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GENERATION AND TRAPPING OF 6,6-DIMETHYL-6-SILAFULVENE

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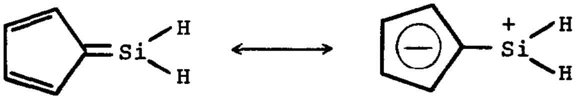
Summary: Flow pyrolysis of allylcyclopentadienyldimethylsilane and of 1-dimethylmethoxysilyl-1-trimethylsilylcyclopentadiene afforded 6,6-dimethyl-6-silafulvene which was either trapped or allowed to dimerize.

6-Silafulvene (1) has been suggested as a molecule containing a silicon-carbon double bond which could be a stable compound.[1] This idea is derived from the qualitative view that the less electronegative the element in the 6-position, the more available will be the six π-electrons to the cyclopentadienyl ring. The CNDO calculations of 1 by Ustynyuk[2] do indeed predict a large ground-state dipole moment.



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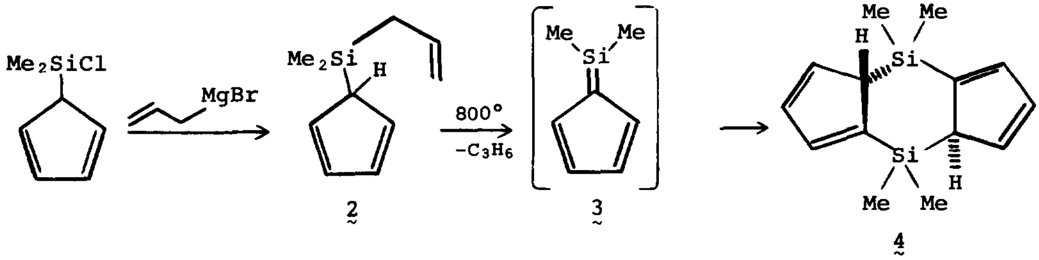
Although we believe that the lack of "stability" of silenes is to a large extent due to enhanced reactivity because of this bond polarity rather than weakness of the (p-p)π bond,[3] we set out to prepare such a molecule. We present here strong evidence for the generation of 6,6-dimethyl-6-silafulvene (3).

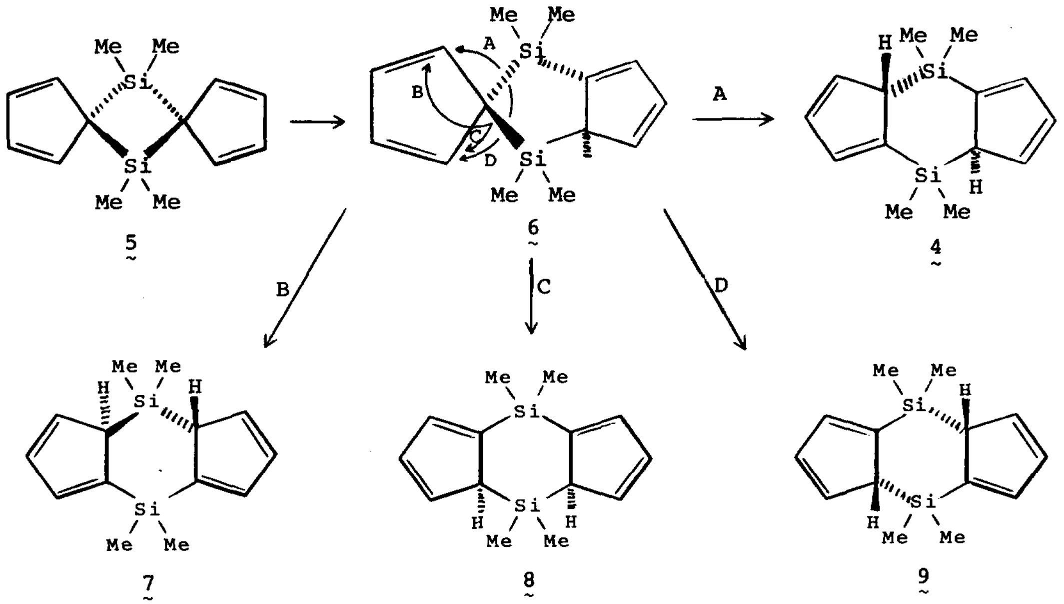
The retroene route to silenes introduced by Block[4] has recently been employed by us to prepare silatoluene[5] and methylsilacyclopentadiene;[6] thus, allylcyclopentadienyldimethylsilane (2) should thermally eliminate propene to yield 3. Synthesis[7] of 2 was accomplished in 72% yield from the coupling of cyclopentadienyldimethylsilyl chloride[8] and allylmagnesium bromide. The NMR spectrum indicated that 2 is a mixture of isomers, 5- and 1-cyclopentadienyl silanes in the respective ratio of 3.6:1 (based on the areas of the SiMe singlets at δ -0.05 and 0.15). The 1-isomer is formed from 1,5-hydrogen migration on the ring.[9] As pyrolysis was the ultimate fate of 2, no attempt was made to separate the isomers.

Pyrolysis of 2 was conducted in a vacuum flow system (800°, 6×10^{-4} Torr) and afforded, in 17% isolated yield, a white, crystalline material (mp 106 - 107.5°) whose mass spectrum was consistant with a dimer of 3 (calcd. for $C_{14}H_{20}Si_2$, 244.1104; measured 244.1101). However, the NMR spectrum [δ(CCl_4)

-1.44 (s, 0.6H), -0.53 (s, ~3H), 0.30 (narrow mult. of 3 spikes, ~3H), 0.52 (like mult at δ 0.30, ~4H), 3.47 (brd. s, ~1.3H), 3.74 (brd. s, ~0.7H), 6.46 - 7.13 (hump, 7H)] was far too complex and unsymmetrical to fit any dimeric structure which we could imagine. Thus, the structure was determined to be that of 4 by single-crystal X-ray diffraction.[10]



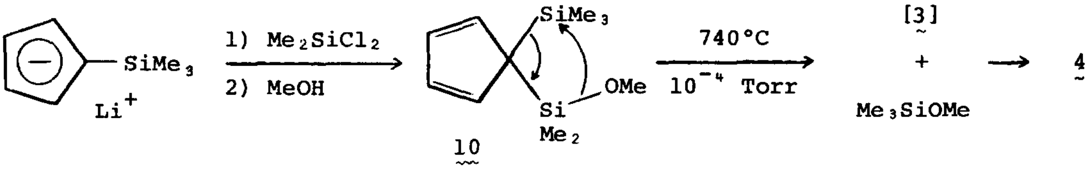
Since the highly symmetrical structure of 4 clearly did not fit the NMR spectrum, several crystals were first shown by photographs to be crystallographically identical to the crystal whose structure was determined, and then dissolved to obtain the same NMR spectrum as before. However, heating to 75° in the NMR probe caused coalescence to two broad singlets centered at δ ca. 6.1 and δ ca. -0.3, and cooling back to ambient temperature reproduced the original spectrum. The same spectrum, but with significant changes in relative peak areas, could be obtained by dissolving crystals of 4 in $DCCl_3$ at -30° and immediately obtaining the NMR spectrum at that temperature.



This latter result effectively eliminates the possibility that isomerization is occurring through prototropic rearrangements, since prototropic rearrangements in cyclopentadienyl silanes always occur slowly compared to the NMR time scale.[9,11] Thus, in solution 4 immediately established an isomeric equilibrium through a variety of facile 1,5-sigmatropic silyl migrations. The possible isomers of 4, which could interconvert by 1,5-silyl migrations, include structures 5 through 9.

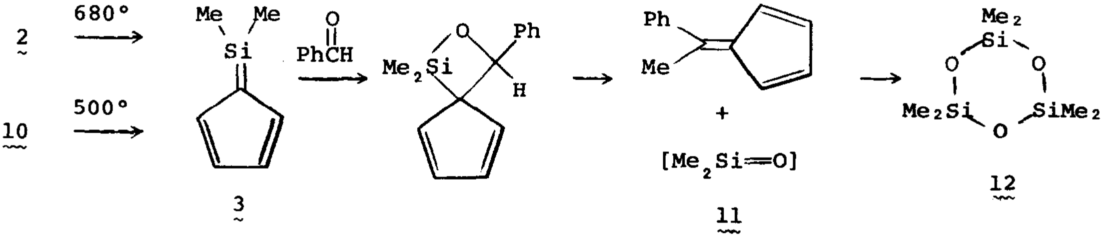
While 4 could be formed directly from dimerization of 3, precedents in silene chemistry[1] suggest that the initial dimer be 1,3-disilacyclobutane 5.

In order to strengthen the claim that thermolysis of 2 affords 3, an alternate route to 3 was investigated. 1-Dimethylmethoxysilyl-1-trimethylsilylcyclopentadiene (10) was prepared in 52% yield from the coupling of trimethylsilylcyclopentadienyl lithium and dichlorodimethylsilane followed by methanolysis [colorless oil; calcd. for $C_{11}H_{22}OSi_2$, m/e 226.1209, measured m/e 226.1206]. The NMR spectrum of 10 [CCl_4) δ -0.07 (s, 9H), -0.13 (s, 6H), 3.36 (s, 3H), 6.94 (AA'BB' center, 4H)] reveals the interesting fact that 10 is locked at room temperature as the 1,1-isomer. Presumably this is due to attractive interaction of the methoxy oxygen and the Me_3Si group possible only in this isomer. Thermolysis of 10 (740° C, 10^{-4} Torr) also afforded dimer 4 in 31% yield accompanied by the extrusion product, trimethylmethoxysilane, in 34% yield.

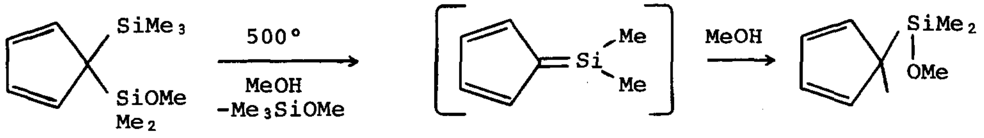


To our knowledge this is the first example of silene generation through the thermolysis of the $Me_3Si-CR_2-SiMe_2OMe$ unit. The lower thermal requirements as compared to retroene elimination make this an attractive alternate.

That silafulvene 3 is indeed initially formed is indicated by the results of nitrogen-flow pyrolyses of both 2 (680°) and 10 (500°) in the presence of excess benzaldehyde. Cycloaddition[1] of the carbonyl group and the Si-C double bond of 3 followed by extrusion and trimerization of dimethylsilanone (11) afforded hexamethylcyclotrisiloxane (12) in 17% and 29% yields respectively.[12]



A N_2-flow copyrolysis of 2 and methanol (660°) produced a complicated product mixture. However, the milder (500°) copyrolysis of 10 and methanol afforded the desired product (13)[13] of alcohol addition across the Si-C π bond of 3 in 58% yield. Adduct 13 was shown to decompose at 600° in a flow experiment, thus providing a rationalization for the failure of the copyrolysis of 2 and methanol.



10 3 13

Experiments are currently in progress for direct, spectral observation of 3.

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References and Footnotes

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3. For an excellent discussion of the role of polarity in the π-bond of silenes see, R. Ahlrichs and R. Heinzmann, *J. Am. Chem. Soc.*, **99**, 7452 (1977).
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10. Full crystallographic details are available from the Cornell authors, and will be published elsewhere.
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12. Although 6-phenylfulvene is also formed in this reaction (27%, GCMS and NMR analysis), taken alone this proves nothing since trimethylsilylcyclopentadiene will itself thermally react with benzaldehyde to produce this fulvene.
13. Identified by spectral comparison with an authentic sample.

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