Tetrahedron Letters,Vol.23,No.50,pp 5323-5326,1982 0040-4039/82/505323-04$03.00/0
Printed in Great Britain

OXASILACYCLOPROPANE. ISOLATION AND CHARACTERIZATION

Wataru Ando*, Yoshitaka Hamada and Akira Sekiguchi
Institute of Chemistry, University of Tsukuba
Sakura-mura, Niihari-gun, Ibaraki 305, Japan

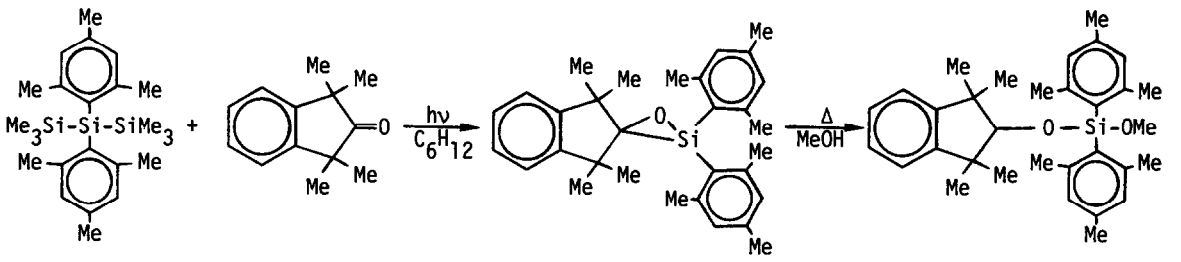
Katsuhiko Ueno
Research Institute for Polymers and Textile
Yatabe-cho, Ibaraki 305, Japan

Summary: A crystalline oxasilacyclopropane was isolated by the reaction of photochemically induced dimesitylsilylene with 1,1,3,3-tetramethyl-2-indanone, and the exact structure of the oxasilacyclopropane was comfirmed by X-ray crystal analysis.

Synthesis of strained small ring compounds containing a silicon atom is one of the current topics in silicon chemistry owing to their high reactivities resulting from the strain energy. Relatively stable silacyclopropanes[1], silacyclopropenes[2] and trisilacyclopropane[3] have been synthesized. However, there is no precedent for the isolation of three membered ring compounds containing silicon and oxygen such as oxasilacyclopropanes. We have already demonstrated the formation of oxasilacyclopropane derivatives as transient intermediates by the reaction of dimethylsilylene with carbonyl compounds[4]. However, oxasilacyclopropanes are found to react with ketones to form dioxasilacyclopentanes or dimerized to dioxadisilacyclohexanes under the reaction conditions.

It seems that oxasilacyclopropane can be stabilized by the protection of the bulky substituents around the ring system. We now wish to report the first synthesis of a stable crystalline oxasilacyclopropane in the reaction of photochemically generated dimesitylsilylene with 1,1,3,3-tetramethyl-2-indanone.

A cyclohexane solution of 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane 1 (687mg, 1.66mmol) and 1,1,3,3-tetramethyl-2-indanone (404mg, 2.15mmol) in a quartz tube was irradiated at room temperature with a low pressure mercury lamp for 18 hr. The resulting reaction mixture was concentrated, and the residue was subjected to separation by HPLC (JAIGel column) to give colorless crystals of the oxasilacyclopropane 2 (462mg, 61%), recrystallyzed from hexane, mp. 202.5-203.5°C.



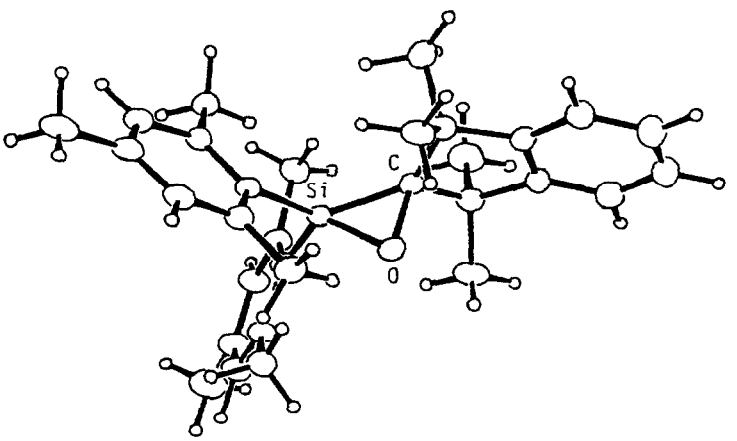
1 2 3

The structure of the oxasilacyclopropane 2 has been characterized by its ^{1}H NMR, ^{13}C NMR, IR, and Mass spectra. The ^{1}H NMR spectrum (CCl_4, δ) shows aromatic protons at 7.04(s,4H), 6.79(s,4H), two singlet peaks attributed to methyl protons of the mesityl groups, ortho 2.70(s,12H), para 2.25(s,6H), and two singlet aliphatic methyl protons, 1.31(s,6H), 0.97(s,6H); ^{13}C NMR ($CDCl_3$, δ) 149.9(s,aromatic C), 145.5(s,aromatic C), 142.8(s,aromatic C), 140.2(s,aromatic C), 129.4(d,aromatic C), 128.7(s,aromatic C), 128.4(d,aromatic C), 126.7(d, aromatic C), 122.0(d,aromatic C), 89.9(s, Si-C-O), 49.5(s, C-C$(CH_3)_2$), 32.3 (q, CH_3), 27.6(q, CH_3), 25.1(q, CH_3), 23.2(q, CH_3), 21.1(q, CH_3); IR (KBr) 1075cm^{-1} (Si-O-C); Mass m/e 454 (M^+). Elemental analysis also supports its

structure, Calcd for $C_{31}H_{38}OSi$: C,81.88; H,8.42. Found: C,82.13; H,8.53. Our finding that oxasilacyclopropane 2 does give an adduct 3[5] upon methanolysis at reflux temperature lends further support of the three membered ring structure of 2.

X-ray crystal analysis established the exact structure of the oxasilacyclopropane 2. The crystal has triclinic space group $P\bar{1}$ with a=8.416(2)Å, b=10.159(4)Å, c=16.007(6)Å and α=85.52(3)°, β=89.39(3)°, γ=78.49(3)° with V=1337.1(8)Å^3. Intensity data were collected on a four circle diffractometer with graphite monochromated Mo/Kα radiation. A total of 3848 independent reflections were obtained within θ<53°, 4723 had intensities greater than $3\sigma|F_o|$ and were used for structure analysis. The structure was refined to an R value of 0.075. Perspective view of the molecular structure of the oxasilacyclopropane 2 is shown in Figure; bond angles: C-Si-O,50.4°; Si-C-O,58.5°; C-O-Si,71.0°: bond lengths: Si-C,1.849Å; Si-O,1.668Å; C-O,1.507Å. It is quite interesting that the oxasilacyclopropane 2 is not isosceles triangle but silacyclopropane[6], silacyclopropene[7] and trisilacyclopropane[3] are. For additional crystallographic details consult reference 8.

Figure. Perspective view of the structure of oxasilacyclopropane 2



References

(1) (a) R. L. Lambert, Jr. and D. Seyferth, J. Am. Chem. Soc., 1972, 94, 9246.
(b) M. Ishikawa and M. Kumada, J. Organomet. Chem., 1974, 81, C-3.

(2) (a) R. T. Conlin and P. P. Gaspar, J. Am. Chem. Soc., 1976, 98, 3715.
(b) D. Seyferth, D. C. Annarelli, and S. C. Vick, Ibid., 1976, 98, 6382.
(c) M. Ishikawa, T. Fuchikami, and M. Kumada, Ibid., 1977, 99, 245.
(d) H. Sakurai, Y. Kamiyama, and Y. Nakadaira, Ibid., 1977, 99, 3879.
(e) M. Ishikawa and M. Kumada, Adv. Organomet. Chem., 1981, 119, 51, and references cited therein.
(f) P. P. Gaspar, "Advances in Silylene Chemistry 1977 to 1979", a chapter in Reactive Intermediates, edited by M. Jones, Jr. and R. A. Moss, Wiley, N. Y., (1980).

(3) S. Masamune, Y. Hanzawa, S. Murakami, T. Bally, and J. F. Blount, J. Am. Chem. Soc., 1982, 104, 1150.

(4) (a) W. Ando, M. Ikeno, and A. Sekiguchi, J. Am. Chem. Soc., 1977, 99, 6447.
(b) W. Ando, M. Ikeno, and A. Sekiguchi, Ibid., 1978, 100, 3613.

(5) mp. 164-166°C. ^{1}H NMR (CCl_4,δ) 7.02(s,4H), 6.71(s,4H), 3.94(s,1H), 3.41(s,3H), 2.34(s,12H), 2.20(s,6H), 1.22(s,6H), 1.07(s,6H). ^{13}C NMR ($CDCl_3$,δ) 148.5, 144.4, 144.2, 139.2, 129.7, 129.1, 129.0, 126.8, 122.8, 90.6, 49.9, 45.8, 28.0, 26.5, 26.4, 23.9, 23.8, 21.2. IR (KBr) 1060cm^{-1} (Si-O-C). Mass m/e 486 (M^+). Elemental analysis; Calcd for $C_{32}H_{42}O_2Si$: C,78.95; H,8.69. Found: C,79.05; H,8.68.

(6) G. L. Delker, Y. Wang, G. D. Stucky, R. L. Lambert, Jr., C. K. Haas, and D. Seyferth, J. Am. Chem. Soc., 1976, 98, 1779.

(7) K. Hirotsu, T. Higuchi, M. Ishikawa, H. Sugisawa, and M. Kumada, J. C. S. Chem. Comm., 1982, 726.

(8) Final crystallographic coordinates have been deposited with the Cambridge Crystallographic Data Centre.

(Received in Japan 27 August 1982)