

AD-A127 343

ORGANOSILICON CHEMISTRY(U) UNIVERSITY OF SOUTHERN
CALIFORNIA LOS ANGELES DEPT OF CHEMISTRY W P WEBER
DEC 82 AFOSR-TR-83-0242 AFOSR-80-0006

1/1

UNCLASSIFIED

F/G 7/3

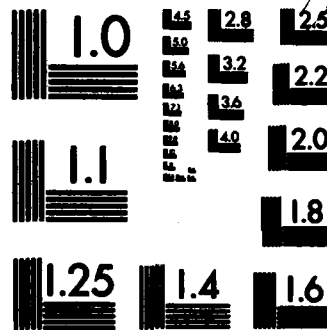
NL

END

FORMED

11

DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

4

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER AFOSR-TR- 83 - 0242'		2. GOVT ACCESSION NO. AD-A127 343	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Organosilicon Chemistry		5. TYPE OF REPORT & PERIOD COVERED Final Report	
7. AUTHOR(s) William P. Weber		6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Southern California Department of Chemistry Los Angeles, CA 90089-1062		8. CONTRACT OR GRANT NUMBER(s) AFOSR-80-0006	
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force of Scientific Research/NC Bolling AFB, DC 20332		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2303/B2	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE Dec 82	
		13. NUMBER OF PAGES 12	
		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	

16. DISTRIBUTION STATEMENT (of this Report)
Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Silylenes	Cyclic Polysilanes
Dimethylsilylene	Siloxane
Alkoxydimethylsilanes	Alkyl Lithium
Synthesis	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

SEE OTHER SIDE

83 04 20 238

DTIC ELECTE
S APR 27 1983 **D**
E

AD A127 343

DTIC FILE COPY

20. Abstract (cont)

Several new aspects of the chemistry of silylenes, divalent reactive silicon intermediates, have been explored. Insertion reactions of dimethylsilylene into O-H bonds of primary, secondary, and tertiary alcohols were studied. This provides an efficient route to alkoxydimethylsilanes. It was found that solvent significantly affects the reactivity of dimethylsilylene in such insertion reactions. The insertion of dimethylsilylene into Si-O bonds of alkoxy silanes permits the synthesis of a novel series of cyclic polysilanes. New insertion reactions of dimethylsilylene into silicon-sulfur and sulfur-sulfur bonds were discovered. In the chemistry of siloxane oligomers it was found that secondary and tertiary alkyl lithium reagents will add to the carbon-carbon bond of vinyl di- or trisiloxanes at low temperatures to yield alpha-lithio di- or trisiloxanes with no attack by the alkyl lithium reagent on the siloxane bond.



JAN 1983

FINAL SCIENTIFIC REPORT

Period Covered October 1, 1979 to December 30, 1982

Grant Number AFOSR 80-0006

Air Force Office of Scientific Research

Accession For		
NTIS GRA&I	<input checked="" type="checkbox"/>	
DTIC TAB	<input type="checkbox"/>	
Unannounced	<input type="checkbox"/>	
Justification		
By _____		
Distribution/		
Availability Codes		
Dist _____/or		
Dist _____		
A		

ORGANOSILICON CHEMISTRY

Principal Investigator: William P. Weber

Department of Chemistry

University of Southern California

University Park

Los Angeles, California 90089-1062



83 04 20 238

Approved for public release;
distribution unlimited.

ORGANOSILICON CHEMISTRY

Period Covered October 1, 1979 to December 30, 1982

Final Scientific Report

Personnel Employed at Various Times on This Project

Professor William P. Weber served as principal investigator, Professor Alan Marchand spent part of his sabbatical leave from the University of Oklahoma working with us. The following people were employed as post-doctoral research associates: Drs. Heinrich Firgo and Dongjaw Tzeng. In addition, a number of graduate students were employed as research assistants: James Chih, Dongjaw Tzeng, Kent Steele, Jeff Mullis, Samir Kazoura, Yi-Ming Pai, Lih-Jeng Juang, Mark Rubino, Steve Carr, Robert Swain, and Tai-Yin Yang Gu.

Equipment Purchased during Grant Period

None.

Publications

1. Insertion of Dimethylsilylene into O-H and N-H Single Bonds. Tai-Yin Yang Gu and William P. Weber, J. Organometal. Chem., 184, 7 (1980).
2. Mechanism of the Reactions of Dimethylsilylene with Oxetanes, Tai-Yin Yang Gu and William P. Weber, J. Am. Chem. Soc., 102, 1641 (1980).
3. Mass Spectrometry of Aryl-substituted Di- and Tri-Siloxanes, Robert E. Swain and William P. Weber, J. Organic Mass Spectrometry, 15, 304 (1980).
4. Mechanism of Reaction of Dimethylsilyl with α,β -Unsaturated Epoxides, Dongjaw Tzeng and William P. Weber, J. Am. Chem. Soc., 100, 1451 (1980).
5. Flash Vacuum Pyrolysis of 2-Methylbenzophenones and 2-Methyldiphenyl-Ketimines: Mechanism of the Vapor Phase Elbs Reaction, T.Y. Gu and William P. Weber, J. Organic Chemistry, 45, 2542 (1980).

6. Insertion Reaction of Dimethylsilylene into Si-H and Si-OR Bonds, Tai-Yin Yang Gu and William P. Weber, J. Organometal. Chem., 195, 29 (1980).
7. Solvent Modified Reactivity of Dimethylsilylene, Kent P. Steele and William P. Weber, J. Am. Chem. Soc., 102, 6095 (1980).
8. Kinetic Isotope Effects for Silylene Insertions into Oxygen-Hydrogen and Silicon-Hydrogen Bonds, Kent P. Steele and William P. Weber, Inorganic Chem., 20, 1302 (1981).
9. Regiospecific Synthesis of Allylic Dimethylmethoxysilanes, Dongjaw Tzeng and William P. Weber, J. Org. Chem., 46, 265 (1981).
10. Reactions of Allylic and Benzylic Methyl Ethers with Sodium and Trimethylchlorosilanes. Evidence for the Intermediacy of Allylic and Benzylic Radicals and Anions, Dongjaw Tzeng and William P. Weber, J. Org. Chem., 46, 693 (1981).
11. Insertion Reactions of Dimethylsilylene into Silicon-Sulfur and Sulfur-Sulfur Single Bonds, Abdelkrim Chihi and William P. Weber, J. Organometal. Chem., 210, 163 (1981).
12. Reaction of Dimethylsilylene with Allylic Methyl Sulfide, Abdelkrim Chihi and William P. Weber, Inorganic Chemistry, 20, 2822 (1981).
13. Evidence for the Intermediacy of 1,1-Dimethyl-2-phenyl-1-sila-1,3-butadiene in the Photochemistry and Pyrolysis of 1,1-Dimethyl-2-phenyl-1-sila-2-cyclobutene, Dongjaw Tzeng, Raymond H. Fong, and William P. Weber, J. Organometal. Chem., 219, 153 (1981).
14. Mechanistic Studies of the Reaction of Oxetanes with Methylthio-trimethylsilane, Heinrich Firgo and William P. Weber, J. Organometal. Chem., 222, 201 (1981).
15. Oxidation of Alkenyldisilane by *m*-Chloroperbenzoic Acid, Timothy A. Dixon, Kent P. Steele, and William P. Weber, J. Organometal. Chem., 231, 299 (1982).
16. Insertion Reactions of Dimethylsilylene: Relative Reactivity Towards Oxygen-Hydrogen, Silicon-Hydrogen, and Silicon-Alkoxy Bonds, Kent P. Steele, Dongjaw Tzeng, and William P. Weber, J. Organometal. Chem., 231, 291 (1982).
17. Mass Spectrometry of Allyloxy Di- and Trimethylsilanes, Kent P. Steele and William P. Weber, J. Organic Mass Spectrometry, 17, 222 (1982).
18. Regiospecificity of Reactions of Epoxides and Oxetanes with Trimethylsilyl Cyanide, Jeffrey C. Mullis and William P. Weber, J. Org. Chem., 47, 2873 (1982).

19. Reaction of Secondary and Tertiary Alkyl Lithium Reagents with Vinyl Di- and Trisiloxane. Synthesis of α -Silyl Silanols, Heinrich Firgo and William P. Weber, Organometallics, 1, 649 (1982).
20. Mechanism of Reactions of Oxetanes with Sodium and Dimethyldichlorosilanes, Synthesis of 1-oxa-2-silacyclopentanes, Dongjaw Tzeng and William P. Weber, J. Org. Chem., 47, 1976 (1982).
21. Selectivity in the Reactions of Alkyl Lithium Reagents with α,ω -Dichloropermethyilsiloxanes, Samih Amine Kazoura and William P. Weber, J. Organometal. Chem., in press (1983). Manuscript appended.

Seminars

Seminars were presented on work supported by the AFOSR at the following institutions:

California State University at Long Beach, Organosilicon Chemistry,

February 27, 1981.

Harvey Mudd College, Claremont, Organosilicon Chemistry, March 4, 1980.

AFOSR/AFWAR Workshop on Organosilicon Chemistry and Its Applications to

Materials. Wright-Patterson Air Force Base, Ohio, October 20, 1981.

University of California at Los Angeles, Silylene Reactivity, November

13, 1980.

Virginia Polytechnic Institute, Organosilicon Chemistry, February 3, 1981.

University of Southern California, Organosilicon Chemistry, March 13, 1981.

San Diego State University, Organosilicon Chemistry-Silylene Reactivity,

November 13, 1981.

California State University at Northridge, Organosilicon Chemistry-

Silylene Reactivity, November 18, 1981.

University of California at Santa Cruz, Organosilicon Chemistry-

Silylene Reactivity, January 4, 1982.

University of Connecticut, Organosilicon Chemistry-Silylene Reactivity,

March 9, 1982.

Meetings

- Dr. Weber attended the IUPAC Meeting on Organometallic Reagents in Organic Synthesis, Ft. Collins, Colorado, August 2-7, 1981.
- Organosilicon Symposium at Central Regional Meeting, Midland, Michigan, June 16-18, 1982.
- 19th Conference in Reaction Mechanism held at University of Utah, June 21-24, 1982.

Papers Given at Scientific Meetings

Unusual Reactions of Dichlorocarbene under Phase Transfer Catalysis Conditions, W.P. Weber, Invited talk at PTC Symposium, March 24, 1980 at the American Chemical Society National Meeting, Houston, Texas.

Mechanism of Reaction of Dimethylsilylene with α,β -Unsaturated Epoxides, D.J. Tzeng and W.P. Weber, March 24, 1980 at the American Chemical National Meeting, Houston, Texas.

Solvent Modified Reactivity of Dimethylsilylenes, K.P. Steele and W.P. Weber, March 27, 1980 at the American Chemical Society National Meeting, Houston, Texas.

Substituted and Solvent Effects on the Photooxidation of Aryl Substituted Disilanes, R.E. Swain and W.P. Weber, March 28, 1980 at the American Chemical Society National Meeting, Houston, Texas.

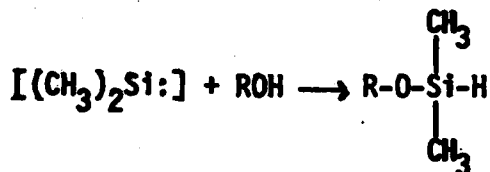
Reaction of Secondary and Tertiary Alkyl Lithium Reagents with Vinyl Di- and Trisiloxanes. Synthesis of α -Silyl Silanols, W.P. Weber and H. Firgo, March 31, 1982 at the American Chemical Society National Meeting in Las Vegas, Nevada.

**Steric Effects in the Reaction of Dimethylsilylene with Sulfoxides--
A Mechanistic Study, W.P. Weber and I. Alnaimni, American Chemical Society Regional Meeting, October 18, 1982, San Francisco, California.**

Research Accomplishments

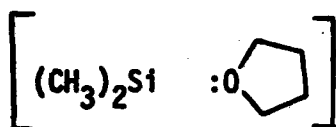
Most of our work has been published (see list of papers). Often, however, results related to a single goal or objective are the subject of more than one publication. For this reason, I will attempt to summarize the scientific success of the last three years, which has been achieved with the support of the Air Force Office of Scientific Research Contract 80-0006. I hope this will bring our work into clearer focus.

The chemistry of dimethylsilylene has been perhaps the central focus. Several new aspects of the chemistry of silylenes, divalent reactive silicon intermediates, have been explored. We have studied the insertion reaction of dimethylsilylene into O-H bonds of primary, secondary, and tertiary alcohols. This provides an efficient route to alkoxydimethylsilanes.



T.Y. Yang-Gu and W.P. Weber, *J. Organometal. Chem.*, 184, 7 (1980).

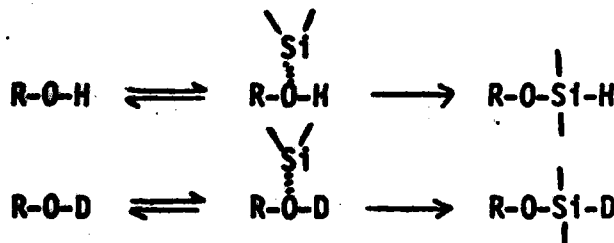
We have found that solvent significantly affects the reactivity of dimethylsilylene in such insertion reactions. Specifically, in relative reactivity studies dimethylsilylene shows no discrimination between primary and tertiary alcohols in hexane solvent but shows considerable selectivity in favor of the less hindered primary alcohols in ether solvents such as THF. This decreased reactivity and increased selectivity in ether solvents has been interpreted in terms of formation of a complex between the electrophilic silylene and the oxygen of the ether.



K.P. Steele and W.P. Weber, J. Am. Chem. Soc., 102, 6095 (1980).

Dimethylsilylene reactivity also depends on the concentration of alcohol in hydrocarbon solvents. Apparently different alcohol aggregates, monomer versus dimers for example, show different reactivity toward dimethylsilylene. K.P. Steele, D. Tzeng, and W.P. Weber, J. Organometal. Chem., 231, 291 (1982).

An effect isotope $k_H/k_D \approx 2$ on the rate silylene insertion is observed on substitution of a deuterated alcohol ROD for a normal alcohol with an O-H bond. This is consistent with a silylene complex with the oxygen of the alcohol which rearranges in the rate determining step to the insertion product.



K.P. Steele and W.P. Weber, Inorganic Chemistry, 20, 1302 (1981).

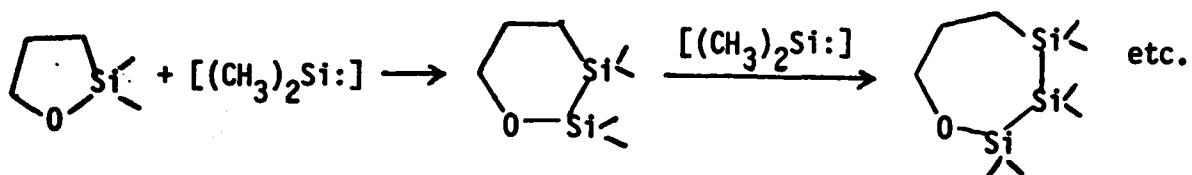
Our study of the insertion of dimethylsilylene into Si-H and Si-O bonds of alkoxy silanes is closely related to this work.

T.Y. Yang-Gu and W.P. Weber, J. Organometal. Chem., 195, 29 (1980).

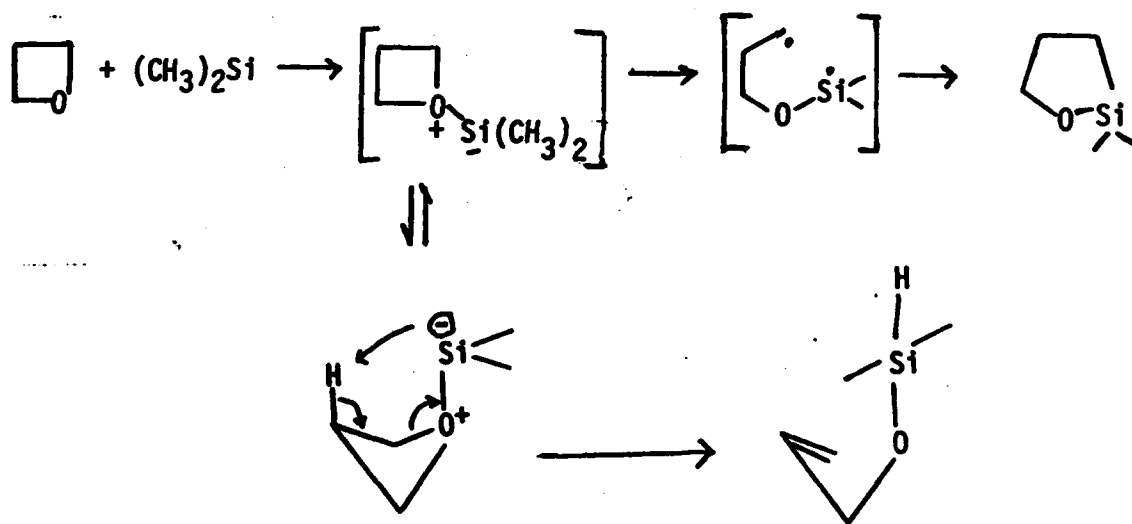
K.P. Steele and W.P. Weber, Inorganic Chemistry, 20, 1302 (1981).

K.P. Steele, D. Tzeng, and W.P. Weber, J. Organometal. Chem., 231, 291 (1982).

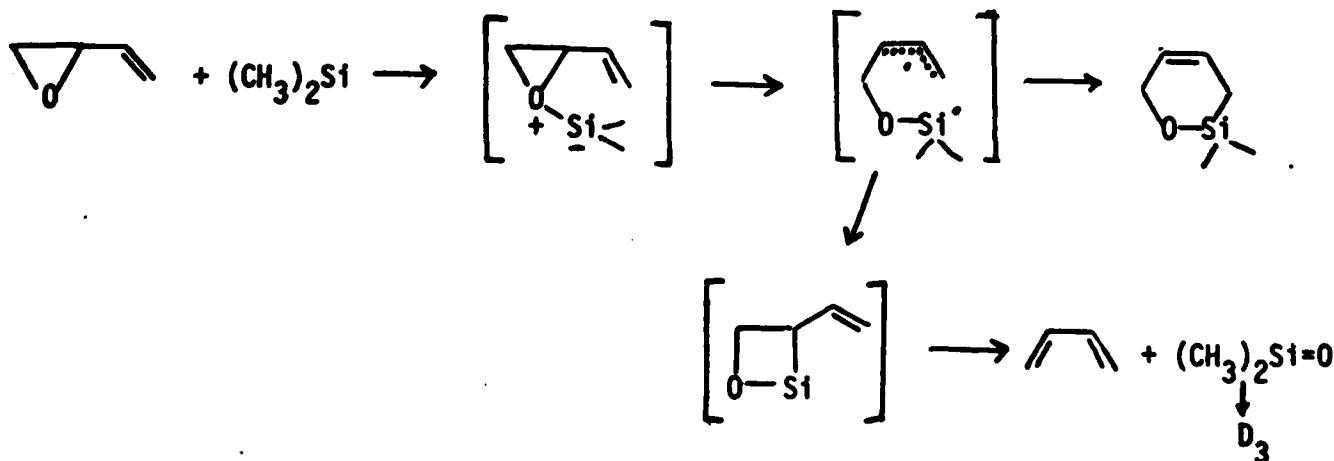
The insertion of dimethylsilylene in Si-O bonds of alkoxy-silanes permits the synthesis of a novel series of cyclic polysilanes.



A second major area of research has been the study of the reaction of dimethylsilylene with ring strained ethers, such as epoxides and oxetanes. These reactions apparently occur by initial complexation of the silylene with the ether oxygen to form a zwitterionic intermediate which rearranges to yield the final products as outlined below.

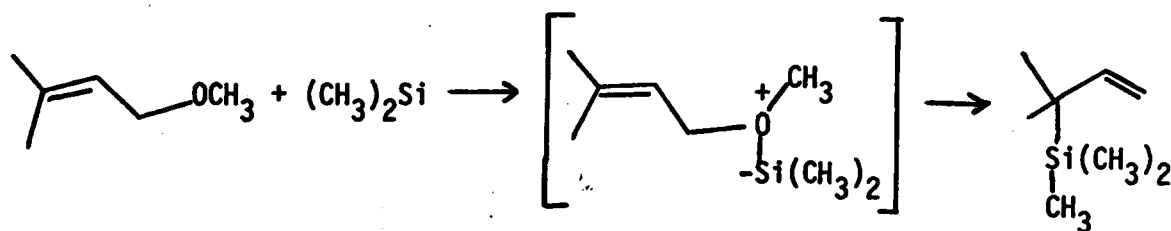


T.Y. Yang-Gu and W.P. Weber, J. Am. Chem. Soc., 102, 164 (1980).



D. Tzeng and W.P. Weber, J. Am. Chem. Soc., 102, 1451 (1980).

The regiospecific reaction of dimethylsilylene with allylic methyl ethers to yield allylic dimethylmethoxysilanes may proceed through an analogous zwitterionic intermediate which undergoes 2,3-sigmatropic rearrangement to yield products.



D. Tzeng and W.P. Weber, J. Organometal. Chem., 46, 265 (1981).

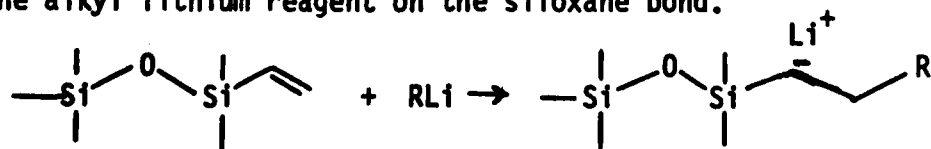
The reaction of dimethylsilylene with allylic methyl sulfides to yield allylic dimethyl thiomethylsilanes appears to proceed via a similar reaction pathway.

A. Chihi and W.P. Weber, Inorganic Chem., 20, 2822 (1981).

New insertion reactions of dimethylsilylene into silicon-sulfur and sulfur-sulfur bonds have been discovered.

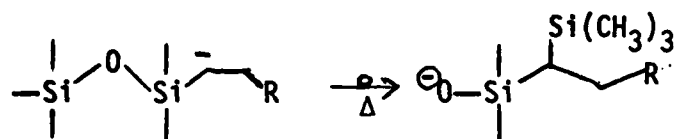
A. Chihi and W.P. Weber, J. Organometal. Chem., 210, 163 (1981).

A third area we have begun to study is the possibility of carrying out chemistry on siloxane oligomers. We have found that secondary and tertiary alkyl lithium reagents will add to the carbon-carbon bond of vinyl di- or trisiloxanes at low temperatures to yield α -lithio di- or trisiloxanes with no attack by the alkyl lithium reagent on the siloxane bond.



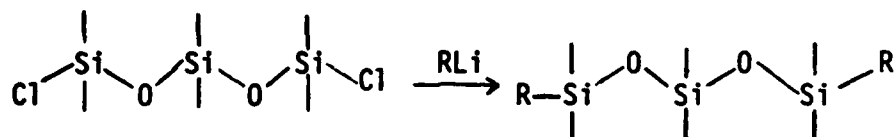
However, on warming these undergo rearrangement to yield α -silyl silanols.

H. Firgo and W.P. Weber, *Organometallics*, 1, 649 (1983).



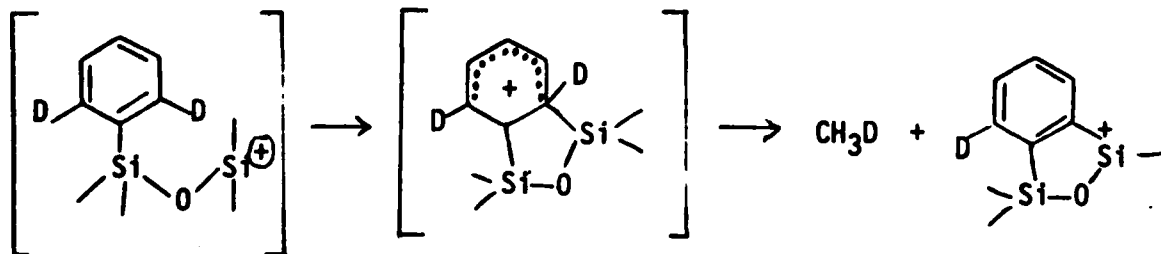
This provides a novel route to such sterically hindered silanols. Of interest, these are quite stable to dehydration.

We have also found that alkyl lithium reagents react selectively with the Si-Cl bonds of α,ω -dichloro permethylsiloxanes with no cleavage of Si-O bonds to yield α,ω -dialkyl permethylsiloxanes.



S.A. Kazoura and W.P. Weber, *J. Organometal. Chem.*, in press (1983).

A fourth area, is the mass spectrometry of organosilicon compounds. Mass spectral fragmentation pathways and rearrangements of aryl substituted di- and trisiloxanes as well as those of allyloxy di- and trimethylsilanes have been studied.



R.E. Swain and W.P. Weber, *J. Organic Mass Spectrometry*, 15, 304 (1980).

K.P. Steele and W.P. Weber, *J. Organic Mass Spectrometry*, 17, 222 (1982).

We have had significant results on a number of smaller projects which have been reported in individual publications which are listed.