

Triisopropylsilyl triflate and diphenylmethylsilyl triflate were similarly prepared from their corresponding chlorides.

Tris(alkylthio)silyl chloride was prepared in ca. 95% yield (estimated by ^{29}Si NMR) from SiCl_4 and *i*-PrSH (3 equiv) using the method described in the literature for the preparation of tris(alkylthio)silane from trichlorosilane.¹¹ The reaction of the chloride with 1 equiv of triflic acid gave a ca. 65% yield of the triflate (estimated by ^{29}Si NMR). Unreacted triflic acid in the reaction mixture was removed by addition of the required amount of 2,4,6-tri-*tert*-butylpyridine. An aliquot of the solution was used for NMR studies (transferred to an NMR tube under nitrogen).

BBr_3 was doubly distilled, followed by distillation from aluminum powder, in an all glass distillation apparatus, until it was completely colorless. It was then stored in a drybox. BCl_3 (Matheson) was used as received. All aromatic compounds were commercial samples of highest purity and were used as received.

The ^{29}Si and ^{11}B NMR spectra were recorded on a Varian FT-80A instrument. The silicon chemical shifts were referenced to Me_4Si , whereas the boron shifts were referenced to $\text{BF}_3 \cdot \text{Et}_2\text{O}$. GC analyses were performed on a Varian Model 3700 gas chromatography using a capillary as well as a short packed column (OV 101).

Complexation of Silyl Triflates with BX_3 . The triflate (1 mL) was placed in an NMR tube and was cooled in dry ice/acetone under dry nitrogen with exclusion of moisture. After slow addition of BCl_3 (ca. 2 mL) and vortex mixing, the sample was first studied by ^{29}Si NMR directly in BCl_3 solvent, followed by ^{11}B NMR analysis usually after removal of excess BCl_3 and SO_2ClF as solvent. With BBr_3 , whereas the addition was initially done at low temperature, the NMR tube was allowed to warm up slowly

to room temperature prior to NMR studies. Same procedure was followed for the reaction of Me_3SiOR with BCl_3 and BBr_3 .

For reactions with aromatics, the donor-acceptor complexes formed upon reaction of Me_3SiOTf or Et_3SiOTf with BCl_3 at low temperature were added to an excess of the aromatic compound precooled to ca. -40°C with efficient magnetic stirring under dry nitrogen. The temperature was then allowed to warm up slowly to room temperature, followed by an additional 30 min of mixing at room temperature. The remaining BCl_3 was then removed by passing a fast flow of nitrogen through the reaction mixture, and the mixture was analyzed by GLC. In some cases, the reaction mixtures were also subjected to aqueous workup and ether extraction prior to GLC analysis.

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Registry No. $\text{Me}_3\text{SiOTf} \cdot \text{BCl}_3$, 91158-42-8; $\text{Me}_3\text{SiOTf} \cdot \text{BBr}_3$, 91158-43-9; $\text{Et}_3\text{SiOTf} \cdot \text{BCl}_3$, 91158-44-0; *n*- $\text{Bu}_3\text{SiOTf} \cdot \text{BCl}_3$, 91158-45-1; $\text{Me}_2(i\text{-Pr})\text{SiOTf} \cdot \text{BCl}_3$, 91158-46-2; $\text{Ph}_2(\text{Me})\text{SiOTf} \cdot \text{BBr}_3$, 91158-47-3; $\text{Ph}_2(\text{Me})\text{SiOTf} \cdot \text{BCl}_3$, 91158-48-4; Me_3SiCl , 75-77-4; Me_3SiBr , 2857-97-8; Et_3SiCl , 994-30-9; *i*- Pr_3SiCl , 13154-24-0; *n*- Bu_3SiCl , 995-45-9; $\text{Me}_2(i\text{-Pr})\text{SiCl}$, 3634-56-8; $\text{Me}_2(t\text{-Bu})\text{SiBr}$, 76358-45-7; $\text{Ph}_2(\text{Me})\text{SiBr}$, 17571-61-8; $\text{B}(\text{OTf})_2$, 91158-32-6; $\text{B}(\text{OTf})\text{Br}_2$, 91158-33-7; Me_3SiOTf , 27607-77-8; Et_3SiOTf , 79271-56-0; $\text{Et}_2\text{Si}(\text{OTf})_2$, 91158-34-8; *i*- Pr_3SiOTf , 80522-42-5; *n*- Bu_3SiOTf , 91158-35-9; $\text{Me}_2(i\text{-Pr})\text{SiOTf}$, 91158-36-0; $\text{Me}_2(t\text{-Bu})\text{SiOTf}$, 69739-34-0; $\text{Ph}_2(\text{Me})\text{SiOTf}$, 91158-37-1; BCl_3 , 10294-34-5; BBr_3 , 10294-33-4; AlBr_3 , 7727-15-3; AlCl_3 , 7446-70-0; Me_3SiOMe , 1825-61-2; Me_3SiOEt , 1825-62-3; Me_3SiOPh , 1529-17-5; MeOBBR_2 , 29877-99-4; EtOBBR_2 , 91158-38-2; PhOBBR_2 , 91158-39-3; MeOBCl_2 , 867-46-9; EtOBCl_2 , 16339-28-9; PhOBCl_2 , 75088-70-9; cumene, 98-82-8; tris(isopropylthio)silyl triflate, 91158-40-6; chlorotris(isopropylthio)silane, 91158-41-7.

(11) Wolinski, L.; Tiechmann, H.; Post, H. W. *J. Org. Chem.* 1951, 16, 395.

Thermolysis of 6-Oxa-3-silabicyclo[3.1.0]hexanes: A New Convenient Route to Silicon-Oxygen π -Bonded Species

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The direct generation of silanones and germanones from easily prepared 6-oxa-3-metallabicyclo[3.1.0]hexanes is reported. Application of this method to the transient formation of an $[\text{O}=\text{Si}=\text{O}]$ species is given. This silicon analogue of carbon dioxide was trapped by hexamethylcyclotrisiloxane to yield 2,2,4,4,6,6,10,10,12,12,14,14-dodecamethyl-2,4,6,8,10,12,14-heptasila-1,3,5,7,9,11,13,15-octaaxaspiro[7.7]-pentadecane, the expected spiro adduct, in 60% yield.

Silanones, compounds containing a silicon-oxygen double bond, have been postulated as transient intermediates in a variety of reactions.¹ Most of these reactions involve the conversion of other unsaturated silicon intermediates into silanones. For example, reaction of non-enolizable aldehydes or ketones with silenes,²⁻⁶ silamines,^{7,8}

or disilenes⁹⁻¹¹ yield silanones. Likewise, reaction of silylenes with sulfoxides give silanones.¹²⁻¹⁷ On the other

(4) D. N. Roark and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, 167 (1973).

(5) P. B. Valkovich and W. P. Weber, *J. Organomet. Chem.*, 99, 231 (1975).

(6) I. M. T. Davidson, C. E. Dean, and F. T. Lawrence, *J. Chem. Soc., Chem. Commun.*, 52 (1981).

(7) C. M. Golino, R. D. Bush, and L. H. Sommer, *J. Am. Chem. Soc.*, 96, 614 (1974).

(8) D. R. Parker and L. H. Sommer, *J. Organomet. Chem.*, 110, C1 (1976).

(9) T. J. Barton and J. A. Kilgour, *J. Am. Chem. Soc.*, 96, 2278 (1974).

(1) For a general review of π -bonded silicon see: L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.*, 79, 529 (1979).

(2) T. J. Barton and E. A. Kline, Third International Symposium on Organosilicon Chemistry, Madison, WI, Aug 1972.

(3) W. Ando, A. Sekiguchi, and T. Migita, *J. Am. Chem. Soc.*, 97, 7159 (1975).

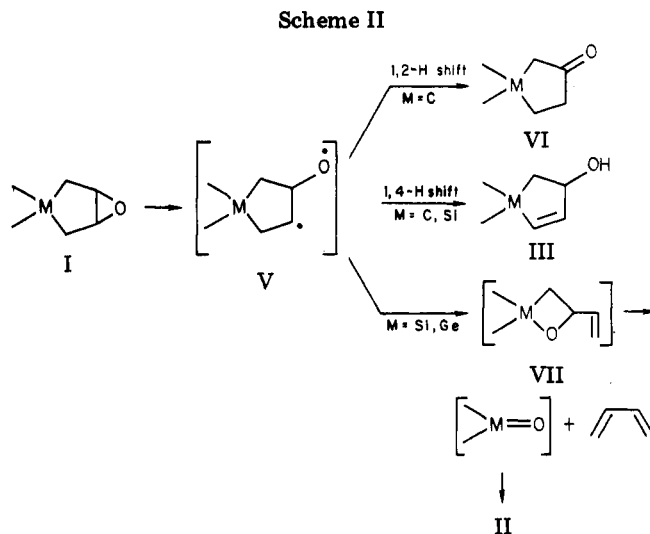
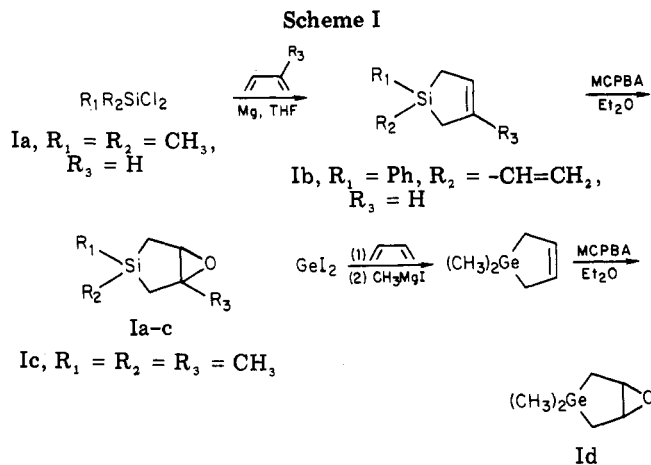


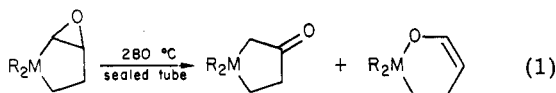
Table I. Absolute Yields of Derivatives II and III and Percentage Decomposition Observed in the Pyrolysis of I

I	M	R ₁	R ₂	% butadiene	% II	% III	% decompn
a	Si	Me	Me	85	61	7	95
b	Si	Ph	Vi	75	61	12	90
d	Ge	Me	Me	88	70	0	90

hand, silapyran-Diels Alder adducts extrude silanones directly.^{18,19}

We wish to report a simple general route to generate a variety of silicon²⁰ (or germanium) analogues of carbonyl derivatives including the carbon dioxide isologue.

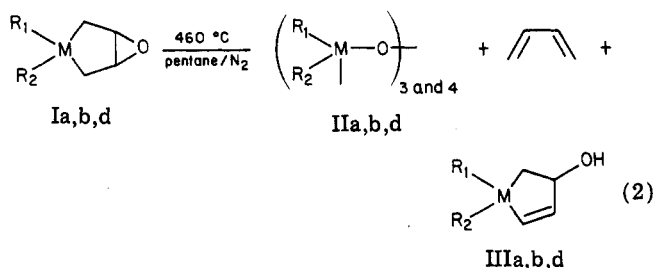
In previous papers,^{21,22} it has been shown that thermolysis of 6-oxa-2-sila(or germa)bicyclo[3.1.0]hexanes leads to 3-sila (or germa) cyclopentan-1-ones and 1-oxa-2-sila(or germa)cyclohex-5-enes (eq 1).



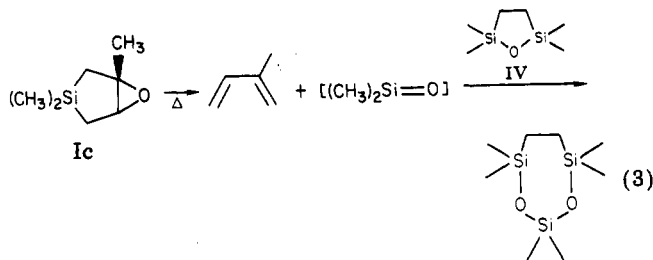
Formation of 1-oxa-2-sila(or germa)cyclohex-5-enes is of particular interest since it demonstrates the existence of intramolecular interactions between the oxygen and the metal atom. For this reason, we investigated the thermal behavior of 6-oxa-3-sila(or germa)bicyclo[3.1.0]hexanes (I) in the hope that a transannular reaction would lead to silanones or germanones.²³⁻²⁵

The starting epoxides I were synthesized in two steps²⁶⁻³⁰ in up to 90% yield (Scheme I).

Thermolysis of derivatives Ia,b,d in a flow system, at 460 °C, gave rise to cyclosiloxanes (or germoxanes) (II) and 1,3-butadiene. Depending on the nature of the metal atom and substituents, a small quantity of 3-metallacyclopent-4-en-1-ols (III)^{31,32} was also detected (Table I).



Copyrolysis of Ic and an excess of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (IV) leads to isoprene and 2,2,4,4,7,7-hexamethyl-1,3-dioxo-2,4,7-trisilacycloheptane, the expected product of trapping dimethylsilanone by IV.^{33,34}



The formation of cyclosiloxanes and germoxanes (II) has often been interpreted as evidence for the intermediacy

(10) T. J. Barton and J. A. Kilgour, *J. Am. Chem. Soc.*, **98**, 7231 (1976).

(11) M. J. Fink, D. J. De Young, and R. West, *J. Am. Chem. Soc.*, **105**, 1070 (1983).

(12) T. J. Barton and W. F. Goure, *J. Organomet. Chem.*, **199**, 33 (1980).

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

(14) I. S. Alnaimi and W. P. Weber, *J. Organomet. Chem.*, **241**, 171 (1983).

(15) W. Ando, M. Ikeno, and Y. Hamada, *J. Chem. Soc., Chem. Commun.*, 621 (1981).

(16) W. Ando, M. Ikeno, and A. Sekiguchi, *J. Am. Chem. Soc.*, **99**, 6447 (1977).

(17) R. E. Swaim and W. P. Weber, *J. Am. Chem. Soc.*, **101**, 5703 (1979).

(18) T. J. Barton and W. D. Wulff, *J. Am. Chem. Soc.*, **101**, 2735 (1979).

(19) G. Hussmann, W. D. Wulff, and T. J. Barton, *J. Am. Chem. Soc.*, **105**, 1263 (1983).

(20) G. Bertrand and G. Manuel, reported at the 17th Organosilicon Symposium, Fargo, ND, June 1983.

(21) M. Lesbre, G. Bertrand, G. Manuel, and P. Mazerolles, *C.R. Acad. Sci. Paris, Ser. C*, **284**, 709 (1977).

(22) G. Manuel, G. Bertrand, and P. Mazerolles, *J. Organomet. Chem.*, **146**, 7 (1978).

(23) For a general review of multiply bonded germanium species see: J. Satgé, *Adv. Organomet. Chem.*, **21**, 241 (1982).

(24) J. Barrau, M. Bouchaut, H. Lavayssière, G. Dousse, and J. Satgé, *J. Organomet. Chem.*, **243**, 281 (1983).

(25) J. Barrau, G. Rima, H. Lavayssière, G. Dousse, and J. Satgé, *J. Organomet. Chem.*, **246**, 227 (1983).

(26) G. Manuel, P. Mazerolles, and G. Cauquy, *Synth. React. Inorg. Met.-Org. Chem.*, **4**, 133 (1974).

(27) G. Manuel, P. Mazerolles, and J. C. Florence, *J. Organomet. Chem.*, **30**, 5 (1971).

(28) G. Manuel, P. Mazerolles, M. Lesbre, and J. P. Pradel, *J. Organomet. Chem.*, **61**, 147 (1973).

(29) P. Mazerolles, G. Manuel, and F. Thoulmas, *C.R. Acad. Sci. Paris, Ser. C*, **267**, 619 (1968).

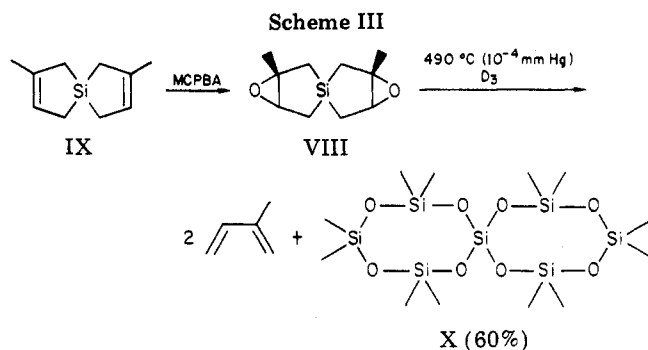
(30) G. Manuel, P. Mazerolles, and J. C. Florence, *C.R. Acad. Sci. Paris, Ser. C*, **269**, 1553 (1969).

(31) G. Manuel, G. Bertrand, and F. El Anba, *Organometallics*, **2**, 391 (1983).

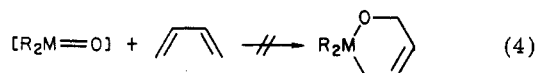
(32) A. Laporterie, G. Manuel, J. Dubac, and P. Mazerolles, *Nouv. J. Chim.*, **6**, 67 (1982).

(33) H. Okinoshima and W. P. Weber, *J. Organomet. Chem.*, **155**, 165 (1978).

(34) T. H. Lane and C. L. Frye, *J. Organomet. Chem.*, **172**, 213 (1979).



of silanones and germanones. This result along with the trapping experiment and the observation of 1,3-butadiene or isoprene is consistent with extrusion of metallanones from I. No [2 + 4] cycloaddition reaction of metallanones was observed with 1,3-butadiene or isoprene even when the thermolysis reactions were carried out in the presence of an excess of diene (eq 4). 1-Oxa-2-silacyclohex-4-enes have been shown to be stable under the pyrolysis conditions.¹³



It is interesting to compare our findings with those reported in the case of the carbon isologue. Flowers and Penny³⁵ studied the gas-phase thermolysis of 6-oxabicyclo[3.1.0]hexane (I) between 400 and 470 °C and observed formation of cyclopentanone (VI) (66%) and cyclopent-2-en-1-ol (III) (34%). A mechanism involving homolytic cleavage of a carbon-oxygen bond that leads to diradical (V), followed by 1,2- and 1,4-hydrogen shift has been postulated (Scheme II).

In the silicon and germanium series, initial formation of diradical (V) also seems reasonable. However, a 1,2 hydrogen shift that would lead to 3-metallacyclopentan-1-one (VI) was not observed under our experimental conditions, where this derivative is stable. The 1,4-hydrogen shift that gives rise to 3-metallacyclopent-4-en-1-ols (III) is a minor process. For this reason, a third route, specific to metal 4B epoxides, must be considered. We propose attack on the metal atom by the oxygen radical, with transient formation of unstable metallaoxetanes (VII)³⁶ that decomposes to silanones or germanones and 1,3-butadiene or isoprene (Scheme II).

To illustrate the wide applicability of this reaction, the possibility of generating the silicon isologue of carbon dioxide was investigated. Several diagonal silicon intermediates such as 2-silaallene³⁷⁻⁴⁰ [CH₂=Si=CH₂], silaketene³⁷ [CH₂=Si=O], and silacarodiimides⁴¹ [RN=Si=NR] have been the subject of experimental as well as theoretical studies. Note that an [O=Si=O] species has already been postulated.^{37,42}

With this goal in mind, 2,7-dimethyl-2,3,7,8-diepoxy-5-silaspiro[4.4]nonane (VIII) was synthesized by treatment of 2,7-dimethyl-5-silaspiro[4.4]nona-2,7-diene (IX) with *m*-chloroperbenzoic acid.⁴³ It was copolylyzed with a fivefold excess of hexamethylcyclotrisiloxane (D₃). Isoprene was found in essentially quantitative yield. In addition 2,2,4,4,6,6,10,10,12,12,14,14-dodecamethyl-2,4,6,8,10,12,14-heptasila-1,3,5,7,9,11,13,15-octaoxaspiro[7.7]pentadecane (X)^{44,45} was isolated in 60% yield (Scheme III).

These results may be interpreted in terms of insertion of a reactive intermediate [O=Si=O] into the silicon-oxygen single bond of two molecules of hexamethylcyclotrisiloxane. Obviously, an alternative possibility is that the reactive silicon-oxygen double bonds are generated stepwise.

Conclusion

These results emphasize the role of the metallic Si or Ge heteroatoms on the thermal behavior of 6-oxa-3-metallabicyclo[3.1.0]hexanes. In contrast with the carbon series, a transannular reaction takes place leading to transient metallaoxetanes. Since the starting materials are easily available, this method allows the facile generation of various metal 4B-oxygen π -bonded species.

Experimental Section

¹H NMR spectra were obtained on JEOLCO-90FX-Q or IBM-Brucker WP-270-SY spectrometer operating in the FT mode using 5% solution of deuteriochloroform. Chloroform was utilized as the internal standard. The integration of the NMR spectra sometimes gave too small intensities for the SiCH₃ signals because of saturation problems. However, in all cases the integration was within 10% of the calculated value. ¹³C NMR spectra were obtained on an IBM-Brucker WP-270-SY using 10–15% solution in deuteriochloroform. Chloroform was utilized as an internal standard. ¹³C spectra were run with broad-band proton decoupling.

IR spectra were obtained on a Perkin-Elmer 281 or Nicolet MX-1 Fourier Transform spectrometer. Low-resolution mass spectra were obtained on a Hewlett-Packard 5985 GC-MS at an ionizing voltage of 70 eV. A 20 in. \times 1/8 in. in 2% OV-10 on 100/120 mesh chromosorb W column was used in the gas chromatography inlet of the mass spectrometer. High-resolution mass spectra were obtained on an A.E.I. MS-902 at 70 eV. Exact mass were determined by peak matching against peaks of known mass of perfluoro kerosene. GLPC analysis as performed on a Hewlett-Packard F&M 700.

1,1-Dimethyl-1-silacyclopent-3-ene,^{26,46} 1,1,3-trimethyl-1-silacyclopent-3-ene,^{28,46} 1,1-dimethyl-1-germacyclopent-3-ene,^{28,48} and the corresponding epoxides 3,3-dimethyl-6-oxa-3-silabicyclo[3.1.0]hexane,²⁷ 1,3,3-trimethyl-6-oxa-3-silabicyclo[3.1.0]hexane,²⁷ 3,3-dimethyl-6-oxa-3-germabicyclo[3.1.0]hexane,²⁸ and 3,3-dimethyl-3-silacyclopent-4-en-1-ol^{31,47} were prepared by previously reported methods and had spectral and physical properties in complete agreement with literature values.

Synthesis of 3-Phenyl-3-vinyl-6-oxa-3-silabicyclo[3.1.0]hexane (Ib). A solution of 1-phenyl-1-vinyl-1-silacyclopent-3-ene²⁸ (9.45 g, 0.05 mol) in ether (50 mL) was added dropwise to a stirred solution of *p*-nitroperbenzoic acid (10.2 g, 0.05 mol) in ether (50 mL), at 0 °C. After filtration, the solution was washed with a 10% NaOH solution and then with water. After drying

(35) M. C. Flowers and D. E. Penny, *J. Chem. Soc., Faraday Trans. 1*, **70**, 355 (1974).

(36) Up to now, only one example of stable siloxetane have been reported. G. Märkl and M. Horn, *Tetrahedron Lett.*, **24**, 1477 (1983).

(37) G. Bertrand, G. Manuel, and P. Mazerolles, *Tetrahedron*, **34**, 1951 (1978).

(38) J. C. Barthelat, G. Trinquier, and G. Bertrand, *J. Am. Chem. Soc.*, **101**, 3785 (1979).

(39) M. S. Gordon and R. D. Koob, *J. Am. Chem. Soc.*, **103**, 2939 (1981).

(40) M. H. Lien and A. C. Hopkinson, *Chem. Phys. Lett.*, **80**, 114 (1981).

(41) W. Ando, H. Tsumaki, and M. Ikeno, *J. Chem. Soc., Chem. Commun.*, 597 (1981).

(42) C. M. Golino, R. D. Bush, and L. H. Sommer, *J. Am. Chem. Soc.*, **97**, 7371 (1975).

(43) D. Terunuma, S. Hatta, T. Araki, T. Ueki, T. Okazaki, and Y. Suzuki, *Bull. Chem. Soc. Jpn.*, **50**, 1545 (1977).

(44) D. W. Scott, *J. Amer. Chem. Soc.*, **68**, 357 (1946).

(45) K. A. Andrianov, M. A. Sipyagina, and N. P. Gashnikova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2493 (1970).

(46) D. R. Weyenberg, L. H. Toporcer, and L. E. Nelson, *J. Org. Chem.*, **33**, 1975 (1968).

(47) A. Laporterie, J. Dubac, and P. Mazerolles, *J. Organomet. Chem.*, **202**, C87 (1980).

(48) A. Laporterie, G. Manuel, J. Dubac, P. Mazerolles, and H. Iloughmane, *J. Organomet. Chem.*, **210**, C33 (1981).

over Na_2SO_4 , ether was removed at reduced pressure (15 mmHg). Distillation led to 8.1 g of Ib (79% yield): bp 170 °C (30 mmHg); n_D^{20} 1.5578; IR (neat) $\bar{\nu}$ 1590 cm^{-1} ($\text{CH}=\text{CH}_2$); $^1\text{H NMR}$ (CCl_4) δ 0.8–1.7 (m, 4 H, SiCH_2), 3.3 (m, 2 H, CH), 5.4–6.7 (m, 3 H, $\text{CH}=\text{CH}_2$), 7.1–7.7 (m, 5 H). Anal. Calcd: C, 71.23, H, 6.97. Found: C, 71.26; H, 6.87.

Synthesis of 3-Phenyl-3-vinyl-3-silacyclopent-4-en-ol (IIIb). A pure sample of IIIb was prepared by photooxygenation of 1-phenyl-1-vinyl-1-silacyclopent-3-ene followed by reduction of the resulting hydroperoxide according to the procedure previously described by Laporterie et al.³²

The photooxygenation of 1-phenyl-1-vinyl-1-silacyclopent-3-ene (3.7 g, 0.02 mol) was followed by reduction of the crude hydroperoxide in methanol by NaBH_4 (5 g, excess). After removal of the solvent, the residue was extracted with ether (200 mL) and the etheral solution washed with water (2×50 mL). After the solution was dried over Na_2SO_4 , the ether was removed. Fractional distillation led to 2.7 g of IIIb (66% yield): bp 120 °C (0.2 mmHg); IR (neat) 3310 (OH), 1590 ($\text{HC}=\text{CH}_2$), 1560 cm^{-1} ($\text{CH}=\text{CH}_2$); $^1\text{H NMR}$ (CCl_4) SiCH_2 (two AB parts of two ABX systems corresponding to the two diastereoisomers 50/50, δ_A 1.56, δ_B 0.99, $J_{AB} = 15$ Hz, $J_{AX} = 2$ Hz, $J_{BX} = 1.4$ Hz and δ_A' 1.69, δ_B' 0.88, $J_{A'B'} = 15.2$ Hz, $J_{A'X'} = 2$ Hz, $J_{B'X'} = 1.4$ Hz), OH (4.3 ppm), CHOH (4.9 ppm, m), $\text{CH}=\text{CH}_2$ and $\text{SiCH}=\text{CH}$ (5.6–6.8 ppm, m), $\text{SiC-H}=\text{CH}$ (rest A of an ABX system centered at 7.05 ppm, $J_{AB} = 10$ Hz, $J_{AX} = 2$ Hz), (7.2–7.8 ppm, 5 H). Anal. Calcd: C, 71.26; H, 7.07. Found: C, 71.35; H, 7.11.

Synthesis of 2,7-Dimethyl-5-silaspiro[4.4]nona-2,7-diene (IX).⁴³ Crude diethoxydichlorosilane, obtained by heating SiCl_4 (34 g, 0.2 mol) and $\text{Si}(\text{OEt})_4$ (41.6 g, 0.2 mol), in a sealed tube, at 160 °C, for 3 days, is added to a THF solution (500 mL) containing Mg (24.3 g, 1 mol) and isoprene (68 g, 1 mol). The mixture was stirred under reflux for 24 h under a nitrogen atmosphere. Water (200 mL) was added dropwise to the reactive mixture, and the organic layer was separated and evaporated. The pentane extracts of the residue was dried over CaCl_2 . Evaporation and distillation gave 55.1 g of IX (84% yield from SiCl_4 (lit.⁴³ 52%)): bp 104–106 °C (30 mm Hg) (lit.⁴³ 140 °C (105 mm Hg)); $^1\text{H NMR}$ (CCl_4) δ 1.3–1.6 (m, 8 H, SiCH_2), 1.7–1.9 (m, 6 H, CH_3), 5.45–5.70 (m, 2 H, CH).

Synthesis of 2,7-Dimethyl-2,3,7,8-diepoxy-5-silaspiro[4.4]nonane (VIII). To a stirred solution of *m*-chloroperbenzoic acid (8.7 g, 0.05 mol) in ether (100 mL), at –10 °C, was added a solution of IX (4.1 g, 0.025 mol) in ether (30 mL) dropwise. The resulting mixture was stirred at room temperature for 10 h, then washed with a 10% NaOH solution (3×40 mL) and with water (2×50 mL), and dried on CaCl_2 . Evaporation and distillation gave 3.8 g of VIII (77% yield (lit.⁴³ 65.3%)): bp 81 °C (0.4 mm Hg) (lit.¹⁹ 80 °C (0.45 mm Hg)); $^1\text{H NMR}$ (CCl_4) δ 0.7–1.3 (m, 8 H, SiCH_2), 1.35 (s, 6 H, CH_3), 3.05 (br s, 2 H, CHO).

Pyrolysis of 6-Oxa-3-metallabicyclo[3.1.0]hexanes (Ia,b,d). The pyrolysis were conducted in a 30-cm vertical Pyrex tube packed with Pyrex chips and enclosed in a tube furnace heated to 460 °C. A 20% solution of I in pentane was mechanically added at a rate of 2 mL/h concomitant with a nitrogen flow of 20 mL/mn. The pyrolysate was collected in a liquid-nitrogen-cooled

trap, and the major products were identified. One of these was identified as 1,3-butadiene by comparison of its GC retention time and its GC-MS with those of an authentic sample. Cyclosiloxanes and cyclogermoxanes as well as 3-silacyclopent-4-en-1-ols were purified by preparative GC on a 20 ft \times 0.25 in. 15% SE-30 column and their IR and $^1\text{H NMR}$ spectra compared with those of authentic samples. Yields were determined by gas chromatography using authentic samples of the products as internal standards. Percentage of decomposition and yield of 1,3-butadiene were estimated by ^1NMR of the crude pyrolysate.

Pyrolysis of 2,7-Dimethyl-2,3,7,8-diepoxy-5-silaspiro[4.4]nonane (VIII). Compound VIII was copyrolyzed with a fivefold excess of hexamethylcyclotrisiloxane through a 30-cm quartz tube that was heated to 490 °C with a pressure of 10^{-4} torr. The pyrolysate was collected in a liquid-nitrogen-cooled trap. Isoprene was found in essentially quantitative yield. In addition, 2,2,4,4,6,6,10,10,12,12,14,14-dodecamethyl-2,4,6,8,10,12,14-heptasila-1,3,5,7,9,11,13,15-octaoxaspiro[7.7]pentadecane was isolated, in 60% yield, by preparative GLPC on a 4 ft \times 0.25 in. 20% SE-30 column: $^1\text{H NMR}$ (CDCl_3) δ 0.103 (s, 24 H), 0.075 (s, 12 H); $^{13}\text{C NMR}$ (CDCl_3) δ 0.761 (8 C), 0.599 (16 C); IR 1100, 1060 cm^{-1} ($\nu_{\text{Si-O}}$); mass spectrum, *m/e* (relative intensities) 489 (30%, $M - 15^+$), 401 (69%), 385 (15), 227 (12.6), 147 (11.3), 73 (100); high-resolution mass spectrum ($M - 15$)⁺ calcd for $\text{Si}_7\text{C}_{11}\text{H}_{33}\text{O}_8$ ⁺ 489.0560, found 489.0577.

Copyrolysis of 1,3,3-Trimethyl-6-oxa-3-silabicyclo[3.1.0]hexane (Ic) and 2,2,5,5-Tetramethyl-1-oxa-2,5-disilacyclopentane (V). 1,3,3-Trimethyl-6-oxa-3-silabicyclo[3.1.0]hexane (Ic) (1 g, 7 mmol) was copyrolyzed with 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (3.5 g, 21.86 mmol) through a 30-cm quartz tube that was heated to 490 °C with a pressure of 10^{-3} torr. The pyrolysate was collected in a liquid-nitrogen-cooled trap. Isoprene was found in quantitative yield. In addition, D_3 (40%), D_4 (18%), and 2,2,4,4,7,7-hexamethyl-1,3-dioxa-2,4,7-trisilacycloheptane (41%) were isolated. 2,2,4,4,7,7-Hexamethyl-1,3-dioxa-2,4,7-trisilacycloheptane has the following spectral properties:^{33,34} $^1\text{H NMR}$ (CDCl_3) δ 0.714 (s, 4 H), 0.071 (s, 12 H), 0.040 (s, 6 H); mass spectrum, *m/e* (relative intensities) 219 (100, $M^+ - 15$), 191 (87), 141 (61), 133 (14), 117 (71), 88 (28), 74 (90), 73 (63).

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