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EVIDENCE FOR CYCLOPROPENE FORMATION IN THE REACTIONS OF 4,4-DIMETHYL-4-SILACYCLOHEXADIENYLIDENE

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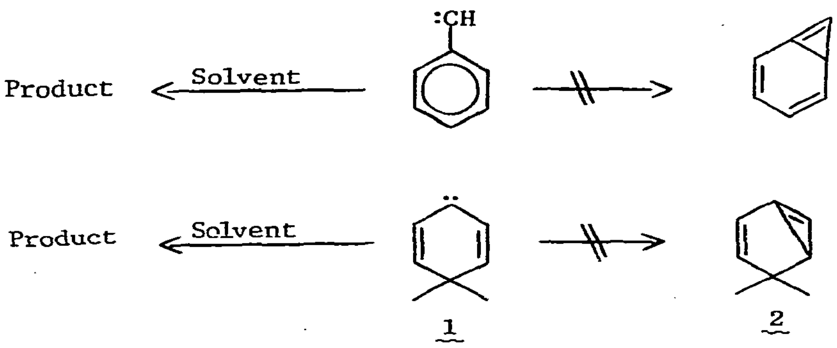
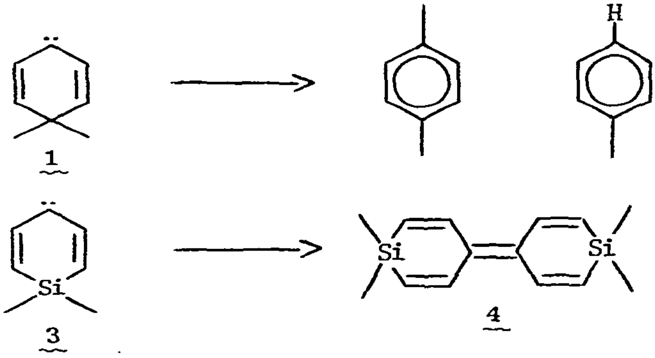
SUMMARY

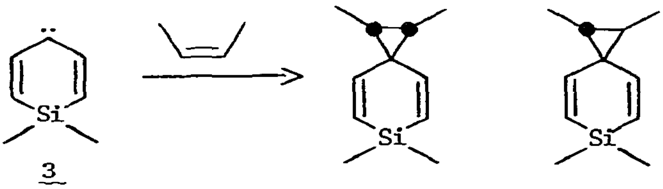
In the reactions of 4,4-dimethylcyclohexadienylidene no evidence for cyclopropene formation has been found. By contrast, 4,4-dimethyl-4-silacyclohexadienylidene yields a product on reaction with butadiene that is best rationalized by intramolecular cyclopropene formation.

Vinylcarbenes have long been known to provide an efficient source of cyclopropenes [1]. Indeed, together with the addition of carbenes to acetylenes, the intramolecular cyclization of vinylcarbenes must account for most modern cyclopropene syntheses. But modification of the structure of the vinylcarbene should render the cycloaddition less facile and thus allow intermolecular reactions to compete with intramolecular closure. Two such modifications have been used and found effective. Inclusion of the double bond of the vinylcarbene in an aromatic system suffices to retard closure so that in reactions of simple phenylcarbenes attack on solvent prevails [2]. However, if the aromatic system is annelated, addition can proceed at lower cost in loss of aromaticity and often occurs even in solution [3]. Similarly, inclusion of the double bond in a five- or six-membered ring was expected to induce sufficient strain in the product cyclopropene to prevent closure, at least in solution [4]. To our knowledge no evidence for cyclopropene formation in small cyclic systems exists. For example, no sign of the formation of **2** was found in the reactions of **1** in solution [4]. Conventional addition and insertion reactions won out at all times. We report here the discovery that substitution of silicon for the quaternary carbon allows the detection of reactions most easily attributed to a cyclopropene formed by intramolecular cycloaddition.

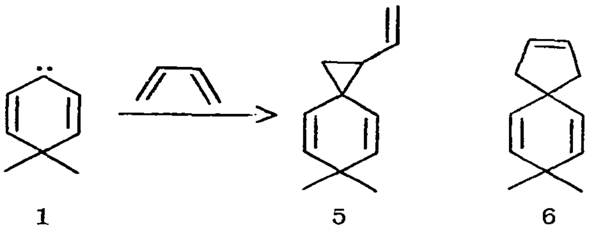


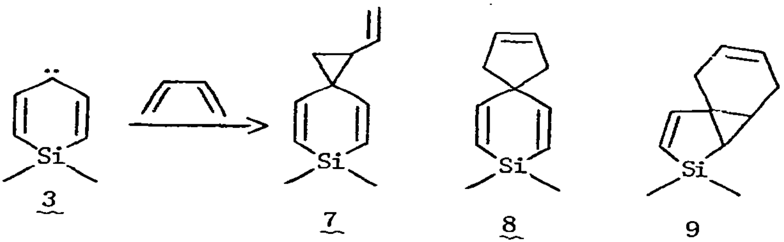
We had long seen 4,4-dimethyl-4-silacyclohexadienylidene (3) as a potential source of silabenzenes [5]. In our hands, however [6], generation of 3 in the gas phase, where competing intermolecular reactions should be minimized, and where 1 rearranges to aromatic compounds with ease [7], results only in the isolation of 4, the formal dimer of 3 [8]. Frustrated by our repeated failures to convert 3 to an aromatic compound, we turned to an investigation of the chemistry of 3 in solution in order to be certain that 3 behaved similarly to 1. Initially no significant differences were seen. Thus 3 adds overwhelmingly stereospecifically to *cis*-2-butene, as does 1 to *cis*-4-methyl-2-pentene [4]. Other typical carbene reactions of 3 have been observed by us and others [8,9].





However, the reaction with butadiene revealed surprising differences. Here 1 yields only the sensitive vinylcyclopropane 5 and small amounts of the product of pyrolysis of 5, cyclopentene 6.[*] By contrast, generation of 3 in butadiene gives not only 7 and 8, the silicon-substituted analogs of 5 and 6, but a new compound 9 as well. The overall yield is 66%, and 7, 8 and 9 are produced in the ratio 53/9/38. Compound 9 is not formed by photolysis or pyrolysis of 7 or 8.





The elemental analysis of 9 establishes its composition as $C_{11}H_{16}Si$. In the infrared spectrum (see Table 1) bands appear, *inter alia*, at 1659 and 1552 cm^{-1}. The band at 1649 cm^{-1} in cyclohexene [10] is only slightly changed by incorporation of a three-membered ring as in bicyclo[4.1.0]hept-3-ene [11,12]. Other such systems are reported at similar or even higher frequencies [13,14]. Thus the 1659 cm^{-1} band is appropriate for 9 and there seems no chance that an unsubstituted cyclopentene (ca. 1611 cm^{-1}) [10,15] could be incorporated. However, a cycloheptene (ca. 1650 cm^{-1}) [15] must be considered and for the moment will be carried along as a possibility.

The band at 1552 cm^{-1} requires a 3-silacyclopentene. A large series of such compounds has been described [16] and values between 1550 and 1560 cm^{-1} given. 1,1-Dimethyl-2-silacyclohexene is reported [17] to absorb at 1600 cm^{-1} and the analogous 1,1-dichloro compound [18] at 1595 cm^{-1}. A number of silacyclohexadienes produced in this work showed a pair of bands for the carbon-carbon double bond, one weak, the other strong, centered at roughly 1650 cm^{-1}.

Confirmation that the molecule contains only two double bonds comes from the ^{13}C NMR spectrum which shows only four olefinic carbons (157.9,

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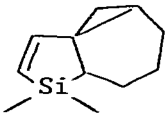
[*] This reaction was reported in reference 4 and repeated by us. No products other than 5 and 6 could be found.

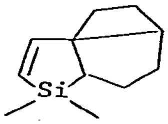
TABLE 1: SPECTRA OF 9

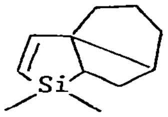
^1H NMR (δ,$CDCl_3$)	^{13}C NMR (ppm,$CDCl_3$)		IR (cm^{-1})		
0.04 (shoulder)	157.9	27.8	3034(s)	1341	1041
0.16 (singlet)	127.0	25.9	2979(s)	1272(w)	1011
0.85 (triplet, 1H)	123.7	10.4	2899(s)	1251(sh)	973
2.40 (multiplet, 4H)	122.7	0.0	2837(s)	1248	969
5.54 (multiplet, 3H)	35.9	-3.2	1659	1216	934
6.71 (doublet, 1H)	30.9		1552(s)	1191	909(w)
			1436	1172(w)	889(s)
			1398	1139	864(s)
			1380(w)	1119	842(s)
			1356	1070	

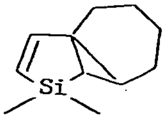
127.0, 123.7, and 122.7 ppm; see Table 1). Similarly, the ^1H NMR spectrum shows only four olefinic hydrogens. Thus, there are no hidden tetrasubstituted double bonds that might account for our 1659 cm^{-1} band, and the two double bonds are disubstituted. The remarkable shift to low field of the olefinic carbon β to the silicon had been noticed by us previously in other compounds, and recently a collection of spectra has reached the literature [19].

The ^1H NMR spectrum yields another important fact that ultimately allows a determination of the size (six- or seven-membered) of the carbocyclic ring. The hydrogen on the carbon β to silicon is coupled only to the hydrogen on the α carbon. There is no hydrogen on the γ carbon which therefore must be tetrasubstituted. Were the carbocyclic ring to be seven-membered, it can only be attached to the silacyclopentene in a fused fashion as shown below. In order to make the γ carbon tetrasubstituted, the size of the seven-membered ring must be reduced in one of the four ways possible. In any event, we no longer have a cycloheptene. Thus, the second double bond must be contained in a cyclohexene.

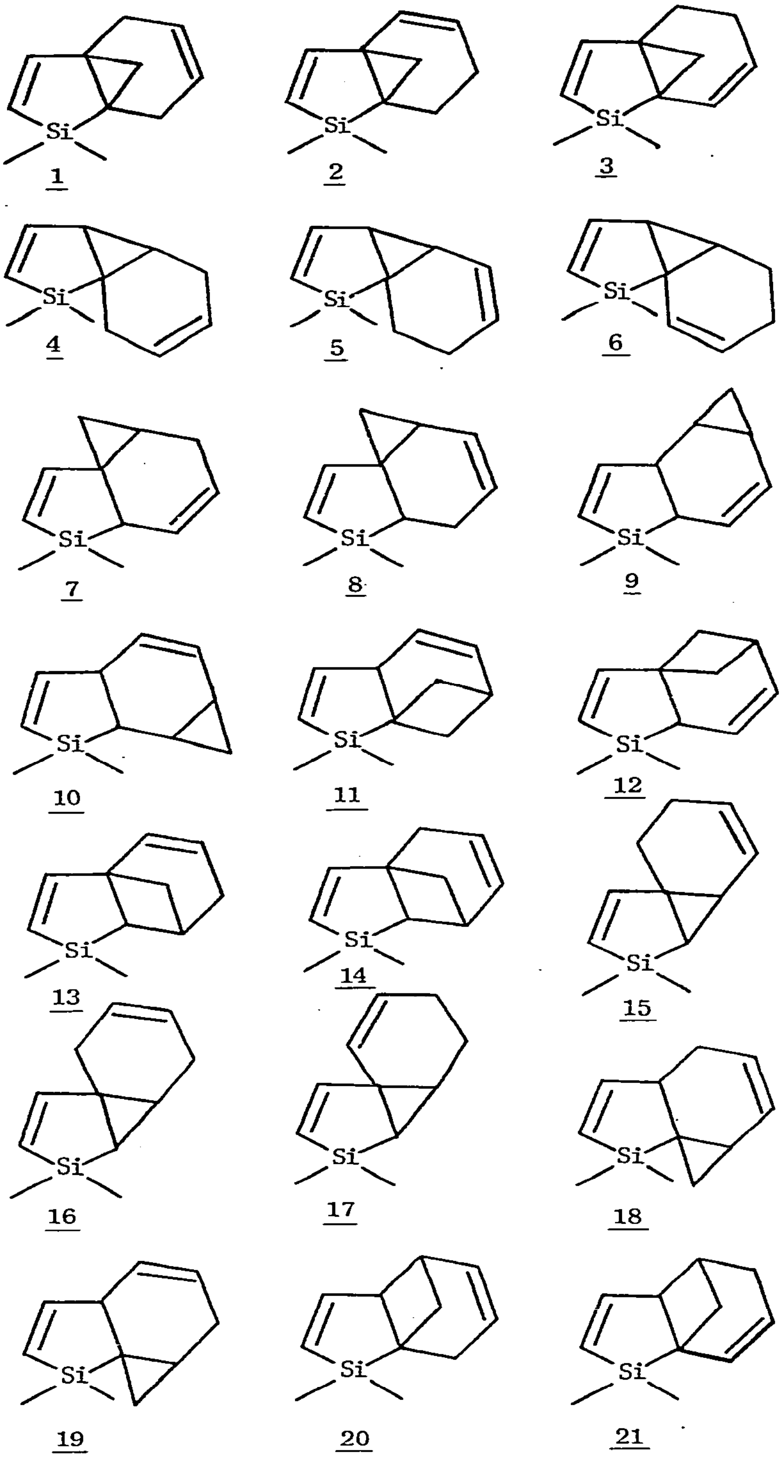








Application of CONGEN [20], with the only constraints being the absence of silenes and siliranes, and the presence of the cyclohexene and silacyclopentene demonstrated previously, led to a list of 21 structures (see Fig. 1). The off-resonance decoupled ^{13}C NMR spectrum revealed a



1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21

FIGURE 1

single quaternary carbon, thus eliminating isomers 1, 2, 3, 9 and 10. As the γ carbon must be tetrasubstituted, compounds 4, 5, 6, 9, 10, 11, 18, 19, 20 and 21 were ruled out. The ^{1}H NMR spectrum further showed that two high-field protons were coupled to each other, and that neither was coupled to an olefinic hydrogen (see Schematic Coupling Chart). One of the high-field

SCHEMATIC COUPLING CHART
(^{1}H NMR)

1H	0.04
6H	0.16
1H	0.85
4H	2.40
3H	5.54
1H	6.71

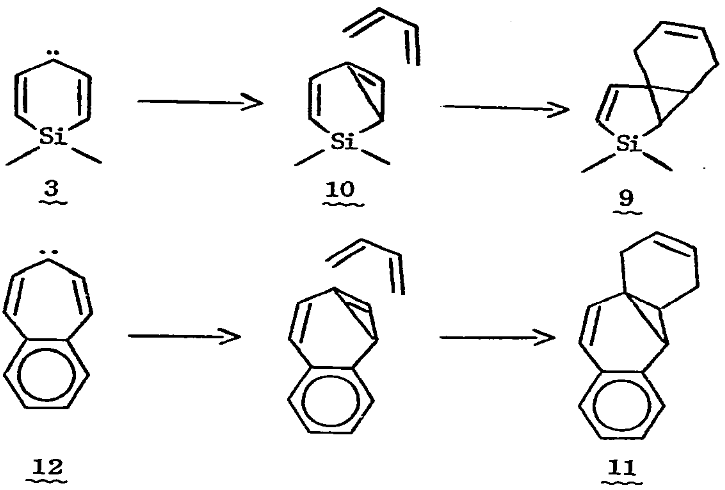
hydrogens was coupled, however, to the four-proton multiplet at 2.4 δ. The presence of two high-field hydrogens, each integrating for a single proton coupled in this way, rules out several isomers previously eliminated (4, 5, 6, 9, 11, 20 and 21) and allows us to discard for the first time 7, 12 and 15 (and probably 13 and 14 as well).

Thus of the original twenty-one, only three, 8, 16 and 17 (and perhaps 13 and 14) remain. Of these, 16 alone possesses the four non-cyclopropyl allylic hydrogens required by the ^{1}H NMR spectrum. This criterion also rules out 2, 3, 5, 6, 7, 9, 10, 12, 13, 14, 15, 18, 19, 20 and 21.

Of the original twenty-one, only three (1, 8 and 17) have been eliminated by a single criterion. Two of these (8 and 17) contain the bicyclo-[4.1.0]hept-2-ene system, the parent compound of which is reported to absorb in the infrared at 1632 cm^{-1}, significantly lower than that observed. Compound 1 suffers a conspicuous lack of mechanistic probability as well as containing two quaternary carbons.

Thus we feel that enough redundancy has been built into our analysis to warrant a confident claim for the structure of 16 = 9.

Given the structure of 9 and its formation as a primary product, the intervention of the cyclopropene 10 as precursor becomes most attractive. A similar process has been invoked by Coburn and W. M. Jones to account for the formation of 11 from 12 [21].



3 10 9

12 11

Beyond noting that other acyclic dienes undergo the same reaction with 3, we cannot yet comment upon the generality of the effect. Experiments designed to uncover the source of the changes induced by the substitution of silicon for carbon are under way.

EXPERIMENTAL

1-Diazo-4,4-dimethyl-4-silacyclohexadiene. This was made by either the method of Barton and Banasiak [8] or by the method of Jones et al. [4] from the known 4,4-dimethyl-4-silacyclohexadien-1-one [22].

Pyrolysis of 1-diazo-4,4-dimethyl-4-silacyclohexadiene. 80 µℓ of 1-diazo-4,4-dimethyl-4-silacyclohexadiene, in 5 µℓ portions, was pyrolyzed at 620° and 5×10^{-3} Torr. The pyrosylate was collected at -196° C and, after the pyrolysis was complete, dissolved in carbon tetrachloride. Analysis of this solution on a 10' 20% SE30 on Chromosorb W column at 190° gave the dimer 4 [8] as the only identifiable product.

Photolytic generation of 3 in cis-2-butene. A sample of 87 mg 1-diazo-4,4-dimethyl-4-silacyclohexadiene in ~ 10 ml *cis*-2-butene was photolyzed in a sealed 10 mm OD Pyrex tube, using a Hanovia L679A high-pressure mercury arc lamp at 10° C. After photolysis, the *cis*-2-butene was removed by distillation and the residue dissolved in carbon tetrachloride. Analysis on a 6' 10% SF96 on Chromosorb W at 135° showed cis- and trans- adduct in a ratio of 92:8 (overall yield 54%) as the only volatile products.

Assignment of stereochemistry rests on the appearance of two quartets for the vinyl hydrogens in the cis adduct and only one in the trans.

Analyses were by high-resolution mass spectroscopy: (cis adduct) Found: 178.1176. (trans adduct) Found: 178.1176. $C_{11}H_{18}Si$ calcd.: 178.1178.

NMR (CCl_4, cis adduct): 0.33 δ (6H,s), 1.37 δ (8H,bs), 5.72 δ (2H,m), 6.24 δ (2H,q). NMR (CCl_4, trans adduct): 0.35 δ (6H,s), 1.42 δ, shoulder 1.25 δ (8H,d,m), 5.98 δ (4H,q).

Photolytic generation of 3 in butadiene. A sample of 90 mg of 1-diazo-4,4-dimethyl-4-silacyclohexadiene in ~ 10 ml butadiene was photolyzed at 10° for 3 h. Separation on a 12' x 1/4" 10% DC 710 on Chromosorb P at 130° gave 35% 7, 6% 8, and 25% 9.

NMR (C_6D_{12}, 7): 0.08 δ (6H,s), 0.98-1.95 δ (3H,m), 4.83-6.70 δ (7H,m). NMR (C_6D_{12}, 8): 0.07 δ (6H,s), 3.40 δ (3H,s), 6.27 δ (4H, AB quartet), 5.61 δ (2H,s).

Analysis: (9) Found: C, 74.73; H, 9.13. (7) Found: C, 74.71; H, 9.12. $C_{11}H_{16}Si$ calcd.: C, 74.93; H, 9.15. (8, mass spectrum) Found: 176.1018. $C_{11}H_{16}Si$ calcd.: 176.1021.

Control experiments. A sample of ~ 5 mg 7 was dissolved in perdeuteriocyclohexane in a sealed NMR tube. Photolysis, using a Hanovia L 679A high-pressure mercury arc lamp at 10° for 3.25 h, left the sample unchanged. Heating the tube at 135°-140° for 2 h converted 7 cleanly to 8. Irradiation of the solution of 8 for 3 h formed no 9.

ACKNOWLEDGMENT

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