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SILATHIACYCLOPROPANE. ISOLATION AND CHARACTERIZATION

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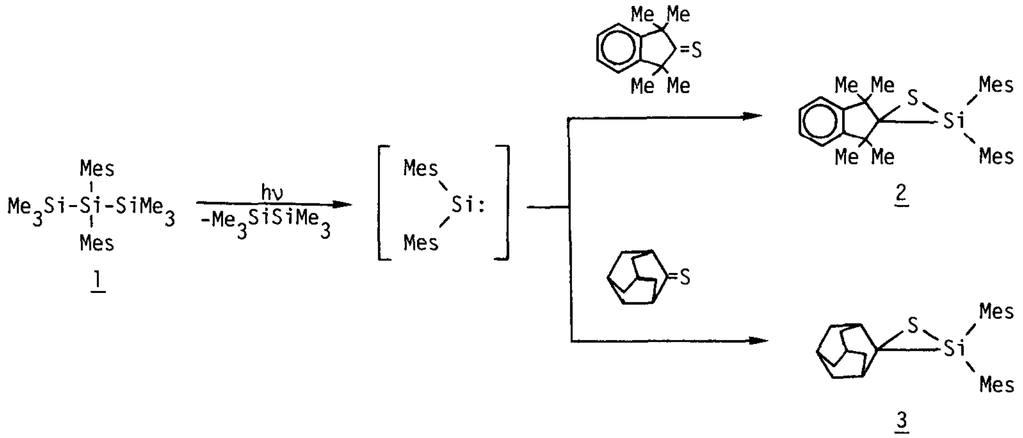
Summary: A crystalline silathiacyclopropane was isolated from the reaction of dimesitylsilylene with 1,1,3,3-tetramethyl-2-indanethione, and the exact structure of the silathiacyclopropane was comfirmed by X-ray crystal analysis. Similar silathiacyclopropane was also synthesized by the reaction of dimesitylsilylene and adamantanethione.

The chemistry of silicon three membered ring compounds is one of the most considerable advanced fields in recent years, and the use of the appropriate sterical blockades has permitted the isolation of stable silacyclopropenes,1) disilacyclopropane,2) trisilacyclopropanes3) and diazasilacyclopropane.4) During the course of our studies of the reaction of silylenes and carbonyl compounds5) we have been successful in the isolation and characterization of oxasilacyclopropane as stable compound containing three membered ring.6) It is of interest to prepare the sulfur analogues which cannot be found in any literature yet. We now wish to report the first synthesis of silathiacyclopropanes by the reaction of silylene and thiocarbonyl compounds.

A cyclohexane solution of 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane 1 (503.6mg, 1.22mmol) and 1,1,3,3-tetramethyl-2-indanethione(327.9mg, 1.61mmol) in a quartz tube was irradiated at room temperature with a low pressure mercury lamp for 15 hours. The resulting reaction mixture was treated by methanol/ether, and concentrated, the residue was subjected to separation by HPLC (JAI Gel culumn) to give colorless crystals of silathiacyclopropane 2 in 82% yield,7) recrystallized from hexane, m.p. 210.5-211.5°C. This silathiacyclopropane 2 is quite stable in atmosphere of oxygen or moisture, and not decomposed by heating to its melting point.



^{1}H and ^{13}C NMR, Mass spectra and elemental analysis are consistent with the structure of 2.8) The ^{13}C NMR signal at 66.7(s) is attributed to the carbon in the three membered ring system.

The X-ray crystallographic analysis of 2 showed triclinic space group P$\bar{1}$ with a=8.547(2)Å, b=10.142(3)Å, c=15.845(4)Å and α=95.07(2)°, β=92.52(2)°, γ=81.46(2)° with V=1352.3(7)Å^3. Intensity data were collected of a four circle diffractometer with graphite monochromated Mo/Kα radiation. A total of 4453 independent reflections were obtained within $2\theta<155°$, 4775 had intensities greater than $3\sigma|Fo|$ and were used for structure analysis. The structure was refined to an R value of 0.088. Perspective view of the molecular structure of 2 is shown in Figure; bond lengths: Si-C, 1.903Å; S-C, 1.905Å; Si-S, 2.093Å:

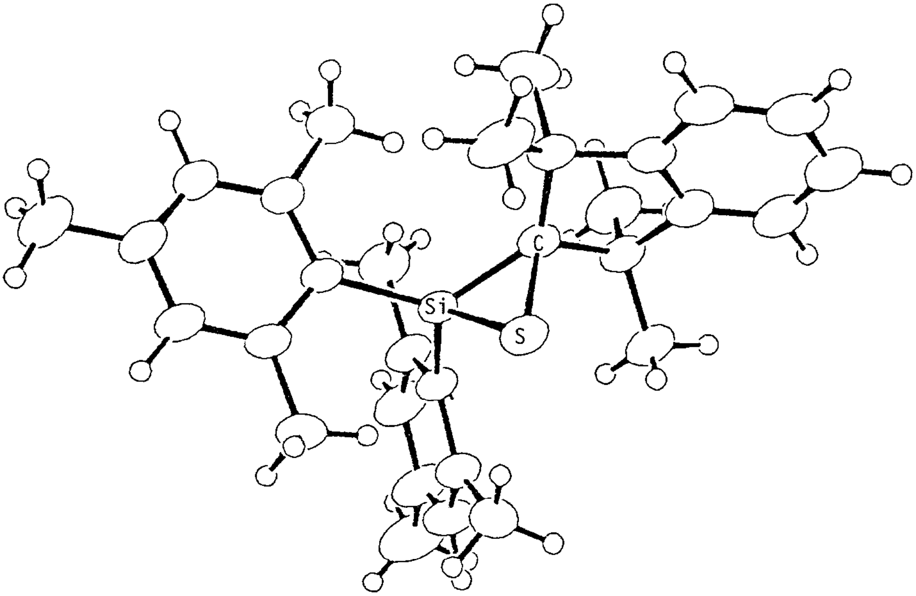


Figure: Perspective view of the structure of silathiacyclopropane 2

bond angles: C-Si-S, 56.7°; C-S-Si, 56.6°; Si-C-S, 66.7°. It is of interest to note that the silathiacyclopropane 2 is an isosceles triangle, in spite of the three different elements constituting the ring system. For additional crystallographic details consult reference 9.

The similar silathiacyclopropane 3 was isolated as stable form by the photolysis of the trisilane 1 in the presence of adamantanethione in 29% yield,[10)] along with the dimer of adamantanethione(43%). This is contrast to the report that adamantanone reacted with dimesitylsilylene to give 2:1 adduct instead of oxasilacyclopropane.[11)] The compound 3 is also inert to oxygen or moisture, and not decomposed by heating to its melting point (193.0-194.0°C). The ^{13}C NMR signal attributed to the ring carbon was observed at 53.6 ppm.

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(7) The silathiacyclopropane 2 was inert to the attack of nucleophile such as methanol, and ring opening reaction did not take place even at benzene reflux temperature.

(8) ^{1}H NMR (CCl_4,δ) 7.11(s,4H), 6.80(s,4H), 2.71(s,12H), 2.23(s,6H), 1.40 (s,6H), 1.22(s,6H).

^{13}C NMR at -50°C ($CDCl_3$,δ) 150.6(s), 145.7(s), 142.3(s), 139.7(s), 129.9 (d), 128.8(s), 128.3(d), 126.6(d), 121.6(d), 66.7(s), 50.2(s), 32.2(q), 29.7(q), 28.4(q), 24.5(q), 21.1(q).

Mass m/e 470 (M^+).

Elemental analysis; Calcd for $C_{31}H_{38}SSi$: C,79.08; H,8.13. Found: C,79.06; H,8.19.

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

(10) ^{1}H NMR ($CDCl_3$,δ) 6.85(s,4H), 2.67(s,12H), 2.48-2.28(m,2H), 2.28(s,6H), 2.05-1.58(m,12H).

^{13}C NMR ($CDCl_3$,δ) 144.1(s), 139.6(s), 128.8(s), 128.8(d), 53.6(s), 38.7(t), 38.2(t), 37.8(d), 36.3(t), 28.0(d), 27.1(d), 24.5(q), 21.1(q).

Mass m/e 432 (M^+).

Elemental analysis; Calcd for $C_{28}H_{36}SSi$: C,77.71; H,8.38. Found: C,77.74; H,8.57.

(11) W. Ando, Y. Hamada, and A. Sekiguchi, J. Chem. Soc., Chem. Commun., in contribution

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