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Preliminary communication

Preparation of hexamethyl-1,2-disila-3-cyclobutene

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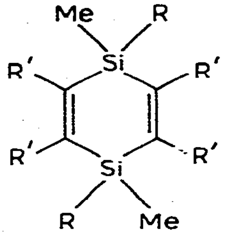
We have previously reported on the formation of silylenes from the thermolysis of methoxy substituted polysilanes[1-4]. One of the most studied reactions of silylenes has been that with acetylenes[5-8]. In all cases reported to date the isolated product of such reaction is the corresponding 1,4-disilacyclohexadiene derivative.

$$(MeO)MeRSiSiRMe(OMe) + RC{\equiv}CR' \rightarrow MeRSi(OMe)_2 +$$

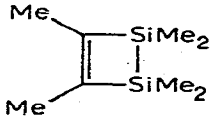
(R = Me or OMe, R′ = Me, Et, Ph or H)



While most of these studies have been carried out under static conditions in sealed tubes[5], some vapor phase flow thermolysis work has been described[1,2,9].

We now wish to report that the vapor phase thermolysis of 1,2-dimethoxytetramethyldisilane in the presence of dimethylacetylene gives hexamethyl-1,2-disila-3-cyclobutene (I), the first reported example of this ring system[9].

$$(MeO)Me_2SiSiMe_2(OMe) + MeC{\equiv}CMe \xrightarrow[-Me_2Si(OMe)_2]{400^\circ}$$



(I)

A mixture of 20 g (0.11 mole) of 1,2-dimethoxytetramethyldisilane and 9.0 g (0.17 mole) of dimethylacetylene was passed through a quartz tube* heated to 400°,

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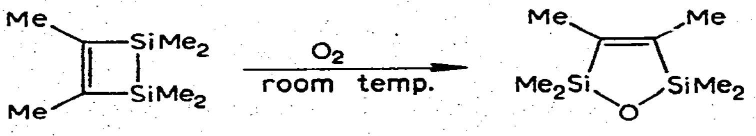
* For a description of the tube and thermolysis equipment see experimental section ref. 10.

using a flow rate of ca. 10 ml/h. The reaction products were collected under dry nitrogen and distilled to give 3.0 g (31%) of I, b.p. 53–55°/15 min (purity ca. 90%). The NMR spectrum (neat with TMS as internal reference) showed singlet proton absorptions for C–Me at τ 8.30 and SiMe at τ 9.80, in a 1/2 ratio, respectively. The mass spectrum gave a molecular weight of 170 and showed a large m/e 116 peak (Me_4Si_2), further supporting the assigned structure. To date, no attempt has been made to optimize the yield of I in this reaction.

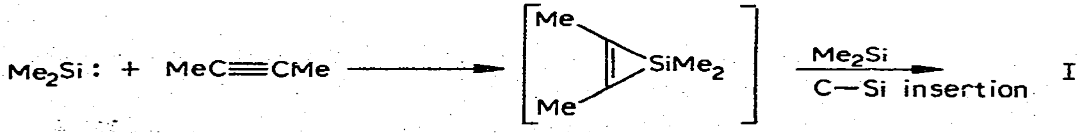
Compound I proved difficult to isolate in the pure state because of its high reactivity toward oxygen. Merely passing oxygen over an open vial containing a relatively pure sample of I resulted in a mild exotherm and a nearly quantitative conversion to hexamethyl-1-oxa-2,5-disilacyclopentene (II) in a matter of minutes*



(I) (II)

The NMR spectrum (neat with TMS as internal reference) of II showed singlet proton absorptions for C–Me at τ 8.26 and SiMe at τ 9.89 in a 1/2 ratio, respectively. The mass spectrum (mol. wt. 186) and IR data (ν (SiOSi) at 920 cm^{-1} and ν(C=C) at 1552 cm^{-1})* provided additional support for the strained cyclosiloxane structural assignment.

At present the route to formation of I is unknown. However, in view of the known ability of carbenes to insert into the carbon–silicon bond of strained rings[13], a path involving dimethylsilylene insertion into an intermediate silacyclopropene seems worthy of consideration.



While the high reactivity of compound I should be useful in future studies on the reactivity of silicon–silicon bonds, this work suggests that a study of the general use of silylenes for the synthesis of new silicon ring systems is warranted.

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* Similar reactivity toward oxygen has been reported for octamethylcyclotetrasilane (ref. 11).

** 2,2,5,5-Tetramethyl-1-oxa-2,5-disilacyclopentene shows ν(SiOSi) at 920 cm^{-1} and ν(C=C) at 1625 cm^{-1} (ref. 12).

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