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Studies on dimethylsilylene

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Studies on dimethylsilylene

by

James Bailey Kimble III

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

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For the Graduate College

Iowa State University
Ames, Iowa
1977

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DEDICATION

To Barb, my wife, my friend and my greatest inspiration

HISTORICAL

When considering organosilicon compounds it is often easiest to compare the chemistry of these systems with the analogous carbon systems. In keeping with this tradition a similar tack will be taken here. A review of the organic literature reveals certain molecules or molecular systems that generate special interest among researchers. The origins of this interest are varied, from unusual and mysterious chemistry to extreme difficulty in synthesis. Among these especially well-described systems are the cyclopentadiene, cyclopropane and norbornadiene systems. It is the organosilicon analogues of these systems that will be discussed here.

It is perhaps unusual to find all of these discussed in one work. There is, however, a unifying thread that joins these areas. They are all associated with silylenes, the silicon analogues of carbenes. Silacyclopentadienes and 7-silanorbornadienes are involved in the generation of silylenes, and silacyclopropanes are thought to be important in some reactions of silylenes. Each of these compounds is of interest to the chemist because of its own chemistry, as is shown by the wealth of work discussed below. Their involvement with silylenes will be of special interest here.

Silylenes

Silylenes are the divalent silicon species analogous to carbene. While the known chemistry of carbenes (1) is extensive, much less is known about the reactions of silylenes (2-5). The work presented in this dissertation is an attempt to increase our knowledge in this area.

As with carbenes, the chemistry of silylenes is much affected by the substituents on the central atom, silicon. The dihalosilylenes are an important area in this field (2,6). A considerable amount is known about them, however they lie outside the scope of this work, and for the most part will be neglected here. The parent molecule, $:SiH_2$, has also been the object of much investigation, especially by Hass and Ring (7), Jenkins et al. (8) and Sefiek and Ring (9). Again a complete discussion of this area is impossible here and will be neglected unless it has some particular relevance to this work. This dissertation will be concerned with the diaryl and dialkyl derivatives of silylene, and in particular their reactions with acetylenes and olefins.

The first diorganosilylenes were postulated in 1959 by Gilman and coworkers (10,11) when they proposed that the product of various disilanes and silyl anions, a polysilane, could be explained by the involvement of a silylene (1). In a similar vein Wiberg et al. (12), postulated the intermediacy of dimethylsilylene in the decompositions

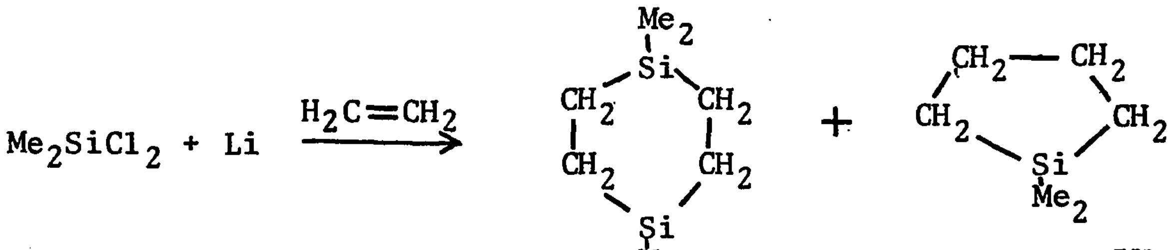
$$\varphi_3SiK + \varphi_3SiSiCl_3 \longrightarrow \varphi_3SiSi\varphi_3 + KCl + [:SiCl_2]$$
$$n[:SiCl_2] \longrightarrow (SiCl_2)_n \qquad \text{I}$$

$$Zn(Si\varphi_3)_2 \longrightarrow Zn + Si\varphi_4 + [:Si\varphi_2]$$
$$n[:Si\varphi_2] \longrightarrow (Si\varphi_2)_n \qquad \text{II}$$

$$3\ Hg(SiMe_3)_2 + 2\ Al \longrightarrow 3\ Hg + Al(SiMe_3)_3$$
$$Al(SiMe_3)_3 \longrightarrow AlMe_3 + (:SiMe_2)$$
$$n[:SiMe_2] + Hg(SiMe_3)_2 \longrightarrow Me_3(SiMe_2)_nMe \qquad \text{III}$$

of $Zn(SiMe_3)_2$ (II) and $Hg(SiMe_3)_2$ in the presence of Al (III) to form polysilanes. While these explanations are possible, other mechanisms not involving silylenes are also satisfactory and these authors provided no definitive evidence for their mechanism.

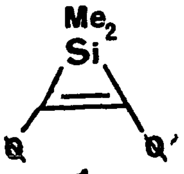
The intermediacy of a silylene was also postulated by some Russian workers (13). They reacted dichlorodimethylsilane with lithium. They formed polysilane products similar to those mentioned earlier. When these reactions were run in the presence of various olefinic traps, products consistent with the intermediacy of silylenes were formed (IV). Similar results were obtained when a cyclic polysilane was heated in the presence of these traps (14). While these organometallic reactions were first thought to go



IV

through silylenes, Weyenberg at al. (15) have shown that they probably do not, as analogous products are formed when Me_3SiCl is used instead of Me_2SiCl_2.

Volpin et al. (16,17) and Leites et al. (18) was the first to react silylenes with acetylenes when he heated $(SiMe_2)_{55}$, a cyclic polysilane, in the presence of diphenylacetylene. He recovered a high-melting white solid to which he originally assigned the structure of a silacyclopropene (1). Similar products resulted from dimethylgermylene.



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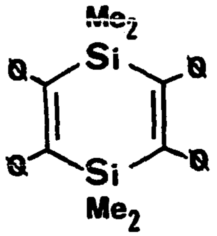
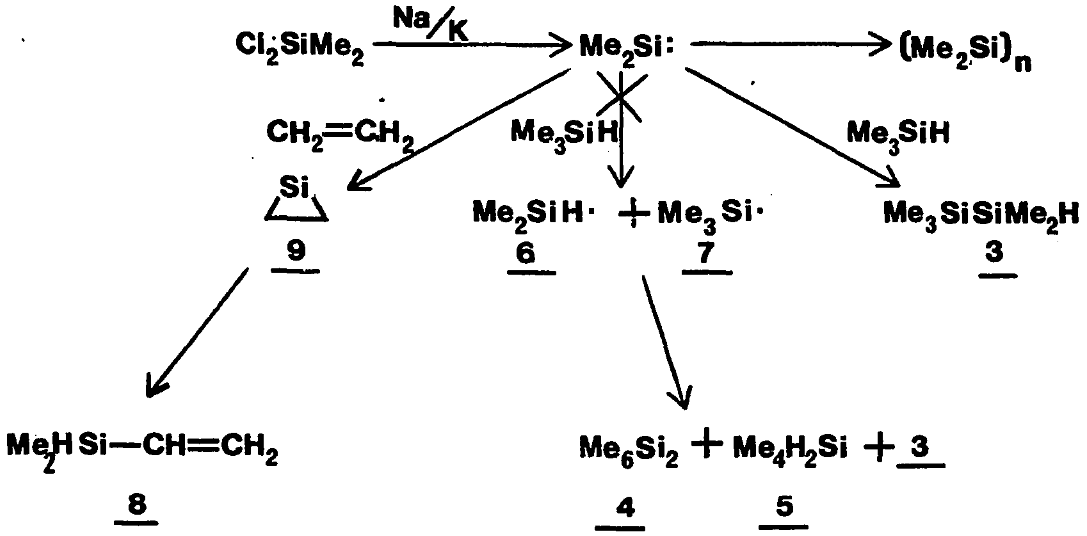


2

Unfortunately his structure assignment proved to be wrong. Johnson et al. (19) showed by mass spectroscopy that the molecule was actually the dimer (2) of 1. West and Bailey (20) later confirmed this disilacyclohexadiene structure by freezing point studies.

The first evidence for the existence of diorganosilylene was furnished by Skell and Goldstein (21). When Me_2SiCl_2 was passed into a Na/K vapor the product obtained was a polysilane. When the reaction was run in the presence of Me_3SiH the product was the disilane 3. This product can be explained by the insertion of the silylene into the Si-H bond of the trap. It is important that neither disilane 4 or 5 were found in the product mixture. If the silylene reacted as a triplet, then the primary reaction would produce diradicals 6 and 7. If these were produced then all three of the disilanes 3, 4 and 5 would be formed. That 4 and 5 were not produced is taken as evidence that the silylene reacts as a singlet by concerted insertion into the Si-H bond. Skell also found the reaction of dimethylsilylene with ethylene produced dimethylvinylsilane (8). This product was rationalized as coming from the intermediate silacyclopropane (9). This work is summarized in Figure 1. These latter ideas were reinforced in a succeeding paper (22). Two other methods that likely give silacyclopropanes

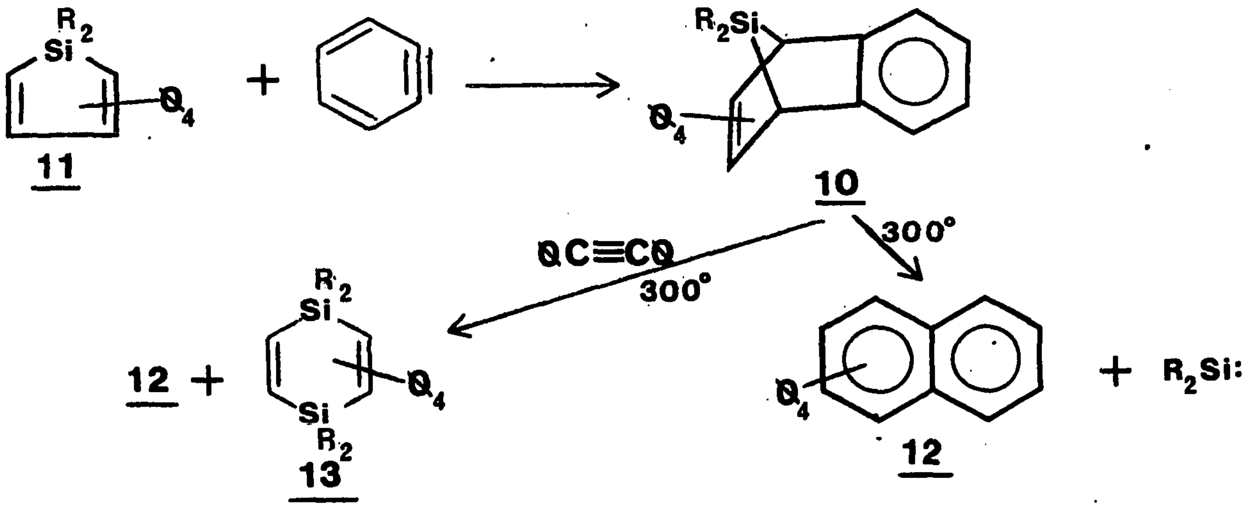


also give dimethylvinylsilane as the only product (V).

$$Me_3SiCHCl_2 \xrightarrow{Na/K} \underline{8} \xleftarrow{Na/K} Me_2Si(CH_2Cl)_2 \qquad V$$

Some reservations have appeared (1) as alternative explanation of these results are possible, however, subsequent study has not produced any evidence that refutes the proposals made by Skell and Goldstein.

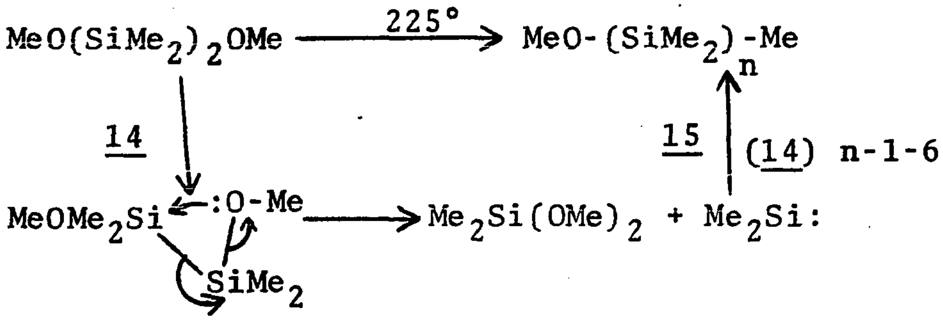
In 1964 Gilman, Cottis, and Atwell (23a,b) showed that 7-silanorbornadienes are good generators of silylenes. When the Diels-Alder adduct (10) of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (11) (R=Me) and benzyne were heated to 300° the elements of dimethylsilylene were extruded and the tetraphenylnaphthalene (12) was recovered. When this reaction was carried out in the presence of diphenylacetylene, tetraphenyldisilacyclohexadiene (13) (R=Me) was recovered in greater than 50% yield (see above). This is much higher than the yield of the analogous products from Volpin's work. The results are the same when 11 (R=Φ) was used



Gilman has shown that several other dienophiles, i.e. phenylacetylene, dimethylacetylenedicarboxylate and maleic anhydride react with silacyclopentadienes to give adducts analogous to 10. Many of these also thermally extrude silylene, if an aromatic residue can be produced, just as 10 does. However, this reaction is very dependent on the substituents as other reactions take the place of the silylene elimination in some systems.

Much work has been done on these interesting 4+2 adducts. In a later section the varied chemistry of these molecules will be discussed, but here a few words on the elimination of silylene are in order. Balasubramanian and George (24) have found the substituents on the silicon have a significant role in determining if silylene will be eliminated. Maruca and coworkers (25) have studied five systems with varying degrees of substitution on the carbon base of the silanorbornadiene system. They concluded that decreasing the number of substituents and the electron withdrawing ability of the substituents around this base would lower the temperature at which the silylene is eliminated. A French group (26) has studied the 4+2 adduct of 1,1-dimethyl-2,5-diphenylsilacyclopentadiene with trichlorogermylacetylene and found that this molecule undergoes elimination of silylene at 70°.

In 1966 Atwell and Weyenberg (27,28) and Atwell et al. (29) published the first of a series of papers that introduced a new general method for producing silylenes. When sym-dimethyoxytetramethyldisilane (14) is pyrolyzed at 225° a mixture of polysilanes (15) results (VI). Kinetic work on this reaction



VI

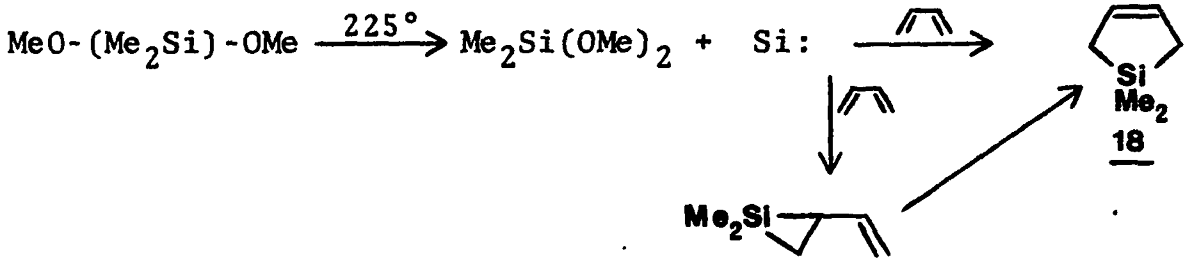
showed that this conversion proceeds first by a unimolecular decomposition of 14 to produce dimethylsilylene and dimethoxydimethylsilane (15) n=1. The silylene thus produced then inserts into the Si-O bonds of starting material or products to produce the observed mixture of polysilanes. It was also demonstrated that any disilane with substituents that have unshared pairs of electrons also undergo this reaction. For instance dichlorotetramethyldisilane also reacts to eliminate dimethylsilylene and leave dichlorodimethylsilane. Sakurai et al. (30a,b) has shown that silyl hydrides undergo a similar type of α elimination when heated to 300° (VII). Pentamethyldisilane (16) yields a mixture of polysilanes 17 when pyrolyzed. In this case

$$\underset{16}{Me_3SiSiMe_2H} \xrightarrow{300^\circ} \underset{17}{Me_3Si(SiMe_2)_nH} \qquad \text{VII}$$

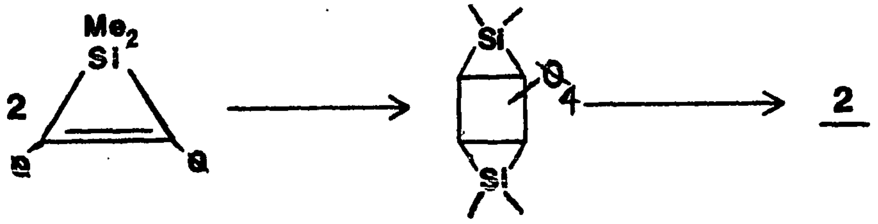
the silylene inserts into the Si-H bond of 16 as was seen in Skell's work. Recently hexamethyldisilane has been shown to undergo this same reaction, however temperatures of over 500° were required (31).

The Atwell-Weyenberg method of producing silylenes is an improvement over previous methods as the starting material is much more convenient to synthesize, and the silylene can be used to make products in very high yield. Atwell and Weyenberg used it to make disilacyclohexadiene (2). With this method of silylene generation they discovered a new reaction of silylenes - that with dienes (28). The product of this reaction is a 1,1-dimethylsilacyclopentene (18). It is believed that this reaction proceeds through the intermediacy of a silacyclopropane, followed by 1-3 migration of the silicon. This latter reaction has precedent in the carbon literature.

Fig. 3

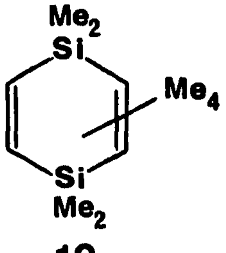


Since the determination of the correct structure of the product from the reaction of Me_2Si: and acetylenes by Johnson (19) and West (20), the process for its formation has intrigued organosilicon chemists. Gilman (23) hypothesized its formation proceeded through the silacyclopropene (1), which the dimerized in a 2+2 fashion (VIII).



VIII

With this new, convenient silylene precursor Atwell and Weyenberg tested this hypothesis (28). They pyrolyzed dimethoxytetramethyldisilane (14) in the presence of diphenylacetylene and 2-butyne. If the silacyclopropene was formed and underwent $2\pi+2\pi$ dimerization then disilacyclohexadienes 2, 19, and 20 would have been formed. The critical product



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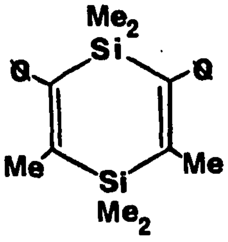

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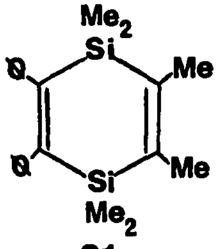
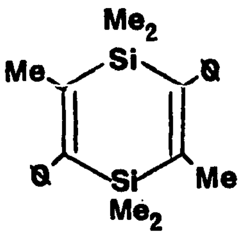


21

is 20, as it is the only mixed product possible if the $2\pi+2\pi$ dimerization operates. The products of the reaction were 2, 19, and 21; no 20 was formed. When the reaction was run with phenylpropyne the products were 22 and 23; no 24 was found as is demanded by the $2\pi+2\pi$ dimerization. As the



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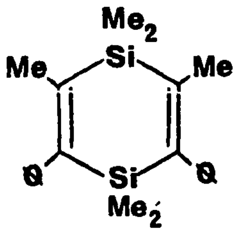

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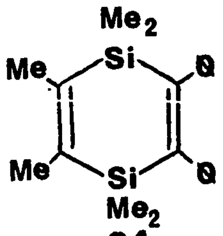
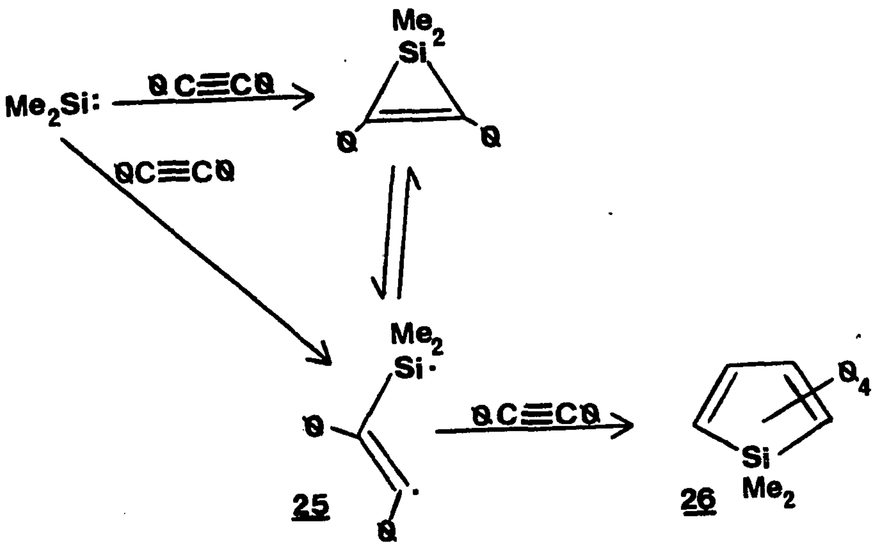
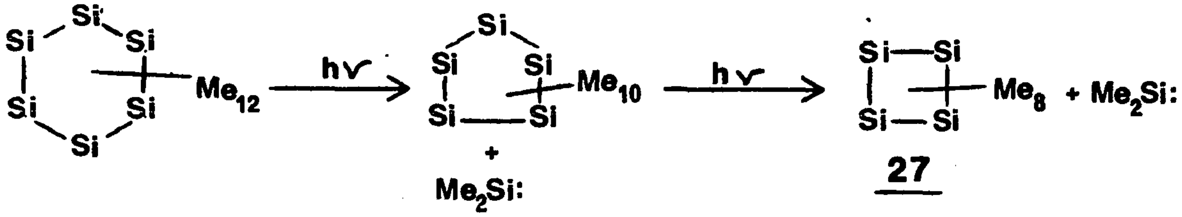


24

$2\pi+2\pi$ dimerization is not operative, alternatives must be considered. One alternative is a mechanism involving a diradical, 25, as shown in Figure 4. If this diradical were involved, one would expect excess acetylene to react to form a silole (26). This product was not found, thus the diradical is an unlikely intermediate.

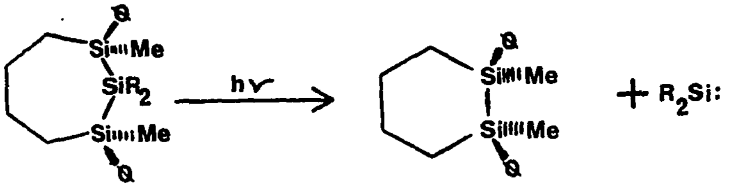


Another method of generating silylene has been developed by Japanese chemists. In 1966 Ishikawa and Kumada showed that permethylpolysilanes eliminate Me_2Si: when photolyzed in the U.V. (32a,b,c). Cyclosilanes also eliminate silylene. Ishikawa and Kumada were able to easily synthesize the previously unknown permethylcyclobutasilane (27) from permethylcyclohexasilane (33)



IX

(IX). Sakurai et al. modified this method to develop his "tailor-made" silylene generator (28) (34a,b). He showed that elimination of dimethylsilylene proceeds with retention at the terminal silicons (X).

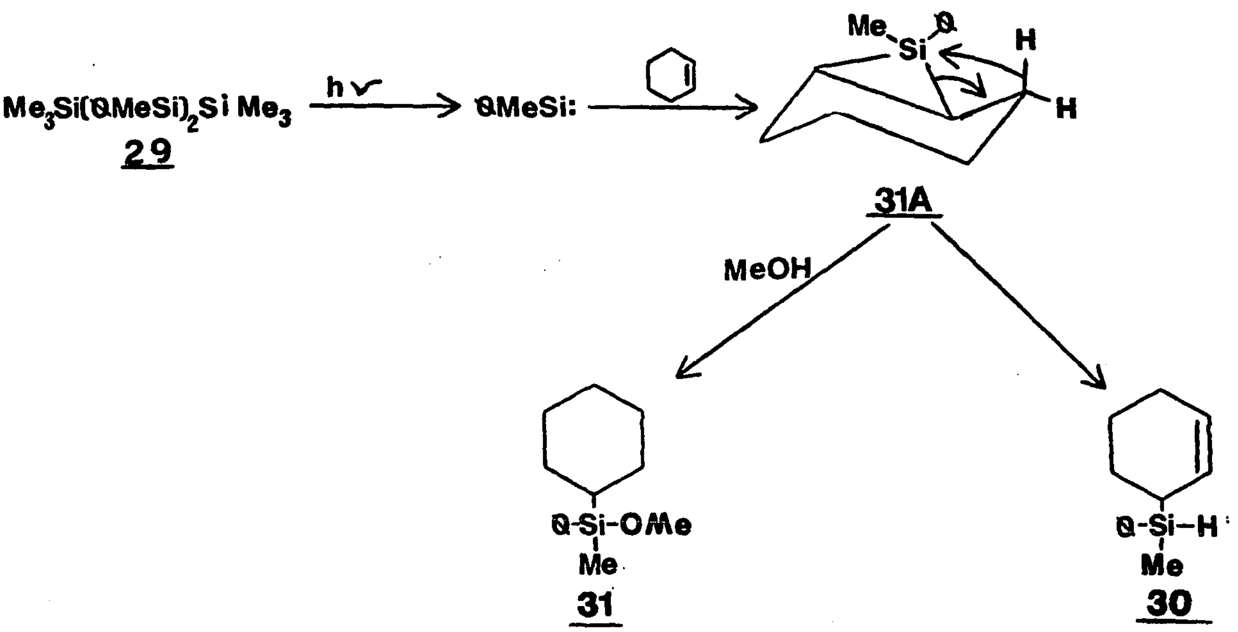


28

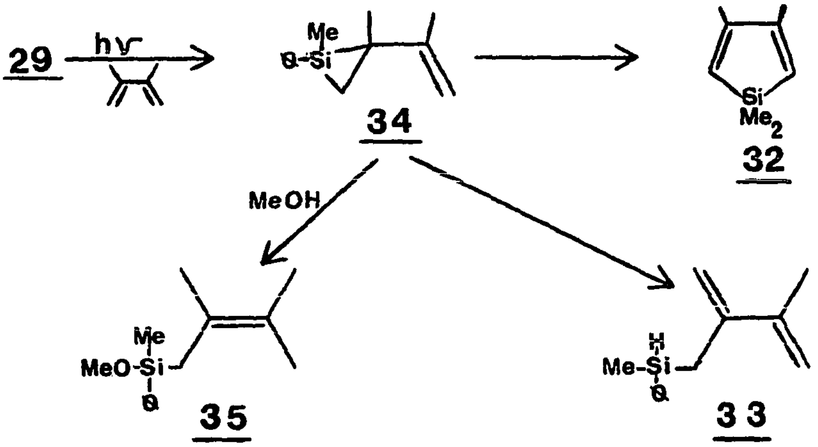
X

Ishikawa et al. (35a,b) used their polysilane photolysis for generation of a silylene to synthesize what is apparently the first stable silacyclopropane formed via a silylene reaction. When φMeSi: is generated by photolysis of polysilane (29) in a quartz vessel with cyclohexene as the solvent, the only product is the allylic insertion product 30. However, if a Vycor filter is used, a new product is formed in solution. If this solution is photolyzed through quartz then 30 is once again formed. If methanol is added then a new product, silyl methyl ether 31, is formed. This is the expected product from the reaction of silacyclopropane 31a. Although no other evidence has been presented, it is likely that a process like that shown below is operating. A similar sort of reaction has been seen by Gilman in a thermal reaction (36).

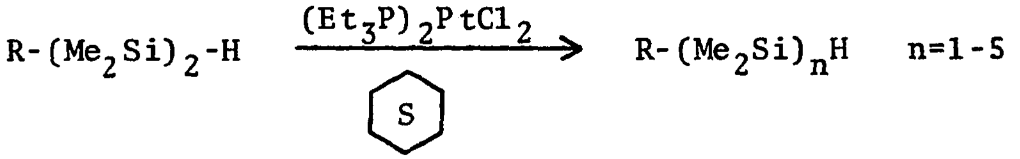
Ishikawa et al. have also investigated the reaction of silylene with dienes (37). When 29 is photolyzed with 2,3-dimethylbutadiene not only is the expected



silacyclo-3-pentene (32) produced but also silyl butadiene 33, as shown below. The formation of this new product is understandable if silacyclopropane 34 is an intermediate. More evidence in this regard is gained when the reaction is performed in the presence of methanol. Under these conditions 32 and 33 are replaced by silylether 35 as the only product.

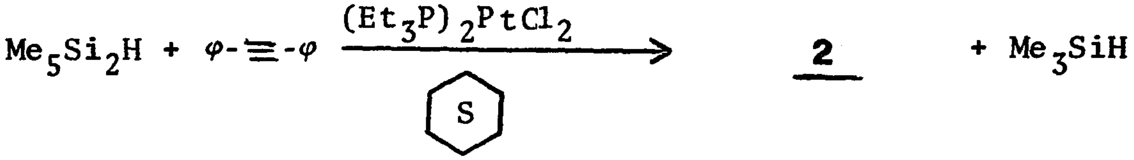


Yamamoto et al. has developed what could become a convenient method to produce silylenes (38,39). When disilylhydrides are heated in the presence of a platinum calalyst, one obtains a mixture of polysilanes (XI). The possibility



$$R\text{-}(Me_2Si)_2\text{-}H \xrightarrow[\text{S}]{(Et_3P)_2PtCl_2} R\text{-}(Me_2Si)_nH \quad n=1\text{-}5$$

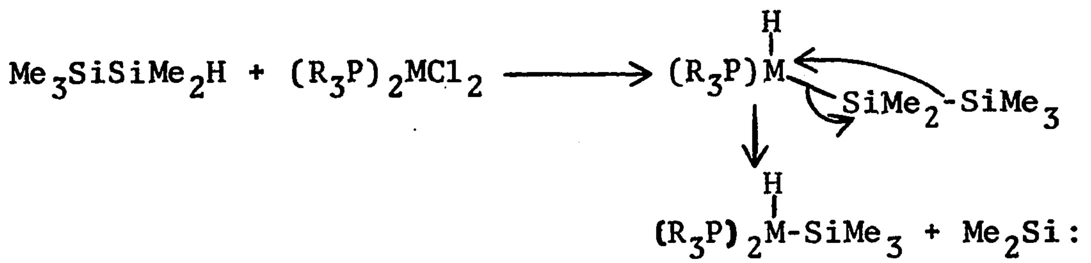
XI



$$Me_5Si_2H + \varphi\text{-}\equiv\text{-}\varphi \xrightarrow[\text{S}]{(Et_3P)_2PtCl_2} \underline{\mathbf{2}} + Me_3SiH$$

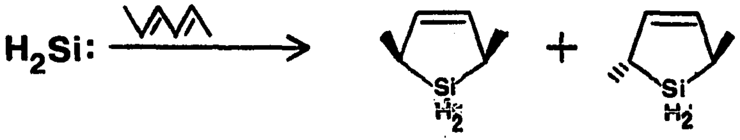
XII

that a silylene is involved was increased by the finding that when the reaction was run in the presence of diphenylacetylene, trimethylsilane and disilacyclohexadiene $\underline{2}$ were isolated. Kumada has suggested that this reaction proceeds by an oxidative addition of the silylhydride bond to the metal. This is followed by an α-elimination to produce a new silicon metal bond and dimethylsilylene (see below). Other metals are known to react in a similar fashion, particularly nickel and palladium (40,41). However, when metals or ligands are changed, the reaction changes which probably means that there is no free silylene involved, but a metal silenoid of some type.



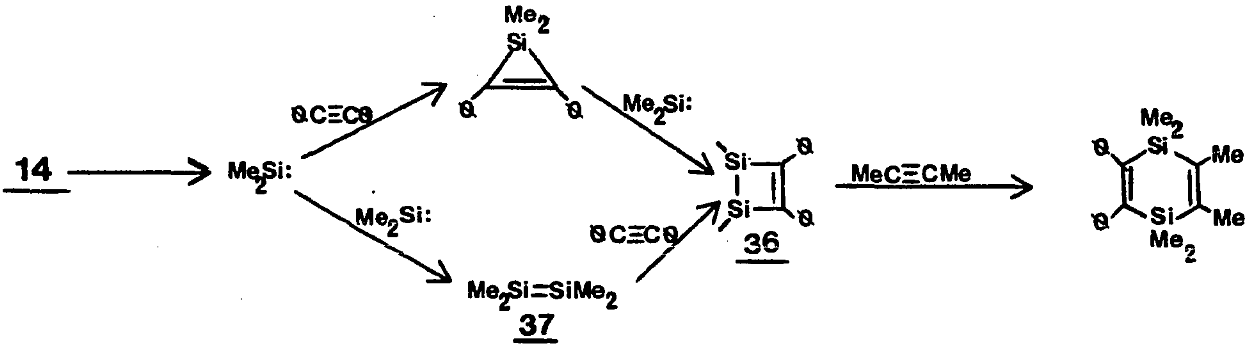
$$Me_3SiSiMe_2H + (R_3P)_2MCl_2 \longrightarrow (R_3P)\overset{H}{M}\text{-}SiMe_2\text{-}SiMe_3 \longrightarrow (R_3P)_2\overset{H}{M}\text{-}SiMe_3 + Me_2Si:$$

Gaspar has pioneered the production of H_2Si: via nuclear recoil (42). Phosphine molecules are bombarded by fast neutrons and transformed into ^{31}Si atoms. These abstract hydrogen atoms from molecules of phosphine yielding H_2Si:. This method does not allow the generation of silylene in synthetic quantities, but one can investigate some aspects of the way these intermediates react. Gaspar found that silylene can insert into Si-Si bonds (43). He then investigated the reaction of silylene with dienes (44). He found that when silylene reacted with trans,trans-2,4-hexadiene he obtained an approximately 1:1 ratio of cis- and trans-silacyclo-3-pentene (below). It was concluded that there

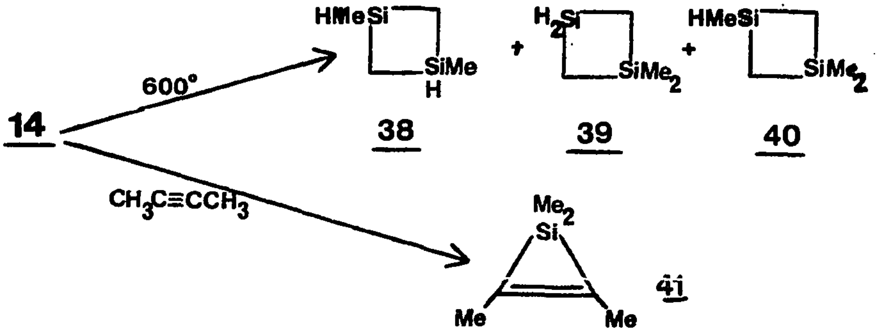


was a diradical on the reaction surface that had allowed bond rotation to occur. It has been shown, however, that the multiplicity of the silylene produced by this method is in a ratio of 4:1 triplet to singlet (45a,b). Also the singlet is the ground state, therefore it is likely that Gaspar's results are an artifact of this method of silylene production.

Returning to the reaction of silylene with acetylenes. Atwell and Uhlman have shown that disilacyclobutane 36 is formed in the reaction of dimethylsilylene (from disilane 14) with diphenyl acetylene in a gas flow if the concentrations are adjusted correctly (46). Barton and Kilgour have shown that if this molecule is pyrolyzed in a sealed tube in the presence of more acetylene, disilacyclohexadienes are produced (47). They also showed that the disilacyclohexadienes produced in the case where two different acetylenes are used, are the ones required by the Atwell and Weyenberg work (see below). This silacyclobutane

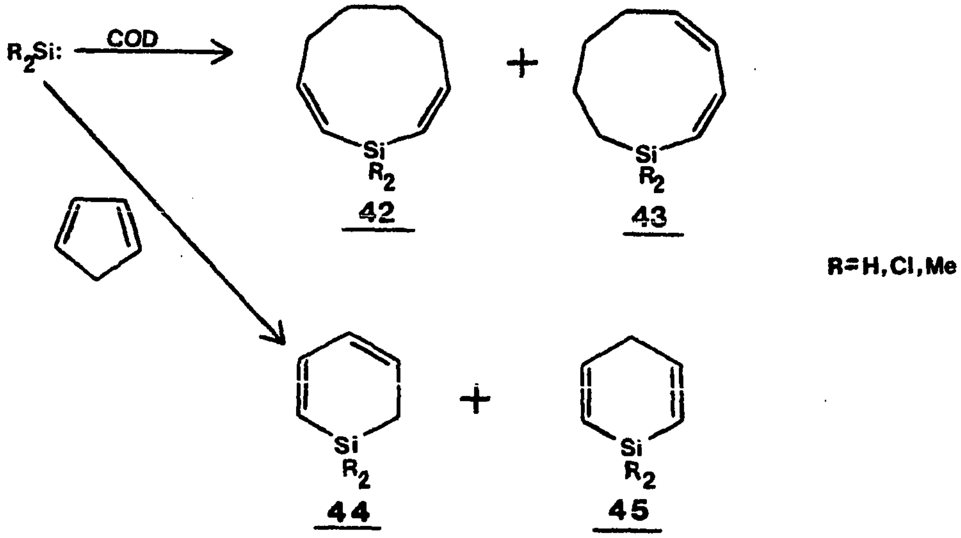


can be formed in two general ways. Initial formation of silacyclopropene 7 followed by insertion of another silylene, either into a Si-C σ-bond or into the C=C double bond followed by rearrangement to form the product 36. Alternatively the silylene could dimerize to a disilene like 37, then undergo what is formally a 2π+2π cycloaddition reaction with diphenylacetylene to form 36. Gaspar and Conlin have supported both of these possibilities (48,49) by showing that dimethylsilylene will dimerize when reacted with propyne at temperatures above 600° C. He obtained products 38, 39, and 40 from this reaction (XIII). Peddle had previously shown that these are the products of the reaction of disilene with acetylenes (50). Recently, Peddle and Roark have achieved the first synthesis of a silacyclopropene (50). When 14 is pyrolyzed in the presence of a tenfold excess of 2-butyne, disilacyclopropene 41 is isolated in very high yield. However, the dimerization of dimethylsilylene did not occur at temperatures below 400°. Since disilacyclohexadiene formation occurs at temperatures as low as 200° it seems unlikely that disilene is involved.



XIII

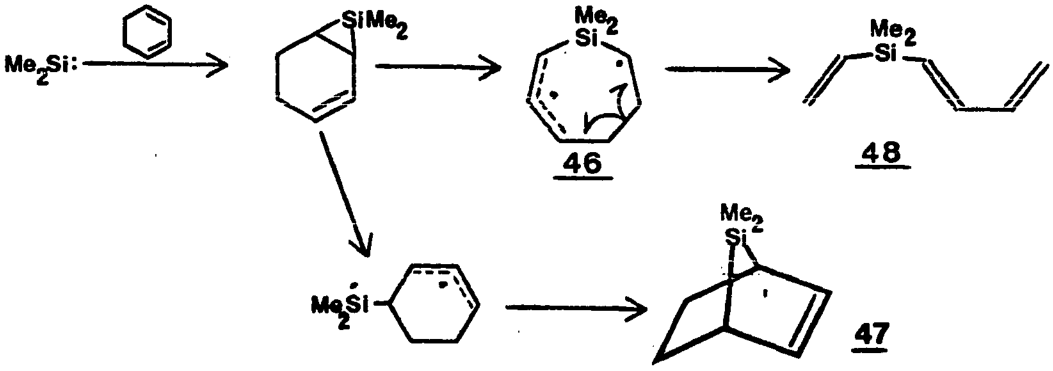
An interesting reaction of silylenes has been described by Childs and Weber (51). In this work silylene was added to cyclooctadiene to yield cyclodienes 42 and 43. Although it was not referenced by Weber, a similar reaction had been discussed by Chernyshev et al. (52) earlier. Chernyshev et al. added dichlorosilylene to cyclopentadiene to yield 1,1-dichloro-1-silacyclo-2,4-hexadiene (44). Hwang et al. has clarified this situation (53). He found that dimethylsilylene with



cyclopentadiene yielded a mixture of 44 and 45. Weber had earlier explained his findings in terms of a diradical intermediate analogous to 46 (Figure 11). Gaspar found in the reaction of dimethylsilylene and 1,3-cyclohexadiene, 7-silanorbornene (47), and 3-sila-1,4,6-heptatriene (48). These products are most easily explained in terms of diradical 46 (see below). In the five and eight numbered ring cases the external Si-C bond does not break and the ring does not cleave in 46. Instead different hydrogen abstractions yield the observed products 42-45.

The reaction of silylenes and cyclooctatetraene has been investigated by Barton and Juvet (54), and Chernyshev et al. (55). They obtained 1-silaindane and 1-silaindene. If the previously proposed mechanism is operative, it is easy to understand the formation of 8,9-dihydrosilaindene. From here hydrogen shifts or eliminations form the products. Another explanation of these results is possible (54). A concerted conrotatory ring opening yields cis,cis,cis,trans-silanonatetraene A ring closing yields the previously discussed dihydrosilanindene. Interestingly if orbital symmetry considerations hold, the dihydrosilaindene showld be trans-fused. This later mechanism has precedent in other heterocyclic systems.

Seyferth and Anorarelli recently developed a very promising new method for generating silylene (56). When hexamethylsilacyclopropane (49) is heated to 70°, it extrudes dimethylsilylene. This silylene was trapped by insertion into Si-H

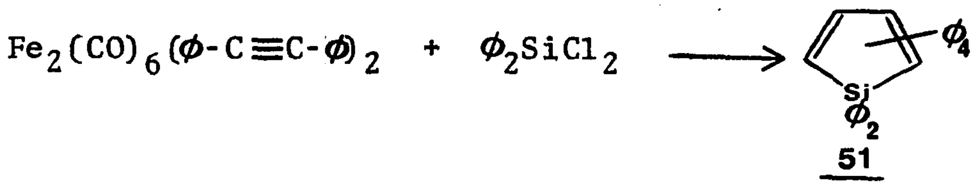


bonds. It does not seem to be very reactive toward olefinic or acetylenic systems. This is obviously because these reactions have higher activation energies.

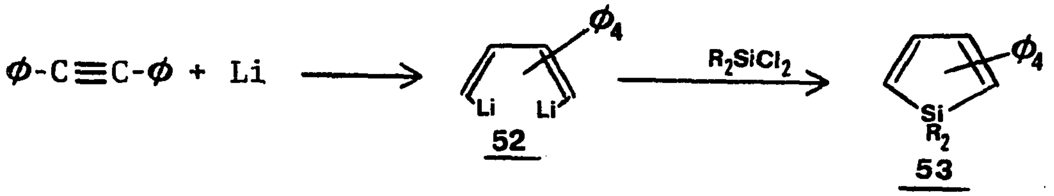
Silacyclopentadienes

The rich chemistry of cyclopentadiene has spurred interest in analogues of this compound with various heteroatoms replacing the methylene group of the parent molecule. Of special interest in this regard is the aromaticity of any of several six π electron species, the metal complexes produced by these aromatic species, and Diels-Alder adducts produced by reaction with suitable dienophiles. Because of its position directly below carbon on the periodic table, silicon has received substantial interest in this regard. Much of the interesting chemistry associated with silacyclopentadienes has recently been reviewed (57); only a summary of items of particular interest to this work will be presented here.

The first synthesis of a silacyclopentadiene was accomplished by Braye and Hüebel in 1959 (58). They reacted the diiron carbonyl complex of diphenyl acetylene (<u>50</u>) with diphenyl dichlorosilane to yield hexaphenylsilacyclopentadiene (<u>51</u>) (XIV). These same authors developed a general method of synthesizing these compounds (59). Diphenylacetylene reacts with lithium to form a 1,4-dilithiobutadiene (<u>52</u>). This compound reacts with dichlorosilanes to produce tetraphenylsilacyclopentadienes (<u>53</u>) with a variety of substituents at the silicon atom (XV). This method has been



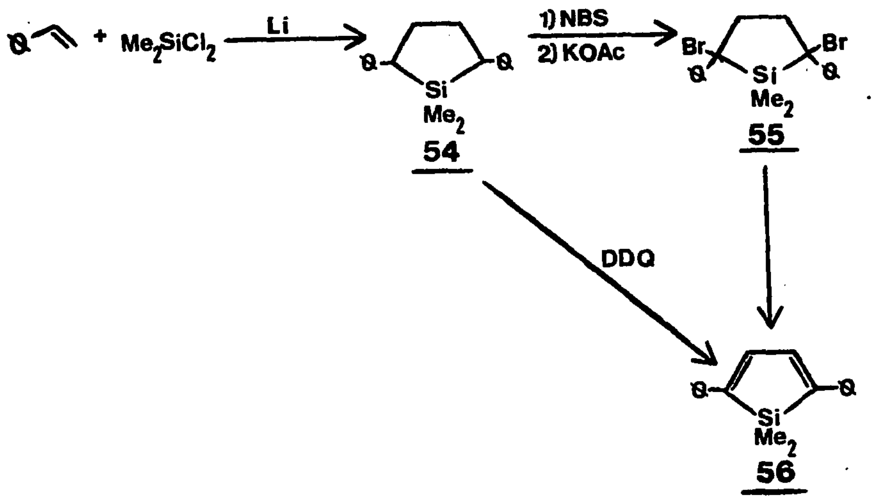
XIV



XV

used by several authors to make a wide variety of silacyclopentadienes (60,61).

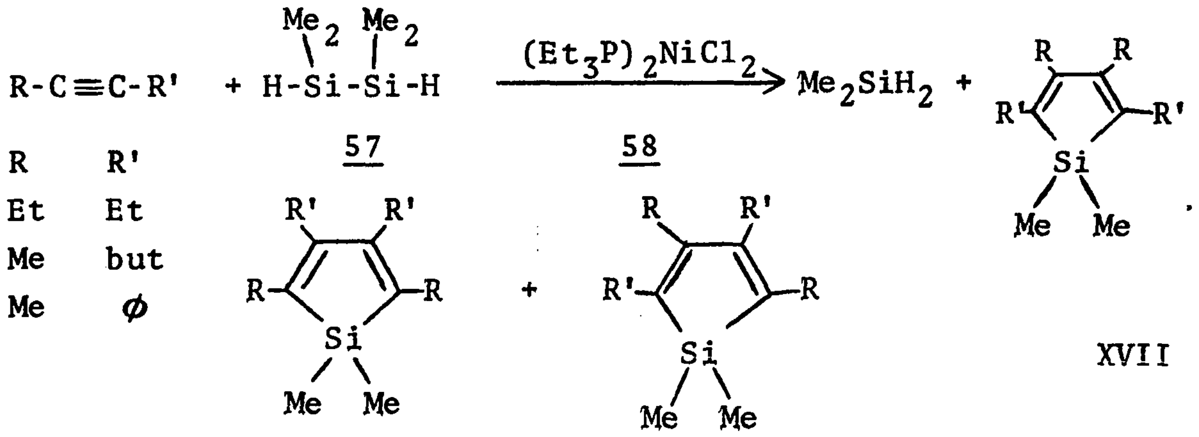
A less substituted silacyclopentadiene has been synthesized by Gilman and Atwell (62) and Atwell et al. (63). When styrene is treated with lithium in the presence of dichlorodimethylsilane, silacyclopentane (<u>54</u>) is formed. This molecule is brominated with N-bromosuccinimide to form <u>55</u>, which is dehydrobrominated to yield 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (<u>56</u>). Other dichlorosilanes can be used to yield different silacyclopentadienes. This method has recently been improved by Barton and Gottsman (64) through the use of DDQ to directly convert <u>54</u> to <u>56</u> (XVI).



XVI

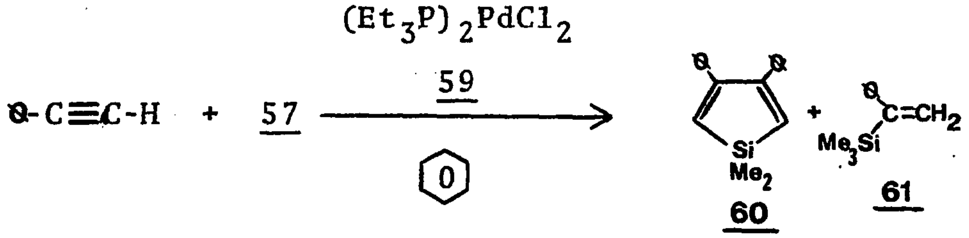
It should be emphasized that these methods only provide access into systems with two or four phenyls on the butadiene portion of the 5 membered ring. Work to reduce the substitution around the ring has been unsuccessful. The 1,1-dimethylsilacyclopentadiene has been reported by two groups (65,66). In both cases the saturated silacyclopentane was passed over a metal catalyst at high temperature to obtain very low yields of silacyclopentadiene. However, fourteen years have elapsed since the appearance of this work and no further chemistry has been reported by these or other groups. These reports are therefore generally regarded as erroneous. In 1961 and 1962 Benkeser at al. reported the synthesis and some chemistry of the parent silacyclopentadiene (67), however, the author later reported this work to be in error (68). Therefore until very recently, investigation of the chemistry of these systems was hindered by the heavy phenyl substitution of all known silacyclopentadienes.

Yamamoto et al. have increased the number of known silacyclopentadiene derivatives (40). When internal acetylenes are heated with sym-tetramethyldisilane (57) in the presence of a nickel [0] catalyst (58) silacyclopentadienes are produced in very high yield (XVII). Some acetylenes, those with electron withdrawing substituents and terminal acetylenes, fail to undergo this reaction to form silacyclopentadienes. Instead they simply underwent the well-precedented oligimerization to form substituted benzenes.



XVII

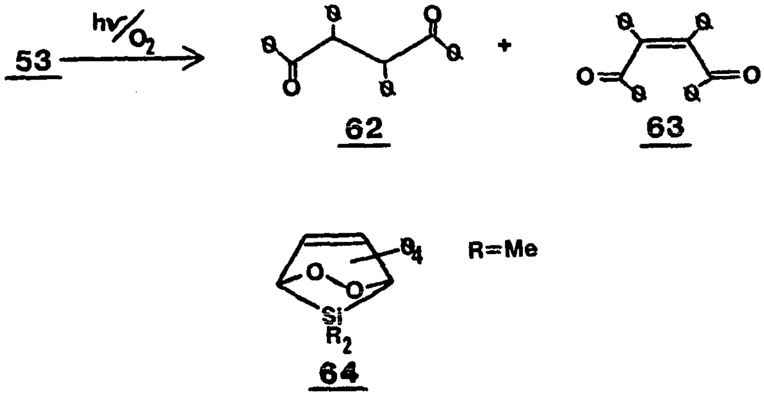
It has now been shown that palladium catalysts will induce terminal acetylenes to enter into this type of reaction (41) (XVIII). Phenylacetylene, and 57 are heated in the presence of a catalytic amount of palladium compound (59) to yield silacyclopentadiene (60) and styrene 61. This new compound 60 is the first derivative of silacyclopentadiene



XVIII

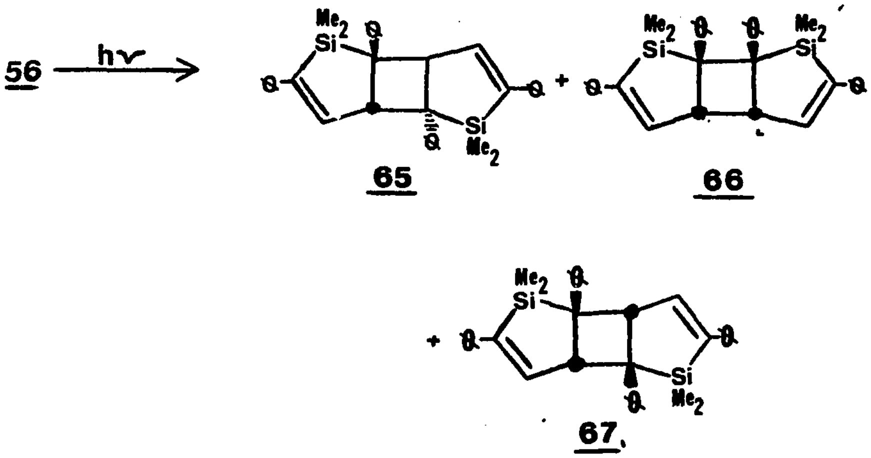
to have hydrogens in the 2- and 5-positions. Unlike the 2,5-diphenylsilacyclopentadienes 53 and 56, 60 is colorless and unstable on contact with air.

The silacyclopentadiene system has shown some very interesting chemistry. When tetraphenylsilole 53 (R=Me) is photolyzed in a stream of oxygen, 1,2,3,4-tetraphenyl-1,4-butadiene (62) and a mixture of cis-and trans-dibenzoylstilbene (63) results (69). The authors felt these products arose via intermediate peroxide (64). Barton and Nelson



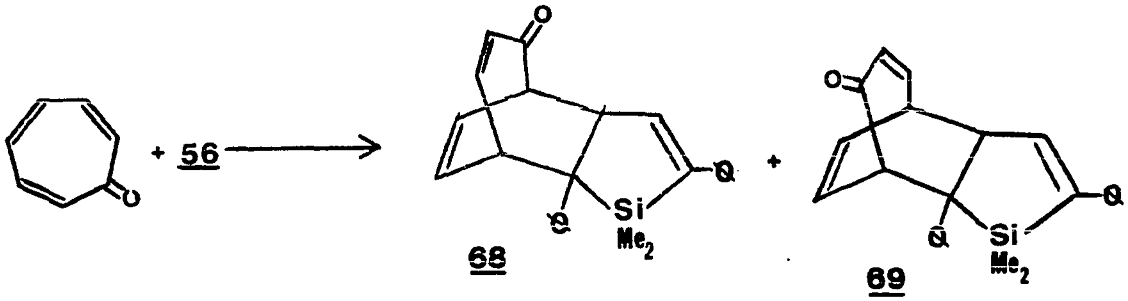
XIX

showed that photolysis of the 2,5-diphenylsilole (56) in an inert atmosphere yielded a 2 +2 dimer (70). Later X-ray determinations showed that the major product of this dimerization is the head-to-tail cis-trans dimer (65) (71). Small amounts of the head to head cis-trans dimer 66, and the head-to-tail cis-cis dimer 67 were found in some solvents. Interestingly, the major product is the orbital symmetry allowed product for a thermal dimerization.



XX

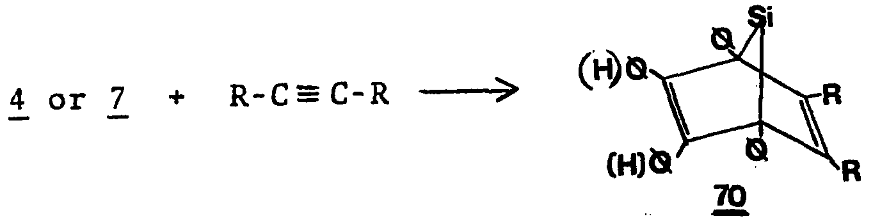
Silacyclopentadiene derivatives enter into Diels-Alder reactions as either dienes or dienophiles. Tropone reacts with 56 to yield adducts 68 and 69, in both cases the silacyclopentadiene has entered into the reaction as a dienophile (72). In the reaction with chlorosulfonyl



XXI

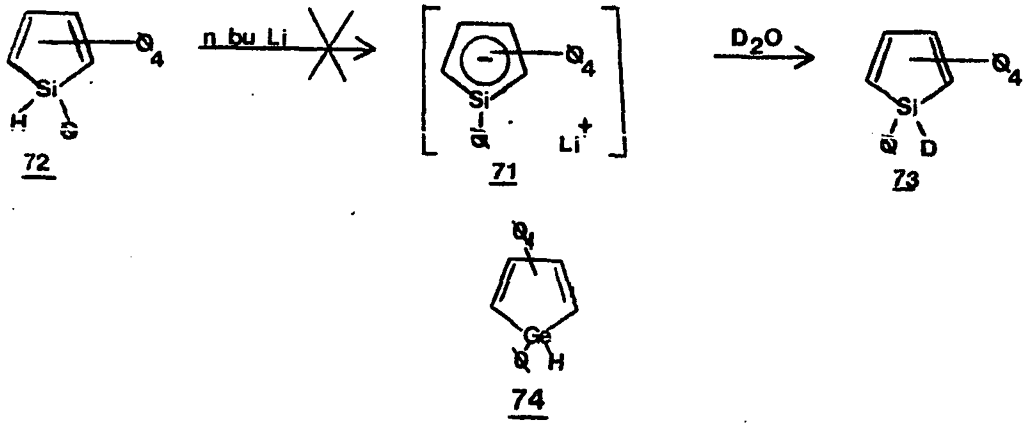
isocyanate 56 also acts as an unconjugated olefin (73).

However, with acetylenes 53 and 56 have been shown to act as dienes and yield 7-silanorbornadienes (70) (74-76). These compounds will be discussed later.



XXII

Curtis has investigated the possibility of there being some aromatic character in ions such as 71. Treatment of compound 72 with n-butyllithium followed by D_2O quench afforded no 73, as is required if 71 is formed (77). His work in the germacyclopentadiene system has allowed him to



XXIII

estimate that 74 is 10^6 more acidic than is triphenylgermane (75) (78). Presumably this is due to the intermediacy of an aromatic ion analogous to 71.

Hanzen et al. has studied the alkali metal reduction of several silacyclopentadienes (79). He sees the formation of diradical anions and dianions, but no evidence for any cyclic conjugation indicating d-orbital participation on silicon.

Curtis was also unable to make any "sandwich" complexes from silacyclopentadienes (78). Since that time several complexes have been made with iron, cobalt, manganese, and ruthenium (80,81). However, the chemistry of these complexes and the X-ray structure of one of them (81) is best explained as being the result of the π interaction of a diene and a metal.

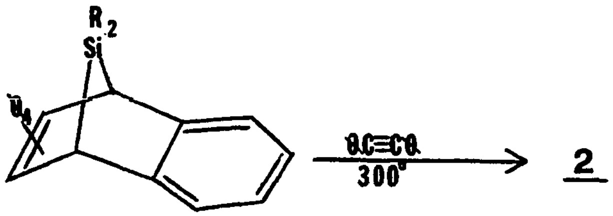
7-Silanorbornadienes

Norbornadienes have a rich chemistry. Thermally they eliminate the elements of carbene and leave a residue of benzene at temperatures in the range of 100-200° C. The temperature is determined by the stability of the fragments produced (82). While this reaction is a symmetry-allowed cheleotropic fragmentation, it is generally believed that this reaction proceeds via a diradical intermediate (82).

Norbornadiene photoisomerizes to quadricyclane when sensitized with benzophenone or acetophenone. Quadricylane itself thermally reverts back to norbornadiene then to benzene and carbene (83). Some quadricyclanes formed by photolysis of 7-heteronorbornadienes, do proceed thermally to 7-membered rings, i.e. oxepin and azepin (84,85).

Of principal interest to this dissertation is the chemistry that suggests the elimination of silylenes from a silanorbornadiene. 7-Silaquadracyclanes and silapins are unusual molecules and only a few examples are known (86). A study of their possible formation was envisioned at the start of this work.

The first 7-silanorbornadienes were made by Gilman, et al. in 1964 (23). They reacted hexaphenylsilacyclopentadiene (51) and 1,1-dimethyltetraphenylsilacyclopentadiene (56) with benzyne to yield 75 (R=ϕ or Me). When these compounds are

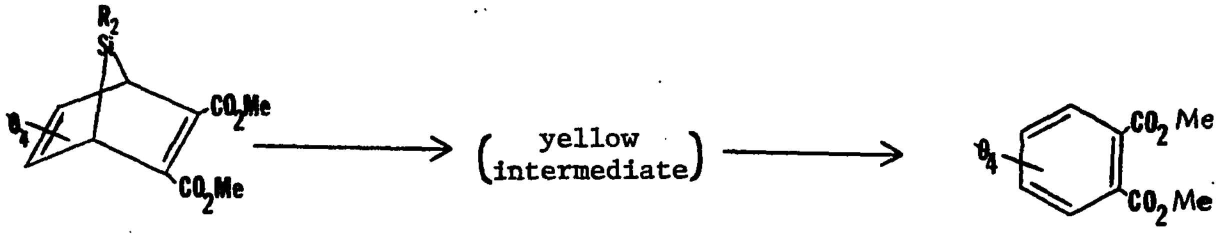


75

XXIV

heated to 300° they decompose to silyenes and naphthalenes as shown by the isolation of disilacyclohexadiene 2. A number of similar adducts have been made with other tetraphenylsiloles and some other dienophiles (61,87). This later work has shown that the substitution on the silicon atom affects the temperature of decomposition. The substitution, both in the number and in the kind, around the basal portion of the molecule has been shown to have a greater effect on the ease of elimination (88).

Gilman, Cottis and Atwell used a number of dienophiles besides benzyne. Of particular interest are adducts 76 formed when hexa- and tetraphenylsilacyclopentadienes are reacted with dimethylacetylenedicarboxylate. Both adducts react with

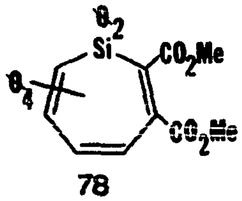


76

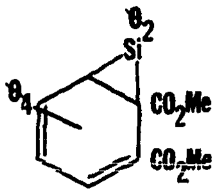
77

XXV

ethanol to yield a yellow intermediate which decomposes to dimethyltetraphenylphthalate (77). When R=ϕ the yellow intermediate is insoluble as a yellow crystal. It was shown to be isomeric with the starting material and its nmr spectrum revealed two different carbomethoxy groups. Structures 78 and 79 were proposed as likely but no conclusive data has been obtained to date.

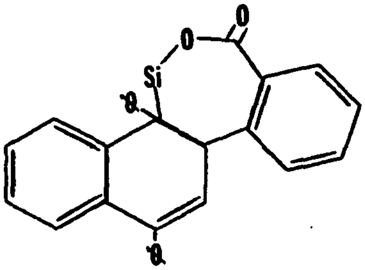


78



79

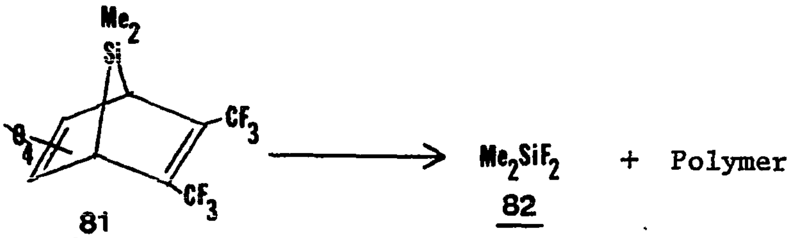
Barton et al. have shown that 1,1-dimethyl-2,5-diphenylsilacyclopentadiene also adds to benzyne (89). At temperatures above 0° C , however, the adduct eliminates silylene and yields diphenylnaphthalene. When the benzyne is produced from benzenediazoniumcarboxylate the initial adduct is not isolated as it adds another molecule of benzyne precursor to yield 80.



80

Maruca has reported the formation of an adduct between diphenylacetylene and 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (90). An X-ray determination of this species by Clardy and Barton revealed that it is in fact a solid complex and not a true adduct (91). The forces responsible for this complex are not understood.

Hata and Willis have reported the hexafluoro-2-butyne with dimethyltetraphenylsilole and isolated an adduct identified as 7-silanorbornadiene 81 (74). Heating of this

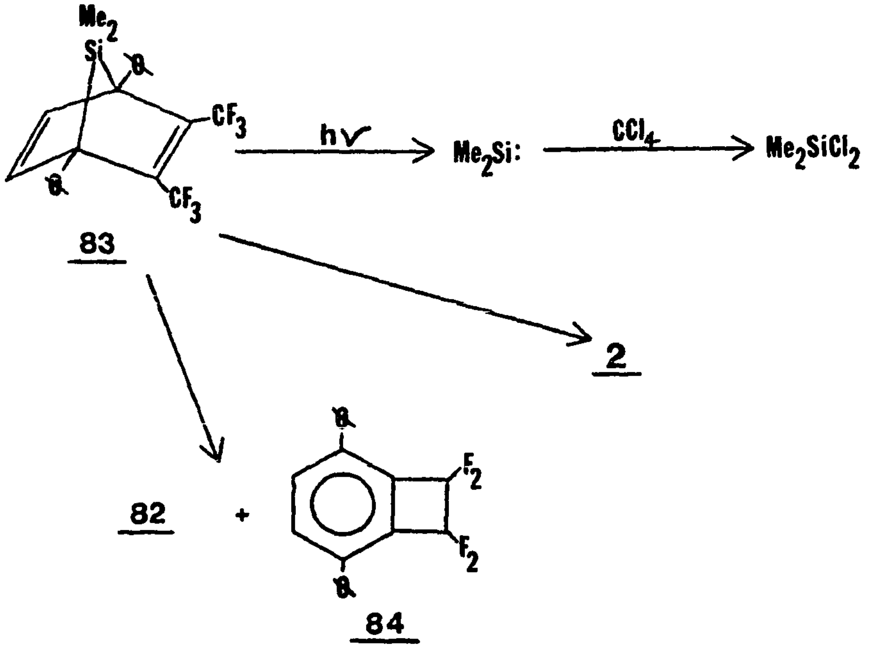


XXVI

product did not yield the expected substituted benzene. Instead they found only polymer and dimethyldifluorosilane (82). Barton and Wittiak have investigated the chemistry of the diphenylsilacyclopentadiene adduct (83) with perflouro-2 butyne (92,93). They also obtained 82 and benzocyclobutane (84). They showed that these products arise through a diradical analogous to the one involved in the all carbon situation (Reaction XXVII).

Some other chemistry of these systems has been discussed (93,94). 7-Silanorbornadienes react with bases and acids by cleaving a ring Si-C bond to give silanols. They also react with silica gel and alumina to give the same products. Wittiak found 83 decomposed with acetone or ethanol but no products were isolable.

The photolysis of some 7-silanorbornadienes have been carried out (93). When diphenyl adduct 83 is photolyzed



XXVII

it apparently eliminates dimethylsilylene, as shown by the isolation of disilacyclohexadiene 2 (XXVII). No evidence for the rearrangement to quadricyclane was found.

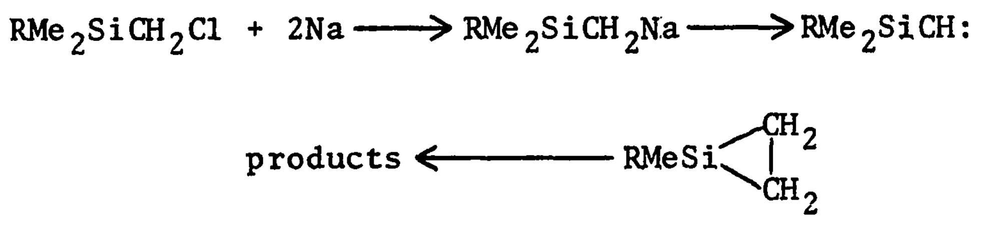
Silacyclopropenes and Silacyclopropanes (95)

Three membered silicon containing rings are of interest for a number of reasons. They are highly strained and an understanding of them can add to our knowledge of structure and bonding. Because of their strain they are unstable and thus present synthetic challenges with which to test our abilities to control chemical transformations. Perhaps most importantly for this work, they are implicated in several reactions as reactive intermediates. Therefore, their isolation and study will add to our understanding of these reactions.

The first cyclic organosilicon compound made in 1915 by Bygden (96), was 1,1-dichlorosilacyclohexane. The ring size was not reduced below five members until 1954 when Sommer and Baum (97) isolated the first silacyclobutane. It revealed some of the future problems of reducing the size of the ring further, as it was much more reactive than previously known silacarbocycles. It had a C-Si-C ring angle of 80°, however, this same angle in the three membered ring was calculated to be only 48°. This number predicts both great internal strain and high reactivity. Some hope could be taken in the fact that the phosphorane has a C-P-C angle of only 47.4°, yet had been isolated. It was felt that both the size of the silicon atom and the length of the Si-C bond would help to make the silirane isolable (95).

The first recorded attempt to make a silacyclopropane was in 1954 when Roberts and Dev (98) reacted bisiodomethyldimethylsilane with zinc and magnesium. They found only polymeric products. Researchers incorrectly assigned a silacyclopropene structure to the product of the reaction between dichlorodimethylsilane, sodium and diphenylacetylene (16-20).

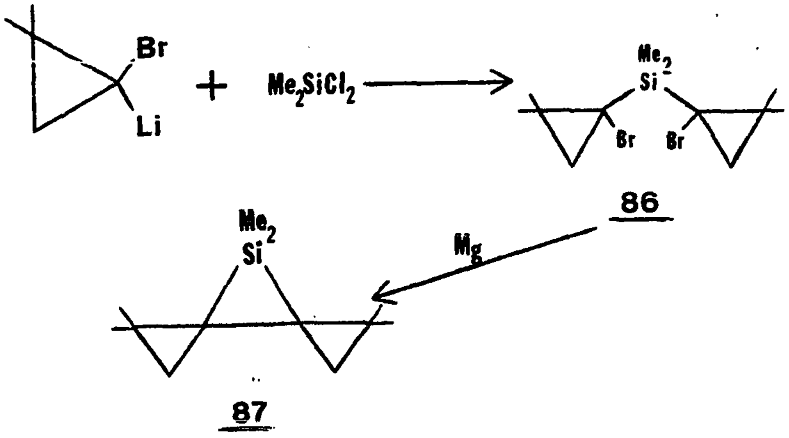
Several authors have found involvement of a silacyclopropane an attractive method of explaining observed products. A silacyclopropane was proposed to explain the formation of dimethylvinylsilane from several silane reactions with sodium/potassium vapor (21,22). This work is more completely discussed in the first part of this dissertation. Connally proposed this intermediate to explain some of the products he observed in the reaction of chloromethyltrialkylsilanes with sodium (99) (XXVIII). Ionic intermediates



XXVIII

could explain his observations. Gilman, Atwell and Weyenberg have discussed the possible involvement of silacyclopropenes and silacyclopropanes in the reaction of silylene with acetylenes and dienes (23,28).

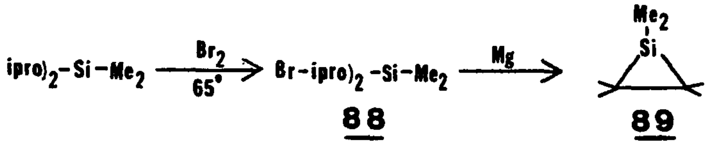
The first stable silacyclopropane was made by Lambert and Seyferth (100). They reacted α-bromolithiopropanes with dimethyldichlorosilanes to obtain bicyclopropylsilanes 86. When these compounds are treated with magnesium at room temperature they eliminate bromine to close the three membered ring and thus form silacyclopropanes (87) (XXIX). The silacyclopropanes are white solids. They possess surprising thermal stability, decomposing only slowly at 150°. They are much more reactive to both neucleophilic and electrophilic reagents than are silacyclobutanes (101, 95), as they suffer ring cleavage to give addition products



XXIX

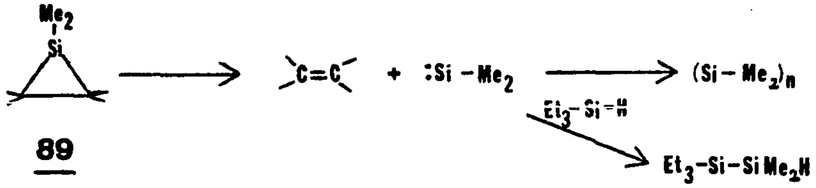
at room temperature. The crystal structure has confirmed the proposed structures for silacyclopropanes (102). This structure has a ring C-Si-C bond angle of 49.2°, very close to the estimate of 48° mentioned earlier.

Recently Seyferth and Annarelli have reported a nonspiro annulated silacyclopropane (103). When bisbromoisopropyldimethylsilane (88), synthesized as shown below, is reacted with magnesium it also undergoes ring closure to yield hexamethylsilacyclopropane (89) (XXX). This silacyclopropane is



XXX

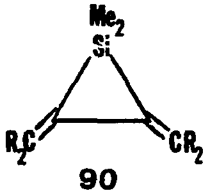
much less thermally stable than are the previously mentioned silacyclopropanes (56). When heated in solution to only 70°, 89 quickly decomposes to silylene and tetramethylethylene (XXXI). The silylene polymerizes unless a compound



XXXI

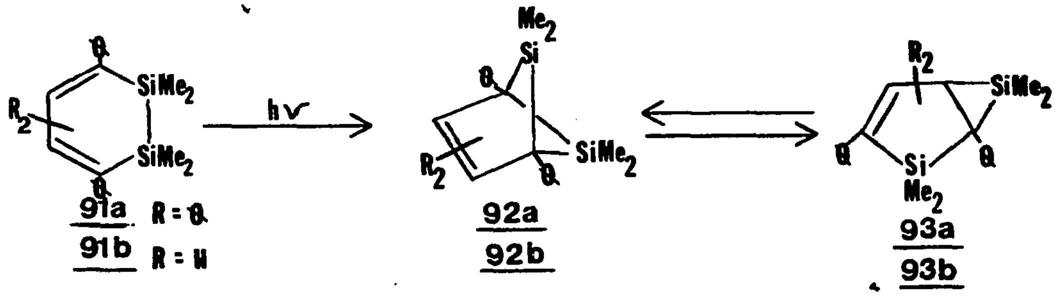
with a silicon hydrogen bond is present as a trap. In these cases silylene insertion products are obtained. Olefins and dienes have not been shown to be useful as traps, as they are for silylenes generated by other methods. One must remember that these other methods generate the silylene by high temperature or by photolysis. It is therefore not surprising that some reactions that occur under those more stringent conditions do not occur under these mild conditions.

The instability of the hexamethylsilacyclopropane relative to its cyclopropyl counterparts is of interest. A possible explanation lies in the known stabilizing influence of sterically bulky groups. However, molecular orbital calculations show that significant electronic effects contribute to the stability of the cyclopropyl substituted systems (104). These calculations describe the occurrence of bonding interactions between the d-orbitals on silicon and the π system of the spiro-cyclopropyl substituent. They predict that similar interactions could occur between silicon and the methylene substituent in 90. These interactions are not possible in the hexamethyl case 89.



90

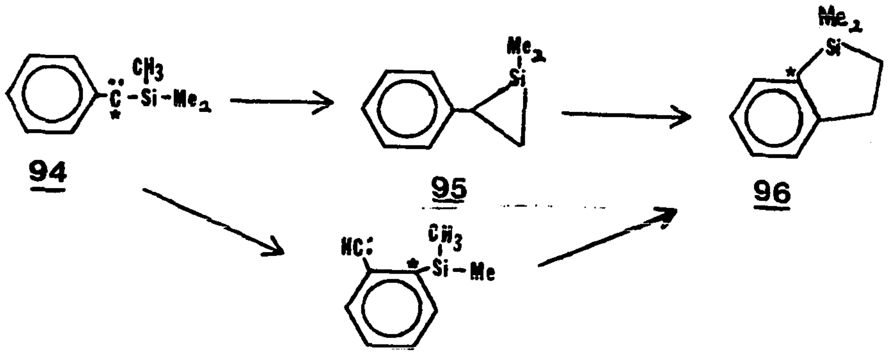
Some other examples of what are apparently stable silacyclopropanes have recently been reported. Nakadaira et al. (105) photolyzed disilacyclohexadienes 91a and b. The primary product in both cases is disilabicyclohexene 92a and b. Further photolysis of 92b generated the bicyclic compound 93b. Heating 93b regenerates 92b. Strangely, further



XXXII

photolysis of 92a does not form 93a, however, heating to 115° does. Photolysis of 93a regenerated 92a. This conversion of 93a and b to 92a and b is the rearrangement postulated by Atwell and Weyenberg for the formation silacyclopentenes from the reaction of silylenes with dienes. Other examples of stable silacyclopropanes are found in the work of Ishikawa described in the first section of this work (35,37).

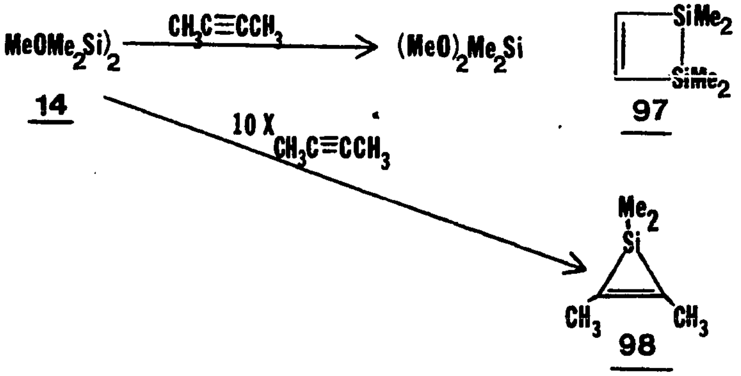
Since the synthesis of a stable silacyclopropane, the popularity of this ring system as a reactive intermediate has increased. Ando et al. used a silacyclopropane 95 to account for the formation of silaindane 96 from the production of phenyltrimethylsilylcarbene (94) (106). Barton et al.

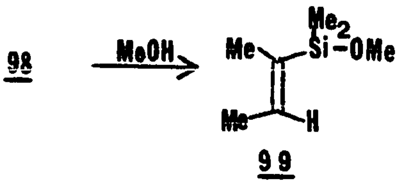


XXXIII

used a labeling experiment to show that the reaction proceeded via a well known phenylcarbene rearrangement, and did not involve the proposed silacyclopropane (XXXIII) (107).

Some work has also gone into forming small unsaturated rings containing silicon. Atwell and Uhlman synthesized octamethyldisilacyclobutane (97) via the flow pyrolysis of dimethoxytetramethyldisilane (14) with 2-butyne as a trap (Figure 12) (46). Gaspar and Conlin have carried out this gas flow reaction with a ten-fold excess of 2-butyne (48). The product under these conditions is silacyclopropene (98). Its existence was proved by spectral evidence and the formation of methylether (99) when the product is treated with methanol.



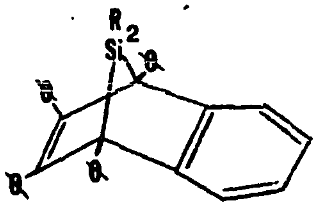


RESULTS AND DISCUSSION

The chemistry of divalent silicon is currently an active area of research. This dissertation will describe some work done in this area during the last five years. The reaction of dimethylsilylene, $Me_2Si:$, with acetylenes is of principal interest, however, a substantial amount of varied organosilicon chemistry will be involved.

Silacyclopentadienes

When this work was begun, it was deemed desirable to develop milder methods for generating silylenes than were then known. The known methods were photolysis of polysilanes (34,35), pyrolysis of methoxypolysilanes (28), and pyrolysis of 7-silanorbornadienes (23). The literature concerning the pyrolysis of 7-silanorbornadienes showed encouraging indications that structural modifications could significantly lower the temperature at which silylene elimination occurred. The Diels-Alder adducts between tetraphenylsilacyclopentadienes and benzyne (10) were shown not



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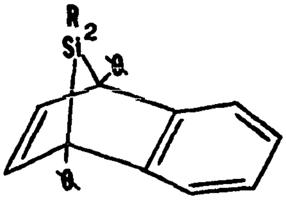
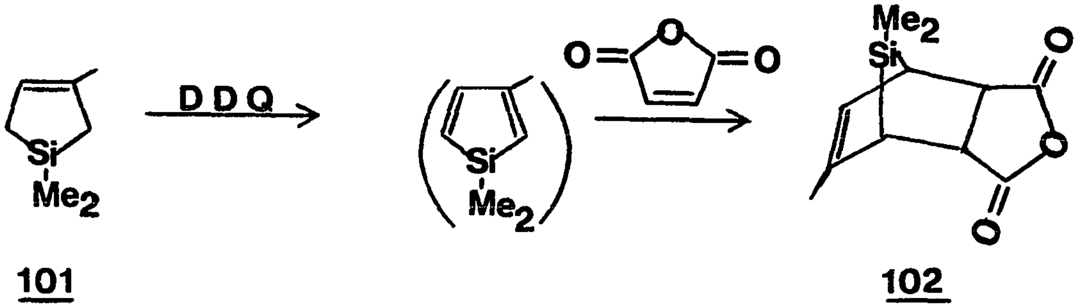


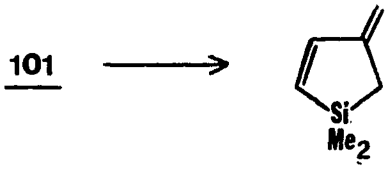
100

to decompose before 300°; while the adduct of benzyne and 2,5-diphenylsilacyclopentadiene (100) decomposed below room temperature. Most substituent modifications around the carbon base of the molecule were not possible as the requisite silacyclopentadienes were not available.

Barton and Gottsman have shown that dichlorodicyanoquinone (DDQ) is an effective oxidant for the synthesis of 2,5-diphenylsilacyclopentadiene (64). They have also treated 1,1,3-trimethyl-1-silacyclopentene (101) with DDQ. When maleic anhydride was used as a trap, the Diels-Alder adduct (102) of a new silacyclopentadiene was isolated in 3% yield (57). The fate of the remainder of the starting material was undetermined. Other dienophiles, i.e. hexafluoro-2-butyne, did not increase the amount of silacyclopentadiene trapped.



The reaction between 101 and DDQ is very fast even at temperatures below 0°, and the hydroquinone is consistently produced in very high yields. We undertook a careful examination of this reaction in order to determine the fate of the majority of 101. Distillation of the filtered product mixture, followed by preparative gas chromatography allowed the isolation of the major product of this reaction (40% isolated yield). This molecule was assigned structure 103 on the basis of its spectral properties. Its high

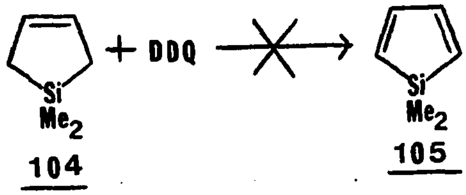


103

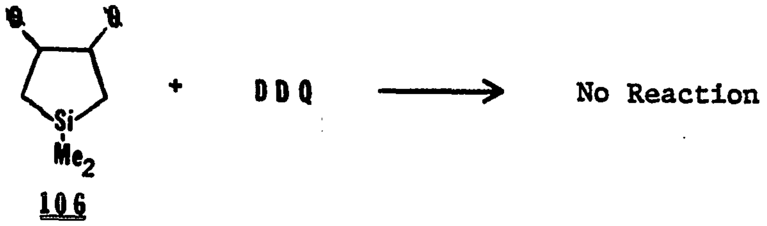
resolution mass spectrum showed a parent ion of 124.071303 (caL for $C_6H_{12}Si$-124.070824), and its NMR spectrum showed the following absorbances; (ppm δ) .17 (singlet, 1 H), 1.48 (triplet, J-1.5 Hz, 2 H's), 5.0 (multiplet, 2 H's), 6.12 (doublet, J-10 Hz, 1 H) and 6.97 (doublet, J-10 Hz, 1 H).

Since the reaction of 101 with DDQ is so rapid, it was of interest to compare its rate with the rates of dehydrogenation of some hydrocarbons. The reactions of DDQ with 101, cycloheptatriene and 1,3-cyclohexadiene in acetic acid were followed by the UV absorption of DDQ at 390 nm. These reactions produce precipitates that interfere with the collection of accurate rate data, however, 101 was seen to react slower than cycloheptatriene and 1,3-cyclohexadiene. When solutions equimolar in cycloheptatriene or 1,3-cyclohexadiene and 101 were added to a deficient amount of DDQ, work-up showed that no 101 had reacted.

Silacyclopentene 104 can be prepared by the reaction of 1,4-dibromo-2-butene, dichlorodimethylsilane and magnesium in ether (108). The reaction between 104 and DDQ is much slower than between 101 and DDQ. Silacyclopentene 104 reacts completely only after refluxing for several hours in methylene chloride with two equivalents of DDQ. Even then, none of the desired 1,1-dimethylsilacyclopentadiene (105) is isolated. Trapping experiments with maleic anhydride failed



to indicate the formation of 105. Similar results were obtained with 3,4-diphenyl-silacyclopentane (106). Silacyclopentene 106 was synthesized according to the procedure of Weyenberg et al. (109). DDQ fails to react with 106

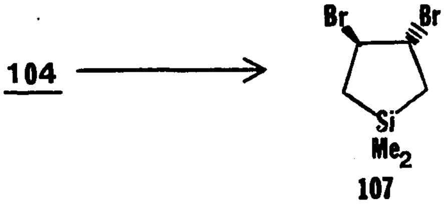


even when refluxed in benzene for 15 hours.

Thus DDQ has failed to dehydrogenate several precursors to silacyclopentadienes. Only with 101 did the reaction proceed readily. The origin of this rapid reaction is unknown but possibly lies in the "transoid" relationship of the hydrogens that are abstracted.

Several other routes for the conversion of 104 to 105 are available. Bromine reacts smoothly with 104 at -78°. When this crude mixture, still at -78°, was treated with diazabicycloundecene (DBU), a white precipitate appeared (DBU-HBr). However, 105 was not isolated from this reaction mixture. Maleic anhydride and tetracyanoethylene were found to react with DBU to produce black polymeric tars. Therefore, tetrachloroethylene was used in an unsuccessful attempt to trap any 105 produced from 104.

Work-up of the reaction of 104 and bromine afforded 107 in 75% yield. Dibromide 107 decomposes when heated,

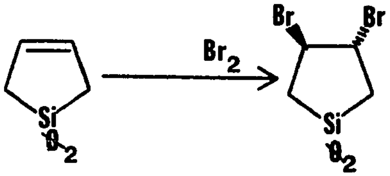


107

obtaining a mass spectrum was impossible, however, its elemental analysis was satisfactory. The NMR spectrum of 107 consists of a singlet at 0.27 ppm (6 H's), a doublet of multiplets at 1.3 ppm (J - 15 Hz, 2 H's), a doublet of doublets at 1.81 ppm (J - 15 Hz, 2 H's) and a multiplet at 4.7 ppm (2 H's). Decoupling the spectrum reinforces this structural assignment. Irradiation of the multiplet at 4.7 ppm simplifies the area between 1.0 and 2.0 ppm to an AB quartet. Upon irradiation at 1.55 ppm, the multiplet at

4.7 ppm collapses to a singlet. The trans relationship between the bromine atoms is implied by the singlet for the Si-Me absorption at 0.27 ppm.

Diphenylsilacyclopentene 108 can be synthesized in a fashion completely analogous to 104 (108). Likewise it can be brominated to yield 109. The structure 109 is

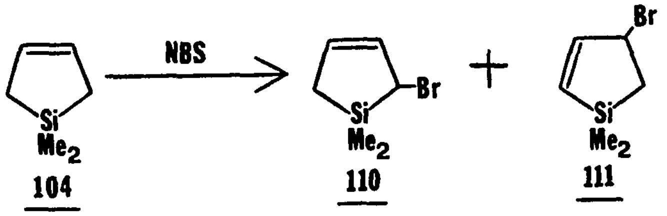


108 109

supported by a satisfactory elemental analysis and an NMR spectrum which is reminiscent of the spectrum of 107 with a doublet of multiplets at 1.75 ppm (J - 16 Hz, 2 H's), a doublet of doublets at 2.25 ppm (J - 16 Hz, 2 H's), a multiplet at 4.67 ppm (2 H's) and a multiplet 7.1-7.6 ppm (10 H's). The *trans* relationship of the bromine atoms is assigned by analogy with 107. Both 107 and 109 have been reported by Manuel et al. since this work was complete (110).

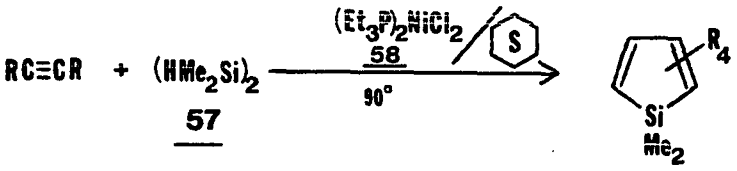
Treatment of purified samples of 107 or 109 with DBU again resulted in the precipitation of a white solid, presumably DBU·HBr, but no products were identified. Other dehydrohalogenating agents were employed, but the results were similar. DBN, potassium t-butoxide and lithium-2,2,6,6-tetramethylpiperylamide all reacted to form complex polymeric mixtures that had no olefinic absorptions in their NMR spectra.

Another possible route for the synthesis of 105 involves initial allylic bromination of 104 with NBS. The reaction

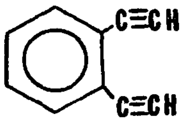


of the resulting bromides with dehydrohalogenation agents could be more successful than that with 107 and 109. Reaction of NBS, initiated by photolysis or by a radical initiator, yielded only a mixture of polysilanes or siloxanes. Manuel et al. (111) and Brunet et al. (112) have recently synthesized 110 and 111 via NBS reactions, however, no attempts at dehydrohalogenation were reported.

While this work was in progress, Yamamoto et al. (40) reported the synthesis of a number of previously unknown silacyclopentadienes. When nonterminal acetylenes and sym-tetramethyldisilane (57) are heated to 90° with a catalytic amount of



bis(triethylphosphino) nickel/dichloride (58), silacyclopentadienes result. We have investigated the scope of this reaction in anticipation that some new and unusual molecules would be synthesized. Yamamoto had reported that reactions with terminal acetylenes were unsuccessful. This was confirmed by us when no reaction was observed with diyne 112.



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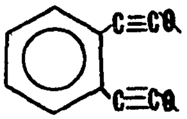


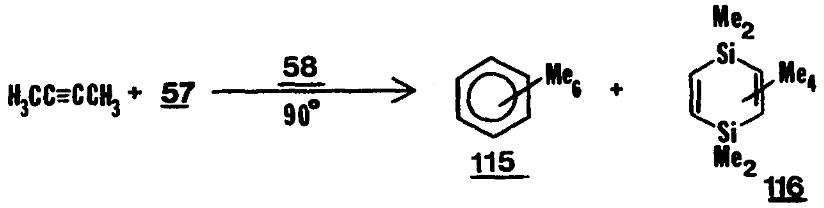
113

Reaction did occur with 1-hexyne, but only an intractable tar resulted. If diyne 113 was placed under the reaction conditions, decomposition of the disilane was observed, but the starting acetylene was recovered unchanged. When silylacetylene 114 was heated under the above conditions no

$$\underset{\underline{114}}{Me_3SiC{\equiv}CCl} + \underline{57} \xrightarrow[90^\circ]{\underline{58}} \text{No Reaction}$$

reaction occurred. Benzene and n-butyl ether were substituted for cyclohexane as solvents but still no reaction occurred. When a neat mixture of 114, 57, and a small amount of 58 were heated to 180° the slow decomposition of 57 was observed. Heating at 220° for four hours completely decomposed 57 but no reaction with 114 was detected by NMR.

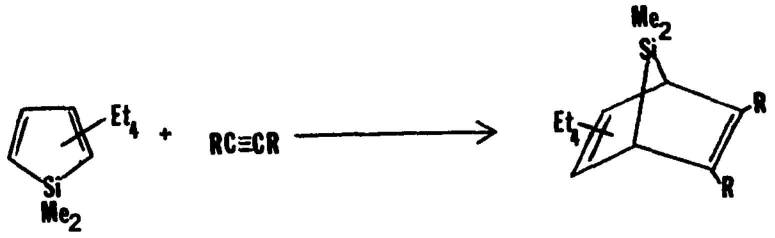
It was reported that 3-hexyne and 2-heptyne were both converted quantitatively to silacyclopentadienes. It was expected that 2-butyne would react in an analogous fashion.



However, no hexamethylsilacyclopentadiene resulted, instead a mixture of hexamethylbenzene (115) and octamethyl-1,4-disilacyclohexadiene (116) were isolated. The ratio of these products was variable, but 116 was consistently the major product. This catalyst, 58, is known to trimerize acetylenes, therefore, the production of 115 is not surprising. The other product, however, was surprising. The mechanistic change that has resulted in this new product can only be the result of the change in steric requirements when the ethyl groups of 3-hexyne are replaced by methyls. This is indicative of close dependency between the exact arrangement of the ligands around the nickel in an intermediate complex and the products formed.

7-Silanorbornadienes

The reaction of 3-hexyne with 57 and 58 does produce silacyclopentadiene 117 in greater than 90% yield. The



117

reactions of this molecule as a diene were investigated. Gilman and Wittiak had independently observed the rearrangement of adducts between silacyclopentadienes and dimethyl acetylenedicarboxylate (DMADC), to compounds that were tentatively identified as silacycloheptatrienes (23a-b,93). An adduct between this new silacyclopentadiene <u>117</u> and DMADC could produce a silacycloheptatriene whose structure could hopefully be proved by an X-ray determination. When <u>117</u> and DMADC were mixed, an exothermic reaction occurred. An NMR spectrum of this solution revealed a new absorbance in the Si-Me region. However, only starting materials could be isolated.

Dicyanoacetylene is also a powerful dienophile and has the advantage of containing no oxygen or fluorine atoms. These atoms form very strong bonds with silicon, and in some cases direct reaction away from silylene elimination and toward formation of these strong bonds (74,92). Dicyanoacetylene was synthesized by dehydration of acetylenedicarboxamide (113), and vacuum transferred to a reaction vessel containing <u>117</u> at -196°. The mixture was then allowed to warm. With the melting of dicyanoacetylene, a fast reaction began and considerable heat was released. A black tar resulted, from which no identifiable products could be obtained.

Perfluoro-2-butyne is also a powerful dienophile. It reacts with 117 when the two are heated in carbon tetrachloride at 50° for 10 hours. The product proved impossible to purify, however, elution through a short column and sublimation at 100° yielded an impure solid (m.p. 110-145°). Recrystallization from several solvents did not improve the melting point. Structure 118 is based on the method of synthesis and the spectral properties of the molecule. The mass spectrum showed a parent ion (m/e-384) and a fragmentation pattern that were consistent with 118. The NMR spectrum consisted of two Si-Me peaks at 0.18 and 0.27 ppm, a multiplet centered at 1.0 ppm and a quartet of doublets centered at 2.2 ppm.

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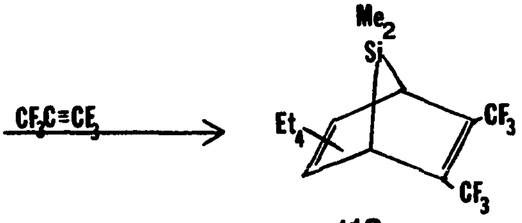
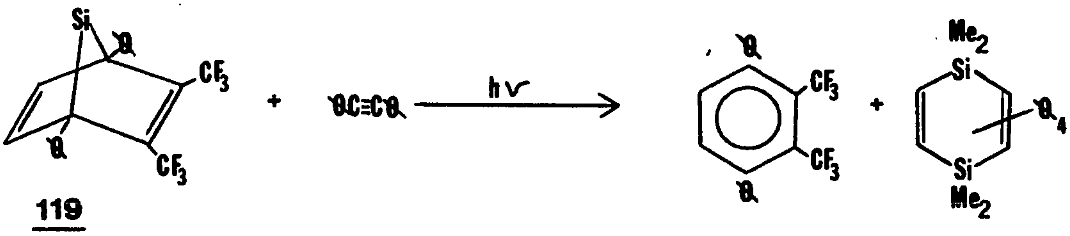


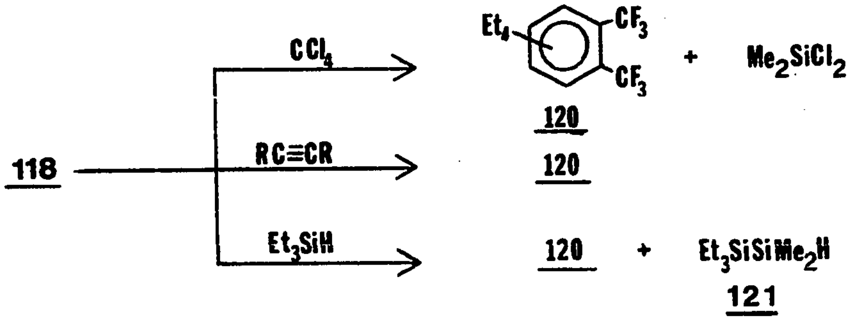
118

When 118 was heated above its melting point, no change was observed until the temperature reached 200°, at which time rapid decomposition, accompanied by evolution of gas was observed. Unfortunately these thermal conditions do not represent an improvement over other methods of silylene production. At any rate, 118 would be expected to thermally eliminate Me_2SiF_2 instead of dimethylsilylene (74,92,93), and this is presumably the gas that is evolved.

The adduct (119) between hexafluoro-2-butyne and 2,5-diphenylsilacyclopentadiene has been shown to eliminate dimethylsilylene when photolyzed (93). Adduct 118 was

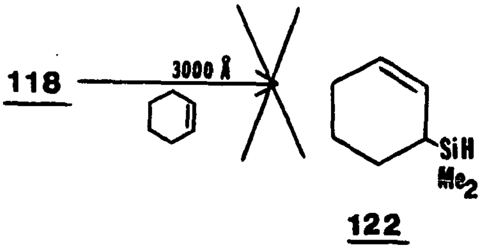


photolyzed to determine if the bridgehead phenyl groups are necessary for this elimination to occur. When 118 was irradiated at 3000 Å in carbon tetrachloride, substituted benzene 120 and dimethyldichlorosilane resulted. Diphenylacetylene masked the absorption of light by 118, therefore,

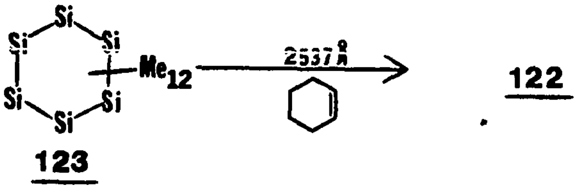


3-hexyne and hexafluoro-2-butyne were used as traps. When a cyclohexane solution of 118 and either acetylene were irradiated only 120 was isolated. None of the expected disilacyclohexadienes were recovered. A dimethylsilylene adduct was formed when triethylsilane was used as a trap. Disilane 121 was isolated from this reaction mixture, so apparently $:SiMe_2$ was generated.

Ishikawa has shown that dimethylsilylene generated from the photolysis of permethyltetrasilane reacts with cyclohexene to form an allylic insertion product, 122 (35). Silanorbornadiene 118 was photolyzed in cyclohexene, however, the desired product 122 was not found when the reaction



mixture was examined by NMR or IR spectroscopy. Photolysis of 123 (114) at 2537 Å showed that dimethylsilylene will



react with cyclohexene under these conditions. After irradiation of a solution of 123 in cyclohexene, 122 was observed in the product mixture. That photolysis of 118 in cyclohexene does not produce 122 is of concern as it casts doubt on the involvement of silylene in this process. Radical processes can explain most of the reactions of

7-silanorbornadienes, and in some cases are the only explanation (92). They are usually neglected, as silylene mechanisms have to date adequately explained existing data. Indeed the results reported here may be the consequence of the different light energies that must be used to decompose 118 and 123. In any event more work should be done in this area.

To summarize, a nonphenyl substituted 7-silanorbornadiene 118 was synthesized and some of its chemistry was studied. Unfortunately, it did not offer any advantages over existing methods for silylene generation. Since these studies were completed, 1,1-dimethyl-3,4-diphenylsilacyclopentadiene (124) has been synthesized (41). This is the first example of

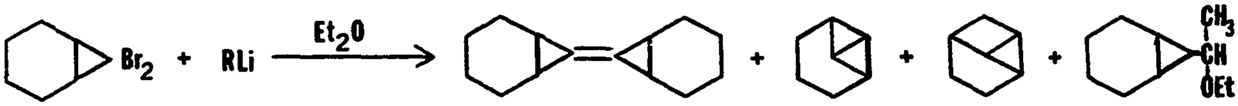
124

a silacyclopentadiene system with hydrogen atoms at the 2 and 5 positions. This could change its chemistry and the chemistry of its acetylene adducts and 124 should be investigated in the future.

Photolytic Preparations of Silacyclopropanes

Lambert and Seyferth have prepared the first stable silacyclopropanes (100). This work tells us which olefins can be expected to yield stable silacyclopropanes when dimethylsilylene is added to them. Of the possible precursor olefins, 125 was the easiest to synthesize, thus it was selected for these studies.

Olefin 125 is readily prepared by the reaction of alkyllithium with 7,7-dibromonorcarane (126) (115). Moore and



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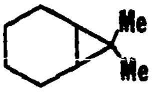
125

Ward have shown that in addition to a 30% yield of 125 several carbene insertion products are obtained (116). In our investigation g.c.-mass spectral examination of the product mixture showed that several other products are also formed in variable quantities. Compounds 127, 128 and 129 are the products of alkylation and metal-halogen exchange reactions.

127



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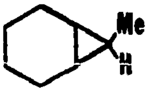
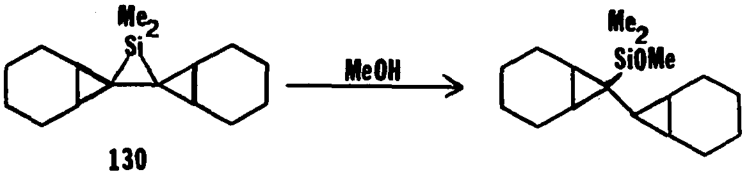


129

Photolysis of polysilanes was selected as the method of generating dimethylsilylene, as moderate temperatures are involved. By analogy to the all-carbon systems, silacyclopropanes could be photolabile, however, alternative methods for dimethylsilylene generation required temperatures 50° higher than those at which silacyclopropanes had been shown to decompose (100). This thermal decomposition had produced intractable tars, so thermal methods were of no use to us. Cyclohexasilane 123 was selected as the dimethylsilylene precursor since its photolysis readily generated dimethylsilylene (33), and it was easily prepared (114).

Olefin 125 was found to be photostable under the reaction conditions except in n-butyl ether. Even here the decomposition of 125 was much slower than the decomposition of 123. Photolysis of solutions of 123 and 125 in cyclohexane, n-butylether, and heptane was carried out in a Rayonet photolysis chamber with 2537 Å lamps. When the decomposition of 123 was shown by gas chromatographic analysis to be complete, methanol was added. Methanolysis of the desired product 130 has been shown to yield 131 (95,100). Work up by column or gas chromatography showed no trace of the desired silylether 131.



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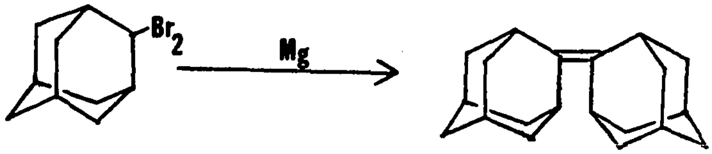
131

One explanation for the stability of 130 is the steric bulk of the spirocyclopropyl groups. If this is an important effect then a spiroadamantane should be better. The desired olefin 132 was available by the method of Bartlett



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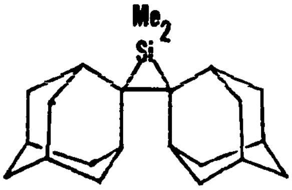
132

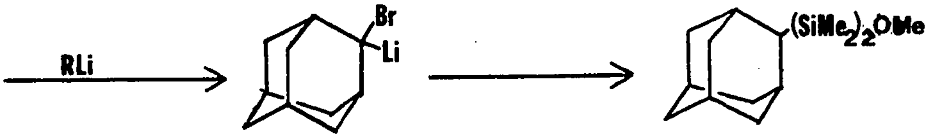
and Ho (117). Photolysis of 123 and 132 was carried out in the same manner as the photolysis of 123 and 125. Work-up yielded no evidence for the formation of 134, as no methanolysis products were obtained.



134

The preparation of 134 by the route of Lambert and Seyferth was attempted. Treatment of 133 by methyl- or butyllithium at -78° followed by addition of dichlorodimethylsilane yielded, after addition of methanol, only one silicon containing product 135. Apparently the adamantane group is too bulky to get two of them around the silicon atom. In addition to 135, adamantanone and 2-bromoadamantane were isolated.

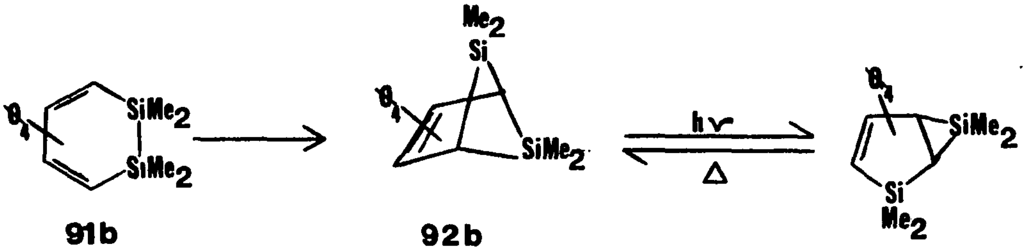
133



135

This work was terminated at this point as its goal was apparently achieved by other workers (35). However, to date some doubts exist and more work is expected in this area.

Nakadaira et al. have found that upon irradiation 1,2-disilacyclohexadienes 91a and b (Page 36) rearrange to 92a and b (105). Under the reaction conditions 92b further rearranges to 93b. Heating 93b regenerates 92b. It seemed to us that 92b was likely to thermally eliminate silylene as doing so would increase conjugation in the all-carbon portion of the molecule. Any strain associated with the disilacyclobutane ring in 92b would also be relieved by such a reaction. A sample of 91b was obtained from a co-worker and 92b was prepared and isolated in a straightforward manner. This

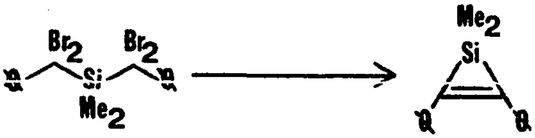


91b 92b 93b

compound 92b was isolated as a yellow gum that could not be made to crystallize. An NMR spectrum was obtained that was consistent with the literature. A mass spectrum of the gum showed a parent ion of 472 m/e and a fragmentation pattern consistent with the proposed structure. A solution of 92b decomposed upon heating to cleanly form a new solution with a single Si-Me absorption in the NMR, but sample quantities prevented identification of the components of this mixture. At this time a new sample of 91b was prepared. Photolysis followed by heating of this compound produced a sample of 92b identical by all spectral properties with that earlier discussed. However, heating a solution of this newly prepared 92b, even to 230° for 24 hours, brought about no reaction. Evidently, in the first sample were undetected quantities of an unknown compound that catalyzed its decomposition.

The Reactions of Bis(α,α-dibromobenzyl)-dimethylsilane

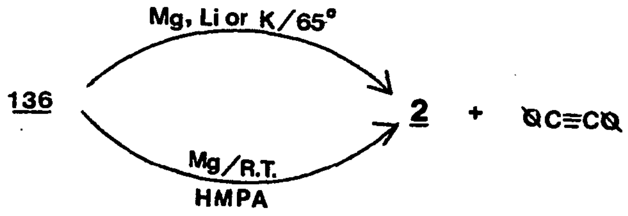
Silacyclopropenes have long been proposed as reactive intermediates in the reactions of silylenes with acetylenes, but when this work was begun, none had been isolated. We began a program designed to prepare one of these elusive molecules. Lambert and Seyferth (100) had succeeded in synthesizing the first isolable silacyclopropanes by dehalogenating bis(α-dibromo)silanes with magnesium. A similar dehalogenation of bis(α,α-dibromo)silanes was envisioned as a route into the silacyclopropene system. In particular it was hoped that bis(α,α-dibromobenzyl)dimethylsilane (136) would dehalogenate to silacyclopropene 137.


136

137

Brook and Peddle had prepared 136 from the NBS bromination of dibenzyldimethylsilane (118). In THF, 136 reacts wtih powdered magnesium only when refluxed for 12 hours. Disilacyclohexadiene 2 and diphenylacetylene were isolated from the resulting mixture. Lithium and potassium also react with 136 under these conditions, to produce the same products.

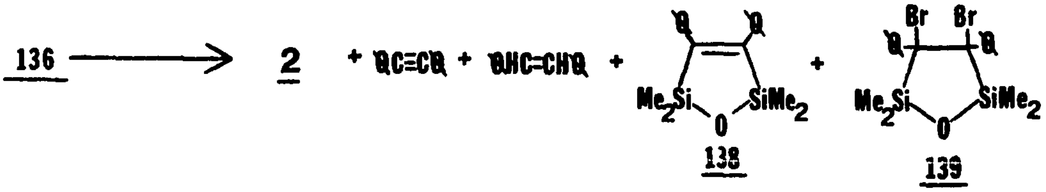
Better yields of both 2 and diphenylacetylene can be obtained if 136 is stirred with magnesium in HMPA at room temperature. From these conditions each product can be isolated in 30% yield. Although 137 was not isolated, the products isolated are easily explained via a silacyclopene intermediate. Several other possibilities exist as well, therefore we studied this reaction in greater detail.



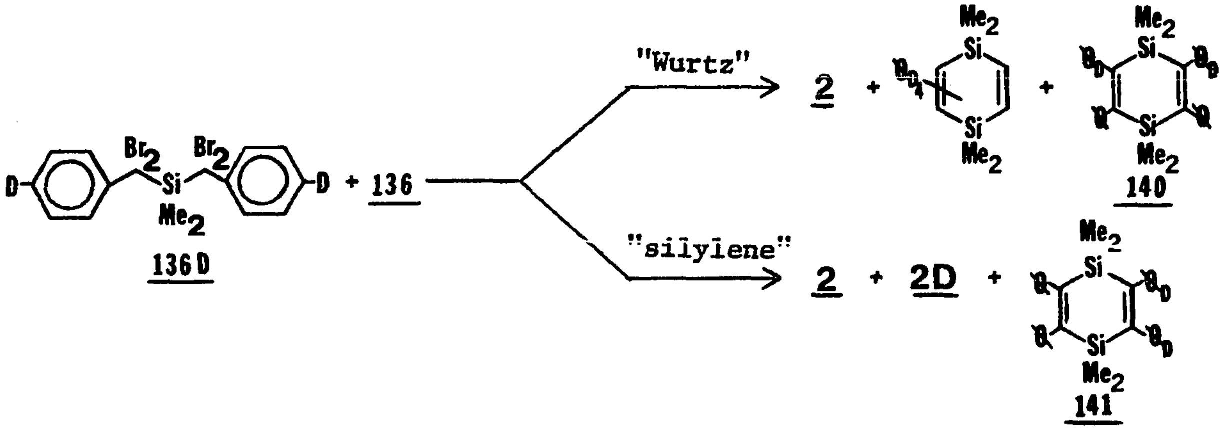
Rieke and Bales have described a method for preparing extremely active metal surfaces (119). By this method, magnesium chloride is reduced by potassium, to produce a slurry of finely divided, very active magnesium. Added salts, for instance potassium iodide, increase the activity of this suspension evidently by altering the surface structure of the magnesium particles.

$$MgCl_2 + 2K + \xrightarrow[\Delta]{THF/KI} 2KCl + Mg^*$$

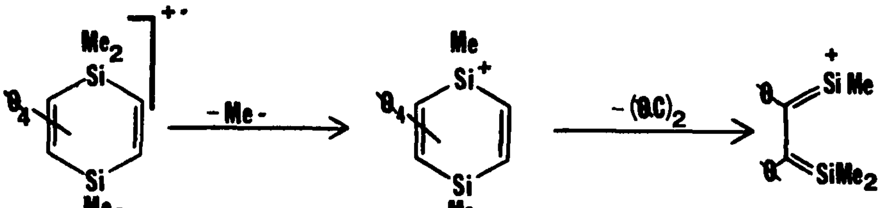
Magnesium prepared in this manner, would dehalogenate 136 when stirred in THF at 0°. From these conditions a number of products could be isolated. Besides 2, still formed in 30% yield, and diphenylacetylene, now formed in less than 10% yield, a mixture of cis- and trans-stilbene was isolated in 30% yield. Also formed was the disilaoxacycle 138. If the amount of magnesium used was reduced, 139 could be found in substantial quantity. The NMR spectra of 138 and 139 are consistent with their proposed structures, but as one might expect, not conclusive. The IR spectra clearly show the Si-O stretch at 1250 cm^{-1}, and other diagnostic bands at 1000-1100 cm^{-1} and 850 cm^{-1}. The structures are based mainly on the mass spectra of these compounds. For 139 the exact mass and the isotope distribution of the parent ion are both satisfactory. The exact mass of the parent ion of 138 is also satisfactory. The fragmentation pattern for both compounds is consistent with their proposed structures.



A variety of reaction sequences can be used to explain the products seen. Our first interest was in the disilacyclohexadiene 2. It could arise from the direct, and to us uninteresting, coupling of two molecules of 136 by magnesium. This "Wurtz" type process was tested by reacting a 1:1 mixture of 136D and 136 with activated magnesium under these conditions. The Wurtz type coupling would produce a mixture of 2, 140, and 2D in 1:2:1 ratio. Mechanisms involving dimethylsilylene or an intermediate in the acetylene/dimethylsilylene reaction would be expected to produce a mixture of 2, 141 and 2D in a 1:2:1 ratio.



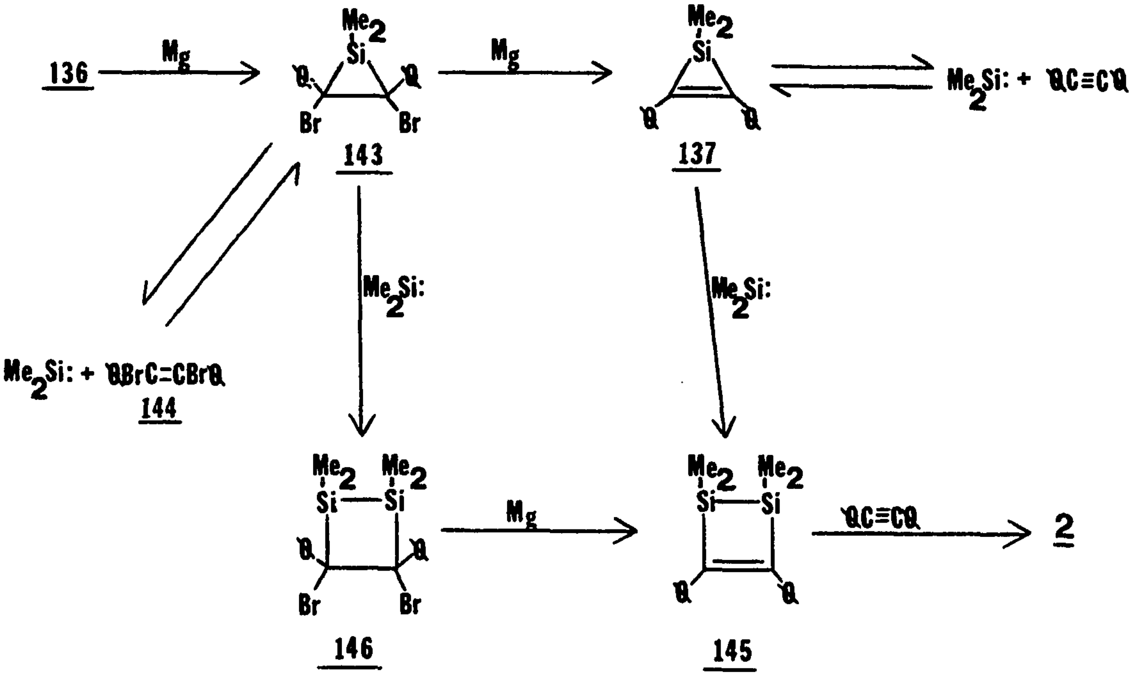
These product mixtures can be differentiated by mass spectroscopy. Maruca et al. have shown an important process observed in the mass spectra of tetraaryl-1,4-disilacyclohexadienes is the loss of methyl followed by loss of diarylacetylene, producing ion 142 (m/e 279) (120). This ion from the Wurtz type

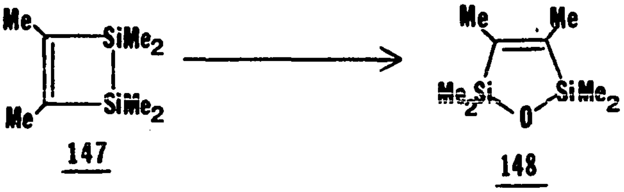


14

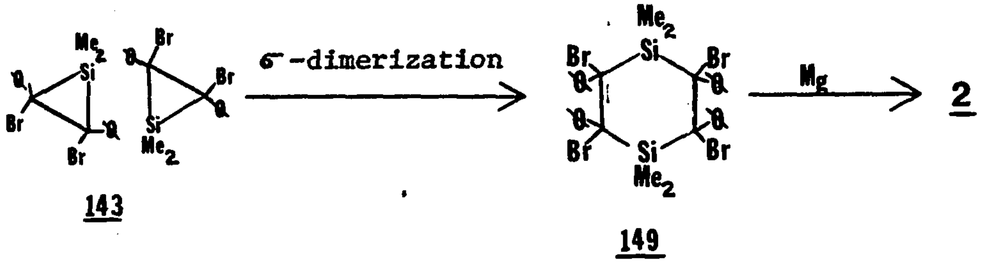
reaction mixture would produce an enhanced isotope distribution of 1:2:1 for D_0(m/e 279) : D_1(m/e 280) : D_2(m/e 281). From the silylene type reaction mixture we expect an isotope distribution of 1:1 for D_0(m/e 279) : D_2(m/e 281); no D_1(m/e 280) species should be produced. After isolation and purification of the disilacyclohexadienes produced by this reaction, the mass spectrum showed a distribution of 100:54:92 for the D_0:D_1:D_2 species. The starting material 136D was 25% D_1 and the P+1 for the natural abundance 279 peak is 27%. Therefore, this spectrum shows that no 2 was formed via a Wurtz type process. These data also rule out any sort of π-dimerization of an intermediate silacyclopropene.

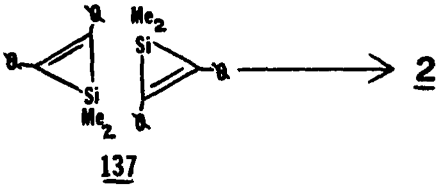
Several mechanisms are still possible. Silacyclopropane 143 could be produced from 136 and magnesium. Further reaction with magnesium would produce 137. These molecules, 137 or 143, could eliminate dimethylsilylene to produce diphenylacetylene or dibromostilbene 144 respectively. The dimethylsilylene produced could insert in 137 or 143 to produce 145 or 146 respectively. Reaction of 146 with magnesium would produce 145. Products 138 and 139 imply that 146 and 145 are produced under these conditions. Atwell and Uhlmann have shown that hexamethyl-1,2-disilacyclobutene (147) adds oxygen to form 148 (46). A similar process, occurring during work-up would produce 138 and 139.





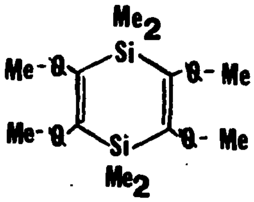
Disilacyclohexadiene 2 could be formed by reaction of 145 with diphenylacetylene as Barton and Kilgour have shown (47). A σ-dimerization of 137 or 143, however, also will account for the production of 2.



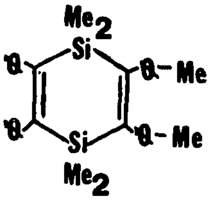


To test these possibilities 136 was reacted with activated magnesium in the presence of ditolylacetylene 150. The yield of the disilacyclohexadiene was greatly reduced, but careful examination of the reaction mixture showed 2 was the only one present. An authentic sample of 151 was prepared for comparison, but it was not found in this reaction. The "mixed" molecule 152 could not be found either.

$\underline{136} + \text{Me-}\phi\text{-C}{\equiv}\text{C-}\phi\text{-Me} \xrightarrow{\text{Mg}} \underline{2}$



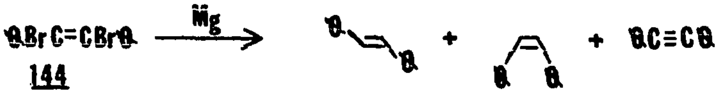
151



152

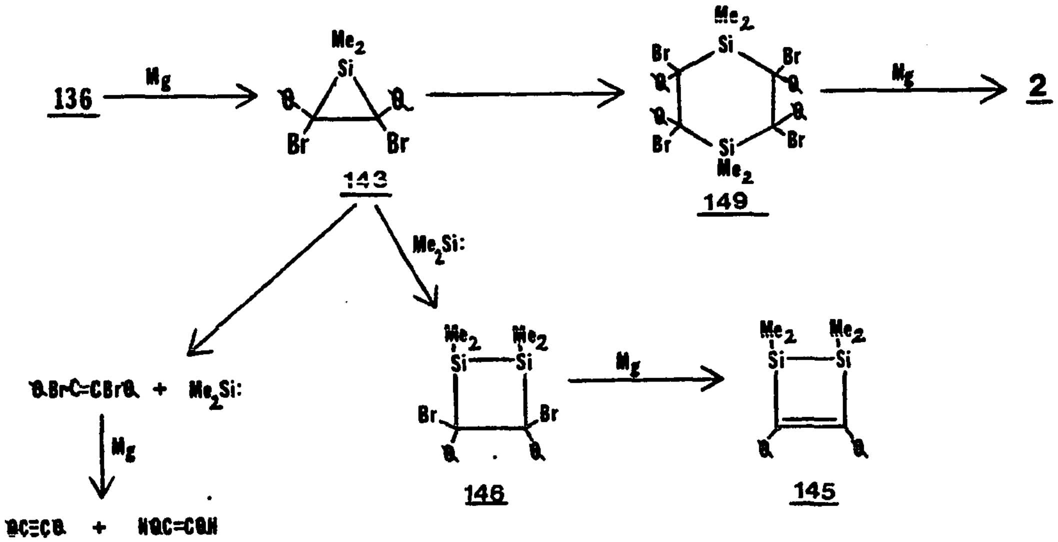
Several mechanistic ideas can be derived from the failure to form 151 and 152. If 137 eliminates dimethylsilene to form diphenylacetylene, the silylene formed does not react to reform 137. If it did, because of the presence of a large amount of ditolylacetylene relative to diphenylacetylene, tolyl groups would certainly be incorporated into the disilacyclohexadiene products. The same reasoning rules out the reaction of 145 with acetylene to produce 2. The only possibilities left for the formation of 2 are the σ-dimerizations of 137 and 143.

The formation of stilbenes in the reaction of 136 with activated magnesium was surprising. No straightforward mechanism accounts for their formation. Dibromostilbene (144) was made by the addition of bromine to diphenylacetylene. When 144 was treated under the reaction conditions with

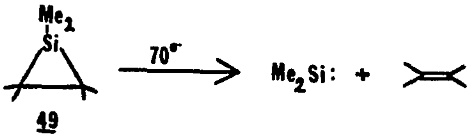


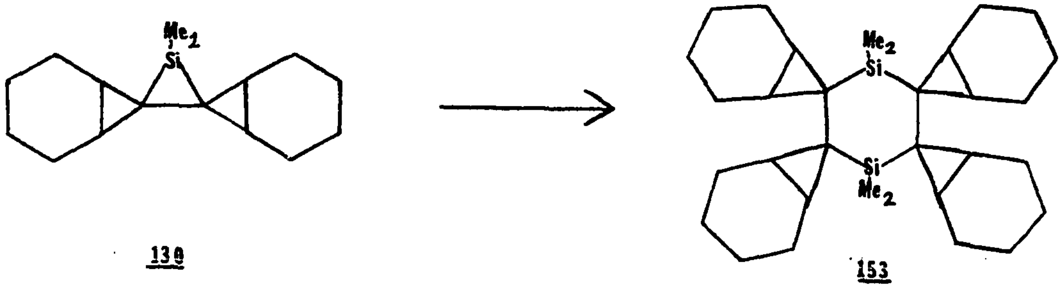
activated magnesium, not only diphenylacetylene was produced, but also <u>cis</u>- and <u>trans</u>-stilbene were formed in a total 30 % yield.

These facts allow us to account for the products formed without the involvement of silacyclopropene <u>137</u>. The following mechanism is proposed. After formation from <u>136</u>, <u>143</u> suffers two fates. It dimerizes along a Si-C ring bond to form <u>149</u> or it eliminates dimethylsilylene to form olefin <u>144</u>. The silylene produced reinserts into <u>143</u> producing <u>146</u> which then can be dehalogenated to <u>145</u>. Disilacyclohexane <u>150</u> can be dehalogenated to form <u>2</u>.

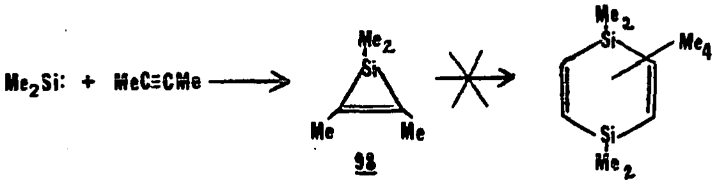


Seyferth and Anorarelli have observed the loss of silylene from hexamethylsilacyclopropane (49) to form tetramethylethylene (56). These authors have also reported the dimerization of 130 to form 153 when heated (56).





Seyferth and Anorarelli have recently reported the first silacyclopropene, 98 (56). They reported that this molecule

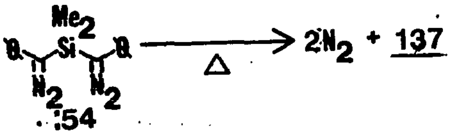


does not dimerize to the octamethyldisilacyclohexadiene even when heated to 150°. This work also implies that 137 is not involved in this reaction. It is possible that substituting phenyl groups for the methyl groups of 98 could lower the activation energy of this reaction sufficiently to allow it to occur.

This system has no direct relationship to the reaction between dimethylsilylene and acetylenes, however, some of the conclusions reached here bear on that problem. In particular the σ-dimerization of silacyclopropanes or silacyclopropenes must be considered as viable possibilities in considering this reaction.

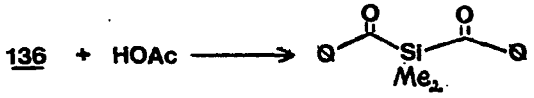
Attempts to Prepare a α-α' Bisdiazosilane

Unsaturated three-membered rings can also be prepared by heating 1,3-bisdiazo compounds (121). For this method to be applied to the synthesis of a silacyclopropene, an α,α'-bisdiazosilane such as 154 is required. Tetrabromide



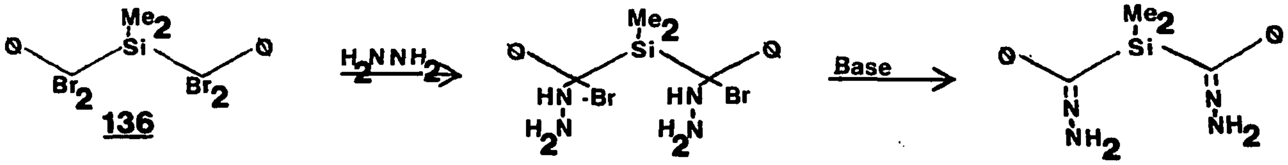
154

136 appears to be a possible precursor to 154. Unfortunately, Brook had already established that diketone 155, if formed in the hydrolysis of 136, was too unstable to be isolated (118). Without the isolation of 155 this route to 154 is not reasonable.



155

Other routes to 154 can be envisioned. If hydrazine would displace two bromine atoms from 136, dehydrohalogenation would produce dihydrazone 156. This molecule could

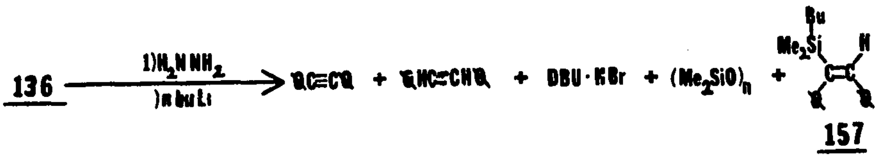


be converted to 154 via anion formation with a strong base, followed by heating. When 136 was treated with tosylhydrazine, followed by treatment with two equivalents of DBU, diphenylacetylene, DBU hydrobromide and cyclic polysiloxanes were isolated. If DBU was replaced by n-butyllithium a mixture

$$\underline{136} \xrightarrow[\text{2) DBU}]{\text{1) } H_2NNH_2} \text{Ø}\text{-}C\equiv C\text{-}\text{Ø} + (Me_2SiO)_n + DBU\cdot HBr$$

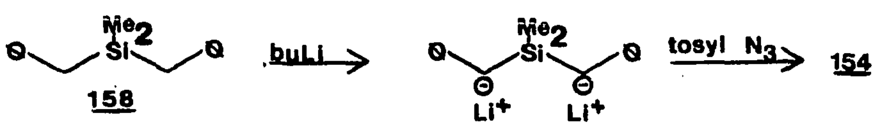
$n=3,4,5$

of cis- and trans-stilbene formed, besides the products mentioned above. Preparative, high-pressure, liquid chromatography also allowed the isolation of silylstilbene 157. This

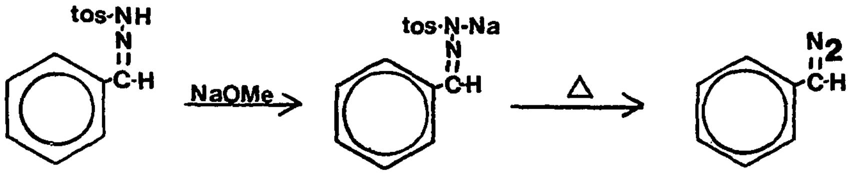


product was identified by its exact mass and its NMR spectrum which showed a singlet at 0.30 ppm (6 H's), a broad multiplet at 1.5-1.0 ppm (9 H's), a singlet at 6.6 ppm (1 H) and a broad aryl multiplet centered at 7.4 ppm (10 H's). The stereochemistry is assigned by analogy with cis-stilbene in which the vinyl proton appears at 6.54 ppm. Although this product appears to be formed from silacyclopropene 137, this reaction was not investigated further. It does seem that this might be a fruitful area for future work.

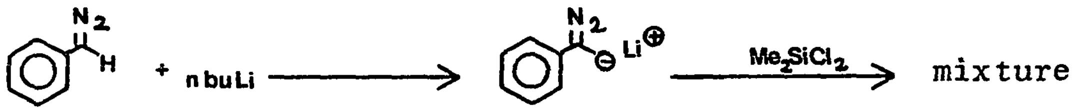
Treatment of tosylazide with carbon anions has been shown to yield diazo compounds (122). Treatment of dibenzyldimethylsilane (158) with n-butyllithium followed by tosylazide was envisioned as a route to 154. Unfortunately the dianion required was not produced in sufficient quantities to make this route feasible.



Diazo compounds prepared from aldehydes can, when treated with strong base, form stable carbanions. These in turn have been used to form C-Si bond from chlorosilanes. Phenyldiazomethane was prepared by treating benzaldehyde tosylhydrazone with sodium methoxide, then warming the dry salt to 80°.



Treatment of phenyldiazomethane with n-butyllithium yielded carbanion 159. When this ion was added to dimethyldichlorosilane a complex mixture of products resulted. It is possible that 154 was a component in this mixture, however, it could not be isolated and purified. The mixture was not stable to silica gel or alumina, decomposed when heated, and could not be crystallized.



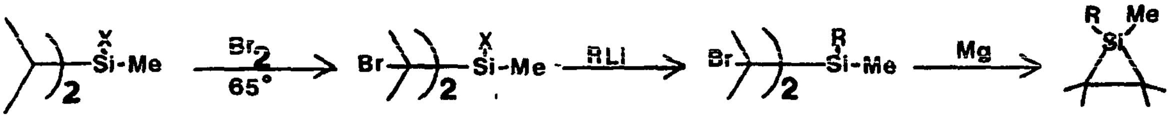
159

Thus some encouraging indications were found that this general approach might prove successful. In particular the isolation of 157 is very promising. Unfortunately, time did not allow more detailed investigation. This area does, however, deserve more work.

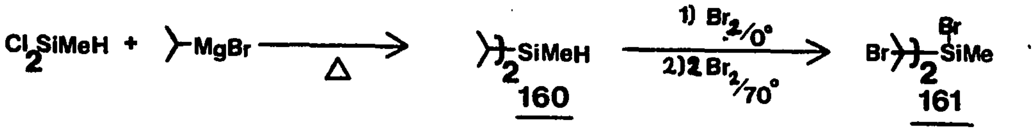
Reactions of Bis(bromoisopropyl)-silane Systems

Carbenes are known to undergo a number of interesting rearrangements if the correct substituents are present. To date, this area of silylene chemistry has been relatively ignored. No organic substituents except phenyl, methyl and methoxide have even been studied as part of the silylene species. Our inability to synthesize the proper precursor for these substituted silylenes has greatly hindered development in this area.

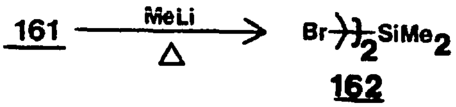
Dimethylsilylene can be generated from hexamethylsilacyclopropane (49) under very mild conditions (56). The preparation of 49 is relatively easy, and offers the possibility for substituting various kinds of functionality for methyl on the silicon atom. As the synthesis involves bromination at 65° in one step, if the new group contains unsaturation, its incorporation must occur after this step. Thus, the sequence shown below can be envisioned, where the new organic group is introduced by an organolithium compound.



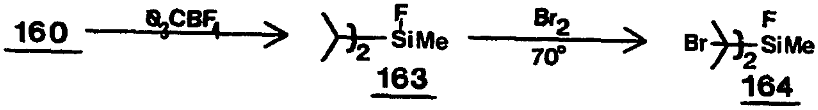
Diisopropylmethylsilane (160) was prepared by adding isopropyl Grignard to dichloromethylsilane. Silylhydrides are easily converted to silylbromides by reaction with bromine, so treatment with three equivalents of bromine should make 161. The reaction of bromine with silylhydrides



is an exothermic process, thus the addition of the first equivalent of bromine was accompanied by external cooling. After one equivalent was added the temperature was raised to 70° and the remaining two equivalents were added at a rate such that the solution stayed only slightly orange. This sequence allowed the preparation of 161 in about 60% yield, however, it was contaminated with substantial di-*t*-butyl- quantities of an unidentified impurity. The purification of 161 was not accomplished, but treatment of an impure sample with methyllithium in refluxing THF failed to produce any of the desired 162.



Treatment of 160 with tritylfluoroborate allows the preparation of fluoride 163 in at least 90% yield. Reaction with two equivalents of bromine at 70° produces 164 in 80% yield. The purification of 164 was much easier than that for 161 and pure samples were obtained. Neat samples of 164 were heated to reflux with one equivalent of two molar solutions of methyllithium and vinyllithium in THF for 15 hours, but no reaction occurred.



The steric bulk of the 2-bromoisopropyl group is larger than the t-butyl group. Substitution reactions on di-t-butylsilanes have been shown to be difficult (123). It is reasonable then that the bulky groups around the silicon are preventing the desired reaction from occurring. This problem may be alleviated by use of a better leaving group, however, at present fluoride is the best available.

EXPERIMENTAL

Instrumentation

All melting points were determined using a Thomas Hoover melting point apparatus and are uncorrected.

Nuclear magnetic resonance (NMR) spectra were recorded on on a Hitachi Perkin-Elmer R-20 B High Resolution spectrometer or a Varian Associates HA-60 spectrometer. Chemical shifts are all relative to tetramethylsilane.

Infrared spectra were recorded on a Beckman Model 12 or a Model 18 infrared spectrometer. Spectra were recorded on thin films between sodium chloride plates or as potassium bromide pellets.

Low resolution mass spectra were recorded on an Atlas CH-4 mass spectrometer or on a Perkin-Elmer Model 270 gas chromatographic mass spectrometer. High resolution mass spectra were recorded on a MS-902 mass spectrometer manufactured by AEI.

High pressure liquid chromatography (HPLC) was carried out on a Waters 202/401 high pressure liquid chromatograph.

Elemental analyses were conducted by Ilse Beitz . Mikroanalytisches Laboratorium, Kronach, West Germany.

Preparation and Experiments

Reaction of 1,1,3-trimethyl-1-silacyclo-3-pentene (101) with dichlorodicyanoquinone (DDQ) in the presence of perfluoro-2-butyne.

A sample of DDQ (2.3 g.; 10 mmoles) was placed in a 100 ml. flask. Perfluoro-2-butyne (9.7 g.; 60 mmoles), 101 (124) (1.0 g.; 7.9 mmoles) and methylene chloride (ca. 100 ml.) were vacuum transferred into the flask which was cooled to -196°. As soon as most of the solvent had melted, a reaction began as evidenced by the appearance of the tan hydroquinone. After the reaction mixture had warmed to room temperature, the volatile components were distilled. The residue consisted of unreacted DDQ and DDQ-hydroquinone. The volume of the distillate was reduced to approximately 3 ml. by careful evaporation. This solution was separated by preparative gas chromatography. Besides the solvent, only two components were observed in the mixture. They were shown by mass spectrometry to be 101 (parent ion at m/e 126) and 103 (parent ion at m/e 124).

Preparation of 1,1-dimethyl-4-methylene-1-silacyclo-2-pentene (103)

A quantity of DDQ (4.0 g.; 17.5 mmoles) was placed in a flask. Methylene chloride (ca. 150 ml.) and 101 (2.0 g.; 16 mmoles) were distilled into the flask, which was cooled to -196°. The reaction mixture was warmed to room temperature and stirred for 5 hours. The volatile components were removed by vacuum distillation. The distillate was then carefully reduced to approximately 5 ml. This mixture was separated by preparative gas chromatography on a 6 ft. by 1/4 in. 5% SE-30 column at a temperature of 50°. The major product, 103, was isolated in 40% yield.

The structure of this molecule, 103, was assigned on the basis of its spectral properties. Its high resolution mass spectrum showed a parent ion of mass 124.070824 (calculated for $C_7H_{12}Si$ - 124.071303). Its nmr spectrum consisted of absorptions at δ 0.17(6H,s), 1.48(2H,t,J=1.5), 5.0(2H,m), 6.12(1H,d,J=10) and 6.97(1H,d,J=10).

Determination of the rate constants for the reaction of 101 and cycloheptatriene with DDQ

The general experiment was conducted as follows. A stock methylene chloride solution, 9.9×10^{-3} molar in DDQ was prepared. Two methylene chloride solutions, one 5.0×10^{-2} molar in cycloheptatriene and the other 1.07×10^{-1} molar in 101 were also prepared. A 3 ml. cuvette was charged with a sample of DDQ solution, from 0.25 to 1.0 ml. The volume was increased to 2 ml. with methylene chloride. One ml. of substrate solution was injected, a stopwatch started, and the cuvette inserted in a Cary 14 spectrometer. The spectrometer was adjusted to follow the decrease in the concentration of DDQ by monitoring its absorbance at 390 nm. The pseudo first-order rate constant for the disappearance of DDQ was calculated from the slope of the line from a plot of the absorbance vs. time. The second order rate constant was calculated by division by the substrate concentration:

$$k_1/[\text{substrate}] = k_2 \ .$$

Cycloheptatriene forms first a charge transfer complex, then a 1:1 adduct with DDQ. This adduct precipitates as a black solid which soon makes the solution opaque. These phenomena prevent accurate data from being obtained. The other substrate (101) was well-behaved and gave a straight line for several half lives.

Final DDQ] x 10^3	[Cyclophetatriene] x 10^2	k_1(1./min.)	k_2(1./mole-min.) x 10^{-1}
2.49	1.7	0.692	4.1
1.65	1.7	0.656	3.9
0.83	1.7	0.87	5.1
	[101] x 10^2		
3.3	3.6	0.163	0.45
2.49	3.6	0.153	0.43
1.65	3.6	0.167	0.45
0.83	3.6	0.133	0.37

Reaction of 101 and cycloheptatriene with DDQ

A 1:1 mixture of 101 and cycloheptatriene in methylene chloride was prepared. After obtaining an nmr spectrum, one equivalent of DDQ was added. The black precipitate, which began to form immediately after the addition of the DDQ, was filtered and an nmr spectrum was recorded. There were no absorbances above δ1.0 except the Si-Me absorption for 101, indicating no reaction between 101 and DDQ. The absorptions from cycloheptatriene had almost completely disappeared.

The reaction of 101 and 1,4-cyclohexadiene with DDQ

One equivalent of DDQ was added to a 1:1 mixture of 101 and the cyclohexadiene in methylene chloride. The mixture was stirred for one hour and filtered. An nmr spectrum was obtained. As in the reaction with cycloheptatriene, no Si-Me absorptions were observed except that for 101. The cyclohexadiene was completely converted to benzene.

Synthesis of 1,1-dimethyl-1-silacyclo-3-pentene (104) and 1,1-diphenyl-1-silacyclo-3-pentene (108)

A 250 ml. round bottom flask was fitted with a Friedrich condenser and two addition funnels. This flask was charged with 70 ml. of dry ether, magnesium (4.8 g.; 0.2 moles) and a magnetic stirring bar. Into one funnel was put a solution of 1,4-dibromo-2-butene (8.6 g.; 0.04 moles) in 40 ml. of ether. Into the other funnel was put a solution of dimethyldichlorosilane (5.2 g.;0.04 moles) in 40 ml. of ether. A crystal of iodine and 10 ml. of the dibromide solution were added to the stirred ether solution. This mixture was refluxed while the remaining solutions were added simultaneously over a two hour period. After all the solutions were added, the mixture was refluxed for two days. After hydrolysis and evaporation of the ether the residue was distilled to yield 3.0 g. (70%) of 104 (b.p. 99-100°) (lit 99-100°) (124). Use of dichlorodiphenylsilane instead of dichlorodimethylsilane led to 108 (b.p. 140-150°;1 torr) (lit 132°;0.02 torr) (108) in 75% yield.

Reaction of 104 with DDQ

DDQ (0.25 g.;1.1 mmoles), maleic anhydride (1.1 g.; 11 mmoles) and 104 (0.16 g.;1.4 mmoles) were dissolved in 15 ml. of methylene chloride. An nmr spectrum was recorded of the starting mixture and it was heated to reflux. After 21 hours of heating, considerable DDQ-hydroquinone was seen and little DDQ color remained in the solution. However, an nmr spectrum showed that starting material was still present and no new products were observable. Another portion of DDQ (0.25 g.;1.1 mmoles) was added and refluxing was continued for 18 hours. An nmr spectrum showed no starting material was left unreacted. Filtration yielded 0.12 g. (25%) of DDQ-hydroquinone. Evaporation of the filtrate to approximately 2 ml. followed by filtration yielded 0.85 g. (77%) of maleic anhydride. Column chromatography of the filtrate failed to yield any

1,1-dimethylsilacyclopentadiene or its maleic anhydride, 2+4 adduct. Similar results were obtained with the 1,1-diphenyl analogue (108).

Reaction of 1,1-dimethyl-3,4-diphenyl-1-silacyclopentane (106) with DDQ

DDQ (0.2 g.;0.8 mmoles) with 106 (0.1 g.;0.4 mmoles) were refluxed in 15 ml. of methylene chloride for 15 hours. At this time a trace of what was apparently DDQ-hydroquinone was visible. Workup by filtration and chromatography yielded no products, only an 80% recovery of starting material (106).

Reaction of 104 with bromine and DBU

A 25 ml. three necked flask was charged with 104 (0.25 g.;2.2 mmoles) and 10 ml. of methylene chloride. This solution was cooled to -75° with a dry ice-isopropanol bath. Bromine (0.35 g.;2.2 mmoles) was slowly added to this cooled solution. After the bromine color had disappeared, a solution of DBU (0.7 g.;4.6 mmoles) was added. This solution was stirred as it warmed to room temperature. A bulky white precipitate (DBU·HBr) fell out. The hydrolytic workup followed by column chromatography yielded no silacyclopentadiene or Diels-Alder adduct.

Reaction of 104 with bromine and DBU with tetrachloroethylene as a trap

A flask was fitted with a reflux condenser, two addition funnels and a magnetic stirring bar. The flask was charged with 10 ml. of methylene chloride and 104 (0.25 g.;2.2 mmoles). One funnel was charged with bromine (0.35 g.;2.2 mmoles) in 15 ml. of methylene chloride, the other with DBU (0.7 g.;4.6 mmoles) and tetrachlorethylene (3.6 g.;22 mmoles) in 20 ml. of methylene chloride. The flask was cooled to -75° by a dry ice-isopropanol bath and the bromine was added dropwise. Ten minutes after the last addition of bromine, the red color had completely disappeared. The DBU solution was then added dropwise. With the first drop of DBU solution, a white precipitate appeared. After the addition of DBU, the solution was allowed to warm to room temperature and stir for 10 hours. The slurry was filtered, extracted with water and dried over magnesium sulfate. Evaporation of the solvent yielded an oil. The nmr spectrum of this mixture showed only absorptions for Si-Me protons.

Synthesis of 3,4-dibromo-1,1-dimethyl-1-silacyclopentane (107)

A 100 ml. flask was fitted with a magnetic stirring bar and a septum. This flask was charged with 104 (5.0 g.; 45 mmoles) and 50 ml. of carbon tetrachloride. This solution was cooled to -75° and bromine (7.2 g.;45 mmoles) was slowly added. The solution was warmed to room temperature and the solvent was evaporated. The resulting cloudy oil was passed through a silica gel column with hexane-ether (9:1) as the eluent. Evaporation of the eluent yielded 107 (82% yield). The product decomposed on excessive heating, thus obtaining a mass spectrum was prevented. It did give a satisfactory elemental analysis: carbon = 26.67%, hydrogen = 4.41%, bromine - 58.56%, and silicon = 10.18% (calculated for $C_6H_{12}Br_2Si$: carbon = 26.49%, hydrogen = 4.44%, bromine = 58.74%, and silicon = 10.32%). The nmr spectrum for 107 showed absorptions at δ0.27(6H,s), 1.3(2H,d,J=15), 1.81(2H,d of d,J=15) and 4.7(2H,m).

Synthesis of 3,4-dibromo-1,1-diphenyl-1-silacyclopentane (109)

This molecule, 109, was synthesized in a manner completely analogous to 107. The diphenylsilacyclopentene, 108, was used instead of 104. Unlike the earlier synthesis, chromatography of the reaction mixture did not yield a satisfactory pure sample of 109. The clear oil was therefore distilled at reduced pressures (110° at 5 torr). In this manner a sample which gave a satisfactory elemental analysis was obtained: carbon = 48.44% and hydrogen = 3.99% (calculated for $C_{16}H_{16}Br_2Si$: carbon = 48.48% and hydrogen = 4.04%). The nmr spectrum of 109 consisted of absorptions at δ1.75(2H,d of m,J=16), 2.25(2H,d of d,J=16), 4.67(2H,m) and 7.35(10H,m).

Reaction of 107 with DBU

An nmr tube was charged with a concentrated solution of 107 in carbon tetrachloride. An nmr spectrum was recorded and one drop of DBU was added. Despite the presence of a good deal of white precipitate, an nmr spectrum revealed no new proton absorptions. Several more drops were added until recording an nmr spectrum was prevented by the bulkiness of the precipitate. NMR spectra were recorded after each drop of DBU was added, but only a decrease in the intensity of the starting material absorptions was observed. No new absorptions were observed. When a large excess of DBU was added a new absorbance near $\delta 5.2$ appeared, however no products were isolated.

Reaction of 107 with DBU

A three necked flask was charged with 107 (0.8 g.; 3 mmoles) and 15 ml. of THF. The flask was fitted with an addition funnel and a magnetic stirring bar. The solution was cooled to 0° with an ice bath and a solution of DBU (0.9 g.;6 mmoles) in 25 ml. of THF added dropwise. After the last portion of DBU was added, the slurry was stirred at room temperature for 1 hour. The white solid was removed by filtration and the solvent was removed from the filtrate to yield a red oil. The white solid was shown by mass spectrometry to be DBU·HBr. The red oil was chromatographed on a silica gel column with hexane as the eluent. A clear oil was obtained, which showed nmr absorptions only in the area between δ0.5 and 0.0. The mass spectrum of this oil showed many fragments with m/e values in excess of 500 mass units.

Reactions of 107 with other bases

When DBN (0.125 g.;1 mmole) was allowed to react with 107 (0.272 g.;1 mmole) in the same manner as in the DBU reaction, a similar product was formed. Chromatography over silica gel yielded a clear oil which had only Si-Me absorptions in its nmr spectrum and showed fragments with molecular weights in excess of 500 mass units in its mass spectrum.

The hindered base, lithium 2,2,6,6-tetramethylpiperylamide, was allowed to react with 107 in the manner described previously. The oil obtained was also shown to be a polymeric mixture by mass spectrometry.

No reaction was observed when 107 was dissolved in ether and stirred with potassium tert-butoxide for 24 hours.

Reaction of 109 with bases

When 109 (1.2 g.;3 mmoles) was treated with DBU (0.9 g.; 6 mmoles) again the expected white precipitate (DBU·HBr) was obtained. Hydrolytic work up and chromatography over silica gel yielded an oil whose nmr spectrum showed only aryl proton absorbances. It was concluded that this product was also polymeric in nature.

Reaction of 109 (0.40 g.;1 mmole) with potassium tert-butoxide (0.225 g.;2 mmoles) in refluxing ether for 4 hours yielded, after washing with water and evaporation of the ether, a brown oil which had some olefinic absorbances in its nmr spectrum. No material eluted from a silica gel column.

Reaction of 104 with NBS

NBS (0.178 g.;1 mmole) and 104 (0.112 g.;1 mmole) were placed in a flask and 15 ml. of carbon tetrachloride were added. The flask was fitted with a reflux condenser and a magnetic stirring bar. A small quantity of benzoyl peroxide was added and the solution was refluxed for 6 hours. At this time all the NBS was completely converted to succinimide which was removed from the solution by filtration. The filtrate was concentrated and an nmr spectrum was recorded. No absorptions except those in the Si-Me area were observed.

Reaction of syn-tetramethyldisilane (57) and terminal acetylenes

The disilane (0.12 g.;1 mmole), *o*-diethynylbenzene (0.13 g.;1 mmole) and *bis*-triethylphosphinonickel dichloride (58) (0.07 g.;0.02 mmole) were dissolved in 15 ml. of cyclohexane. This mixture was degassed by several freeze-thaw cycles and sealed in a thick-walled glass tube. This tube was heated for 18 hours at 90°. After cooling, the tube was opened and an nmr spectrum was obtained. It showed that no reaction had taken place.

A similar reaction was run with 1-hexyne (0.33 g.; 4 mmoles) replacing the substituted benzene. A brown intractable tar resulted. The nmr spectrum of this tar revealed no olefinic protons.

Reaction of 57 with o-bis(phenylethynyl)benzene (113)

A thick-walled glass tube was charged with 57 (0.2 g.; 1.5 mmoles), 113 (0.4 g.;1.5 mmoles) and 58 (0.07 g.; 0.02 mmoles). Approximately 15 ml. of cyclohexane was added and the mixture was degassed by several freeze-thaw cycles. The tube was sealed and heated at 90° for 18 hours. Evaporation of the solvent yielded a dark tar. The nmr spectrum of this tar showed that 57 had completely decomposed. The only material isolated after column chromatography was starting acetylene, 113.

Reaction of phenyltrimethylsilylacetylene (114) and 57

Three nmr tubes were prepared, each containing 114 (0.25 g.;1.5 mmoles), 57 (0.18 g.;1.5 mmoles) and a small amount of 58. In one tube approximately 0.75 ml. of cyclohexane was added, in another approximately the same amount of benzene was added, and in the third no solvent was added. Each tube was degassed and sealed, then heated for 18 hours at 90°. No reaction was seen in any tube. The neat sample was heated at 180° for 24 hours, but only slight decomposition of 57 was seen. This same tube was heated at 235° for 36 hours to completely decompose 57. However, as judged from the nmr spectrum of the product, a large number of products were formed and isolation was not attempted.

Reaction of 2-butyne and 57

The butyne (1.1 g.;20 mmoles), 57 (2.4 g.;20 mmoles) and 58 (0.4 g.;0.1 mmole) were dissolved in 50 ml. of cyclohexane. This solution was degassed by several freeze-thaw cycles sealed in a thick-walled glass tube and heated at 90° for 18 hours. The solvent volume was reduced to approximately 10 ml. and white crystals (m.p. 160-162°) fell out. This compound was shown to be hexamethylbenzene (115) on the basis of its nmr spectrum (singlet at δ 2.2) and its mass spectrum (parent ion at m/e 162).

Further evaporation of the solvent from the product mixture yielded more 115 and a clear oil. Column and gas chromatography of this material allowed the isolation of octamethyldisilacyclohexadiene (116). This structure was assigned on the basis of its nmr spectrum (2 singlets of equal intensity at δ1.75 and 0.06) and mass spectrum (parent ion at m/e 224). A sample of 116 from this reaction would not crystallize, therefore, a mixed melting point could not be obtained.

Reaction of 1,1-dimethyl-2,3,4,5-tetraethyl-1-silacyclopentadiene (117) with dimethylacetylenedicarboxylate (DMADC)

In an nmr tube was put 117 (40) (0.90 g.;0.4 mmoles), DMADC (0.142 g.;1 mmole) and approximately 0.5 ml. carbon tetrachloride. Heat was evolved and an nmr spectrum showed slight changes from the expected nmr of the starting materials. However, a thin layer chromatogram showed that the product was identical with the starting materials.

Reaction of 1,1-dimethyl-2,3,4,5,-tetramethyl-1-silacyclopentadiene (117) with dicyanoacetylene

Dicyanoacetylene (113) (125) (0.25 g.;2.5 mmoles) was distilled into a flask containing 117 (0.22 g.;1.0 mmoles) at -196°. This mixture was allowed to warm. When melting occurred, a very fast and exothermic reaction began, producing a black, intractable tar as the product.

Reaction of 117 with perfluoro-2-butyne

Perfluoro-2-butyne (1.3 g.;8 mmoles) and 117 (0.22 g.; 1 mmole) were dissolved in a small amount of carbon tetrachloride. This solution was degassed, sealed in a glass tube and heated to 50° for 20 hours. The tube was opened, the solvent evaporated and the resulting oil was chromatographed to yield impure 7,7-dimethyl-3,4-bis(trifluoromethyl)-1,4,5,6-tetraethyl-7-silanorbornadiene (118). Several attempts were made to recrystallize 118 from a variety of solvent systems but no satisfactory conditions were found. Thin layer chromatography and sublimination at 0.25 torr and 100° only partially purified the product. This structural assignment is supported by the method of synthesis and the spectral properties of the major product. The nmr spectrum showed absorptions at δ0.18(s), 0.27(s), 1.00(t of d) and 2.20 (q of d). The material was too impure to obtain satisfactory integration values. The mass spectrum showed a parent ion at m/e 222.

Pyrolysis of 2,3,bis(trifluoromethyl)-7,7-dimethyl-1,4,5,6-tetraethyl-7-silnorbornadiene (118)

A quantity of 118 was put into a capillary melting point tube. The tube was then submerged in an oil bath at 200°. The sample immediately melted and quickly a gas evolved, presumably difluorodimethylsilane.

Photolysis of 118 in carbon tetrachloride

A sample of 118 was dissolved in carbon tetrachloride and put in a quartz nmr tube. This solution was photolyzed at 2537 Å in a Rayonet photolysis apparatus. An nmr spectrum showed that the starting material had disappeared in 3 hours. The nmr spectrum showed the quartets assigned to the methylene protons had shifted downfield by 0.5 ppm. Also a sharp new singlet had appeared at δ0.78 which was shown to be dimethyldichlorosilane by comparison with authentic samples.

Photolysis of 118 with acetylenes

In a quartz tube were put 118 (1.0 g.;2.6 mmoles), 2-hexyne (1.5 g.;18 mmoles) and approximately 15 ml. of cyclohexane. This tube was degassed, sealed, and photolyzed at 3000 Å for 3 hours. The solvent was removed by evaporation. An nmr spectrum revealed the downfield shift of methylene protons seen before. The complex mixture was separated by column chromatography. The only identifiable product obtained was a 20% yield of tetramethyl-*bis*-trifluoromethylbenzene (120). The mass spectrum of 120 showed a parent ion at m/e 326. The nmr spectrum showed a triplet of doublets at δ1.0 and a quartet of doublets at δ2.70.

Photolysis of 118 with triethylsilane

In a 25 ml. flask was put 118 (0.2 g.;0.5 mmoles), triethylsilane (2.0 g.;17 mmoles) and 10 ml. of cyclohexane. This flask was fitted with a reflux condenser and photolyzed at 3000 Å for 3 hours. The solution volume was reduced to approximately 2 ml. and the mixture was separated by preparative gas chromatography. This allowed the isolation of 50 mg. of triethyldimethylsilane (121). The nmr spectrum of this compound consisted of absorptions at δ0.28(6H,d,J=5), from 1.5 to 5.0(15H,m) and 4.0(1H,h,J=5). This spectrum was decoupled, when the multiplet at δ4.0 was irradiated, the doublet at δ0.25 collapsed to a singlet. When the doublet at δ0.25 was irradiated, the multiplet at δ4.0 collapsed to a singlet. A mass spectrum showed a parent ion of m/e 174.

Photolysis of 118 in cyclohexene

The silanorbornadiene 118 (0.2 g.;0.5 mmoles) was dissolved in 6 ml. of cyclohexene. This mixture was photolyzed at 3000 Å for 3 hours. The reaction mixture volume was reduced to 2.5 ml. by distillation and both the distillate and the pot residue were examined by nmr and infrared spectrometry. No evidence for the formation of the expected silylhydride was found. In particular there was no infrared absorption in the area of 2100 cm.$^{-1}$ where silylhydrides typically absorb.

Photolysis of permethylcyclohexasilane (123) in cyclohexene

Approximately 1 ml. of cyclohexene was distilled into a quartz nmr tube that contained permethylsilacyclohexane (123) (114) (0.2 g.;0.5 mmoles). This solution was deoxygenated by bubbling argon through it. An nmr spectrum was taken and the solution was photolyzed at 2537 Å for

48 hours. The existence of a silylhydride bond was indicated by the appearance of a heptet at $\delta 4.0$ in the nmr spectrum. The infrared spectrum also showed a strong absorption near 2100 cm.$^{-1}$. These are consistent with the formation of <u>122</u>.

Reaction of 7,7-dibromonorcarane (126) with methyl lithium

A 25 ml. three necked flask was fitted with a reflux condenser, an addition funnel and a septum. The flask was flame dried and a slow nitrogen sweep was begun. The flask was charged with a magnetic stirrer, 10 ml. of ether, and <u>126</u> (1.0 g.;4 mmoles). The solution was cooled to -78° and 5.9 ml. of a 1.7 M methyl lithium (10 mmoles) was added slowly with constant stirring. After the addition of base, the solution was stirred for 0.5 hours, then allowed to warm to room temperature. The reaction mixture was poured onto ice and the organic compounds were collected by 3 ether washes. After drying, the volume was reduced to approximately 1 ml. This mixture was analyzed by gas chromatography-mass spectrometry.

As reported by Moore and Ward (115-116), two isomers of molecular weight 94 and olefin <u>125</u> were obtained. In addition the following compounds were found in substantial yield (the yield varied in other runs).

	Fragment weight	% base peak
C_8H_{14} (127)	$M^{+\cdot} = 110$	30%
	95	25%
	81	95%
	67	100%
C_9H_{16} (128)	$M^{+\cdot} = 124$	40%
	109	50%
	95	17%
	81	100%
	67	81%
$C_8H_{13}Br$ (129)	$M^{+\cdot} = 190$	15%
	188	15%
	148	5%
	146	5%
	109	35%
	95	50%
	81	60%
	67	100%

Another compound with a $M^{+\cdot}$ of 154 was also formed in a large yield but was not identified.

Photolysis of 123 in the presence of norcaranylidene norcarane (125)

A solution of 123 (0.7 g.;2 mmoles) and 125 (0.05 g.; 0.5 mmoles) in cyclohexane (13 ml.) was degassed by several freeze-thaw cycles and photolyzed in a quartz tube at 3000 Å for 6 hours. The quartz tube was opened in an argon atmosphere and most of the cyclohexane was removed. The residue was treated with damp ether and then the ether was evaporated. The resulting oil was chromatographed over silica gel using hexane as the eluent. No identifiable products were obtained from the column except unreacted starting material.

Similar reaction were followed by gas chromatography but no products other than those expected from the decomposition of 124 were seen.

Photolysis of 123 with adamantylidene adamantane (132)

A solution of 132 (117) (0.27 g.;1 mmole) and 123 (0.7 g.;2 mmoles) in cyclohexane was photolyzed in a quartz tube at 3000 Å for 6 hours. After this time the solution was treated with methanol and the solvent was removed. No identifiable products were obtained by chromatography of the residue.

Attempted synthesis of 2,3-dispiroadamantyl-1,1-dimethyl-1-silacyclopropane (134)

Methyl lithium (2 mmoles) was slowly added to a solution of 2,2-dibromoadamantane (0.6 g.;2 mmoles) in THF at -95°. The mixture was allowed to stir for 30 minutes, then dimethyldichlorosilane (0.13 g.;1 mmole) was added and the solution was allowed to warm to room temperature. Through a side arm, magnesium powder (0.24 g.;10 mmoles) was added and the mixture was stirred for 15 hours. At this time the mixture was treated with methanol. The mixture was then worked up hydrolytically and the solvents evaporated off. The residue was chromatographed over silica gel to yield several fractions. Two nonsilicon containing products, adamantanone and 2-bromoadamantane were isolated and identified by their mass spectra. Also one silicon containing product was isolated and its nmr and mass spectra were consistent with structure 134. The mass spectrum showed a parent ion at m/e 282. The nmr was also consistent, showing absorptions at δ0.1(s), 0.3(s), 1.6(m) and 3.46(s).

Synthesis of 5,5,6,6-tetramethyl-1,2,3,4-tetraphenyl-5,6-disilabicyclo[2,1,1]hept-2-ene (92b)

A sample of 1,2-disilacyclohexadiene (91b) (1.75 g.; 3.7 mmoles) was irradiated for 48 hours at 3000 Å in benzene. The tube was then heated at 95° for 36 hours. The solvent was removed and the brown residue was dissolved in pentane. A yellow crystalline material (0.300 g.) did not dissolve. This material was shown to be the tetraphenylsilacyclopentadiene by comparison of its nmr spectrum with that of an authentic sample and by its mass spectrum.

The pentane was removed and a yellow, amorphous material was obtained. Its mass spectrum showed a parent ion of m/e 472, therefore, the material is isomeric with the starting material. The nmr spectrum of this material showed absorptions at δ0.52 and 1.75(6H) and in the aryl region, δ6.7 to 7.2(10H).

Reaction of 92b with diphenylacetylene

Diphenylacetylene (0.18 g.;1.0 mmoles) and 92b (0.95 g.; 0.2 mmoles) were dissolved in benzene-D_6 and heated at 140° for 2 hours. An nmr showed complete disappearance of the starting material peaks and almost quantitative appearance of a new peak at δ -0.07. I was unable to isolate any material with this absorbance in its spectrum.

More starting material (91b) was prepared according to the method of Nakadaira et al. (105) and this was converted to 92b. This sample was almost identical to that prepared earlier except for some minor impurities with absorbances in the area of the Si-Me absorptions of 92b.

This newly prepared material, 92b, was heated for 36 hours. The temperature was raised, in increments, from 140° to 200°, but no decomposition occurred.

Diphenylacetylene and 92b were heated for 24 hours at 230°, but very little decomposition occurred. The reaction that did occur was not the same as observed earlier.

Reaction of bis(α,α-dibromobenzyl)dimethylsilane (136) with magnesium in THF

A three necked flask was fitted with a condenser and a magnetic stirring bar. This system was charged with 136 (118) (1.4 g.;2.5 mmoles), magnesium (0.25 g.; 10 mmoles) and 20 ml. of dry THF. This mixture was refluxed for 5 hours, then filtered. The filtrate was hydrolyzed in the usual manner and the solvents were evaporated leaving a yellow oil as a residue. Column chromatography yielded diphenylacetylene (12%) and disilin 2 (8%). These were identified by comparing their nmr spectra with authentic samples and by their mass spectra (parent ions - m/e 178 and m/e 472 respectively).

Similar reactions were run with potassium or lithium instead of magnesium and similar yields of the same two products were obtained.

Reaction of 136 with magnesium in HMPA

Magnesium powder (0.25 g.;10 mmoles) and 136 (2.8 g.; 5 mmoles) were put into a 100 ml. three necked flask and approximately 50 ml. of HMPA were distilled from lithium aluminum hydride into the flask. The mixture was stirred for two days. The solution was filtered through celite and about 100 ml. of hexane was added. The solution was washed 5 times with water to remove the HMPA and the organic layer was dried. After the solvent was evaporated, the residue was chromatographed to yield diphenylacetylene and 2 (25% and 20%). A product later identified as 138 was also detected in the nmr spectrum of the initial product mixture.

Reaction of 136 with activated magnesium in THF

Magnesium (1.0 g.;40 mmoles) was produced in the manner of Rieke and Bales (119). After the reduction was complete, the THF slurry was cooled to 0° and a solution of 136 (5.6 g.;10 mmoles) in THF was added dropwise. The mixture was stirred for 30 minutes while it warmed to room temperature. The reaction mixture was quenched with methanol and worked up by normal hydrolytic procedures.

After evaporation of the solvents, the residue was chromatographed over 100 g. of silica gel with hexane or hexane/ether as eluents. A mixture of *cis*- and *trans*-stilbene (0.55 g.;31%) was isolated after 750 ml. of hexane. The identities of these compounds was shown by nmr and by retention times on high pressure liquid chromatography. HPLC showed this mixture to be 15% cis and 85% trans. This ratio was consistent with the nmr spectrum recorded.

After 3000 ml. of hexane, 2 (1.93 g.) eluted from the column. This material was recrystallized from hot benzene to yield 2 (0.70 g.;30%) m.p. 319-322° (literature values: 322-324°). The identity of 2 was confirmed by nmr and mass spectrometry ($M^{+\bullet} = 72$).

In succeeding runs varying amounts of 138 and 139 were also isolated from this reaction sequence.

Synthesis of 3,4-diphenyl-2,2,5,5-tetramethyl-2,5-disila-1-oxa-3-cyclopentene (138)

Powdered magnesium (0.5 g.;20 mmoles) and 136 (2.8 g.;5 mmoles) were put in a flask and 50 ml. of HMPA was distilled from LAH into the pot. The reaction was stirred for 1 day and worked up in the usual manner. Chromatography of the resulting oil over silica gel yielded several fractions, including diphenylacetylene and disilin. Along with the disilin, 2, 138 eluted. Recrystallization of 2, from benzene provided 138 in pure form. The structure of 138 was assigned principally from its high resolution mass spectrum which showed a parent ion of 310.117588 ± 0.0016 (calculated for $C_{18}H_{22}OSi_2$ as 310.12092). The infrared spectrum showed an absorption at 1250 cm.$^{-1}$, characteristic of an Si-O absorption. The nmr is consistent, showing a singlet at δ 0.4(6H) and an aryl multiplet (5H).

Synthesis of 3,4-dibromo-3,4-diphenyl-2,2,5,5-tetramethyl-2,5-disila-1-oxa-cyclopentane (139)

A reaction similar to the one above was run using 136 (5.6 g.;10 mmoles) and only one equivalent of magnesium (0.5 g.;20 mmoles). Chromatography over a silica gel column yielded several fractions. Diphenylacetylene eluted first followed immediately by a fraction containing 139. Later fractions showed 138 and 2 were also produced.

The fraction containing 139 was purified by preparative HPLC and recrystallized from methylene chloride. The nmr spectrum showed a singlet at δ 0.25(6H) and a broad singlet at δ 7.2(5H). The mass spectrum of the compound showed a triplet at m/e 468, 470, and 472. The compound's infrared spectrum showed an absorption at 1250 $\mathrm{cm.}^{-1}$ similar to 138. The melting point was 162-164°.

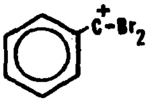
Synthesis of 136d

To a slurry of magnesium (48.0 g.;2 moles) in THF was added dropwise a solution of p-bromotoluene (200 g.; 1.17 moles) in THF. After the addition was complete the solution was stirred until it returned to room temperature. Deuterium oxide (30 g.;1.5 moles) was slowly dropped into the mixture. The precipitate was filtered off and the organic solution was extracted with water and dried over magnesium sulfate. Distillation yielded 100 g. (92%) of p-deuterotoluene (b.p. = 105-110°). The nmr was consistent with this assignment.

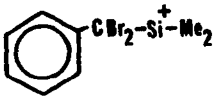
In a 1000 ml. flask was put 600 ml. of carbon tetrachloride, previously made p-deuterotoluene (100 g.; 1.07 moles) and n-bromosuccinimide (195 g.; 1.1 moles). This mixture was refluxed for 5 hours. At this time all the solid had risen to the surface of the solution. The mixture was filtered and the filtrate distilled. The desired product, p-deutero-benzylbromide, 125 g. (68%) was collected between 100-102° at 15 torr. The nmr spectrum was consistent with the desired product, showing a singlet at δ4.95(2H) and a quartet at δ7.25(4H).

A three necked flask was fitted with a true bore stirrer and addition funnel and a reflux condenser. This flask was charged with magnesium (24 g.;1 mole) and 500 ml. of THF. A solution of p-deutero-benzylbromide (115 g.; 0.67 moles) and dichlorodimethylsilane (43 g.;0.33 moles) in 200 ml. of THF, was introduced into the addition funnel. This solution was added slowly to the magnesium. After addition of the solution, the mixture was stirred for 15 hours and then hydrolyzed and worked up in the normal fashion. Evaporation of the solvent yielded a white solid which was recrystallized from ethanol to yield the desired bis(p-deuterobenzyl)dimethylsilane (50 g.;61%).

This material was converted by the method of Brook and Peddle (118) to 136d, (m.p.=124-126°). Mass spectral analysis showed the product was 75% dideuterated. This is shown by the isotope distribution in two fragment ions.



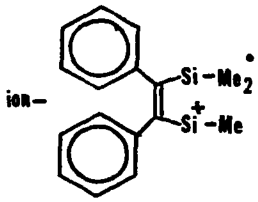
Natural abundance		Deuterated compound	
m/e = 246	0%	m/e = 247	6.5%
247	50%	248	50 %
248	4%	249	17 %
249	100%	250	100 %
250	8%	251	14 %
251	48%	252	48 %



304	0%	305	6%
305	50%	306	51%
306	8%	307	20%
307	100%	308	100%
308	16%	309	19%
309	52%	310	52%

Reaction of 136 with activated magnesium

A mixture of 136 (1.4 g.;2.5 mmoles) and 136d (1.4 g.; 2.5 mmoles) were subjected to the same conditions as when 136 was used alone. The disilins produced were collected and subjected to mass spectral analysis. When compared to the natural abundance material, the mass spectrum shows all the deuterium is situated on the same side of structure 2.



Natural abundance		Deuterated compound	
227	11%	277	11%
278	7%	278	7%
279	100%	279	100%
280	27%	280	54%
281	12%	281	92%
282	2%	282	25%

Synthesis of ditolylacetylene

Tolualdehyde (180 g.;1.5 moles) was reacted with potassium cyanide (15 g.;0.23 moles) according to the procedure of Fieser and Williamson (125).

This product was converted first to the substituted benzil, then to ditolylacetylene using nitric acid and hydrazine followed by yellow mercuic oxide. In these procedures Fieser's methods were also used. The nmr spectrum implied the desired product had been formed, showing a singlet at δ 2.5(3H) and a quartet centered at δ 7.3(5H).

Reaction of 136 and ditolylacetylene with magnesium

Ditolylacetylene (1.0 g.;5 mmoles) and 136 (2.8 g.; 5 mmoles) were stirred with magnesium to HMPA for 15 hours. The mixture was diluted with ether and extracted with several portions of water. The solvents were evaporated and chromatographed over silica gel to remove the excess ditolylacetylene, which comes off with hexane. A yellow granular compound was brought off with 20% ether-80% hexane. The yellow solid was rechromatographed over silica gel with 3% ether in hexane as the eluent. A pure sample of 138 was recovered. The other samples were a mixture of 138 and 2 as shown by nmr, which showed only two Si-Me absorbances and no absorbances in the area of δ 2.0-3.0 where tolylmethyl should absorb. The mass spectrum of this sample showed molecular ions for only 138 (m/e 310) and 2 (m/e 472).

This type of reaction was also run with some alterations, using activated magnesium and THF and increasing the ditolylacetylene concentration or using 136d with diphenylacetylene. However, the results were similar to those reported here.

Reaction of dibromostilbene (149) with activated magnesium

Dibromostilbene (149) was prepared by addition of one equivalent of bromine to diphenylacetylene in carbon tetrachloride. Evaporation and recrystallization from chloroform yielded 144 (m.p. = 195-199°) in 60% yield.

Reaction of 144 with activated magnesium in THF under the reaction conditions used to form stilbenes from 136 yielded a mixture of diphenylacetylene and *cis*- and *trans*-stilbene. After work up by hydrolysis and evaporation of solvent, the stilbenes are easily identified by the absorptions of the olefinic protons which absorb at δ6.96 (trans) and δ6.54 (cis). These are well shifted out of the aromatic absorbances, so integration allowed an estimate of the concentration of the stilbenes. *Cis*- and *trans*-stilbene were found in about 30% combined yield.

Reaction of 136 with tosylhydrazine followed by DBU

Tosylhydrazine (3.70 g.;20 mmoles), DBU (6.1 g.; 40 mmoles) and 136 (5.6 g.;10 mmoles) were dissolved in 150 ml. of dry THF. The solution was stirred overnight, at the end of this time there was 3.65 g. of a white precipitate formed which was shown by nmr to be DBU·HBr. The solvent was removed from the filtrate to yield a yellow oil. Examination of this oil by mass spectrometry showed it to be a mixture of diphenylacetylene ($M^{+\cdot}$= m/e 178) and cyclic polysiloxanes ($M^{+\cdot}$= m/e 207, 281, 255).

Reaction of 136 with tosylhydrazine followed by butyl lithium

Tosylhydrazine (3.7 g.;20 mmoles) and 136 (5.6 g.; 10 mmoles) were dissolved in THF and stirred for 15 hours. *n*-butyl lithium (60 mmoles) was added dropwise over a 3 hour period. After the addition of 2/3 of the butyl lithium, each drop was accompanied by extensive frothing. After complete addition of the organometallic reagent, the solution was hydrolyzed and the solvents removed by distillation.

The residue was distilled to yield a clear oil. A solid which contained the silicon-containing compounds was collected in the distillation tube.

The distillate was chromatographed over silica gel to yield three fractions. The first contained cyclic polysiloxanes, shown by mass spectrometry to be the pentamer and hexamer ($M^{+\cdot} - 15$ = m/e 355 and 429).

The second and third fractions were subjected to HPLC over a u-porasil column to yield 157, diphenylacetylene and *cis*- and *trans*-stilbene. The hydrocarbons were implied by comparing their HPLC retention times and nmr spectra with authentic samples. Their exact molecular weights, determined by high resolution mass spectrometry, were satisfactory.

The identity of 157 was implied by its exact molecular weight (294.18006, calculated for $C_{28}H_{26}Si$ is 294.18038). Its nmr spectrum showed a singlet at δ 0.1, a multiplet at δ1.8-1.0(9H's), and a multiplet at δ 6.7-7.4.

Reaction of dibenzyldimethylsilane (158) with butyl lithium followed by D_2O

The silane, 158, (0.5 g.;2 mmoles) was dissolved in THF and the solution was stirred. Butyl lithium (5 mmoles) was carefully syringed into the solution and the mixture was stirred for 3 hours. One ml. of deuterium oxide was carefully injected and the solution was stirred for

10 minutes. Drying and evaporation of the solvents yielded a yellow solid (0.49 g.;98%) that proved to be only the starting material. An nmr analysis showed that the recovered material was only 16% deuterated.

Reaction of phenyldiazomethane with butyl lithium followed by dichlorodimethylsilane

Phenyldiazomethane (1.2 g.;10 mmoles) was distilled into a flask and dissolved in 10 ml. of THF. Butyl lithium (10 mmoles) was carefully syringed into the solution and it was stirred for 2 hours. At this time dichlorodimethylsilane (0.65 g.;5 mmoles) was added and stirring continued for 2 hours. The reaction was quenched with a saturated bicarbonate solution and the organic layer was dried over magnesium sulfate. Evaporation of the solvent yielded a red oil. The nmr spectrum was very complex. The mixture decomposed exothermically when exposed to silica gel or alumina. It was also unstable toward heat. Attempts to recrystallize from benzene, methylene chloride, and ethanol were unsuccessful.

Synthesis of diisopropylmethylsilane (160)

A solution of dichloromethylsilane (115 g.;1 mole) and isopropyl bromide (370 g.;3 moles) in 150 ml. of dry ether was added to magnesium turnings (80 g.;3.3 g.) over a 4 hour period. After the addition was complete, the mixture was refluxed for 18 hours. The reaction mixture was quenched with saturated ammonium chloride. The ether was washed with three portions of saturated ammonium chloride and dried over magnesium sulfate. The solution was distilled and the fraction boiling between 115 and 123° (105 g.;80%) (lit 122°) (126) was collected.

Reaction of diisopropylmethylsilane (160) with bromine

A neat sample of 160 (14.4 g.;0.1 mmole) was cooled in a three necked flask to 0°. One equivalent of bromine was added over a 30 minute period. The temperature of the reaction was raised to 70° and two more equivalents of bromine were added at a rate such that the solution was just orange at all times. The mixture was vacuum distilled to yield three fractions. None were pure, however, most of the desired product was collected below 30°. The nmr spectrum was consistent with a singlet at 0.4(1H) and a singlet at 1.1(2H).

Reaction of bis(2-bromoisopropyl)bromomethylsilane (161) with methyl lithium

This material was treated with methyl lithium at room temperature in THF for 2 hours. The mixture was quenched with methanol and worked up hydrolytically. Distillation of the solvents yielded a clear oil. The nmr spectrum showed a significant reaction had occurred with the

Si-Me absorption shifted to 0.9. However, the isopropylmethyl absorption has been converted quantitatively to a doublet, indicating metal halogen exchange at the alkyl position was the only reaction that occurred.

Synthesis of diisopropylfluoromethylsilane (163)

Tritylfluoroborate (33 g.;0.1 mmole) was mixed with 10 ml. of THF. The silane, 160, (14.4 g.;0.1 mole) was slowly added to this stirred mixture. The yellow color disappeared at the completion of the addition. All the volatile products were removed by vacuum distillation. The distillate was redistilled at atmospheric pressure to yield 163, b.p. = 116°, (13.5 g.;91%). The structure was confirmed by its nmr spectrum which showed a doublet at 0.1(3H,J=8) and a broad singlet at 1.1(13H).

Synthesis of bis(2-bromoisopropyl)fluoromethylsilane (164)

Bromine was added slowly to a neat sample of 163 (15 g.; 0.1 mole) while the temperature was maintained at 70°. After the final cooling the reaction mixture was distilled to yield 164 (25 g.;80%). The nmr spectrum of 164 is consistent with this structural assignment: 0.65(1 H,d,J=6.5) and 2.0(14 H,d,J=2). A four bond coupling of the isopropylmethyl protons with fluorine explains the doublet at 1.0.

Reaction of 164 with methyl lithium

Methyl lithium (10 mmoles) was added to a solution of 164 (3.5 g.;10 mmoles) in THF and stirred for 3 hours. The reaction was quenched with water and the organic layer was dried and solvents evaporated. Distillation allowed an 80% recovery of 164. No other products were isolable.

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