CHEMISTRY OF NEW SILICON CONTAINING POLYMERS TRIPLY BONDED SILICON INTERN (U) UNIVERSITY OF SOUTHERN CALIFORNIA LOS ANGELES DEPT OF CHEM. W P WEBER UNCLASSIFIED DEC 85 AFOSR-TR-86-0131 AFOSR-82-0333
A method to generate $[\text{O} \equiv \text{Si} = \text{O}]$ in the gas phase by flash vacuum pyrolysis (FVP) of 2,3:4,7 diepoxy 5-silaspiro[4.4]nonane was developed. Reactive $\pi$-bonded silicon nitrogen double bonds intermediates were generated by FVP of dimethoxymethylsilyl-bis(trimethylsilyl) amine. Photolysis of dodecamethylcyclohexasilane yields both dimethylsilylene and methylsilene. The oxidation of dimethylsilylene with sulfoxides yields silanones.

**Chemistry of New Silicon Containing Polymers Triply Bonded Silicon Intermediates**

**Silanes, Photolysis, Silanones**
Sterically hindered t-butyldimethyl-silanedi permits control in the silyl hydroformylation reaction. FINAL REPORT: Chemistry of New Silicon Containing Polymers Triply Bonded Silicon Intermediates. AFOSR-82-0333.
PROGRESS REPORT #6 / FINAL REPORT

Period Covered: 31 August 1982 to 31 October 1985

Grant Number: AFOSR 82-0333

Title: Chemistry of New Silicon Containing Polymers
Triply Bonded Silicon Intermediates

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COMPLETED PROJECT SUMMARY

1. TITLE: Chemistry of New Silicon Containing Polymers Triply Bonded Silicon Intermediates

2. PRINCIPAL INVESTIGATOR: Professor William P. Weber

3. INCLUSIVE DATES: August 31, 1982 to October 31, 1985

4. GRANT NUMBER: AFOSR 82-0333

5. COSTS AND FY SOURCE:

6. SENIOR RESEARCH PERSONNEL:

Professor W. P. Weber, principal investigator worked on this contract ten percent of his time during the academic years 8-31-1982 to 10-31-1985 and one hundred percent of his time for two months each Summer 1983, 1984, and 1985.

Professor K. L. Servis worked one month during the Summer 1984 as a consultant on $^{29}\text{Si}$ NMR.

Professor Kyung Tae Kang, on sabbatical leave from the Department of Chemistry of Pusan University, Pusan, South Korea, has worked on this contract 1-15-1985 to 10-31-1985.

POSTDOCTORAL RESEARCH ASSOCIATES:

Dr. S. Kazoura, 9-1-1983 to 5-31-1984. Dr. Kazoura received his Ph.D. from USC under my supervision.

Dr. Y. M. Pai, 2-1-1985 to 10-31-1985. Dr. Pai received his Ph.D. from USC under my supervision.
Dr. E. Wanek, 3-3-1983 to 6-30-1984. Dr. Wanek is a graduate of the Technical University, Graz, Austria.

Dr. A. Bacereido, 8-1-1985 to 10-31-1985. Dr. Bacereido is a graduate of the Universite Paul Sabatier, Toulouse, France.

7. JUNIOR RESEARCH PERSONNEL:

TECHNICAL ASSISTANTS:

F. Berchier, 11-15-1984 to 7-31-1985. Ms. Berchier is a graduate of the University of Lausanne, Lausanne, Switzerland.

GRADUATE RESEARCH ASSISTANTS:

S. Kazoura, 8-31-1982 to 7-31-1983
J. Mullis, 8-31-1982 to 8-31-1983, and 6-1-1984 to 8
Y. M. Pai, 8-31-1982 to 8-31-1983, and 6-1-1984 to 12-
S. Hedayati, 6-1-1983 to 8-31-1983.
C. P. Kuan, 6-1-1985 to 8-31-1985.

UNDERGRADUATE RESEARCH ASSISTANTS:

D. Dowd, 5-30-1984 to 7-25-1984
C. Smith, 5-31-1984 to 6-27-1984
8. PUBLICATIONS:


8. Thermolysls of 6-Oxa-3-Sila Bicyclo[3,1,0]hexanes: A New Convenient Route to Silicon-Oxygen $\pi$-Bonded Species, G. Manuel, G. Bertrand,


16. Silicon Dioxide [$O=Si=O$]: New Routes to Cyclic Spirosiloxanes; Chemical Vapor Deposition of SiO$_2$, J. Wiley & Sons, in press;


9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A method to generate \([\text{O} = \text{Si} = \text{O}]\) in the gas phase by flash vacuum pyrolysis of 2,3:4,7 diepoxy 5-silaspiro [4.4] nonane (I) has been developed. Co-pyrolysis of I and cyclic siloxanes permits the facile synthesis of spirosiloxanes.

\[
\begin{align*}
2 \quad \text{SiO} & \quad + \quad [\text{O} = \text{Si} = \text{O}] \\
\quad \text{Si} & \quad \text{Si} \\
\end{align*}
\]

FVP of I alone yields a high surface area (300 \(\text{M}^2/\text{g}\)) silica which has been further characterized by scanning and transmission electron microscopy. See publications 8, 11, 16 and 21.

Reactive \(\pi\)-bonded silicon nitrogen double bonds intermediates have been generated by FVP of dimethoxymethylsilyl-bis(trimethylsilyl)amine. These intermediates have been reacted with silicon-oxygen single bonds of cyclic siloxanes to yield new heterocycles.

\[
\begin{align*}
\text{(CH}_3\text{O)}_2\text{Si} - \text{N}[\text{Si(CH}_3\text{)}_3]_2 & \quad \xrightarrow{\Delta} \quad \text{(CH}_3\text{)}_3\text{SiOCH}_3 + \left[\text{CH}_3\text{O} \quad \text{Si} = \text{N} \quad \text{Si(CH}_3\text{)}_3\right] \\
\quad \text{Si} & \quad \text{Si} \\
\end{align*}
\]

See publications 5, 6 and 11.
We have prepared 1,3-bis(silyl)adamantanes as outlined below.

\[
\begin{align*}
\text{Cl} & \quad \text{Pd/C} \quad \text{Cl} \\
\text{Cl} & \quad \text{Li}^+ \\
\text{Si(CH}_3)_2O & \quad \text{H}_2\text{O} \\
\text{N}_2\text{HCO}_3
\end{align*}
\]

See publications 7 and 15.

We have chlorinated \(\alpha,\omega\text{-bis(trimethylsiloxy)polymethylhydrosiloxane}\) polymers to yield \(\alpha,\omega\text{-bis(trimethylsiloxy)polymethylchlorosiloxanes}\). These reactive polymers have been reacted with alkyl lithium reagents to yield \(\alpha,\omega\text{-bis(trimethylsiloxy) polyalkylmethylsiloxanes}\).

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{SiO} & \quad \text{Si}(\text{CH}_3)_3 \\
\text{CH}_3\text{Cl} & \quad \text{Pd/C} \\
\text{Si} & \quad \text{RLi}
\end{align*}
\]

See publications 2 and 14.

We have found that photolysis of dodecamethylcyclohexasilane (II) yields both dimethylsilylene and methylsilene. The ultraviolet spectra of dimethylsilylene in solution and the kinetics of its reaction with various substrates have been determined. See publications 9 and 10.
The oxidation of dimethylsilylene with sulfoxides yields silanones. The reaction of m-chloroperbenzoic with II selectively oxidizes Si-Si bonds adjacent to Si-O bonds.

See publications 1 and 3.

We have found that the use of the sterically hindered t-butyldimethylsilane permits control in the silyl hydroformylation reaction.

See publications 18 and 19.

We have utilized $^{29}\text{Si}$ NMR to explore $T_1$ (relaxation times) of polymethylhydrosiloxane polymers. See publication 12.
Deuterium isotope effects on $^{29}$Si chemical shifts have been observed for the first time. See publication 20.
END

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