rection varied from 0.986 to 1.027. Owing to the low absorption coefficient (1.97 cm^{-1}) no absorption correction was applied. Of the 2651 unique normalized structure factors, 2138 had $F_o^2 \geq 2\sigma(F_o^2)$, where a value of 0.03 was used for p, the ignorance factor[27] in calculating $\sigma(F_o^2)$.

The position of the sulfur atom was assigned from a sharpened origin-removed Patterson map. Positions of the remaining nonhydrogen atoms were obtained from electron density syntheses based on phases derived from atoms in known positions. On convergence of refinement with anisotropic thermal parameters, the proper choice of enantiomers was tested by changing all coordinates to their negatives and refining this model to convergence. Both models converged to $R_1 = 0.0903$.[27] Refinement of the original model was continued with inclusion of hydrogen atoms in fixed idealized positions (see Table E[17]) and converged to $R_1 = 0.063$ and $R_2 = 0.058$. In the final cycle of refinement, the average shift per error was 0.008. At this point the choice of enantiomer was again checked and again the models were found to be indistinguishable based on the R values.

A total of 2138 reflections were used to refine 199 variables. A final difference map was essentially featureless. The highest peak (0.5 e $Å^{-3}$) was 0.9 Å from the sulfur atom. Examination of groups of reflections ordered on $\sin \theta/\lambda$ or $|F_o|$ revealed no significant trends in disagreement with the model. Zerovalent scattering curves from Cromer[28] were used for S, O, N, and C. Those for hydrogen were taken from Stewart.[29] Corrections for anomalous dispersion due to S, O, N, and C were made.[30] The final values of $|F_o|$ and F_c are listed in Table F.[17]

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Supplementary Material Available: Tables A–F, containing atomic positions, bond lengths, angles, root mean square displacements of anisotropic thermal ellipsoids, anisotropic thermal parameters, hydrogen fractional atomic coordinates, and observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Mechanism of the Reactions of Dimethylsilylene with Oxetanes

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Abstract: Dimethylsilylene reacts with oxetane to give high yields of allyloxydimethylsilane and 2,2-dimethyl-1-oxa-2-silacyclopentane. These products result from decomposition of an initial 1,2-zwitterionic intermediate which is formed by coordination of the electrophilic dimethylsilylene with the oxygen of oxetane. Similar results have been obtained from the reactions of dimethylsilylene with 2-methyloxetane, 2,2-dimethyloxetane, 3,3-dimethyloxetane, and 2-vinyloxetane.

We should like to report a novel insertion reaction of dimethylsilylene into the strained carbon-oxygen single bonds of oxetanes.[1] For example, dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane[2] in oxetane solvent at 0 °C yields allyloxydimethylsilane[3] (I, 38%) and 2,2-dimethyl-1-oxa-2-silacyclopentane[4] (II, 41%). The yields reported are based on the generation of two dimethylsilylenes from each dodecamethylcyclohexasilane.[2] It should be noted that in control experiments no reaction of dimethylsilylene with unstrained aliphatic ethers such as tetrahydrofuran or diethyl

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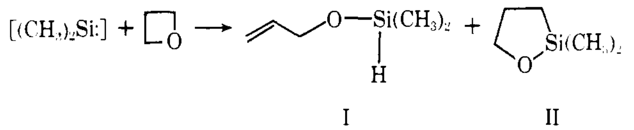
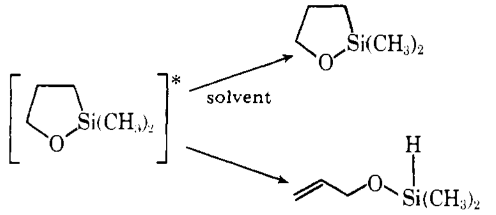
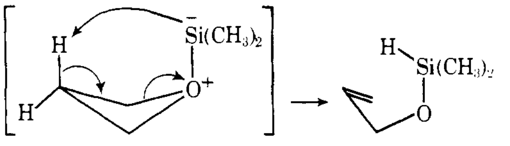

I II

ether was observed.[5] The reaction of dimethylsilylene with oxetane to yield II must be quite exothermic (at least 100 kcal/mol) on the basis of thermochemical bond additivity. Thus, the reaction involves breaking a carbon-oxygen single bond (85.5 kcal/mol), formation of new silicon-carbon (76 kcal/mol) and silicon-oxygen (106 kcal/mol) single bonds,[6] and release of the oxetane strain energy (≃25 kcal/mol).[7] This calculation is incomplete owing to the lack of knowledge concerning the probably small strain energy of II, which may result from constraint of a Si-O-C bond in a five-membered heterocycle. The facile polymerization of II may reflect this strain energy.[8]

If II is formed by direct insertion of dimethylsilylene into a carbon-oxygen single bond of oxetane in a single step, one might assume that II would be formed in a vibrationally excited ground state. This excess vibrational energy could be lost by collisional deactivation with solvent or by undergoing a retro-hydrosilation reaction to yield I.[9] To test this hypothesis, the photolysis of dodecamethylcyclohexasilane in oxetane solvent was carried out at −98 °C in a quartz Dewar. Under these conditions, we expected the ratio of I:II, which is approximately 1:1 at 0 °C, to shift in favor of II. However, under these conditions, the only product formed is I.

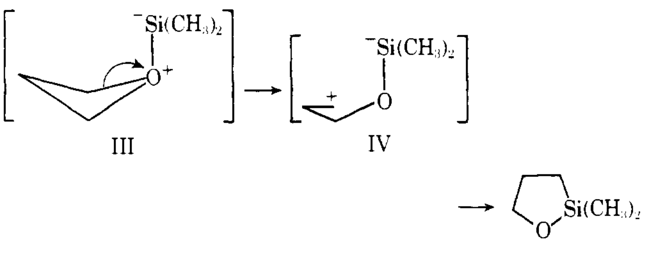


This led us to propose the following alternative hypothesis. Initial electrophilic attack by dimethylsilylene on a lone pair of electrons of the oxygen of the oxetane yields a zwitterionic intermediate (III) which can react further by two pathways.

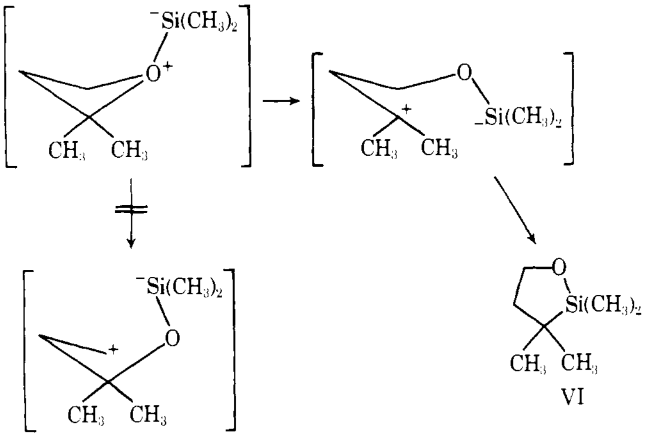

III

The first involves intramolecular proton abstraction from C-3 of the oxetane ring by the negatively charged silicon with simultaneous fragmentation to yield I. A unique low-energy vibrational puckering mode of the oxetane ring exists.[10] If a similar vibrational mode exists for the zwitterionic intermediate, it may permit the facile attainment of a nonplanar puckered conformation which will bring a hydrogen atom on C-3 and the negatively charged silicon center into close proximity. This would favor this reaction pathway.

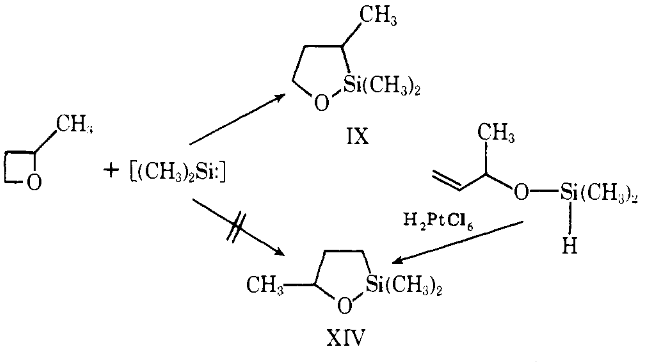
The second pathway involves heterolytic fragmentation of a carbon-oxygen single bond of the zwitterionic intermediate to yield a carbonium ion-silyl anion, a 1,5 zwitterion (IV), which combines by cyclization to yield II. The fact that at −98 °C only I is formed indicates that the second pathway has a higher energy of activation than the first.


III IV

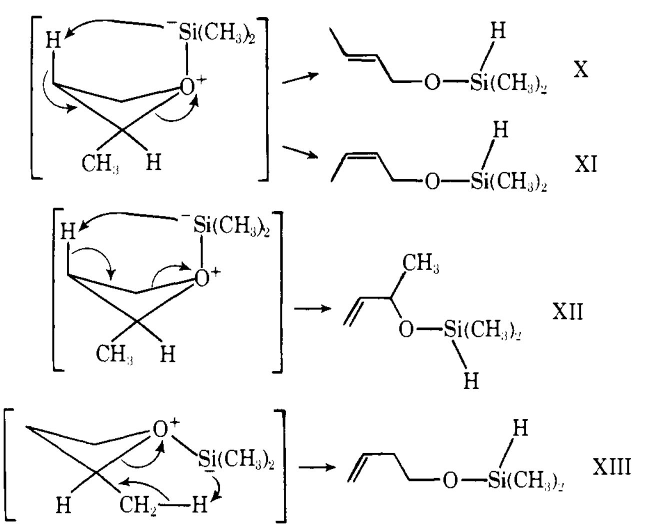
Additional support for this proposal comes from the following four experiments. Reaction of dimethylsilylene with 3,3-dimethyloxetane yields only 2,2,4,4-tetramethyl-1-oxa-2-silacyclopentane (V, 90%).[11,12] Reaction of dimethylsilylene with 2,2-dimethyloxetane yields only 2,2,3,3-tetramethyl-1-oxa-2-silacyclopentane (VI, 26%), 3-methyl-2-butenyloxydimethylsilane (VII, 44%),[3] and 3-methyl-3-butenyloxydimethylsilane (VIII, 13%). The regiospecific formation of VI is expected since heterolytic fragmentation of a carbon-oxygen single bond of the zwitterionic intermediate is expected to lead to a tertiary carbonium ion in preference to a primary one. The formation of VII in preference to VIII is favored by the greater stability of the more substituted alkene product and by the more facile abstraction of a proton from a secondary carbon compared to a primary one. On the other hand, reaction of dimethylsilylene with 2-methyloxetane yields 2,2,3-trimethyl-1-oxa-2-silacyclopentane (IX, 29%), (*E*)-2-butenyloxydimethylsilane (X, 26%), (*Z*)-2-butenyloxydimethylsilane (XI, 22%), 1-methylallyloxydimethylsilane (XII, 1%), and 3-butenyloxydimethylsilane (XIII, 2%).[3] These latter two minor products were only identified by comparison of their GLC retention times with those of authentic samples.


VI

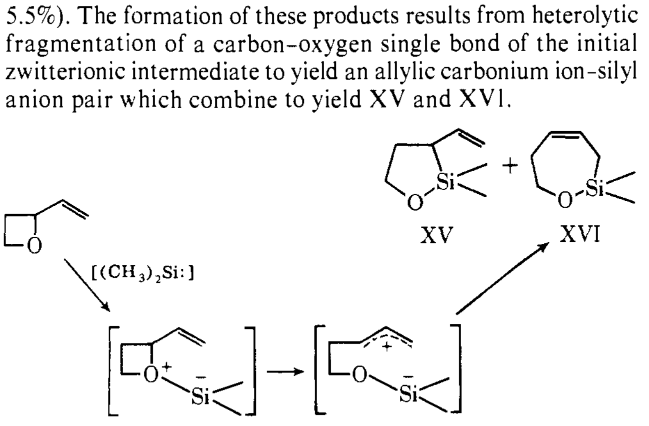
The regioselective formation of IX is expected since heterolytic fragmentation of a carbon-oxygen single bond of the zwitterionic intermediate is expected to lead to a secondary carbonium ion in preference to a primary one. The formation of IX was confirmed by independent synthesis of the other possible isomer, 2,2,5-trimethyl-1-oxa-2-silacyclopentane (XIV),[13] by an intramolecular hydrosilation reaction of 1-methylallyloxydimethylsilane catalyzed by chloroplatinic acid.[3] The predominant formation of X and XI rather than XII may result from preferential fragmentation of the 1,2-zwitterionic intermediate to form the more stable alkenes. The relative ease of proton abstraction from a secondary carbon compared to a primary carbon may control the relative amounts of XIII and XI formed.



IX XIV



Finally, reaction of dimethylsilylene with 2-vinyloxetane yields 2,2-dimethyl-3-vinyl-1-oxa-2-silacyclopentane (XV, 74%) and 2,2-dimethyl-1-oxa-2-silacyclohept-4-ene (XVI, 5.5%). The formation of these products results from heterolytic fragmentation of a carbon-oxygen single bond of the initial zwitterionic intermediate to yield an allylic carbonium ion-silyl anion pair which combine to yield XV and XVI.



Based on these results we believe that the mechanism of reaction of dimethylsilylene with oxetanes involves initial electrophilic attack by dimethylsilylene on an oxygen lone pair of electrons to yield a 1,2-zwitterionic intermediate which further decomposes to yield a variety of products. These results should encourage caution in the interpretation of experiments involving dimethylsilylene carried out in "inert" ether solvents. Thus, while dimethylsilylene does not react with unstrained aliphatic ethers to yield products, it may well form a complex with them. Such a zwitterionic complex might be capable of delivering dimethylsilylene to various substrates. The reactivity of dimethylsilylene may well be influenced by such solvation. This question is under active investigation.

Experimental Section

IR spectra were determined as CCl_4 solutions on a Perkin-Elmer 281 spectrometer. NMR spectra were recorded on a Varian XL-100 spectrometer using 5% solutions in $CDCl_3$ with an internal standard of chloroform. Mass spectra were determined on a Du Pont 21-492 at an ionizing voltage of 70 eV. Samples of all compounds for spectra analysis were purified by preparative vapor phase chromatography on a Hewlett-Packard F&M 700. Yields of products were determined by GLC with cyclooctane added as internal standard. Yields are based on 2 mol of dimethylsilylene per mol of dodecamethylcyclohexasilane.

Many of the starting materias and products are known compounds. They had physical and spectral properties in complete agreement with literature values. In those cases where spectral data have not been previously reported, we have included these data.

Reaction of Dimethylsilylene with Oxetane. A solution of dodecamethylcyclohexasilane[14,15] (105 mg, 0.3 mmol) in oxetane[16] (1.16 g, 20 mmol) was placed in a 5-mm quartz NMR tube. The solution was photolyzed with a 450-W medium-pressure Hanovia Hg lamp housed in a water-cooled quartz well for 90 min at 5 °C in an ice-water bath. GLC analysis of the resulting colorless solution on a $^1/_4$ in. × 12 ft 20% SE-30 on Chromosorb W 60/80 mesh column showed the formation of 2,2-dimethyl-1-oxa-2-silacyclopentane[4] (41%) and allyloxydimethylsilane[3] (38%).

2,2-Dimethyl-1-oxa-2-silacyclopentane had the following spectral properties: NMR δ 3.82 (t, 2 H, J = 6 Hz), 1.85 (tt, 2 H, J = 7.5 and 6 Hz), 0.72 (t, 2 H, J = 7.5 Hz), 0.18 (s, 6 H); IR Si-O and C-O broad 1050 and 1085 cm^{-1}; mass spectrum parent *m/e* 116 (13%), P − 1 115 (1.7%), P − 15 101 (100%), P − 17 99 (16.9%), P − 28 88 (22.4%).

Allyloxydimethylsilane has the following spectral properties: NMR δ 5.93 (ddt, 1 H, J = 17.1, 10.2, and 4.8 Hz), 5.23 (dq, 1 H, J = 17.1 and 1.7 Hz), 5.09 (dq, 1 H, J = 10.2 and 1.7 Hz), 4.62 (septet, 1 H, J = 2.8 Hz), 4.16 (ddd, 2 H, J = 4.8, 1.7, and 1.7 Hz), 0.21 (d, 6 H, J = 2.8 Hz); IR Si-H 2110, C=C 1650, Si-O and C-O 1030, 1080 cm^{-1}; mass spectrum parent *m/e* 116 (4.6%), P − 1 115 (22%), P − 15 101 (79.7%), P − 17 99 (59%), P − 31 85 (15.6%), 75 (100%).

Reaction of Dimethylsilylene with Oxetane at −98 °C. A 5-mm quartz NMR tube containing a solution of dodecamethylcyclohexasilane (17 mg, 0.05 mmol) in oxetane[16] (812 mg, 14 mmol) was placed in a quartz Dewar with a transparent end of i.d. 0.8 × 3 cm. Dry ice-methanol slush was used to achieve the temperature of −98 °C. Photolysis was carried out for 60 min. Allyloxydimethylsilane was identified to be the only product by GLC analysis.

Reaction of Dimethylsilylene with 3,3-Dimethyloxetane. A solution of dodecamethylcyclohexasilane in 3,3-dimethyloxetane[16] was prepared and photolyzed for 90 min at 5 °C in an ice-water bath to yield 2,2,4,4-tetramethyl-1-oxa-2-silacyclopentane (90%).[11,12] It had the following spectral properties: NMR δ 3.49 (s, 2 H), 1.03 (s, 6 H), 0.66 (s, 2 H), 0.21 (s, 6 H); IR Si-O 1020 cm^{-1}; mass spectrum parent *m/e* 144 (14%) (calcd $C_7H_{16}OSi$ 144.097, found 144.099), P − 15 129 (13%), 99 (33%), 89 (100%), 88 (54%).

Reaction of Dimethylsilylene with 2-Methyloxetane. A mixture of dodecamethylcyclohexasilane (90 mg, 0.26 mmol) and 2-methyloxetane[16] (360 mg, 5 mmol) in ether (630 mg, 8.5 mmol) was placed in a quartz NMR tube. The solution was photolyzed as above and the resulting colorless solution was analyzed by GLC on a $^1/_4$ in. × 28 ft 20% SE-30 on Chromosorb W 60/80 mesh column. (*E*)-2-Butenyloxydimethylsilane (26%), (*Z*)-2-butenyloxydimethylsilane (22%), and 2,2,3-trimethyl-1-oxa-2-silacyclopentane (29%) were isolated.

(*E*)-2-Butenyloxydimethylsilane had the following spectral properties: NMR δ 5.71-5.56 (m, 2 H), 4.61 (septet, 1 H, J = 2.8 Hz), 4.09 (d, 2 H, J = 3.9 Hz), 1.68 (d, 3 H, J = 4.7 Hz), 0.20 (d, 6 H, J = 2.8 Hz); IR Si-H 2115 Si-O and C-O 1080 and 1030 cm^{-1}; mass spectrum parent *m/e* 130 (15.1%) (calcd $C_6H_{14}OSi$ 130.081, found 130.081), P − 1 129 (6.2%), P − 15 115 (74.2%), P − 17 113 (5.9%), 85 (17.7%), 75 (100%).

(*Z*)-2-Butenyloxydimethylsilane has the following spectral properties: NMR δ 5.71-5.49 (m, 2 H), 4.62 (septet, 1 H, J = 2.8 Hz), 4.22 (d, 2 H, J = 4.7 Hz), 1.70-1.60 (m, 3 H), 0.21 (d, 6 H, J = 2.8 Hz); IR Si-H 2120, Si-O and C-O broad 1055 cm^{-1}; mass spectrum *m/e* 130 (20%) (calcd $C_6H_{14}OSi$ 130.081, found 130.081), P − 1 129 (15%), P − 15 115 (60%), 85 (16%), 75 (100%).

2,2,3-Trimethyl-1-oxa-2-silacyclopentane has the following spectral properties: NMR δ 3.84-3.44 (m, 2 H), 1.84-1.59 and 1.52-1.24 (m and m, 1 H and 1 H, CCH_2C), 0.94 (d, 3 H, J = 6 Hz), 0.85-0.65 (m, 1 H), 0.066 and 0.05 (s and s, 3 H and 3 H, $Si(CH_3)_2$); IR Si-O and C-O broad 1035 and 1015 cm^{-1}; mass spectrum parent *m/e* 130 (20%) (calcd $C_6H_{14}OSi$ 130.081, found 130.081), P − 15 115 (100%), 89 (27.6%), 88 (40%), 87 (12.1%), and 75 (35.2%).

1-Methylallyloxydimethylsilane was prepared by reaction of 3-buten-2-ol with chlorodimethylsilane in the presence of *N*,*N*-dimethylaniline. It had the following spectral properties: NMR δ 5.83 (ddd, 1 H, J = 17.1, 10.3, and 5.6 Hz), 5.14 (dt, 1 H, J = 17.1 and 1.5 Hz), 5.00 (dt, 1 H, J = 10.3 and 1.5 Hz), 4.63 (septet, 1 H, J = 2.9 Hz), 4.26 (dq, 1 H, J = 5.6 and 6.3 Hz), 1.23 (d, 3 H, J = 6.3 Hz), 0.19 (d, 3 H, J = 2.9 Hz), 0.18 (d, 3 H, J = 2.9 Hz); IR Si-H 2110, C=C 1640, Si-O and C-O broad 1070 and 1020 cm^{-1}. 1-Methylallyloxydimethylsilane undergoes an intramolecular hydrosilation reaction catalyzed by chloroplatinic acid to yield 2,2,5-trimethyl-1-oxa-2-silacyclopentane. The procedure used was modeled after that of Mironov.[3] A mixture of 150 mg of 1-methylallyloxydimethylsilane and 6 μL of 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol was heated to boiling and then over a period of 2 h the main portion (3 g) of the 1-methylallyloxydimethylsilane was added. After cooling to room temperature, the reaction mixture was checked by IR to observe complete disappearance of Si–H absorption. 2,2,5-Trimethyl-1-oxa-2-silacyclopentane was then collected from a simple bulb to bulb distillation. It had the following spectral properties: NMR δ 4.02–3.90 (m, 1 H), 2.03–1.91 and 1.44–1.31 (m and m, 1 H and 1 H, CCH_2C), 1.19 (d, 3 H, $J = 6$ Hz), 0.89–0.63 (m, 2 H), 0.16 (s, 6 H); IR Si–O and C–O 1045 and 1010 cm^{-1}; mass spectrum parent *m/e* 130 (0.5%), P − 1 129 (1.7%) (calcd $C_6H_{13}OSi$ 129.074), found 129.074), P − 15 115 (100%), P − 28 120 (30.5%), P − 29 101 (7.4%), 87 (30.9%), 75 (17.5%).

(*E*)-2-Butenyloxydimethylsilane was prepared independently by photolysis of dodecamethylcyclohexasilane with the commercial (*E*)-2 buten-1-ol in ether. This reaction involves insertion of dimethylsilylene into the O–H single bond.[19] 3-Butenyloxydimethylsilane was prepared from 3-buten-1-ol. By comparison of GC retention times, 1-methylallyloxydimethylsilane (1%) and 3-butenyloxydimethylsilane (2%) were found in the photolysis of dodecamethylcyclohexasilane in 2-methyloxetane.

2,2-Dimethyloxetane was prepared from 4-bromo-2-methyl-2-butanol[17] and tributylmethoxytin[18] following literature methods[17,18] and was purified by preparative GLC: NMR δ 4.00 (t, 2 H, $J = 8$ Hz), 2.05 (t, 2 H, $J = 8$ Hz), 1.00 (s, 6 H).

Reaction of Dimethylsilylene with 2,2-Dimethyloxetane. A solution of dodecamethylcyclohexasilane in 2,2-dimethyloxetane was prepared and photolyzed as above. Analysis of the resulting colorless solution by GLC on a 1/4 in. × 28 ft 20% SE-30 on Chromosorb W 60/80 mesh column showed the formation of 3-methyl-3-butenyloxydimethylsilane (13%),[3] 3-methyl-2-butenyloxydimethylsilane (44%), and 2,2,3,3-tetramethyl-1-oxa-2-silacyclopentane (26%). They had the following spectral properties.

3-Methyl-3-butenyloxydimethylsilane:[3] NMR δ 4.76 (br s, 1 H), 4.71 (br s, 1 H), 4.60 (septet, 1 H, $J = 2.9$ Hz), 3.72 (t, 2 H, $J = 7.0$ Hz), 2.25 (t, 2 H, $J = 7.0$ Hz), 1.73 (s, 3 H), 0.19 (d, 6 H, $J = 2.9$ Hz); IR Si–H 2110, C═C 1650, Si–O and C–O broad 1085 and 1060 cm^{-1}; mass spectrum parent *m/e* 144 (2.5%) (calcd $C_7H_{16}OSi$ 144.097, found 144.098), P − 1 143 (1.7%), P − 15 129 (40.6%), 101 (11.1%), 99 (7.6%), 89 (100%), 87 (10.5%), 75 (24.7%).

3-Methyl-2-butenyloxydimethylsilane: NMR δ 5.33 (t, 1 H, $J = 6.6$ Hz), 4.61 (septet, 1 H, $J = 2.8$ Hz), 4.14 (d, 2 H, $J = 6.6$ Hz), 1.72 (s, 3 H), 1.65 (s, 3 H), 0.20 (d, 6 H, $J = 2.8$ Hz); IR Si–H 2110, C═C 1670, Si–O and C–O broad 1050 and 1025 cm^{-1}; mass spectrum parent *m/e* 144 (5.8%) (calcd $C_7H_{16}OSi$ 144.097, found 144.099), P − 1 143 (0.9%), P − 15 129 (46.2%), 101 (9.4%), 89 (7.9%), 75 (100%).

2,2,3,3-Tetramethyl-1-oxa-2-silacyclopentane: NMR δ 3.86 (t, 2 H, $J = 6.2$ Hz), 1.61 (t, 2 H, $J = 6.2$ Hz), 1.02 (s, 6 H), 0.11 (s, 6 H); IR Si–O and C–O 1030 and 1020 cm^{-1}; mass spectrum parent *m/e* 144 (23.7%) (calcd $C_7H_{16}OSi$ 144.097, found 144.098), P − 15 129 (51.7%), 101 (9.4%), 99 (4%), 89 (24%), 88 (20%), 75 (100%).

2-Vinyloxetane was prepared from 5-chloropent-1-en-3-ol[20] and tributylmethoxytin[18] following the literature method[17,18] and was purified by preparative GLC: NMR δ 6.28–5.94 (m, 1 H), 5.27 (dm, 1 H, $J = 15.2$ Hz), 5.21–5.18 (m, 1 H), 5.13 (dm, 1 H $J = 7$ Hz), 4.76–4.39 (m, 2 H), 2.95–2.28 (m, 2 H).

Reaction of Dimethylsilylene with 2-Vinyloxetane. A solution of dodecamethylcyclohexasilane (70 mg, 0.2 mmol) and 2-vinyloxetane[20] (336 mg, 4 mmol) in ether (750 mg, 10 mmol) was placed in a 5-mm quartz NMR be and photolyzed as above for 60 min. Prompt GLC analysis of the resulting colorless solution indicated the formation of 2,2-dimethyl-3-vinyl-1-oxa-2-silacyclopentane (74%) and 2,2-dimethyl-1-oxa-2-silacyclohept-4 ene (5.5%).

2,2-Dimethyl-3-vinyl-1-oxa-2-silacyclopentane has the following spectral properties: NMR δ 5.81 (ddd, 1 H, $J = 17.2$, 10.0, and 7.8 Hz), 4.89 (dm, 1 H, $J = 17.2$ Hz), 4.82 (dm, 1 H, $J = 10.0$ Hz), 4.12–3.65 (2 H, m), 2.12–1.87 (m, 3 H), 0.21 (s, 3 H), 0.10 (s, 3 H); IR C═C 1635, Si–O and C–O broad 1035 cm^{-1}; mass spectrum parent *m/e* 142 (56.3%) (calcd $C_7H_{14}OSi$ 142.0814, found 140.0808), P − 15 127 (100%) (calcd $C_6H_{11}OSi$ 127.0579, found 127.0551), 101 (15.2%), 99 (47.4%), 97 (69.2%), 88 (43.4%), 75 (42.5%), 59 (14.1%).

2,2-Dimethyl-1-oxa-2-silacyclohept-4-ene has the following spectral properties: NMR δ 6.36–5.54 (m, 2 H), 3.75 (dd, 2 H, $J = 5.05$ and 5.0 Hz), 2.13 (dt, 2 H, $J = 6$ and 5 Hz), 1.47 (d, 2 H, $J = 6.5$ Hz), 0.126 (s, 6 H); IR Si–O and C–O broad 1045 cm^{-1}; mass spectrum parent *m/e* 142 (67.8%) (calcd $C_7H_{14}OSi$ 142.0814, found 142.081), P − 15 127 (97.7%), 112 (24.8%), 101 (26.7%), 99 (48.5%), 97 (100%), 88 (87.2%), 75 (89.7%), 59 (41.6%).

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References and Notes

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