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ORGANOSILICON COMPOUNDS AND ORGANOSILICON POLYMER INTERMEDIATES--ETC(U)
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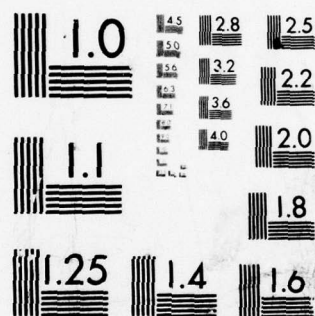


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FINAL SCIENTIFIC REPORT
Grant No. AF-AFOSR-76-2917

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"Organosilicon Compounds and Organosilicon
Polymer Intermediates"

Principal Investigator: Professor Dietmar Seyferth

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Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

November 21, 1978

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A summary of three years of research directed mainly at a development of the chemistry of silacyclopropanes and sila- cyclopropenes.			

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

A. Period Covered and Personnel

1. Period Covered

1 October 1975 30 September 1978

2. Personnel*

a. Senior Investigator: Professor Dietmar Seyferth

b. Postdoctoral Investigators:

T.F.O. Lim (North Texas State University)
W. Holderich (Univ. of Karlsruhe)

c. Predoctoral Investigators**

D. Dagani (Ph.D.)
C.K. Haas (Ph.D.)
D.P. Duncan (Ph.D.)
J.L. Lefferts (Ph.D.)
D.C. Annarelli (Ph.D.)
S.C. Vick (Ph.D.)
P. Holl (Ph.D., Technical Univ. of Munich)
M.L. Shannon

ACCESSION for

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* Personnel are listed whose salaries and/or research costs were covered totally or in part by this Grant.

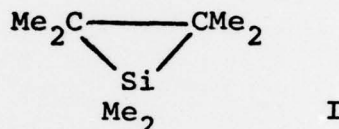
** Those whose name is followed by (Ph.D.) obtained their Ph.D. degree during the grant period.

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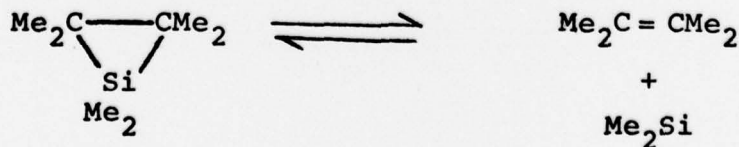
B. Research Accomplishments

1) Silacyclopropanes and Silacyclopropenes

The first silacyclopropanes to be reported were prepared during the previous AFOSR Grant (AF-AFOSR-72-2204). During the present Grant period the chemistry of one of these, hexamethylsilacyclopropane,

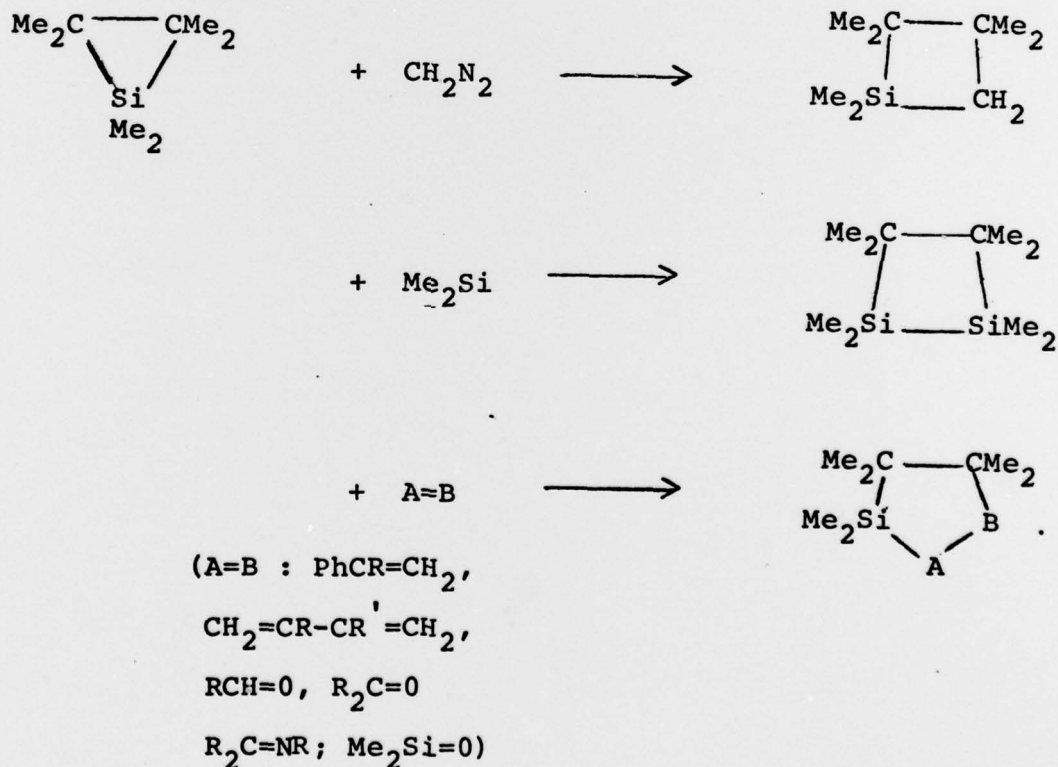


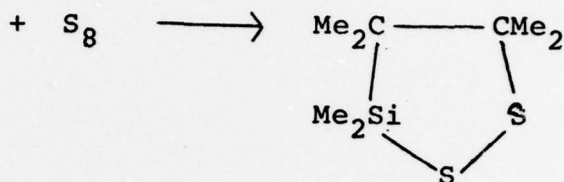
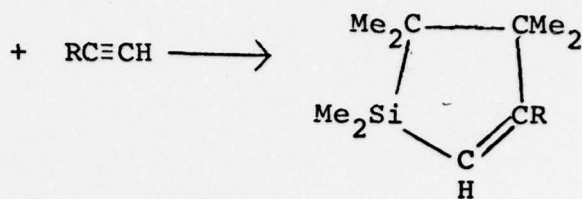
was developed in some detail. Because of its high ring strain (the C-Si-C bond angle in the SiC_2 cycle is $\sim 49^\circ$), this compound is hyper-reactive. Many reagents attack the SiC_2 ring of I under mild conditions, often exothermally, which do not react with the Si-C bonds of unstrained silacarbycles. Such attack generally results in ring cleavage or ring enlargement processes. Also of interest is the thermal decomposition of I under exceptionally mild conditions (70°C), which occurs reversibly:



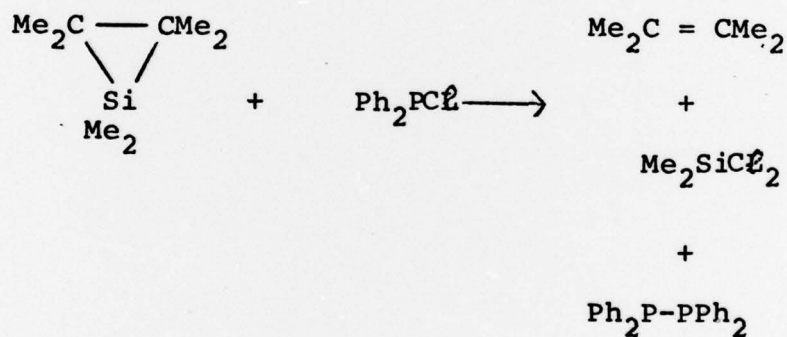
Among the areas of hexamethylsilacyclopropane chemistry which were studied are the following:

- a) Its use as a source of dimethylsilylene under exceptionally mild conditions.
- b) Insertions into its SiC_2 ring: diazomethane, dimethylsilylene, "two-atom" insertions of activated olefins, 1,3-dienes, terminal acetylenes, aldehydes and ketones, imines, dimethylsilanone, elemental sulfur.

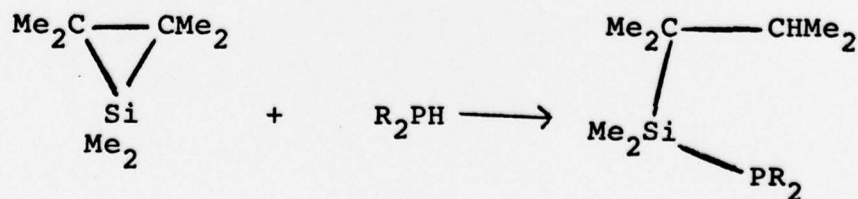




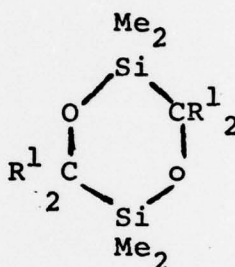
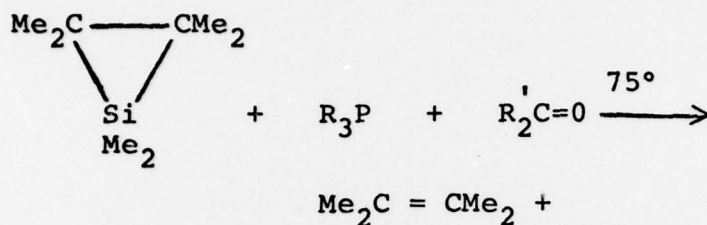
c) fragmentation reactions with chlorophosphines, e.g.,



d) ring-opening reactions with primary and secondary phosphines and a mercaptan, e.g.,

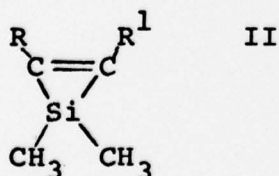


e) its use in the generation of $R_3P^+ - \bar{Si}Me_2$:



R_3P is recovered but is involved as the $R_3P^+ - \bar{Si}Me_2$ intermediate.

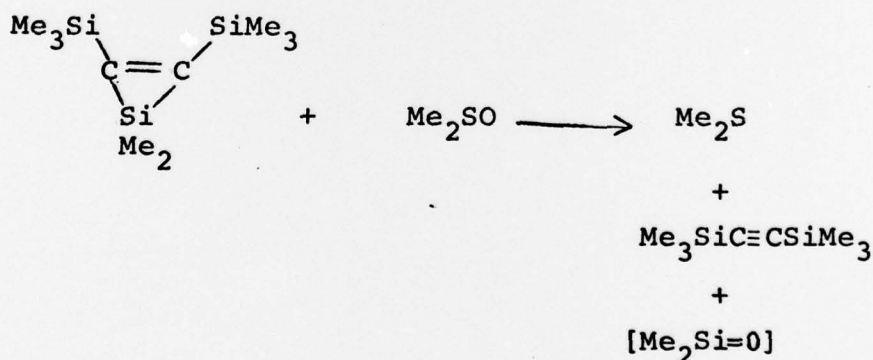
Among the more interesting of the Me_2Si transfer reactions of I are those to olefins. When the right olefins were used, these reactions gave the first silacyclopropenes ever to be isolated and characterized, compounds IIa-IIe.



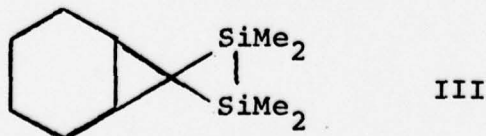
	<u>R</u>	<u>R¹</u>
a	Me_3Si	Me_3Si
b	Me_3Si	Me_3C
c	Me_3Si	CH_3
d	Me_3C	CH_3
e	Me_2HSi	Me_2HSi

Noteworthy is the unexpectedly high thermal stability and the exceptionally high reactivity of these compounds. Our attention was focussed on the chemistry of IIa. This compound is much more stable than I but at the same time is much more reactive. Among the reactions of IIa which were studied are the following:

- a) ring-opening by alcohols and water
- b) insertion reactions into its SiC_2 ring: dimethyl-silylene, "two-atom" insertion reactions of activated olefins, 1,2-dienes, terminal acetylenes, aldehydes and ketones, dimethylsilanone.
- c) Oxidation under very mild conditions by Me_2SO to give $\text{Me}_2\text{Si=O}$ as a trappable intermediate:



During the course of these studies the first disilacyclopropane, III, was generated in solution.



The silacyclopropanes and silacyclopropenes which were prepared during the course of our studies are the most reactive of all organosilicon compounds which have only Si-C bonds, and they show a particularly rich chemistry because of this. The starting materials to the silacyclopropane system are easily prepared and the ring is easily closed, so they are viable intermediates in organosilicon syntheses.

2) Halogenated Organometallics

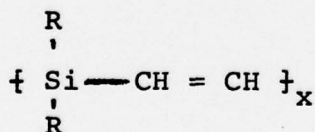
(Completion of projects begun under AF-AFOSR-72-2204)

1) Reactions of gem-dichloroallyllithium with element halides

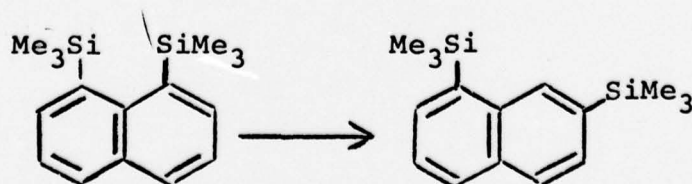
2) Synthesis of α -bromovinylsilanes

3) Miscellaneous

1) Attempted synthesis of 1,2-dilithioethylene. This was unsuccessful, but interesting chemistry. It was aimed at the production of silicon-containing polymers with potentially reactive C=C bonds of type



2) Synthesis and isomerization of 1,8-bis(tri-methylsilyl) naphthalene:



C. Publication List

Published

1. Halomethyl-Metal Compounds. LXXVIII. Cyclohexyl- and β -Phenylethyl(trihalomethyl) mercury Compounds as Dihalo-carbene Precursors at Room Temperature
J. Organometal. Chem., 104, 9 (1976)
D. Seyferth, C.K. Haas and D. Dagani
2. Halomethyl-Metal Compounds. LXXIX. The Generation of Isopropylidene Carbene by the Organomercury Route.
J. Organometal. Chem., 104, 145 (1976)
D. Seyferth and D. Dagani
3. Molecular Structure and Bonding of a Silacyclopropane, Dimethyl Dispiro[bicyclo[4.1.0]heptane-7,2'-silacyclopropane-3,7"-bicyclo[4.1.0]heptane].
J. Amer. Chem. Soc., 98, 1779 (1976).
G.L. Delker, Y. Wang, G.D. Stucky, R.L. Lambert, Jr., C.K. Haas and D. Seyferth
4. Evidence for the Generation of a Disilacyclopropane in Solution.
J. Organometal. Chem., 111, C21 (1976)
D. Seyferth and D.P. Duncan
5. 1,1,3,3-Tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-disilacyclobutane and Its 1,3-Digerma- and 1,3-Distanna Analogs: Unexpected Products from the Reaction of Bis(trimethylsilyl)bromomethyl lithium with Dimethyldihalo Derivatives of Silicon, Germanium and Tin.
J. Organometal. Chem., 116, 257 (1976)
D. Seyferth and J.L. Lefferts
6. Dimethylsilylene Transfer from Hexamethylsilirane to Olefins.
J. Organometal. Chem., 117, C51 (1976)
D. Seyferth and D.C. Annarelli
7. 1,1-Dimethyl-3,3-bis(trimethylsilyl)-1-silirene, a Stable Silacyclopropene
J. Amer. Chem. Soc., 98, 6382 (1976)
D. Seyferth, D.C. Annarelli and S.C. Vick
8. 7,7-Dimethyl-7-siladispiro [2.0.2.1]heptane Derivatives. The First Silacyclopropanes
J. Organometal. Chem., 122, 311 (1976)
D. Seyferth, R.L. Lambert, Jr. and D.C. Annarelli

9. Novel Two Atom Insertions into the Silacyclopropane and Silacyclopropene Rings
J. Organometal. Chem., 125, C5 (1977)
D. Seyferth, D.P. Duncan and S.C. Vick
10. The Preparation of a 1,2-Disilacyclobutane and a 1,2-Disilacyclobut-3-ene by Dimethylsilylene Insertion into the Silacyclopropane and Silacyclopropene Ring Systems. New Silacyclopropenes
J. Organometal. Chem., 125, C11 (1977)
D. Seyferth and S.C. Vick
11. Two Atom Insertions Into the Silacyclopropane and Silacyclopropene Rings: Mechanistic Considerations
J. Organometal. Chem., 135, C37 (1977)
D. Seyferth, S.C. Vick, M.L. Shannon, T.F.O. Lim and D.P. Duncan
12. The Reaction of gem-Dichloroallyllithium with Aldehydes, Ketones and Other Organic Substrates. An Example of Electronic Control of Regioselectivity in the Reactions of an Ambident Nucleophile
J. Amer. Chem. Soc., 99, 5317 (1977),
D. Seyferth, G.J. Murphy and B. Mauze
13. The Reactions of gem-Dichloroallyllithium with Halides of Silicon, Germanium, Tin and Mercury, and With Triphenylborane. Equilibrium vs. Kinetic Control of Regioselectivity
J. Organometal. Chem., 141, 71 (1977).
D. Seyferth, G.J. Murphy and R.A. Woodruff
14. Synthesis of 1,8-Bis(trimethylsilyl-) and 1,8-Bis(trimethylstannyl)naphthalene. The Relative Steric Effects of Carbon, Silicon and Tin in the 1,8-Bis(trimethylelement)naphthalenes
J. Organometal. Chem., 141, 173 (1977)
D. Seyferth and S.C. Vick
15. Reactions of Bis(trimethylsilyl)bromomethylolithium and Tris(trimethylsilyl)methylolithium. The Synthesis of α -Bromovinylsilanes
J. Organometal. Chem., 142, 39 (1977)
D. Seyferth, J.L. Lefferts and R.L. Lambert, Jr.
16. Organolithium Routes to 1,2-Disubstituted Ethylene Derivatives. An Attempted Synthesis of 1,2-Dilithioethylene
J. Organometal. Chem., 144, 1 (1978)
D. Seyferth and S.C. Vick

17. The Reactions of 1,1-Dimethyl-2,3-bis(trimethylsilyl)-1-silirene and Hexamethylsilirane with Dimethyl Sulfoxide. Insertion of Dimethylsilanone into the Silirene and Silirane Rings
J. Amer. Chem. Soc., 100, 1626 (1978)
D. Seyferth, T.F.O. Lim and D.P. Duncan
18. The Extraordinary Reactivity of the Ring Si-C Bonds in 1,1-Dimethyl-trans-2,3-bis(2',2'-dimethylcyclopropylidene)-1-silacyclopropane
J. Organometal. Chem., 152, 131 (1978)
D. Seyferth, C.K. Haas, R.L. Lambert, Jr. and D.C. Annarelli
19. Reactions of Hexamethylsilirane with Primary and Secondary Phosphines and with Chlorophosphines
J. Organometal. Chem., 153, 299 (1978)
W. Holderich and D. Seyferth
20. Hyper-reactive Organosilicon Compounds: Silacyclopropanes and Silacyclopropenes
Science-Ciencia, 5, 144 (1978)
D. Seyferth, R.L. Lambert, Jr., D.C. Annarelli, S.C. Vick, T.F.O. Lim, D.P. Duncan and M.L. Shannon
21. Reactions of Silacyclopropanes with 1,2-Dipolar Reagents: Diazomethane and Methylenetrimethylphosphorane
J. Organometal. Chem., 159, 137 (1978)
D. Seyferth, D.P. Duncan, H. Schmidbaur and P. Holl

D. Lectures Presented on AFOSR Research during Grant Period

Stevens Inst. of Technology
Hunter College
Williams College
Rohm & Haas Co. (Spring House, Pa.)
University of Karlsruhe
Technical University of Munich
172nd ACS National Meeting (San Francisco)
McGill University
Univ. of Oklahoma
North Texas State University
32nd Southwest Regional ACS Meeting (Fort Worth)
11th Organosilicon Symposium (Kansas City, Missouri)
Vanderbilt University
International Symposium on Strained Rings (SUNY Binghamton)
Dow Corning Corp.
West Virginia University
University of Puerto Rico
9th Caribbean Chemical Conference (San Juan, PR)

D. Lectures Presented on AFOSR Research during Grant Period (cont.)

Duke University
North Carolina State Univ. at Raleigh
Harvard University
12th Organosilicon Symposium (Ames, Iowa)
University of Bordeaux
Paul Sabatier Univ. (Toulouse)
University of Languedoc (Montpellier)
University of Marseille
1978 Gordon Research Conference on Heterocyclic Chemistry
BASF-Wyandotte Company
Fifth International Symposium on Organosilicon
Chemistry (Karlsruhe)

E. Special Recognition of AFOSR-Sponsored Research

- a) Election of principal investigator to membership
in the Deutsche Akademieder Naturforscher Leopoldina
- b) Election of principal investigator as a Fellow of
the American Association for the Advancement of Science
- c) J.L. Carrico Lecturer, North Texas State University
- d) Lyman Wood Memorial Lecturer, St. Louis University
- e) Plenary lecturer at International Symposium on
the Chemistry of Strained Rings, Ninth Caribbean
Chemical Conference, Group d'Etudes de Chimie
Organometalliques VI and Fifth International Symposium
on Organosilicon Chemistry.