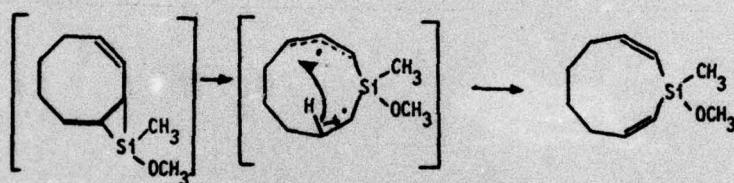


Work on the effect of neighboring trimethylsilyl groups on the photochemical and mass spectral fragmentation pathways of S-alkyl thioacetates was an outgrowth of this work. Both sulfur-alkyl and sulfur-aryl bond scission were shown to be primary processes. ω -(Trimethylsilyl)-alkyl methyl sulfides and sulfones were prepared and their spectrum studied. Little work had previously been done on intramolecular interactions between silicon and sulfur (see publications 9 and 10).

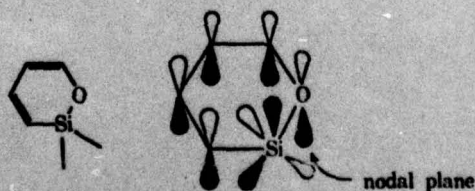


The insertion reaction of silylenes into various unsaturated organic molecules was found to be a more direct approach to the preparation of unsaturated organosilicon heterocycles.

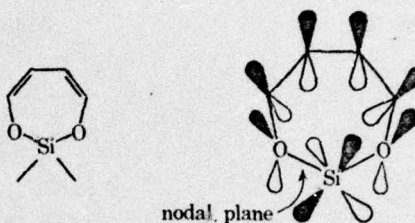
Thus the reaction of methoxymethylsilylene with 1,3-cyclooctadiene led to 1-methoxy-1-methyl-1-sila-2,8-cyclononadiene. The formation of this product was consistent with an addition mechanism involving a vinyl-sila-cyclopropane intermediate which opened by carbon-carbon bond scission rather than by carbon-silicon scission to yield a diradical which underwent a trans-annular 1,5-hydrogen transfer.



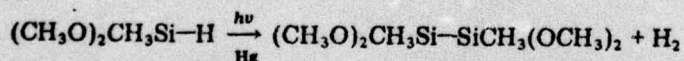
Most recently, the reaction of methoxymethylsilylene with 2,5-dimethyl furan has been shown to yield 2-methoxy-2,3,6-trimethyl-1-oxo-2-silacyclohexa-3,5-diene and 2-methoxy-2,4,7-trimethyl-1,3-dioxo-2-silacyclohepta-4,6-diene. In the first compound, interaction of a lone pair of electrons on oxygen with both an empty 3d orbital on silicon and the diene system would yield a 6π electron system possessing a nodal plane. Such a system is predicted to be antiaromatic by the Mobius concept.



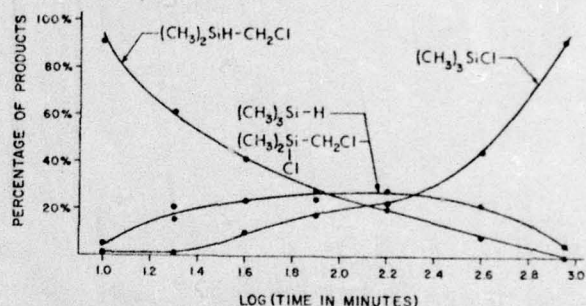
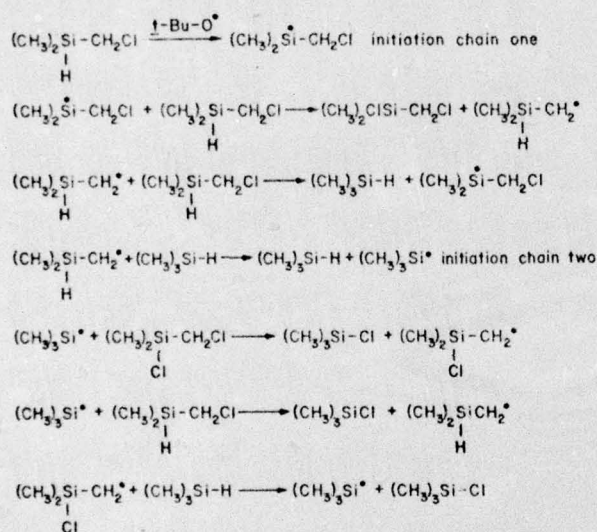
In the second compound, on the other hand, interaction of two lone pairs of electrons from the two oxygen atoms with both an empty 3d orbital on silicon and the diene system would yield an 8π electron system possessing a nodal plane. Such a system is predicted to be aromatic by the Mobius concept. Ultraviolet and other spectral properties of these compounds, however, did not indicate any special stabilization (see publications 13 and 19).



Clearly, the reaction of silylenes with unsaturated cyclic organic compounds provides an extremely direct efficient synthetic route to unsaturated organosilicon heterocycles. This provided the incentive to develop better methods to prepare silylene precursors. Specifically, the pyrolysis of sym-tetramethoxy-1,2-dimethyldisilane has been shown to yield silylene and trimethoxymethylsilane. An efficient synthesis of sym-tetramethoxy-1,2-dimethylsilane was developed. Photolysis of dimethoxymethylsilane in the gas phase in the presence of mercury vapor yields the desired sym-tetramethoxydimethyldisilane and hydrogen (see publication 14).

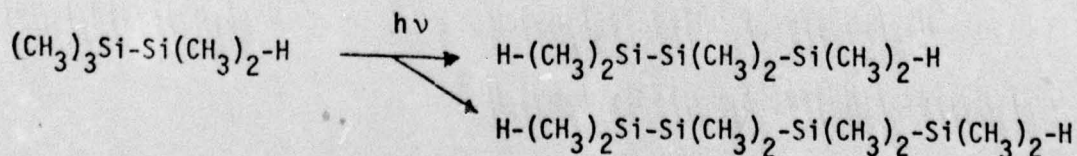


An attempt to extend this reaction to the photolysis of chloromethyldimethylsilanes led to the discovery of an interesting pair of radical chain reactions leading to formation of trimethylsilane and chloromethyldimethylchlorosilane at short reaction times and trimethylchlorosilane at long reaction times. Similar results were found when the reaction was initiated by di-*t*-butyl peroxide decomposition (see publication 18).



Time dependence of the product ratios in the radical chain reactions of chloromethyldimethylsilane initiated by di-*tert*-butyl peroxide.

On the other hand, it was shown that photolysis of pentamethyldisilane in the vapor phase in the presence of mercury permits the synthesis of 1,3-dihydrohexamethyltrisilane and 1,4-dihydrooctamethyltetrasilane (see publication 20).

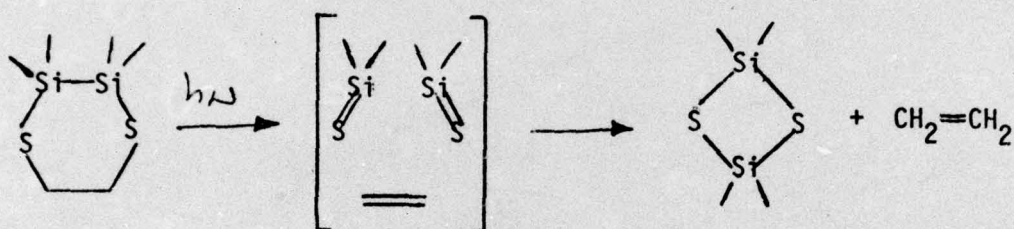


The chemistry of polysilanes possessing sulfur atoms directly bonded to silicon has been actively explored. Preliminary results in this area are most exciting.

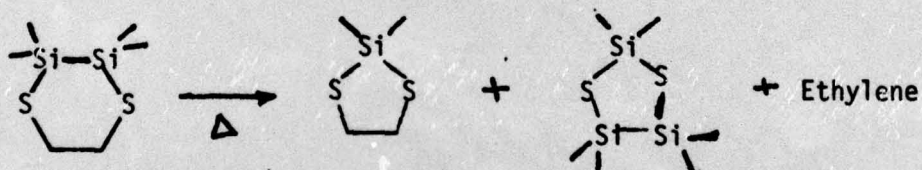
Photolysis of 2,2,3,3-tetra-2,3-disila-1,4-dithiacyclohexane yields ethylene and 2,2,4,4-tetramethyl-2,4-disila-1,3-dithiacyclobutane.

This reaction may involve silicon-sulfur doubly bonded intermediates.

Experiments designed to trap such a silicon-sulfur doubly bonded intermediate are in progress.



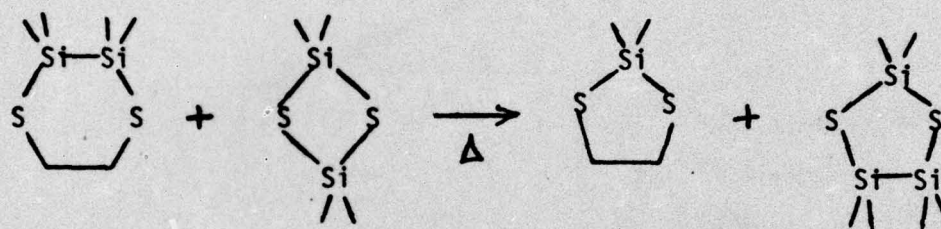
Pyrolysis of 2,2,3,3-tetramethyl-2,3-disila-1,4-dithiacyclohexane at 230° in solution yields ethylene, 2,2-dimethyl-2-sila-1,3-dithiacyclopentane, and 2,2,3,3,5,5-hexamethyl-2,3,5-trisila-1,4 dithiacyclopentane in a ratio of approximately 1:1:1.



Experiments designed to detect the presence of dimethylsilylene as an intermediate in this reaction - pyrolysis in the presence of dimethylphenylsilane as solvent - were negative. Dimethylsilylene is known to insert into Si-H bonds.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Summary of the scientific accomplishments of the past four years (October 1, 1972 to September 30, 1976) achieved by principal investigator and co-workers while working on AFOSR grant 73-2424.		

The following experiment served to demonstrate that 2,2,4,4-tetramethyl-2,4-disila-1,3-dithiacyclobutane may be an intermediate in the pyrolysis of 2,2,3,3-tetramethyl-2,3-disila-1,4-dithiacyclohexane. Co-pyrolysis of 2,2,3,3-tetramethyl-2,3-disila-1,4-dithiacyclohexane and 2,2,4,4-tetramethyl-2,4-disila-1,3-dithiacyclobutane yields a 1:1 mixture of 2,2-dimethyl-2-sila-1,3-dithiacyclopentane and 2,2,3,3,5,5-hexamethyl-2,3,5-trisila-1,4-dithiacyclopentane. This reaction has been shown not to involve free dimethylsilylene.



Finally, both 2,2-dimethyl-2-sila-1,3-dithiacyclopentane and 2,2,3,3,5,5-hexamethyl-2,3,5-trisila-1,4-dithiacyclopentane were shown to be stable under the pyrolysis conditions.

The following series of compounds was prepared $\text{CH}_3\text{S}-[(\text{CH}_3)_2\text{Si}]_n-\text{SCH}_3$ from $n = 1$ to 4. They had the following ultra-violet spectra. Photochemistry and thermal chemistry of these compounds are under study.

$\text{CH}_3\text{S}-[(\text{CH}_3)_2\text{Si}]-\text{SCH}_3$	λ_{max}	2246 Å	ϵ	2.24×10^3
$\text{CH}_3\text{S}-[(\text{CH}_3)_2\text{Si}]_2-\text{SCH}_3$	λ_{max}	2466 Å	ϵ	2.26×10^3
$\text{CH}_3\text{S}-[(\text{CH}_3)_2\text{Si}]_3-\text{SCH}_3$	λ_{max}	2526 Å	ϵ	2.40×10^3
$\text{CH}_3\text{S}-[(\text{CH}_3)_2\text{Si}]_4-\text{SCH}_3$	λ_{max}	2572 Å	ϵ	6.05×10^3