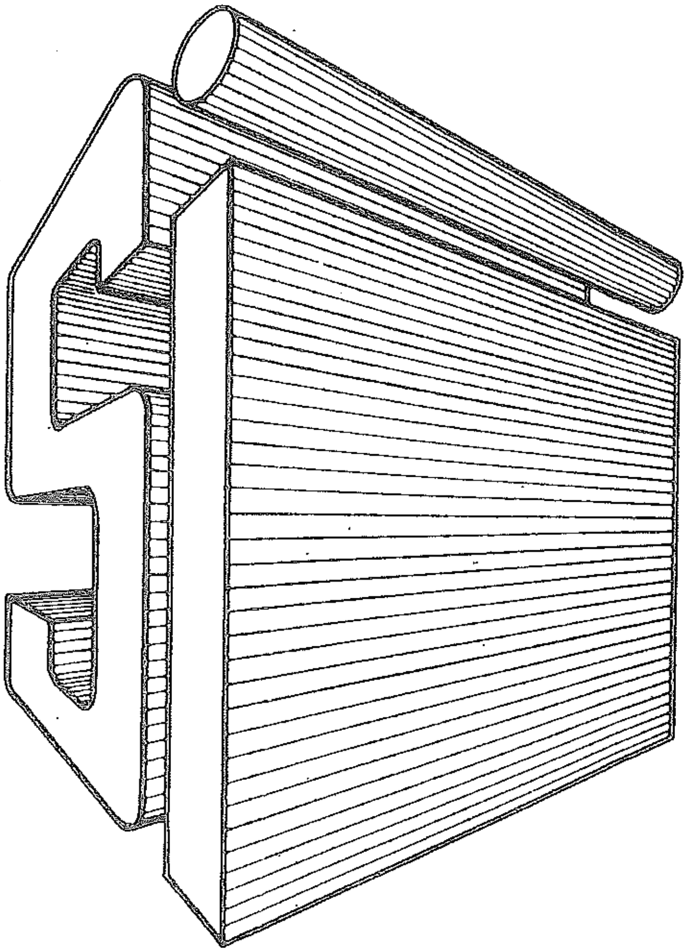

XXII

ORGANOSILICON SYMPOSIUM

April 7-8, 1989

PENN TOWER HOTEL

XXII Organosilicon Symposium
April 7-8, 1989

ORGANIZERS: BARRY ARKLES, JERRY LARSON
PETRARCH SYSTEMS

IN MEMORIAM

EUGENE R. COREY

A SCIENTIST, AN EDUCATOR, A FRIEND....

Hüls America, Inc./Petrarch Systems Silanes and Silicones is pleased to host the XXII Organosilicon Symposium with the special support and cooperation of The DuPont Company. Additional financial support was provided to the Symposium by the organizations listed below. Without the support received through these generous contributions this Symposium would not have been possible.

Dow Corning Corporation

The DuPont Company

General Electric Corporation

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Loctite Corporation

Mobay Chemicals

PCR Corporation

Union Carbide Corporation

Wacker Silicone Corporation

PROGRAM

All meetings will be held in the Ball Room area on the second floor of the Penn Tower Hotel.

THURSDAY APRIL 6th

5:30-7:00 REGISTRATION AND COCKTAIL HOUR

FRIDAY APRIL 7th

8:15-8:30 OPENING REMARKS

SESSION A (Moderator Barry Arkles)

8:30-9:15 **PLENARY LECTURE 1** "Structure - Transport Property Relationships in Organic Modified Silicone and Silicone Modified Organic Polymers." Chi-Long Lee (Dow Corning).

9:15-9:35 **A 1** "Telechelic Norbornene Silicone Elastomers Cured by the Thiolene Reaction" <u>Steven T. Nakos</u>, Anthony F. Jacobine.

9:35-9:55 **A 2** "Synthetic Routes to Silicone Polycarbonate Copolymers from Aryl Terminated Siloxane Precursors" <u>P. J. McDermott</u>, T. E. Krafft, J D. Rich.

9:55-10:15 **A 3** "New Polysiloxanes with a Carbonate Group in the Side Chains: Synthesis and Properties" G. de Marignan, D. Teyssie, J. M. Yu, <u>S. Boileau</u>.

10:15-10:45	**BREAK**
10:45-11:05	**A 4** "Synthesis of Organopolysilanes Using Crown Ethers" Masaie Fujino, Hiroaki Isaka, Nobuo Matsumoto.
11:05-11:25	**A 5** "The Photophysics and Photochemistry of Polysilanes" J. M. Zeigler, R. Hochstrasser, J. R. G. Thorne, P. Ohsako.
11:25-12:10	**PLENARY LECTURE 2** "Organosilicon Chemistry. A Tool for Control of Macromolecular Synthesis" Dotsevi Y. Sogah (DuPont Co.).
12:10-2:00	**LUNCH**

SESSION B (moderator C. Blankenship)

2:00-2:45	**PLENARY LECTURE 3** "Trialkylsilyl Subsituted Control of Chemo-, Regio- and Stereoselectivity in Cobalt-Mediated Total Syntheses of Natural and Unnatural Products" K. Peter C. Vollhardt.
2:45-3:05	**B 1** "The Conversion of Acylsilanes into Chiral (Non-Silicon) Containing) Alcohols" John D. Buynak, Byron Strickland.
3:05-3:25	**B 2** "Silacyclohexanones as Templates for the Synthesis of Chiral Acyclic Synthons" John A. Soderquist, Alvin Negron.
3:25-3:45	**B 3** "Carbocyclization Procedures Featuring Organosilicon Chemistry" George Majetich, Clay Ringold, Derric Lowery, Vikram Khetani.
3:45-4:15	**BREAK**
4:15-4:35	**B 4** "Silicon-Promoted Ring Contractions and Total Synthesis of (-)-Solavetivone" Reuben J-R. Hwu, John M. Wetzel.

4:35-4:55 **B 5** "Organosilicon Aminoacid Building Blocks in Peptide Design" Stephen R. Wilson, Martin J. DiGrandi, Gong-Hua Pan.

4:55-5:15 **B 6** "A Systematic Study of the Stability/Reactivity of Silyl Ethers to Various Reagents" Ram Chawla, Craig Polsz Gerald L. Larson.

SESSION C (moderator Robert A. Smith)

2:00-2:45 **PLENARY LECTURE 4** "Ultraviolet Curable Epoxysilicone and Epoxysiloxane Systems" Richard P. Eckberg (General Electric).

2:45-3:05 **C 1** "The Dimethylzirconocene Catalyzed Polymerization of Alkyl Silanes" William H. Campbell, Terrence K. Hilty.

3:05-3:25 **C 2** "Polysilane Substituted with Phenol Moiety. UV Absorption and NMR Spectroscopy in Polar Solvents" Shuzi Hayase, Rumiko Horiguchi, Yasunobu Onishi, Toru Ushirogouchi.

3:25-3:45 **C 3** "Synthesis, Properties and Photochemistry of Amorphous Alkylsilicon Network Polymers" T. W. Weidman, W. L. Wilson, E. W. Kwock, P. A. Bianconi.

3:45-4:15 **BREAK**

4:15-4:35 **C 4** "Vinylic Polysilanes - A Perspective" C. L. Schilling, Jr.

4:35-4:55 **C 5** "Trimethylsilyl Triflate as Initiator for the Cationic Polymerization of Hetercyclics and Alkenes. Model Reactions for the Cationic Grafting from Polysilanes" Jeffrey S. Hrkach and Krzysztof Matyjaszewski.

4:55-5:40 **PLENARY LECTURE 5** "Liquid, Crosslinked and Surface-Bonded Silicone Stationary Phases for Gas Chromatography" Harald Rotzsche (DDR).

5:45-5:55 **SPECIAL FEATURE** "Silicone Formulation Strategies for Prosthetics Medical Sculpture" Robert Erb, Doretta Erb, Christine Jansen and Harold Heller.

6:00-8:30 **POSTER SESSION** (moderator Gerald L. Larson)

8:00-8:30 **MEETING TO ORGANIZE FUTURE MEETINGS**

SATURDAY APRIL 8th

SESSION D (moderator Frank K. Cartledge)

8:30-9:15 **PLENARY LECTURE 6** "The Synthesis, Structure and NMR Spectral Studies on Organosilanes and Silylmetal Derivatives" John P. Oliver, Jeff Kampf, Srini DeMel, Greg Hendershot, and Mike Sierra.

9:15-9:35 **D 1** "Mechanism and Dynamics of Rearrangements Involving Organosilicenium Ions in the Gas Phase" K. A. Reuter and D. B. Jacobson.

9:35-9:55 **D 2** "Electron Beam Sensitivities of Some Poly-1-Sila- and -1,3-Disilacyclobutanes" E. Babich, J. Paraszczak, S. Rishton, N. Chou, and H. Linde.

9:55-10:15 **D 3** "Regioselective One- and Two-Bond Cleavages in the Solution Phase 185 NM Photochemistry of (E) and (Z)-1,1,2,3-Tetramethylsilacyclobutane" Mark G. Steinmetz and Hao Bai.

10:15-10:45 **BREAK**

10:45-11:05 **D 4** "Determination of the Absolute Rate Constants for the Gas-Phase Reactions of Cl2Si and Br2Si with Various Substrates" V. Sandhu, O. P. Strausz, and T. N. Bell.

11:05-11:25 **D 5** "Relative Reactivities in Anionic Attack on Tetravalent Silicon" Larry W. Burggraf and Larry P. Davis.

11:25-11:45 **D 6** "Excited States of Oligosilanes and Polysilanes" V. Balaji and J. Michl.

11:45-12:30 **PLENARY LECTURE 7** "Hydrosilylation Catalyzed by Transition Metal Complexes" Iwao Ojima.

SESSION E (moderator Walter Hertler)

9:15-9:35 **E 1** "Chemical and Spectroscopic Characterization of Trialkylsilylcuprates Derived from CuCN and CuBr DMS" Sunaina Sharma and Allan C. Oehlschlager.

9:35-9:55 **E 2** "Rhodium Catalyzed Hydrosilylation of Allyl Methacrylate to Prepare Dimethylketene Bis-(Trimethylsilyl) Acetal and the Mechanism Thereof" Anthony Revis.

9:55-10:15 **E 3** "Synthesis and Characterization of A Molybdenum Disilene Complex" Donald H. Berry, Jean Chey.

10:15-10:45 **BREAK**

10:45-11:05 **E 4** "New Reformations and Migrations of OligosilylIron Complexes" Keith Pannell, J. Rozell, L. Wang and J. Cervantes.

11:05-11:25 **E 5** "Polysilazanes and Silicon Nitride Processing" S. T. Schwab, R. C. Graef and C. R. Blanchard-Ardid.

11:25-11:45 **E 6** "Phenyl(trimethylsilyl)germanes as Photochemical Precursors of Germylenes. New Insight into the Mechanisms of Addition of Germylenes to Dienes" K. L. Bobbitt and P. P. Gaspar.

11:45-12:05	**E 7**	"Silanamidines and Related Compounds" G. E. Underiner, R. West.
12:05-12:25	**E 8**	"Photolysis of Vinyltris(trimethylsilyl)silane" S. Zhang, R. T. Conlin.
12:30-2:00	**LUNCH**	

SESSION F (moderator Cecil Frye)

2:00-2:45	**PLENARY LECTURE 8**	"Gas Phase Ion Chemistry of Organosilicon Compounds" R. Damrauer.
2:45-3:05	**F 1**	"Theoretical Studies of Highly Strained Rings" Mark S. Gordon and J. A. Boatz.
3:05-3:25	**F 2**	"Why Silaketones are Colored" Roger S. Grev and Henry F. Schaefer.
3:25-3:45	**F 3**	"Thermal Isomerizations of Silylallenes and Silylheteroallenes" T. J. Barton, G. R. Magrum and B. L. Groh.
3:45-4:05	**F 4**	"The Thermal Rearrangements of Two Silacyclobutadienes" Mark J. Fink, Dhananjay B. Puranik, and M. Pontier Johnson.
4:05-4:35	**BREAK**	
4:35-4:55	**F 5**	"Hetercycles with Silicon Nitrogen Bonds...Silenoids or Silene Precursors?" Paul R. Jones and S-N. Uang.
4:55-5:15	**F 6**	"Silaaziridines and 1-Sila-3-azacyclobutanes from the Reaction of Silenes with Isonitriles" A. G. Brook, A. K. Saxena, Y. K. Kong and J. F. Sawyer.

5:15-5:35	**F 7**	"Novel Living Anionic Polymerization of Masked Disilenes to Polysilylene High Polymers and Block Copolymers" Hideki Sakurai, Kenkichi Sakamoto, Kuninori Obata, Hiroki Hirata, Masahi Nakajima, and Masaru Yoshida.
5:35-5:55	**F 8**	"Synthesis and Characterization of an Unusual Disiladiphosphane with Butterfly Structure: 1,1,3,3-Tetramesityl-1,3,2,4-Disiladiphosphabicyclo-[1.1.0]butane" Matthias Driess and Robert West.
5:55-6:15	**F 9**	"Disilenes: New Structures, New Reactions" Robert West, Brian D. Shepherd and Gregory R. Gillette.

6:15-7:30 **COCKTAIL HOUR**

7:30-10:00 **BANQUET**

Dr. Isaac Asimov will speak on "Carbon and Silicon in Cooperation"

Robins Bookstore of Philadelphia has agreed to have several copies of some of Dr. Asimov's more recent books available for purchase between the hours of 4:00 and 7:30 Saturday afternoon. They will be located outside the Ball Room. Dr. Asimov has kindly agreed to autograph books after his talk.

BACKGROUND DR. ISAAC ASIMOV

Author, Biochemist Dr. Isaac Asimov was born in Russia and came to the United States in 1923. He was naturalized in 1928.

He received his B.S. from Columbia University in 1939, his M.A. in 1941, and his Ph.D. in 1949 all from Columbia and all in chemistry.

Dr. Asimov has been associated with Boston University School of Medicine since 1949 where he is Professor of Biochemistry.

He is the recipient of many awards including, the American Chemist Society Award in 1965 and the AAAS Westinghouse Science Award in 1967.

He is the author of more than 410 books and many articles printed in national publications.

At 7 years of age Dr. Asimov taught his 5-year old sister to read. He has been fortunate to be born with a restless and efficient brain with a capacity for clear thought and an ability to put that thought into words.

He is the beneficiary of a lucky break in the genetic sweepstakes, Dr. Asimov states.

SPECIAL FEATURE

SILICONE FORMULATION STRATEGIES FOR PROSTHETICS MEDICAL SCULPTURE

Robert Erb, Doretta Erb, Christine Jansen and Harold Heller

Franklin Research Institute
A Division of the Franklin Institute
Physical and Life Science Department
Philadelphia, PA

Dr. Robert Erb leads an interdisciplinary team consisting of a physiologist, an artist and an engineer in the development of prosthetic devices, human simulators and medical models. They employ a full spectrum of chemical, sculptural, visual and mechanical techniques in their efforts. Immediately following a short introduction and overview of these interesting applications of organosilicon chemistry by Dr. Erb at the main session, he will hold a demonstration in the poster area during the poster session.

PLENARY LECTURES

We are pleased to have a distinguished line up of plenary lecturers for the XXII Organosilicon Symposium with talks concerning the chemistry of polysiloxanes, the use of organosilanes in the synthesis of polymers, applications to gas chromatography, hydrosilylation, structural features, gas phase chemistry and applications to the synthesis of complex molecules. We are thankful to the plenary lecturers for their important participation.

Plenary Lecture-1	Chi-Long Lee (Dow Corning) "Structure - Transport Property Relationships in Organic Modified Silicone and Silicone Modified Organic Polymers."
Plenary Lecture-2	Dotsevi Y. Sogah (DuPont Co.) "Organosilicon Chemistry. A Tool for Control of Macomolecular Synthesis."
Plenary Lecture-3	K. Peter C. Vollhardt (U. C. Berkeley) "Trialkylsilyl Substituted Control of Chemo-, Regio- and Stereoselectivity in Cobalt-Mediated Total Syntheses of Natural and Unnatural Products."
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Plenary Lecture-5	Harald Rotzsche (VEB Chemiewerk Nünchritz) "Liquid, Crosslinked and Surface-Bonded Silicone Stationary Phases for Gas Chromatography."
Plenary Lecture-6	John P. Oliver (Wayne State University) "The Synthesis, Structure and NMR Spectral Studies on Organosilanes and Silylmetal Derivatives."
Plenary Lecture-7	Iwao Ojima (State University of New York at Stony Brook) "Hydrosilylation Catalyzed by Transition Metal Complexes."
Plenary Lecture-8	Robert Damrauer (U. of Colorado-Denver) "Gas Phase Ion Chemistry of Organosilicon Compounds."

PLENARY LECTURE 1

STRUCTURE - TRANSPORT PROPERTTIES RELATIONSHIPS IN ORGANIC MODIFIED SILICONE AND SILICONE MODIFIED ORGANIC POLYMERS

BY

CHI-LONG LEE

SILICONE RESEARCH DEPARTMENT
DOW CORNING CORPORATION
MIDLAND, MICHIGAN 48686-0994

The structure of silicone and organic polymers can be modified with organics or silicones respectively to change their physical properties to meet specific requirements for the desired applications. The modification of polymer structure can be achieved by block copolymerization, grafting or polyblend technique. This paper deals with the effect of the structure of organic modified silicone and silicone modified organic polymers on the transport properties, namely (a) gas permeability, (b) drug permeability, (c) ionic conductivity, and (d) release of volatile compounds such as air fragnances or pheromones.

Quantitative relationships between the polymer structure and above transport properties will be reviewed for the following classes of polymers; (1) poly dimethylsiloxane modified by replacing one of the methyl group with an aryl or an alkyl side chain (R), i.e., $(MeRSiO)_x$, (2) polydimethylsiloxane modified by replacing every other oxygen atom in the polymer backbone with an arylene or an alkylene segment (Z), i.e., $(Me_2SiOMe_2SiZ)_x$, (3) polydimethylsiloxane grafted with polyethyleneoxide side chain (G) , i.e., $[(Me_2SiO)_x MeGSiO]_y$, (4) poly-dimethylsiloxane-polyethyleneoxide-polymethylmethacrylate block copolymers, (5) polydimethylsiloxane-polyurethane block copolymers, (6) polydimethylsiloxane-poly-alpha-methylstyrene block copolymers, (7) trimethylsilyl substituted polyacetylene, $(MeC{=}CSiMe_3)_x$, and polyethylene, $(CH_2CHSiMe_3)_x$, (8) silicone modified polystyrenes, (CH_2CH--$Z)_x$, where Z is a silicon containing substituent, and (9) polydimethylsiloxane-polyethylene polyblends.

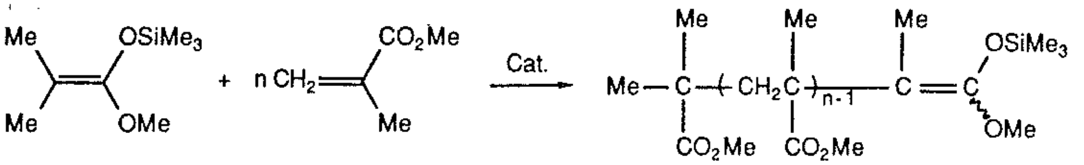
PLENARY LECTURE 2

ORGANOSILICON CHEMISTRY. A TOOL FOR CONTROLLED MACROMOLECULAR SYNTHESIS

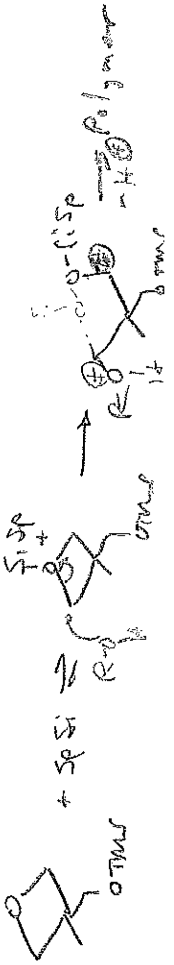
Dotsevi Y. Sogah
Central Research and Development Department
E. I. du Pont de Nemours and Company, Inc.
Experimental Station, P. O. Box 80328
Wilmington, DE 19880-0328

Cationic Poly

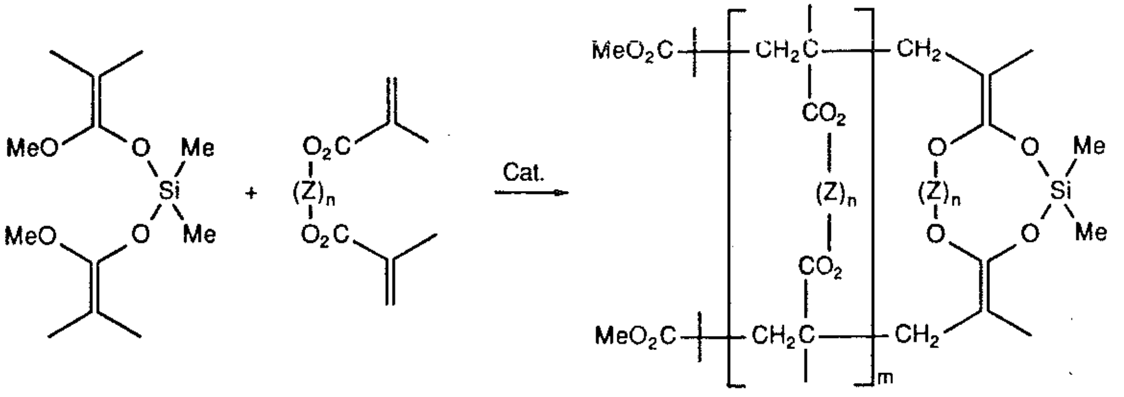
A current trend in polymer chemistry is to control the architecture of polymers from common monomers. Group Transfer Polymerization (GTP) has been shown to be a living polymerization suitable for preparation of acrylic polymers of well-controlled architecture. The reaction, catalyzed by anions and Lewis acids, involves the transfer of a silyl group from the initiator (a silyl ketene acetal) to the incoming monomer (Equation 1).



(1)



In a related process, termed Aldol Group Transfer Polymerization, aldehydes initiate polymerization of silyl vinyl ethers to give poly(vinyl alcohol). This new method facilitates control of hydrophilicity of copolymers. In both types of GTP, a reactive functional group originally present in the initiator is regenerated in the terminal position of the chain upon reaction with monomer in such a fashion that undesirable chain transfer and termination reactions are minimized. A key advantage of group transfer polymerizations is that they operate above room temperature, thus enabling us to control molecular weight and polydispersity, as well as monomer sequences under industrially significant conditions. Thus, block, star, graft and random copolymers have been readily prepared, and incorporation of various functional groups is facile. In our continued investigation of GTP we found that, by a rational design of initiators, ladder polymers of suitable acrylic monomers could be prepared (Equation 2).

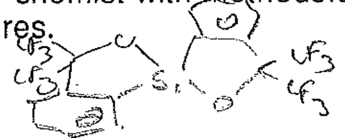


(2)

$\left(\begin{array}{l} Z = -CH_2 \\ n = 2-7 \end{array}\right)$

H$_2$O-Sol Polymers P

GTP, therefore, provides the synthetic polymer chemist with methodologies for macromolecular engineering of unique structures.



Lewis Acid

DYS/ta
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PLENARY LECTURE 3

Trialkylsilyl Substituent Control of Chemo-, Regio-, and Stereoselectivity in Cobalt-Mediated Total Syntheses of Natural and Unnatural Products.

K. PETER C. VOLLHARDT, Department of Chemistry, University of California at Berkeley, Berkeley, California 94720.

Recent advances in the use of cobalt catalysts for the construction of complex polycycles by the cyclization of unsaturated precursors will be described. Particular emphasis will be placed on approaches to the natural products illudol, stemodin, and lysergic acid, as well as the theoretically interesting linear and angular phenylenes. The pivotal role of trialkylsilyl substituents attached to alkynyl groups in determining the chemo-, regio-, and stereoselectivity of these reactions will be stressed. In addition, the utility of these substituents as protecting and masked functional groups in both starting materials and cobalt-complexed or uncomplexed products will be discussed, in conjunction with a mechanistic rationale for the strong steric and electronic influence of the silyl moiety on the outcome of the reported transformations.

PLENARY LECTURE 4

ULTRAVIOLET CURABLE EPOXYSILICONE AND EPOXYSILOXANE SYSTEMS

Richard P. Eckberg

General Electric Company
Silicone Products Division
Waterford, NY 12188

ABSTRACT

Organofunctional Silicon-containing polymers and oligomers based on cycloaliphatic epoxy moieties linked to siloxane structures are efficiently cured (crosslinked) when irradiated with ultraviolet light in the presence of certain iodonium photocatalysts. Synthesis of epoxysilicones is accomplished by hydrosilation addition of olefin epoxy monomers to preformed methylhydrogen siloxanes. Cured films of these materials are release coatings finding application in the tag and label industry. Diepoxy-stopped silicon- and siloxane- monomers display remarkable uv-cure speed and completeness of cure compared to analogous organic diepoxides, both when cured alone and with hydroxy-containing materials. The novel silicon-based uv-curable monomers and oligomers are potentially important new compositions for the radiation cure industry.

LIQUID, CROSSLINKED AND SURFACE-BONDED SILICONE STATIONARY PHASES FOR GAS CHROMATOGRAPHY

Harald Rotzsche

Analytical Department, VEB Chemical Works Nünchritz
8122 Radebeul/Dresden, G.D.R.

In the last years, basic investigation on coating, bonding and cross-linking of silicone stationary phases on the inner walls of glass lined and fused silica capillary columns have been carried out by several chromatogrpahic research teams, in order to improve the performance of chromatogrpahic columns. The results, which will be summarized in this paper, are believed to be of general importance for wetting and coating silica surfaces by poly(organosiloxanes) and for substrate pretreatment and coat behavior at thermal strain.

After a survey of methods for the characterization of silica surfaces and the conditions for the wettability, the deactivation of silanol sites by high temperature silylation and the wettability of silylated silica surfaces will be discussed. The stability of coherent poly(diorganosiloxane) films on silica surfaces which, if thermally strained leaves much to be desired, can be much improved by cross-linking and bonding reactions. If the organosiloxane is weakly cross-linked and chemically bonded to the substrate, the rearrangement of the siloxane film, i.e. the decrease of the interfacial energy at the liquid/gas interface and hence the danger of the formation of droplets, can be prevented and a chromatographic stationary phase, treated in this way, can keep its efficiency much longer.

Such immobilization reactions will be presented and the influence of the purification and cross-linking of poly(diorganosiloxanes) on their thermal behavior at very low and very high temperatures will be shown.

The Synthesis, Structure and NMR Spectral Studies on Organosilanes and Silylmetal Derivatives.

John P. Oliver, Jeff Kampf, Srini DeMel, Greg Hendershot, Mike Sierra

Department of Chemistry
Wayne State University
Detroit MI 48202

The synthesis and structures of a number of aromatic silanes and of a series of organosilylmetal derivatives (metals include lithium, magnesium, cadmium, mercury, aluminum, tin and lead) will be described. Multinuclear NMR studies (primarily ^{1}H, ^{29}Si, and ^{13}C) on the solutions of these systems will be presented, including some variable temperature data. Based on these results, structures for the species present in solution will be proposed along with possible exchange path-ways for the exchange reactions which involve the transfer of silyl groups between these species. Solid state CP/MAS NMR studies on the organosilanes along with limited studies on the silylmetal compounds will be reported. The correlation between the solid state structures, CP/MAS NMR, and solution NMR results will be discussed.

Hydrosilylation Catalyzed by Transition Metal Complexes

Iwao Ojima

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794

Recent advances in the hydrosilylation of unsaturated substrates, such as alkenes, alkynes, dienes, carbonyl compounds, conjugated carbonyl compounds catalyzed by Group VIII transition metal carbonyl clusters in our laboratory will be reviewed. For the catalysts of hydrosilylations, transition metal carbonyl clusters have been attracting little interests. Recently, our research group started an extensive study on the behavior of those metal carbonyl clusters, such as $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, $CoRh(CO)_7$, and their phosphine as well as isonitrile complexes. It has been found that those metal carbonyl clusters show unique selectivities which are very different from those achieved by e.g., $RhCl(PPh_3)_3$ and $Co_2(CO)_8$ in some cases, which strongly suggests the intermediacy of silyl-$Rh_nCo_m(CO)_x$ or $(silyl)_2Rh_nCo_m(CO)_{x-1}$ species. Possible mechanisms for the homogeneous hydrosilylations as well as organometallic chemistry of those metal clusters relevant to silicon chemistry will also be discussed.

PLENARY LECTURE 8

Gas Phase Ion Chemistry of Organosilicon Compounds

R. Damrauer
Department of Chemistry
University of Colorado at Denver
1200 Larimer Street
Denver Colorado 80204

After a brief description of conventional and tandem flowing afterglow techniques as applied to the study of anion-molecule reactions in the gas phase, a general discussion of the application of these techniques to problems in organosilicon chemistry will be presented. Particular emphasis will be placed on the preparation of unusual silicon-containing anions, their thermodynamic properties, and their gas phase reaction chemistry. Stability and reactivity comparisons with analogous carbon-containing species will also be made as will specific discussions of multiply bonded sila-analogs (eg. silaformaldehyde, silaacetaldehyde, silamethylformate, and silaacetic acid).

SESSION A

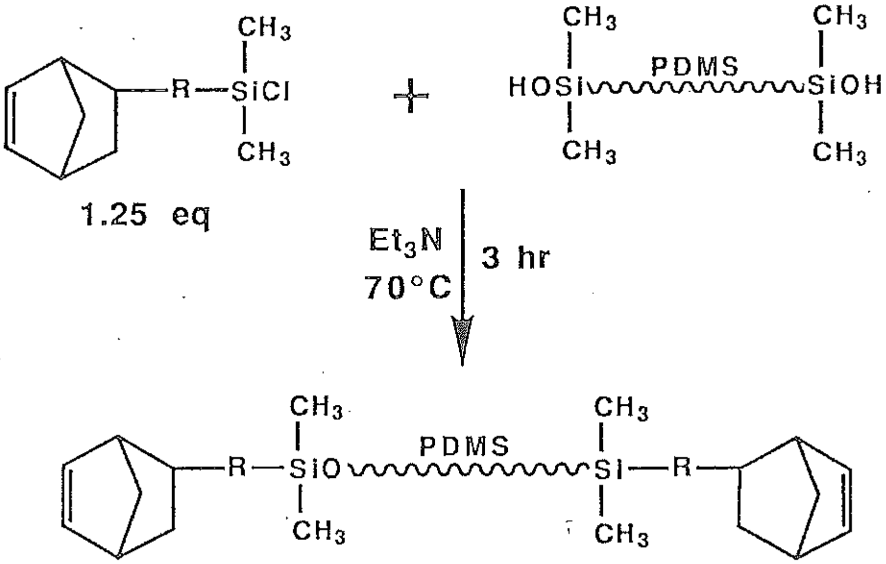
A 1

TELECHELIC NORBORNENE SILICONE ELASTOMERS CURED BY THE THIOLENE REACTION

Steven T. Nakos and Anthony F. Jacobine
New Technologies
Loctite Corporation
705 North Mountain Road
Newington, Ct 06111

The hydrosilylation of 5-alkenyl-2-norbornenes with chlorodimethylsilane has enabled the preparation of a new class of norbornene-functional silicone oligomers that are readily polymerized by a UV-initiated thiolene condensation:

Preparation of Telechelic Norbornene Siloxanes



These materials exhibit cure times that are much shorter than conventional RTV silicones of similar molecular weight, with comparable bulk properties:

A 1

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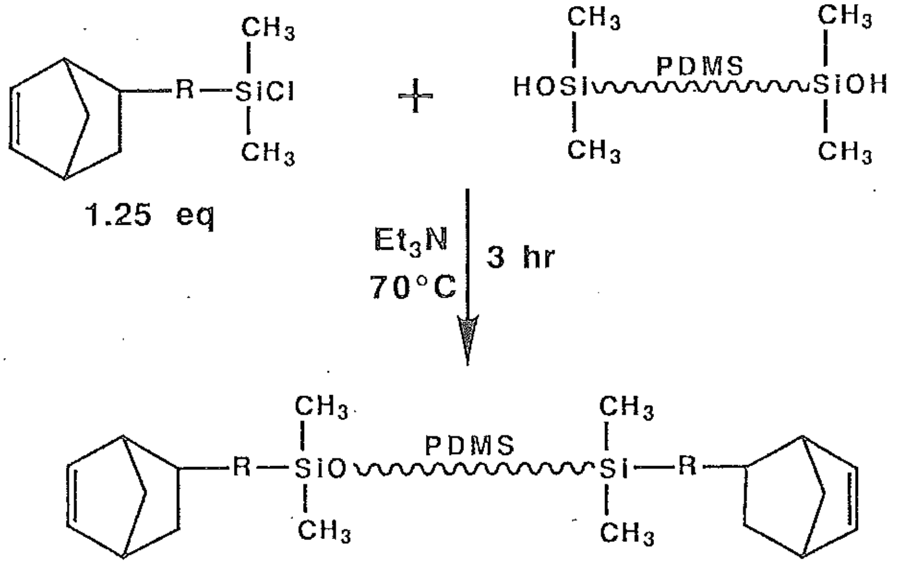


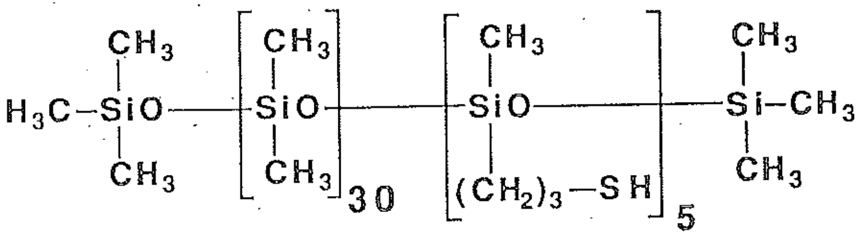
These materials exhibit cure times that are much shorter than conventional RTV silicones of similar molecular weight, with comparable bulk properties:

UV CURED 28,000 MW TELECHELIC NORBORNENE SILICONE CONTAINING 3K5M (100 EQ% THIOL)

70 mW/cm^2 Medium Pressure Hg Lamp
35% Fumed Silica
2% DEAP

Property	Seconds/Side 30	 45	 60
Tensile Strength (psi)	804	936	988
Elongation (%)	490	518	504
Tear (pli)	155	140	145
Durometer (Shore A)	35	36	40

The preferred crosslinker is a 3000 MW trimethylsilyl-terminated polysiloxane containing 5 pendant mercaptopropylmethyl units (3K5M):



$$H_3C-\overset{CH_3}{\underset{CH_3}{Si}}O-\left[\overset{CH_3}{\underset{CH_3}{Si}}O\right]_{30}-\left[\overset{CH_3}{\underset{(CH_2)_3-SH}{Si}}O\right]_{5}-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

3000 MW
1.5 meq SH/g

Suitable photoinitiators include α,α–diethoxyacetophenone (DEAP) or other silicone-soluble acetophenones.

Because thiolene cure is essentially additive in nature, this system may incorporate difunctional thiol chain extenders which reduce crosslink density. This allows the preparation of high elongation, low durometer elastomers without the use of high viscosity silicone oligomers.

This norbornene/thiol system has the following advantages:

1. **Dry-to-the-touch cure in air (no oxygen inhibition).**
2. **UV Cure times of 30 to 60 seconds per side @ 70 mW/cm^2 (medium pressure Hg) onto a 0.070 inch plate give cured properties similar to RTVs.**
3. **Addition cure allows tailoring of cured properties with the appropriate crosslinker and chain extender.**

A 2

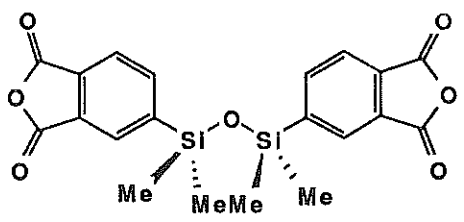
SYNTHETIC ROUTES TO SILICONE POLYCARBONATE COPOLYMERS FROM ARYL TERMINATED SILICONE PRECURSORS

P. J. McDermott, T. E. Krafft, and J. D. Rich

GE Corporate Research and Development
P.O. Box 8
Schenectady, N. Y. 12301

Several synthetic routes to silicon polycarbonate copolymers utilizing aryl-terminated siloxanes have been examined. Siloxanes with varying D_p units (1) were prepared by the acid equilibration of 1,3-bis-phthalic anhydride tetramethyldisiloxane. These siloxanes were then imidized with aminophenol to the corresponding "bis phenol" (2). Reaction of these materials with 4,4'-isopropylidene diphenol (BPA) and phosgene (both interfacially and non-interfacially) gives the corresponding silicone polycarbonate copolymer (3). Synthesis of these copolymers was also achieved using bis-chloroformate derivatives of 4,4'-isopropylidene diphenol (monomer and oligomers). The different synthetic routes significantly affect the thermal and mechanical properties as well as the composition of these copolymers.

Use of aryl-terminated siloxane precursors in the synthesis of silicone polycarbonate copolymers offers potential advantages over conventional siloxane precursors. These materials do not contain a hydrolyzable Si-O-C group which may afford improved hydrolytic stability in the polymers. Some of the polymers synthesized in this study also exhibit improved thermal and mechanical properties.



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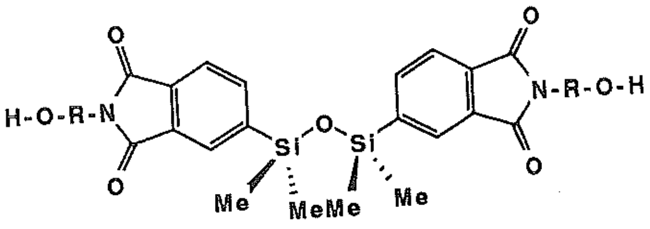

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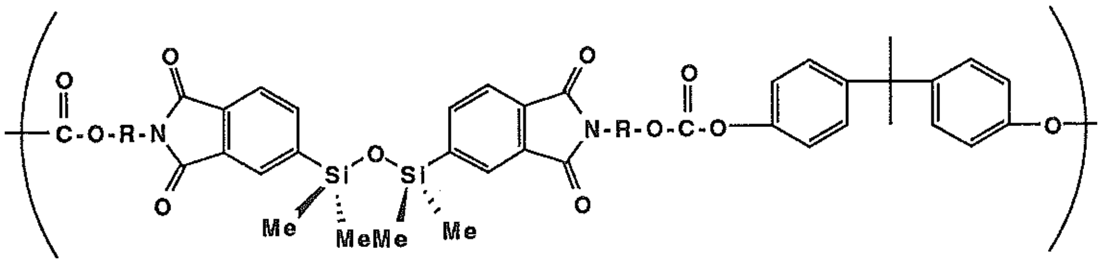


NEW POLYSILOXANES WITH A CARBONATE GROUP IN THE SIDE CHAINS : SYNTHESIS AND PROPERTIES.

G. de MARIGNAN, D. TEYSSIE, J.M. YU and S. BOILEAU

Collège de France, 11 place Marcelin Berthelot, 75231 Paris Cédex 05, France.

A series of new mesomorphic side chain polysiloxanes with a carbonate group in the spacer was prepared by hydrosilylation of nematic allyl carbonates with polymethylhydrosiloxane (PMHS). Side reactions during the hydrosilylation step were identified by ^{1}H NMR and new experimental conditions were determined in order to get pure polymers. Thermal properties of the resulting polysiloxanes were analysed in terms of the nature of the spacer and of the nature and length of the tail group on the mesogenic moiety. The properties of these polymers were compared to those of similar polymers with an ether linkage in the spacer instead of a carbonate group.

On the other hand, water soluble polysiloxanes were prepared by partial modification of PMHS with monoallyl polyethylene oxide. The remaining SiH functions were subsequently modified with allyl carbonates. The resulting polymers were used as models for studying controlled drug release. Kinetics of the carbonate bond scission were followed as a function of the pH of buffered aqueous solutions.

A 4

SYNTHESIS OF ORGANOPOLYSILANES USING CROWN ETHERS

Masaie Fujino, Hiroaki Isaka, and Nobuo Matsumoto

NTT Basic Research Laboratories
Musashino, Tokyo 180, Japan

In the synthesis of organopolysilanes, increasing the polymerization yield within a short polymerization time and controlling the molecular weight distribution are topics of current interest. We report that a method using crown ethers as cocatalysts very effectively overcomes these problems for many kinds of organopolysilanes. The effects of the side chains of the polymers and of the cavity size and content of crown ethers on the polymerization yield and molecular weight distribution are discussed. The polymerization time dependence is also discussed.

Table 1 shows the side chain dependence of the yield for polymers synthesized in toluene for 30 minutes using a catalytic amount of crown ether (10 mol%). The yields of alkyl and phenetyl polysilanes synthesized with crown ether were 4-300 times larger than those obtained without crown ether. The yields were increased by increasing crown ether content. The yield of phenylpolysilane slightly decreased and 5.2% was obtained at the crown ether content of 100 mol%. The cavity size effect of crown ether is shown in table 2 for dihexylpolysilane. Polymerization time dependence of the yield is shown in table 3: The yield gradually saturated when crown ether was used as cocatalyst, although continuous increase was observed in the case without crown ether.

Molecular weight distributions conducted with crown ether were changed from bimodal (Mw$\sim$1,000,000 and $\sim$10,000) to monomodal with a medium molecular weight of Mw$\sim$100,000 for all the types of alkylpolysilanes used in this work. Use of higher content of crown ether reduced the molecular weight. In phenetyl and phenyl polysilanes, however, only low molecular weight polymers (Mw$\sim$10,000) were synthesized.

In conclusion, crown ethers were shown to be such good cocatalysts as to obtain alkylpolysilanes in high yield within a short polymerization time, accompanied by monomodal molecular weight distributions.

Table 1.

polysilane	polymerization yield (%) 18-crown-6/none	 10 mol%
-MeMeSi-	3.0	38.8
-MePrSi-	11.1	38.8
-MeHexSi-	3.0	34.7
-MeDodecylSi-	0.4	21.0
-Me(cycloHex)Si-	0.8	46.3
-HexHexSi-	0.05	16.7
-Me(β-phenetyl)Si-	2.6	13.3
-MePhSi-	21.0	13.4

Table 2.

crown ether	p. yield (%)
none	0.05
12-crown-4	31.1
15-crown-5	16.8
18-crown-6	16.7

(-HexHexSi-)

Table 3.

p. time (h)	p. yield (%) 18-crown-6/none	 10 mol%
0.5	0.05	16.7
2.0	2.2	45.6
5.0	8.1	52.9

(-HexHexSi-)

A 5

PHOTOPHYSICS AND PHOTOCHEMISTRY OF POLYSILANES

J. M. Zeigler[1], R. M. Hochstrasser[2], J. R. G. Thorne[2], and
P. Ohsako[2]

[1] Division 1812, Sandia National Laboratories, Albuquerque, NM 87185-5800

[2] Department of Chemistry, University of Pennsylvania, Philadelphia, PA
19104-6323

Recent studies of the photophysics of polysilanes in our laboratories and elsewhere show that the excited singlet states in polysilanes are highly delocalized, and vibrationally decoupled, with rapid energy transfer among the absorbing chain segments. Like the absorbtion, the singlet emission exhibits thermochromism both in solution and in the solid state attributable to conformational transitions. The triplet emission is much lower in intensity (quantum yields typically 10^{-4}), vibrationally coupled, but still mobile, since strong delayed fluorescence is observed. In this paper, we report new photophysical investigations which provide insight into the nature of the excited states, their ability to bring about photoscission of the polysilane backbone, and the products so formed. Hole-burning experiments suggest a homogeneous bandwidth for the absorption of < 4 cm^{-1}. These same experiments indicate that photochemical reactions occur primarily after energy transfer to the segments having the lowest transition energy ("longest"). Fluorescence anisotropy measurements indicate that energy transfer is complete within a few tens of picoseconds. Although singlet exciton annihilation has been shown by Kepler, et al. to be an important decay mechanism for loss of singlets, transient absorption studies of the photolysis of $(PhMeSi)_n$ in solution demonstrate that the formation of the PhMeSi: photoproduct is linear in the laser intensity, thereby suggesting that biexciton states are not important in the photochemical reaction which generates this product. While our experiments strongly indicate the operation of multiple pathways leading to the photochemical scission, we present additional evidence for the hypothesis first offered by one of us earlier that triplet states are an important element in initiating the photochemistry of polysilanes. The fate of the polymer chain after the initial bond breakage is strongly dependent on the electronic, structural, and physical properties of the specific polysilane polymer under examination. Although a full understanding of the photochemistry of polysilanes is still in the future, our current understanding of this complex area will be summarized.

*Work performed at Sandia National Laboratories was supported by the U. S. Department of Energy under contract number DE-AC04-76DP00789.

SESSION B

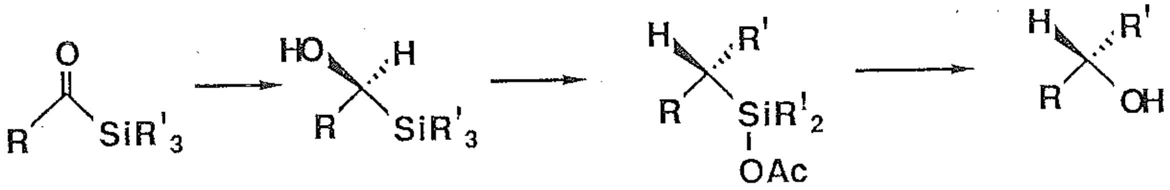
B 1

THE CONVERSION OF ACYLSILANES INTO CHIRAL (NON-SILICON CONTAINING) ALCOHOLS

John D. Buynak and Byron Strickland

Department of Chemistry
Southern Methodist University
Dallas, TX 75275 U.S.A.

The reactions of acylsilanes with a variety of chiral reducing agents and nucleophiles has been explored. These materials can be converted to α-acetoxy silanes and thermally rearranged. The rearrangement proceeds with migration of acetate from carbon to silicon and migration of one alkyl group from silicon to carbon with inversion of configuration at carbon. The resulting silafunctional silanes are converted to non-silicon containing alcohols with retention of configuration by standard methods.

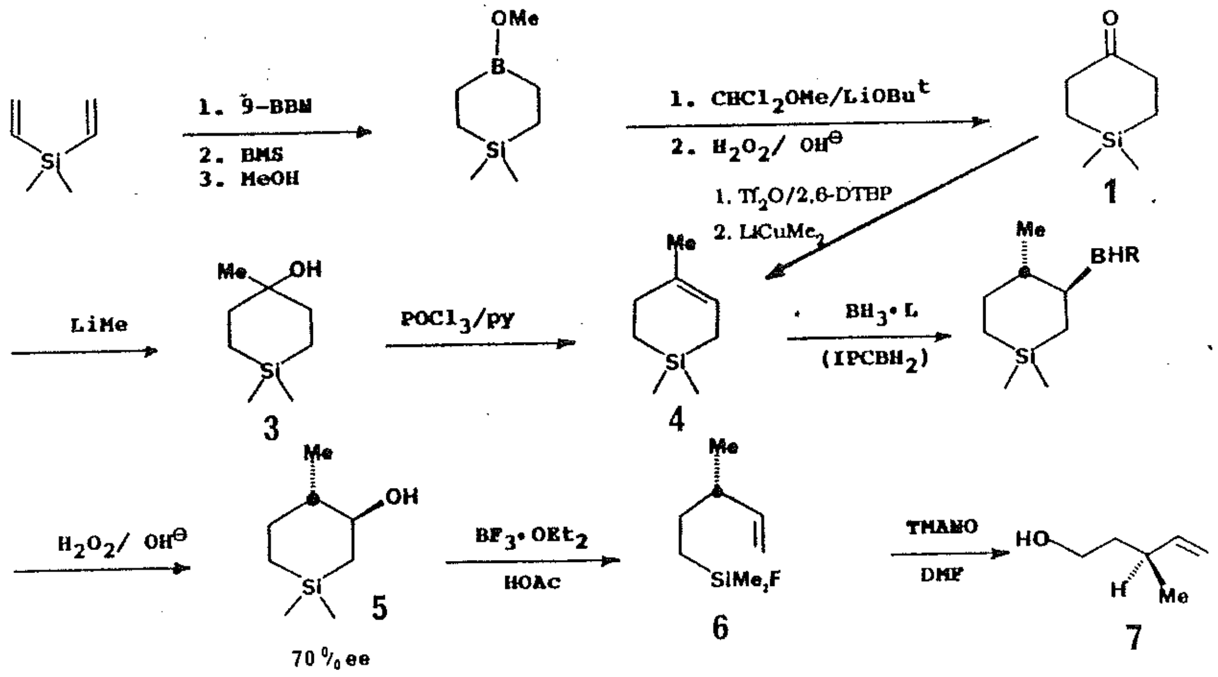


B 2

SILACYCLOHEXANONES AS TEMPLATES FOR THE SYNTHESIS OF CHIRAL ACYCLIC SYNTHONS

John A. Soderquist and Alvin Negron
Department of Chemistry
University of Puerto Rico
Rio Piedras, Puerto Rico 00931

A detailed study of the conversion of divinyl derivatives of silicon and germanium to the corresponding 1-metalla-4-borinanes was carried out with their subsequent conversion to the metallacyclohexan-4-ones (**1**). The silicon ketone (MR_2 = $SiMe_2$) was converted in good yield to the isomerically pure allylsilane (**4**) *via* the reaction of $LiCuMe_2$ with the vinyl triflate (**2**). **4** was also prepared from the dehydration of **3** with either I_2 or $POCl_3$/pyr, but in lower yields and isomeric purity. The asymmetric hydroboration of **4** provides the β-hydroxysilane (**5**) in 70% ee. Conversion of **5** to **7** was accomplished *via* treatment with BF_3/HOAc followed by oxidation of the resulting fluorosilane (**6**) with anhydrous Me_3NO in DMF. This study provides the basis for a new approach to asymmetric synthesis based upon silicon heterocycles as templates for stereodifferentiation.



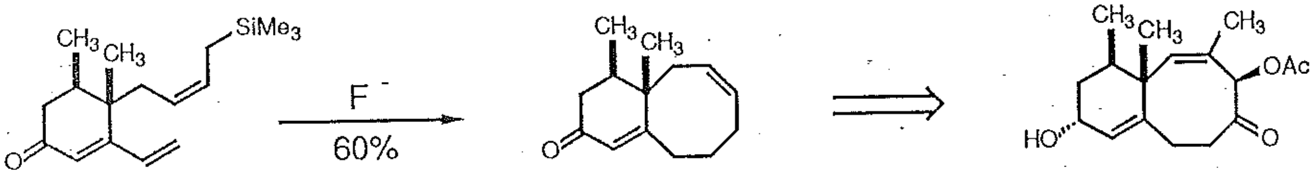
B 3

CARBOCYCLIZATION PROCEDURES FEATURING ORGANOSILICON CHEMISTRY

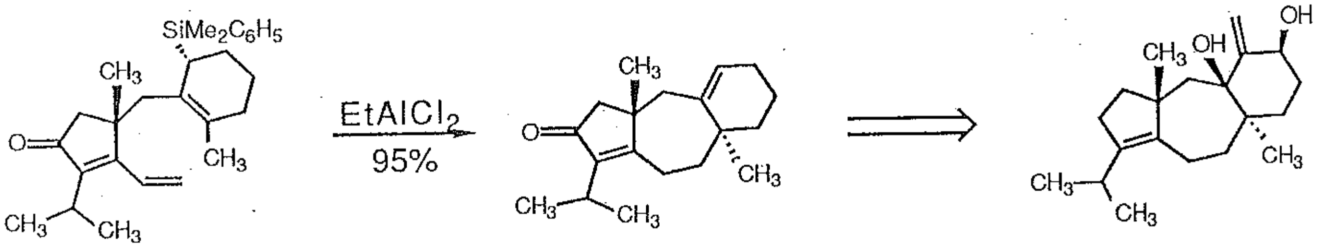
George Majetich, Clay Ringold, Derric Lowery and Vikram Khetani

Box 218, Department of Chemistry, *The University of Georgia*

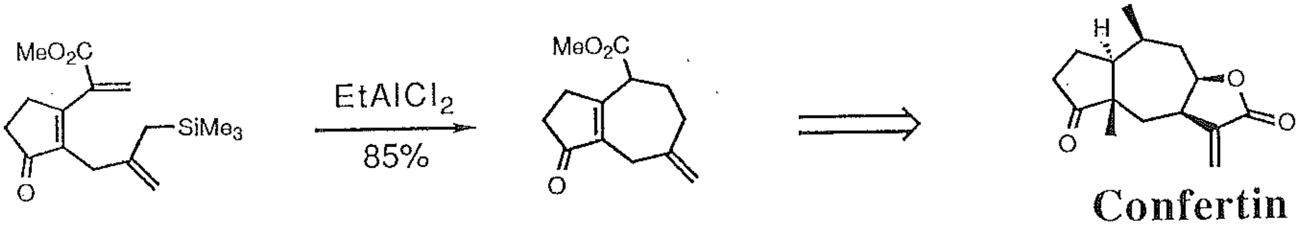
We have demonstrated that the intramolecular addition of allylsilanes to electrophilic olefins can be used to produce not only the common ring sizes but also polycyclic systems having seven- or eight-membered rings. The key transformations for several syntheses have been studied. Our progress towards the synthetic goals illustrated below will be presented.



Neolemnane



Isoamijiol



Confertin

B 4

Abstract for Oral Presentation

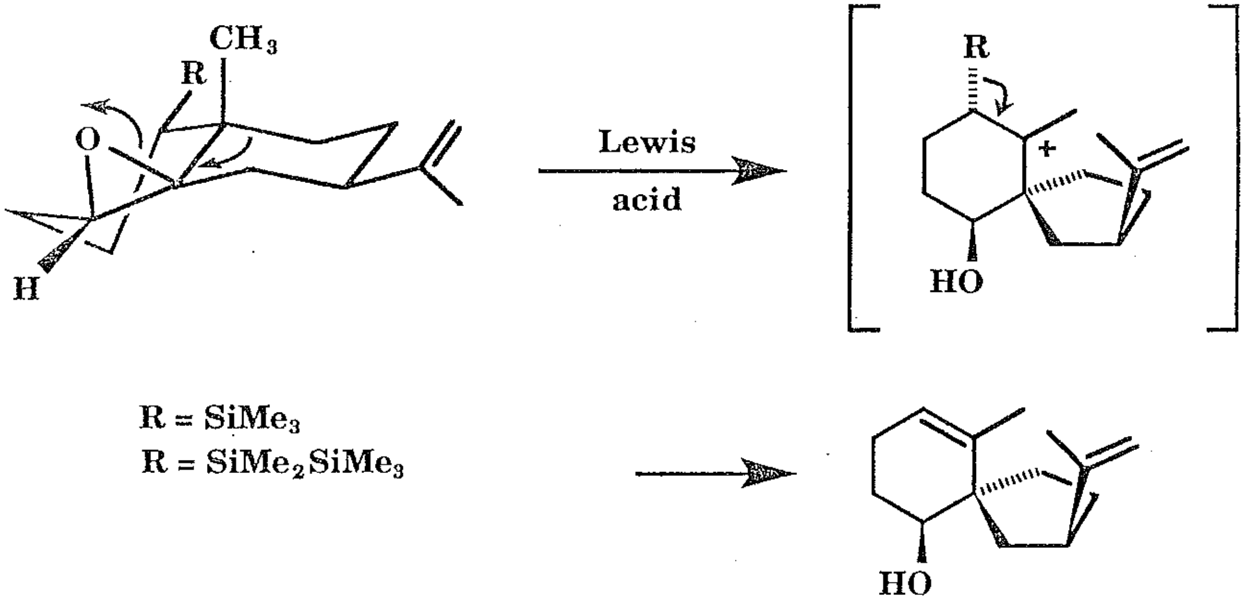
Title: Silicon-Promoted Ring Contractions and Total Synthesis of (–)-Solavetivone

Authors: Reuben Jih-Ru Hwu and John M. Wetzel

Address: Department of Chemistry, The Johns Hopkins University,
Baltimore, MD 21218

Trimethylsilyl (Me_3Si) and 1,1,2,2,2-pentamethyldisilanyl (Me_3SiMe_2Si) groups were found to promote ring contractions (e.g., see Scheme I). This unprecedented ring contraction was applied as the key step in the first total synthesis of optically active solavetivone, a vetispirane antifungal metabolite (Scheme II). Use of the newly developed silicon-promoted reaction solves three major problems associated with the synthesis of carbocyclic spiro compounds: (1) formation of the quaternary carbon spiro center; (2) stereochemical control of the spiro center during its formation; (3) control of the chiral centers on both rings. This reaction also allows localization of a carbon–carbon double bond at the desired endocyclic position.

Scheme I



A SYSTEMATIC STUDY OF THE STABILITY/REACTIVITY OF SILYL ETHERS TO VARIOUS REAGENTS

Ram Chawla, Craig Polsz and Gerald L. Larson

Hüls America, Inc./Petrarch Systems Silanes and Silicones
Bartram Road
Bristol, PA 19007

The silyl ethers of n-butanol, cyclohexanol, tert-butanol, allyl alcohol, benzyl alcohol, and phenol with the trimethylsilyl, triethylsilyl, 2,3-dimethylpropyldimethylsilyl, tert-butyldimethylsilyl, tert-butyldiphenylsilyl, cyclohexyldimethylsilyl and thexyldimethylsilyl groups were prepared. These representative silyl ethers of primary, secondary, tertiary, allylic, benzylic and aryl alcohols were subjected to a variety of reaction conditions in order to ascertain their relative stabilities and reactivities. They were also subjected to several conditions known to be used to for the deprotection (protodesilylation) of silyl ethers to again study their relative reactivities. Not surprisingly, the more hindered silyl ethers proved to be the more stable. Acid catalyzed protodesilylations are effective for all systems, being slower for the tertiary ethers and for the more hindered silyl groups. All are stable to lithium reagents with the exception of the allyl ethers, which react at the allyl group with loss of the lithium trialkylsiloxide. Stability to Grignard reagents, lithium aluminum hydride, and the Wittig reagent was also observed. Some reaction with oxidizing agents was noted with the less hindered silyl ethers.

These results will be discussed with an emphasis on synthetic utility.

SESSION C

THE DIMETHYLZIRCONOCENE CATALYZED POLYMERIZATION OF ALKYL SILANES

William H. Campbell, Terrence K. Hilty
Dow Corning Corporation, Midland, Michigan 48640

ABSTRACT

Polysilanes are receiving an increased amount of attention in the literature due to their potential uses as positive and negative photoresist materials, as photopolymerization catalysts, as photoconductive polymers and as precursors to and reinforcing agents in ceramic materials. The only viable route to high molecular weight polysilanes to date has been through the Wurtz coupling reaction, which has several drawbacks: 1) poor control over molecular weight and large polydispersity, 2) potential hazards associated with the use of molten alkali metals, and 3) a large amounts of salt waste generated.

Recently, the possibility of using transition metals to catalyze Si-Si catenation has been addressed using group VII and group VIII transition metal complexes, but the best results for preparing longer Si-Si chains catalytically has been with group IV transition metal catalysts in the catenation of primary alkyl and aryl silanes. Our work in this area has shown some interesting and important results that bear on the feasibility of transition metal catalyzed routes of polysilane preparation.

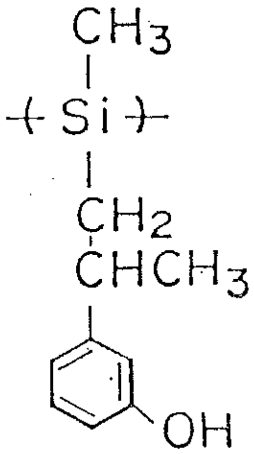
We carried out the polymerization of n-butylsilane using bis-(η^5-cyclopentadienyl)dimethyl zirconium (IV) as the catalyst. Rapid conversion of the silane to low molecular weight catenated Si-Si oligomers did take place, but the characterization revealed that a large percentage of the Si_5 and higher oligomers were cyclic, whereas previous reports cited only linear products from similar reactions. Running the reaction at higher temperature increases the degree of cyclic formation. Oligomers with degrees of polymerization (Dp) of 2 through 8 were also observed showing another clear distinction between our work and that previously reported.

The differences in products are believed to be due to the ability of zirconium to react reversibly with both primary and secondary alkyl silanes. The lability of the zirconium-silicon bond allows for a dynamic equilibrium in which intermediate products may be liberated from the metal center. These intermediates undergo further reaction including cyclization. Previously postulated mechanisms do not adequately account for the formation of cyclics or low Dp intermediates. Some possible mechanistic implications are discussed in light of the previous literature postulates.

Polysilane substituted with phenol moiety. UV absorption and NMR spectroscopy in polar solvents.

Shuzi Hayase, Rumiko Horiguchi, Yasunobu Onishi and Toru Ushirogouchi
Chemical Laboratory, Research and Development Center, Toshiba Corporation, Komukai-Toshiba cho, Kaiwai-ku Kawasaki 210 JAPAN

Although many kinds of polysilane polymers have been synthesized, almost all bear only hydrophobic substituents such as alkyl or aryl groups, and are therefore insoluble in polar solvents. Recently we have synthesized a polysilane with a hydroxy aryl ring substituent, (I). The presence of the phenolic OH group makes (I) soluble in alcohols and in weakly basic aqueous media.



(I)

We now report the UV absorption spectra, NMR spectroscopy of (I) as well as several chemical reactions of (I) leading to new functionalized polysilane polymers.

Reference
1) R. Horiguchi, Y. Onishi and S. Hayase, Macromolecules, 21(2), 304 (1988)

We thank Professor R. West for helpful discussions.

SYNTHESIS, PROPERTIES, AND PHOTOCHEMISTRY OF AMORPHOUS ALKYLSILICON NETWORK POLYMERS. T. W. Weidman, W. L. Wilson, E. W. Kwock, and P. A. Bianconi. AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

High intensity ultrasound was employed to mediate the reductive condensation of alkylsilicon trihalides with liquid NaK alloy emulsions in inert alkane solvents. Subsequent addition of tetrahydrofuran, alkylation of residual Si-Cl moieties, followed by aqueous workup and reprecipitation afforded amorphous soluble powders or gells of composition $[R_{1+x}Si]$ (with $0 < x < 0.25$). Applying the same procedure to a variety of $RSiCl_3$ monomers indicated that simple n-alkyl substituents of more than three carbons favored the formation higher molecular weight (20,000 -50,000 by GPC) soluble gels, while branching (especially at the alpha carbon) favored oligomeric material with molecular weights under 5,000. All chemical and spectroscopic data suggest a structure composed of tetrahedral (sp^3) alkylsilyne fragments irregularly assembled via silicon-silicon sigma bonds into amorphous networks. In solution or as thin films, these materials (hereafter termed polysilynes) exhibit intense near UV absorption band edges and visible luminescence centered around 500 nm. Time-resolved single photon counting experiments revealed that this emission exhibits complex multi-exponential decay behavior better resembling that of amorphous semiconductors than the simple sigma-sigma* emission observed for linear polysilanes. Heating the higher molecular weight polymers past 400°C. results in the loss of alkenes as the primary volatile product, leaving behind mixtures of a-Si:H and SiC. Exposure to UV light and oxygen results in a wavelength dependent photo-oxidative bleaching and crosslinking reaction, producing insoluble silsequioxane-like network materials.

C 4

VINYLIC POLYSILANES - A PERSPECTIVE

Curtis L. Schilling Jr.

Union Carbide Corporation
Specialty Chemicals Division
Tarrytown, New York, 10591

Recent reports on adverse reactions of vinylmethyldichlorosilane with sodium metal in refluxing toluene[1-3] have prompted a more detailed structural examination of Union Carbide Vinylic Polysilane Y-12044. The latter, a polymeric precursor[4] for silicon carbide ceramic compositions, has demonstrated a viable combination of economics, performance, and scalability.

$$Me_3SiCl + MeSiHCl_2 + CH_2{=}CHSiMeCl_2 \xrightarrow[\text{Solvent Blend}]{\text{Na}} \xrightarrow{\text{Workup}} \text{Y-12044}$$

Analytical results (NMR, GC/MS) show that low molecular weight species are clearly vinylic polysilanes, as $Me_3Si(SiMeH)_x(SiMeCH{=}CH_2)_y$-$SiMe_3$ or $Me_3Si(SiMeH)_x(SiMeCH{=}CH_2)_yH$, where $x = 0$ or 1 and $y = 1$-4. Higher molecular weight fractions contain both vinylmethylsilane units and units which show that reaction of vinyl groups has occurred. Cleavage of silicon-silicon bonds in vinylic polysilanes with NaOMe/-MeOH in tetrahydrofuran has proven to be uniquely effective in structure determination, and shows that more than 60% of theory of the vinyl groups are present as such in the product.

Model chemistry reveals cases in which vinyl groups do and/or do not react; factors affecting retention of vinyl groups will be discussed. The use of blended solvents in the synthetic reaction appears to be critical in retaining a majority of the vinyl groups as such.

1. R. West, J. Organomet. Chem., 300, 327(1986)

2. H. Stueger and R. West, Macromolecules, 18, 2349(1985)

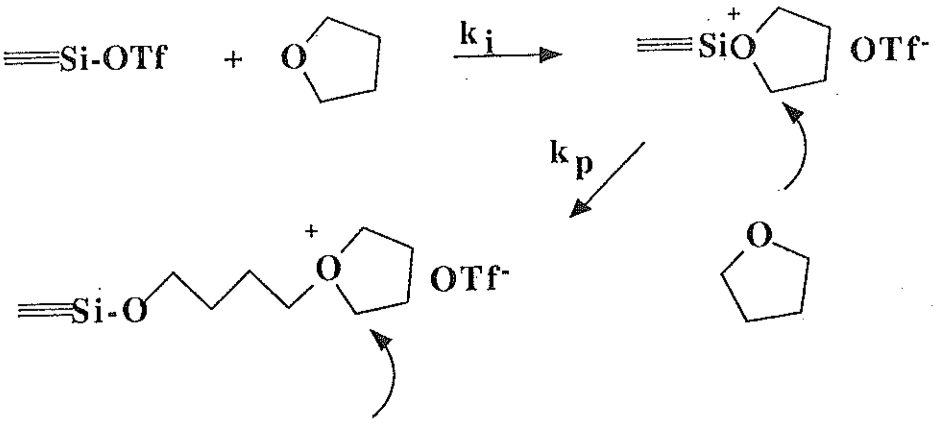
3. D. J. Worsfold, Abstract PS2-12 from meeting, "Advances in Silicon-Based Polymer Science", November 21-24,1987

4. C. L. Schilling Jr., U. S. Patent 4,783,516; Brit. Polym. J., 18, 355(1986)

Trimethylsilyl Triflate as Initiator for the Cationic Polymerization of Heterocyclics and Alkenes. Model Reactions for the Cationic Grafting from Polysilanes.

Jeffrey S. Hrkach and Krzysztof Matyjaszewski
Department of Chemistry
Carnegie Mellon University
4400 Fifth Avenue
Pittsburgh, PA 15213

Trimethylsilyl trifluoromethanesulfonate is one of the strongest silylating reagents. It reacts with a variety of nucleophiles including alcohols, amines, ethers, and esters. Reaction with cyclic ethers, iminoethers, and esters leads to silyl onium ions which initiate polymerization of strained heterocyclic monomers. The reactivity of the first silyl onium ions is lower than that of the subsequent alkyl onium ions. Therefore initiation rate constant (k_i) is lower than propagation rate constant (k_p):



Trimethylsilyl triflate reacts directly only with the most nuceophilic alkenes (N-vinylcarbazole). Polymerization of less reactive styrene is initiated by traces of triflic acid, which is a decomposition product of silyl triflate.

Reaction of poly(phenylmethylsilylene) with triflic acid leads to dearylation of polysilane and formation of very reactive silyl triflate groups along the chain of polysilane. These sites were used to initiate cationic polymerization of various monomers from polysilanes, and to prepare new graft copolymers based on polysilanes.

SESSION D

D 1

MECHANISM AND DYNAMICS OF REARRANGEMENTS INVOLVING ORGANOSILICENIUM IONS IN THE GAS PHASE

K. A. Reuter and D. B. Jacobson

Department of Chemistry
North Dakota State University
Fargo, North Dakota 58105

The mechanism and dynamics of rearrangements involving organosilicenium ions in the gas phase were investigated by using Fourier transform mass spectrometry (FTMS) and specific isotopic labeling. Specific organosilicenium ions were generated by chloride abstraction using trimethylsilylium, process 1.

$$Si(Me)_3^+ + SiR_3(R')(Cl) \longrightarrow ClSi(Me)_3 + SiR_3(R')^+ \qquad (1)$$

This allows the synthesis of distinct isomers that can be subsequently studied. For example, the following ions have been generated by chloride abstraction from appropriate precursors.

$$(Me)_2\overset{+}{Si}-(CH(CH_3)_2) \qquad (Me)_3Si-\overset{+}{C}H-CH_3 \qquad (Me)_3Si(CH_2CH_2)^+$$

1 2 3

$$(Me)_3Si\overset{+}{C}H_2 \qquad (Me)_2HSi\overset{+}{C}H_2 \qquad H_3Si\overset{+}{C}H_2 \qquad H_2\overset{+}{Si}CH_3$$

4 5 6 7

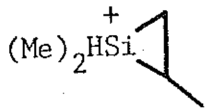
The $C_5H_{13}Si^+$ isomers, 1 and 2, undergo facile rearrangement to 3 upon collisional activation (CA) resulting in elimination of ethene, process 2. A

$$SiC_5H_{13}^+ \xrightarrow{CA} SiC_3H_9^+ + C_2H_4 \qquad (2)$$

novel hydrogen/methyl exchange reaction occurs exclusively between $SiH(Me)_2^+$ and propene, process 3. Cyclopropane reacts in an analogous fashion. The

$$SiH(Me)_2^+ + \text{propene} \longrightarrow Si(Me)_3^+ + C_2H_4 \qquad (3)$$

mechanism for both reactions 2 and 3 appear to involve a common intermediate, presumably the pentacoordinated silycyclopropane ion 8. The details of these



8

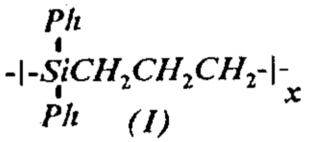
results concerning the mechanism and dynamics of organosilicenium

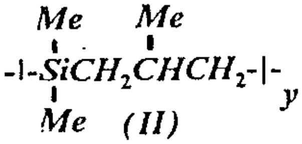
ELECTRON BEAM SENSITIVITIES OF SOME POLY-1-SILA- AND -1,3-DISILACYCLOBUTANES

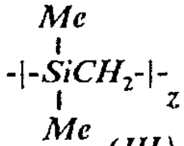
E.Babich, J.Paraszczak, S.Rishton, N.Chou
IBM T.J.Watson Research center,p.o.box 218,Yorktown Heights,N.Y.10598

H.Linde
IBM Essex Junction, Vermont

The E-beam sensitivities of high molecular weight polysiltrimethylenes and polysilmethylenes having the following structures:

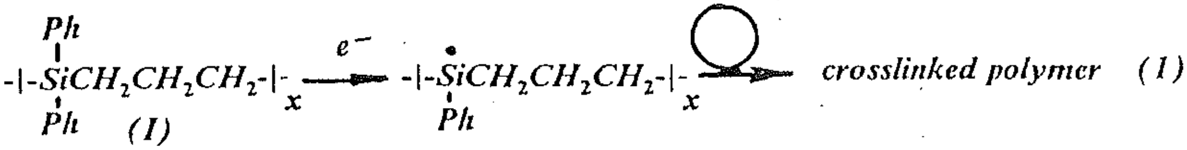

$-|-\underset{Ph}{\overset{Ph}{Si}}CH_2CH_2CH_2-|-_x$ (I) ,


$-|-\underset{Me}{\overset{Me}{Si}}CH_2\overset{Me}{C}HCH_2-|-_y$ (II) and

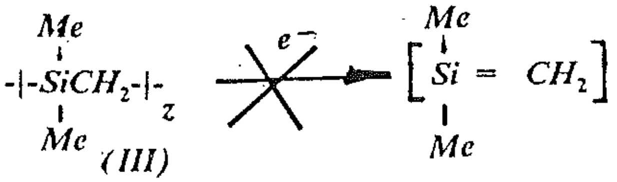

$-|-\underset{Me}{\overset{Me}{Si}}CH_2-|-_z$ (III)

prepared by thermal polymerization of corresponding 1-sila- and 1,3- disilacyclobutanes was investigated.It was found that irradiation with electrons at 25 kV causes a crosslinking of thin polymer films. It was shown that polymers of the type (II) have very high sensitivities (up to 0.5 μC/cm²).The influence of the molecular weight upon e-beam sensitivity was investigated and found that it drops linearly with the decrease of the molecular weight.

In contrast to Ph-containing polysiloxanes polymers (I) were found to have much higher sensitivities (up to 10 μC/cm² and a contrast of 1.3 when the molecular weight $1.4x10^6$ and the dispersivity 5.4) while their thermostability is rather high (up to 400 C).The crosslinking reaction includes scission of Si-C(aryl) bonds according to scheme 1:


$-|-\underset{Ph}{\overset{Ph}{Si}}CH_2CH_2CH_2-|-_x \xrightarrow{e^-} -|-\underset{Ph}{\overset{\bullet}{Si}}CH_2CH_2CH_2-|-_x \longrightarrow$ crosslinked polymer (1)

Polymers of the type (III) in contrast to polyisobutylenes undergo crosslinking, but not the scission reaction (2):


$-|-\underset{Me}{\overset{Me}{Si}}CH_2-|-_z \xrightarrow{e^-} \left[\underset{Me}{\overset{Me}{Si}} = CH_2\right]$ (2)

Polysilmethylenes I - III due to a high silicon content have low etch rates in oxygen plasmas and can be used for fine line lithography as imageable masking layers.

REGIOSELECTIVE ONE- AND TWO-BOND CLEAVAGES IN THE SOLUTION PHASE 185 NM PHOTOCHEMISTRY OF (E) AND (Z)-1,1,2,3-TETRAMETHYLSILACYCLOBUTANE.

Mark G. Steinmetz and Hao Bai
Department of Chemistry, Marquette University, Milwaukee, WI 53233.

We report 185 nm photolyses of (E) and (Z)-1,1,2,3-tetramethylsilacyclobutane **1** in 0.5 M methanol in pentane or heptane as the solvent, which in marked contrast to pyrolyses, lead to regioselective scission of a Si-C bond in the S_1 (σ,σ^*) excited state. With (E)-**1** the products of two-bond cleavage were propene and (E),(Z)-2-butenes, formed in a 1 : 3.3 ratio, respectively, with a total quantum efficiency of 0.28, in addition to methoxytrimethylsilane (**2**) and ethyl(methoxy)-dimethylsilane (**3**), produced in a ratio of 2.2 : 1 and ϕ (**2** + **3**) = 0.26, via trapping of the corresponding dimethyl- and trimethylsilenes. In addition to (Z) to (E) isomerization (ϕ = 0.044), Si-C bond cleavage resulted in intramolecular diradical disproportionation products: (2-methyl-3-butenyl)-dimethylsilane (**4**), ϕ = 0.018, and (2-methylbutyl)methoxydimethylsilane (**5**) plus (2,3-dimethylpropyl)methoxydimethylsilane (**6**), the latter in a 1.9 : 1 ratio (ϕ (**5** + **6**) = 0.058). Silene precursors to **5** and **6** were supported by exclusive monodeuteration of the Si methyl groups, as shown by mass spectroscopy and ^{2}H NMR after photolysis in 0.5 M methanol-O-d_1 as the solvent; no deuterium was detected in the C_5H_{11} alkyl substituents of **5** or **6**. Disproportionation products of initial scission of the C_2-C_3 or C_3-C_4 bonds were not detected. The results obtained for the E isomer of **1** were similar, although the total quantum yield for two-bond cleavages was lower, 0.16. Excited state bond orders and bond distances obtained from MNDO calculations with configuration interaction were in complete agreement with the experimental results, indicating a preference for cleavage of the more substituted Si-C bond in the S_1 excited state.

XXII ORGANOSILICON SYMPOSIUM

DETERMINATION OF THE ABSOLUTE RATE CONSTANTS FOR THE GAS-PHASE REACTIONS OF Cl_2Si AND Br_2Si WITH VARIOUS SUBSTRATES.

V. Sandhu and O.P. Strausz, Chemistry Department, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2.

and T.N. Bell, Chemistry Department, Simon Fraser University, Burnaby, British Columbia, Canada, V5A 1S6.

Using the flash photolysis–kinetic absorption spectroscopy technique we have determined the absolute rate constants for the gas-phase reactions of Cl_2Si with N_2O and 1,3-butadiene and of Br_2Si with O_2 and NO. Both Cl_2Si and Br_2Si were generated by photolysing their precursors, Si_2Cl_6 and $SiBr_4$ respectively, with single flashes of 2900J. Concentrations of these transient species during their decay in the absence or in the presence of added substrate were monitored using the $\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ transition of their recently–discovered absorption spectrum in the UV region. All the decay reactions follow first order kinetics.

In comparison with Cl_2Si, Br_2Si reacts slowly with O_2 and NO, but the rate constants for the $Br_2Si + O_2$ and $Br_2Si + NO$ reactions follow a trend similar to that observed for the analogous reactions of Cl_2Si.

RELATIVE REACTIVITIES IN ANIONIC ATTACK ON TETRAVALENT SILICON

Larry W. Burggraf and Larry P. Davis
Directorate of Chemical and Atmospheric Sciences
Air Force Office of Scientific Research
Bolling AFB DC 20332-6448

Anionic attack on tetravalent silicon compounds can proceed by two competing pathways: nucleophilic addition to silicon to form a pentacoordinated siliconate, or attack on a ligand to produce a variety of products. In many cases, both pathways are activationless or nearly so, so that transition state theories are not able to predict relative reactivities. We have analyzed the relative reactivities of nucleophilic addition vs ligand attack on several tetravalent silicon compounds using a dynamic trajectory analysis, the Dynamic Reaction Coordinate (DRC) method in the semi-empirical molecule-orbital program MOPAC. Reactivities are presented for a variety of kinetic energies and relative orientations of the incoming nucleophile.

EXCITED STATES OF OLIGOSILANES AND POLYSILANES

V. Balaji and J. Michl
Center for Structure and Reactivity
Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712-1167, U.S.A.

We report the results of *ab initio* calculations on (i) the nature of the lowest vertical excited states of oligosilanes up to tetrasilane and (ii) the photochemical paths leading to silylene extrusion reactions and to homolytic bond cleavage to radicals, using SCF and MC SCF procedures followed by large-scale configuration interaction and basis sets of at least double zeta quality. The effects of the addition of polarization functions on silicon (d) and hydrogen (p) and of Rydberg functions (s,p) have been examined as well.

The issues addressed are (i) the ordering of $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, and Rydberg excitations, the assignment of the observed intense UV absorptions of oligosilanes, the effects of chain conformation and methyl substitution, and (ii) the nature of the electronic states responsible for the competing photochemical processes. A simple explanation is proposed for the much lower $\sigma \rightarrow \sigma^*$ excitation energies of oligosilanes compared with alkanes. The difference might be surprising at first sight since the C-C and Si-Si bond energies are comparable.

The results support the picture provided by earlier semiempirical calculations for oligosilanes and the proposed extrapolation to high-molecular weight polysilane chains, in which these are viewed as collections of loosely coupled chromophores localized for any one chain conformation within approximately all-trans chain segments of various lengths.

Acknowledgement. This work was supported by the Air Force Office of Scientific Research.

SESSION E

E 1

Organic Chemistry

Chemical and Spectroscopic Characterization of Trialkylsilylcuprates Derived from CuCN and CuBr·DMS

Sunaina Sharma
Allan C. Oehlschlager

Department of Chemistry
Simon Fraser University
Burnaby, British Columbia
CANADA V5A 1S6

CHEMICAL AND SPECTROSCOPIC CHARACTERIZATION OF TRIALKYLSILYLCUPRATES DERIVED FROM CuCN AND CuBr·DMS. Sunaina Sharma and Allan C. Oehlschlager Department of Chemistry, Simon Fraser University, Burnaby, B.C., CANADA, V5A 1S6

Low-temperature ^{29}Si, ^{13}C, ^{1}H and ^{7}Li NMR and infrared spectroscopy were used to probe the composition of solutions generated by mixing dimethyphenylsilyl lithium (ØMe$_2$SiLi) with CuCN and CuBr·DMS. In THF addition of increasing amounts of ØMe$_2$SiLi (prepared from ØMe$_2$SiCl and Li, therefore containing LiCl) to CuCN gave sequentially ØMe$_2$SiCu(CN)Li (1:1), (ØMe$_2$Si)$_2$Cu(CN)Li$_2$ (2:1) and (ØMe$_2$Si)$_3$CuLi$_2$ (3:1). Similarly, the addition of ØMe$_2$SiLi to THF solutions of CuBr·DMS gave (ØMe$_2$Si)$_3$CuLi$_2$ (3:1).

$$\begin{tikzcd}
\text{ØMe}_2\text{SiLi} + \text{CuCN} \arrow[r, shift left] & \text{ØMe}_2\text{SiCu(CN)Li} \arrow[l, shift left] \arrow[d, shift left, "\text{ØMe}_2\text{SiLi}"] \\
\text{LiCN} + (\text{ØMe}_2\text{Si})_3\text{CuLi}_2 \arrow[r, shift right] & (\text{ØMe}_2\text{Si})_2\text{Cu(CN)Li}_2 \arrow[u, shift left] \arrow[l, shift right, "\text{ØMe}_2\text{SiLi}"']
\end{tikzcd}$$

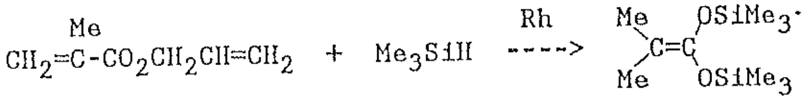
NMR studies indicated the absence of free ØMe$_2$SiLi in solutions containing CuCN or CuBr·DMS at ratios of silyl anion to copper cation of 1:1 to 3:1. In agreement with this observation solutions containing ØMe$_2$SiLi and CuCN underwent nearly exclusive 1,4-addition to cyclohex-2-en-1-one, reacted with alkynes *via* silylcupration (rather than by hydrogen abstraction) and gave negative Gilman tests.

E 2

RHODIUM CATALYZED HYDROSILYLATION OF ALLYL METHACRYLATE TO PREPARE DIMETHYLKETENE BIS-(TRIMETHYLSILYL)ACETAL AND THE MECHANISM THEREOF.

Anthony Revis, Fluids Resins and Process Industries, Dow Corning Corporation, Midland, M
48686

Silyl ketene acetals have found increased applications in Aldol condensation and Group Transfer Polymerization(GTP) of acrylates. Hydrosilylation is one method of preparing functionalized silyl ketene acetals. The rhodium catalyzed hydrosilylation of allyl methacrylate by trimethylsilane unexpectedly gave dimethylketene bis-(trimethylsilyl)acetal instead of the allyl-functional silyl ketene acetal. The product is formed via a mechanism which involves beta-elimination of propene and trimethylsilyl methacrylate. Insitu hydrosilylation of trimethylsilyl methacrylate gave the silyl ketene acetal in 64% yield.



orgsil89.abs

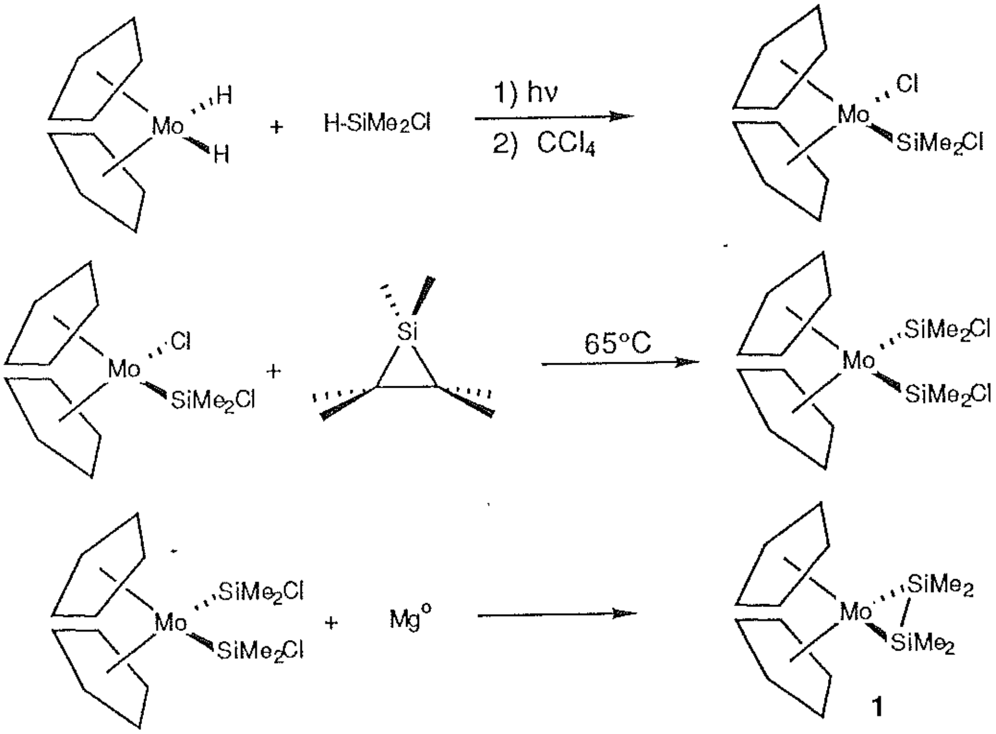
E 3

SYNTHESIS AND CHARACTERIZATION OF A MOLYBDENUM DISILENE COMPLEX

Donald H. Berry and Jean Chey

Department of Chemistry
University of Pennsylvania
Philadelphia, PA 19104-6323

A new strategy for the synthesis of metal disilene / disilametallacyclopropane complexes has been developed, based on the reductive coupling of cis chlorosilyl ligands. The bis(chlorosilyl) molybdocene complex $Cp_2Mo(SiMe_2Cl)_2$ was synthesized from Cp_2MoH_2 in three steps as shown below. Reduction of $Cp_2Mo(SiMe_2Cl)_2$ with Mg in THF followed by recrystallization yields 50% of pure $Cp_2Mo(SiMe_2SiMe_2)$ (**1**) as an orange microcrystalline solid. Complex **1** has been characterized by NMR (^1H, ^{13}C, ^{29}Si) and MS. On the basis of spectroscopic properties and reactivity, **1** appears to exhibit a high degree of π-backbonding from the metal to the $Me_2SiSiMe_2$ fragment; i.e. **1** may be formulated as a $MoSi_2$ ring system.



1

E 4

New Reformations and Migrations of Oligosilyl Iron Complexes

Keith Pannell[1], James Rozell[1], Lih-Ji Wang[1], and Jorge Cervantes[2]
Departments of Chemistry, 1. University of Texas at El Paso, El Paso, Texas, 79968, USA, 2. Universidad de Guanajuato, Guanajuato, Mexico.

Disilanes of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2$-disilyl readily react photochemically to form the corresponding $(\eta^5\text{-}C_5H_5)Fe(CO)_2$-monosilyl complexes via a series of silyl(silylene)iron complexes upon loss of CO (Organometallics, 1986, 5, 1056).

We have extended such studies to oligosilyl complexes containing up to six silicon atoms and reported a new metal facilitated rearrangment process that results in the formation of tris(silyl)silane complexes of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$, (Fp), system as outlined below, equations 1,2 (Organometallics, 1989, 8, 550).

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}(SiMe_2)_3SiMe_3 \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}Si(SiMe_3)_3 \qquad 1$$

$$Fp(SiMe_2)_5SiMe_3 \xrightarrow{h\nu} FpSi(SiMe_3)_2(SiMe_2)_2SiMe_3 \qquad 2$$

Full experimental details will be provided along with illustrations of the importance of ^{29}Si NMR analysis of the reaction mixtures including observation of intermediates. Extension of the chemistry to η^5-indenyl metal systems will also be described.

In related studies we have shown that di-Fp substituted silanes and oligosilanes exhibit both single and double migrations to the cyclopentadienyl rings upon treatment with bases such as lithiumdiisopropylamide (LDA), equation 3.

$$\begin{tikzcd}
Fp\text{-}(SiMe_2)_n\text{-}Fp \arrow[rr, "LDA/MeI"] \arrow[dr, "LDA/MeI"'] & & Fp\text{-}(SiMe_2)_n\text{-}(\eta^5\text{-}C_5H_4)Fe(CO)_2Me \arrow[dl, "LDA/MeI"] \\
& Me(CO)_2Fe(\eta^5\text{-}C_5H_4)\text{-}(SiMe_2)_n\text{-}(\eta^5\text{-}C_5H_4)Fe(CO)_2Me &
\end{tikzcd} \qquad 3$$

This research has been supported by the NSF and the R. A. Welch Foundation, Houston, Texas.

Polysilazanes and Silicon Nitride Processing

Stuart T. Schwab, Renee C. Graef, and Cheryl R. Blanchard-Ardid
Department of Materials Sciences
Southwest Research Institute
6220 Culebra Road
San Antonio, Texas 78284

Current techniques of advanced ceramic fabrication are based on pressureless consolidation technology in which voids often remain in the final microstructure. These voids act as stress concentrators and promote catastrophic failure of ceramic components. Much of this porosity is induced when the organic binder used in consolidation is burned off. One approach to minimizing void formation is through the replacement of the traditional fugitive binder with an organometallic polymer ("preceramic polymer") which will decompose into a predetermined ceramic when heated. The void space normally induced during binder burn-out would be replaced by the ceramic produced through the pyrolysis of the preceramic polymer.

Silicon nitride (Si_3N_4) is a ceramic material in great demand for its superior high-temperature properties and excellent strength to weight ratio. Unfortunately, like other covalent ceramics, silicon nitride is difficult to sinter because of its low diffusivity. Densification can be achieved without applied pressure if sintering aids are used; however, the presence of these glassy materials in the ceramic seriously detracts from the material's strength at high temperature.

The pyrolytic decomposition of polysilazanes into silicon nitride is well known. Nonetheless, the effects of polysilazane binders on the handling characteristics of the green body and the microstructural characteristics of the sintered body have not been fully investigated. To explore these effects, we have synthesized a number of polysilazanes bearing different organic substituents, and have evaluated their performance as binders in cold pressing and pressureless sintering operations. We have found that powder compacts made using these preceramic binders exhibit excellent green strengths, and unusual whisker-enriched microstructures develop in these ceramics during pressureless densification. Major changes in the microstructures are induced by subtle changes in polysilazane chemistry.

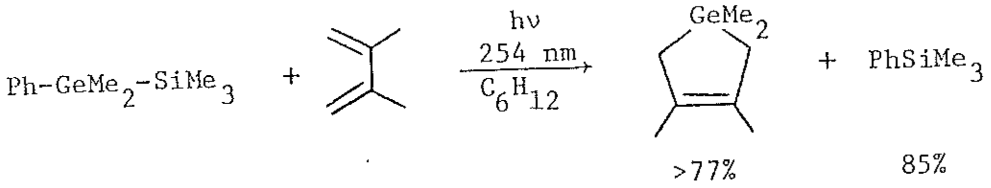
In addition to implications for the pressureless sintering of silicon nitride, the potential utility of polysilazanes for *in situ* whisker growth and low temperature processing will be presented.

Phenyl(trimethylsilyl)germanes as Photochemical Precursors of Germylenes. New Insight into the Mechanisms of Addition of Germylenes to Dienes.

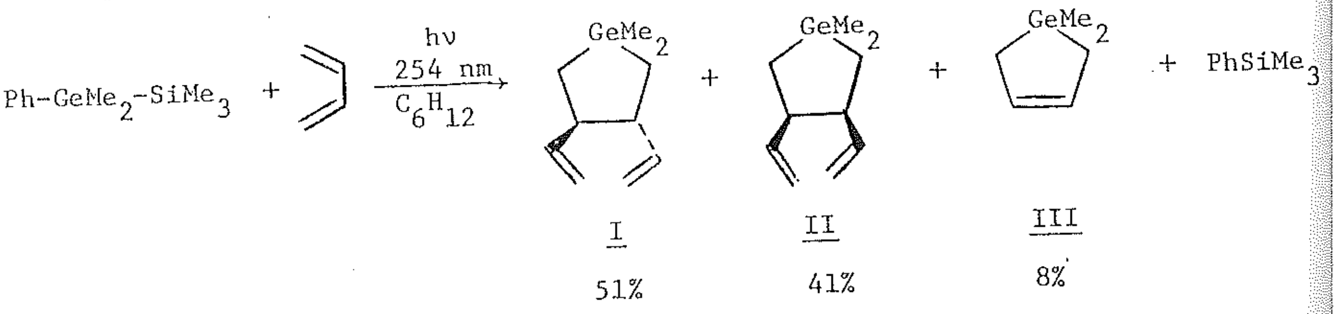
Kevin L. Bobbitt and Peter P. Gaspar

Department of Chemistry
Washington University
Saint Louis, MO 63130

Photolysis of phenyl(trimethylsilyl)germanes in the presence of 1,3-dienes leads to the isolation of phenyltrimethylsilane and high yields of products attributable to the corresponding germylene. The following reaction encourages the belief that dimethyl(phenyl)(trimethylsilyl)germane may be a convenient and efficient dimethylgermylene generator:



When butadiene is employed as the substrate for addition, the major products are apparent 1:2 adducts of dimethylgermylene to the diene, compounds I and II, formed in high yield. The 1:1 adduct, germacyclopent-3-ene III is a minor product:



The mechanism of this intriguing 1:2 addition reaction, first reported by Neumann in a thermal reaction,[1] is the subject of this report. Questions to be addressed include: 1. Are free germylenes involved? 2. Are there vinylgermirane intermediates? 3. What is the relationship between the new 1:2 addition and the better-known 1:1 addition of germylenes that has been shown to be stereospecific,[2] and for which Neumann has proposed a concerted 1,4-addition mechanism.[3] 4. Are there significant mechanistic differences between germylene-diene and silylene-diene addition reactions?

We are grateful to the National Science Foundation for support of this work under grant no. CHE-88-02677.

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3. M. Schriewer and W.P. Neumann, J.Am.Chem.Soc., 1983, 105, 897; J. Köcher and W.P. Neumann, ibid., 1984, 106, 3861; R. Marx, W.P. Neumann, and K. Hillner, Tetrahedron Lett., 1984, 25, 625.

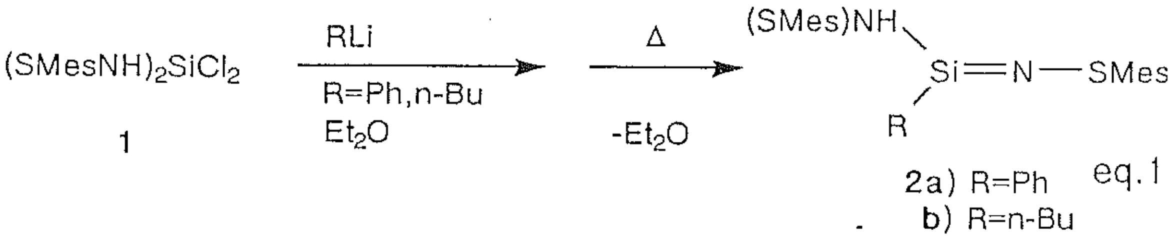
E 7

SILANAMIDINES AND RELATED COMPOUNDS

Gail E. Underiner and Robert West

Department of Chemistry, University of Wisconsin, Madison, WI 53706

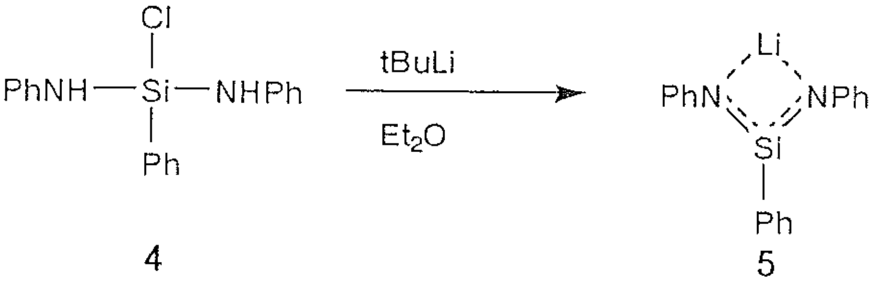
N,N'-Bis(2, 4, 6-tri-tert-butylphenyl)diaminodichlorosilane 1 reacts with phenyllithium and butyllithium to give phenyl- and butylsilanamidines 2a and 2b, respectively (eq.1). Reaction of 1 with tert-butyllithium or potassium hexamethyldisilazane yields the lithium and potassium chlorosilanamidides 3a and3b respectively (eq.2). In these anions silicon forms a partial double bond to each of two different nitrogen atoms. Compounds 2a-b and 3a-b are all colorless, air-sensitive, kinetically stable compounds.



eq.1

eq.2

N,N'-(Diphenyl)diaminophenylchlorosilane 4 also reacts with tert-butyllithium to give the corresponding lithium silanamidide 5 (eq.3). This species contains surprisingly little steric hindrance for a stable compound containing a formal silicon-nitrogen double bond.



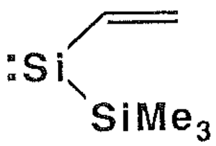
eq.3

E 8

Photolysis of Vinyltris(trimethylsilyl)silane

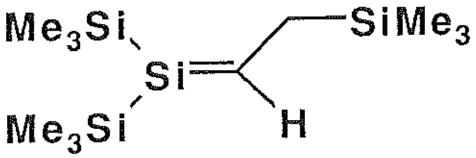
Shizong Zhang and Robert T. Conlin
Department of Chemistry
University of North Texas
Denton, TX 76205

Photolysis of vinyltris(trimethylsilyl)silane at 77 K and at room temperature with 254 nm light produces vinyl(trimethylsilyl)-silylene, **1**, 1,1-bis(trimethylsilyl)-2-trimethylsilene, **2**, and trimethylsilyl radicals, **3**. The transient species have been chemically trapped with triethylsilane and several butadienes. Uv spectra in a 3-methylpentane glass are assigned to each of the reactive intermediates. Mechanistic pathways will be discussed.



1

378 nm



2

316 nm

$Me_3Si\cdot$

3

284 nm

SESSION F

THEORETICAL STUDIES OF HIGHLY STRAINED RINGS

MARK S. GORDON AND JERRY A. BOATZ

DEPARTMENT OF CHEMISTRY
NORTH DAKOTA STATE UNIVERSITY
FARGO, ND 58105

Recent high quality ab initio calculations on silabicyclobutanes and group IV-substituted cyclopropanes will be presented. Bond stretch isomers have been found for all Si-substituted bicyclobutanes. When the two bridgehead atoms are both silicons, the bond stretch isomer is predicted to be the most stable bicyclobutane structure and exhibits little diradical character. When carbons are in the bridgehead positions, the bond stretch isomers are high energy local minima and are essentially diradicals. This suggests that Si-Si bonds can be stretched significantly and still retain most of their identities as bonds. Transition states connecting the "normal" and bond stretch isomers have been identified in each case and the reaction paths connecting the isomers will be presented.

Calculations have also been carried out on cyclopropane, 1,1-difluorocyclopropane, and their 1-sila, 1-germa, and 1-stanna analogs. The energetics of the reactions which form these rings will be presented and discussed.

WHY SILAKETONES ARE COLORED

Roger S. Grev and Henry F. Schaefer
Center for Computational Quantum Chemistry
School of Chemical Sciences
University of Georgia
Athens, Georgia 30602

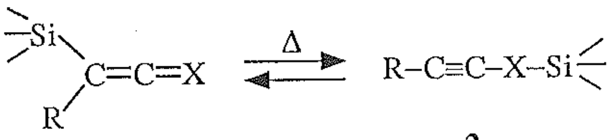
Whereas aromatic and aliphatic ketones are colorless compounds exhibiting broad, weak, structureless $n \longrightarrow \pi^*$ transitions in solution, silaketones are colored compounds with more intense, structured, electronic transitions. Reasons for the dramatic changes in the excitation profiles upon sila-substitution, and a surprising answer to the title question, will be provided from the results of an ab-initio quantum mechanical study of some simple model systems.

Thermal Isomerizations of Silylallenes and Silylheteroallenes

T. J. Barton, G. R. Magrum and B. L. Groh

Department of Chemistry
Iowa State University
Ames, Iowa 50011

The gas-phase kinetics of the thermal isomerizations of the allenic systems **1** and acetylenic systems **2** have been examined in a stirred-flow reactor in order to distinguish between a concerted 1,3-silyl shift and a stepwise mechanism.



1 **2**

(X = CH_2, O, S)

The gas-phase kinetics of the thermal decompositions of **1**/**2** (to produce >Si=X) have also been determined. It is concluded that in contrast to the **1** ⇄ **2** equilibria, the decompositions are initiated by a 1,2-silyl migration.

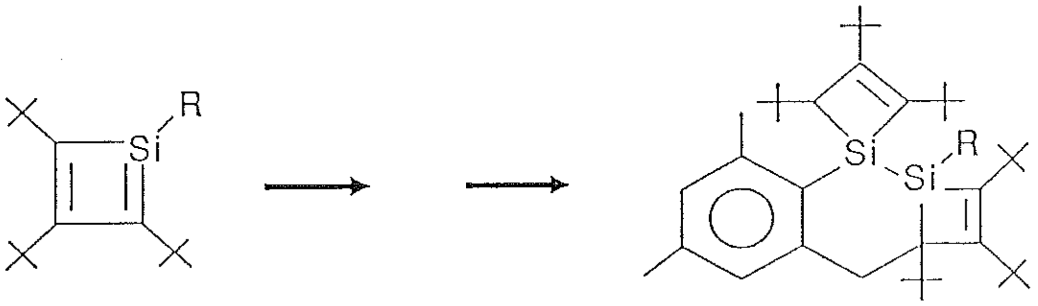
F 4

THE THERMAL REARRANGEMENTS OF TWO SILACYCLOBUTADIENES

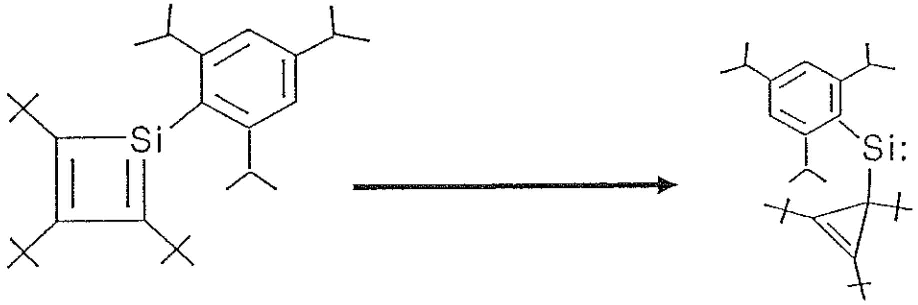
Mark J. Fink , Dhananjay B. Puranik, M. Pontier Johnson

Department of Chemistry, Tulane University
New Orleans, Louisiana 70118

The sterically hindered silacyclobutadienes 1a and 1b can be efficiently generated in 3-methylpentane glass at 77K. Upon warming to room temperature, each silacyclobutadiene decomposes by an initial unimolecular process. For the case of 1a, the unusual disilane 2 is the sole product. An X-ray structure of 2, and a mechanism for its formation, will be presented. Silacyclobutadiene 1b, on the other hand, undergoes a ring contraction isomerization to cleanly give the cyclopropenylsilylene 3. This silylene is <u>stable</u> in 3-methylpentane solution up to 200K before significant decomposition ensues. The unusual kinetic stability of this and similar silylenes will be discussed.



1a 2



1b 3

R = Mesityl; 2,4,6 trimethylphenyl

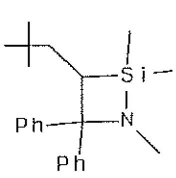
F 5

HETEROCYCLES WITH SILICON NITROGEN BONDS...SILENOIDS OR SILENE PRECURSORS?

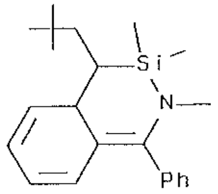
Paul R. Jones and Shi-Nian Uang

Center for Organometallic Research & Education
Department of Chemistry
University of North Texas
Denton, Texas 76203

1,1-dimethyl-2-neopentylsilene reacts with the *N*-methylimine of benzophenone to give both the sila-azetidine, **I**, and the tetrahydro-sila-isoquinoline, **II**, in 35% and 20% yields, respectively.

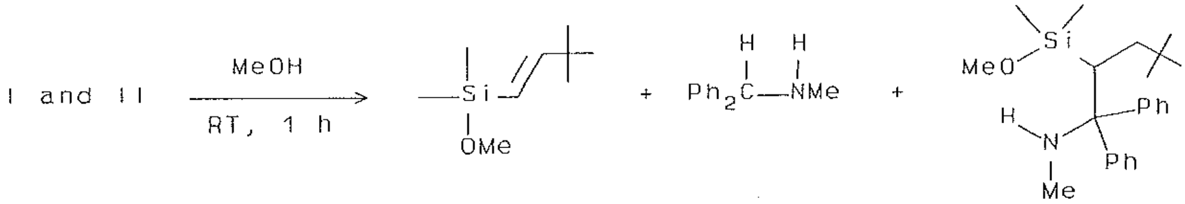


I



II

In contrast to similar compounds reported by Wiberg and coworkers,[1] **I** and **II** do not serve as thermal silene precursors. Heating the compounds to over 280° does not yield 1,3-disilacyclobutanes. In the presence of 2,3-dimethyl-1,3-butadiene typical silene trapped products are not obtained. However, **I** and **II** react rapidly with methanol at room temperature to give the ring-cleaved products **III**, **IV**, and **V**. When **V** is heated to 280° in the presence methanol small amounts the imine and the product expected from methanol addition to the silene are obtained. The major products are dimethoxydimethylsilane and 1,1-diphenyl-2-neopentylethylene.



III IV V

The mechanisms of these reactions will be discussed.

[1] Wiberg, N.; Preiner, G.; Schieda, O. *Chem. Ber.* **1981**, *114*, 3518.

Silaaziridines and 1-Sila-3-azacyclobutanes from the Reaction of Silenes with Isonitriles

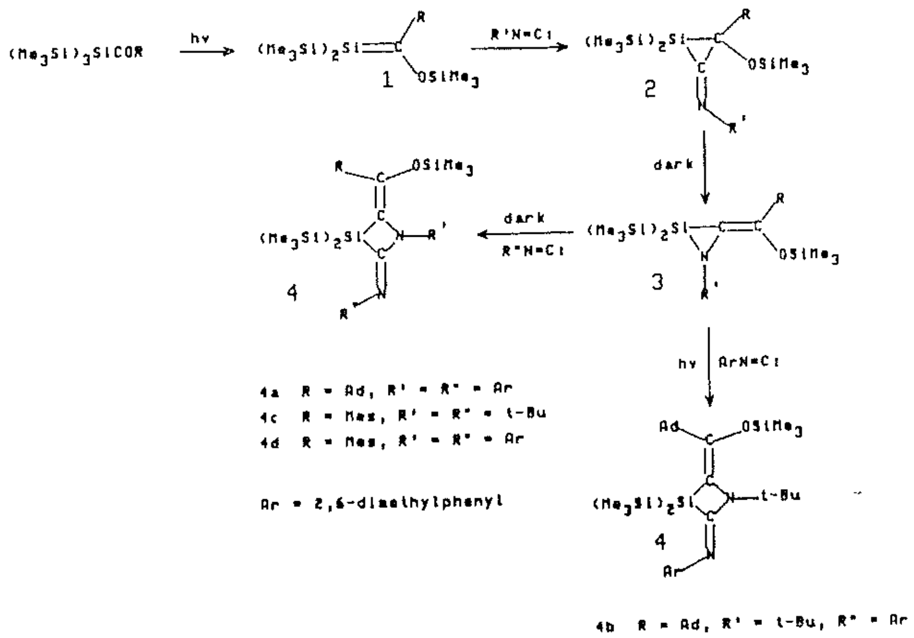
A. G. Brook, A. K. Saxena, Y. K. Kong and J. F. Sawyer

Lash Miller Chemical Laboratories
University of Toronto
Toronto M5S 1A1, Canada

Silenes, 1, of the family $(Me_3Si)_2Si{=}CR(OSiMe_3)$ react with isonitriles R'N=C: yielding unstable silacyclopropanimines 2, which even at -40° rearrange in the dark to silaaziridines 3, the first reported examples of this ring system. When R and R" are both alkyl, the silaaziridines are stable in solution: the crystal structure of one compound was obtained.

When either R or R' is an aryl group, a further reaction of the silaaziridines occurs in which a second molecule of isonitrile inserts into the ring Si-N bond leading to 1-sila-3-azacyclobutanes 4, as shown by a crystal structure.

The scope and mechanisms of these unusual rearrangements will be discussed.



4a R = Ad, R' = R" = Ar
4c R = Mes, R' = R" = t-Bu
4d R = Mes, R' = R" = Ar

Ar = 2,6-dimethylphenyl

4b R = Ad, R' = t-Bu, R" = Ar

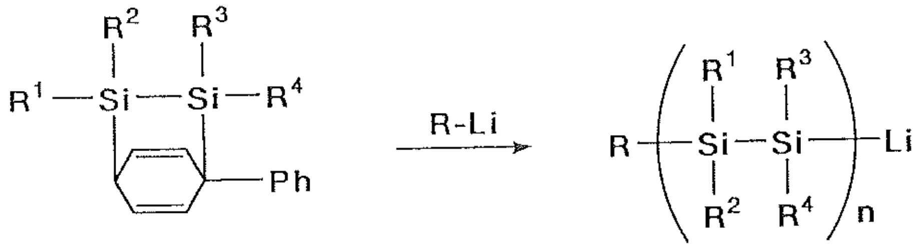
F 7

Novel Living Anionic Polymerization of Masked Disilenes to Polysilylene High Polymers and Block Copolymers

Hideki Sakurai, Kenkichi Sakamoto, Kuninori Obata, Hiroki Hirata, Masashi Nakajima, and Masaru Yoshida
Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980, Japan

Polysilylenes (polysilanes) attract much interests currently because of their unique chemical and physical properties and potential applicabilities. The method of the preparation of polysilylenes is, however, very much limited. The Wurtz type condensation has been only the way to high molecular weight polysilylenes. We now report anionic polymerization of masked disilenes as an entirely novel method of preparing polysilylenes.

Masked disilenes such as 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-dienes with an appropriate initiator led to the formation of the reactive living polysilylenyl anions, R-$(SiR^1R^2SiR^3R^4)_n^-$ (1) which gave the corresponding highly monodispersed polysilylenes (2) upon quenching. The $\overline{Mw/Mn}$ values range from 1.3 to 1.9. The reaction of the living polysilylenyl anions with methyl methacrylate (MMA) afforded well characterized block copolymers (3). Furthermore, the reaction of the living polysilylenyl anions with a variety of electrophiles led to the formation of end-functionalized polysilylenes such as polysilylene carboxylic acids (4).



(1)

$$1 \xrightarrow{ROH} R(SiR^1R^2SiR^3R^4)_nH \quad (2)$$

$$1 \xrightarrow{MMA} R(SiR^1R^2SiR^3R^4)_n\text{-}(MMA)_mH \quad (3)$$

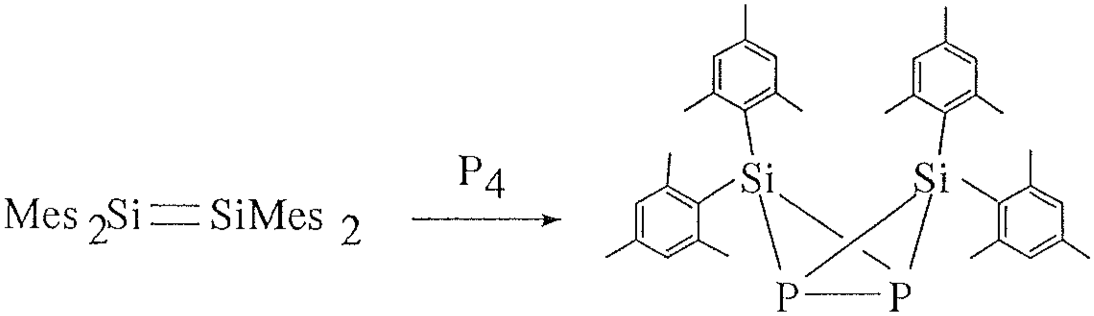
$$1 \xrightarrow{CO_2} R(SiR^1R^2SiR^3R^4)_nCOOH \quad (4)$$

F 8

SYNTHESIS AND CHARACTERIZATION OF AN UNUSUAL DISILADIPHOSPHANE WITH BUTTERFLY STRUCTURE: 1,1,3,3-TETRAMESITYL-1,3,2,4-DISILADIPHOSPHABICYCLO[1.1.0]BUTANE

Matthias Driess and Robert West
Department of Chemistry
University of Wisconsin
Madison, WI 53706 U.S.A.

The high reactivity of the silicon-silicon double bond in disilenes toward electrophiles, e.g. oxygen, sulfur, carbenes and isonitriles, is very useful for the preparation of new classes of small heterocycles containing silicon. We find that tetramesityldisilene reacts easily at +25° C in inert solvents (toluene and pentane) with white phosphorus, leading surprisingly to only one product, the title compound 1.



1

The $^{31}P\{^1H\}$-NMR spectra of 1 shows an strongly upfield resonance signal (δ = -300, 15) typical for bridgehead P atoms in tetraphospha- and diphophabicyclobutane derivatives. The ^{29}Si NMR signal at δ = -49.5 (triplet, J_{SiP} = 77Hz) is in a region characteristic for silicon in three-membered rings. Characterizations and reactions of 1 with transition metal reagents and chalcogens will also be discussed.

DISILENES: NEW STRUCTURES, NEW REACTIONS

Robert West, Brian D. Shepherd and Gregory R. Gillette

Department of Chemistry
University of Wisconsin
Madison, WI 53706 U.S.A.

X-ray crystal structures have been determined for unsolvated, thermochromic tetramesityldisilene (1) and for E-1,2-di-1-adamantyldimesityldisilene (6). These new structures are compared with those already known for disilenes:

Structures of Disilenes, $R^1R^2Si{=}SiR^1R^2$

	R^1	R^2	Si=Si, pm	Twist, °	Pyram, °	Ring Twist, °
1	Mes	Mes	214.3	3	12,14	42, 52, 67, 70
2*	Mes	Mes	216.0	12	18	35, 35, 78, 78
3	DEP	DEP	214.0	10	0	62, 62, 64, 64
4	Is	Is	214.4	3	0	52, 56, 58, 61
5	Mes	t-Bu	214.3	0	0	88, 88
6	Mes	1-Ad	213.6	0	3	87, 87

*Toluene solvate; DEP = 2,6-diethylphenyl; Is = 2,4,6-triisopropylphenyl.

The results illustrate the great variability of stereochemical arrangements possible at the Si=Si double bond. The activation energy for Z--E interconversion in 6, 28.8 Kcal mol^{-1}, is compared with other values for the rotational barrier in disilenes.

The reaction of 1 with the following azides have been investigated: Me_3SiN_3, PhN_3, $MesN_3$, $PhCH_2N_3$, $Me_3SiCH_2N_3$. The reactions follow three different pathways, all leading to the three-membered ring disilaaziridine as final product. Quite different products are obtained from 1 with $C_7H_8SO_2N_3$, $Ph_2P(O)N_3$, or HN_3.

POSTERS

Applications of Simulated Annealing to Siloxane Polymers

Frank Guarnieri, Weili Cui and Stephen R. Wilson
Department of Chemistry
New York University
Washington Square
NY, NY 10003

A new molecular modeling strategy for conformational analysis of flexible molecules has been devised. The simulated annealing algorithm has been applied to the search for the global minimum energy conformation.

Usual conformation searching techniques (grid search or tree search) involve generation of many conformations by rotation about all of the bonds (usually by 60 degrees, 6 points per dihedral angle). This results in the production of thousands of starting conformations. Each conformation is subsequently energy minimized and the duplicates discarded . This method is impractical for all but the smallest structures since the number of starting conformations involved increases as 6^N (N = number of rotatable bonds).

Simulated annealing is a Monte Carlo algorithm which has two major advantages over standard conformational analysis: it allows for energy increases as opposed to just steady minimization, and it employs a gradual temperature reduction which slowly restricts the conformation space. The run is started with the molecule at a high temperature. Initial bond rotation is randomly chosen and rotated by a random amount between -90 to +90 degrees. The energy of this new conformation is calculated. If the energy is lower, this conformation is taken to be the new conformation of the molecule. If the energy is higher, the new conformation is accepted with a Boltzmann probability. Examination of the Boltzmann factor $\exp[-(E2-E1)/kT]$ shows that acceptance of the higher energy structure depends upon the change in energy and the temperature. The higher the temperature and the lower the energy jump, the more probable an energy increase is likely to occur. The polymer molecules are cooled slowly until eventually it goes through some sort of phase transition in which a conformation freezes out.

This poster will describe the simulated annealing algorithm in general and its application to siloxane polymers in particular.

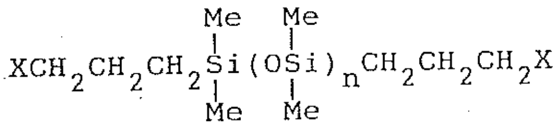
Poster 2

REACTIVE SILOXANE OLIGOMERS

Hisao Motegi and Michio Zembayashi

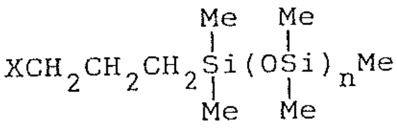
Reseach Laboratory,Toshiba Silicone Co.,Ltd.
133,Nishishinmachi,Ohta-shi,Gunma-ken,JAPAN 373

Reactive siloxane oligomers which have organofunctional groups on terminal have been developed. We have already lined up two types according to the chemical structure. One is diorganofunctional siloxane oligomers(1),and the other is monoorganofunctioal siloxane oligomers(2). Their types have been mainly utilized in order to modify organic polymers.



$$XCH_2CH_2CH_2\underset{Me}{\overset{Me}{Si}}(O\underset{Me}{\overset{Me}{Si}})_nCH_2CH_2CH_2X$$

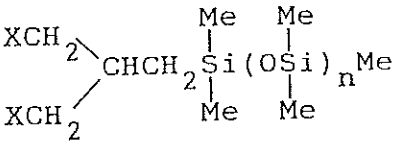
(1)



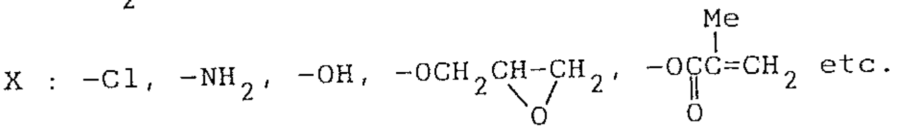
$$XCH_2CH_2CH_2\underset{Me}{\overset{Me}{Si}}(O\underset{Me}{\overset{Me}{Si}})_nMe$$

(2)

We now introduce new types of reactive siloxane oligomers which have two functional groups with the same reactivity on one side of dimethylsiloxane as shown (3). New types have the unique features that they can copolymerize with various organic polymers without incorporating siloxane chain in organic main chain and also serve as the chain extender.



(3)



Molecular Dynamics Simulation Study of Siloxanes.

*David C. Doherty, Thomas H. Lane, and Stelian Grigoras,

* University of Illinois at Chicago
Department of Chemistry
Chicago, Il 60680

Dow Corning Co., FRPI Research
Midland, Mi 48646

Abstract

A molecular dynamics (MD) simulation technique has been aplied to study several organo-siloxanes. MD provided unique insight into the time-dependent conformational behavior of molecules. MD calculations on disiloxane suggest that the coupling between the SiH_3 groups and the dispersion interactions account for a lowering of the average value of the Si-O-Si bond angle which is accompanied by a dramatic decrease in the amplitude of its vibration. These MD simulations, also suggest that the conformational flexibility of octamethylcyclotetrasiloxane, D_4, may be greater than that predicted by time-independent molecular mechanics methods. This technique was used to study the intermolecular motion of D_{12} and explains the unusual NMR relaxation data obtained experimentally by Bassindale and Pannell.

SYNTHESIS AND CHARACTERIZATION OF THE NEW PYRIDINE MOIETY CONTAINING SILICON MONOMERS

Slawomir Rubinsztajn,* Martel Zeldin, Wilmer K. Fife
Indiana University-Purdue University at Indianapolis
Department of Chemistry
1125 East 38th Street
Indianapolis, IN 46205
*Centre of Molecular and Macromolecular Studies
Polish Academy of Sciences
Lodz, POLAND

Siloxane polymers containing the pyridine moiety were found to be highly effective transacylation catalysts in the synthesis of symmetrical and mixed carboxylic anhydrides and the hydrolysis of diphenyl phosphorochloridate under phase-transfer conditions. Unfortunately, the synthesis of the polymer precursors, pyridinyl containing dichlorosilanes, and the handling of such extremely moisture sensitive monomers were difficult.

Now we wish to report a one-pot preparation of pyridinylmethyldiethoxysilanes and their characterization. Diethoxy(methyl)(pyridin-3-yl)silane was prepared by reaction of the 3-lithiopyridine with chloromethyldiethoxysilane or by Grignard reaction involving Mg metal and 3-bromopyridine in the presence methyltriethoxysilane.

Diethoxy(methyl)(pyridin-4-yl)silane was prepared by reaction of the 4-lithiopyridine with chloromethyldiethoxysilane. The new compounds were characterized by IR, ^{1}H and ^{29}Si NMR, and MS. The monomers were transformed into polymers by hydrolysis in the presence of strong base. The polymers were N-oxidized with m-chloroperoxybenzoic acid and shown to be effective catalysts in benzoic anhydrides synthesis.

Poster 5

APPLICATION OF THE DYNAMIC SIMS TECHNIQUE TO THE STUDY OF SILICONE RELEASE COATINGS

Judith Stein, Tracey M. Leonard, and Gary A. Smith

General Electric Company
Corporate Research and Development
Schenectady, NY 12301

ABSTRACT

Secondary Ion Mass Spectrometry (SIMS) depth profiling has been used to determine the location of a controlled release additive (CRA) in a UV cured epoxy functionalized silicone release coating for pressure sensitive adhesives (PSA's). The CRA, prepared by converting a fraction of the epoxy groups to 1,2-hydroxyesters via reaction with d_5 benzoic acid, was found to be uniformly distributed throughout the matrix with no apparent increase at either the air or adhesive interface when a diluent, which compatibilizes the two resins, is present. These results suggest that a minimum concentration at the surface is necessary for tight release, however, this concentration is not greater than that found in the bulk.

Poster 6

AMINOALKOXYSILANE MODIFIED IMIDES

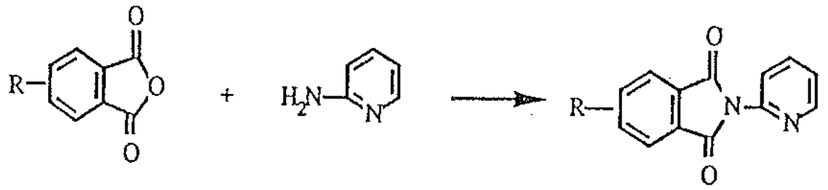
V.M . Van Valkenburgh, J.H. Wengrovius, J.L. Webb

GE Corporate Research and Development
P.O. Box 8
Schenectady, NY 12301

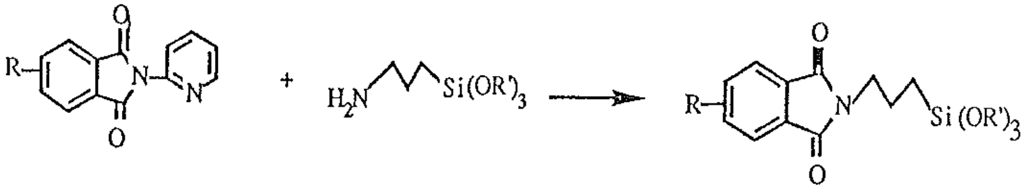
ABSTRACT

The one-step reaction between an aromatic anhydride and an aminopropylalkoxysilane results in hydrolysis and condensation of the alkoxysilane and a gelled reaction mixture. We have prepared alkoxysilylpropylimides in high yield via a two-step transimidation process. The first step involves reaction of the anhydride with an aminoheterocycle, such as 2-aminopyridine, to form the 2-aminopridylimide (1). This is subsequently reacted with an aminopropylalkoxysilane to give a high yield of the desired product, an alkoxysilylpropylimide (2). Alkoxysilylpropylimide-endcapped polyimide polymer was also prepared by the above two-step process. Additionally, silicone polyimides were synthesized via a one-step reaction between a mono-alkoxyaminosilane and an aromatic anhydride (3).

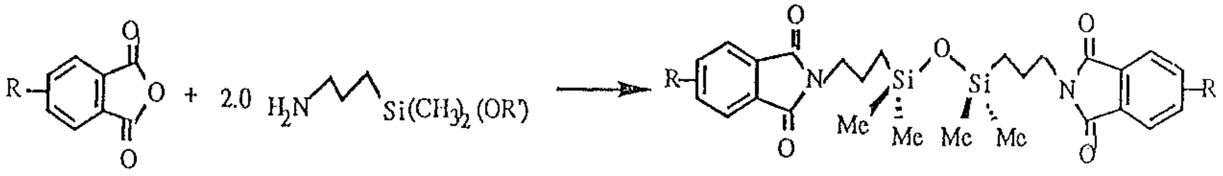
1.



2.



3.



Poster 7

Synthesis and Structures of Some Aluminosiloxane Complexes

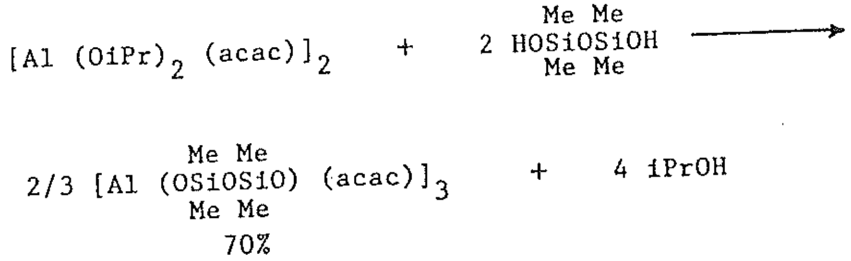
J.H. Wengrovius, V.M. Van Valkenburgh, and G.L. Bryant

GE Corporate Research and Development
P.O. Box 8
Schenectady, NY 12301

ABSTRACT

The natural occurrence of many aluminosilicates suggests that aluminosiloxane polymers may be stable, useful materials. Some aluminosiloxanes have been reported, but their physical properties are inferior to silicone polymers. A better understanding of the structural differences between silicones and aluminosiloxanes may suggest a pathway to new materials.

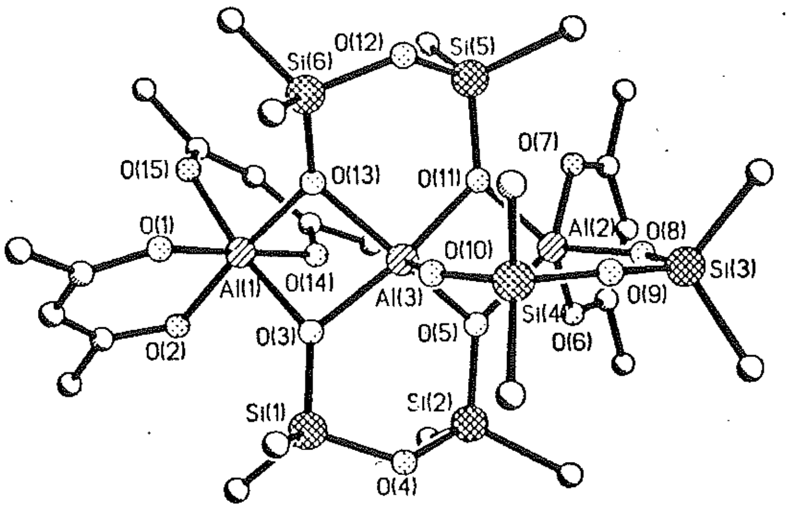
We have prepared a model aluminosiloxane by reaction of two equivalents of a siliconediol with $[Al(OiPr)_2(acac)]_2$ (acac=2,4-pentanedionate). The resulting trimer was characterized by NMR and single crystal X-ray structural analyses. Of special interest is the presence of two rare five-coordinate aluminum metal centers. Related reactions will also be described.



$$[\mathrm{Al}\ (\mathrm{OiPr})_2\ (\mathrm{acac})]_2 \quad + \quad 2\ \mathrm{HO}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{O}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{OH} \longrightarrow$$

$$2/3\ [\mathrm{Al}\ (\mathrm{O}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{O}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{O})\ (\mathrm{acac})]_3 \quad + \quad 4\ \mathrm{iPrOH}$$

70%



Poster 8

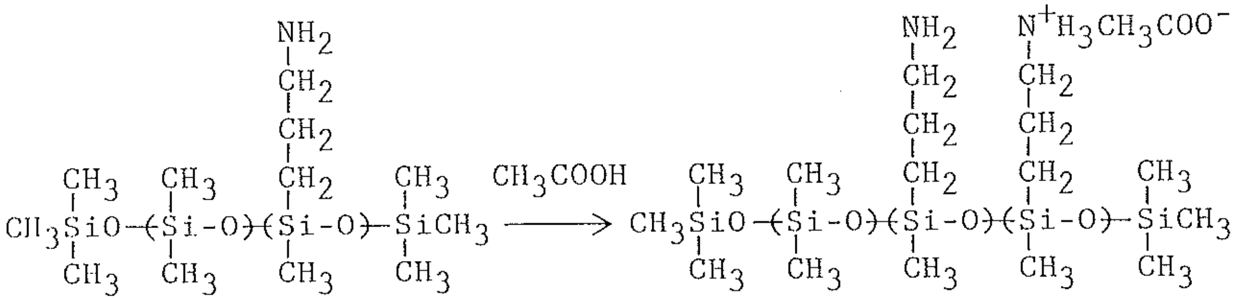
Passage Stability of the Aminosilicone Microemulsion

Noriyuki Meguriya, Masaki Tanaka

Silicone-Electronics Materials Research Center
Shin-Etsu Chemical Co.,Ltd.
2-13-1, Isobe, Annaka, Gunma 379-01, JAPAN

It is well known that the microemulsion named by Shulman et al., 1959 has been defined as a clear or translucent liquid, and the thermodynamically stable mixture of oil, water and surfactant. It is demonstrated that such a stable emulsion generally can be prepared by adding appropriate cosurfactants like alcohol to the mixture, and by introducing some hydrophilic functional groups to oil to impart more affinity for the surfactant as well.

For example:



$$CH_3\overset{CH_3}{\underset{CH_3}{Si}}O-(\overset{CH_3}{\underset{CH_3}{Si}}-O)(\overset{NH_2CH_2CH_2CH_2}{\underset{CH_3}{Si}}-O)-\overset{CH_3}{\underset{CH_3}{Si}}CH_3 \xrightarrow{CH_3COOH} CH_3\overset{CH_3}{\underset{CH_3}{Si}}O-(\overset{CH_3}{\underset{CH_3}{Si}}-O)(\overset{NH_2CH_2CH_2CH_2}{\underset{CH_3}{Si}}-O)(\overset{CH_3COO^-\,{}^+H_3NCH_2CH_2CH_2}{\underset{CH_3}{Si}}-O)-\overset{CH_3}{\underset{CH_3}{Si}}CH_3$$

Affinity property for hydrophilic surfactants in an ordinary aminosilicone can be improved by converting the amino group into its salts. Thus we can obtain the clear aminosilicone microemulsion easily by mixing this oil with water and suitable nonionic surfactants.

But the microemulsion made in such a method tends to become turbid with the passage of time. It is assumed that this phenomenon is closely related to the distribution of the amino group or its salts in the polymer.

This reaction will be discussed.

POSTER SESSION

Title: Ammonia Pyrolysis of Organosilicon Polymers: Preparation and Sintering of Amorphous Silicon Nitride Powders

Authors: Gary T. Burns*, Grish Chandra*, Jeff Ewald** and Prof. Kali Mukherjee**
* Dow Corning Corporation, Midland, Michigan 48686-0995
** Department of Metallurgy, Mechanics and Materials Science
Michigan State University, East Lansing, Michigan 48824-1226

Abstract:

Silicon nitride has emerged as one of the leading candidates for high temperature structural applications. Currently, silicon nitride powders are manufactured by : 1) thermal decomposition of silicon diimide, 2) gas phase reaction of $SiCl_4$ with NH_3, 3) carbothermic reduction of SiO_2 in a nitrogen atmosphere and 4) nitridation of silicon metal. A new route to silicon nitride powders via the ammonia pyrolysis of crosslinked organosilicon polymers was investigated.

Amorphous silicon nitride powders were prepared by the thermal decomposition of various crosslinked organosilicon polymers in an ammonia atmosphere. Polycarbosilane (PCS), methylchloropolysilane (MPS-Cl) and hydridopolysilane (HPZ) were chosen to represent the three major classes of silicon based pre-ceramic polymers . Each polymer was thermally crosslinked at 550, 400 and 400 °C, respectively. The crosslinked polymers were ground into a powder and fired to 400, 500, 600, 700, 800, 925, 1050 and 1200 °C in an ammonia atmosphere and the elemental composition of the powder determined at each temperature. From this data, it was determined that the removal of carbon and the formation of the amorphous Si-N residue occurs between 400 and 600 °C. At higher temperatures (approximately, 1500 °C), the amorphous powders partially crystallize to alpha silicon nitride.

In order to determine the effect of alkyl / aryl substitution on the efficacy of carbon removal, a series of alkyl- and aryl silsesquiazanes was prepared and pyrolyzed to 1200 °C in ammonia. In each case (R= methyl, ethyl, allyl, phenyl and 2-phenethyl), low carbon amorphous silicon nitride powders were obtained. Thus, the removal of carbon was independent of polymer structure and substitution.

The 1200 °C, amorphous silicon nitride powders were hot pressed to > 99 % of theoretical density. The strengths and microstructures were compared to those obtained with a high purity commercial powder (UBE SN-N-10).

CONFORMATIONAL CHANGES IN POLY(DI-N-ALKYLSILANES) INDUCED BY PRESSURE AND BY LOW TEMPERATURE PRECIPITATION*

C.A. Walsh[a], F.C. Schilling[b], R.B. MacGregor, Jr.[b], A.J. Lovinger[b], D.D. Davis[b], F.A. Bovey[b], and J.M. Zeigler[a]

[a]Sandia National Laboratories, Div. 1812, Albuquerque, NM 87185
[b]AT&T Bell Laboratories, 600 Mountain Ave., Murray Hill, NJ 07974

It has been previously demonstrated that poly(di-n-butylsilane) (PDBS) and poly(di-n-pentylsilane) (PDPS) have Si-backbones forming 7/3 helices under ambient conditions, whereas poly(di-n-hexylsilane) (PDHS) has an all-trans Si-backbone. It is shown here that PDBS with a trans-like backbone can be formed with the application of moderate pressure. The UV absorption maximum of the new form is red-shifted by 40 nm from that of the helical form. A trans-like form of PDBS can also be formed by precipition from dilute solution at very low temperatures. However, the polymer prepared in this manner is crystallographically disordered. The effect of pressure on the solid-solid phase transitions in PDBS, PDPS and PDHS is presented.

*Work performed at Sandia National Laboratories supported by the U.S. DOE under contract DE-AC04-76DP00789.

Prefer Poster Session

Poster 11

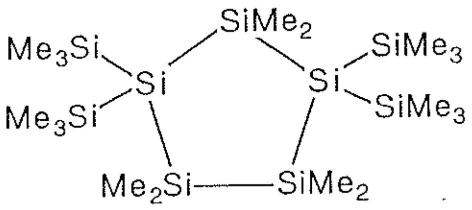
Determination of Silicon Connectivity by ^{29}Si NMR

Alan Fanta, Jim Maxka, and Robert West

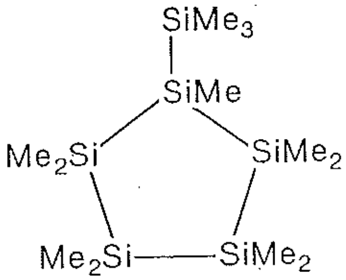
Department of Chemistry, University of Wisconsin, Madison, WI
53706 USA

Silicon connectivity in polysilanes can be obtained using 2-D INEPT-INADEQUATE experiments. However these experiments lack sensitivity due to the small amounts of adjacent ^{29}Si nuclei present in a given compound and, consequently, suffer from long data collection times. A 2-D ^{29}Si-^{1}H correlation experiment can provide the same connectivity information in a fraction of the time necessary for an INEPT-INADEQUATE experiment. The experiment detects $^{2}J_{\text{Si-H}}$ and $^{3}J_{\text{Si-H}}$ in differing magnitudes simultaneously. This means that a methyl group will correlate to the attached silicon atom as well as an adjacent silicon atom. This technique has been applied to the following compounds:

$Si_{10}Me_{22}$,



, and



Poster 12

UV EVIDENCE FOR SEVERAL CONFORMATIONS OF $Me(SiMe_2)_{16}Me$ IN SOLUTION

Robert West, LiMing Huang, Yoshitaka Hamada and Jim Maxka
Department of Chemistry
University of Wisconsin
Madison, WI 53706 U.S.A.

The polysilanes have attracted much interest recently. One of the most intriguing properties of catenated substituted silane derivatives is their remarkable electronic absorption spectra. The behavior of polysilanes, described variously as either a σ-σ^* or a $\sigma^{3d\pi}$ Si-Si transition, depends on chain length, solvent and temperature. In order to gain more understanding of the effect of conformation on the properties of permethylpolysilanes, we synthesized the $Me(SiMe_2)_{10}Me$ (**1**) and $Me(SiMe_2)_{16}Me$ (**2**) oligomers as models for the high polymers, and studied their electronic properties by ultraviolet spectroscopy.

UV absorption of **2** in 3-methylpentane or 2-methylbutane (solution or matrix) between 77K and 150K shows two sharp absorption bands at 310 and 288 nm, indicating the presence of two distinct conformations, tentatively identified as all-*trans* and all-*gauche*.

The behavior of **2** in 2-methyltetrahydrofuran is even more complex. Upon rapid cooling to 77K in this solvent, the spectrum contains three absorption bands, at 310, 285 and 253 nm. Slow warming of the sample, after melting of the matrix, leads to disappearance of the 310 nm band with growth of the 285 nm peak and no change at 253 nm. We suggest that three different conformations, *trans*, *gauche*, and "intermediate" are present at various temperatures in 2-methyltetrahydrofuran.

The shorter chain compound **1** shows similar changes indicating coexistence of at least two conformations, but the effects are less dramatic because of closer spacing of the absorption bands.

Poster 13

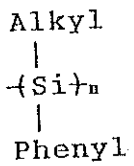
UNUSUAL THERMOCHROMISM OF ARYLALKYLPOLYSILANES

Tetsuya Asuke, Jim Maxka and Robert West

Department of Chemistry
University of Wisconsin
Madison, WI 53706 U.S.A.

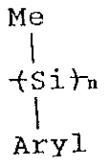
All of the polysilanes are strongly absorbing in the ultraviolet region. The electronic absorption is ascribed to excitations involving Si–Si σ electrons. Thermochromism of polysilanes is observed and appears to be due to conformational changes along the polysilane chain.

Recently we have synthesized a series of polymers.



$$\left(\overset{\text{Alkyl}}{\underset{\text{Phenyl}}{\mathrm{Si}}}\right)_n$$

Alkyl
Me
Et
Hex
Oct



$$\left(\overset{\text{Me}}{\underset{\text{Aryl}}{\mathrm{Si}}}\right)_n$$

Aryl
Ph
Tolyl
Anisyl
Biphenyl

The UV absorption maxima depend upon the electronic effect of the organic substituent groups. Most of the arylalkylpolysilanes show little thermochromism. However the arylalkylpolysilanes which have longer alkyl chains exhibit an unusual blue shift as the temperature is decreased. The conformational features of various polysilanes will be discussed.

Ordered Alternating Silane Copolymers

Rogerio Menescal , Jim Maxka and Robert West

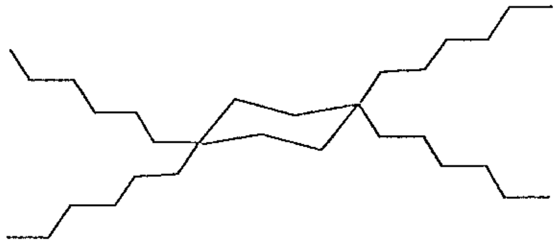
Department of Chemistry
University of Wisconsin
Madison, WI 53706, U.S.A.

Polysilanes with different silicon units have been made by many research groups but only in the form of block or random copolymers. An alternating copolymer has been reported (Matsumoto,N. and Fujino, *J. Polym. Sci.: Polym. Chem. Ed.,* 26, 109 (1988)) but temperature dependent high resolution NMR studies have led us to the conclusion that the fine structure on the ^{29}Si spectrum are due to structural rather than conformational differences in the Si-Si backbone as suggested.
We report here the synthesis of an ordered alternating polysilane, poly[bis(dimethylsilylene)-alt-hexylsilylene] according to the scheme below:

$$\mathrm{Hex_2SiCl_2} + \mathrm{PhMe_2SiLi} \longrightarrow \mathrm{PhMe_2SiSi(Hex)_2SiMe_2Ph} \xrightarrow{\mathrm{HBr,\ AlBr_3}}$$

$$\mathrm{BrMe_2SiSi(Hex)_2SiMe_2Br} \xrightarrow{\mathrm{Na/K\ ,\ toluene,\ reflux}} [\mathrm{Si(Me)_2Si(Me)_2\,Si(Hex)_2)}]_n$$

The 29 Si NMR shows two peaks at -41.7 and -36.5 ppm due to the dimethyl and di-n-hexyl units respectively with linewidths of 13.6 and 2.9 Hz and no fine structure. The main product of the polymerization reaction was however the six membered ring;



no other rings or oligomers were found in appreciable amounts.

An Examination of the β-Effect in an Addition Reaction With Different Ligands on Silicon

Michael A. Brook, Mahmud A. Hadi and Axel Neuy
Department of Chemistry, McMaster University, 1280 Main St. W., Hamilton, Ontario, Canada, L8S 4M1.

Although the β-effect, the ability of organosilicon groups to stabilize a carbonium ion in the β-position, is well documented, little is known of the rôle played by the ligands on silicon: most examples known involve trialkyl or aryl substituted silanes. In this paper, we report a study on the β-effect of silicon bearing a variety of ligands in the addition of bromine to silylstyrenes.

Koenig and Weber[1] demonstrated that in contrast to olefins such as styrene, trimethylsilylstyrene underwent *cis*-addition with bromine. Assuming, as is generally accepted, that hyperconjugation is the mechanism of β-stabilization, the greater the negative charge on the α-carbon, the greater the β-stabilization leading to a greater percentage of *cis*-addition product (the absence of such an extra stabilizing group e.g. methylstyrene (Scheme, Z=Me) leads to *trans*-addition).

Using this rational, we have examined a series of silylsubstituted styrenes in their reaction with bromine. The results are presented in the Table. As the groups on silicon become increasingly electron withdrawing, an increase in the formation of the *trans*-addition product is observed as expected. There is a reasonable correlation between the group electronegativities of the SiXYZ groups and the degree of *cis*-addition (Table). The only exception is trimethoxysilylstyrene.

This procedure for evaluating the β-effect is extremely facile both in the preparation of the starting materials and in the evaluation of the degree of stabilization. Extensions to silyl groups with more or less stabilizing ability should be readily accomplished by modifications to the phenyl group. Further work in this context in the evaluation of the rôle of steric affects of the silyl groups is currently underway.

[1] K.E. Koenig and W.P. Weber, Tetrahedron Lett., 1973, 2533.

Table 1: Degree of *cis*-Addition

SiXYZ	%*cis*-addition	Group Electronegativity
$SiMe_3$	100	2.05
$SiMe_2Cl$	100	2.12
$SiMe_2F$	87	2.23
$Si(OMe)_3$	81	2.47
$SiMeCl_2$	68	2.19
$SiCl_3$	57	2.26
$SiMeF_2$	40	2.41
SiF_3	17[a]	2.59

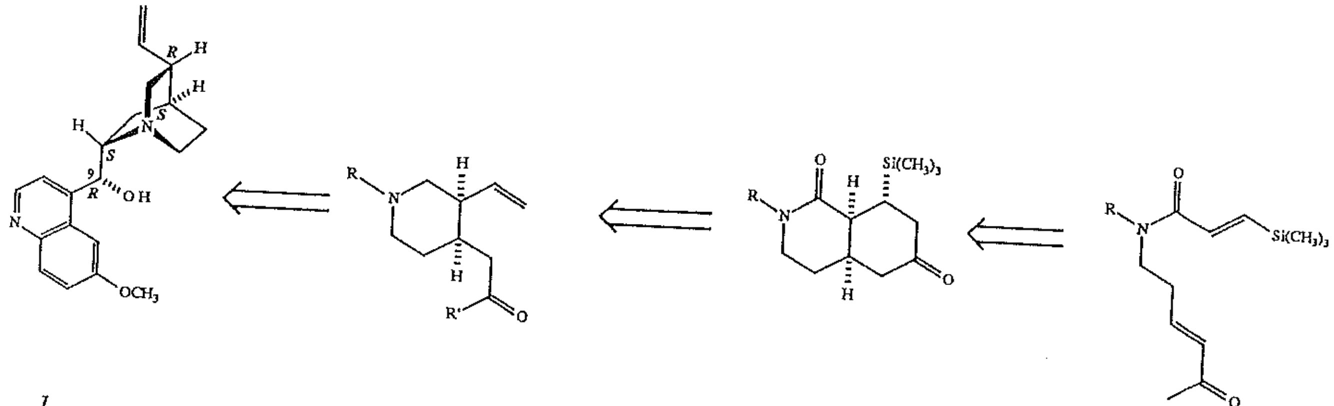
[a] Based on the ratio of bromostyrenes after elimination.

Poster 16

A SILICON DIRECTED SYNTHESIS OF QUININE

Martin J. Di Grandi, Stephen R. Wilson, Department of Chemistry
New York University, Washington Square, New York, N.Y. 10003

Meroquinene *2* (R' = OH, R = H) has been used as a key intermediate in the total synthesis of quinine *1*. In an effort to extend the usefulness of silicon directed fragmentations in the synthesis of natural products, we have prepared *4* (R = Benzyl) in four steps from benzyl amine in an overall yield of 37%.



1 *2* *3* *4*

Enone *4* was converted to lactam *3* with high stereoselectivity via an intramolecular Diels-Alder reaction; the structure of this amidoketone (*3*) was confirmed by single crystal X-ray analysis. This poster will discuss the various fragmentation methods examined for the conversion of *3* to *2* as well as the application of these compounds to a formal synthesis of quinine.

Poster 17

Synthesis and Characterization of some Aryl-Silyllithium Compounds: An Investigation of Steric and Electronic Effects

D. Greg Hendershot, E. Alan Sadurski and John P. Oliver
Department of Chemistry
Wayne State University
Detroit, Michigan 48202

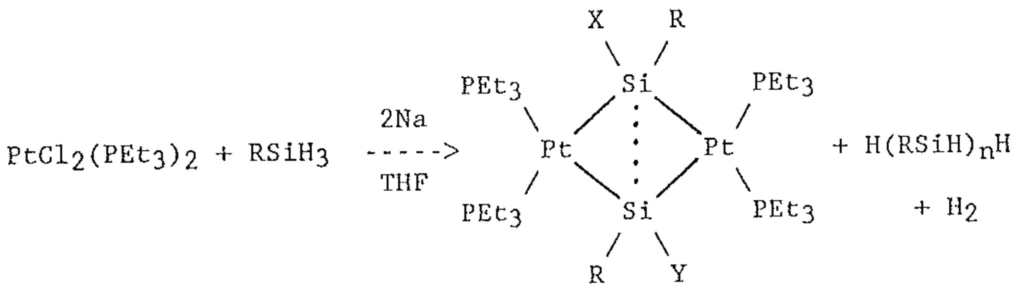
Abstract

As part of our continuing study of silicon-metal chemistry, we seek to understand factors governing the properties of silyllating agents, specifically, those of aryl-silyllithium derivatives. To date, very little is known about these types of compounds, and often reactions involving silyllithiums with main group metal halides lead to undesired products. Thus, we sought to "tune" the nature of our silyllithium. To accomplish this purpose, we chose to examine a series of aryl-silyllithium compounds with varied electronic and steric properties. Our earlier work on substituted arylsilanes demonstrated that the chemical shift of the silicon nucleus was most affected by ortho-substitution of the aryl group. Therefore, by using substitituents of differing size and electronic character, a wide range of behavior in the silyllithiums might be achieved. Thus, we have prepared several substituted aryl-silyllithium compounds of the general formula $Ar_nMe_{3-n}SiLi \cdot$ solvent (where n = 1, 2 or 3) and examined them by multinuclear NMR techniques. Results and observations from these experiments will be presented.

Spectroscopy of Metal-Silicon Dimers

Vance O. Kennedy, Claire Tessier-Youngs, Wiley J. Youngs
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

The work to be presented will stress the spectroscopic (^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR, UV-vis, and IR) characterization of metal-silicon dimers which contain short Si-Si separations. These dimers are of interest as catalytic precursors in the formation of polysilanes. The preparation of these dimers is shown in Equation 1.



(Eq. 1)

R = Ph, Tol, and Cy   X = Y = H, X = Y = Cl, X = H and Y = Cl

The spectroscopic characterization of polysilanes produced will also be presented.

The generality of the reaction in Equation 1 has been tested with other phosphine ligands and other metal (Ni and Pd) ligand systems. The preliminary results from these reactions will also be described.

Ferrocenyl Silyl Ketones

Hemant Sharma, Steven Vincenti, Francisco Cervantes, & Keith Pannell
Department of Chemistry, University of Texas at El Paso, El Paso, Texas, 79968, USA.

In 1974 Reuter and Damrauer reported the first, and only, example of a ferrocenyl silyl ketone, $FcCOSiMe_3$, Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$. The synthesis involved formation of 2-ferrocenyl-2-silyl-1,3-dithiane from ferrocene aldehyde and hydrolysis of this material to form the silyl ketone.

We have a general interest in the chemical, spectral and photochemical properties of organosilicon groups in the coordination sphere of metal ions. We will report on the synthesis (using the dithiane hydrolysis route), single crystal X-ray structural analysis, basicity toward hydrogen bonding phenol, and the relationship between the structure and the basicity of the following silyl ketones: $Fc\text{-}CO\text{-}SiR_3$, R_3Si = Me_3Si, Me_2PhSi, $MePh_2Si$, and Ph_3Si.

Attempts to synthesize oligosilyl ferrocenyl ketones using the same synthetic procedures, e.g. $Fc\text{-}CO\text{-}SiMe_2SiR_3$, SiR_3 as above, led to the exclusive formation of the corresponding monosilyl ketone $Fc\text{-}CO\text{-}SiR_3$. The use of ^{29}Si NMR to facilitate the analysis of such reactions will be illustrated. Hydrolysis of the 2-ferrocenyl-2-disilyl-1,3-dithianes results in the cleavage of the Si-Si bond and migration of the terminal Si group to the 2-position.

$$Fc\text{-}C(S_2C_2H_6)\text{-}SiMe_2\text{-}SiR_3 \ldots\xrightarrow{HgCl_2/CdCO_3/acetone/H_2O} Fc\text{-}CO\text{-}SiR_3$$

Support of this research by the NSF and R. A. Welch Foundation is gratefully acknowledged.

Poster 20

Synthesis of α-cyanoamines Via Organosilicon Chemistry

Mirna Rivera, Eduardo Pena, and Keith Pannell
Department of Chemistry, The University of Texas at El Paso, TX. 79968

The reaction of lithium diisopropylamide (LDA) with ferrocenylaldehyde leads to the formation of the amino alcoholate via attack of the amide upon the carbonyl group.

$FcCHO + LDA \qquad FcCH(N[iPr]_2O^-Li^+$

Treatment of this intermediate with trimethylsilylcyanide leads to the transient intermediacy of the expected siloxy derivative, however this rapidly transforms to the obtained cyano complex, $Fc\text{-}CH(N[iPr]_2)CN$.

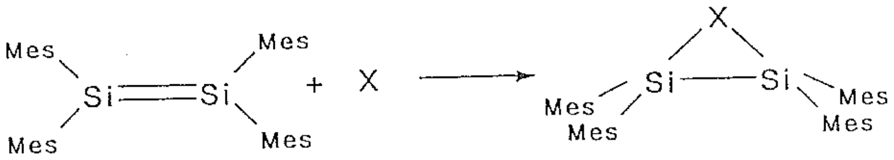
Full mechanistic and spectral details will be provided along with a single crystal X-ray structural determination of the complex which contains an almost planar amino N atom. Extension of this new chemistry to simple organic aldehydes will be presented.

Selenium and Tellurium Adducts of Tetramesityldisilene.

Robin Peng-Koon Tan, Greg Gillette and Robert West

Department of Chemistry,
University of Wisconsin,
Madison, WI 53706, U.S.A.

Reactions of disilene with oxygen and sulfur have been well studied. We now report the reaction of tetramesityldisilene with two other Group VI elements, selenium and tellurium. Both elements react with the disilene to give three-membered ring compounds.



X = Se, Te

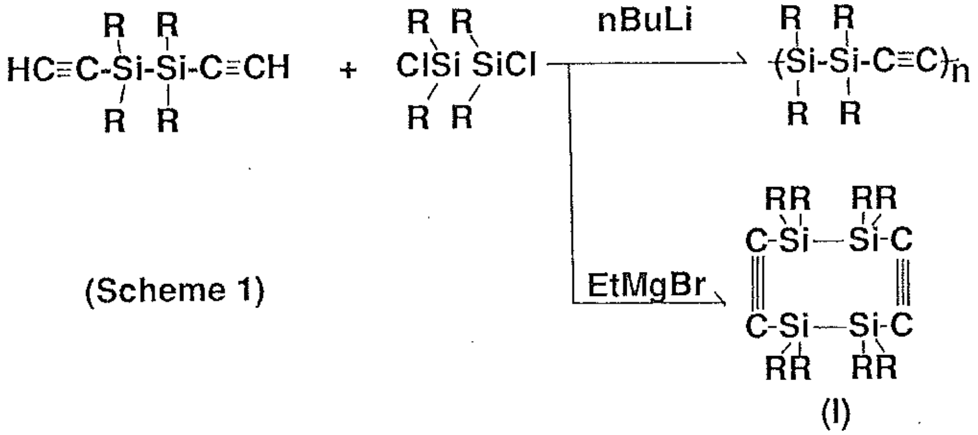
^{29}Si {H} NMR chemical shifts for these compounds are listed below, along with data for the analogous oxygen and sulfur compounds. The sulfur and selenium compounds have rather similar chemical shifts but that for the tellurium compound appears farther upfield, probably because of the greater electron-donating ability of tellurium. Some reactions of these compounds will be discussed.

X	Electronegativity	δ(ppm) $(Mes_2Si)_2X$	δ(ppm) $(t\text{-}BuMesSi)_2X$
O	3.44	-26.9	-8.0
S	2.58	-59.0	-36.1
Se	2.55	-54.6	-
Te	2.10	-89.9	-

Syntheses of ethynylene-disilene copolymers. A new ring opening polymerization of strained cyclic disilanylene-acetylenes,(1,2,5,6-tetrasilacyclo Octa-3,7-diyne)(I)

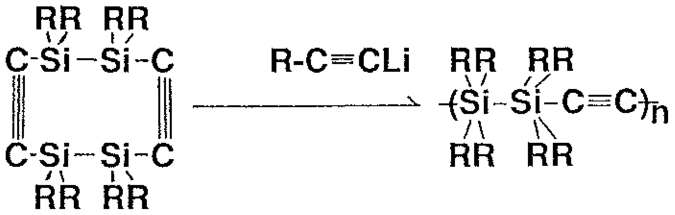
Shuzi Hayase, Takahisa Iwahara and Robert West
Department of Chemistry, University of Wisconsin, Madison, WI 53706, USA.

We have previously reported the syntheses and properties of a new Si-Si σ–π polymeric system, the ethynylene-disilanylene alternating polymers(1). These polymers were synthesized by condensation polymerization.(Scheme 1).



(Scheme 1)

In the course of the investigation, we found that the eight membered ring compound(I) was obtained in high yields by using EtMgBr instead of nBuLi(2). We now wish to report the ring opening polymerization of (I), initiated by R-C≡CLi catalysts.(Scheme 2).



(Scheme 2)

References

1) Iwahara, T. West R. Macromolecules, in press.
2) Iwahara, T. West R. J. Chem. Soc., Chem. Commun., 1988 954

Poster 23

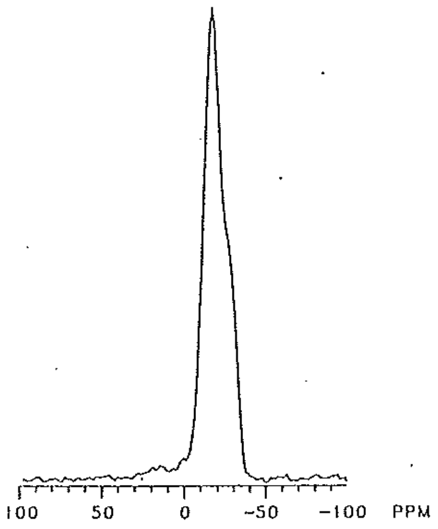
Title: Static Solid State ^{29}Si NMR Studies of Disilenes

Authors: Jeff Cavalieri, James Duchamp*, Robert West,
and Kurt Zilm*

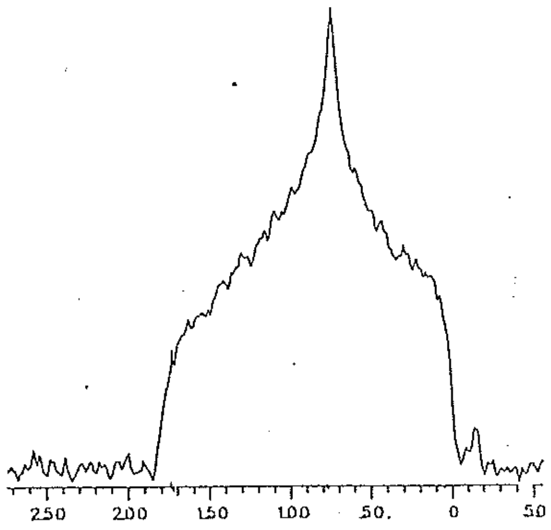
Address:
Department of Chemistry
University of Wisconsin
1101 University Avenue
Madison, WI 53706

*Sterling Labs
Yale University
New Haven, CT 06511

Text: The Chemical Shift Anisotropy (CSA) of the ^{29}Si nuclei in four disilene samples were measured. The three chemical shift tensors for each compound were determined from the spectra.



$(Me_2Si)_6$, single bonds



$Mes_2t\text{-}Bu_2Si_2$, double bond

The patterns are extremely wide compared to CSA patterns for singly-bonded silicon compounds, demonstrating the low symmetry environment of the doubly-bonded silicon atoms. These results will be compared with similar data for multiply-bonded compounds of carbon and other main-group elements, and the implications for chemical bonding will be considered.

Table: CSA tensors and isotropic shifts for some disilenes, in ppm

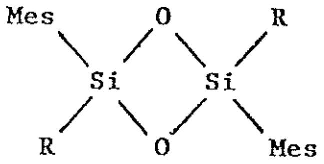
Compound	σ_{11}	σ_{22}	σ_{33}	σ_{iso}
Mes_4Si_2	183	28	-20	63.2
$Mes_4Si_2\cdot THF$	165	40	-25	59.6
trans-$Mes_2(t\text{-}Bu)_2Si_2$	178	77	3	86.1
Is_4Si_2	155	30	-31	53.1/50.8

Mes = 2,4,6-trimethylphenyl
Is = 2,4,6-triisopropylphenyl

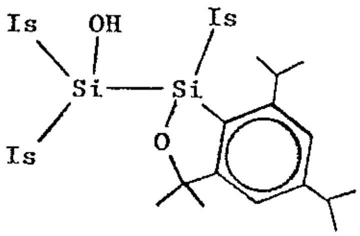
THE OXIDATION OF TETRAKIS(2,4,6-TRIISOPROPYLPHENYL)DISILENE

Anthony J. Millevolte, Lori LaPean and Robert West
University of Wisconsin-Madison
Madison, Wisconsin USA

The solution and solid-state oxidation chemistry of several disilenes has been investigated and shown to give, in addition to some interesting intermediates, compounds with the 1,3- cyclodisiloxane structure 1. Recently, an investigation of the solid-state oxidation chemistry of the considerably more hindered tetrakis(2,4,6-triisopropylphenyl)disilene was reported to yield 2, which has no analog in other disilene oxidations (Watanabe, H., et. al. Chem. Lett. 1988, p. 1343).



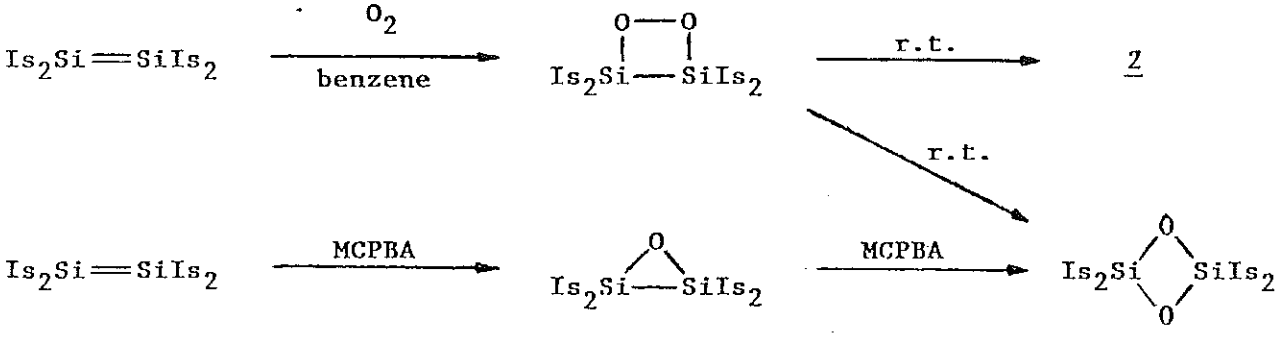
1: R = Mes, t-Bu, $(Me_3Si)_2N$, 1-Ad



2

Mes = mesityl, Is = 2,4,6-triisopropylphenyl

Because of this striking difference, we investigated, and will discuss here, the solution oxidation of this disilene with atmospheric oxygen as well as several other reagents. The air oxidation, which is much slower than for other disilenes, was determined to proceed as shown below. Also notable was the observation that dinitrogen oxide failed to react with this disilene even at 90°C. Rationalizations of these results will be presented.



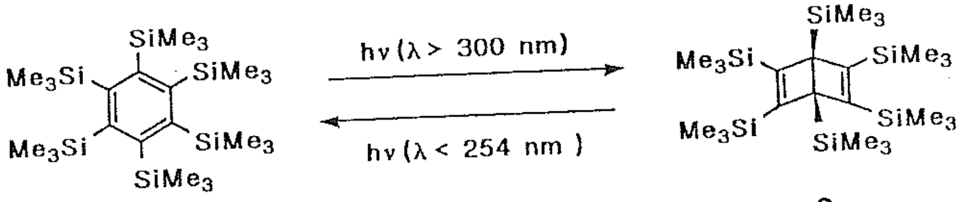
Preparation and Properties of Hexakis(trimethylsilyl)benzene and Related Compounds

Keisuke Ebata, Akira Sekiguchi, Chizuko Kabuto, and Hideki Sakurai
Department of Chemistry and Organosilicon Research Laboratory, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980, Japan

We report herein preparation of hitherto unknown hexakis(trimethylsilyl)benzene (1) and its very interesting properties. The reaction of organometallics derived from hexabromobenzene with trimethylchlorosilane did not afford the target molecule 1 at all as described before. An ingenious device was necessary for the preparation of 1.

The compound 1 was obtained as yellow crystals, mp 216 °C. The X-ray crystallographic analysis indicates a remarkably distorted structure for 1 as shown in Fig. 1. The benzene is deformed to a chair structure. Interestingly, ^{1}H NMR and other evidence show that an isomer with a boat form exists in equilibrium with the chair one. The ratio of chair to boat isomers is 89/11 at 20 °C.

The compound 1 has unusual uv absorption maxima at 320 nm ($\log \epsilon = 1.2$). Irradiation of 1 with a light ($\lambda > 300$ nm) afforded a Dewar-benzene isomer (2) very efficiently. Details of the structure and reactions of these compounds will be presented.



1

2

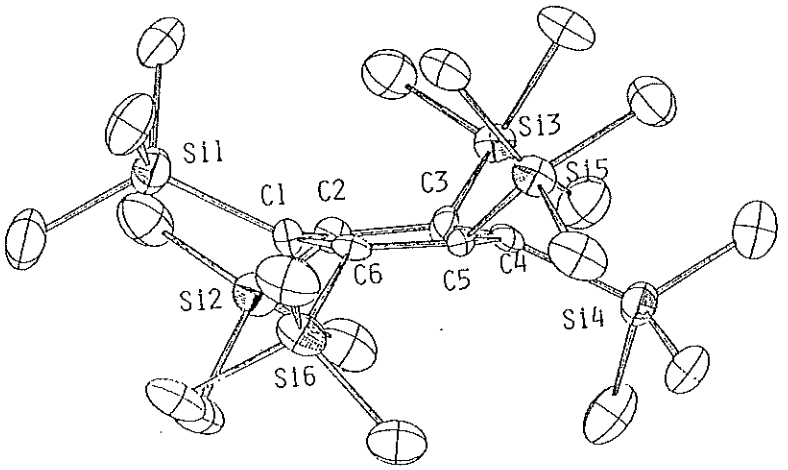


Fig. 1. X-ray crystallographic structure of 1.

Poster 26

Photochemistry of Disilanylquinones. The [3+2] Cycloaddition of Oxasila-m-quinodimethane.

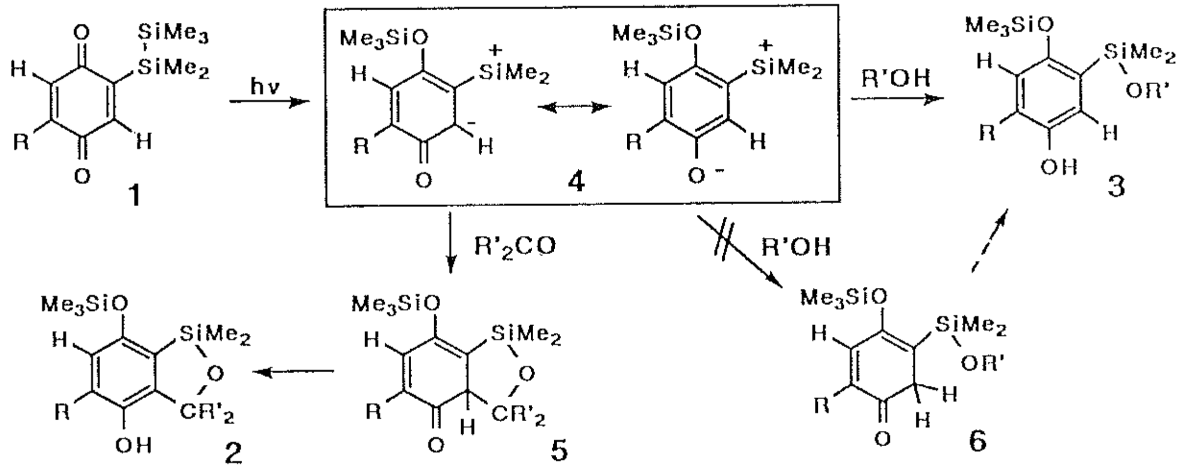
Kenkichi Sakamoto and Hideki Sakurai
Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980, Japan

Disilanylquinones (1) are an interesting class of organosilicon compounds, because the compound contains both electron withdrawing (quinone) and electron releasing (disilane) groups connected directly each other. We have recently succeeded the preparation of several derivatives of 1 and have examined interesting photochemical reactions.

The compounds 1 (R = *t*-Bu, $SiMe_3$) are obtained as reddish orange crystals. Irradiation ($\lambda \geq 520$ nm) of a hexane solution of 1 in the presence of a variety of ketones gave a yellow solution. The color of the solution faded slowly at room temperature. The usual work-up afforded colorless adducts 2. In the presence of alcohol, however, no such adduct was formed and instead an adduct of alcoho 3 was obtained.

The reaction is interpreted in terms of the intermediacy of oxasila-m-quinodimethane 4 which gives an adduct 5 by the reaction with ketone. The intermediate 5 isomerized to 2. For the reaction with alcohols, direct 1,5-addition to 3 instead of 1,3-addition to 6 was indicated by an experiment with ROD.

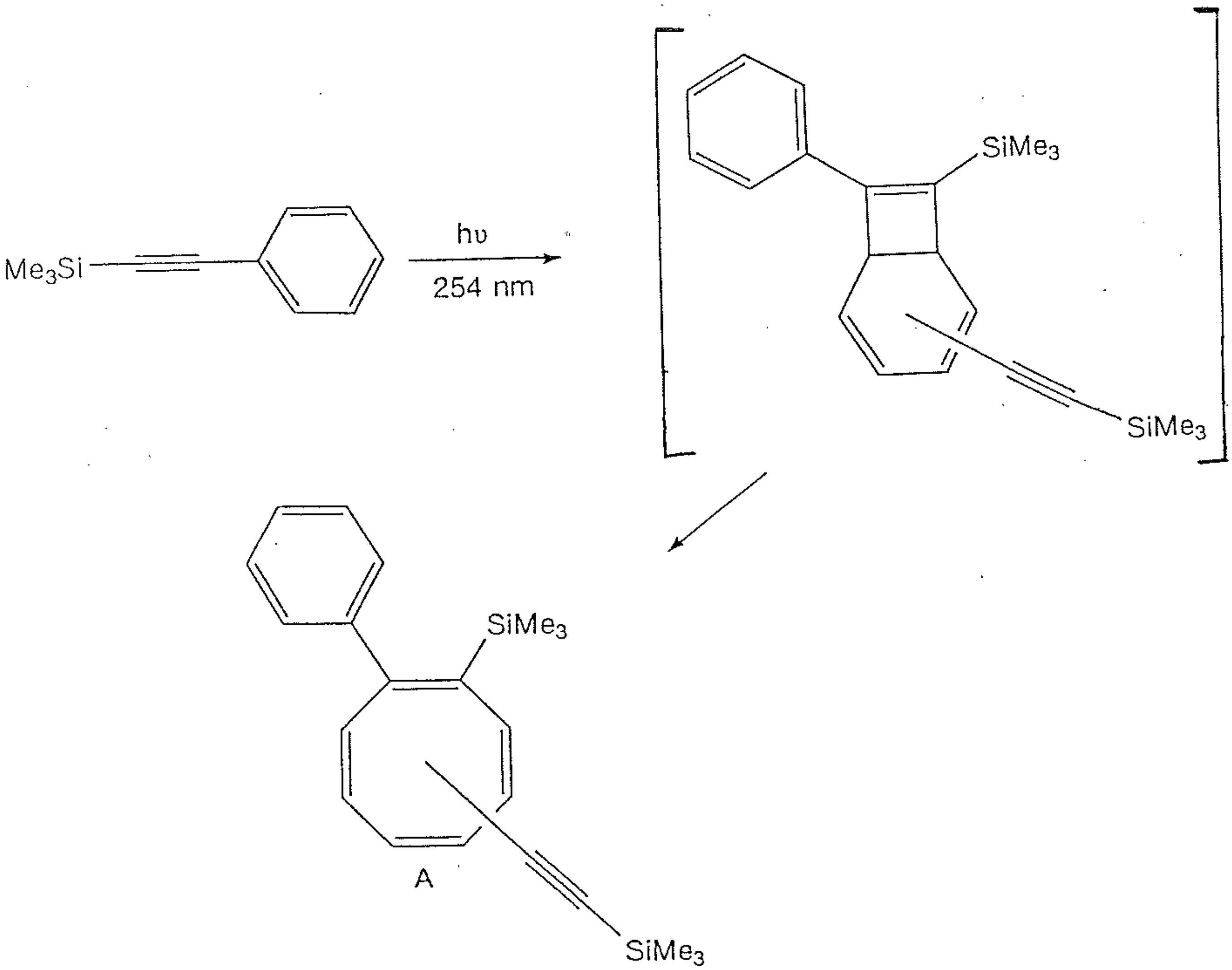
The key intermediate 4 was isolated in 77 K matrices. Spectra and chemistry of 4 indicated that 4 was not a diradical but a zwitter ion.



Photodimerization of Phenylethynyltrimethylsilane

R.S. Archibald, D. Chinnery, R. West*
Department of Chemistry, University of Wisconsin-Madison
1101 University Avenue, Madison, WI, 53706

Phenylethynyltrimethylsilane was found to dimerize when photolysed at 254 nm., either neat or in pentane solution. G.C. analysis indicated that at least three dimeric products are formed in a total yield of 15%. These isomers were analysed by GCMS, IR, ^{1}H NMR, ^{13}C NMR. The data suggest that the dimers are substituted cyclooctatetraenes with the formulas of the type A. Formation of the dimers is thought to occur via a [2+2] intermolecular cyclization between the alkyne and the phenyl group, followed by ring opening to the substituted cycloctatetraenes.



A

VIBRATIONALLY RESOLVED SPECTRA OF JET-COOLED PHENYLSILANES: THE INFLUENCE OF HYPERCONJUGATION

Mark J. Fink, Mark Sulkes, Chin Khuan Teh, and Jeffrey Sipior.

Department of Chemistry, Tulane University
New Orleans, Louisiana 70118

A series of phenylsilanes have been examined by seeding their vapor in a He carrier gas which subsequently undergoes a supersonic expansion. The vibrationally and rotationally cold ($T_{rot} \leq 5K$) isolated molecule samples which are produced have been studied via laser spectroscopy. The spectra of phenylsilane, phenyltrimethylsilane, and phenylpentamethyldisilane show previously unobserved vibrational structure. Unlike analogous spectra of alkylbenzenes, strong S_1 vibrational progressions are seen in these species. These features are not evident from their room temperature gas phase spectra. It is argued that the vibrational progressions arise from differences in hyperconjugation between the ground and excited electronic states.

A COMPARISON OF ALKOXYSILANE HYDROLYSIS RATES BY FT-IR

James A. Steinmetz, Robert Boutier and Barry Arkles
Hüls America, Inc./Petrarch Systems Silanes and Silicones
Bartram Road
Bristol, PA 19007

The relative rates of hydrolysis of alkylalkoxysilanes have been determined as a function of pH and time. Data was collected for methoxy, ethoxy and mixed methoxy/ethoxy silanes. For the mixed systems GC/IR was employed to obtain infrared spectra of each species produced. Hydrolysis studies were carried out using a horizontal internal reflection accessory with a zinc selenide crystal in a trough cell (available from Spectra Tech). All spectra were obtained using a Nicolet System 740 FT-IR Spectrophotometer.

The information obtained to date indicates that the technique of using FT-IR in the study of the hydrolysis of alkoxysilanes is a viable one.

SUPERCRITICAL FLUID FRACTIONATION OF POLYSILANES, POLYSILOXANES, AND POLYCARBOSILANES: *Results Since XXth Organosilicon Symposium*

V.J. Krukonis, P.M. Gallagher, M.P. Coffey

Phasex Corporation
360 Merrimack Street
Lawrence, MA 01843

Increased demands being placed on silicon polymers have taxed the ability of traditional separations processes to provide requisite performance characteristics. For example, molecular distillation is limited in its purification capabilities when a material's vapor pressure is extremely low, and fractional crystallization methods often cannot produce polymer fractions of satisfactory polydispersity. In 1986 the application of the pressure-dependent dissolving power properties of supercritical fluids to the processing of photoresists, high-vacuum environment sealants, and ceramic precursors was described.

Work has continued on the application of supercritical fluids to other difficult polymer/monomer separations, e.g., extraction of octaphenylcyclotetrasiloxane from polydiphenylsiloxanes, fractionation of graft and block dimethylsiloxanes, fractionation of polyvinylsilanes, and purification of functionally-terminated siloxane macromonomers. Results of many silicon polymer and copolymer systems will be presented.

ENHANCED REACTIVITY OF PENTACOORDINATED SILICON ANIONS

Joan A. Deiters
Department of Chemistry, Vassar College, Poughkeepsie, NY 12601

Robert H. Holmes
Department of Chemistry, University of Massachusetts, Amherst, MA
01003

Pentacoordinate silicon anions show enhanced reactivity in nucleophilic displacement reactions compared to neutral tetracoordinate silanes. This experimental result is somewhat unexpected since the pentacoordinate species are more sterically shielded and contain a negative charge compared to the tetracoordinate derivatives. We have carried out ab-initio calculations on the tetracoordinated series, SiH_xF_{4-x}, and on the related anionic pentacoordinated series, $[SiH_xF_{5-x}]^-$ using GAUSSIAN 86 with a 6-31+G* basis set and full geometry optimization. The results show only a small change in charge at silicon between the silanes and the pentacoordinate siliconates. However, a general loosening of all bonds in the pentacoordinate state occurs, particularly for the apical Si-F bonds as the number of hydrogen substitutents increases. This suggests that enhanced reactivity of pentacoordinated species is associated with the presence of a greater leaving group ability and not any significant change in electrophilic character at the silicon center on going from the four- to five-coordinated species.