1973

(p-p) [pi] multiple bonding in silicon

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(p-p) π MULTIPLE BONDING IN SILICON.

Iowa State University, Ph.D., 1973
Chemistry, organic

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(p-p) π multiple bonding in silicon

by

Eugene Arden Kline

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

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1973

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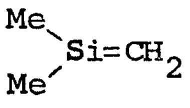
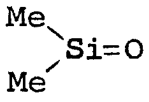
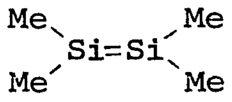
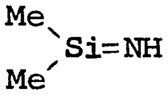
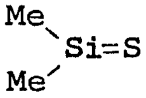
NOMENCLATURE

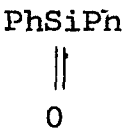
In the literature, one finds several names for $Me_2Si = CH_2$ which is quite common for compounds developed over long periods of time. The official IUPAC names are not yet available, but will probably be issued later this year. However, the following names have been recommended (1) for the respective structures and will be listed along with the others which have been used in the past.

	Dimethylmethylenesilane (1), 1,1-dimethyl-1-silaethylene, 2-methyl-2-silapropene
	Dimethylsilicon oxide (1), dimethyloxosilane (1), dimethylsilaketone, dimethylsilanone
	Tetramethyldisilene (1)
	Dimethylsilicon imide (1), dimethylsilylenimine (1)
	Dimethylsilicon sulfide (1), dimethylthioxosilane (1)

HISTORICAL

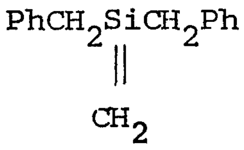
It has been more than three quarters of a century since the first investigations were reported in organosilicon chemistry (2). The area has grown to a stage where we are now only beginning to understand some of the properties of organosilicon compounds, which are quite unique compared to those of its congener-carbon. One such area of interest is the consideration of multiple bonding of silicon which is perhaps one of the oldest, yet one of the least understood, phenomena.

As early as 1866, Dilthey (3) reported the synthesis of diphenylsilanone (1). This was followed in 1909 by an attempted synthesis of dibenzylsilaethylene (2) by Kipping (4) and later by a reported isolation of diphenylsilaethylene (3) by Schlenk and Renning (5). Little did it matter that all of these efforts were failures, as the real impetus for studying the problem of multiple bonding in silicon was made. Only time was necessary before technology reached a point where it could be produced synthetically and be better



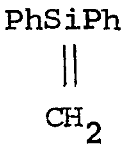
$\mathrm{Ph}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{Si}}\mathrm{Ph}$

(1)



$\mathrm{PhCH_2}\underset{\underset{\mathrm{CH_2}}{\|}}{\mathrm{Si}}\mathrm{CH_2Ph}$

(2)



$\mathrm{Ph}\underset{\underset{\mathrm{CH_2}}{\|}}{\mathrm{Si}}\mathrm{Ph}$

(3)

understood theoretically. Recent additional experimental evidence (6) for the rather well established d-orbital participation in (p-d) π-back-bonding of silicon has only increased the interest. Bonding of the (p-p) π type in silicon until quite recently was thought to be nonexistent (7). There has only been a minimal amount of data to suggest the possibility for (p-p) π-bonding but this has provided the real justification to pursue the investigation of this new type of bonding with silicon.

Pitzer (8) used a limited qualitative basis of pictorial representations to convey that the reason for the lack of (p-p) π-bonding observed in $n > 2$ row elements was the repulsion of inner shell electrons of the adjacent atoms. Mulliken (9, 10) calculated relevant integrals to examine this question and found that inner shell-inner shell overlaps were negligible ($< 10^{-3}$) while inner shell-valence shell integrals had values up to 0.1 which were of some importance. These latter repulsions were no larger for the third row atoms than the second row atoms and thus seemed to negate Pitzer's original explanation (8).

Mulliken also considered (p-p) π-bonding by computing bonding overlap integrals. He showed that $np\pi - np\pi$ $(n > 2)$ overlaps are, in some cases, greater than $2p\pi - 2p\pi$ overlaps at equilibrium bonding distances. He reasoned that one must use overlap integrals at constant ξ, where $\xi = R/(r_a+r_B)$

(R = bond distance, $r_i = n_i^2 a_o/Z_{eff}$ = the maximum in the radial probability curve). The bonding distance R is the sum of the radial maxima for both atoms when $\xi = 1$. At this condition, the (C-C) π-overlaps were found to be greater than (Si-Si) π-overlaps (0.29 + 0.22, respectively). However, under the same circumstances ($\xi = 1$), σ-overlaps of third row elements were larger than those of the second row elements. Mulliken used these data to conclude that the lack of π-bonding in compounds of heavy elements could be explained by relatively stronger σ-bonds being formed when the multiple bonded species polymerizes.

Aside from the fact that there was experimental evidence that the (C-C) σ-bond was stronger than the corresponding (Si-Si) bonds (11), Curtis (12), in the most recent theoretical investigation, pointed out that typical values of ξ range from 0.7 (H-H) to 1.77 (F-F) signifying that the bond distance was not necessarily directly related to the radial maxima of the free atom, but rather to the lowest energy. The use of constant ξ, then, was hardly warranted. Rather, the use of the Mulliken-Wolfgang-Helmholtz (MWH) approximation (13, 14) of off-diagonal elements (Hij): $Hij = 0.5\ K\ Sij\ (Hij + Hij)$ was needed to make an estimate of the Hij elements in the π-bond involved rather than just comparing overlap integrals (15).

The EHMO results of Curtis showed that values associated with 3d π-orbitals were always considerably higher than those with only pπ type orbitals. This showed up when the π (b_1 u) MO overlap population of disilaethylene ($H_2Si{=}SiH_2$) (4) was broken down into separate contributions of (p-p) (0.277), (p-d) (0.348), and (d-d) (0.038) totaling 0.663. The large (p-d) contribution was due to the large (p-d) π-overlap integrals which were responsible for the great sensitivity of π-bond overlap population in disilaethylene. The d-orbitals had less effect on overlap population in the σ-framework which was the same as saying in MO language that polarizability of the π-bond was greater than for the σ-bond. The d-orbitals were acting as polarization functions for the s and p potentials.

Silaethylene ($H_2Si{=}CH_2$) (5) yielded somewhat different results than disilaethylene. Besides differences in bonding and antibonding for the respective MO's (due to differences in symmetry), the carbon-silicon π-bond (b_1) overlap population was 0.327 and was composed of contributions of 2p-3p (0.130) and 2p-3d (0.197). With no d-orbitals, the p-p overlap population was only 0.158. The smaller value of the π-bond overlap population (as compared to disilaethylene), was accompanied by an asymmetric electron distribution being localized primarily in the carbon 2p-orbital. The calculated charges in the π-bond were C (+0.71), Si (+0.71) and C (+0.81), Si (-0.81) with and without d-orbitals, respectively. The charge over the whole molecule was calculated to be C (-1.1) and Si (1.6) when d-orbitals were included. Curtis pointed out that a carbanion-siliconium ion bond polarization seemed to explain the data much better than a diradical, which had earlier been proposed (6, 15).

The CNDO method which contains coulombic interaction (EHMO includes only overlap integrals), showed the carbon-silicon double bond to be quite polar, but much less so than in the former EHMO calculation. The π-bond polarity of silaethylene was C (+0.264), Si (-0.264), compared to that of formaldehyde which was C (0.158), O (-0.158). The dipole moment calculated for $CH_2{=}SiH_2$ by CNDO method was 2.99 D.

Another way to examine the strength of the π-bond, theoretically, was by measuring the barrier to rotation of one end of a π-bond with respect to the other end. The results with and without d-orbitals revealed the ordering of π-bond strengths as $C{=}Si < Si{=}Si < C{=}C$. This agreed with conclusions based on the previous population analyses.

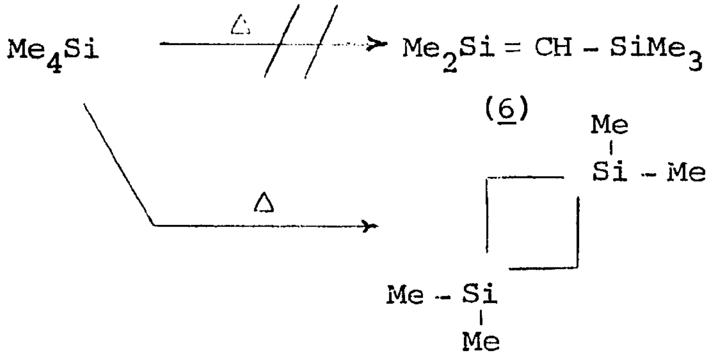
The resulting effect of twisting the planar molecule was a separation of the bonding π MO into "π_C" and "π_{Si}" components. The degree of separation determined whether the singlet or triplet state existed. In twisted silaethylene, the singlet state was calculated to be the lowest energy excited state. This was consistent with an exceedingly polar π-bond with the electrons remaining localized on carbon when it was twisted. The dipole moment was, of course, predicted to be lower than the one calculated with one electron put on both the silicon and carbon atoms (triplet state).

Disilaethylene, not having the asymmetry of silaethylene, was predicted to have the triplet state in its twisted shape. Both the CNDO and EHMO calculations coincided with this conclusion as to multiplicity. They were also in accord with the strength of the π-bond as determined from its rotational barrier and had the same order, C=Si < Si=Si < C=C, as found with overlap integrals.

The high polarity of silaethylene should result in a head to tail dimerization and the calculated LUMO and HOMO with their contributions of each orbital, indicated a net positive overlap (bonding), which was expected between the LUMO and HOMO. The conclusion drawn from these results, in general, was not only the probable existence of silaalkene, but also it was predicted to have a singlet energy state with considerable polarity in the molecule.

Experimental evidence for the transient existence of the silicon-carbon double bond could be found as early as 1914 when Schlenk and Renning (5) reported dehydrating diphenylmethylsilanol to form the diphenylsilaethylene. However, when reinvestigated, Kipping (16) found that the product was the siloxane formed by the loss of one molecule of water from two molecules of silanol, a very common reaction. No evidence for the desired elimination was found in either the vigorous reaction of phosphorus pentoxide or zinc chloride. Heating tribenzylchlorosilane with dimethylaniline or quinoline also produced no elimination. Attempts by West (17) to produce silabenzene from catalytic dehydrogenation of silacyclohexanes with platinum and palladium catalysts demonstrated that the degradation led to mixed olefins above 500°C, with no reaction occurring at lower temperatures.

Fritz and Grobe (18) reported isolation of a molecule containing a silicon-carbon (p-p) π-bond by pyrolyzing tetramethylsilane to give 2,4,4-trimethyl-2,4-disila-2-pentene (6) which reacted with bromine and hydrogen



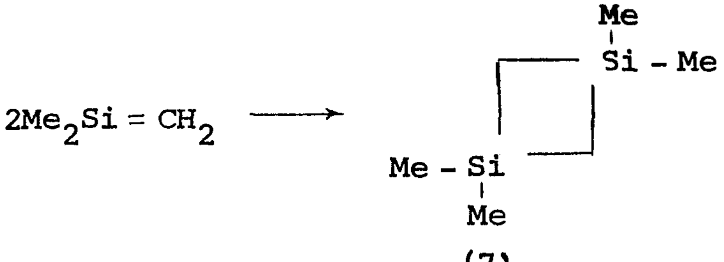
(6)

(7)

$$Me_4Si \xrightarrow{\Delta} Me_3Si\cdot + Me\cdot \qquad 1$$

$$Me_4Si + Me\cdot \rightarrow Me_3SiCH_2\cdot + CH_4 \qquad 2$$

$$Me_3SiCH_2\cdot \rightarrow Me\cdot + Me_2Si{=}CH_2 \qquad 3$$



(7)

4

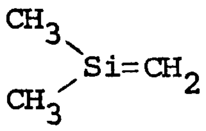
bromide. Later work proved (19, 20) that the product was 1,1,3,3-tetramethyl-1,3-disilacyclobutane (7). Fritz et al. (21) proposed that the correct mechanism for this reaction involved the diradical which dimerizes to the product (7) observed. No attempt was made to explain why only the dimer was formed from diradicals. The same product formed in the catalytic (iron/copper) dechlorination of tris(trichlorosilyl)chloromethane at 250°C (22, 23). The diradical mechanism of Fritz and Grobe was assumed.

Another investigation by Kumada showed halomethyl substituted disilanes eliminated with sodium ethoxide to form the ethoxide (24). A mechanism involving the silaalkene with addition of ethanol was offered, but an alternative mechanism without the silaalkene was later proposed by the same workers (25). Alternative explanations (26) have also been offered to the proposed (27) silaalkene intermediate in the formation of polymeric products from the reaction of dialkyldihalosilanes with lithium.

Bailey and Kaufmann (28) reported that pyrolysis of allyl trimethylsilanes at 600°C yielded propene and silaalkene which is trapped by different butadienes as well as by itself. This has never been substantiated in literature. In fact, there is at least one report (29) of several unsuccessful attempts to reproduce these results. A rather unusual Grignard reaction between benzophenone and dimethylsilylmethylmagnesium bromide (8) to give trimethylsilyldiphenylmethyl ether (9) and pentaphenylmethyldisilane (10)

$$\mathrm{PhCOPh} + \underset{(8)}{\mathrm{Me_2SiHCH_2MgBr}} \rightarrow \underset{(9)}{\mathrm{Me_3SiOCHPh_2}} + \underset{(10)}{\mathrm{Me_2SiHCH_2SiMe_3}}$$

has been reported (30). The silaalkene (11) was thought to be the intermediate most likely to explain the products. However, a later report (31) did not favor this intermediate.



(11)

$$\mathrm{(Me_2SiO)_n(Me_2SiCH_2)_m}$$

(12)

Still another report (32) of a silaalkene being an intermediate was the pyrolysis of cyclic siloxanes (12) which form 1,1,3,3-tetramethyl-1,3-disilacyclobutane (7).

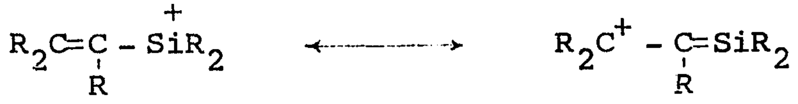
Mass spectral data has been given as evidence for species with (p-p) π multiple bonding involving silicon

(33). The electron bombardment of 1,1,1,3,3,3-hexamethyl-2,2-disubstituted-1,3-disilanes (13) gave very strong peaks at M^+ -30-R. The ions with these masses were consistent

$$\mathrm{Me_3SiCR_1R_2SiMe_3} \xrightarrow[-2\mathrm{Me}]{e^-} [\mathrm{Me_2Si = C_{R1}} \overset{..}{-} \mathrm{SiMe_2}]^+$$

(13) (14)

with an allyl type cation (14) with a Si-C double bond. However, if d-orbital participation stabilizes multiple bonding, as suggested (34), it was almost certain to occur here. Dimmel's other suggestion of the allyl cation needing a Si-C double bond contribution seemed much less convincing, as vinylsiliconium ions could be an adequate explanation.



$$\mathrm{R_2C{=}\underset{R}{C}-\overset{+}{Si}R_2} \longleftrightarrow \mathrm{R_2C^+-\underset{R}{C}{=}SiR_2}$$

One of the most dramatic pieces of evidence for the transient silaalkene comes from the pyrolysis of 1,1-dimethyl-1-silacyclobutane (15) (35), following a similar reaction which has been well-studied in the all-carbon system (36). The silicon system had been studied by Nametkin and co-workers (35) who found polymerization occurred when heating the above compound (15) neat at 160-180°C. However, at a higher temperature in the gas phase, ethylene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane were the sole products (37). The dichloro-analogue, 1,1-dichloro-1-silacyclobutane, gave ethylene and the 1,1,3,3-tetrachloro-1,3-disilacyclobutane (38) to show its generality.

A mass spectral analysis of (15) (39, 40) indicated that the transient silaalkene was an independent species. The mass spectrum of 1,1-dimethyl-1-silacyclobutane (Table 1) showed a metastable loss of 28 (C_2H_4) to form the base peak at m/e 72 $[Me_2Si{=}CH_2]^+$. That this species might exist was further substantiated by a stoichiometric measurement of products in copyrolyses with water to form silanol (41), with ammonia to form silylamine (41) and with dienes to readily form the Diels-Alder adducts (42). Kinetic data (43) confirmed the mechanism involving silaalkene as did the inhibition of the formation of the disilacyclobutane by addition of ethylene and propene (44, 42). No polymeric products resembling those expected from diradical species were observed and it was concluded that the bonding with silicon was of the (p-p) π type.

The isolated species came late in 1971 when Barton and McIntosh (45) pyrolyzed the 1,1-dimethyl-1-silacyclobutane (15). The apparatus, similar to that described by King and co-workers (46), allowed especially short contact times and collection on a cold (-196°C) sodium chloride plate.

Table 1. Mass spectrum of $(CH_3)_2Si(CH_2)_3$ (<u>15</u>) (38)

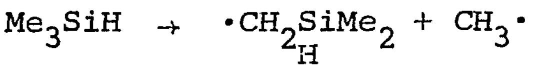
m/e	Rel. Int.
101	1.9
100	16.9
86	1.0
85	7.8
74	3.8
73	9.6
72	100
71	4.8
70	3.9
68	1.0
60	1.0
59	12.4
58	2.9
57	3.6
56	1.1
53	1.9
46	1.0
45	5.1
44	23.4
43	18.5
42	3.0
39	1.0
31	2.2
29	5.1
27	1.3
Metastable	$M^{+}100\text{-}28 \rightarrow [Me_2Si{=}CH_2]^{+\cdot}$

Vacuum pyrolysis at 650°C and collection on a clear NaCl plate allowed an ir spectrum to be taken which contained an additional peak to those of starting material, ethylene and 1,1-dimethyl-1-silacyclobutane. The strong peak at 1407 cm^{-1} disappeared after warming to (-120°C) and did not recur upon cooling to -196°C. This peak was tentatively ascribed to that of dimethylsilaethylene which indicated a rather polar bond.

Kinetic studies (47, 48) of the pyrolysis of trimethylsilane (16) has shown that 1,1,3,3-tetramethyl-1,3-disilacyclobutane (7) is formed and the following complex mechanism has been offered.

$$Me_3SiH \rightarrow Me_3Si\cdot + H\cdot \qquad 1$$

(16)



$$Me_3SiH \rightarrow \cdot CH_2\underset{H}{Si}Me_2 + CH_3\cdot \qquad 2$$

$$H\cdot + Me_3SiH \rightarrow \cdot CH_2Me_2SiH + H_2 \qquad 3$$

$$CH_3\cdot + Me_3SiH \rightarrow \cdot CH_2Me_2SiH + CH_4 \qquad 4$$

$$\cdot CH_2SiMe_2H + HMe_2Si\cdot \rightarrow Me_3SiH + CH_2 = SiMe_2 \qquad 5$$

(11)

$\cdot CH_2SiMe_2H + Me_3Si\cdot \rightarrow Me_3SiH + CH_2 = SiMe_2$ 6

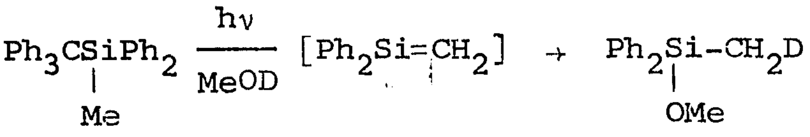
$\cdot CH_2SiMe_2H + \cdot CH_2SiMe_2H \rightarrow Me_3SiH + CH_2 = SiMe_2$ 7

$2CH_2 = SiMe_2 \rightarrow (7)$ 8

Such experimental data has recently been used in theoretical investigations of the nature of the (p-p) π bonding silicon, when Walsh (49) used thermodynamic kinetic data of Flowers and Gusel'nikov (41) and Davidson and Lambert (47, 48). The limits on $D\pi$ were increased to account for maximum experimental errors. The value of $D\pi$ was found to be 138 ± 22 kJ/mole. This was very similar to that estimated by Jackson (50) who used previously measured dissociation energies (51) of diatomic molecules C_2, CSi, Si_2 whose values were 144, 104, and 75 kcal mole^{-1} respectively. Jackson admitted the possibility that these might be a crude measure due to possible differences in hybridization between these diatomic species and "pure" organic molecules. However, he felt it significant that D (Me-Me) plus the π-bond energy in ethylene equaled 147 kcal mole^{-1}. This indicated that the diatomic C_2 was essentially a doubly-bonded molecule where D (Si_2) was only 8 kcal mole^{-1} greater than the "pure" single bond value in the corresponding

($Me_3SiSiMe_3$). This disclosed that π-overlap was very poor in the case of two silicon atoms. The case of Si=C was believed to be intermediate with a value of 28 kcal $mole^{-1}$ which was about half the value for ethylene. This did not suggest that the diradical form might be more stable, but only that reaction with other molecules including those of its own kind should be extremely facile.

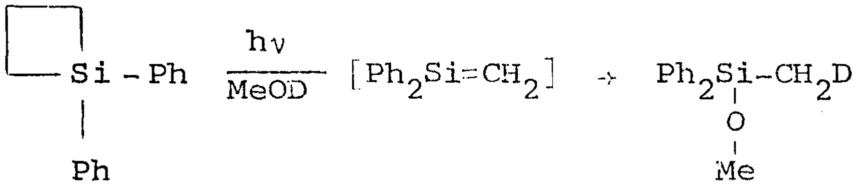
The majority of reports of generation of silaalkenes has been by thermal degradations. However, there are some reports of photochemical generation of the (p-p) π-bonded species. The first example was reported by Barton and Kline (52) and will be explained in the results and discussions of this thesis. A second report (53) followed with the photochemical dehydrosilation of pentaphenylmethyldisilane (<u>17</u>). It was reported that this intermediate of $Ph_2Si{=}CH_2$ (<u>3</u>) was the first such example produced photochemically. The addition of methanol and d_1-methanol provided substantial evidence for a species consistent with the diphenylmethylenesilane (<u>3</u>).



$$Ph_3\underset{\overset{|}{Me}}{C}SiPh_2 \xrightarrow[MeOD]{h\nu} [Ph_2Si{=}CH_2] \rightarrow Ph_2\underset{\overset{|}{OMe}}{Si}\text{-}CH_2D$$

(<u>17</u>) (<u>3</u>)

The third example by the same authors (54) recorded quite similar results by photolyzing 1,1-diphenyl-1-silacyclobutane (18) in the same solvents MeOH, although this reaction provides cleaner products.



(18)

The silicon-oxygen double bond also represents a case where (p-p) π-bonds supposedly exist. Beattie and Gilson (34) proposed that the occurrence of a compound whose structure was such that the efficiency of filling of the d-orbitals was not affected by polymerization, might well be expected to exist. The reports of the silicon-oxygen double bond started back in 1866 with Dilthey (3) who treated diphenyldichlorosilane with water to form the diol. Upon heating to 140°C there was thought to be formed diphenylsilanone ($Ph_2Si=O$) (1) but examination (16) of the molecular weight showed it to be the trimer. Subsequently, several reports have been made of the silanone being produced and these in turn have been followed by a closer examination which refute the isolation of the silanone species. Kipping (55) reported benzylethyldichlorosilane produced the monomer (19) but it was later reported (56) that the observed species was actually the trimeric form. Similar procedures

$$PhCH_2SiEtCl_2 \rightarrow PhCH_2EtSi=0$$

(19)

(4) were utilized to produce the trimeric form with dibenzyldichlorosilane. Stock and co-workers (57, 58) found comparable results with hydration of dibromosilane except a polymer resulted. They proposed the existence of the monomeric silanone (prosilanone) in equilibrium with the polymeric form but this has never been substantiated. Sommer and Tyler (59) found one silandiol (di-t-butylsilandiol) which would not polymerize upon distilling (210°C) but no evidence was ever obtained for the production of the monomeric species under a variety of conditions.

Beatty and Gilson (34) advocated that the polysiloxanes are more stable than the monomeric species due to (d-p) π-bonding in the polymer. They also proposed that if the d-orbitals could be used that perhaps the silanone could be an isolable species.

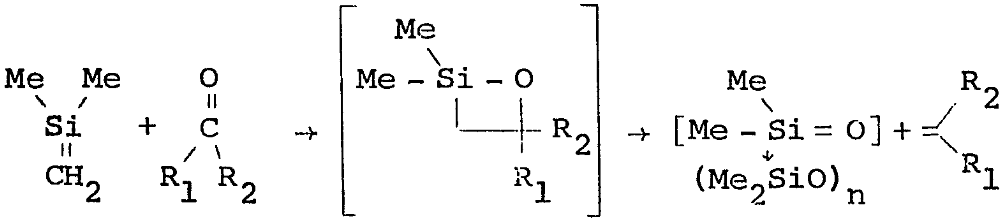
Some experimental evidence was accrued which implies the existence of the multiply bonded silicon-oxygen species. Silicon monoxide has been observed (60) with a mass spectrometer when silicon dioxide and silicon were heated at 1200-1950°K. In fact, some reactions with organic molecules have been investigated and reactions resembling those of both silylene and silanone were observed (61).

Pyrolytic studies by Davidson and Thompson (62) of octamethyltetrasiloxane have produced the cyclic trimeric and

$$(\mathrm{Me_2SiO})_4 \xrightarrow{\Delta} \mathrm{Me_2SiO} + (\mathrm{Me_2SiO})_3 \quad \xrightarrow{(\mathrm{Me_2SiO})_4} (\mathrm{Me_2SiO})_5$$

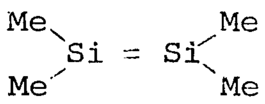
pentameric forms. He indicated this occurs by way of loss and gain of the intermediate monomeric dimethylsilaketone. Similar evidence had been cited in heating cyclic siloxanes which have some methylene groups between two silicon atoms (63). The reaction was complicated by the production of products that could be explained by the silaalkene also being formed.

Barton, McIntosh, and Kline (64) reported the reaction of ketones (acetone and 3-pentanone) with 1,1-dimethyl-1-silacyclobutane in copyrolyses experiments. At 600°C only one product, produced in small amounts, had the molecular weights of the ketones plus m/e 72 ($\mathrm{Me_2Si{=}CH_2}$) which were later found to be trimethylsilylenolates produced from reaction of $\mathrm{Me_2Si{=}CH_2}$ and the enol form of the ketones. At 700°C none of the products (M^+ ketone + 72) were observed, but several components having characteristic mass spectra of cyclosiloxanes were formed. A mechanism involving the intermediacy of a silanone was suggested and further corroborated (65, footnote 4) by formation of styrene in the copyrolysis of benzaldehyde and cyclobutane generator (15).



Comparable results came later (54, footnote 5) when it was reported that heptanal reacted under like conditions at 600°C to form only hexamethylcyclotrisiloxane and 1-octene. A later publication (66) reported that an enolizable ketone (methylpropylketone) under similar conditions gave only the two isomeric trimethylenolates. This was quite different from the results with enolizable aldehydes but this dichotomy was not discussed in any detail. One non-enolizable ketone benzophenone did produce the trimeric cyclic siloxane $(Me_2SiO)_3$ and the olefin (styrene) having an additional methylene group.

Silicon has been observed to be (p-p) π-bonded to atoms other than carbon. In 1969, Peddle and co-workers (67) reported the syntheses and pyrolyses of 7,8-disilabicyclo (2.2.2)-2,5-octadienes. Using the dianions of biphenyl, naphthalene, and anthracene plus dichlorotetramethyldisilane, the bicyclic systems were prepared. Upon heating the pure aromatic with the bicyclic compounds, new Diels-Alder's products were formed. A more thorough report (68) explained the 1,3-disilacyclobutanes in terms of a migration of H back to silicon and formation of disilacyclopropane. Reaction with conjugated dienes such as labelled anthracene and 1,4-diphenylbutadiene, gave the corresponding Diels-Alder products which provided strong evidence for the (p-p) π-type double bond between the silicon atoms. Mass spectral data showing very strong peaks for tetramethyldisilene (21) species gave additional strength to their conclusions.



(21)

RESULTS AND DISCUSSION

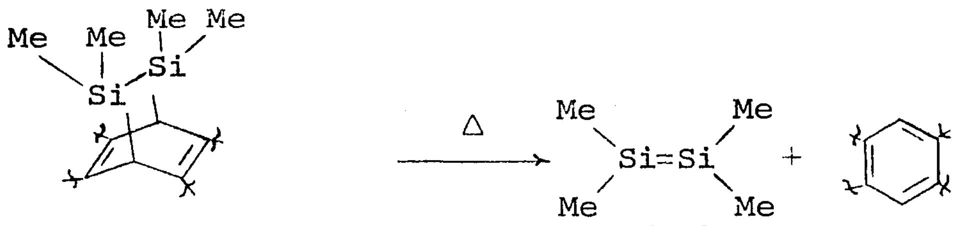
Silaalkene Generator

The transient existence of compounds containing a silicon-carbon double bond seemed quite probable from the preliminary work of Flowers and Gusel'nikov (43) and Barton and McIntosh (45). Therefore, a much more thorough investigation was warranted. This study was to include a preparation of silaalkene by an independent route with more reactions to examine its properties.

There are at least two factors which limit the use of 1,1-dimethyl-1-silacyclobutane, as the synthetic generator of the dimethylmethylenesilane. Perhaps, the most important undesirable feature of this reaction is its reversibility. The addition of excess olefin has been shown to completely inhibit any of the cyclic dimer (7). When such mixtures are present, the data is often much more difficult to interpret. In the case of flash pyrolysis, where one must separate out bands of other species, the presence of starting material further complicates the ir spectrum. The reversibility also impairs the yields of the reactive silaalkene and the separation is more difficult with more components. The second limiting factor in using the 1,1-dimethyl-1-silacyclobutane is the rather high temperature (500°C) required to thermally degrade it. There may be many interesting reactions, the products of which will simply decompose in this temperature region.

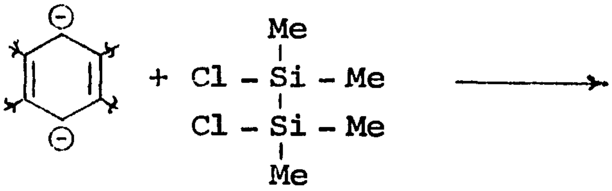
While the undesirable features are obvious, there are some things that can be said in favor of this generator. It is to date, the only system that can produce the silaalkene in any quantity. It is quite easy to prepare and the synthetic procedures are quite general with regard to varying substitution on the silicon. Also ethylene, a product in the thermal degradation, is easily disposed of.

It would be convenient to have a generator which would produce a product not reactive to the coformed silaalkene, once the degradation takes place. Also, a system that would generate the silaalkene at lower temperatures, thermally, and/or photochemically, would be most desirable. One case very similar to a silicon-carbon double bond generator, was tetramethyldisilene (21) generated from different bicyclic generators (22). The aromatic product was somewhat resistant to reaction with the disilene (21). The



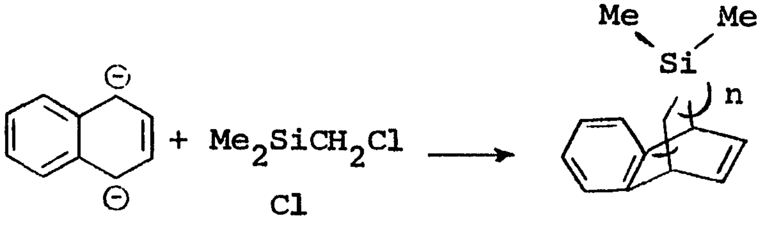
(22) (21)

order of ease of thermal degradation was anthracene > naphthalene > biphenyl. This follows the dienic character of the three species, biphenyl being the least dienic and the most aromatic. The general preparation (68) of the disilabicyclics (22) involved the reaction of the dianion and the dichlorotetramethyldisilane.



(22)

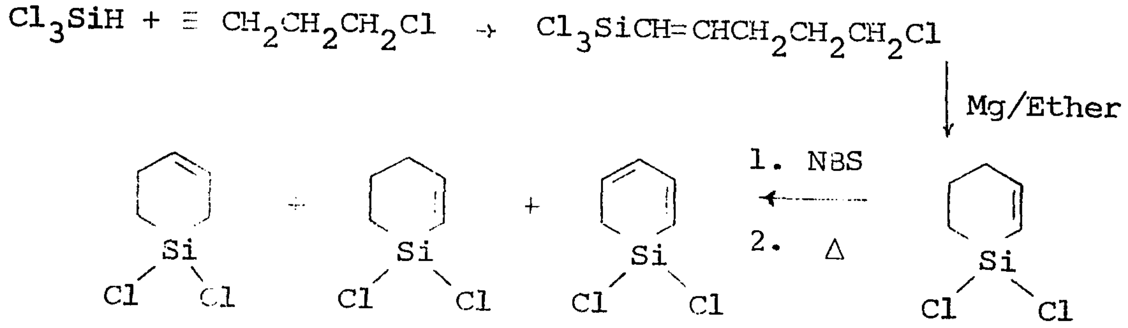
The analogous reaction using chloromethyldimethylchlorosilane (25) was attempted in our laboratory using the same procedure (67). Analysis of the product mixture by gcms indicated a significant amount of the possible product (24, n=1) with M^+ 200. However, other peaks in



(23) (24)

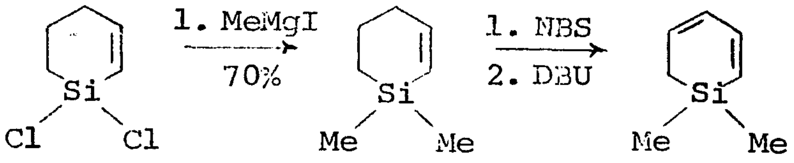
the gas chromatograph nearly as large as that of M^+200, indicated compounds with n=2 and 3 (M^+272 and M^+344). While it is quite possible that this procedure might be found suitable, other methods have been devised which make this reaction less attractive in terms of its generality.

Silahexadienes have been prepared (69) by a rather long, tedious, and expensive sequence of reactions which



(25)

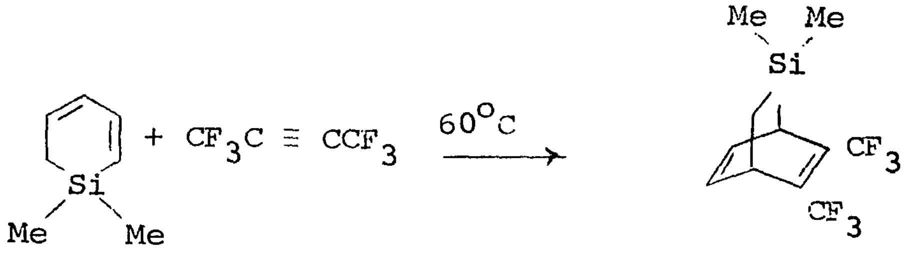
provided a way to get substitution on silicon. One example (69) of a Diels-Alder reaction of the diene with maleic anhydride to form the bicyclic adduct was reported. The very poor yields of the thermal dehydrobromination (18.4%) and the mixture of products made this procedure quite costly. 1,5-Diazobicyclo (5.4.0) undec-5-ene (DBU) is a good dehydrohalogenation agent giving yields substantially higher (70) than the 18% reported in the pyrolytic method (69). The procedure of Benkeser was altered somewhat by the following steps.



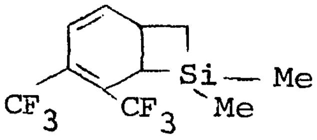
(25) (26)

The overall yield of diene (26) from 1,1-dichloro-1-silacyclohex-2-ene (25) by this new method is 11.2% compared to 0.27% yield of 1,1-diphenyl-1-silacyclohexa-2, 4-diene. This comparison of methyl with phenyl substitution is somewhat dubious, but little effort was spent on maximizing it and small volumes were involved.

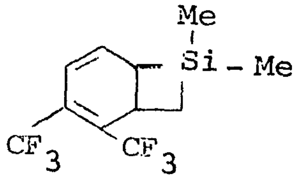
The diene (26) was added to hexafluoro-2-butyne (27) to produce 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo (2.2.2) octa-2,5-diene (28) in 64% yield. The structure was identified by its nmr(δ), 0.11 (s, 6H), 0.48 (d, 2H, J=3.8Hz, $SiCH_2$), 3.58 (d, 1H, J=6.5Hz, SiCH), 4.12 (m, 1H, CH_2CH), 6.16 (m, 2H, CH=CH). That the structure is none of the following cannot be absolutely ruled out. The



(26) (27) (28)



(29)



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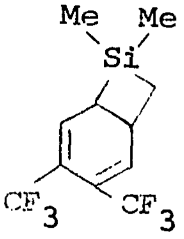
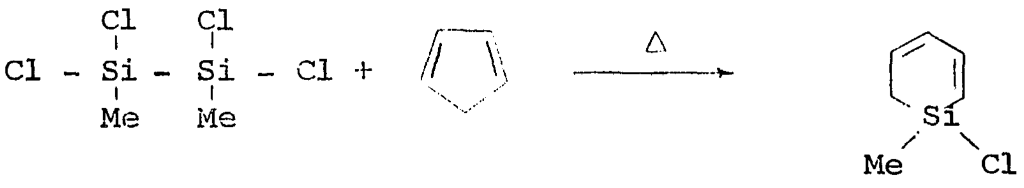


(31)

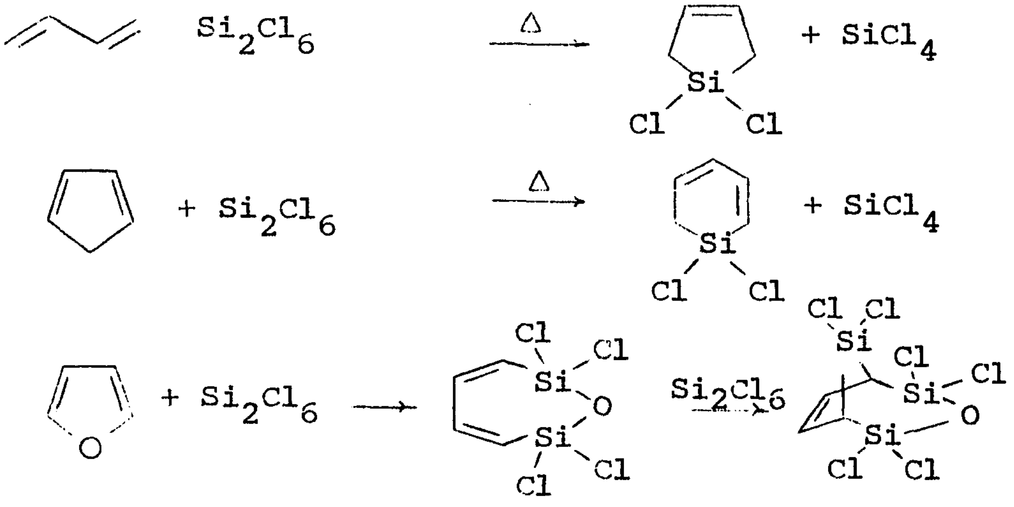
multiplet of the bridgehead hydrogen not adjacent to silicon in (29) would be expected to be more defined, while the bridgehead hydrogen adjacent to silicon in the same structure, would be expected to be more complex than the observed doublet with allylic coupling. The bridgehead hydrogens of (30) probably have greater separation than observed, but (31) is quite difficult to eliminate. In fact, all represent possible silaalkene generators that might be synthesized independently.

A long period of time followed before another method of preparing the diene (26) was developed. Therefore, much preliminary work was done using the compound produced in this long series of reactions.

The solution to a better yield of the silacyclohexadiene came by way of an unpublished result from the laboratories of Dr. William Atwell, Dow Corning, Midland, Michigan. The reaction involved that of the silylene generated from tetrachlorodimethyldisilane (32) and cyclopentadiene. The

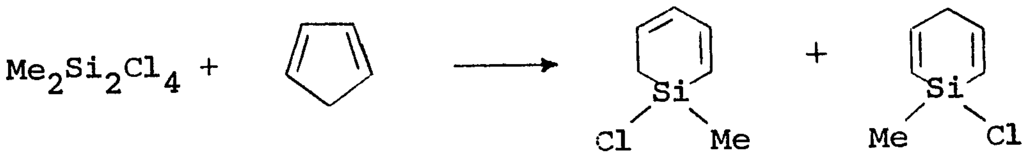

(32) (33)

tetrachlorodisilane (32) presumably formed the methylchlorosilylene species which somehow inserted and was followed by a ring expansion to (33). Similar reactions have since been reported (71).



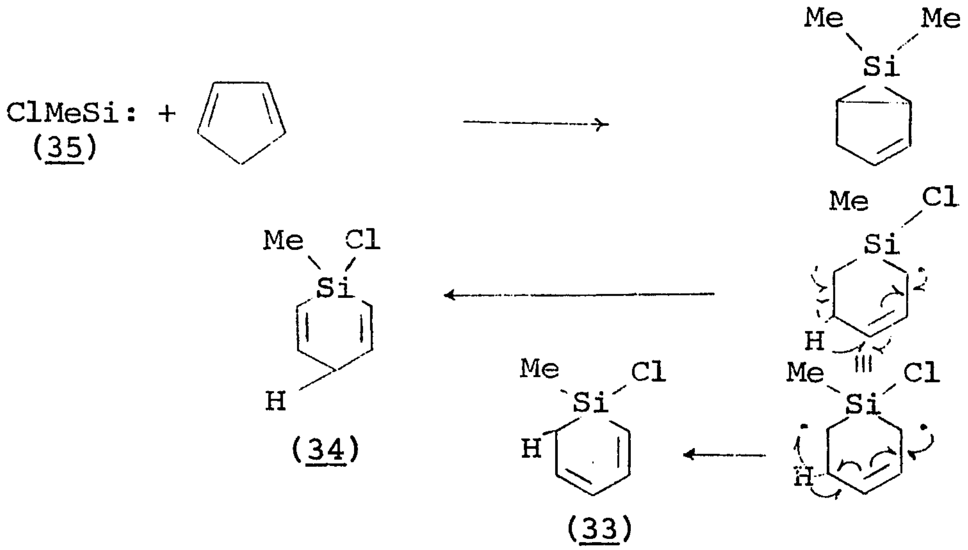
When a similar procedure (72) used in making trichlorotrimethyldisilane was utilized to prepare the tetrachlorodimethyldisilane, a mixture of the tetra- and trichloro species was obtained in 78.1 and 21.9 mol % yields, respectively.

This mixture reacted with cyclopentadiene at the suggested 525°C to give both 1-chloro-1-methyl-1-silacyclohexa-2,4-diene (33) and 1-chloro-1-methyl-1-silacyclohexa-2,5-diene (34). The nmr of the mixture collected at

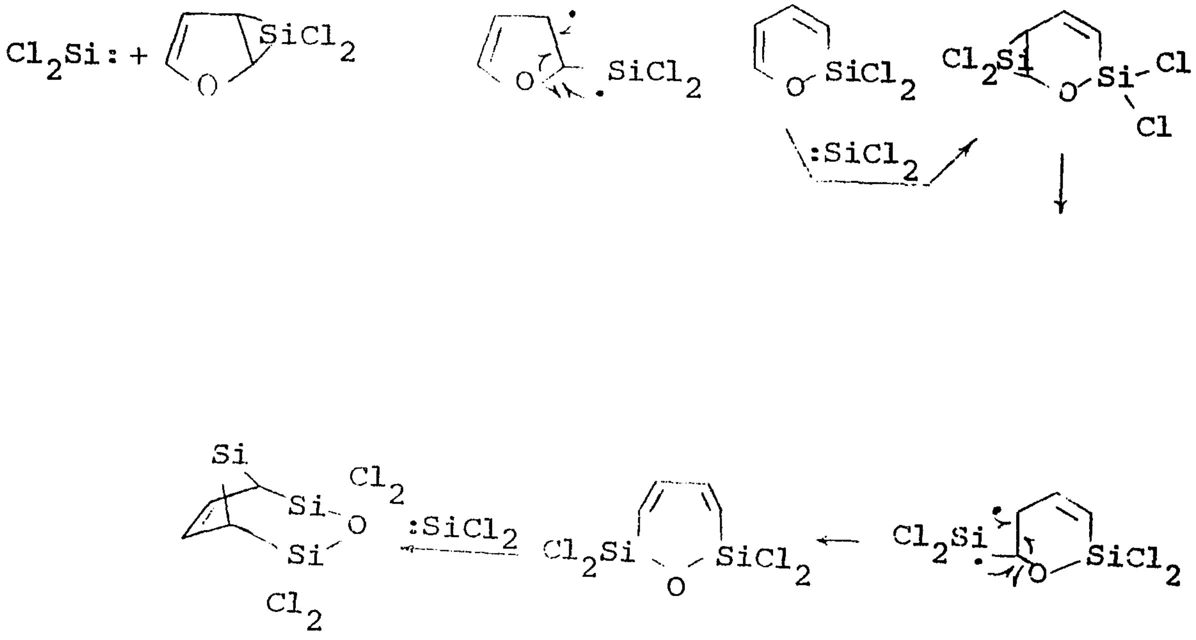


(33) (34)

constant bp (42°/23 mm) consisted of a mixture of $Cl_4Si_2Me_2$ (40 mol %), $Cl_3Si\ Me_3$ (21 mol %), 2,4-diene (33) (25.7 mol %) and 2,5-diene (34) (13.5 mol %). The isomers could be separated and collected by vpc. The 2.5-diene (34) was not particularly desirable so the temperature was raised in an attempt to get less of this isomer. At 600°C a mixture (bp 68-70°/30 mm) of 2,4-diene (82.5 mol %), 2,5-diene (13.15 mol %) and tetrachlorodimethyldisilane (4.4 mol %) was found. Thus this procedure provides a very useful synthetic method for producing silacyclohexa-2,4-dienes. It not only gives good yields, but also has many less steps than the former method (69). One chlorine atom on silicon allows general utility with different substitution on silicon. The mechanism likely involves a silylene (35) reacting with a double bond possibly as seen in the following manner. The mechanism for the reaction of



silylene with furan seems to be somewhat different. The silacyclopropane, if formed at all, always cleaves open toward oxygen in the following manner. The use of hexa-



chlorodisilane would provide an additional number of possible compounds with disubstitutions. It might be the method of choice with its reported higher yields if it was not for the very high cost of hexachlorodisilane.

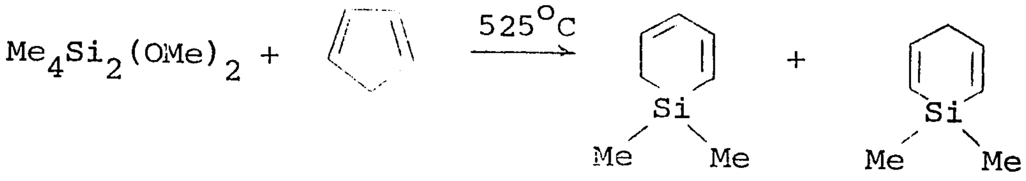
The fact that the Russian workers (71) failed in adding only one silylene to furan was most unfortunate, as the formation of the cyclic dienes with oxygen, sulfur, and nitrogen had appeared quite interesting as generators of dimethylsilicon oxide (36), dimethylsiliconthioxosilane (37), and dimethylsilicon imide (38), respectively.

$Me_2Si = O$ (36) $Me_2Si = S$ (37) $Me_2Si = NH$ (38)

One feature of this reaction that is particularly undesirable is that hydrogen chloride polymerizes cyclopentadiene quite easily. This prohibits the prior mixing of the two starting materials which is no great problem. The more serious disadvantage in this procedure is a build-up of polymer in the heated tube, which puts severe limitations on the amount that can be produced at one time.

There has been (73) considerable success with tetramethyldimethoxydisilane as a silylene generator. It limits the use of the resulting diene in terms of substitution, but the requisite disubstitution is desired in many cases. When dimethoxytetramethyldisilane is mixed with cyclopentadiene, no polymerization occurs in the addition funnel or in the pyrolysis tube during reaction. The product formed at 600°C in 38 % yield, had a bp 78-80°C/14 mm and was identified by comparison of nmr's with an authentic sample of 1,1-dimethyl-1-silacyclohexa-2,4-diene. The alkoxydisilanes are quite easily handled which implies that tetraalkoxydisilanes and even hexaalkoxydisilanes might be used in the future.

When the temperature for the dimethoxytetramethyldisilanecyclopentadiene reaction was 525°C, the products, as with tetrachlorodimethyldisilane, were both of the isomeric dienes (26) and (39) in nearly equal amounts as measured by nmr.



(26) (39)

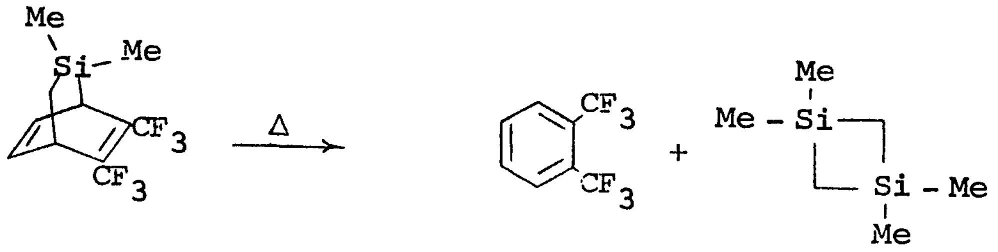
A large amount of hexafluoro-2-butyne was added to hexadiene and a bp 78-80°C/14 mm was observed for the Diels-Alder adduct. One of the really convincing indications that 1,1-dimethyl-1-silacyclobutane (15) would be a good silaalkene generator was its results of electron bombardment in the mass spectrometer (28) (39, 40) with the base peak of m/e 72 being observed. If the bicyclic compound was to be a good generator, a strong peak of m/e 72 was also essential and the results are seen in Table 2.

The strong peak at m/e 72 was, indeed, a good indication that this was to be an excellent silaalkene generator.

Table 2. Mass spectrum of (28) at 70 eV

286	1	171	3	120	1.5	71	5
271	0.25	169	2	119	1.5	70	6
267	0.5	164	3	101	3	69	3
221	1	163	3	99	2	63	4
217	6	151	5	95	3	57	5
214	6	146	2	81	5	55	4
213	1	145	15	77	23	49	6
208	5	140	4	76	2	47	5
195	100	127	2	75	5	45	5
190	8	126	4	74	4	44	27
189	2	125	4	73	7	43	15
176	3	121	3	72	69		

The necessity of degradation of the bicyclic compound (28) was equally essential, but the exact method for doing this was not known. It was hoped that only two products, the 1,2-bis(trifluoromethyl)benzene (43) and 1,1,3,3-tetramethyl-1,3-disilacyclobutane (7) could be isolated.



(28) (30) (7)

The initial studies on the bicyclic compound (28) were carried out in sealed tubes. Small amounts of the generator (28) were placed in the tubes and sealed under a vacuum. Very little reaction took place at temperatures up to 285°C, even after three and one-half hours. Only after heating at 320°C was there significant thermal degradation observed. Many small peaks were observed in vpc analyses, but only the bis-1,2-trifluoromethylbenzene was ever isolated. Results with gcms indicated small amounts of the dimer M^+144(2Si) and M^+306 [M^+286 + HF (20)]. Relatively small amounts of silicon-containing species were observed, indicating polymerization in some way of the silicon moiety. The component with M^+306 might well be formed from the breaking of a Si-C bond and later adding HF. However, this was not investigated.

It became evident very early that the high concentration in sealed tube reactions would not give the desired results. This paralleled a report of Nametkin et al. (35), who obtained silicon polymer when heating the silacyclobutane at 180°C in a sealed tube.

The low concentration, gas phase pyrolyses studies using 1,1-dimethyl-1-silacyclobutane (15) have all had one common procedural aspect--pressures in the range of one torr (10^{-3} mm). It appeared that such would be the case for the bicyclic system (28) as well. Thus, a vacuum system was constructed, so that pyrolyses could be carried out in glass at pressures below 10^{-3} mm.

The initial experiments with the vacuum system were carried out using a Vycor tube 30 cm x 28 mm packed loosely with quartz wool. The first experiment was the pyrolysis ($410^{o}C$) of the bicyclic compound (<u>28</u>) neat at pressures $< 10^{-3}$ mm. Three products were observed and isolated including 0.0014 g dimer (3.9% theoretical), 0.0838 g xylene (95% theoretical) and a large amount of a clear viscous material having M^{+}292. The dimer was verified by identical retention times in the vpc identical mass spectra of an authentic sample (74) and hrms (obs. 144.079553, calc. 144.078892). The xylene was identified by mass spectra (M^{+}214 and characteristic peaks of fluorocarbons at m/e 195, 164, 145, 69). The nmr (m, 7.8 ppm), when expanded, showed AA'BB' pattern with a triplet of doublets consistent with the symmetrical structure. The hrms: obs. 214.021812 and calc. 214.0217704.

The third component had a M^{+}292 and the isotopic analysis showed three silicon atoms. The hrms indicated a molecule consistent with $C_{15}H_{28}Si_{3}$ (obs. 292.148188, calc. 292.14988). No siloxane nor fluorine component was obvious from the mass spectrum, but peaks at m/e 73, 146 and 204 indicated oligomeric silicon-containing material. The nmr showed more than one silyl methyl around 0.0 ppm δ and was of little value. Thus the structure was never completely elucidated.

The temperature was then raised to 500°C and another pyrolysis of neat compound (28) was made. Analysis by gcms indicated 19 different components, the main ones being M^+124 (retro Diels-Alder product), M^+144 (dimer), M^+306 (M^+286 + HF) and M^+214 (xylene). Only after using cyclohexane, pentane, and later nitrogen as carrier gases did pyrolysis at 500°C give only two products--the dimer (7) and xylene (40) in 76% and 94% yields, respectively. This was clear evidence that a silaalkene species similar to that of Flowers and Gusel'nikov (43) had been prepared by an independent route. The yield of 95% for the xylene was a definite indication that reversibility of the reaction was not a problem and this should allow for many more investigations of the $R_2Si{=}CH_2$ species. Indeed, the relative ease and low expense of synthesis of the bicyclic generator and the obvious advantages of nonreversibility clearly makes this way of producing $Me_2Si{=}CH_2$ the method of choice.

Additional simplicity was found after many experiments with the diffusion pump not being effective, due to the high pressures of the carrier gas. In fact, the rough vacuum was eventually replaced by a positive flow of nitrogen gas, which provided distinct advantages. A vertical tube packed with quartz chips was used and one could be much more certain of the relative amounts of materials dropped into the hot part of the tube. The certainty of having a known concentration or even ratios of concentrations is quite sporadic and uncertain when you must depend on vapor pressures of the compounds.

Barton and McIntosh (45) reported the pyrolysis of the 1,1-dimethyl-1-silacyclobutane in a special apparatus which was made available to us. Identical procedures were carried out on the neat bicyclic system (28) altering the oven temperatures over a wide range. The results indicated no isolation at -196°C of the silaalkene (ir 1407 cm^{-1}) under a variety of conditions. The only product observed was the dimer (7) and xylene (46) by means of ir comparisons with authentic samples. While these results are difficult to understand, the absence of any carrier gas in these experiments might help in explaining the difference in results of this reaction and the cyclobutane one.

The feasibility of photochemical production of the silaalkene seemed quite attractive considering the possible driving force obtained from the stability of the newly formed aromatic xylene as well as the absorption of (28) observed in the uv at 295 mμ (ε_{max} 4 x 10^4). Also the practicality of generating the silaalkene at temperatures lower than 400°C seemed most desirable.

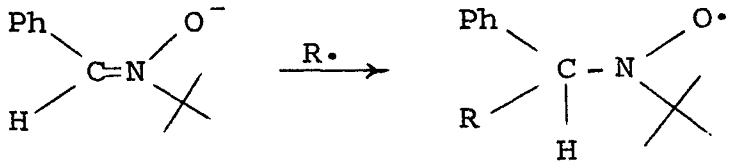
A small amount (5 μl) of compound was coated on a cold

(-196^{o}C) sodium chloride plate. Irradiation with a helium arc through quartz cleanly affords the dimer (7) and xylene (40) without any evidence for the intermediate silaalkene (11). Even at lower temperatures (28^{o}K), the intermolecular reaction of the silaalkene species could not be deterred and no 1407 cm^{-1} absorption was observed. One other experiment feasible for observing the photochemically generated silaalkene intermediate was the matrix isolation of each molecule. Perhaps the molecule of xylene would be so unreactive that it would form and leave the silaalkene in the same matrix for observation. Diluting 5 μl (38) with 3 l. (350 mm) argon, coating a small amount on a sodium chloride plate cooled to 8^{o}K and irradiating with an arc through quartz resulted in some changes in the ir spectrum, but no peak appeared at 1407 cm^{-1}. This experiment was cut short when warming too fast resulted in loss of the organic materials along with the argon. Nevertheless, it seemed quite certain that the silaalkene was not completely independent of the xylene part of the generator when contained in the matrix. Whether a gaseous irradiation experiment can be devised to coat a mixture of argon, photolytically generated silaalkene and xylene on a cold (8^{o}K) plate to separate and isolate the silaalkene is not yet known.

The photochemistry of the bicyclic generator (28) in solution has been somewhat less productive. Irradiation with 2537 Å in quartz nmr tubes of solutions of generator (28) and cyclohexane afford only traces of the dimer (7) and considerable amounts of xylene as analyzed by gcms which implies silaalkene (11) formation.

When acetone was used as solvent for the photolysis, a mildly exothermic reaction was observed. This exothermicity was also observed when mixing 4-methyl-2-pentanone and heptanal, but not when added to benzaldehyde or benzophenone. The one property in common with the compounds which do produce exothermic reactions is that they are enolizable. This explanation was substantiated in similar observations with methanol (MeOH). The structure of the adduct of MeOH and (28), however, could not be completely defined.

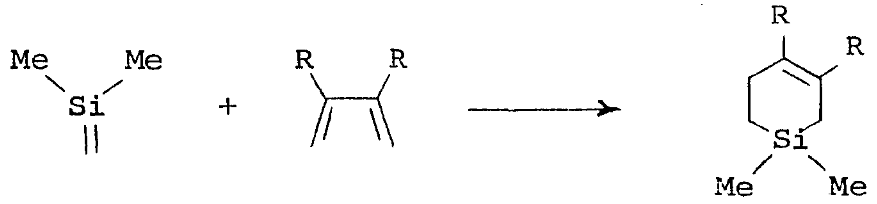
When carbon tetrachloride was used as solvent, analysis by gcms indicated chlorosilanes were formed in the photolysis of (28). This was a good indication of free radicals. One method of testing for these is reaction with spin traps. N-t-Butylphenylnitrone (41) initially prepared by E. G. Janzen of the University of Georgia, Atlanta, Georgia, is such a compound known to trap radicals. The stable radical



(41) (42)

(<u>42</u>) is produced and has characteristic esr spectra. Nitrogen has a spin of 1 and accounts for a triplet while hydrogen has a spin of 1/2 and splits this triplet into a triplet of doublets. The results of photolysis of (<u>28</u>) with 2537Å light from the Rayonette indicated significant absorption in a triplet of doublets. It was clear proof that radical(s) had been generated and one set of splitting constants were $a_H = 3.5$ G and $a_N = 15$ G. It was seen that all the peaks were not of equal height which would not be the case if only one radical was formed in the reaction. The first spectra from irradiation at 2537Å for a short time had the greatest deviation from equal peak heights, which indicated two or more components with fortuitous overlap in some peaks. One might envision that silyl radicals are formed and trapped by the nitrone. The other radical might be the carbon radical formed in the same homolytic cleavage process. As to which radical accounts for which splitting is only speculation and more experiments need to be performed. To be absolutely sure that the generator produces radicals one must run a blank at 2357Å of a mixture of benzene and nitrone. Secondly, it is essential to photolyze a compound known to produce silyl radicals. Examination of the value of splitting constants must be compared to see if they are consistent with those found in the photolysis of (<u>28</u>). These investigations would have been carried out, but the supply of nitrone was not available.

Other properties of the silaalkene might be observed through reactions with a variety of molecules. Addition of butadienes (43) is known, thus unsubstituted, gaseous butadiene (43, R=H) was used to find the conditions necessary to completely suppress formation of dimer in favor of what was assumed to be the Diels-Alder adduct (44). Thus (44) was not characterized.



(11) (43) (44)

Butadiene and 0.031 g of generator were added together through a Vycor tube at 500°C with a pressure on the pump side of a nitrogen cooled trap of ∼ 2 mm. Too much butadiene was used although its evaporation at room temperature made it easy to concentrate the products. Complete suppression of the formation of the dimer was observed and three components including M^+108 (butadiene dimer), M^+126 (silacyclohex-3-ene) (44) and M^+214 (xylene) were present, based on the mass spectra.

Reactions of Silaalkene and Their Mechanisms

The initial investigations of reactions of the silaalkene were made with small amounts of generator (both cyclobutane and bicyclic). These were analyzed by a gas chromatograph-mass spectrometer (gcms) which did not give full proof of structure, but was very useful for following the reactions. Table 3 is a summary of the preliminary results using the bicyclic generator (<u>28</u>), while the cyclobutane generator (<u>15</u>) results are found in Table 4.

At first, a vacuum system was used to allow introduction of the materials into the system by means of their own vapor pressures. This was undesirable for many reasons, including irregular addition of compounds, which resulted in lowering the temperature inside the tube, as evidenced from no decomposition of the generators. One somewhat surprising result was dimerization, in preference to reaction with cyclohexene.

The reaction with cyclopentadiene was of interest, not so much out of novelty, as for its usefulness in other work. It was interesting that when cyclobutane generator was used at 600°C, two different peaks in the gcms had M^+138 in about equal amounts. Whether one isomer was a rearranged product of the Diels-Alder adduct or a 2 + 2 adduct was not determined, but some rather simple experiments might be run. The bicyclic generator at 425°C gives only one

Table 3. Preliminary results of copyrolyses (425°C) with bicyclic generator (28)

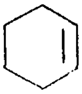
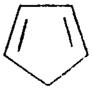
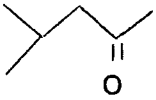
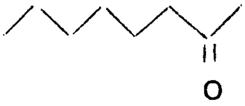
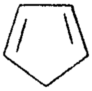
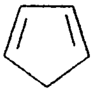
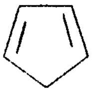
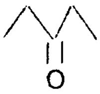
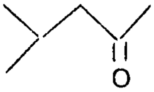
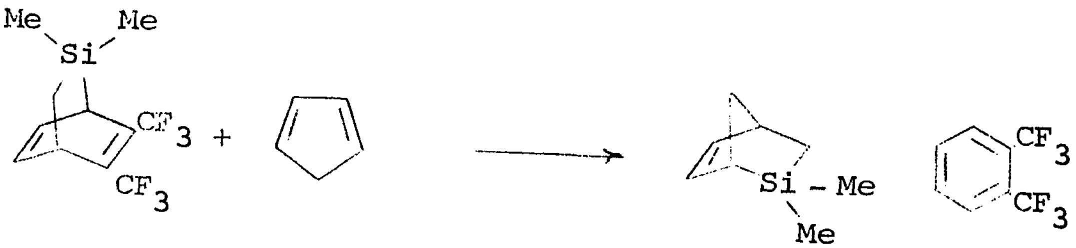
Number	Temp (°C)	Vac./N_2	Reactant	M^+ (likely
1.	500	Vac.		M^+126 (silacyclahexene)
2.	500	Vac.	$Me_2C{=}O$	M^+130
3.	500	Vac.	CO_2	M^+144 (dimer)
4.	500	Vac.	$Cl_2C{=}CH_2$	M^+144 (dimer)
5.	500	Vac.		M^+144 (dimer)
6.	425	N_2		M^+138 (2.2.1)
7.	500	N_2	PhCHO	M^+104 $PhCH{=}CH_2$, m/e 207 $(Me_2SiO)_3$, 281 $(Me_2SiO)_4$
8.	500	N_2		M^+172
9.	500	N_2		M/e 207, 281, 221, 279, 112

Table 4. Preliminary studies of copyrolyses with 1,1-dialkylsilacyclobutane

Number	Temp (^{o}C)	Vac./N_2	Reactant	M^+ (likely
1.	600		Bu MeCOMe	$M^+200 + M^+211$
2.	600		Me MeCOMe	M^+130 (TMS enolate)
3.	500		Me 	M^+138 (2 different isomers)
4.	600		Bu 	M^+222 (2.2.1)
5.	600		Me 	3 peaks M^+138 (isomers)
6.	660		Me 	$M^+156 + M^+236$ (siloxane)
7.	520		Me 	$M^+172 + M^+222$ (siloxane)

isomer (the bicyclic Diels-Alder adduct), which is distinguished from the other in its mass spectrum by the presence of m/e 72.

A larger scale preparation with the bicyclic generator (28) at 425°C and excess cyclopentadiene gave yields (from vpc) of 97% xylene (40) and 55% of 2,2-dimethyl-2-silabicyclo

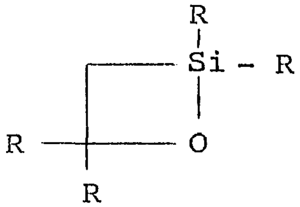


(28) (45) (40)

(2.2.1)-hept-5-ene (<u>45</u>).

One of the properties of the silicon-carbon double bond deemed most probable is its polarity. Curtis has substantiated this with calculations (12) and Barton and McIntosh (45) have supplied experimental data consistent with this assumption. The reaction with itself in a head to tail fashion also gives credence to the dipolar species. Polarity might also be investigated by reacting it with another compound with known polarity. One functional group known to be polar is the carbonyl group. This group has dipole moments in the range of 2.4-3.8 D (75) with oxygen negatively charged and carbon positively charged.

Addition of a carbonyl group to silaalkene would be most interesting. It would produce the first dimethylsiloxetane (<u>46</u>) (a four-membered ring with silicon and oxygen), whose properties in themselves would be of interest. It would show the preferences of the reaction which might reveal information about its polarity. This



(46)

siloxetane might be a good generator of siloxane whose properties are not yet well-defined.

Preliminary results in Table 3 of copyrolysis of the bicyclic generator and acetone indicated formation of a compound having $M^+ 130$ (72 + 58). The mass spectrum resembled other trimethylsilyl ethers (76) with ions at m/e 103, 93, 75, and 73. Originally, copyrolysis was in a vacuum system with large amounts of acetone necessary to get over the less volatile generator. The pressure measured with a McLeod gauge was a combination of the two liquids, and consistent results were impossible. Consequently, the relative amount of component ($M^+ 130$) compared to solvent, was so small that collection was impossible. In fact, the peak would disappear after only a few injections in the vpc. Other ketones were used and their results are also shown in Table 3. It can be seen that a variety of ketones and generators gave small amounts of adducts of the silaalkene and the ketone. The exact structure could not be determined from the mass spectrum alone, thus other methods had to be used to get more isolable compound.

Copyrolysis in a vertical tube with nitrogen provided a way to regulate each of the reactants and the flow rate. The vapor pressures of the components did not greatly affect the results which were quite reproducible under these new conditions. Yields were never measured for the neat pyrolysis, but 97% yields of the xylene were obtained in several copyrolyses and it can be assumed that the yields would be as high when no reactive component was used.

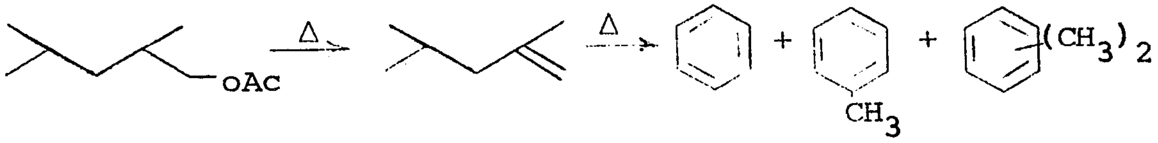
Since the production of bicyclic generator (28) at first was much more difficult than the silacyclobutane (15), the latter was used in many initial experiments. The best conditions, retention times, and other properties could then be duplicated and compared with those of the bicyclic generator (28).

One reason for so many different systems being used was that the retention times of the starting silacyclobutanes and the adduct were too close for good separation on the vpc.

In the case of acetone, the adduct could be separated only when very small samples were used at very low column temperatures (40-50^{o}C). When 1,1-di-n-butyl-1-silacyclobutane was used, the component having M^{+}200 overlapped the silacyclobutane peak having M^{+}184. Finally, the use of 4-methyl-2-pentanone with 1,1-dimethylsilacyclobutane produced products which separated sufficiently. In fact, with an excess (two-three fold) of ketone, the adduct was produced in amounts such that it could be separated and later collected. There was always a small amount of material of M^+172 seen with the mass spectrometer. Components with much smaller peaks of m/e 221 and m/e 279 indicated polysiloxanes. After the mixture was vpc'd twice, the nmr showed the position and nature of peaks to be identical with the nmr of an independently prepared (76) sample of the trimethylsilylenolate.

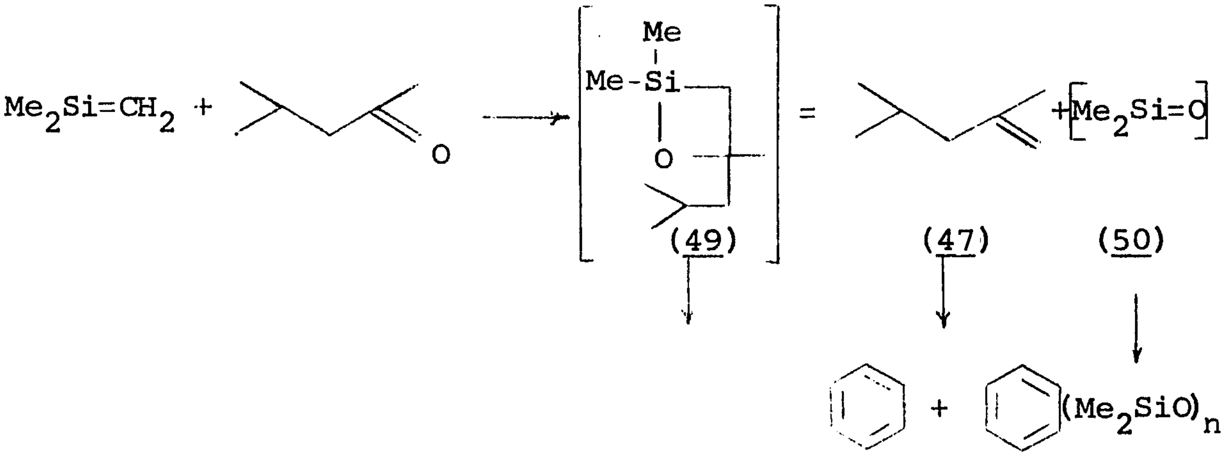
Very recently, Roark and Sommer (66) reported that at 600°C the trimethylsilylenolate was formed from 2-butanone and (15) with only trace amounts of the olefin and hexamethylcyclotrisiloxane. Our yields of 30% of enolate ether compared quite closely to Roark's and Sommer's 35-40%.

At 700-750°C the results were significantly different. Only a very small peak had the same retention time as the predicted olefin, but none was ever isolated. Cyclotrisiloxane (31.8%), cyclotetrasiloxane (52.8%), and cyclopentasiloxane (5.5%) were the silicon-containing species as identified by identical retention times and identical mass spectra with authentic samples. Two other components, benzene (27%) and toluene (20.6%) were identified by equal retention times and hrms (obs. 78.04544, calc'd 78.04692 for C_6H_6 and obs. 92.06260, calcd 92.06259 for C_7H_8). The olefin (47) was prepared by pyrolysis of the acetate (48) at 600°C. When run at 700°C the olefin did not remain, but



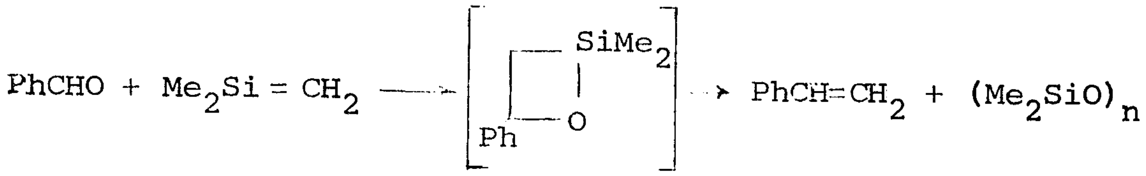
(48) (47)

rather benzene, toluene and xylene were identified. This was not the case with the ketone at 700°C under similar conditions. The mechanism for formation of toluene and benzene from the olefin (47) is not easy to envision. The transient existence of the olefin (47) is substantiating evidence for siloxetane (49) in the reaction of silaalkene and 4-methyl-2-pentanone.



However, this mechanistic interpretation is somewhat clouded by the fact that the trimethylsilylenolate prepared independently (76) and heated at 700°C produces the same products hexamethylcyclotrisiloxane (27.9%), octamethylcyclotetrasiloxane (41.7%), benzene (40%), and toluene (19%). It was not until deuterated ketone was used that siloxetane could be shown to exist.

Other carbonyl compounds were copyrolyzed with 1,1-dimethyl-1-silacyclobutane including 3-pentanone, carbon dioxide and benzaldehyde at 700°C. Only the dimer was formed when carbon dioxide was used as a carrier gas in the vacuum system. The 3-pentanone gave an adduct M^+158 (86 + 72) whose retention time was very close to that of the ketone. The reaction with benzaldehyde, however, at 600°C proved most instructive. A preliminary study showed compounds with peaks at m/e 207 $(Me_2SiO)_3$, m/e 281 $(Me_2SiO)_4$, m/e 104 ($PhCH{=}CH_2$), and m/e 355 $(Me_2SiO)_5$. A larger scale reaction showed identical retention times and mass spectra with authentic samples and the yields measured by vpc were 20% $(Me_2SiO)_4$, 23.4% $(Me_2SiO)_3$, 37% $PhCh{=}CH_2$ and 5.0% $(Me_2SiO)_5$. These results are much clearer evidence for the siloxetane (<u>51</u>) than are those of the reactions with enolizable ketones or aldehydes. The presence of styrene with an additional methylene group to the starting benzaldehyde and 50% of the silicon being accounted for in the cyclosiloxane products definitely favors the four-center intermediate (51).



(51)

The bicyclic generator (28) was copyrolyzed with benzaldehyde (four-fold excess) and similar results were obtained with 21.1% $(Me_2SiO)_3$, 43.5% $(Me_2SiO)_4$, 64% hexafluoroxylene, and 29% $PhCH{=}CH_2$ as determined from vpc. The low yields of xylene probably indicated that a more efficient trap would collect higher yields of all components. The small yields of styrene might be due to its polymerization, but this was not checked.

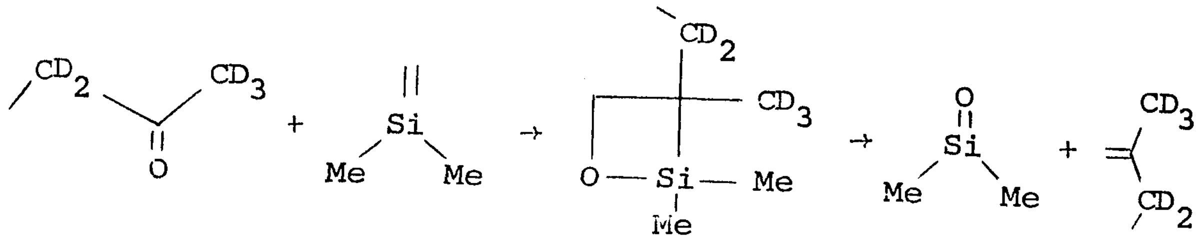
This is the first case of a siloxetane (51) whose only property at the present time is its instability at 500°C. It is a good example of a generator of dimethyloxosilane (50) which might prove to be of value in the future. Davidson and Lambert (62) had earlier reported the intermediacy of dimethyloxosilane (50) from the pyrolysis of tetramethylcyclotetrasiloxane with cyclosiloxanes as products.

Roark and Sommer (54, footnote 5; 66) have reported copyrolyzing heptanal and 1,1-dimethyl-1-silacyclobutane

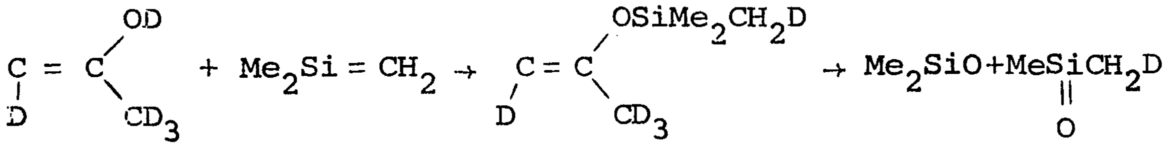
(<u>15</u>) at 600°C. Yields of 35-40% of both the octene and cyclotrisiloxane were noted. They suggested that different mechanisms are observed in aldehydes and enolizable ketones. In the case of aldehydes the mechanism involves the siloxetane intermediate while with enolizable ketones, only trimethylsilylenolate ethers are formed. In no instance do they report observing any more than trace amounts of other components in each case.

Being somewhat inconsistent with our results a closer examination of the reactions seemed essential. One test for the mechanism involved in enolizable ketone copyrolyses would be deuterium labeling. The ketone (4-methyl-2-pentanone) is quite easily deuterated by refluxing in D_2O/K_2CO_3 mixtures, changing the solutions every day. After three days the deuterium incorporation was 86.7% by nmr or 52% d_5, 34% d_4, and 14% d_3.

The use of deuterium to detect whether the mechanism involves the siloxetane and/or enolate ether and the extent that each is taking place can be calculated. The simplest case is the siloxetane mechanism. Assuming there is no random exchange of deuterium atoms with the silylmethyl protons, no deuterium should end up in the final cyclosiloxanes.



Any deuterium found in the final cyclosiloxanes would be an indication that the enol form had further decomposed. The calculations of the amount of deuterium expected is somewhat complicated by the fact that the probability must be figured for several species and then added to get the overall picture. It is further complicated by the fact that the ketone is not 100% d_5. The enolate ether will always have one deuterium in the trimethylsilyl group if there is 100%



d_5 in the ketone. The final product only has two methyl groups so there will be a 2/3 chance of keeping a deuterium and 1/3 chance of losing it. The actual deuterium incorporation expected if 100% d_5 ketone were used is seen in Table 5.

Table 5. Calculated relative intensity of $(Me_2Si)_n$ from TMS-enolate assuming 100% enol deuterium

Specie m/e	d_0 Probability Contribution	d_1 Probability Contribution	d_2 Probability Contribution	Probability Rel. Int.	Total
SiC_2	(1/3)	(2/3)		1/3 + 2/3 = 1	
61		3.4 x .66 = 2.2		2.2	3.2
60	2.3 x .33 = 1.1	7.3 x .66 = 4.8		5.9	8.6
59	7.3 x .33 = 2.4	100 x .66 = 66		69	100
58	100 x .33 = 33			33	47
Si_2C_4	$(1/3)^2$	2(1/3)(2/3)	$(2/3)^2$	1/9 + 4/9 + 4/9 = 1	
120			6.8 x .444 = 3.2	3.2	6.2
119		6.8 x .444 = 3.2	14.6 x .444 = 6.4	10.0	19.4
118	6.8 x .11 = 0.8	14.6 x .444 = 6.4	100 x .444 = 44.4	51.6	100
117	14.6 x .11 = 1.6	100 x .444 = 44.4		46.0	89.2
116	100 x .11 = 11			11.0	21.2

Table 5 (Continued)

Specie	d_0 Prob. Cont.	d_1 Prob. Cont.	d_2 Prob. Cont.	d_3 Prob. Cont.	d_4 Prob. Cont.	Probability Total	Rel. Int.
Si_3C_6	$(1/3)^3$	$3(1/3)^2(2/3)$	$3(1/3)(2/3)^2$	$(2/3)^3$		$1/27 + 6/27 + 12/27 + 8/27 = 27/27$	
179				3.2		3.2	6.5
178			9.8	5.6		10.4	21.2
177		2.4	8.4	29.6		40.4	82.5
176	10.2 x .037 = 0.4	4.2	44.4			49.0	100
175	21.9 x .037 = 0.7	22.2				22.9	46.6
174	100 x .037 = 3.7					3.7	7.6
Si_4C_8	$(1/3)^4$	$4(1/3)^3(2/3)$	$6(1/3)^2(2/3)^2$	$4(1/3)(2/3)^3$	$(2/3)^4$	$1/81 + 8/81 + 24/81 + 32/81 + 16/81 = 81/81$	
238					2.7	2.7	5.6
237				5.2	5.8	11.0	23.0
236			3.6	11.6	19.7	34.9	72.7
235		1.2	8.4	39.4		48.0	100
234	.16	2.8	29.4			32.3	67.3
233	.3	9.5				10.1	20.1
232	1.2					1.2	2.5

The first case is a calculation of the relative peak heights of the loss of one methyl group from d_1-$(CH_3)_3Si$. Based on natural abundances of silicon and carbon and assuming no deuterium the relative peak heights would be m/e 58 (100), 59 (7.3) and 60 (3.4). Hydrogen and oxygen atoms do not contribute significantly to P + 1 and P + 2 isomers, thus the ratio 100: 7.3: 3.4 will always be observed regardless of deuteriums, oxygens, or hydrogens present. Only Si and C are considered in this and future tables as these are the only atoms that will affect the ratio of peak heights. The Si_3C_6 species at m/e 174 will have the same peak heights as $[(CH_3)_2SiO]_3$ at m/e 222. In Si_2C_4, the peak heights are m/e 116 (100), 117 (14.6), and 118 (6.8). These and the other values are shown in the first column in each series in Table 5.

The species which has n-deuteriums always has a $(1/3)^n$ and $(2/3)^n$ probability of having 0 and n deuteriums, respectively where n = no. of silicon atoms. Calculating the probability for two (n-1) deuteriums is somewhat more complicated. In the case of Si_2C_4 there is a (1/3) (1/3) chance of there being no deuteriums while the probability of finding one deuterium is calculated by having no deuterium on one silicon (1/3) and one deuterium on the other (2/3). There is an equal chance that the deuterium and hydrogen are switched and this doubles the chance of finding one deuterium in the whole system. An even more complicated case is where n=4 with two deuteriums. Starting on any Si atom the respective probabilities are H (1/3), H (1/3), D (2/3), and D (2/3). There are six combinations where two deuteriums can be found in Si_4C_8 and this increases the chance by six times or 24/81. It is seen that the final relative intensities is a sum of the mono-,di-,tri-, and tetradeuterated species and the probability is always 1. This assumes completely random losses of methyl groups, 100% d_5-ketone and no scrambling of deuterium with hydrogens in the molecule.

The ketone is not completely d_5, but rather 52% d_5, 34% d_4, and 14% d_3. This would affect the peak heights and the calculations for these are found in Table 6.

The tetradeuterated enol has a 4/5 chance of having a hydroxylic deuterium, thus the chance of a given peak height with d will be reduced by 1/5 or 1/5 x 34% = 6.8% from each of the calculated peaks. The likelihood of d_3-ketone having a hydroxylic deuterium is only 2/5 or 2/5 x 14 = 5.6% of each peak reduced from the 100% d_5-ketone calculation. Thus a total of 5.6 + 6.8 = 12.4% must be subtracted from all peaks except the d_0 species. This subtracted value is the amount present in the species with one less deuterium and must be added to the amount of that species. In the case of Si_3C_6 nothing is subtracted from

Table 6. Calculated relative intensity of $(Me_2SiO)_n$ from TMS-enolate of 52% d_5, 34% d_4, and 14% d_3 methylmethylene ketone

Specie m/e	Contribution	Contribution	Contribution	Rel. Int.	
SiC_2					
61		2.2 - 0.27 = 1.9		1.9	3.0
60	1.1 + 1.9 = 3.0	4.8 - 0.59 = 4.2		7.2	11.0
59	2.4 + 4.2 = 6.6	66.6 - 8.3 = 58.3		65.0	100.0
58	33.3 + 8.3 = 41.6			41.6	64.2
Si_2C_4					
120			3.2 - 0.40 = 2.8	2.8	6.8
119		3.2 - 0.40 + .40 = 3.2	6.5 - 0.76 = 5.6	8.8	15.9
118	0.8 + 0.4 = 1.2	6.4 - 0.76 + .76 = 6.4	44.4 - 5.5 = 38.9	46.5	99.0
117	1.6 + 0.76 = 2.4	44.4 - 5.5 + 5.5 = 44.4		46.8	100
116	11.0 + 5.6 = 16.6			16.6	35.4

Table 6 (Continued)

Specie m/e	Cont.	Cont.	Cont.	Cont.	Cont.	Rel. Int.	
Si_3C_6							
179				2.8		2.8	5.8
178			4.0	4.9		8.9	18.4
177		2.7	7.7	25.9		35.3	75.0
176	0.7	4.9	42.7			48.3	100
175	1.4	24.9				26.3	52.5
174	6.4					6.4	13.2
Si_4C_8							
238					2.4	2.4	5.2
237				4.9	5.0	9.9	21.4
236			3.7	10.7	17.3	11.7	25.2
235		1.5	7.8	37.0		46.3	100
234	0.32	3.5	30.6			34.5	74.5
233	0.66	12.2				12.9	27.8
232	2.4					2.4	5.2

the undeuterated species peaks (3.7, 0.7, 0.4). The monodeuterated species values of 22.2, 4.2 and 2.4 must all be multiplied by 12.4% and these values, in turn, added to 3.7, 0.7 and 0.4, respectively and subtracted from 22.2, 4.2 and 2.4. The summation of the contribution from each species gives the overall ratio of peak heights. A further difficulty in determining the relative peak heights is that the molecular ion is never observed to any extent but the parent ion minus methyl (P-15) is characteristic of the siloxanes. This methyl may or may not have deuterium and the calculations of relative intensities of the peaks are seen in Table 7.

Taking the Si_3C_6 species as an example the undeuterated species will never lose deuterium, so its calculated heights remain unchanged. The monodeuterated species, however, has a 1/6 chance for deuterium being removed in the loss of a methyl group. The peaks at m/e (24.9, 4.9, 2.7) must be reduced by 16.6%. The dideuterated species has a 2/6 chance of eliminating one deuterium with a loss of one methyl group. There is a 2/6 chance that one deuterium is lost from the dideuterated species and a 3/6 chance that deuterium will be eliminated from the trideuterated species.

The experimental results with their calculated values are listed in Table 8.

Table 7. Calculated relative intensity of $(Me_2SiO)_n$ from TMS-enolate of 52% d_5, 34% d_4, and 14% d_3 methyl methylene ketone minus one methyl group

Specie	d_1 Loss Probability	d_1 Loss Probability	d_1 Loss Probability	Rel. Int.	
m/e	d_0 Contribution	d_1 Contribution	d_2 Contribution		
SiC_2	0	(1/2)			
62					
61		1.9 - 1.0 = 0.9		0.9	1.3
60	3.0 + 0.9 = 3.9	4.2 - 2.1 = 2.1		6.0	8.5
59	6.6 + 2.1 = 8.7	58.3 - 29.1 = 29.2		37.9	26.8
58	41.6 + 29.2 = 70.8			70.8	100
Si_2C_4	0	(1/4)	(1/2)		
120			2.8 - 1.9 = 1.4	1.4	2.5
119		3.2 - 0.8 + 1.4 = 3.8	5.6 - 00.8 = 2.8	6.6	11.6
118	1.2 + 0.8 = 2.0	6.4 - 1.6 + 2.8 = 8.6	38.9 - 19.5 = 19.5	30.1	53.0
117	2.4 + 1.6 = 4.0	44.4 - 11.1 + 19.5 = 52.8		56.8	100
116	16.6 + 11.1 = 27.7			27.7	48.7

Table 7 (Continued)

Specie	d_1 Loss Prob.	d_1 Loss Prob.	d_1 Loss Prob.	d_1 Loss Prob.	d_1 Loss Prob.	Rel.	Int.
m/e	Cont.	Cont.	Cont.	Cont.	Cont.		
Si_3C_6	0	(1/6)	(2/6)	(3/6)			
179				1.4		1.4	2.8
178			4.5	2.5		6.0	12.2
177		3.7	7.6	13		24.3	49.2
176	1.2	6.7	41.5			49.4	100
175	2.2	34.9				37.1	75
174	10.6					10.6	21.5
Si_4C_8	0	(1/8)	(2/8)	(3/8)	(4/8)		
238					1.2	1.2	2.7
237				4.3	2.5	6.8	15.4
236			4.6	9.2	8.7	22.5	51.2
235		2.2	9.8	32.2		44.2	100
234	0.5	5.1	36.9			42.5	96.5
233	1.1	18.3				19.4	44
232	3.9					3.9	8.9

Table 8. Mass spectra (70 eV) of $(Me_2SiO)_3$ and $(Me_2SiO)_4$ from the pyrolysis of 1,1-dimethyl-1-silocyclobutane and deuterated 4-methyl-2-pentanone

600°C ($d_5$adduct)

	Obs.	Calculated
179	11	3.1
178	22	20.4
177	100	100
176	89.5	57.8
175	33	21.8
174	11	

700°C

$(Me_2SiO)_3$

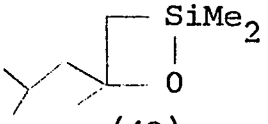
	Obs.	Calculated
215	17	
214	24.8	
213	33.3	
212	41.5	2.8
211	62	12.8
210	83	49.2
209	100	100
208	100	75
207	100	21.5

$(Me_2SiO)_4$

	Obs.	Calculated
288	10	
287	27.4	2.7
286	49.5	15
285	59.5	51
284	89.2	100
283	100	96.5
282	94.6	44
281	75.6	8.9

The results of the deuterated trimethylsilylenolate (M^+172) are not completely unambiguous. There is a peak observed at m/e 174 which should not be present and peaks at both m/e 175 and m/e 176 are larger than calculated.

The observed values for the cyclotrisiloxane are quite different than predicted. There are several peaks m/e 212, 213, 214, and 215 which cannot be explained by either siloxetane mechanism or the enolate mechanism. The high values at m/e 207, and 208, however, are consistent with some siloxetane (49) intermediate.



(49)

The observed results compare much more favorably with the calculated results in the case of cyclotetrasiloxane. A small value is observed for only one peak not calculated (m/e 288). While the observed values for m/e 287 and 286 are a little higher than the calculated values, they are generally agreeable. The big difference is noticed again with much larger peaks at m/e 281 and 282 than the calculated ones which imply the siloxetane intermediate (49). The results indicated that both mechanisms were occurring simultaneously. The extent to which each mechanism occurs could have been calculated, had it not been for the unexplained peaks at higher masses. However, if these higher masses were disregarded, there was a 78/100 ratio of siloxetane to enol intermediate, which is a substantial amount.

This begged the question of why only one type of mechanism with aldehydes was so much different than with enolizable ketones. Aldehydes are quite enolizable (76) and it would seem a priori that a considerable amount of the enolate form would be produced.

Reexamination of Roark's and Sommer's (66) heptanal experiments seemed essential. Heptanal and the cyclobutane generator (15) in a 2:1 ratio by weight, respectively, were dropped in the heated vertical column (700°C) with a nitrogen flow. Only about 1/3 of the material was recovered in a liquid nitrogen trap. The results included many components besides decomposition products of the starting materials. Four components were collected and were found to have m/e 207 (4.1%), 221 (5.1%), 112 (9.8%), and 281 (5.6%) with trace amounts of species with m/e 279, 186, and 355. The nmr of m/e 221 component indicated essentially all silyl methyl groups, thus a polymeric siloxane was implied. The mass spectrum had peaks at m/e 221, 147, 132, 73, all of which are indicative of the linear octamethyltrisiloxane. The ir substantiates this with strong absorptions at 2980, 1260, 1050, 940, 870, and 700 cm^{-1}.

The mass spectrum of the component with m/e 279 was similar to that of the component with m/e 221 with peaks at m/e 279, 221, 206, 147, 132, and 73. This indicated a linear siloxane with one more dimethylsilyl group. It was not isolated and thus the mass spectrum of an impure sample was the only evidence available.

It is known that pyrolysis experiments are often not reproducible with regard to final yields. Some products may well be different depending on the apparatus. However, it is difficult to conceive of such vast differences between these results and Roark's and Sommer's isolation of the olefin and hexamethylcyclotrisiloxane. A similar run at 600°C gave essentially identical results as at 700°C so those at 700°C were utilized.

Deuterated species might again elucidate the mechanism. Indeed, if only the siloxetane is present as suggested (66), no incorporation is expected. Pure enolate would have one deuterium and the calculation of the statistical loss of d to get to Si_nC_{2n} species is the same as for the enolizable ketone assuming 100% d_2-aldehyde. This is shown in Table 5 while Table 9 considers the fact of 51.5% d_2, 31.3% d_1, 18.2% d_0 aldehyde which gives different results than the ketone. Finally, Table 10 considers the loss of deuterium with the loss of methyl to form the only observed ion (P-15).

Table 9. Calculated relative intensity of $(Me_2SiO)_n$ from TMS-enolate with 51.5% d_2, 34% d_1, and 14% d_0 aldehyde

Specie m/e	Contribution	Contribution	Contribution		
SiC_2					
61		2.2 - 0.7 = 1.5		1.5	2.7
60	1.1 + 0.7 = 1.8	4.8 - 1.6 = 3.2		5.0	9.0
59	2.4 + 1.6 = 4.0	66.6 - 22.2 = 44.4		49.4	88.6
58	33.3 + 32.2 = 55.5			55.5	100
Si_2C_4					
120			2.2 - 1.1 = 1.1	2.1	4.4
119		3.2 - 1.1 + 1.1 = 3.2	5.6 - 2.1 = 3.5	7.5	15.6
118	0.8 + 1.1 = 1.9	6.4 - 2.1 + 2.1 = 6.4	44.4 - 14.8 = 29.2	37.9	73.8
117	1.6 + 2.1 = 3.7	44.4 - 14.8 + 14.8 = 44.4		48.1	100
116	11.0 + 14.8 = 25.8			25.8	53.6

Table 9 (Continued)

Specie m/e	Cont.	Cont.	Cont.	Cont.	Cont.		
Si_3C_6							
179				2.1		2.1	4.5
178			4.3	3.7		8.0	17.3
177		3.2	7.5	14.7		30.4	65.5
176	1.2	5.6	39.5			46.3	100
175	2.1	29.3				36.9	68.9
174	10.9					10.9	23.5
Si_4C_6							
238					1.8	1.8	4.1
237				4.4	3.9	8.3	18.8
236			4.1	9.8	13.1	27.0	61.2
235		2.0	9.3	32.9		44.2	100
234	0.20	4.7	32.7			37.6	85.2
233	0.62	16.3				17.5	39.6
232	4.5					4.5	19.8

Table 10. Calculated relative intensity of $(Me_2SiO)_n$ from TMS-enolate from 51.5% d_2, 30.4% d_1, and 18.1% d_0 aldehyde minus one methyl group

Specie	d_1 Loss Probability	d_1 Loss Probability	d_1 Loss Probability	Rel. Int.	
m/e	d_0 Contribution	d_1 Contribution	d_2 Contribution		
SiC_2	0	(1/2)			
61		1.0 - .75 = .75		.75	.9
60	1.8 + 0.8 = 2.6	3.2 - 1.6 = 1.6		4.2	5.4
59	4.0 + 1.6 = 5.6	44.4 - 22.2 = 22.2		27.8	35.8
58	55.5 + 22.2 = 77.7			77.7	100
Si_2C_4	0	(1/4)	(2/4)		
120			2.1 - 1.1 = 1.0	1.0	1.4
119		3.3 - .8 + 1.0 = 3.4	4.3 - 2.1 = 2.1	5.5	10.3
118	1.9 + 0.8 = 2.7	6.4 - 1.6 + 2.1 = 6.9	29.6 - 14.8 = 14.8	23.4	43.4
117	3.7 + 11.6 = 5.3	44.4 - 11.1 + 14.8 = 48.1		53.4	100
116	25.8 + 11.1 = 36.9			36.9	67.5

Table 10 (Continued)

Specie m/e	d_0 Prob.	d_1 Prob.	d_2 Prob.	d_3 Prob.	d_4 Prob.	Rel. Int.	
Si_3C_6	0	(1/6)	(2/6)				
180					0.9	0.9	2.1
179				1.0	2.0	5.7	13
178			3.9	1.8	6.5	19.7	44.3
177		5.6	6.8	9.8		39.6	90
176	1.7	7.2	36.1			43.6	100
175	3.0	38.2				24.3	55.6
174	15.7					6.5	14.9
Si_4C_8	0	(1/8)	(2/8)	(3/8)	(4/8)		
238					0.9		
237				3.7	2.0	1.0	2.2
236			4.7	8.1	6.5	5.7	12.6
235		2.8	10.7	27.1		12.2	49.5
234	0.4	6.4	36.8			45.0	100
233	1.8	2.5				41.2	91.7
232	6.5					15.7	34.9

The products of the reaction of heptanal and the cyclobutane generator (<u>15</u>) were collected and the mass spectra were taken of the deuterated and nondeuterated analogue. The results are summarized in Table 11 for only the cyclic siloxanes produced.

The very high percent of d_0-species in both the tri- and tetrasiloxanes are overwhelmingly in favor of the siloxetane intermediate. The small amount (~20%) of deuterated species is difficult to explain. It might be produced from the enol form or it might involve some random exchange. An experiment was run to check the latter. Undeuterated octamethylcyclotetrasiloxane and deuterated aldehyde were reacted under the same conditions (700°C) as the original reaction, and the results of the collected products are found in Table 12.

The products of the reaction were $(Me_2SiO)_3$ and $(MeSiO)_5$ and starting material $(Me_2SiO)_4$. Only $(Me_2SiO)_3$ and $(Me_2SiO)_4$ were collected and analyzed. The results for $(Me_2SiO)_4$ indicate some random deuterium exchange even without reaction. The major place where deuterium is incorporated is in the $(Me_2SiO)_3$. Evidently, there is some increased affinity for deuterium in the process of losing Me_2SiO. The value of 84% d_0 observed in the case of the same species formed in the copyrolysis of heptanal and silacyclobutane (<u>15</u>) compared very closely to the 80% d_0

Table 11. d-Incorporation results of $(Me_2SiO)_3$ and $(Me_2SiO)_4$ from copyrolysis of $(Me_2SiO)_4$ and deuterated heptanal at 700°C

M/e	Ref.	Sample		
	$(Me_2SiO)_3$			
209	15	20	5	4
208	20	35	15	
207	100	100		
		84% d_0	12.6% d_1	3.4% d_2
	$(Me_2SiO)_4$			
283	20	22	2	2
282	32	38	6	
281	100	100		
		92.9% d_0	5.5% d_1	2.1%d_2

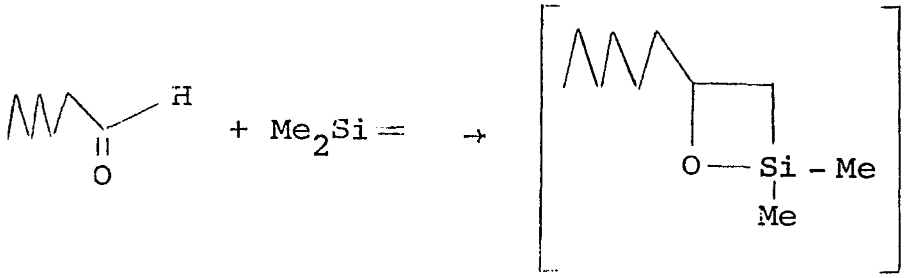
observed when $(Me_2SiO)_4$ is heated in the presence of the same deuterated heptanal. Thus, all but a few percent of deuterated species is explained in the reaction and some if not all of this can be due to error in reading peak heights. It seems quite probable that the formation of the cyclotetrasiloxane would involve similar random deuteration exchange as observed in the formation of cyclotrisiloxane, although it is difficult to test. These results show clearly that essentially all of the cyclotrisiloxane comes from the siloxetane intermediate (52) and it is almost

Table 12. Results from copyrolysis of $(Me_2SiO)_4$ and deuterated heptanal

M/e	Ref.	Sample				Calc'd.
$(Me_2SiO)_3$						
212						2.2
211						12.6
210		4	4 - .4	= 3.6		49.5
209	11	20	9 - 1.8	= 7.2		100
208	20	40	20 - 20	=		91.7
207	100	100				34.9
		78.5% d_0	15.7% d_1	5.7% d_2		
$(Me_2SiO)_4$						
287						2.1
286						13
285		3	3 - .12	2.8 - 0.5	2.3	44.3
284	4	10	6 - 1.2	4.8 - 1.72	3.1	90
283	20	28	8 - 2.9	7.1 - 7.1		100
282	36	50	14 - 14			55.6
281	100	100				14.9
		81% d_0	11.3% d_1	5.75% d_2	2.5% d_3	

certain that the same is true for the newly formed cyclotetrasiloxane. The d-incorporation in $(Me_2SiO)_4$ might have come from the other cyclicsiloxanes known (62) to be in equilibrium.

These results agree with Roark's and Sommer's (66) mechanistic interpretation only to the extent that trisiloxane comes from siloxetane. An important difference



(52)

is that there are two products which substantiate this mechanism instead of the reported one. A more dramatic difference of this copyrolysis experiment with the reported results is the formation in large quantities of siloxane with m/e 221 plus trace amounts of siloxane with 279. The results of their deuterium content is listed in Table 13.

Substantial deuterium incorporation is observed in both of these components. The trimethylsilyl groups would most certainly be the location of the deuterium atoms and it is difficult to understand why more deuterium is not found. One possible explanation is that some other source supplies hydrogen to the silicon methylene besides the hydroxyl group of the aldehydic enol form. That a trimethylsilylenolate was not formed was seen by the thermal stability (at 700°C) of the independently prepared compounds. Also the absence of any peak in the vpc with

Table 13. Deuterium incorporation results of component (M/e 221) and component (M/e 279) from the copyrolysis of (15) and heptanal at 700°C

M/e	Ref.	Sample				
225		8	8	8 - 3.0	5.00 - 2.0	3.0
224		25	25 - 12.7	12.3 - 5.7	6.6 - 6.6	
223	16	54	42.7 - 23.7	19 - 19	6.6 - 6.6	
222	30	100	79 - 79			
221	100	71				
		40% d_0	44.3% d_1	10.7% d_2	3.7% d_3	0.7% d_4
284		10.5	10.5 - 5.7	4.8 - 4.2		
283	8	21	13 - 11.6	2.4 - 4.5		
282	16	36.8	20.8 - 17.6	3.2 - 5.3		
281	24	63	39 - 20.2	19		
280	28	100	72			
279	100	100				
		52.4% d_0	37.6% d_1	10% d_2		

similar retention time corroborated this.

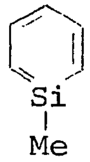
The results of the reactions of deuterated ketone and aldehyde have some similarities as well as some notable differences. Both ketones and aldehydes, whether enolizable or not, form a substantial amount of what one must consider to be a four-center species with silicon, oxygen, and two carbon atoms- the siloxetane. Very little at the present time can be said about the properties of this species except that it was unstable at 425°C and degrades to cyclic siloxanes. The intermediate in this second reaction is dimethyloxosilane, a species of significant interest in itself. Properties of dimethyloxosilane, as with siloxetane, could not be observed under the reaction conditions, but the chance that they might someday be examined seemed greatly improved with these results. The fact of whether an enolizable aldehyde or ketone is used is important only at certain (600°C) temperatures. Above that temperature, the deuteration experiments show that the siloxetane is a main intermediate by showing much less than calculated amounts of total deuterium. The fact that the independently prepared trimethylsilylenolate from the ketone, thermally (700°C), forms the same products as in copyrolysis is some cause for concern and a deuterated trimethylsilylenolate would be of significant value.

The differences between aldehydes and ketones are seen at 600°C. The enolate is formed in the case of enolizable ketones where only traces are observed with aldehydes. However, the two other components including a large amount with m/e 221 and a trace amount with m/e 279 are linear compounds which cannot come solely by reaction with the hydroxyl proton of the enol form. Although calculations were not made for these compounds, it is quite clear that two trimethylsilyl groups would each have one deuterium and peaks at m/e 221, 222, 279, and 280 would be almost negligible compared to those of higher masses.

It becomes necessary with the deuterated aldehyde experiments to invoke a third mechanism--one which has a source of protons which are not alpha to the carbonyl group. Water is one obvious source and some concern might be made as to the dryness of the starting materials. That this was not the case, was seen both in the formation of the dimer M^+144 and in the absence of the hexamethyldisiloxane. Both of these have been indicators of water in the past. This gives one very little basis to even suspect that water might be formed in the copyrolysis. As to exactly what was the extra source of protons was not determined.

Silabenzene

The advent of a silicon-carbon double bond suggests other species which would be most appealing. Silabenzene (53) would, seemingly, be more stable than 1,1-dimethylmethylenesilane (11). Even if it were not aromatic, as



(53)

such, a small amount of conjugation could, quite conceivably, make the double bond less reactive to itself and other addends. Silabenzene is precedented by reports of thiobenzene (77) and the heterobenzenes of the VA family (78, 79, 80). The synthesis of silabenzene has been attempted in at least one case (17), but results were negative.

The thermal degradation is so successful at this moment in time, compared to other methods which have only implied its intermediate existence, that a similar approach might be tried in silabenzenes. Two readily available compounds which have some necessary substitution are 1-chloro-1-methyl-1-silacyclohexa-2,4-diene (<u>33</u>) and 1-chloro-1-methyl-1-silacyclohexa-2,5-diene (<u>34</u>). That either of these might be generated into a silabenzene is seen quite emphatically in the mass spectral results shown in Table 14.

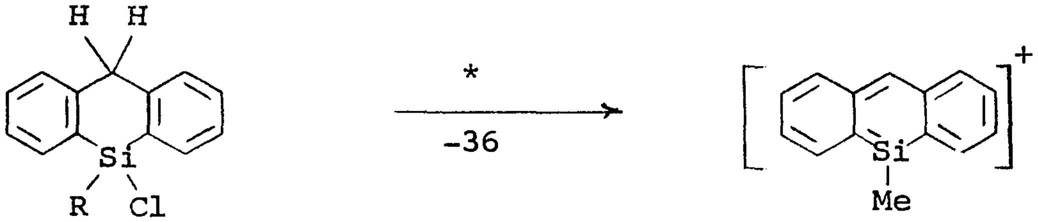
It is quite significant that the behavior of both chlorosilanes (<u>33</u>) and (<u>34</u>) is quite unique in their metastable losses of 36 (HCl) from the molecular ion. There are a number of cases reported where halogens migrate back to silicon in both the mass spectrometer (33) and in synthetic work (81). These halogens migrate to and remain on silicon due to the very strong bond formed (82). The fragmentation of Cl from silicon is rare, but the metastable

Table 14. Mass spectra (70 eV) of (33) and (34)

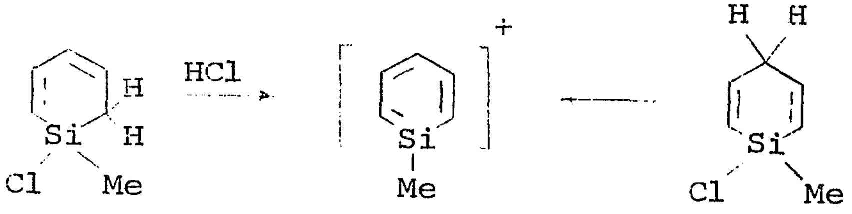
Me	(33)	(34)	Me	(33)	(34)
146	21	18	108	67	48
144	55	47	105	7	6
131	37	37	103	14	13
129	100	100	93	15	12
118	8	5	81	21	17
117	6	6	79	46	33
116	8	6	78	10	7
115	7	12	67	12	15
113	4	12	66	31	38
110	4	4	65	32	33
109	11	18	63	76	78

Metastables	81.0 (144→108)
(33) + (34)	115.6 (144→129)

loss of HCl (36) is reported in one other similar case in the mass spectral studied (83, 84) of dihydrosilaanthracenes, where its loss forms the aromatic-like 9-silaanthracene.



The metastable loss of HCl (36) from both the 2,4- and the 2,5-isomers is substantial evidence for a quite stable species consistent with 1-methyl-1-silabenzene (53). The presence of chlorine seemed essential as no like process was observed with the corresponding dimethyl analogue (26) which only loses Me (15). Dimmel and workers (33) have

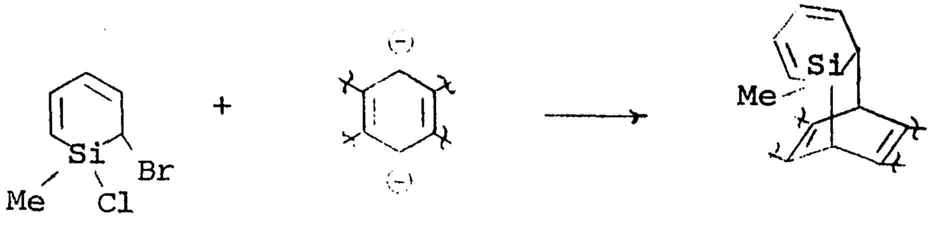


(33) (53) (34)

reported that ionization occurs on chlorine rather than silicon before a species is able to eliminate with a hydrogen.

The method to produce the same aromatic species (53) synthetically is not certain. However, the procedure most likely to work, based on precedent, is a thermal degradation of a species like (54). The formation of the other aromatic species would deter the reversible reaction so that silabenzene (53) could be observed.

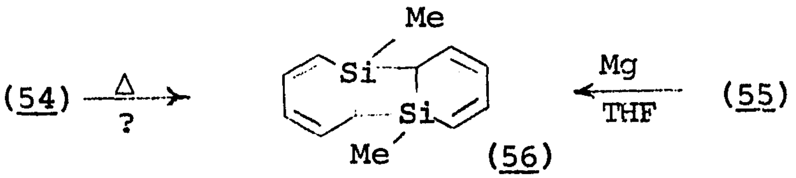
The bicyclic generator (54) might be produced from the dianion and 2-bromo-1-chloro-1-methyl-1-silacyclohexa-2,



(55) (54)

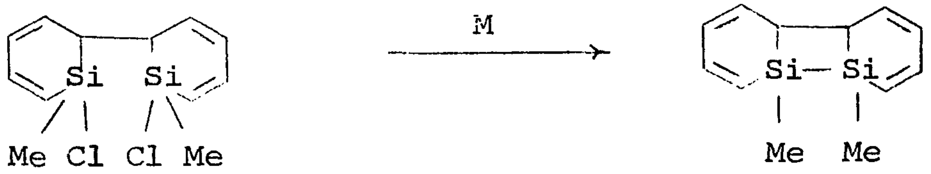
4-diene (55). The latter compound (55) would most likely be prepared from NBS bromination (85) of the diene (33). However, this turned out to be more difficult than first surmised. Refluxing a CCl_4 solution of NBS and diene (33) for four to five hours resulted in much polymeric material. Some compound was isolated under reduced pressure by distillation. The mass spectrum of the product has M^+ 258 (2 Cl, 1 Br) and the nmr is quire complicated, indicating that the desired compound is not formed to any extent.

The product one might expect from reactive silabenzene (53) is the (2+2) adduct (56), as in the case of the more simple analogue (7). In spite of its conjugation, there will probably be some polarity still present and dimerization is quite possible. This adduct might well be produced



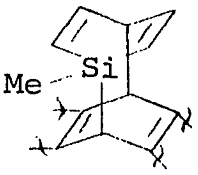
(56)

independently from reacting the brominated diene (55) with magnesium in THF (74). A second approach might be to couple the silicons and allylic carbons separately.



Reversibility might allow the production of silabenzene (53) by thermal degradation in either case.

Bromine at the 4-position in the 2,5-diene (34) might also be utilized to produce a silabenzene generator, although it probably will be much less favorable. The formation of the generator (57) probably would require stereochemistry that would make this much less appealing.



(57)

EXPERIMENTAL

Instrumentation

Proton nmr spectra were recorded on a Perkin-Elmer Model R-20B High Resolution nmr Spectrometer or on a Varian Model A-60 Analytical nmr Spectrometer. All chemical shifts are reported in ppm (δ) downfield from a tetramethylsilane (TMS) standard.

Infrared (ir) spectra were recorded on a Beckman IR 12 Infrared Spectrophotometer and all bands are reported in reciprocal centimeters (cm^{-1}).

Routine mass spectra were recorded on an Atlas CH-4 mass spectrometer and exact mass measurements were carried out using an MS 902 mass spectrometer manufactured by AEI.

Routine analytical and preparative gas chromatography (prep gc) was carried out on an F + M Gas Chromatograph Model using 8' x 1/4" aluminum columns packed with 20% SE-30, DC-550 and Apiezon L on Chromosorb P. Gas chromatographic/mass spectral (gcms) analyses were performed on a Perkin-Elmer 270 mass spectrometer using 6' x 3 mm glass columns packed with 3% OV-1, 3% OV-17 or 3% SE-30 on Chromosorb W.

All microanalyses were performed by Ilse Beetz Mikroanalytishches Laboratorium, Kronach, West Germany.

Procedure for Determining Yields by VPC

VPC yields were determined by considering areas under the peaks and the respective thermal conductivities of each component. A known amount of standard (usually having no functionality and having different retention time than any component), was mixed with the weighed mixture of products. If there was a lot of product, a smaller portion could be utilized. After several (usually 5-7) injections, the areas under the peaks ($A = 1/2\ bh$) were totalled for each component. A known amount of each component was then mixed and injected several times. The area/m mole was calculated for each component. and thermal conductivity factors were derived from this. The observed areas from the product mixture were readjusted to areas that would exist, if equal thermal conductivities prevailed. These adjusted areas were directly related to moles and knowing the number of moles used in the standard, a simple calculation obtained the number of moles of each component in the mixture of products. If a portion was taken from a larger amount, a further calculation was needed to determine total moles.

Illustrative Procedure for Pyrolysis in Vacuum

All pyrolyses in vacuum were carried out with a 28 mm diam x 30 cm Vycor tube with the vacuum gauge on the pump side of the nitrogen cooled trap. Both McLeod and thermal conductivity vacuum gauges were used. The samples were put into bulbs sealed by Fisher and Porter valves. The carrier gas, when a liquid such as cyclohexane was used, was also put into a bulb and sealed until needed. The sample was always degassed and some solvent was allowed through the collecting trap to the second trap before actually starting the pyrolysis. When gases such as butadiene were used, one bulb was replaced with a Brooks gas regulator, to control the flow. Samples were collected in a large trap and transferred to a vial before being weighed. An analysis was often made on the PE-270 mass spectrometer of the resulting products. Small amounts (20-30 μl) of the bicyclic generator (<u>28</u>) were used. The presence of m/e 147 (hexamethyldisiloxane) was invariably indicative of moisture or oxygen which had somehow invaded the reaction chamber. The presence of dimer in the copyrolyses indicated insufficient material was present. Preliminary studies are summarized in Table 3 on page 44.

Illustrative Procedures for Flow Pyrolyses

Vertical tubes (either the 28 mm x 30 cm or a smaller 10 mm x 30 cm) were packed with quartz chips and prepurified nitrogen was passed through the tube. A nitrogen cooled trap was also used, but care had to be taken so that the outlet tube would not freeze up. Pure samples as well as solutions (mixed or injected simultaneously) were dropped into the tube.

Synthetic Procedures and Results

1,1-Dimethyl-1-silacyclohex-2-ene

1-1-Dichloro-1-silacyclohex-2-ene (25) (69) (16.6 g) was added to three-fold excess MeMgI in dry ether and refluxed overnight. Usual work up with dilute HCl, $NaHCO_3$, the etheral solution,was dried ($MgSO_4$) and distilled 8.8 g (70% yield); bp 40°C/35 mm; nmr (CCl_4)δ, 0.0 (S, 6H), 0.62 (m, 2H), 1.85 (m, 4H), 5.52 (d of t, $J = 15$ Hz, 2Hz, 1H), 6.56 ppm (d of t, 1H, $J = 15$Hz, 4Hz); mass spectrum (70 eV) m/e (rel intensity) 126 (40), 111 (100), 94 (60), 59 (50).

4-Bromo-1,1-dimethyl-1-silacyclohex-2-ene

Equivalent amounts of 1,1-dimethyl-1-silacyclohex-2-ene and n-bromosuccinimide in CCl_4 solvent were refluxed with a uv lamp for six hours (85). The succinimide (mp 126°C) was recovered in 92.3% yield and the solvent was distilled. A 50% yield of bromosilacyclohex-2-ene: bp 70-72°C (7 mm); nmr (CCl_4)δ 0.09 (s, 3H), 0.14 (s, 3H), 2.23 (quint, 2H, J = 4.5 Hz), 4.26 (q, 1H, J = 4.5 Hz), 5.74 (d, 1H, J = 14 Hz), 6.76 ppm (d of d, 1H, J = 14Hz, 4.5 Hz); mass spectrum (70 eV) m/e (rel intensity), 204 (1), 124 (35), 109 (100), 81 (30), 59 (45).

1,1-Dimethyl-1-silacyclohexa-2,4-diene (26)

Method I An equivalent amount of 4-bromo-1,1-dimethyl-1-silacyclohexa-2-ene was added to DBU (1,5-diazabicyclo [5.4.0] undec-5-ene) at room temperature. An exothermic reaction was followed by solidification. Work up with 5% HCl extraction with ether and finally distillation gave 42% yield of 1,1-dimethyl-1-silacyclohexa-2,4-diene: bp 70°C (74 mm); nmr (CCl_4) 0.1 (s, 6H), 1.72 (d, 2H, J = 3Hz), 6.95 (m, 3H), 7.92 ppm (m, 1H); mass spectrum 70 eV) m/e (rel intensity) 124 (30), 109 (100), 81 (29), 59 (30); uv (max acetonitrile) 265.5 mμ (ε 35 x 10^3); Anal. calcd for $C_7H_{12}Si$: 124.0708. Found: 124.0709.

Method II 1,2-Dimethoxy-1,1,2,2-tetramethyl-1, 2-disilane was mixed with three equivalents of cyclopentadiene and dropped into 12" x 3/4" Vycor tube with quartz chips at 600°-620°C. The product was collected in a liquid nitrogen cooled flask and was fractionally distilled immediately. The product was a mixture of the 2,5- and 2,4-silacyclohexadienes in a total of 38% yield: bp

70°C (74 mm). 1,1-Dimethyl-1-silacyclohexa-2,5-diene: 10.6% mixture by nmr (CCl_4)δ 0.1 (s, 6H), 2.76 (m, 2H), 6.95 (m, 3H), 7.92 ppm (m, 1H). The rest of the mixture 89.4% was the conjugated 2,4-diene (26).

2,3-Bis(trifluoromethyl-7,7-dimethyl-7-silabicyclo (2.2.2) octa-2,5-diene (28)

1,1-Dimethyl-1-silacyclohexa-2,4-diene (26) was put into a tube to which an excess of perfluoro-2-butyne (Pierce Chemical Co.) was added. The tube was sealed under vacuum and put into oil bath at 60°C for four hours. After the seal was broken and the excess perfluoro-2-butyne was allowed to escape, a yellow viscous liquid resulted shown to be quite pure by vpc was colorless when distilled: bp 78-80°C (14 mm), nmr (CCl_4)δ 0.11 (s, 6H), 0.48 (d, 2H, $J = 3.8$ Hz), 3.58 (d, 1H, 6.5 Hz), 4.12 (m, 1H), 6.16 ppm (m, 2H): ir (neat) 3065 (w), 2980 (w), 1660 (w), 1610 (w) 1415 (w), 1375 (w), 1345 (w), 1300 (vs), 1267 (vs), 1200 (vs), 1150 (vs), 1090 (w), 1050 (w), 1015 (s), 930 (vs); mass spectrum (see Table 2, page 34) uv (max cyclohexane) 295 mμ (ε 4 x 10^4) Anal. Calcd for $C_{11}H_{12}F_6Si$: C, 46.14; H, 4.40; Si, 9.67, 286.06134. Found: C, 46.14; H, 4.22; Si, 9.78, 286.06492.

1,2-Dimethoxy-1,1,2,2-tetramethyl-1,2-disilane

1,2-Dichloro-1,1,2,2-tetramethyl-1,2-disilane prepared (86) from hexamethyldisilane (87) was added dropwise to a slurry of two equivalents of sodium methoxide and dry ether at 0°C. After refluxing for two hours, the mixture was filtered and distilled to give 78% yield of 1,2-dimethoxy-1,1,2,2-tetramethyl-1,2-disilane (73): bp 82-87°C (90 mm); nmr (CCl_4)δ 0.2 (s, 2H), 3.36 ppm (s, 1H), mass spectrum (70 eV) m/e (rel intensity) 178 (86), 148 (100), 118 (18).

1,1,2,2-Tetrachloro-1,2-dimethyl-1,2-disilane

This compound could never be isolated in its pure form, but always had an impurity of 1,1,2-trichloro-1,2,2-trimethyl-1,2-disilane. One mole hexamethyldisilane was added to 4 moles of $AlCl_3$ (anhyd.) and 4 moles of acetyl chloride were added dropwise until about 2 moles were used. Then the temperature was increased to 100°C, the remainder of the acetyl chloride was added and heated five and one half hours more at 110°C. Distillation gave a mixture (bp 65°C/24 mm) of which 78.1% is desired compound making 62.4% overall yield, nmr (CCl_4)δ 1.0 ppm (δ) (88).

1-Chloro-1-methyl-1-silacyclohexa-2,4-diene (33)

A mixture of 79 mol % $Me_2Si_2Cl_4$ and 21 mol % Me_3SiCl_3 was added separately with a three-fold excess of cyclopentadiene to a column 3/4" x 12" at 590-630°C with a nitrogen flow of 250 ml/min. The product mixture was fractionally distilled and a fraction bp: 68-73°C (31 mm) was collected; nmr indicated 1-chloro-1-methyl-1-silacyclohexa-2,4-diene (82.5 mol %) 1-chloro-1-methyl-1-silacyclohexa-2,5-diene (13.2 mol %) and 1,1,2,2-tetrachloro-1,2-dimethyldisilane (4.4 mol %). Proof of structures came with separation of isomers and verifying by nmr (CCl_4)δ 0.52 (s, 3H); 1.83 (d, 2H, J = 4Hz), 5.90 (m, 2H), 6.73 ppm (d of q, J = 2Hz); mass spectrum (see page 80); uv max (cyclohexane) 268 mμ (ε 4.88 x 10^3). Anal. Calcd for C_6H_9SiCl: C, 49.81; H, 6.26; Cl, 24.50; Si 19.41. Found: C, 49.98; H, 6.37; Cl, 24.37.

1-Chloro-1-methyl-1-silacyclohexa-2,5-diene (34)

The best yields were obtained by reducing the temperature of the glass tube to 525°C and keeping everything else the same as above. A mixture, bp 68-73°C (31 mm), gave 40 mol % tetrachlorodimethyldisilane, 21 mol % trichlorotrimethyldisilane; 34% total cyclic diene including 25.7 mol % 2,4-diene (33) and 13.3 mol % 2,5-diene (34): nmr (CCl_4)δ 0.50 (s, 3H) 3.00 (m, 2H), 5.90 (d of t, 2H, J = 15Hz, 2Hz), 6.64 ppm (d of t, 2H, J = 15Hz, 3.5 Hz); mass spectrum (see page 80).

2,2-Dimethyl-2-silabicyclo (2.2.1) hept-5-ene (45)

Method I 2,3-Bis(trifluoromethyl)-2,2-dimethyl-2-silabicyclo [2.2.2] octa-2,5-diene (28) was mixed with cyclopentadiene. A vpc analysis (20% DC-550 Silicon Fluid on Chromosorb P) shows 97% hexafluoro-o-xylene and 55% yield of 2,2-dimethyl-2-silabicyclo (2.2.1) hept-5-ene: nmr (CCl_4)δ 0.00 (s, 3H), 0.2 (s, 3H), 1.35 (d, 2H, J = 9.5 Hz), 1.68 ppm (quint., J = 3Hz) ir (CCl_4) 3030 (s), 2985 (vs), 2825 (s), 1840 (m), 1410 (s), 1290 (vs), 1180 (vs), 1060 (s), 880 (s), mass spectrum (70 eV) m/e (rel intensity) 138 (50), 123 (75), 95 (35), 79 (51), 98 (42), 77 (30), 73 (70), 72 (100), 59 (63), 43 (82). Anal. calcd for $C_8H_{14}Si$: C, 69.62; H, 10.15, Si, 20.21. Found: C, 69.40; H, 10.04.

Method II (attempted) 1,1-Dimethyl-1-silacyclobutane was mixed with cyclopentadiene and copyrolyzed at 600°C. A mixture of two isomers all having M^+138 were observed in gcms, but were never isolated nor further elucidated. The mass spectrum (70 eV) m/e (rel intensity) of other isomer: 138 (86), 123 (100), 101 (50), 73 (32), 59 (65).

Pyrolysis of generator (28) in a sealed tube at 320°C

A small amount (30 μl) of the generator (28) was sealed under vacuum in a glass tube and heated in Wood's Metal bath at 320°C for two hours. Four components were observed on the F and M gas chromatograph (1/4" x 8' 20% DC-550 on chromasorb P), but only two of these were isolated and they had M^+214 and 306. The component at M^+306 was not elucidated, but the other was found to be the hexafluoro-o-xylene (40): mass spectrum (70 eV) m/e (rel intensity) 214 (100), 195 (65), 164 (28), 145 (90).

Reaction of naphthalene dianion and chloromethylchlorodimethylsilane

The same procedure using the identical amounts of reagents substituting only the chloromethylchlorodimethylsilane for the tetramethyldichlorodisilane was used as reported (67). The product was analyzed on the gcms and peaks with silicon had M^+144, 200, 272, and 342. The desired peak at M^+200 was the largest, but other peaks with increasing numbers of $Me_2Si=CH_2$ (M^+72) were present: mass spectrum (70 eV) m/e (rel intensity) 200 (20), 185 (70), 128 (100), 73 (80). The component with M^+272 had mass spectrum (70 eV) m/e (rel intensity) 272 (100), 200 (80), 73 (60).

Flow pyrolysis of neat generator (28) in a vacuum at 420°C

Into a glass bulb with a vacuum valve was placed 0.2564 g (0.0011 mole) of generator (28). When the pressure was $<$ 0.001 mm and the temperature 420°C, the generator was allowed to vaporize into the oven. The pyrosylate, collected in a liquid nitrogen cooled trap was transferred to a vial and it weighed 0.1169 g. Four components were observed in vpc, but only two were isolable. A large amount (0.0838 g) of xylene (40) (71.6%) and 0.015 g of clear viscous material having M^+292, with other peaks at m/e 220, 204, 148, 146, and 73 were observed. The hrms had obs. 292.148188 and calcd 292.1491887 for $C_{15}H_{28}Si_3$. The nmr (HA-100) ($CHCl_3$ = 0.00) - 736.8 (s, 16H), - 727.7 (s), - 717.6 Hz (s, together 139H).

Pyrolysis of neat generator in a vacuum system at 500°C

The procedure was the same as above except more (0.400 g) of the generator was used. The gcms indicated 19 different components, but the main ones had M^+ of 124, 144, 306, and 214. The retention times, mass spectra, and nmr were identical to the M^+144 peak with 1,1,3,3-tetramethyl-1,3-disilacyclobutane which was prepared independently (74). The xylene: nmr (CCl_4)δ 7.8 ppm (t of d, J = 6Hz, 4H); ir (neat) mass spectrum (70 eV) m/e (rel intensity) 214 (100), 195 (65), 164 (28), 145 (90). ir (CCl_4) 3080 (m), 2970 (s), 1960 (w), 1950 (w), 1780 (w), 1660 (w), 1615 (s), 1460 (s), 1320 (vs), 1180 (vs), 1045 (vs), 960 (s), 940 (s). Anal. calcd for $C_8H_4F_6$: C, 44.85; H, 1.93; 214.02177. Found: C, 44.97, H, 1.93, 214.02181.

Tetramethyldisilacyclobutane (7): nmr (CCl_4) - 0.3 (s, 2H), 0.23 (s, 6H); mass spectrum (70 eV) m/e (rel intensity) 144 (27), 129 (100), 100 (15), 73 (13). Anal. calcd for $C_6H_{12}Si_2$: 144.07889. Found: 144.07955 (74).

Pyrolysis of generator (28) with cyclohexane at 500°C

Generator (0.112 g) was added to one bulb, cyclohexane to another, and both were degassed. The cyclohexane was started and the generator was allowed to vaporize with the cyclohexane. Some heat from a heat gun was required to vaporize the generator. The pyrosylate (2.8114 g) was separated in the vpc and 0.086 g xylene (46.2%), 0.028 g (22%) of cyclic dimer. Also 0.010 g of material was collected which appeared to be a silicon-containing polymer and was not further elucidated.

Photolysis of generator (28) in CCl_4

A small amount of generator (28) (0.0307 g) mixed with CCl_4 (0.5695 g) and degassed with Argon was added to a quarts nmr tube. A Rayonette was used with light of 2537 Å. The reaction was followed by nmr and the olefinic protons at 6 ppm moved down field to 7.6 ppm in a multiplet. The bridgehead protons both disappeared and a doublet appeared at 2.76 ppm δ. The doublet of the silyl methylene collapsed to a singlet in same region of 0.53 ppm δ, and the methyl at 0.1 ppm shifted down field to 0.23 ppm and 0.37 ppm. The gcms indicated four components with m/e 113, 93, 63, and M^{+}214. The first three all had chlorine (113 had 2 Cl) and were consistent with $MeSi^{+}Cl_2$, $Me_2Si^{+}Cl$ and $Si^{+}Cl$ respectively. The compounds were not further characterized.

Photolysis of generator (28) in cyclohexane

The same equipment and procedure as above was used. The generator 0.107 g and cyclohexane were added to an nmr tube and followed by nmr when photolyzed in the Rayonette. Essentially, all the olefinic protons had disappeared and new peaks at 7.7 ppm were present. The bridgehead protons were absent, but the silyl methyl protons were 0.12 ppm this time. The silyl methylene protons remained about the same and no doublet at 2.76 ppm was present. The results of the gcms showed xylene (M^{+}214) plus other silicon-containing products whose structures were not obvious from their mass spectra.

Photolysis of generator (28) and 2-methylbut-2-ene

Similar procedures were used as above using 2-methylbut-2-ene as solvent. After one hour in Rayonette with 2537 Å light nearly all the olefinic protons of (28) had disappeared. The silyl methyl protons went into many peaks around 0.0-0.3 ppm and the product mixture was not investigated further.

Methanolysis of generator (28)

Generator (0.03 g) and methanol were added to an nmr tube and a mildly exothermic reaction occurred. The gcms shows basically one component of M^+318 which is 286 + MeOH. The base peak of m/e 89 indicated $Me_2Si=O^+Me$. The product was separated on vpc (8', 1/4", DC-550 Silicone Fluid in Chromosorb P at 100°C): nmr (CCl_4)δ 0.1 (s, 6H), 1.0 (t, 2H, J = 6Hz), 2.9 (m, 1H), 3.33 (s, 1H), 5.9 (m, 2H), 6.55 ppm (m, 1H); mass spectrum (70 eV) m/e (rel intensity) 588 (1), 360 (10), 265 (16), 209 (24), 191 (52), 155 (20), 151 (100), 141 (28), 128 (11), 99 (14), 75 (5), 73 (13).

Copyrolysis of cyclobutane generator (15) and 4-methyl-2-pentanone at 600°C

Generator (15) and ketone were mixed and dropped into a heated tube (600°C). The pyrosylate showed essentially one component having identical mass spectra, nmr, and retention time as an authentic sample of trimethylsilylenolate ether. The yield determined by vpc was 30%.

Copyrolysis of cyclobutane generator (15) and 4-methyl-2-pentanone at 700°C

Generator (15) and ketone were mixed in a ratio of 1:3 respectively and dropped into tube heated at 700°C with nitrogen flow of 250 cc/mm. The pyrosylate showed several peaks, some of which could not be isolated but gcms indicated were gases. Four isolated components, benzene, octamethylcyclotetrasiloxane, toluene, and hexamethylcyclotrisiloxane were identified by identical retention times, mass spectra of authentic samples. Only trace amounts of material having the same retention time as the olefin was observed. Yields for each were 27% benzene, 31.8% cyclictrisiloxane, 52.6% cyclictetrasiloxane, and 20.6% toluene. Anal. calcd for C_6H_6: 78.04692. Found: 78.04554. Anal. calcd for C_7H_8: 92.06260. Found: 92.06260.

Trimethylsilyl-4-methyl-2-pentenolate

Dry (CaH_2) dimethylformamide (200 ml) (76), dry (LAH) triethylamine (121 g), and chlorotrimethylsilane (65.2 g) were added to a flame dried 1000 ml three neck flask with a magnet stirrer. The mixture, kept dry with nitrogen, was refluxed for 48 hours. Work up was with cold $NaHCO_3$ solutions, and one extraction with cold 5% HCl was followed by a cold $NaHCO_3$ extraction, dried ($MgSO_4$) and distilled (bp 47-52°C/30 mm). The nmr indicated a mixture of starting ketone and enolate in 0.45 mol % and 0.55 mol % yields, respectively. The enolate was separated from ketone with vpc (8' 10% Apiezon L on Chromosorb P): nmr (CCl_4)δ 0.17 (m, 9H), 0.92 (d, 6H, J = 6.5 Hz), 1.72 (s, 3H), 1.95 (m, 1H), 4.20 ppm (q, 1H, J = 10Hz); mass spectrum (70 eV) m/e (rel intensity) 172 (6), 157 (40), 130 (20), 117 (20), 117 (56), 115 (44), 103 (8), 101 (4), 75 (70), 73 (100); ir (CCl_4) 750 (s), 830 (s), 1000 (s), 1210 (s), 1260 (s), 1550 (s), 2960 (w).

Pyrolysis of trimethylsilyl-4-methyl-2-pentenolate at 600°C

Trimethylsilyl-4-methyl-2-pentylenolate (0.269 g) was dropped into a tube at 600°C. VPC analysis of material collected (0.0689 g) indicated very little thermal degradation and mainly pure enolate ether.

Pyrolysis of 4-methyl-2-pentenolate at 700°C

4-Methyl-2-pentenolate was dropped into the heated tube (700°C) and four products were collected, including benzene (40%), hexamethylcyclotrisiloxane (27.9%), toluene (19%), and octamethylcyclotetrosiloxane (41.7%), as determined by vpc. These compounds had identical mass spectra and retention times as the authentic samples.

Copyrolysis of cyclobutane generator (15) and benzaldehyde at 600°C

Cyclobutane generator (15) (0.309 g) and benzaldehyde (0.7054 g) were copyrolyzed at 600°C. A gcms analysis indicated $(Me_2SiO)_4$, $(Me_2SiO)_3$, Ph $CH=CH_2$, and $(Me_2SiO)_5$. Further vpc analysis gave yields of 20.3%, 23.4%, 37.5% and 5.3%, respectively. The products were analyzed by identical mass spectra and retention times as authentic samples.

Copyrolysis of generator (28) and benzaldehyde at 450°C

Generator (0.60 g) and benzaldehyde (1.00 g) were mixed and pyrolyzed at 450°C. The products were $(Me_2SiO)_4$ (21.1%), $(Me_2SiO)_3$ (43.5%), xylene (64%), and Ph $CH=CH_2$ (29%). The styrene was identified by identical nmr with an authentic sample. The other components were identified by identical retention times and mass spectra of authentic samples.

Pyrolysis of 2,4-dimethyl-1-pentene at 700°C

A small amount of 2,4-dimethyl-1-pentene (89) was collected with vpc after being produced by pyrolysis of 2,4-dimethyl-1-pentylacetate at 600°C. The subsequent pyrolysis of the olefin at 700°C resulted in benzene, toluene, and xylene as identified by mass spectra and identical retention times with authentic samples.

Deuteration of 4-methyl-2-pentanone

4-Methyl-2-pentanone (25 g) was added with D_2O (4.0 g) and a small amount of K_2CO_3. The D_2O/K_2CO_3 solution was replaced twice in three days and it was held at refluxing temperatures. The nmr indicated 86.7% of the original protons adjacent to the carbonyl had been replaced with deuterium. This was corroborated with results of reference ketone mass spectrum (18 eV) m/e 100 (100) and the deuterated species, 103 (5.5), 104 (13.5), 105 (20.5), and 106 (2.5) which calculates to be 52% d_5, 34% d_4, and 14% d_3.

Copyrolysis of cyclobutane generator (**15**) and deuterated 4-methyl-2-pentanone at 600°C

Deuterated ketone and generator were mixed in about 3:1 ratio and pyrolyzed at 600°C. One component was found and separated with the vpc. The mass spectrum (16 eV) m/e (rel intensity) 174 (11), 175 (33), 176 (89.5), 177 (100), 178 (22), 179 (11), (see Table 8 , page 64); the reference sample: 172 (100), 173 (14.7), 174 (3.8).

Pyrolysis of cyclobutane generator (**15**) and deuterated 4-methyl-2-pentanone at 700°C

The generator and ketone were mixed in 1:3 ratio and pyrolyzed at 700°C. The four components were separated and mass spectra (16 eV) m/e (rel intensity) $(Me_2SiO)_3$ m/e 207

(100), 208 (100), 209 (100), 210 (83), 211 (62), 212 (41.5), 213 (33.3), 214 (24.8) and 215 (17.0); $(Me_2SiO)_4$ 280 (55), 281 (75.6), 282 (94.6), 283 (100), 283 (89.2), 285 (59.5), 286 (49.5), 287 (27.4), and 288 (10); C_6H_6, 78 (16.2) 79 (100), 80 (89.2), 81 (71.4), and 82 (43.3); C_7H_8, 91 (15), 92 (100.0), 93 (96), 94 (100), 95 (96), 96 (75.5), 97 (45), 98 (25.4), and 99 (10.2). Reference spectrum (16 eV) m/e (rel intensity) $(Me_2SiO)_3$ 207 (100), 208 (28), 209 (18); $(Me_2SiO)_4$ 281 (100), 292 (29), 283 (19); C_6H_6 78 (100), 79 (8); C_7H_8 91 (15), 92 (100), 93 (9).

Deuteration of heptanal

Heptanal (16.6 g), D_2O (5 g) and K_2CO_3 (0.5 g) were mixed and left to reflux for 24 hours. The D_2O/K_2CO_3 solution was replaced twice and the resulting heptanal was washed, dried and distilled. The nmr indicated substantial decrease in protons adjacent to the carbonyl; mass spectra (70 eV) m/e (rel intensity) 95 (10), 96 (100), 97 (10), 98 (4), 99 (2) for reference. The deuterated sample: 95 (4), 96 (40), 97 (70), 98 (100), 99 (14), 100 (6), 101 (2). This calculated d_0 18.2%, d_1 30.4%, d_2 51.5%.

Copyrolysis of (15) and heptanal at 700°C

Generator and heptanal were mixed in a 1:3 ratio and pyrolyzed at 700°C. Collection of the product mixture by vpc resulted in four components with m/e 207 (4.1%), 221 (5.1%), 112 (9.8%), 281 (5.6%). Also trace amounts of components with m/e 279, 186, 355 and higher molecular weight siloxanes were observed. The components with m/e 207 and 281 were seen to be cyclic siloxanes by having identical mass spectra, retention times, and ir spectra as authentic samples. The component with m/e 112 had identical retention times, ir, and nmr as an authentic sample of 1-octene purchased from Aldrich Chemical Co. The component with m/e 221: nmr (CCl) 0.00 (s, 1H), 0.24 (s, 1H), 0.24 ppm (s, 6H); ir (CCl_4) 2960 (vs), 2900 (m), 1425 (w), 1340 (w), 1260 (s), 1120 (w), 1050 (s), 940 (vs), 870 (vs), 700 (s); mass spectrum (70 eV) m/e (rel intensity) 221 (100), 208 (3), 206 (6), 191 (2), 189 (5), 147 (9), 132 (6), 130 (4), 104 (14), 96 (4), 73 (80), 59 (8), 45 (7). Anal. calcd for $C_7H_{21}O_2Si_3$: 221.0849. Found: 221.0843. The component at m/e 279 could never be isolated but the mass spectrum indicated a siloxane with peaks at m/e 279, 221, 206, 147, 132, 73. Further elucidation was not made.

Copyrolysis of cyclobutane generator (15) and deuterated heptanal at 700°C

Generator and heptanal were mixed in 1:3 ratio and pyrolyzed at 700°C. Collection was with the vpc and the mass spectra (18 eV) m/e (rel intensity 207 (100), 208 (40), 209 (20), 210 (8); 281 (100), 282 (50), 283 (28), 284 (101), 285 (3); 221 (75), 222 (100), 223 (585), 224 (37.5), 225 (8.3); 279 (100), 280 (100), 281 (63), 282 (37), 283 (21), 214 (10); reference spectra (18 eV) m/e (rel intensity) 207 (100), 208 (20), 209 (11); 281 (100), 282 (36), 283 (20), 284 (4); 221 (100), 222 (27), 223 (18); 279 (100), 280 (28), 281 (24), 282 (16), 283 (8).

Trimethylsilylheptenolate

Heptanal (57 g), dimethylformaamide (200 ml), triethylamine (121 g) and chlorotrimethylsilane (65.2 g) were added together to flame dried three neck 1000 ml flask with magnetic stirring bar and refluxed for 48 hours with nitrogen to keep it dry (76). Work up included cold $NaHCO_3$ extractions, one quick cold 5% HCl extraction, followed by a $NaHCO_3$ extraction, then dried (Mg SO_4) and distilled (bp 68°C/11 mm). vpc indicated two isomers which were separated.

cis-Isomer: nmr (CCl_4)δ 0.17 (s, 9H), 0.97 (m, 3H), 1.27 (m,6H), 2.02 (d, 2H, J = 7Hz), 4.4 (q, 1H, J = 7Hz), 6.04

ppm (d of t, 1H, J = 7Hz, 1.3 Hz), mass spectrum (70 eV) m/e (rel intensity) 186, (3), 171 (5), 129 (23), 75 (11), 73 (100). Anal. calcd for $C_{10}H_{22}SiO$: C, 65.14; H, 12.03; Si, 15.19; O, 8.68. Found: C, 6525, H 12.02, Si, 14.95.

trans-Isomer: nmr (CCl_4)δ 0.15 (s, 9H), 0.95 (m, 2H), 1.3 (m, 6H), 1.8 (m, 2H), 4.84 (m, 1H), 6.07 ppm (d of t, 1H, J = 12Hz, 1.7 Hz), mass spectrum (70 eV) m/e (rel intensity) 186 (8), 171 (13), 129 (62), 75 (25), 73 (100). Anal. calcd for $C_{10}H_{22}SiO$: C, 65.14; H, 12.03; Si, 15.19; O, 8.68. Found: C, 65.17; H, 12.04; Si, 14.87.

Control pyrolyses

The following substances were put through the heated tube at 700°C under the same conditions. The results were similar in that besides a few very volatile components, these components were isolated in quite pure form. 4-Methyl-2-pentanone, heptanal, mixture of trimethylsilylheptenolates , 1-octene.

1,1-Di-n-butyl-1-silacyclobutane

To a three-fold excess of n-butyl magnesium chloride was added 1,1-dichloro-1-silacyclobutane (90) and it was refluxed overnight. Usual work-up with dilute HCl, $NaHCO_3$, NaCl, the etheral solution was dried ($MgSO_4$) and the ether evaporated. The resulting mixture was distilled and found to contain 82.5% di-n-butyl-1-silacyclobutane: bp 92°C (1.9 mm); nmr (CCl_4) 1.32 (t, 8H, J = 4.5 Hz), 1.86 (m, 14H), 2.00 ppm (quint, 2H); ir (neat) 2960 (vs), 2920 (vs), 2820 (vs), 1460 (m), 1120 (s), 1080 (w); mass spectrum (70 eV) m/e (rel intensity) 184 (10), 156 (46), 143 (14), 129 (82), 99 (100), 81 (30), 86 (92), 85 (40), 72 (40), 71 (100), 70 (72).

Diphenylethynyldimethylsilane

Ethylbromide (24 g) was added to magnesium and when cooled, phenylacetylene was added to the Grignard (91). After 15 minutes, dimethyldichlorosilane (12.8 g) was added and left stirring for 24 hours. Work up by H_2O, NaCl dried ($MgSO_4$) and evaporation of ether. Recrystallization twice in Skelly A gave 1.40 gms white crystals mp 78-79°C (92). A second crystallization gave 2.85 gms: nmr (CCl_4)δ 0.48 (s, 6H) 7.26 ppm (m, 12H); mass spectrum (70 eV) m/e (rel intensity) 264 (7), 249 (16), 205 (13), 173 (68), 162 (10), 161 (10), 159 (10), 145 (18), 144 (70), 143 (100), 135 (29), 131 (10).

Reaction of diphenylethynyldimethysilane and hydrogen bromide

Hydrogen bromide gas was bubbled into a solution of 1.0 g silane and 150 ml $CHCl_3$ (93). The crude product had nmr showing many different silyl methyls at 0.47, 0.32, 0.08, 0.15, 0.17 ppm. Separation on silica gel column with Skelly B resulted in α-bromostyrene determined from nmr and mass spectrum (M^+182) and α,β-dibromostyrene (M^+260). Other components M^+170 (w/Si-Me), M^+174 were observed, but not elucidated.

Reaction of n-butyllithium with diphenylethynyldimethylsilane

n-BuLi (0.024 mols) was added to 1 g silane in 50 ml dry ether (93). A clear colorless liquid resulted. Thick layer preparative chromatography (silica gel) with Skelly B as solvent resulted in one basic compound M^+216. nmr (CCl_4)δ 0.3 (s, 6H), ca 1.2 (m, 9H), ca 7.82 ppm (m, 5H). This was consistent with n-BuSiMe$_2$Ph.

Hydrogenation of diphenylacetylenyldimethylsilane with Pd/BaSO$_4$

Hydrogenation of dyphenylacetylenylsilane was carried out three different times, altering conditions (quinoline-2 drops/10 ml MeOH, 10 ml byridine-solvent, quinoline-4 drops/10 ml MeOH). The amount of hydrogen used varied from excessive to equivalent amounts to less than equivalent amounts. In all cases, hydrogenation occurred seemingly without any selectivity. A mixture of diacetylenic silyl methyls (0.48 ppm δ), transolefin, acetylenic (0.39 ppm) trans, trans (0.29), cis, acetylenic (0.24), cis, trans (0.15) cis, cis (0.01 ppm) were observed.

Hydroboration of diphenylacetylenylsilane

Diphenylacetylenylsilane (1 g) was added to $NaBH_4$ and borontrifluoride etherate (94). The nmr indicated a mixture of acetylenic and styryl silanes with a ratio 28.5% to 71.5% respectively at 0.48 and 0.24 ppm. The latter has one styryl and one phenylacetylene. Maximum conditions came with using R_2BH at 0^oC in 10% excess for one half hour in diglyme when cis, cis (0.02 ppm δ) (10%) and cis-trans (0.10 ppm δ) (55%) were isolated from column chromotography (silica gel with Skelly B).

Photolysis of di-cis-styryldimethylsilane

A Hanovia lamp (450 watt) was put into a solution of 0.430 g distyrylsilane and 450 ml dry ether (95). The distyrylsilane was 95% di-cis. After 30 minutes the simple olefin doublet in nmr split and much isomerization to trans was evidenced. After 70 minutes about half of the cis styryl groups had isomerized. At no time was there any evidence for cyclobutyl protons or an increase in phenyl protons due to formation of 1,4-dipheylbutadiene.

di-trans-Styryldimethylsilane

Styryl magnesium bromide (96) was prepared and kept cool < 15°C. Dimethylchlorosilane was added slowly and left overnight. Workup with H_2O, dry ($MgSO_4$), and evaporation (under reduced pressure) of ether gave mixture: styrene (36.7%), cis, cis (0.017 ppm δ) (40%), cis, acetylene (0.16 ppm δ) (8%), trans, trans (0.32 ppm δ) (25.6%), and trans acetylene (.39 ppm δ) (25.6%). The di-olefin could be concentrated by column chromatography (silica gel) with Skelly B.

Photolysis in rayonette of di-trans-styryldimethylsilane

A number of attempts were made to close the system by a 2 + 2 cycloaddition (95). When d_6-acetone was used with di-trans olefin at 2537 Å in quartz, very little change occurs. At 3000 Å in pyrex, the 0.39 peak decreases and one at 0.19 increases. More splitting in the olefinic region is observed. With benzophenone in CCl_4, the acetylenic peaks at 0.15 and 0.39 grew at the expense of the olefinic protons which disappeared until only diacetylene was observed.

Dimethylsilacyclobutane (15)

To a three-fold excess of MeMgI was added 1,1-dichloro-1-silacyclobutane (90) and left to reflux overnight. Work up included dilute HCl, $NaHCO_3$, dried ($MgSO_4$) and distilled:

bp 82°C (760 mm); nmr (CCl_4) 0.3 (s, 6H) 1.0 (t, 4H, J = 8Hz), 2.1 ppm (quint, 2H, J = 8Hz); ir (neat) 3960 (vs), 2930 (vs), 1420 (w), 1390 (m), 1245 (vs), 920 (s), 905 (s), 880 (s), 840 (s), 800 (s), 730 (s), 700 (s), 640 (s); mass spectrum (see Table 1 , page 13).

Pyrolysis of octamethylcyclotetrasiloxane

Pyrolysis (62) of the octamethylcyclosiloxane at 750°C gave three products which were separated on the vpc (8' x 1/4" DC-550 Silicone Fluid on Chromasorb P) to give hexamethylcyclotrisiloxane: mp 64°C; mass spectrum (70 eV) m/e (rel intensity) 207 (50), 149 (100), 132 (22), 131 (10), 117 (25), 116 (15), 115 (30), 105 (16), 104 (16), 103 (9), 73 (25).

Octamethyl cyclotetrasiloxane

Mass spectrum (70 eV) m/e (rel intensity 281 (100), 265 (6), 207 (7), 132 (12), 73 (9); ir (neat) 3000 (ms), 3000 (ms), 1430 (mw), 1270 (s), 1085 (vs), 820 (vs).

Decamethylcyclopentasiloxane

Mass spectrum (70 eV) m/e (rel intensity) 355 (100), 340 (14), 266 (26), 105 (13), 77 (8), 75 (9), 74 (19), 73 (75).

SUMMARY

A method for producing a silicon-carbon double bond of the (p-p) π type was developed. The advantage of using 2,3-bis (trifluoromethyl)-7,7-dimethyl-7-silabicyclo [2.2.2] octa-2,5-diene over 1,1-dimethyl-1-silacyclobutane include its irreversibility and its lower temperature (400°C) required for its pyrolysis. Neither the number of steps, the overall yields, nor the ability to have various substitution offer any great advantage. While the expense at present might be slightly more due to the high cost of hexafluoro-2-butyne, the probable use in the future of other cheaper acetylenes will make this a very economical source of silaalkene.

The additional advantage of photolytic elimination of silaalkene at much lower temperatures, although not completely worked out, is quite appealing.

Perhaps the most dramatic result of this method of silaalkene generation is the fascinating possibilities, heretofore only dreamed about, that are implied. These will surely be most instrumental in elucidating a very basic, yet still poorly understood part of chemistry. The possibility of silabenzene produced by a thermal cleavage to examine cyclic conjugation with or without d-orbital participation (97) seems now to be much more than a fancy.

The substitution of various groups on silicon and the methylene will allow a more thorough investigation of the silicon-carbon π-bond and perhaps even the isolation of some species are within reach. Changing the methylene group for other heteroatoms (O, S, NR) offers a tremendous amount of hope for studying in the near future (p-p) π-bonding with silicon to other atoms.

In the meantime, the reaction of silaalkene with non-enolizable carbonyl-containing compounds suggests other generators of oxosilanes, thioxosilanes, and iminosilanes from four-membered rings produced under conditions milder than 400°C. These newly generated species, besides being most interesting in themselves, will come from compounds whose properties will be equally, if not more, important.

It is believed by the author that this work, rather than being definitive, terminal or conclusive, is only the beginning of what will surely be a most productive and worthwhile area of investigation with both synthetic and theoretical importance.

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ACKNOWLEDGMENTS

It is impossible to mention each person who has given assistance and encouragement in making this work a reality. While I am grateful to many, I would like to note a few to whom I am especially appreciative. I would like to acknowledge Dr. T. H. Kinstle, now at Bowling Green State University, Bowling Green, Ohio, for having introduced me to and intrigued me with the problem of multiple bonding in silicon. I am especially grateful to Dr. T. J. Barton for his ingenuity and enthusiastic direction in getting some very interesting results. His constant efforts at being a good research group leader has made my years at Iowa State University most interesting and enjoyable.

Dr. C. L. McIntosh did the flash pyrolysis work, Dr. J. Pecansky ran the argon matrix isolation studies, and Dr. J. Gerlock assisted with esr experiments. Dr. W. Atwell of Dow Corning, Midland saved us a lot of time with his synthesis. I shall remain ever indebted to each of them.

There are many faculty members and group members to whom I owe a great deal, but I will not attempt to single out anyone. I must thank my mother not only for her support throughout, but also for her assistance in preparing this thesis. Finally, a big thanks to my wife, Ruth Ann, and

daughter Natalie Joan for their encouragement and sometimes perseverence through all of this. We are all glad for this part to be completed.