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THE UNIVERSITY OF ALBERTA

THE THERMAL DECOMPOSITION OF 7,8-DISILABICYCLO[2.2.2]OCTA-2,5-DIENES: EVIDENCE FOR THE TRANSIENT EXISTENCE OF SILICON-SILICON DOUBLE BONDS

by

David Roark

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

FALL, 1970

UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

THE THERMAL DECOMPOSITION OF 7,8-DISILABICYCLO[2.2.2]OCTA-2,5-DIENES:
EVIDENCE FOR THE TRANSIENT EXISTENCE OF SILICON-SILICON DOUBLE BONDS

submitted by David Roark in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

G. J. D. Peddle
Supervisor

Graham

H. Baadsgaard

John Hogg

Karl R. Kopecky

A G Brook
External Examiner

Date Sept. 17, '70

TO MY WIFE

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ABSTRACT

In order to determine whether a transient species containing a silicon-silicon double bond could exist, a series of 7,8-disilabicyclo[2.2.2]octa-2,5-dienes were synthesized and their reactions studied. Two synthetic routes to the desired disilabicyclooctadienes were attempted. The first route involved the synthesis of a 5,6-disila-1,3-cyclohexadiene followed by the Diels-Alder addition of an acetylenic dienophile. The synthesis of the disilacyclohexadiene was accomplished, but the Diels-Alder addition could not be made to take place. The second route to the desired disilabicyclooctadienes involved the addition of 1,1,2,2-tetramethyl-1,2-dichlorodisilane to various aromatic radical-anions. In this manner three different 7,8-disilabicyclo[2.2.2]octa-2,5-dienes were prepared: the anthracene, naphthalene, and biphenyl adducts of tetramethyldisilene.

These three compounds were found to decompose thermally in a sealed tube to give respectively; anthracene, naphthalene, and biphenyl; and a viscous white oil. A flow pyrolysis gave two major volatile silicon containing products: 1,1-dimethyl-1,3-disilacyclobutane and 1,3-dimethyl-1,3-disilacyclobutane.

Pyrolysis of the naphthalene adduct in the presence of silicon hydrides gave 1,1,2,2-tetramethyldisilane as a major product. Pyrolysis of all three adducts in the presence of various dienes resulted in the transfer of the tetramethyldisilene.

A mass spectral study of the three adducts indicated that they should thermally dissociate to give tetramethyldisilene. This evidence as well as the evidence gained by the various reactions mentioned above led us to postulate the formation of a transient species containing a silicon-silicon double bond.

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CHAPTER 1: INTRODUCTION

PREVIOUS ATTEMPTS TO MAKE pπ BONDS TO SILICON

Since the turn of the century there have been attempts to prepare compounds containing pπ bonds to silicon. Some investigators have reported the isolation of compounds containing double bonds to silicon; however, in all the cases which have been subsequently reinvestigated, the reported compounds were not found. Recently there has been evidence that a number of unstable intermediates containing the elusive double bond to silicon do, in fact, exist.

Silicon-Oxygen Double Bonds

In 1907 Potter[1] first reported the high temperature (1300°K) reaction between silicon dioxide and elemental silicon to give gaseous silicon monoxide. Subsequent to this discovery there were numerous spectroscopic and thermochemical investigations of this reaction. These investigations were reviewed in 1954 in a paper by Brewer and Edwards.[2] Brewer and Edwards state that the data from these investigations indicate that gaseous silicon monoxide is monomeric and the silicon analogue of carbon monoxide.

$$\mathrm{SiO_2 + Si \xrightleftharpoons{1300^\circ K} 2\ SiO}$$

In 1917 Stock, Somieski, and Wintgen[3-4] studied the reactions of dibromosilane with water and reported the isolation of a volatile compound which they believed to be the silicon analogue of formaldehyde. It is now well known that silicon dihalides react rapidly with water to form polysiloxanes,[5] and there has been no subsequent verification of the formation of silicon-oxygen double bond contain-

$$\mathrm{H_2SiBr_2 + H_2O \longrightarrow H_2Si{=}O + (H_2\overset{|}{Si}{-}O{-})_n}$$

ing products from these reactions. In fact, Dasent[6] reported in 1965 that there is no record of an isolable compound containing a silicon-oxygen double bond.

One of the reasons for failure to form the silicon-oxygen double bond is the extreme ease with which silicon diols undergo intermolecular dehydration to give polymers.[5]

$$R_2Si(OH)_2 \longrightarrow (\text{-}O\text{-}SiR_2\text{-})_n + H_2O$$

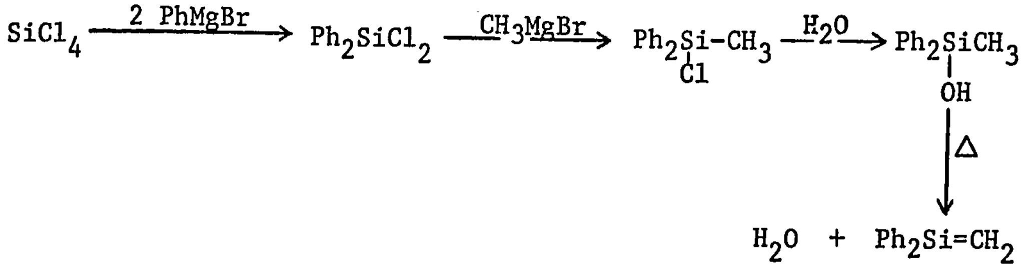
In 1954, Sommer and Tyler reported an attempt to prepare a silicon-oxygen double bond.[7] They prepared di-(tert. butyl)-dihydroxysilane, hoping that the bulky t-butyl groups would make intermolecular dehydration impossible, and this was found to be the case. However, they found that no intramolecular dehydration occurred either, even when the material was heated to temperatures as high as 450°C. in the presence of calcium oxide, alumina, or soda-lime.

Silicon-oxygen double bonds have frequently been proposed in the mass spectral fragmentation of silyl ethers.[8] These fragments can generally be represented as below:

$$R_2Si^{+}\text{-}O\text{-}R' \longleftrightarrow R_2Si{=}O^{+}\text{-}R'$$

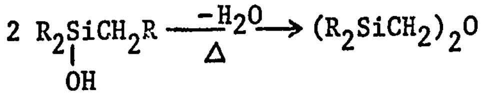
Silicon-Carbon Double Bonds

In 1912, Schlenk and Renning[9] reported the isolation of 1,1-diphenyl-1-silaethene. They obtained this product by treating tetrachlorosilane with two equivalents of phenyl magnesium bromide, followed by one equivalent of methyl magnesium iodide. To the resulting mixture they added water and then, by distillation, they isolated a product whose analysis and molecular weight were consistent with the structure: $Ph_2Si{=}CH_2$. The route they postulated is shown below. They reported that their product did not react with bromine or potassium permanganate.



$$SiCl_4 \xrightarrow{2\ PhMgBr} Ph_2SiCl_2 \xrightarrow{CH_3MgBr} Ph_2\underset{Cl}{Si}{-}CH_3 \xrightarrow{H_2O} Ph_2\underset{OH}{Si}CH_3 \xrightarrow{\Delta} H_2O + Ph_2Si{=}CH_2$$

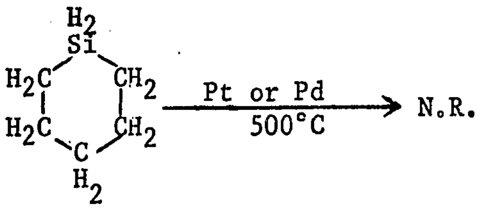
Kipping[10] repeated Schlenk and Renning's[9] experiment and found that he could not duplicate the results which they had reported. In this same paper[10] Kipping reviews the unsuccessful attempts he had made to generate a silicon-carbon double bond by dehydration of silanols and by the thermal dehydrohalogenation of chlorosilanes.



$$2\ \underset{\textstyle OH}{R_2\overset{}{Si}}CH_2R \xrightarrow[\Delta]{-H_2O} (R_2SiCH_2)_2O$$

$$R_2SiClCH_2R \xrightarrow{\Delta} N.R.$$

In 1954, West[11] attempted unsuccessfully to prepare silicon containing analogues of benzene and toluene by the dehydrogenation of 1-silacyclohexane and 1-methyl-1-silacyclohexane with platinum and palladium catalysts at 500°C.

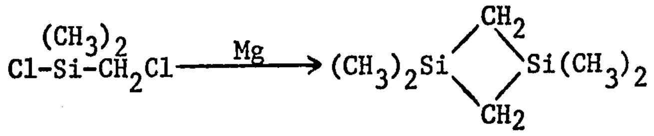


Fritz and Grobe[12] reported in 1961 the isolation of 2,4,4-trimethyl-2,4-disila-2-pentene, 1, from among the products obtained by

$$(CH_3)_4Si \xrightarrow{\Delta} (CH_3)_2Si{=}CHSi(CH_3)_3$$

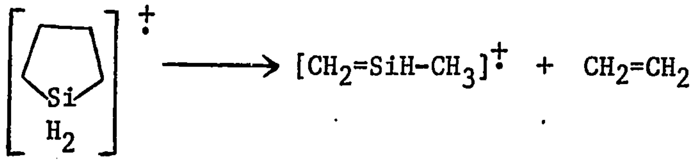
1

the pyrolysis of tetramethylsilane. However, in later publications[13-14] it was shown that this compound was identical to an authentic sample of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, 2.



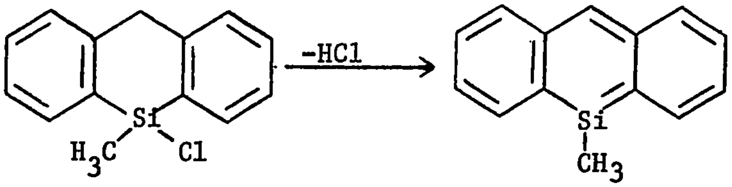
2

Van der Kelen, Volders, van Onckelen, and Eeckhaut[15] found that a fragment of high abundance in the mass spectrum of methylsilane had a mass to charge ratio of 44. They felt that it might best be represented as the radical-cation of silaethene, $(H_2Si{=}CH_2)^{+\cdot}$. Also in the mass spectral fragmentation of silacyclopentane, **3**, Duffield, Budzikiewicz, and Djerassi[16] suggested that the m/e 58 peak was the radical-cation of 2-silapropene.



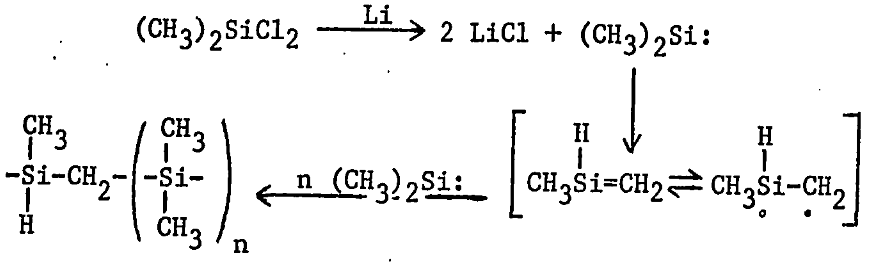
3

Jutzi[17] has reported the preparation and mass spectrum of 9-methyl-9-chloro-9,10-dihydro-9-silaanthracene, **4**. The mass spectrum of **4** showed that the main path of decomposition on electron impact is the loss of hydrogen chloride to give the radical-cation of 9-methyl-9-silaanthracene, **5**. Jutzi states that treatment of **4** with tertiary amine yielded a quantitative amount of hydrogen chloride, but no **5** could be isolated. He did not identify any other products from this reaction.



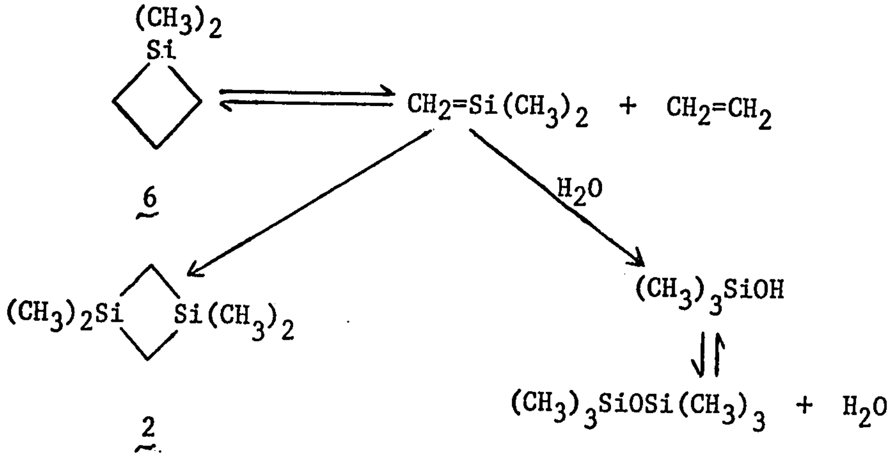
4 **5**

Nefedov, Garzo, Szekely and Shiryaev[18] suggested that an intermediate containing a silicon-carbon double bond might explain the presence of silicon-methylene-silicon bridges in the polymerization of dimethyldichlorosilane by lithium. If the dimethylsilylene initially formed were to undergo a 1-2 hydrogen shift, then the resulting 2-silapropene could be incorporated into the polymer to form the observed methylene bridges. Kirmse[19] has reported similar 1-2 hydrogen shifts in carbenes to give carbon-carbon double bonds.



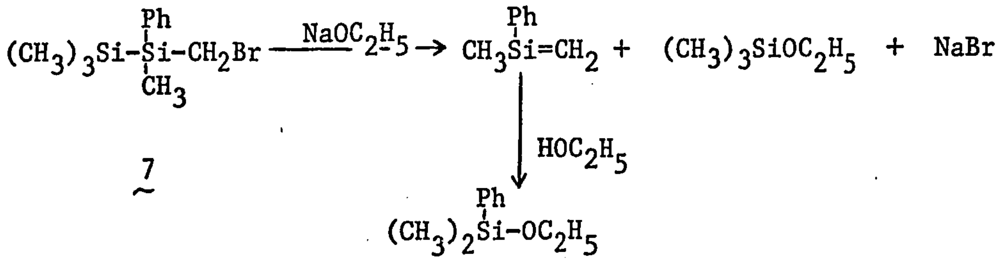
$$RCH_2\ddot{C}\text{-}H \longrightarrow R\text{-}CH{=}CH_2$$

Gusel'nikov and Flowers[20] reported in 1967 that the low pressure gas-phase pyrolysis of 1,1-dimethyl-1-silacyclobutane, 6, gave ethylene and a transient species, which they postulated to contain a silicon-carbon double bond. This species reacted with water to give trimethylsilanol and in the absence of a trap it dimerized to 1,1,3,3-tetramethyl-1,3-disilacyclobutane, 2. Based on this evidence, the reaction scheme below was proposed.



Gusel'nikov and Flowers[21] later reported a kinetic study of the thermal decomposition of 6. They found that the low pressure gas-phase thermolysis of 6 was a first order reaction which was inhibited by ethylene. These two findings help substantiate the first step of the proposed reaction sequence. These workers also state that not only was no evidence found for diradical behavior of the 2-methyl-2-silapropene, but for this intermediate to be a diradical it must be in the triplet state and this would require a spin inversion in the first step of the decomposition. The Arrhenius parameters which were found were inconsistent with such a spin inversion.

Kumada, Jamao, Ishikawa, and Matsuno[22] suggested the formation of an intermediate containing a silicon-carbon double bond in order to rationalize the ethanolysis of 1-halomethyl-1-phenyldisilanes. For example, they postulated the reaction scheme below for the ethanolysis of 1-bromomethyl-tetramethyl-1-phenyldisilane, 7.



$$\underset{7}{(CH_3)_3Si-\underset{CH_3}{\overset{Ph}{Si}}-CH_2Br} \xrightarrow{NaOC_2H_5} CH_3\overset{Ph}{Si}=CH_2 + (CH_3)_3SiOC_2H_5 + NaBr$$

$$CH_3\overset{Ph}{Si}=CH_2 \;\big\downarrow{\scriptstyle HOC_2H_5}\; (CH_3)_2\overset{Ph}{Si}-OC_2H_5$$

Strausz and co-workers[23-24] in their study of the photolysis of methylsilane, have found strong evidence for the formation of 1-silaethene, 8, which they refer to as a 1,2-diradical. One of the primary steps on irradiation of methylsilane-d_3 at 1470Å is the molecular elimination of hydrogen-deuteride to give 1,1-dideutero-1-silaethene, 8-d_2. This intermediate, 8-d_2, then proceeds to polymerize. Photolysis at 1236Å also produces 8-d_2, but instead of polymerizing it pro-

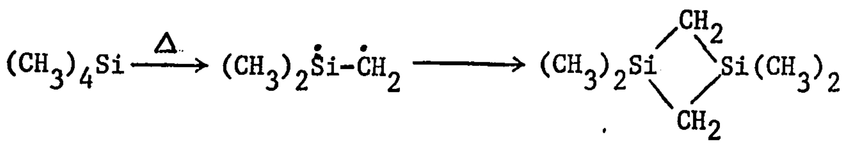
$$H_3CSiD_3 \xrightarrow{1470Å} HD + \underset{8\text{-}d_2}{H_2C{=}SiD_2} \longrightarrow \text{polymer}$$

ceeds to lose another molecule of hydrogen-deuteride to give 1-deutero-1-silaethyne. Some of the 1-deutero-1-silaethyne thus formed loses another molecule of hydrogen-deuteride to give silicon carbide.

$$H_3CSiD_3 \xrightarrow{1236Å} HD + \underset{8\text{-}d_2}{H_2CSiD_2} \longrightarrow HD + HCSiD \longrightarrow HD + CSi$$

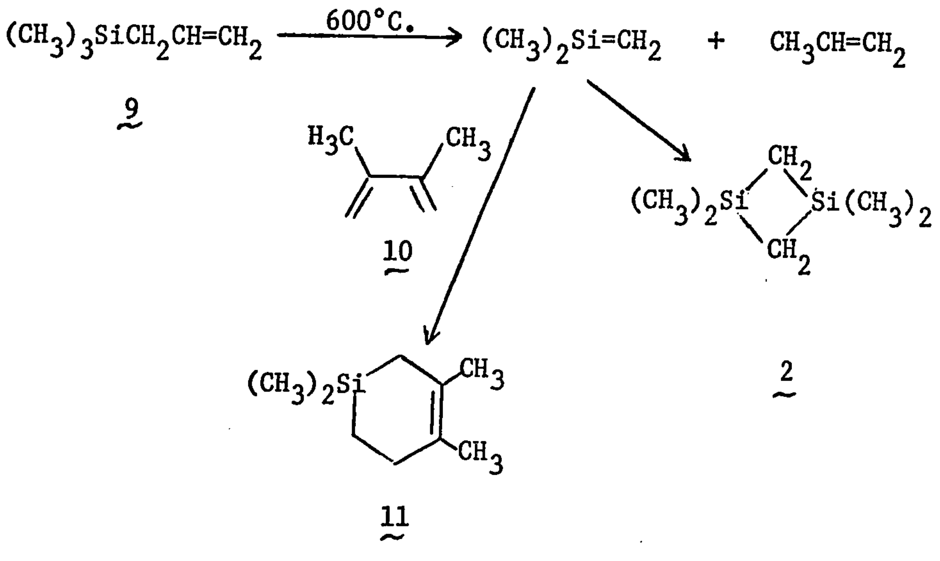
Strausz and co-workers[24] also mention that the 1,2-diradical, 8, appears to be relatively stable.

Fritz, Grobe, and Kummer[25-26] have suggested the intermediacy of silicon containing 1,2-diradicals in the pyrolysis of tetramethylsilane. In this pyrolysis there are a great many products formed,



most of which can be rationalyzed by radical intermediates.

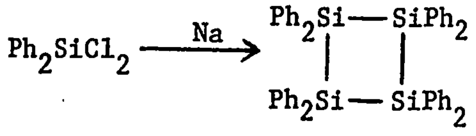
More evidence for the transient existence of compounds containing a silicon-carbon double bond was reported by Bailey and Kaufman.[27] They found that pyrolysis of trimethylallylsilane, 9 at 600°C. gave the disilacyclobutane, 2. When 2,3-dimethyl-1,3-butadiene, 10, was added to the reaction mixture, the product obtained was 1,2,4,4-tetramethyl-4-sila-1-cyclohexene, 11. They rationalized these results by suggesting the formation of 2-methyl-2-silapropene as an intermediate.



Silicon-Silicon Double Bonds

The earliest reported attempt to form a silicon-silicon double bond was by Kipping in 1921.[28-32] He found that one of the products of the reaction between diphenyldichlorosilane and sodium was highly reactive; he called this product the "unsaturated" compound, although he soon realized that it did not contain a silicon-silicon double bond. The structure he finally assigned to this "unsaturated" compound was the 1,4-diradical of 1,1,2,2,3,3,4,4-octaphenyltetrasilane.

Gilman, Peterson, Jarvie, and Winkler[33-34] reinvestigated the reaction of diphenyldichlorosilane with sodium. Their results showed that the highly reactive compound found by Kipping was in fact the cyclic tetramer, octaphenylcyclotetrasilane, 12.



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Kipping and co-workers[35] also looked at the reaction of phenyltrichlorosilane with sodium, but found that, rather than a silicon-silicon triple bond being formed, a polymeric mixture was produced.

In 1950, Milligan and Kraus[36] reported that the reaction of triphenylgermyl sodium and tetrachlorosilane gave, as one of the products, an amorphous material which they thought might be tetrakis-(triphenylgermyl)-disilaethene, 13. The silicon and germanium

$$Ph_3GeNa \; + \; SiCl_4 \longrightarrow NaCl \; + \; Ph_6Ge_2 \; + \; \underset{13}{(Ph_3Ge)_2Si{=}Si(GePh_3)_2}$$

analysis were in agreement with this structure, but the molecular weight determined by cryoscopic measurements in benzene gave values of 867 and 872, while the molecular weight calculated for 13 is 1271. No reactions of this compound were reported.

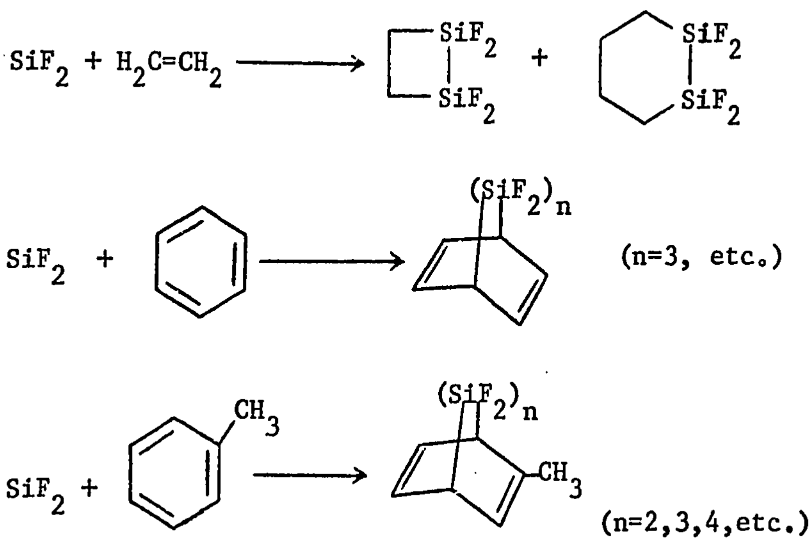
In 1958 Urry reported the preparation of a silicon analogue of hexachlorobenzene in which all of the carbons were replaced by silicon.[37] However, later in a footnote in Eaborn's book, Organosilicon Compounds,[38] Urry is reported to have reinterpreted his results "along quite different lines."

In 1965, Margrave and co-workers[39] started a study of the reactions of difluorosilylene at low temperatures. This study led to the first evidence for the existence of a highly reactive species with a molecular formula Si_2F_4.

Margrave and co-workers[40] prepared difluorosilylene, by passing tetrafluorosilane over silicon at 1000°C. and freezing the resultant products in a krypton matrix at 20°K. At this temperature the difluorosilylene is stable, and its infrared spectrum was obtained. When the difluorosilylene was allowed to warm, a new series of infrared bands began to appear at about 35°K. At 50°K. this new series of bands as well as those for difluorosilylene had all disappeared and were replaced by bands due to the final product, a difluorosilylene polymer.

A number of experiments were performed by co-condensing a reactant with the difluorosilylene at 20°K., then allowing the mixture to warm and following the reaction's progress by infrared spectrometry. In this manner it was found that the intermediates formed at 35°K. could be readily trapped. The major products were nonvolatile, but the following products could be identified in the small volatile fraction.[39-42]

$$SiF_2 + BF_3 \longrightarrow F_3Si\text{-}SiF_2BF_2$$



In order to explain these results Margrave suggested that the difluorosilylene reacted by first dimerizing to form a dimeric diradical, which then continued to add difluorosilylene to form the trimeric, tetrameric, etc. diradicals.

An ESR study[43] showed that, while the difluorosilylene was diamagnetic, as the sample was warmed a broad absorption appeared at about 35°K. This shows that at least some of the species formed were triplets.

Theoretical Calculations

The reason for the obvious difference in stability between multiple bonded compounds of the first row elements and those of the second row has been the subject of considerable discussion. Pitzer[44] showed qualitatively that repulsion of inner shell electrons in second row elements should result in a decrease in p-overlap, thus resulting in weaker multiple bonds.

Mulliken[45] performed detailed calculations using Slater models and the overlap integral,S, and concluded that the multiple bonds to second row elements should be about as strong as to first row elements, but that the single bonds between second row elements should be stronger. He therefore, rationalized the instability of compounds containing multiple bonds to second row elements as being due not to a "loosening of multiple bonds for these atoms (second row) as compared with first row atoms, but of a lesser tightening for multiple than for single bonds." However, while there is still considerable question as to the exact strength of silicon-silicon bonds, there seems to be little doubt that they are weaker than carbon-carbon bonds.[46]

Mulliken did not include d-orbitals in his calculations, but it has been subsequently shown that the inclusion of d-orbitals would have little effect.[47]

Beattie and Gilson[48] have suggested that the instability of multiple bonds to second row elements is due to the more efficient use of d-orbitals in singly bonded compounds. This argument, however, cannot apply to a silicon-silicon multiple bond.

Thus to date there is no adequate theoretical explanation for the failure to isolate stable compounds containing multiple bonds to silicon.

The purpose of this thesis is to describe the results of a systematic attempt to obtain a compound containing a methyl substituted silicon-silicon double bond: tetramethyldisilene.

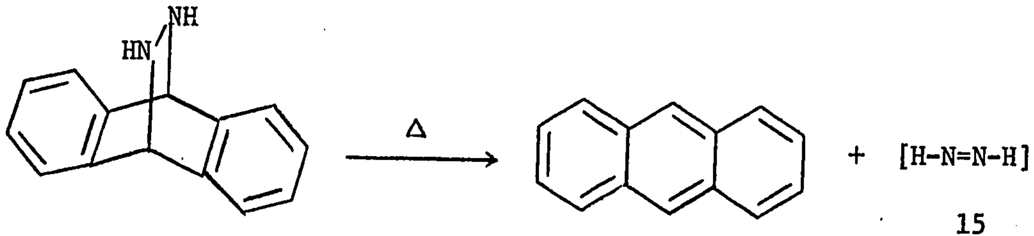
POSSIBLE APPROACHES TO TETRAMETHYLDISILENE

Once it was decided to attempt to generate a tetramethylsubstituted silicon-silicon double bond, the question of how this might best be done arose. There are three possible approaches to double bonds: Addition, combination, and elimination. Addition, which involves the addition of some reactant across a triple bond, must be ruled out as a possible approach since silicon-silicon triple bonds are unknown. Combination would require the dimerization of dimethylsilylene; this would be directly analogous to Margrave's work on difluorosilylene.[39] However, extensive studies of dimethylsilylene have failed to give products directly attributable to tetramethyldisilene.[49] Elimination seemed to offer the most promise as a method for generating silicon-silicon double bonds.

One reasonable approach might be the dehalogenation of a vicinal dihalide. However, we found that 1,1,2,2-tetramethyl-1,2-dichlorodisilane was unreactive with zinc dust, and, although this disilane reacts with alkali metals, the very presence of these alkali metals in the reaction mixture makes it difficult to find suitable traps for any tetramethyldisilene which might be formed.

The success which has been encountered using thermal decompositions to generate intermediates containing silicon-carbon double bonds,[20-21] led us to look for a suitable method for generating a silicon-silicon double bond via a thermal decomposition. One process used to generate compounds with unstable multiple bonds is the retrodiene reaction (or reverse Diels-Alder reaction).[50]

Corey and Mock[51] used the thermal decomposition of 2:3, 5:6-dibenzo-7,8-diaza-bicyclo[2.2.2]octa-2,5-diene, **14**, to generate diimide, **15**.



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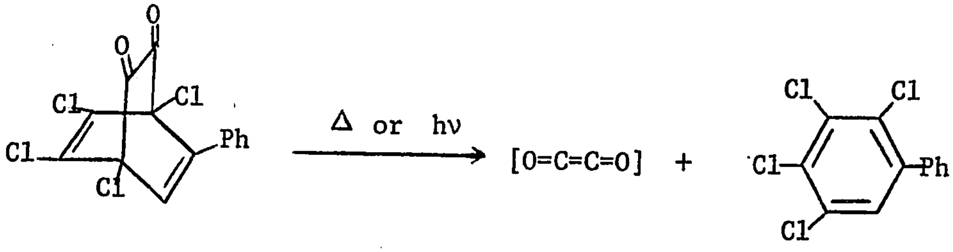
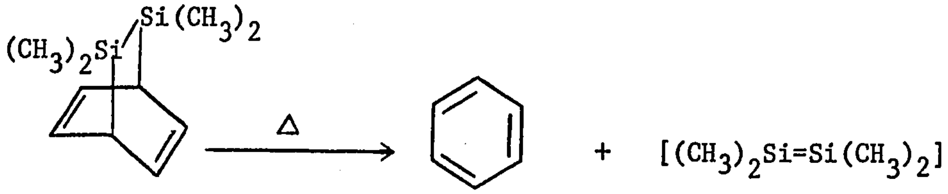
15

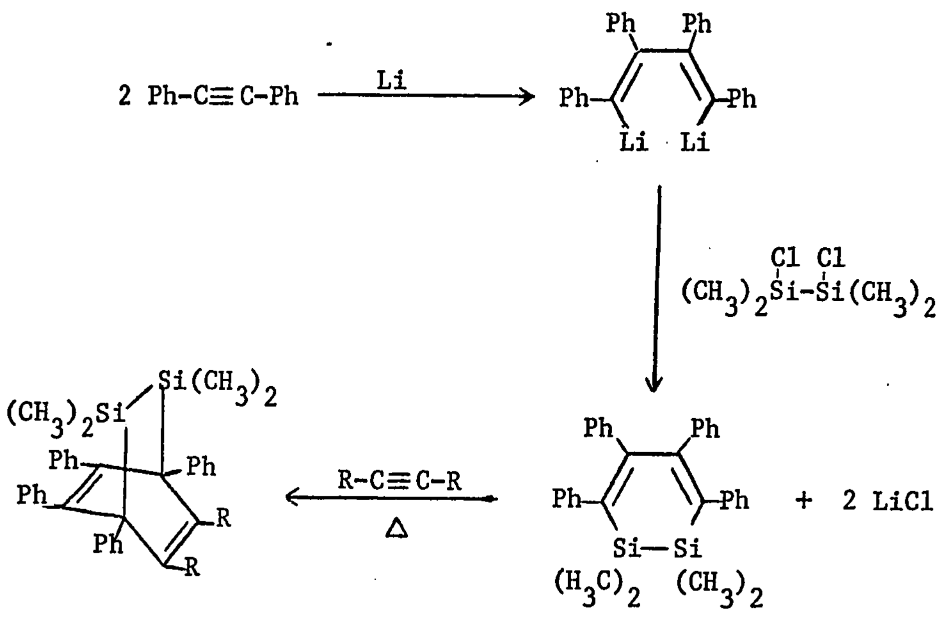
Strating, Zwanenberg, Wagenaar, and Udding[52] have used this type of approach to obtain evidence for the formation of the elusive bis-carbon monoxide by the pyrolytic and photolytic decomposition of bicyclo[2.2.2]octadienediones.

Thus it was felt that a possible route to a methyl-substituted silicon-silicon double bond might be via the thermal decomposition of 7,8-disilabicyclo[2.2.2]octa-2,5-dienes.

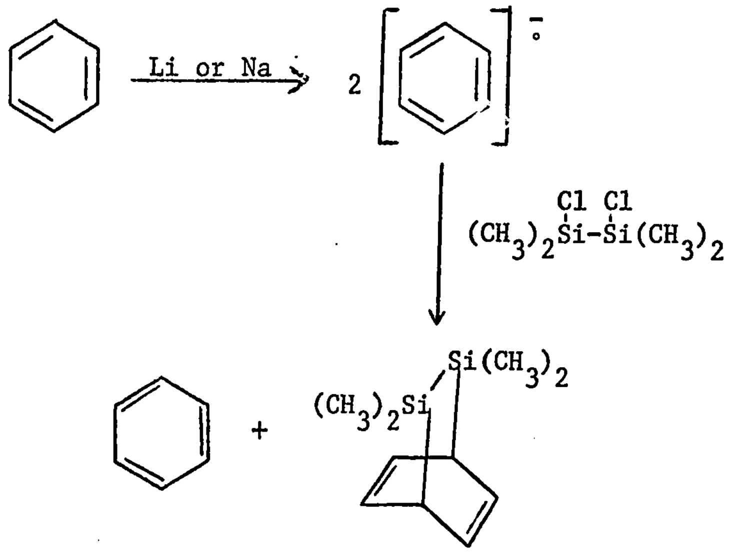




Two possible routes were devised for the synthesis of these disilabicyclooctadienes. The first was a route analogous to that used by Gilman, Cottis, and Atwell[53] in the snythesis of 7,7-dimethyl-7-silanorbornadienes.



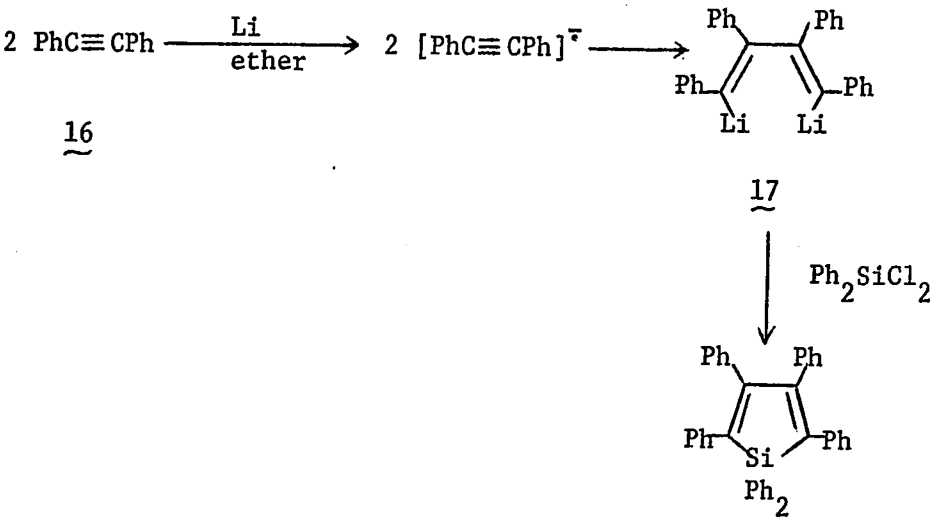
The second route would take advantage of the well-studied reaction between silicon chlorides and the radical-anions of various aromatic hydrocarbons.[54-60] In this route, 1,1,2,2-tetramethyl-1,2-dichlorodisilane would be added to the radical-anions or dianions of various aromatic hydrocarbons. This route is shown below:



CHAPTER 2: PREPARATION AND CHEMISTRY OF 1,2,3,4-TETRAPHENYL-5,5,6,6-TETRAMETHYL-5,6-DISILA-1,3-CYCLOHEXADIENE

PREPARATION

When diphenylacetylene (tolan), 16, is allowed to react with lithium in ether, it first forms the radical-anion of diphenylacetylene; this is followed by coupling of two radical-anions to form 1,2,3,4-tetraphenyl-1,4-dilithio-1,3-butadiene, 17.[61] Brayl, Hubel, and Caplier[62] used this dilithio reagent, 17, to form a number of heterocyclic analogues of cyclopentadiene. Among these was 1,2,3,4,5,5-hexaphenyl-5-sila-1,3-cyclopentadiene (hexaphenylsilole), 18. Following an analogous procedure, Gilman, Cottis, and Atwell[53] prepared 1,2,3,4-tetraphenyl-5,5-dimethyl-5-sila-1,3-cyclopentadiene, 19.



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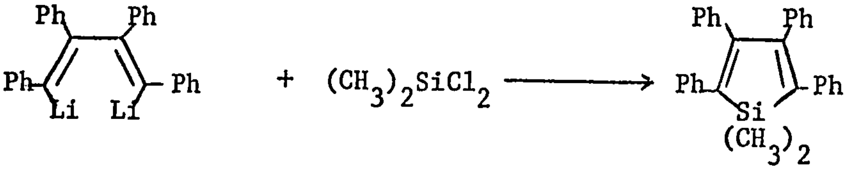

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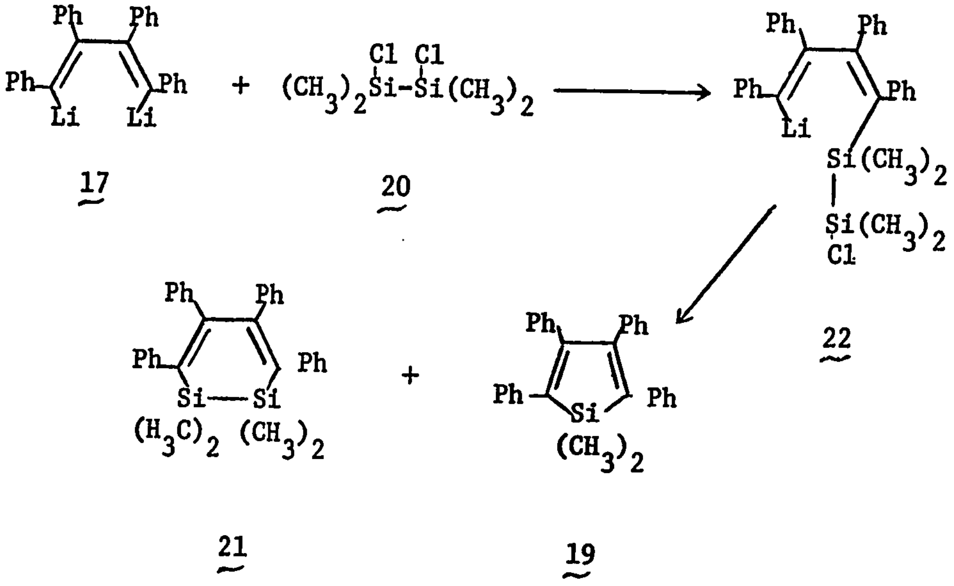
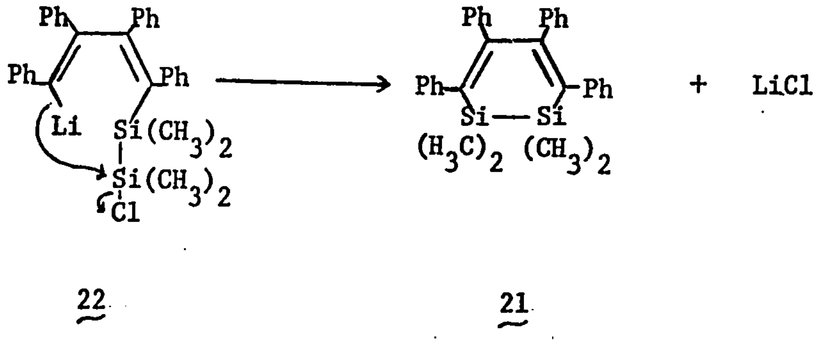
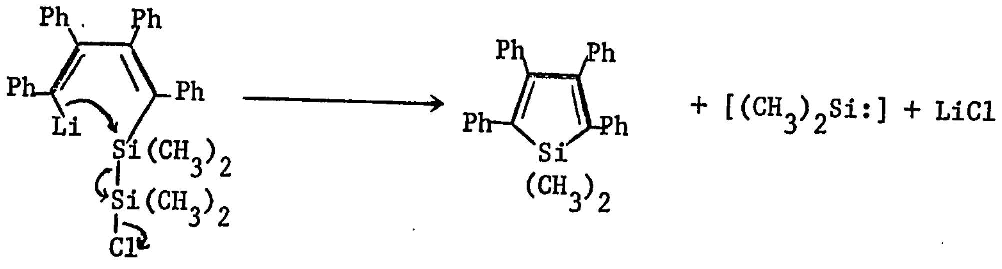
Based on these results, it was felt that the dilithio reagent, 17, should react with 1,1,2,2-tetramethyl-1,2-dichlorodisilane, 20, to give the desired 1,2,3,4-tetraphenyl-5,5,6,6-tetramethyl-5,6-disila-1,3-cyclohexadiene, 21. When the reaction was carried out we obtained two major products. One was identified as the known silacyclopentadiene, 19, which was obtained in a 13% yield. To the other product, obtained in a 35% yield, we assigned the structure of the disilacyclohexadiene, 21.



The intermediate, 22, which is formed in the first step of the reaction, can undergo ring closure by two methods. The first method involves attack on the silicon containing the chlorine atom to give the disilacyclohexadiene 21. The second method of ring closure



involves attack on the other silicon with loss of dimethylsilylene to give the silacyclopentadiene 19.



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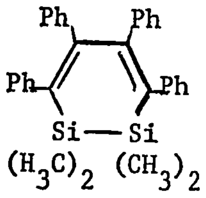
One would predict that attack would occur primarily on the most electropositive silicon, i.e., the one bonded to the chlorine atom. However, Fisher-Hirshfelder-Taylor models indicate that ring closure to form the five-membered ring is much more favorable from steric considerations, than ring closure to form the six-membered ring.

Compound 21 was a yellow crystalline solid, m.p. 168.5-170°C. It had a parent peak in its mass spectrum at m/e 472 and a carbon-hydrogen analysis in agreement with the molecular formula $C_{32}H_{32}Si_2$. Its NMR spectrum showed a multiplet at τ= 2.7-3.3 and a singlet at τ=9.8 which integrated in a ratio of 5:3 respectively. These data are consistent with the product being either 5,6-disilacyclohexadiene, 21, or the 3,6-disilacyclohexadiene, 23.



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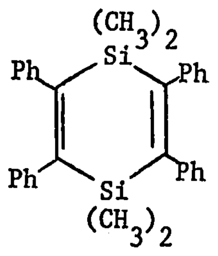

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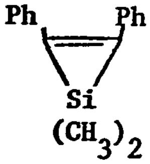
The 3,6-disilacyclohexadiene, 23, is a previously known compound. Vol'pin, Koreshkov, Dulova, and Kursanov[63] studied the reaction of dimethylsilylene with diphenylacetylene and isolated a product whose molecular weight by the Rast method in camphor was 240. On the basis of this evidence, they assigned structure 24, whose molecular weight is 236. It is known that determination of molecular weight by



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the Rast method in camphor does not work well for silicon compounds.[64] West and Bailey redetermined the molecular weight of this product by vapor phase osmometry and found it to be 475.[64] They also prepared the p-tolyl analogue of this product and found that only one aromatic methyl resonance was present in its NMR spectrum. They felt that these data indicated that the product of the reaction between dimethylsilylene and diphenylacetylene had structure 23.

In 1965 Johnson, Gohlke, and Nasutavicus[65] did a mass spectral study on Vol'pin's product. They assigned the structure 23 to the compound, partially because "the complete absence of a $[C_4(C_6H_5)_4]^{+\cdot}$ fragment...suggests that the silicon compound must have structure 23 rather than 21."[65] This reasoning is apparently fallacious since we observed that while the mass spectrum of 21 was significantly different from that of 23, it also did not have a $[C_4(C_6H_5)_4]^{+\cdot}$ fragment.

The structure of Vol'pin's compound was finally established by an X-ray study which showed conclusively that it had structure 23.[66] It, therefore, only remained for us to show that the compound we had obtained was different than that obtained by Vol'pin.

Compound 23 has a melting point of 324-326°C. and is thermally stable to this temperature.[53] Compound 21 on the other hand has a melting point of 168.5-170°C. and rapidly decomposes at 250°C. Compound **21** also gives a mass spectral fragmentation pattern which is significantly different than that reported for **23**.[65] This evidence together with the method of preparation is good evidence that **21** is in fact the 5,6-disilacyclohexadiene.

ATTEMPTED DIELS-ALDER ADDITIONS

After having synthesized 1,2,3,4,-tetraphenyl-5,5,6,6-tetramethyl-5,6-disila-1,3-cyclohexadiene, 21, the next and last step in the formation of the desired 7,8-disilabicyclo[2.2.2]octa-2,5-diene was the Diels-Alder addition of an acetylenic dienophile. When 21 was heated with a number of such dienophiles at temperatures up to 200°C. (see table I), no reaction involving the silicon compound occurred. At temperatures above 200°C. Compound 21 decomposed at a sufficient rate to rule out attempts at the Diels-Alder addition.*

Gilman, Cottis, and Atwell[53] found that the silacyclopentadiene 19 would react with dimethyl acetylenedicarboxylate at 70°C. and with diphenylacetylene at 300°C. One would expect the disilacyclohexadiene 21 to react less readily than the silacyclopentadiene 19, since in the homologous hydrocarbon series from cyclopentadiene to cis-cis-1,3-cyclooctadiene there is a great decrease in reactivity.[67] Therefore, while the disilacyclohexadiene 21 might undergo a Diels-Alder reaction with more forcing conditions, its ease of thermal decomposition prohibits the use of more extreme conditions.

TABLE I: REACTIONS OF COMPOUND 21 WITH ACETYLENIC DIENOPHILES

Dienophile	Temp.	Time	Solvent	Silicon containing products
$CH_3O_2C\text{-}C\equiv C\text{-}CO_2CH_3$	160°C	5 hr.	none	none
$PhC\equiv CPh$	200°C	21 hr.	none	none
$PhC\equiv CCH_3$	200°C	23 hr.	none	none
Benzyne	70°C	----	THF	none

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* For further information on thermal decomposition of 21 see appendix I.

In some instances Diels-Alder reactions have been promoted via photolysis.[68] However, this could not be employed since 21 is photolytically unstable; decomposing to give the silacyclopentadiene 19 as the product.** That the silacyclopentadiene 19 formed during the preparation of the disilacyclohexadiene was not due to a photo-induced side reaction was confirmed by synthesizing 21 in the dark.

Thus the failure of the Diels-Alder addition forced this route to the 7,8-disilabicyclo[2.2.2]octa-2,5-dienes to be abandoned.

** For further information of photolysis of 21 see appendix I.

CHAPTER 3: PREPARATION AND CHEMISTRY OF 7,8-DISILABICYCLO[2.2.2]OCTA-2,5-DIENES

PREPARATION AND PHYSICAL PROPERTIES

It has been known for over a century[69] that aromatic hydrocarbons will react with alkali metals to form intensely colored adducts. There are several recent reviews covering the chemistry of these aromatic radical-anions and dianions.[69-71]

The reaction between aromatic hydrocarbons and alkali metals involves the transfer of one or two electrons from the metal to the hydrocarbons forming the radical-anion or the dianion respectively. These added electrons go into the lowest unoccupied orbital (the lowest anti-bonding orbital). In figure 1, we see the highest occupied orbital and two lowest unoccupied orbitals of some typical aromatic hydrocarbon. Figure 1a is a representation of the occupancy and spacing of orbitals in the parent compound, figure 1b of orbitals in the radical anion, and figure 1c of orbitals in the dianion. In the gas phase it is slightly harder to add the second electron to form the dianion than it is to add the first. This is due to electron repulsion between the two electrons in the anti-bonding orbital.[70] When a radical anion or dianion absorbs light, an electron is promoted from the lowest anti-bonding orbital to the next lowest anti-bonding orbital, while in the parent compound an electron is promoted from the highest bonding to the lowest anti-bonding orbital. This latter transition generally requires more energy than the former two.[70]

For this reason naphthalene is colorless while its radical-anion and dianion are highly colored.[70]

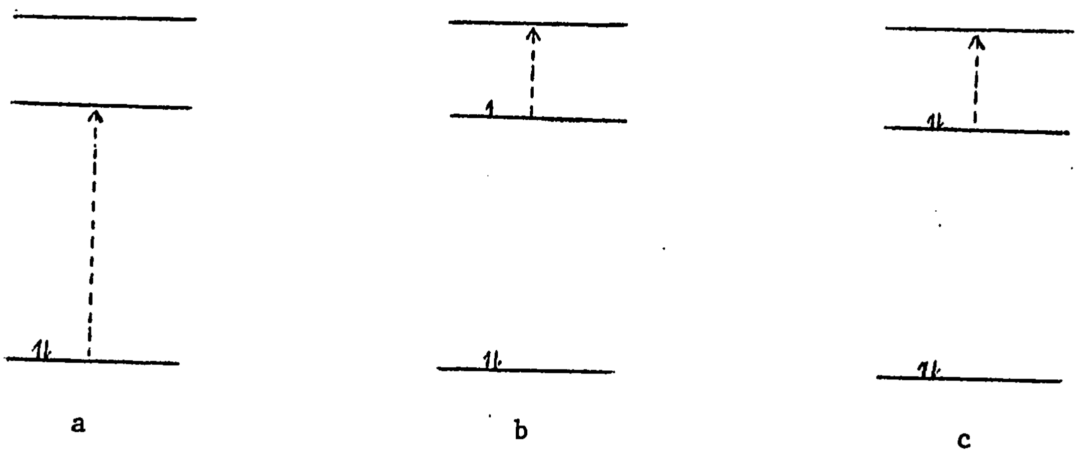
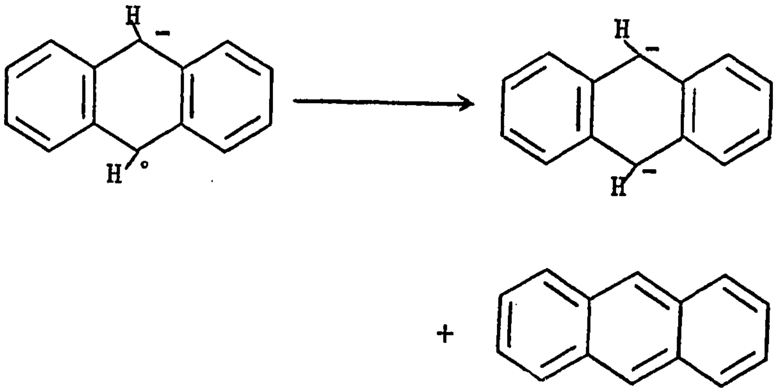
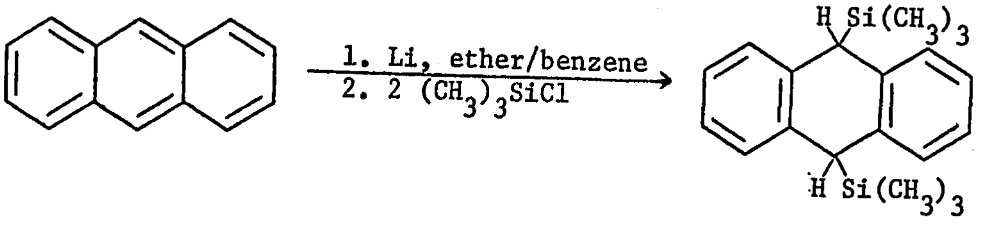


Figure 1: Electron Addition to Aromatic Hydrocarbons

The reduction of aromatic hydrocarbons in solvent is a much more complex reaction. In solvents disproportionation of radical-anions can be quite important due to the increased solvation of the dianion compared to the radical-anion.[71] For example, in THF only the disodium adduct of anthracene can be formed since the radical-anion undergoes the above disproportionation.[72] The dissociation between ion-pairs and solvated ions is influenced by the cation, solvent, and temperature.[71]



The reaction of silicon chlorides and aromatic radical-anions and dianions has been widely studied. Petrov and Chernysheva[54] reported in 1952 that shaking anthracene and lithium for 70 hr. in an ether/benzene solvent followed by addition of two moles of trimethylchlorosilane gave 9,10-bis(trimethylsilyl)-9,10-dihydroanthracene, 25. When only one mole of trimethylchlorosilane was added then 9-trimethylsilyl-9,10-dihydroanthracene, 26, was obtained after aqueous work-up.[54-55] In a similar manner Petrov and Chernysheva[56] also prepared 1-trimethylsilyl-4-phenyl-1,4-dihydrobenzene, 27; 1,4-bis-(tributylsilyl)-4-phenyl-1,4-dihydrobenzene, 28; and 1,4-bis-(trimethylsilyl)-1,4-dihydronaphthalene, 29. Chernyshev and Kozhevnikova[57] carried



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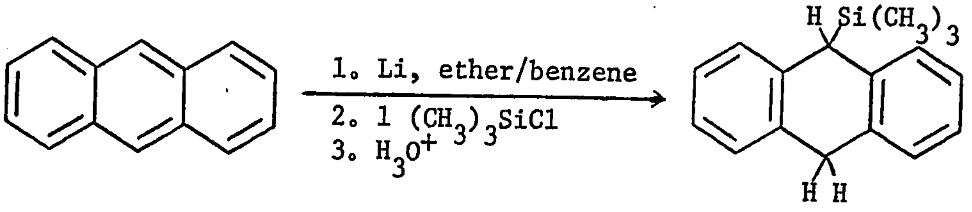

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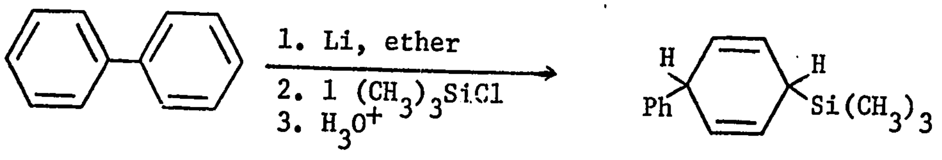

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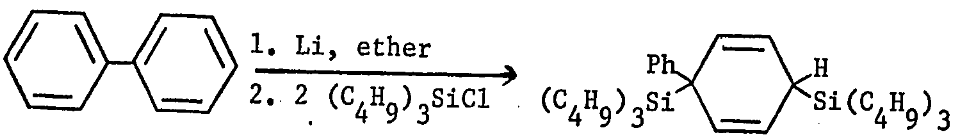

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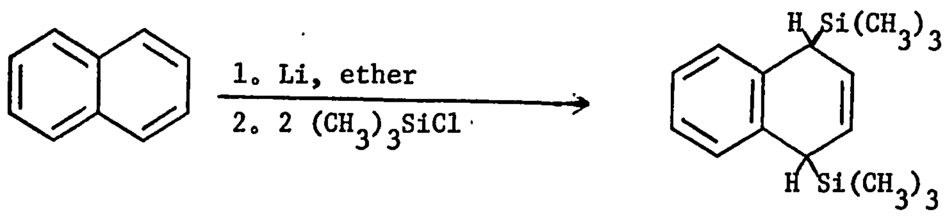

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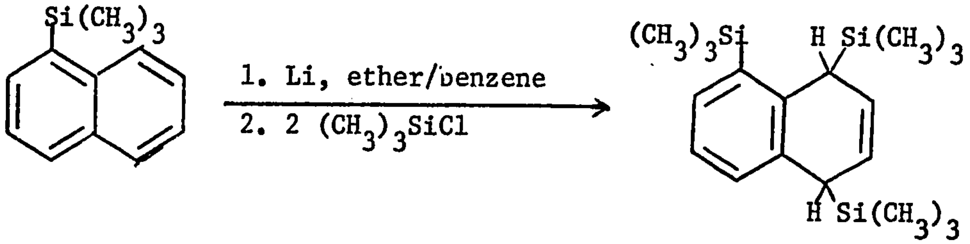
out the same reaction with 1-trimethylsilylnaphthalene, 30, and obtained 1,4,8-tris-(trimethylsilyl)-1,4-dihydronaphthalene, 31.



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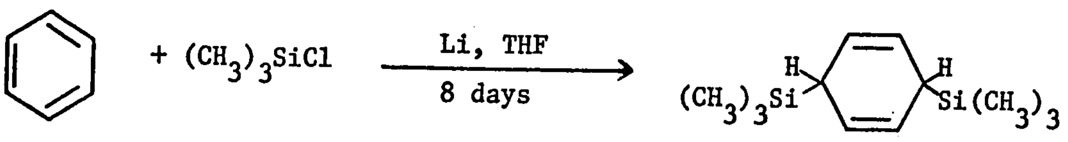
Theshelashvili, Andrianov, and Nogaideli reported the reaction of phenylmethyldichlorosilane[58] and diphenyldichlorosilane[59] with 1,4-dilithio-1,4-dihydronaphthalene to give 1,4-bis-(phenylmethylchlorosilyl)-1,4-dihydronaphthalene and 1,4-bis-(diphenylsilyl)-1,4-dihydronaphthalene respectively.

Weyenberg and Toporcen[60] reported that when a mixture of benzene, lithium, trimethylchlorosilane, and THF was stirred for 8 days at room temperature they obtained 1,4-bis-(trimethylsilyl)-1,4-dihydrobenzene, 32. Substituting chloromethoxydimethylsilane for the trimethylchlorosilane gave 1,4-bis-(dimethylmethoxy)-1,4-dihydrobenzene, 33.



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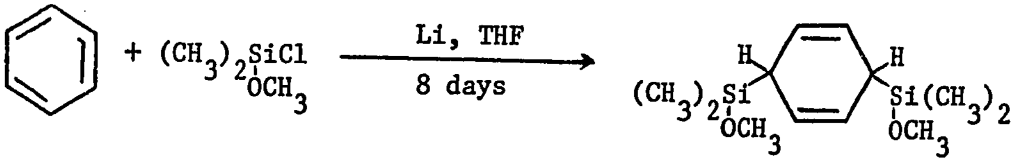

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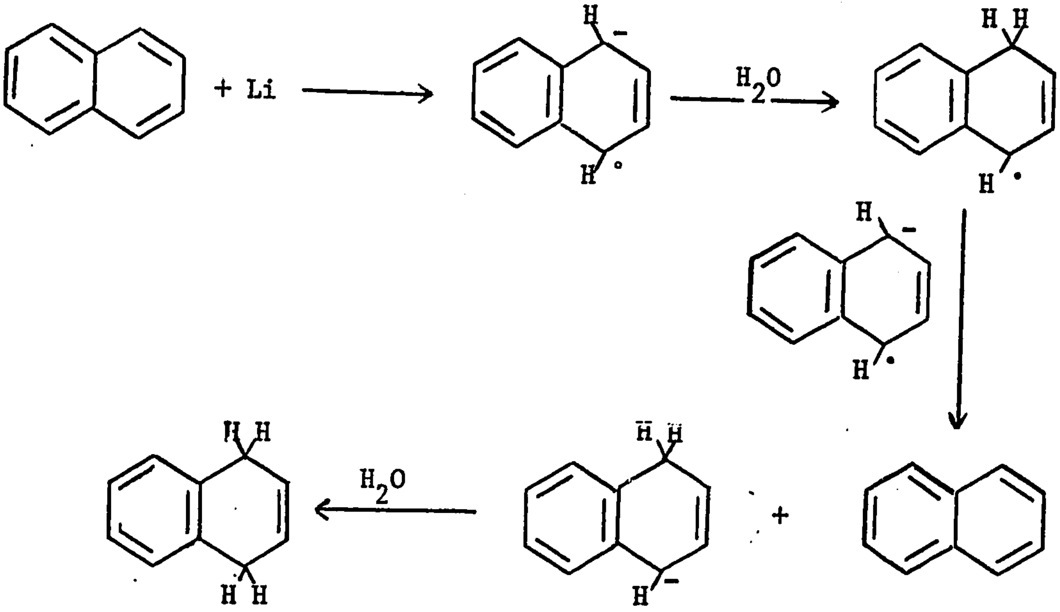
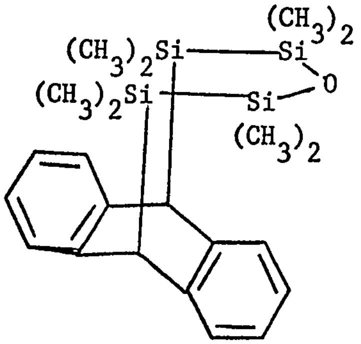
The products obtained in all of the reactions between silicon chlorides and the aromatic hydrocarbon-metal adducts were those expected from reaction of the dianion, although under many of the conditions employed it is known that the radical-anion was in fact the species present.[71] This is because the intermediate radical formed by the reaction of the radical-anion is rapidly converted into an anion via a facile electron transfer reaction. This is typified below in the reaction of the radical-anion of naphthalene with water.[72]



Thus the same product could be obtained using either the dianion or radical-anion; however, since the product we desired involved a double displacement we first investigated the use of the dianion.

When one equivalent of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, 20, was added to one equivalent of the disodium adduct of anthracene in THF at room temperature, a 2% yield of the desired 2:3, 5:6-dibenzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene, 34, was isolated following work-up.

In an attempt to increase the yield of 34, the same cation and solvent were used but the temperature was lowered to -78°C. for the addition. Following aqueous work-up the only product, 35, which could be isolated (1% yield) gave a mass spectral parent peak at m/e 426 and its NMR showed a singlet at τ=2.8, a singlet at τ=6.0, and two singlets at τ=9.7 and τ=10.2. These peaks integrated in the ratio of 8:2:12:12. This spectral data indicated the structure given below for compound 35.



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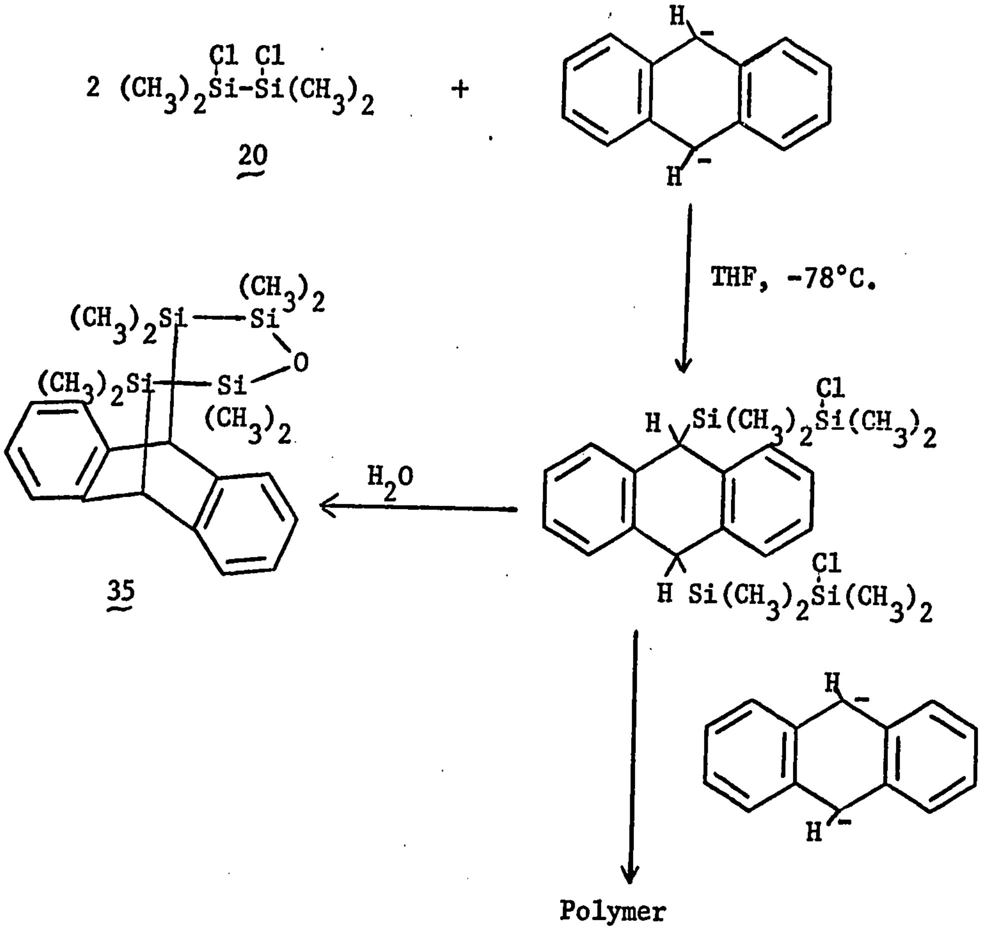
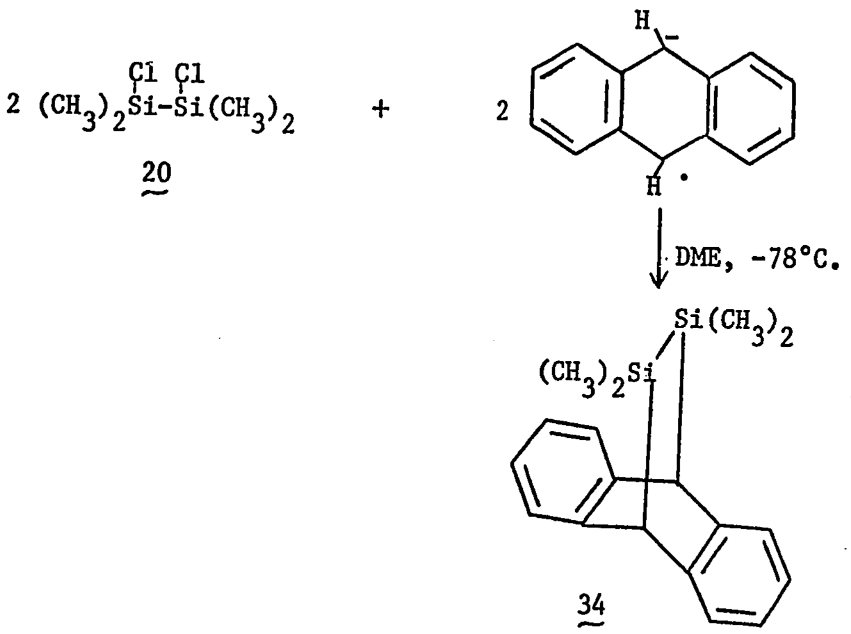
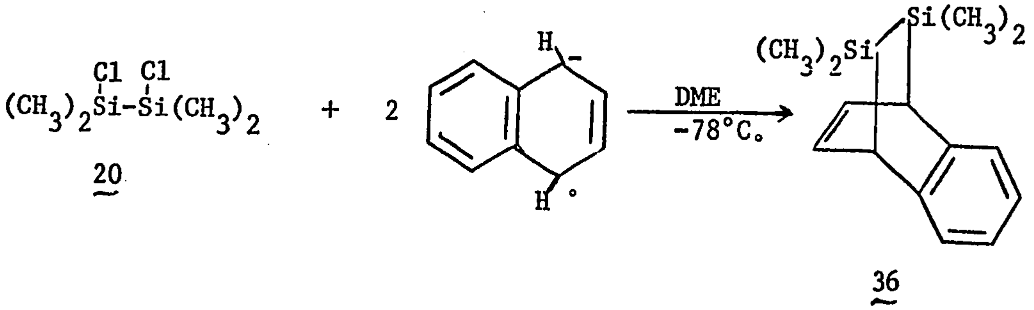
This compound, 35, was probably formed by addition of two molecules of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, 20, to one molecule of the disodium adduct of anthracene followed by hydrolysis on work-up.



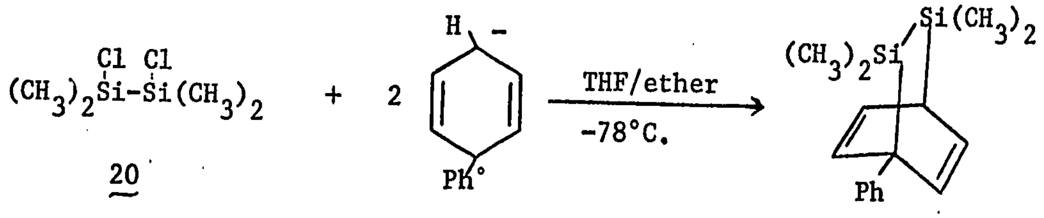
In the next attempt to increase the yield of 34, the dichlorodisilane, 20, was added to the lithium radical-anion of anthracene in 1,2-dimethoxyethane, DME, at -78°C. This gave a good yield (27%) of the desired compound, 34.



2:3-Benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene, 36, was similarly prepared in a 42% yield by adding the dichlorodisilane, 20, to the lithium radical-anion of naphthalene in DME.



Two attempts to prepare 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene, 37, by adding the dichlorodisilane, 20, to the lithium radical-anion of biphenyl first in THF then in DME, gave no isolatable product. However, a third attempt using a mixed solvent of one part THF and two parts diethyl ether gave compound 37 in a 13% yield.



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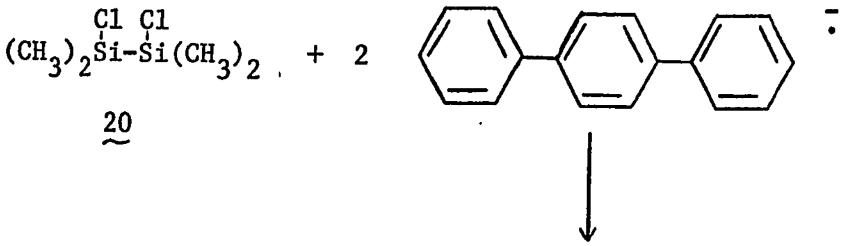
An attempt to make 7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]-octa-2,5-diene by stirring the dichlorodisilane, 20, benzene, lithium, and THF together for 11 days gave no adduct of benzene. Also an attempt to make an adduct of p-terphenyl and tetramethyldisilene gave an inseparable mixture.



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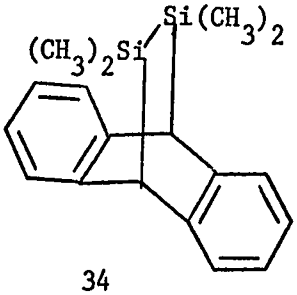
inseparable mixture

The low yields are not unexpected since obviously a variety of side reactions such as polymerization can occur.

The anthracene-tetramethyldisilene adduct, 34, is a colorless solid, m.p. 162-164°C., which sublimes at 120°C./ 0.1 Torr. Its mass spectrum shows a parent peak at m/e 294 and peaks at m/e 178, [anthracene]$^{+\cdot}$, and at m/e 116, $[(CH_3)_2Si=Si(CH_3)_2]^{+\cdot}$. The NMR spectrum of 34 showed singlets at τ=2.8, τ=6.1, and τ=9.8 with relative intensities of 8:2:12 respectively. It can be stored indefinitely in the dark in a stoppered vial, but it appears to be oxidized in the presence of light.



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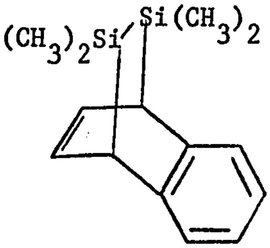
The naphthalene-tetramethyldisilene adduct, 36, is a colorless solid, m.p. 64-66°C., which sublimes at 60°C./ 0.1 Torr. The mass spectrum of compound 36 showed a parent peak at m/e 244 as well as



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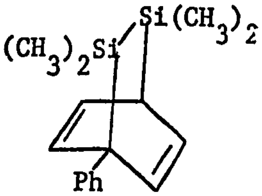
peaks at m/e 128, [naphthalene]$^{+\cdot}$, and at m/e 116, $[(CH_3)_2Si{=}Si(CH_3)_2]^{+\cdot}$. The NMR spectrum of compound 36 showed a singlet at τ=2.9, a double-doublet at τ=3.9-4.1, a double-doublet at τ=6.5-6.7, and two singlets at τ=9.8 and τ=10.2 with relative intensities of 4:2:2:6:6 respectively. The bridgehead protons couple with both of the olefinic protons resulting in the double-doublets. This compound decomposes slowly in a stoppered vial stored in the dark, apparently as a result of oxidation, since mass spectra of the compound taken after such storage show a new parent peak at m/e 260. An exact mass on this peak showed it to have the molecular formula $C_{14}H_{20}Si_2O$.

The biphenyl-tetramethyldisilene adduct, 37, is also a colorless solid, m.p. 118-121°C. The mass spectrum of compound 37 showed a parent peak at m/e 270 as well as peaks at m/e 154, [biphenyl]$^{+\cdot}$, and at m/e 116, $[(CH_3)_2Si{=}Si(CH_3)_2]^{+\cdot}$. The NMR spectrum of compound 37 showed a multiplet at τ=2.5-2.9, a multiplet at τ=3.7-4.2, a triple-triplet at τ=6.8-7.2, and two singlets at τ=9.8 and τ=10.1 with



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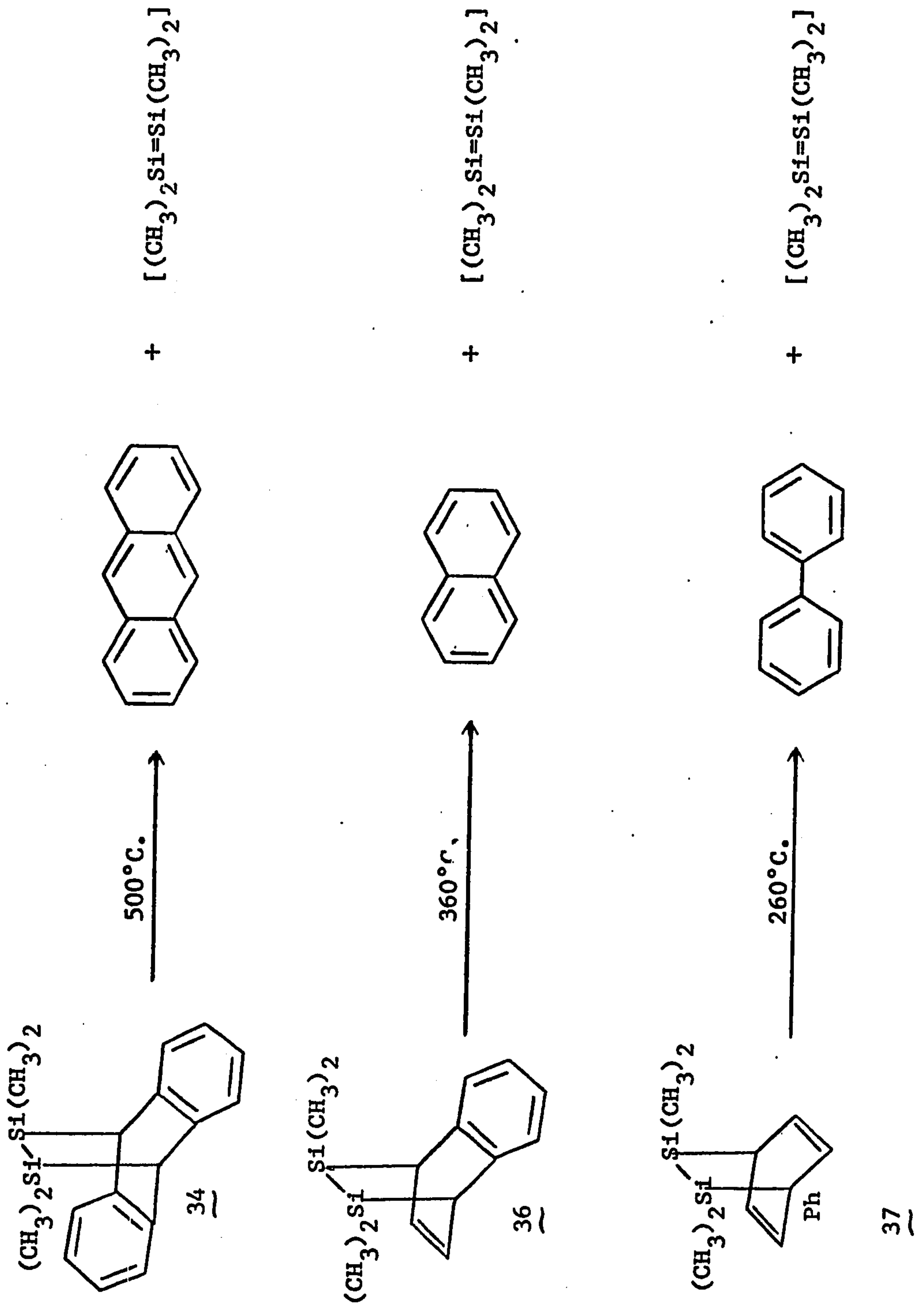
relative intensities of 5:4:1:6:6 respectively. It decomposes on standing in a stoppered vial in the dark.

The foregoing spectral data as well as the method of synthesis and reactions are in agreement with the structures assigned to 34, 36, and 37.

NEAT DECOMPOSITION

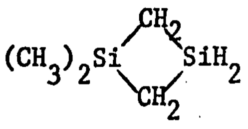
The three 7,8-disilabicyclo[2.2.2]octa-2,5-dienes; **34**, **36**, and **37**; were found to thermally decompose when heated in a sealed tube at 500°C., 360°C., and 260°C. respectively. The products obtained were the respective aromatic hydrocarbons in quantitative yield, a trace of trimethylsilane, and an involatile viscous white oil which was highly soluble in organic solvents. The NMR spectrum of the white oil gave only peaks in the silicon methyl region, while the infrared spectrum showed a broad weak silicon-hydride absorption. The properties of this material were not analogous with those reported for polydimethylsilenes; the low molecular weight cyclic forms are volatile while the linear form is insoluble in most organic solvents. This white oil is probably a polymer resulting from polymerization of rearranged tetramethyldisilene. Some additional evidence for this was found by flow pyrolysis of the tetramethyldisilene adducts.

The relative stabilities of the anthracene, naphthalene, and biphenyl-tetramethyldisilene adducts; **34**, **36**, and **37**; offer some insight into the mechanism of their decomposition. When a dienophile reacts with an aromatic diene, a decrease in resonance energy results, with the amount of decrease depending on the particular aromatic diene.[73] The larger the decrease in resonance energy, the greater the energy barrier to reaction will be. This has been used to explain why maleic anhydride reacts smoothly with anthracene, slightly with naphthalene and not at all with benzene.[73] Reversing this argument a biphenyl-adduct should undergo the retro-diene reaction more easily than a naphthalene-adduct, and a naphthalene-adduct should disproportionate more easily than an anthracene-adduct. The observed relative thermal stabilities of the tetramethyldisilene-adducts are therefore consistent with decomposition via a retrodiene reaction.

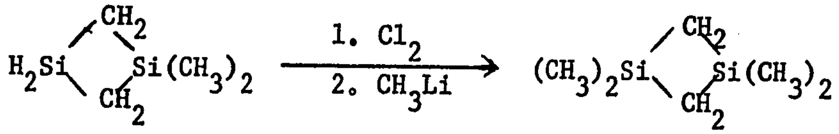

(CH3)2Si–Si(CH3)2
34
500°C.
+
[(CH3)2Si=Si(CH3)2]
(CH3)2Si–Si(CH3)2
36
360°C.
+
[(CH3)2Si=Si(CH3)2]
(CH3)2Si–Si(CH3)2
Ph
37
260°C.
+
[(CH3)2Si=Si(CH3)2]

A flow pyrolysis was performed on both 36 and 37 using the apparatus shown in the experimental section. The technique was to slowly sublime the compound through the oven at low pressures, catching any products in a liquid nitrogen cold trap. After all the material had been sublimed through the oven, the trap was allowed to warm and the volatile material was condensed into a second trap containing cyclopentane at -196°C.

The cyclopentane solutions from the pyrolysis of both 36 and 37 contained, in addition to the respective aromatic hydrocarbons, the same five peaks in the g.l.c. With the aid of a gas chromatograph coupled directly to a mass spectrometer, the mass spectra of all five compounds were determined. The most volatile compound, 38, had a fragmentation pattern and a retention time identical to authentic trimethylsilane. The next two most volatile compounds, 39 and 40, had molecular weights of 118; and the remaining two, 41 and 42, had molecular weights of 116. Compound 41 was the major product (30% yield), and 7 mg. of this material was obtained by preparative gas chromatography. The infrared spectrum of 41 showed a sharp peak at 2142 cm^{-1} which indicated the presence of a silicon hydride. The NMR spectrum of 41 in dichloromethane had a quintuplet at $\tau=5.5-5.7$, a singlet at $\tau=9.7$, and a triplet at $\tau=9.8$. These peaks integrated in the ratio of 2:6:4. The only possible structure which seemed consistent with this spectral data was 1,1-dimethyl-1,3-disilacyclobutane, 41. The addition of chlorine to 41 resulted in the evolution of a gas. Methyl lithium was then added to the reaction mixture and the resulting product had a mass spectrum and g.l.c. retention time identical to that of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, 2. These results are consistent with the structure



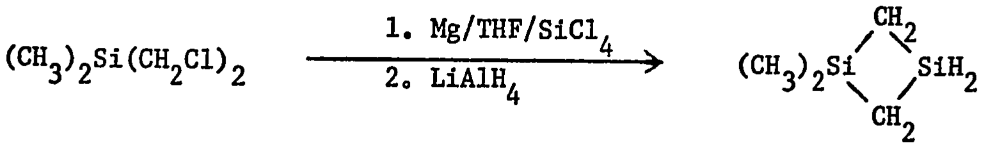
41



41 2

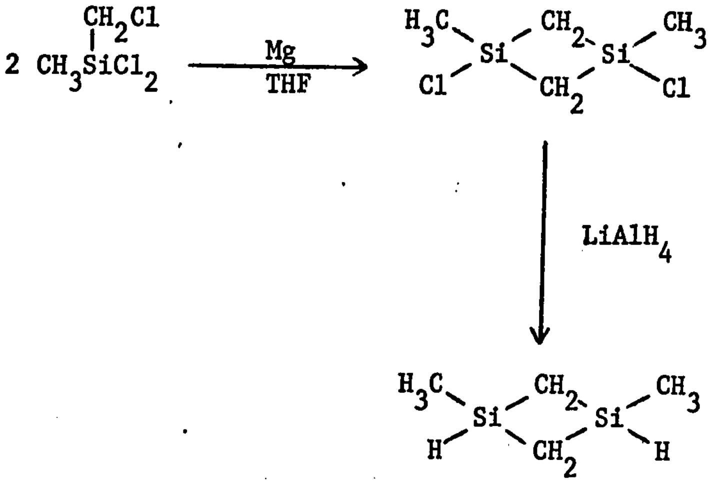
assigned to 41.

An attempt to prepare an authentic sample of compound 41 by the route shown below was made, but none of the desired compound was obtained. The major products formed appeared to be high molecular weight polymers.



41

Compound 42 had a similar mass spectral fragmentation and retention time to 41, so it was felt that it might be 1,3-dimethyl-1,3-disilacyclobutane. This compound was prepared by a known method,[74] and gave identical retention time and mass spectral fragmentation to compound 42.



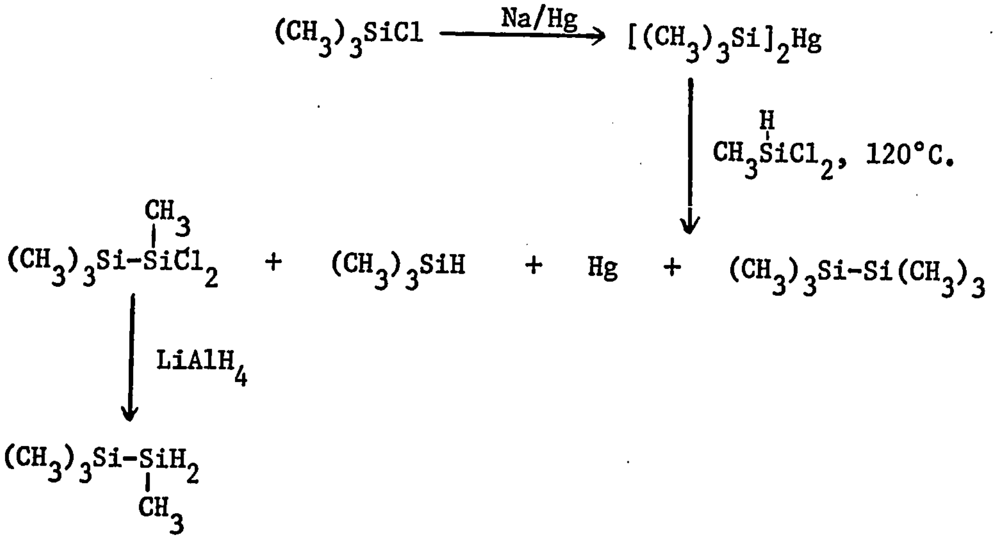
42

In order to determine the identity of compounds 39 and 40, five isomers with the molecular formula $C_4H_{14}Si_2$ were synthesized. The first was 1,1,2,2-tetramethyldisilane, 43, which was prepared by the reduction of 1,1,2,2-tetramethyl-1,2-dichlorodisilane.[75]

$$(CH_3)_2\overset{Cl}{Si}-\overset{Cl}{Si}(CH_3)_2 \xrightarrow{LiAlH_4} (CH_3)_2\overset{H}{Si}-\overset{H}{Si}(CH_3)_2$$

43

The second compound was 1,1,1,2-tetramethyldisilane, 44, which was synthesized by the route shown below. The coupling reaction



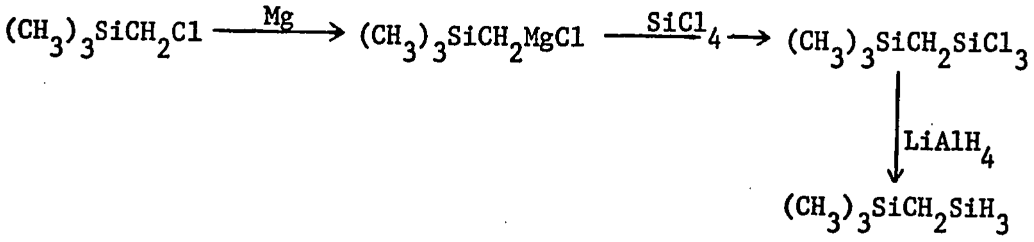
$$(CH_3)_3SiCl \xrightarrow{Na/Hg} [(CH_3)_3Si]_2Hg \xrightarrow{CH_3\overset{H}{Si}Cl_2,\ 120°C.} (CH_3)_3Si-\overset{CH_3}{Si}Cl_2 + (CH_3)_3SiH + Hg + (CH_3)_3Si-Si(CH_3)_3$$

$$(CH_3)_3Si-\overset{CH_3}{Si}Cl_2 \xrightarrow{LiAlH_4} (CH_3)_3Si-\underset{CH_3}{Si}H_2$$

44

between silicon hydrides and bis-silyl mercurials has been recently reported by Urry and co-workers.[76]

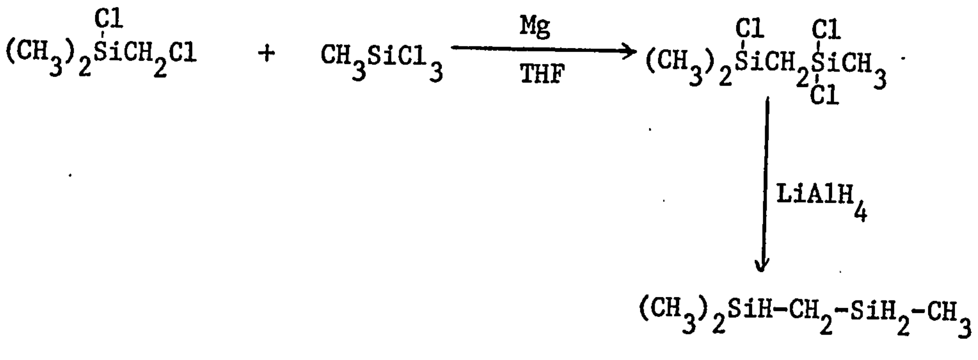
The third compound; 2,2-dimethyl-2,4-disilabutane, 45, was prepared by the reaction shown below.



$$(CH_3)_3SiCH_2Cl \xrightarrow{Mg} (CH_3)_3SiCH_2MgCl \xrightarrow{SiCl_4} (CH_3)_3SiCH_2SiCl_3 \xrightarrow{LiAlH_4} (CH_3)_3SiCH_2SiH_3$$

45

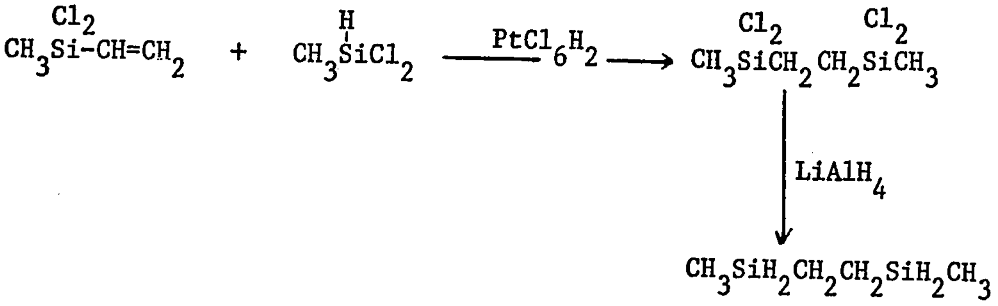
The fourth compound, 2-methyl-2,4-disilapentane, 46, was prepared in a similar manner.



$$(CH_3)_2\overset{Cl}{Si}CH_2Cl + CH_3SiCl_3 \xrightarrow[THF]{Mg} (CH_3)_2\overset{Cl}{Si}CH_2\underset{Cl}{\overset{Cl}{Si}}CH_3 \xrightarrow{LiAlH_4} (CH_3)_2SiH\text{-}CH_2\text{-}SiH_2\text{-}CH_3$$

46

The last isomer prepared was 2,5-disilahexane, 47, which was prepared by means of the platinic acid catalyzed hydrosilation of methylvinyldichlorosilane by methyldichlorosilane,[77] followed by reduction with lithium aluminum hydride.

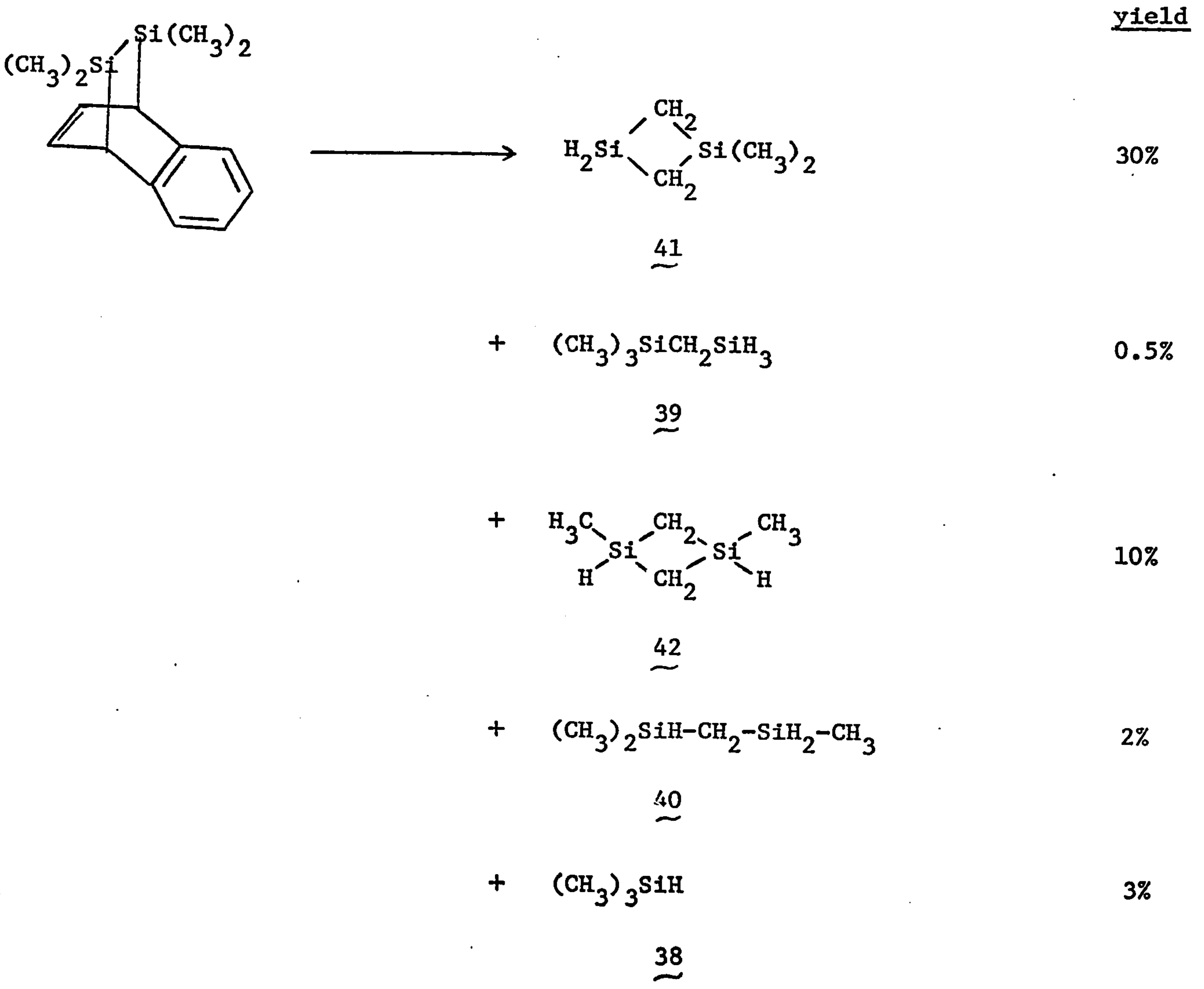


$$CH_3\overset{Cl_2}{Si}\text{-}CH{=}CH_2 + CH_3\overset{H}{Si}Cl_2 \xrightarrow{PtCl_6H_2} CH_3\overset{Cl_2}{Si}CH_2CH_2\overset{Cl_2}{Si}CH_3 \xrightarrow{LiAlH_4} CH_3SiH_2CH_2CH_2SiH_2CH_3$$

47

Comparison of mass spectral fragmentation and g.l.c. retention times showed that compounds 39 and 45 were identical, and also that compounds 40 and 46 were identical.

The five products from the neat flow pyrolysis are shown below with their yields.



yield

41 — 30%

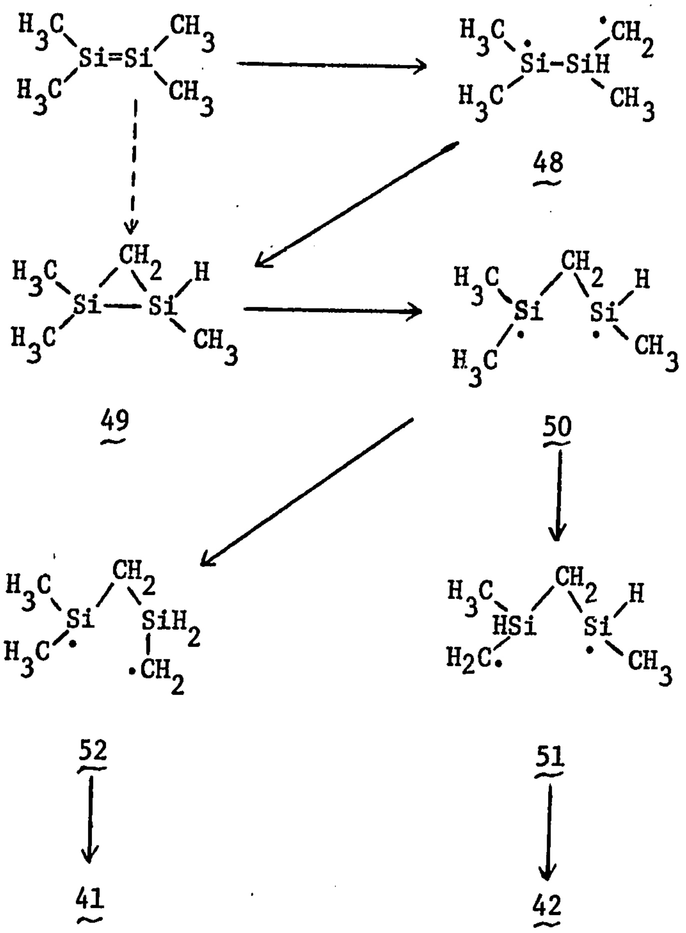
+ $(CH_3)_3SiCH_2SiH_3$ 39 — 0.5%

42 — 10%

+ $(CH_3)_2SiH-CH_2-SiH_2-CH_3$ 40 — 2%

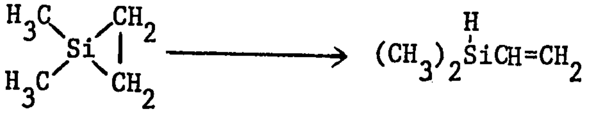
+ $(CH_3)_3SiH$ 38 — 3%

A reasonable pathway for the formation of the two major products, 41 and 42, can be drawn. This rearrangement of tetramethyldisilene



can be divided into two parts. The first step is the rearrangement to form the disilacyclopropane, 49. Three membered ring compounds containing silicon have been previously postulated as intermediates,[78-79] but to date they have never been isolated.

Skell and Goldstein[78] have shown that 1,1-dimethyl-1-silacyclopropane, 53, appears to undergo a facile rearrangement to form vinylsilane, 54. The rearrangement of tetramethyldisilene to 49 is



53 54

very similar to the reverse of the cyclopropane to propene rearrangement.[80]

The second step in the overall reaction is the rearrangement of the disilacyclopropane, **49**, to the two 1,3-disilacyclobutanes, **41** and **42**. In this step the strain in the three-membered ring, **49**, causes the silicon-silicon bond to rupture giving the diradical, **50**. It can be noted here that if diradical **50** abstracts two hydrogens, the minor product **40** will be formed. Of the two radicals in **50**, the

$$\underset{\mathbf{50}}{(CH_3)_2\overset{\circ}{Si}\text{-}CH_2\text{-}\overset{\circ}{Si}(CH_3)H} \xrightarrow{2\ [H]} \underset{\mathbf{40}}{(CH_3)_2SiH\text{-}CH_2\text{-}Si(CH_3)H_2}$$

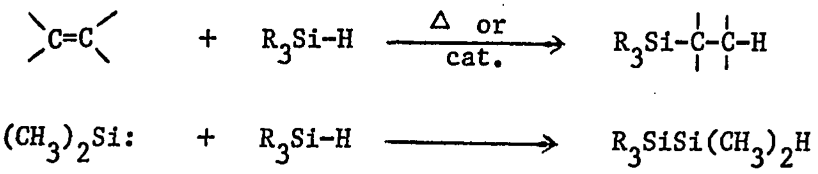
secondary radical should be inductively the least stable and rearrange faster than the tertiary radical. This would result in more **41** being formed than **42**, and in fact, this is what is observed. This second step of the rearrangement is in many ways similar to the thermal rearrangement of hexamethyldisilane.[81]

$$(CH_3)_3Si\text{-}Si(CH_3)_3 \xrightarrow{\Delta} (CH_3)_3Si\text{-}CH_2\text{-}SiH(CH_3)_2$$

The comparatively low yields of volatile products encountered in the neat pyrolysis of these tetramethyldisilene-adducts is not surprising since all of the postulated intermediates should be very prone to polymerization.

REACTION WITH SILICON HYDRIDES

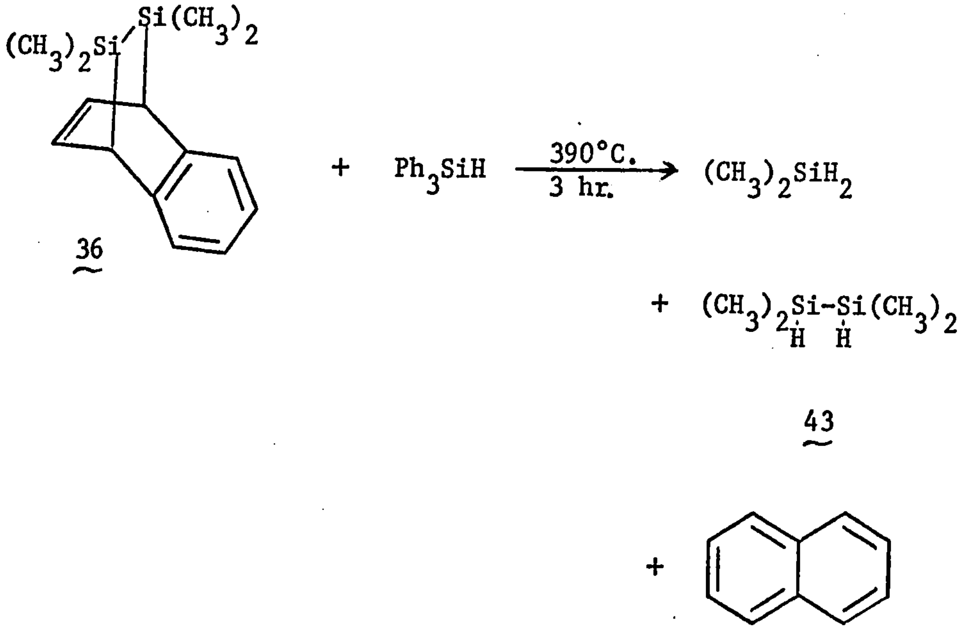
Silicon hydrides are known to add across carbon-carbon double bonds.[77] They have also been used as traps for dimethylsilylene.[82] It therefore seemed reasonable to investigate silicon hydrides as possible traps for tetramethyldisilene.



$$>C=C< \; + \; R_3Si\text{-}H \xrightarrow[\text{cat.}]{\Delta \text{ or}} R_3Si\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}H$$

$$(CH_3)_2Si: \; + \; R_3Si\text{-}H \longrightarrow R_3SiSi(CH_3)_2H$$

The first silicon hydride used was triphenylsilane. When the naphthalene-tetramethyldisilene adduct, 36, was decomposed in the presence of triphenylsilane, the major products obtained were dimethylsilane, 1,1,2,2-tetramethyldisilane, 43, and naphthalene.

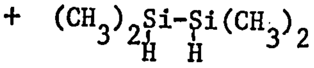


The other products were too involatile to permit their isolation by g.l.c.

We then employed phenyldimethylsilane, 55, in order to obtain more volatile products and observed analogous results. However, a control reaction of neat 55 showed that it underwent thermal disproportionation to give dimethylsilane and diphenyldimethylsilane as major products. This disproportionation also gave a trace amount of tetramethyldisilane, 43. When the reaction was done in the presence of the naphthalene-tetramethyldisilene adduct, 36, the relative amount of 43 was much greater.

$$Ph(CH_3)_2SiH \xrightarrow[17\ hr.]{400°C.} (CH_3)_2SiH_2 + Ph_2(CH_3)_2Si$$

55



$$+ (CH_3)_2\underset{H}{Si}-\underset{H}{Si}(CH_3)_2$$

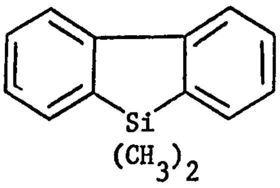
43

This thermal disproportionation probably occurs in a similar manner to the free radical catalyzed disproportionation of phenyldimethylsilane, 55, reported by Nelson, Angelotti, and Weyenberg.[83] These workers observed the formation of dimethylsilane and diphenyldimethylsilane.

Mares and Chvalovsky[84] reported that the pyrolysis of phenyldimethylsilane, 55, at 603°C. gave diphenyldimethylsilane; 9,9-dimethyl-9-silafluorene, 56; benzene; toluene; and polymer.

$$Ph(CH_3)_2SiH \xrightarrow{603°C.} Ph_2(CH_3)_2Si \quad +$$

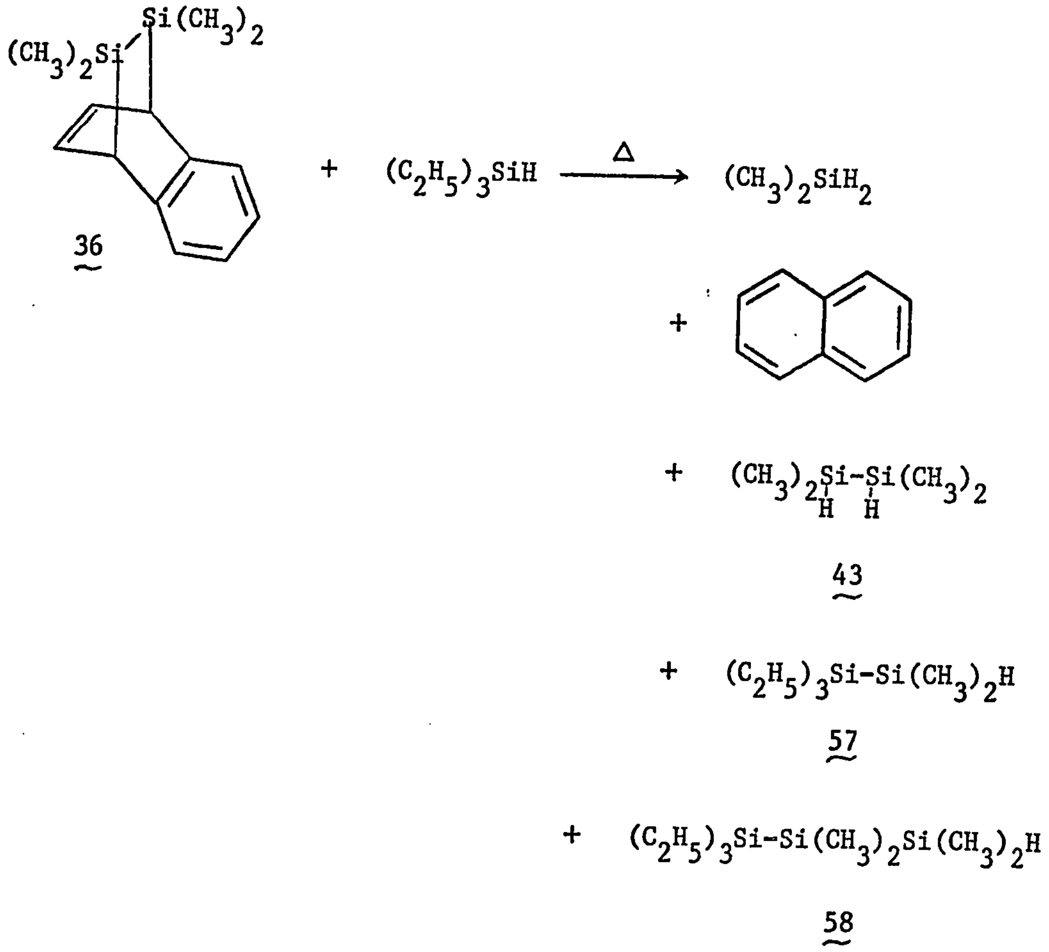
55



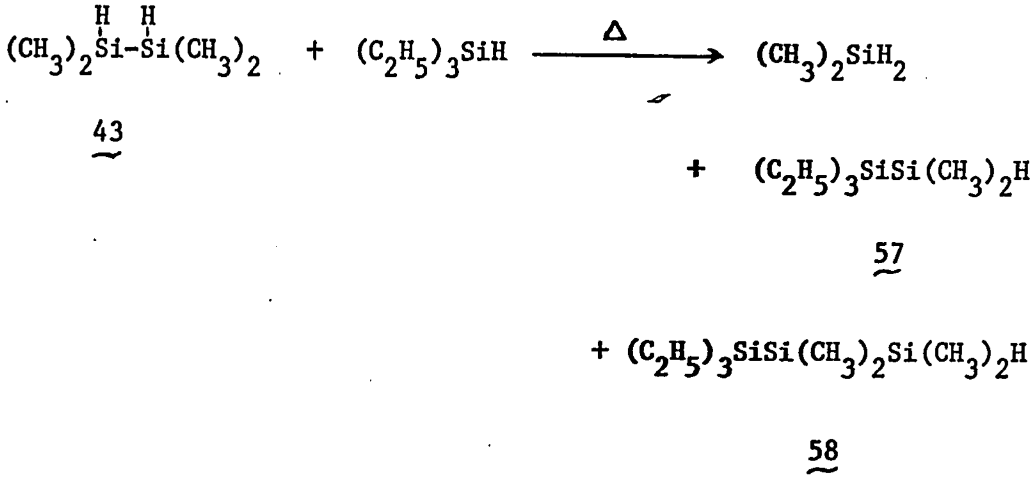
56

$$+ C_6H_6 + PhCH_3 + polymer$$

We next investigated the use of triethylsilane. This silicon hydride was chosen not only for its lower volatility, but also because it contains no methyl groups; therefore, any products containing methyl groups must come initially from the tetramethyldisilene. A series of tube pyrolysis of the naphthalene-tetramethyldisilene adduct, 36, in the presence of 3 to 8 fold excesses of triethylsilane was carried out at 350°-400°C. for periods from 1-3 hr. In each case a complex mixture of approximately 50 different products was formed. The five major products which comprised approximately 70% of the total volatile material are shown below.



The major silicon containing product was 1,1,1-triethyl-2,2-dimethyldisilane, 57, which was obtained in a 46% yield. It was found that the longer the reaction time, the larger the ratio of 57 to 43. This indicates that at least some of 57 is formed by the reaction of the tetramethyldisilane, 43, with the triethylsilane. This was demonstrated by pyrolyzing a mixture of the tetramethyldisilane, 43, and triethylsilane. The major products of this reaction are shown below. There were also many minor products formed.



$$\underset{\underset{\sim}{43}}{(CH_3)_2\overset{H}{\overset{|}{Si}}-\overset{H}{\overset{|}{Si}}(CH_3)_2} + (C_2H_5)_3SiH \xrightarrow{\Delta} (CH_3)_2SiH_2 + \underset{\underset{\sim}{57}}{(C_2H_5)_3SiSi(CH_3)_2H} + \underset{\underset{\sim}{58}}{(C_2H_5)_3SiSi(CH_3)_2Si(CH_3)_2H}$$

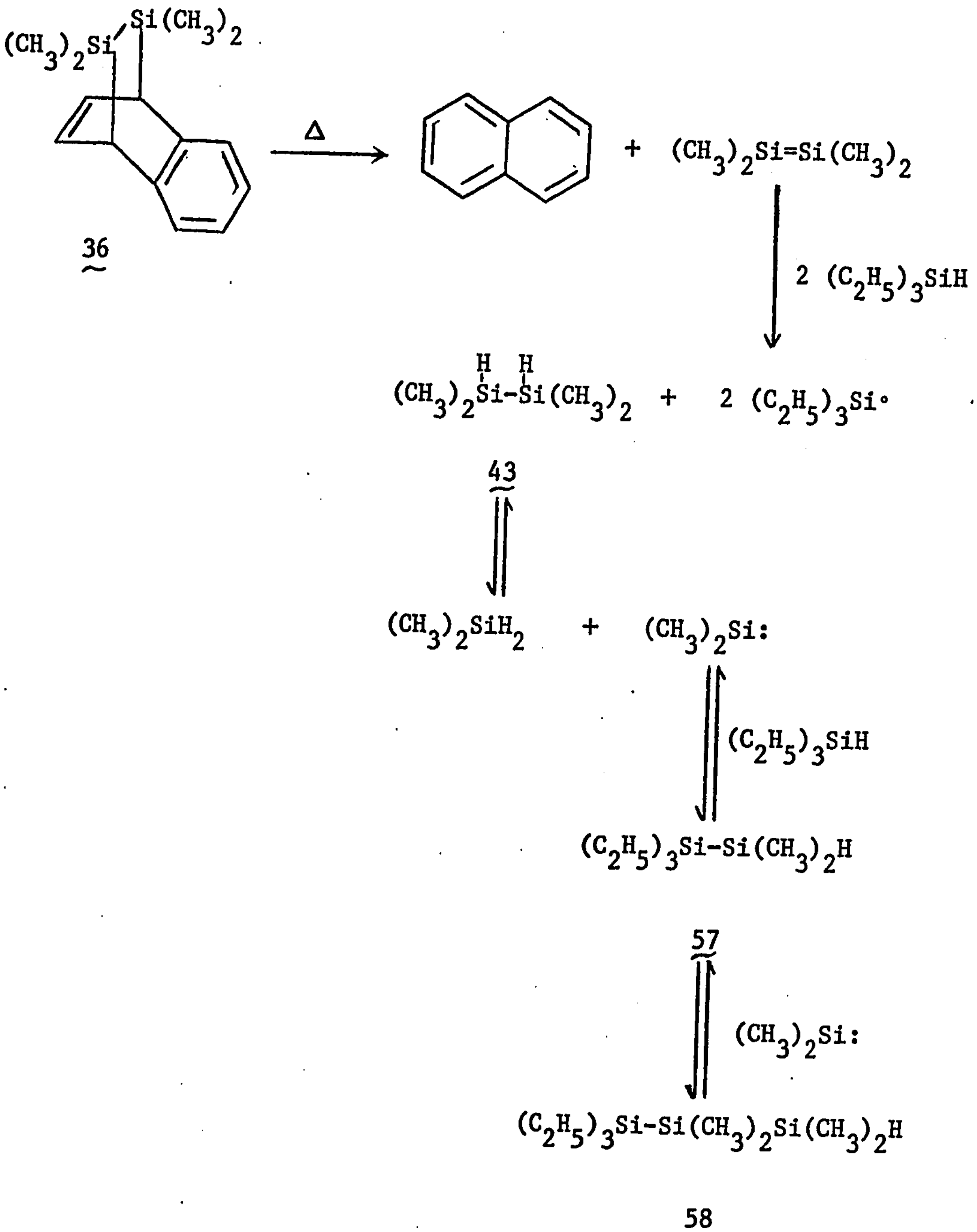
Sakurai, Hosomi, and Kumada[85] carried out similar redistribution reactions with pentamethyldisilane.

$$(CH_3)_3SiSi(CH_3)_2H \xrightarrow{300°\text{-}325°C.} (CH_3)_3Si[Si(CH_3)_2]_nH$$

$$n=0-4$$

The observed results can be rationalized in terms of the dissociation of the naphthalene-tetramethyldisilene adduct, 36, to give tetramethyldisilene. The tetramethyldisilene may then insert into the silicon-hydride bond of the triethylsilane to give 1,1,1-triethyl-2,2,3,3-tetramethyltrisilane, 58, which then undergoes redistribution to give some of the observed products. However, the primary reaction of tetramethyldisilene must involve hydrogen abstraction to generate the tetramethyldisilane, 43, since the relative concentration of 43 decreases with increasing reaction time.

The observed results can be rationalized by the following reaction sequence. The reaction sequence from the tetramethyldisilane, 43, to dimethylsilane, 57, and 58 is analogous to the results from the control reaction.



36

43

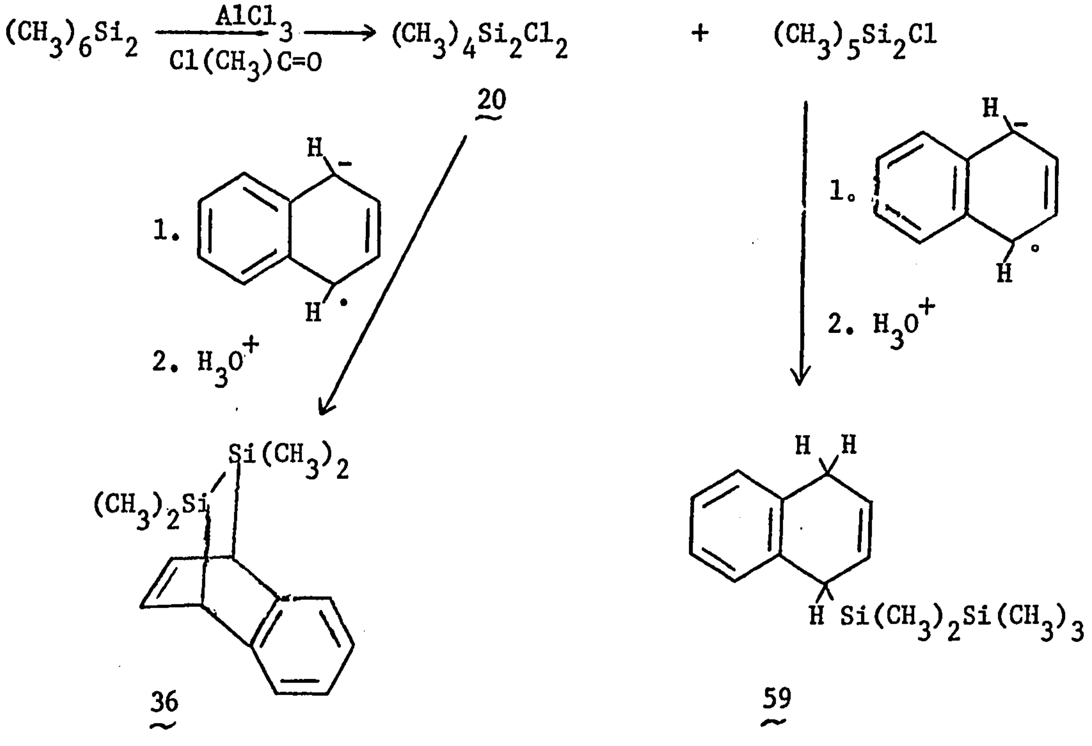
57

58

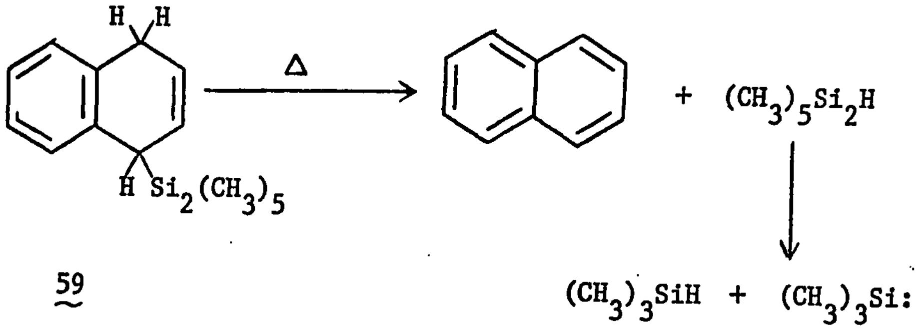
The major unanswered question in this proposed reaction sequence is the fate of the triethylsilyl radicals. The expected product hexaethyldisilane was not present in the reaction mixture. However, at temperatures above 200°C. it was found that hexaethyldisilane underwent a complex thermal decomposition to give triethylsilane as the major volatile product plus a complex mixture of other products. Thus much of any hexaethyldisilane formed would be reconverted to triethylsilane while the rest would be presumably incorporated into the numerous uncharacterized products.

Trimethylsilane is formed in very small amounts in every experiment in which any one of the three 7,8-disilabicyclo[2.2.2]-octa-2,5-dienes are pyrolyzed. While most of this trimethylsilane is probably arising via some rearrangement of tetramethyldisilene, some of it may also be arising due to the presence of a minor impurity.

The 1,1,2,2-tetramethyl-1,2-dichlorodisilane, 20, was prepared by cleavage of hexamethyldisilane with aluminum chloride and acetyl chloride,[86] which gave 20 and a major impurity, pentamethylchlorodisilane. A small amount of pentamethylchlorodisilane remained even after distillation through an annular teflon spinning band column. This pentamethylchlorodisilane would be expected to react with the radical-anion of naphthalene to give 1-pentamethyldisilyl-1,4-dihydronaphthalene, 59, after work-up. The other radical-anions would react to give analogous products.



It is known that silyldihydronaphthalenes disproportionate on heating to give silicon hydrides[87] and, therefore, 59 should undergo a similar reaction to give pentamethyldisilane, which has been shown to readily disproportionate to give trimethylsilane.[85]

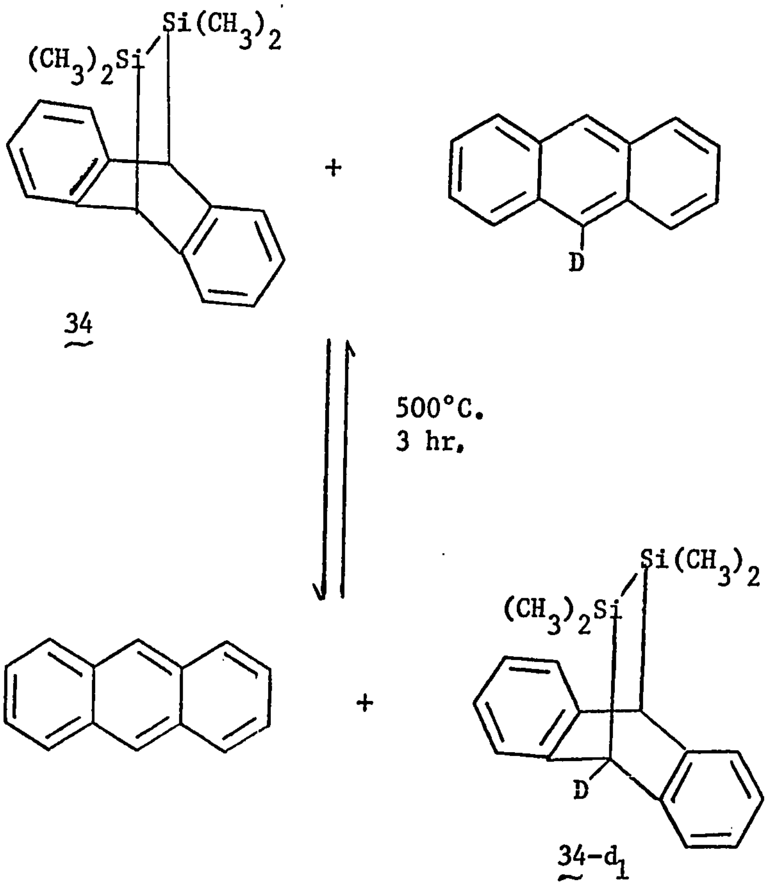


59

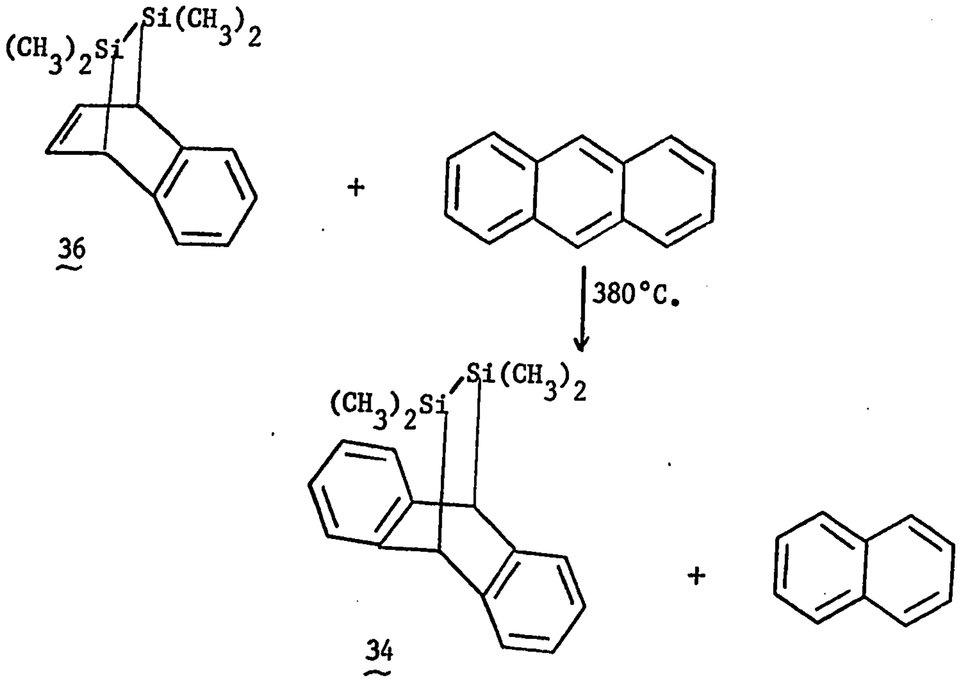
REACTION WITH DIENES

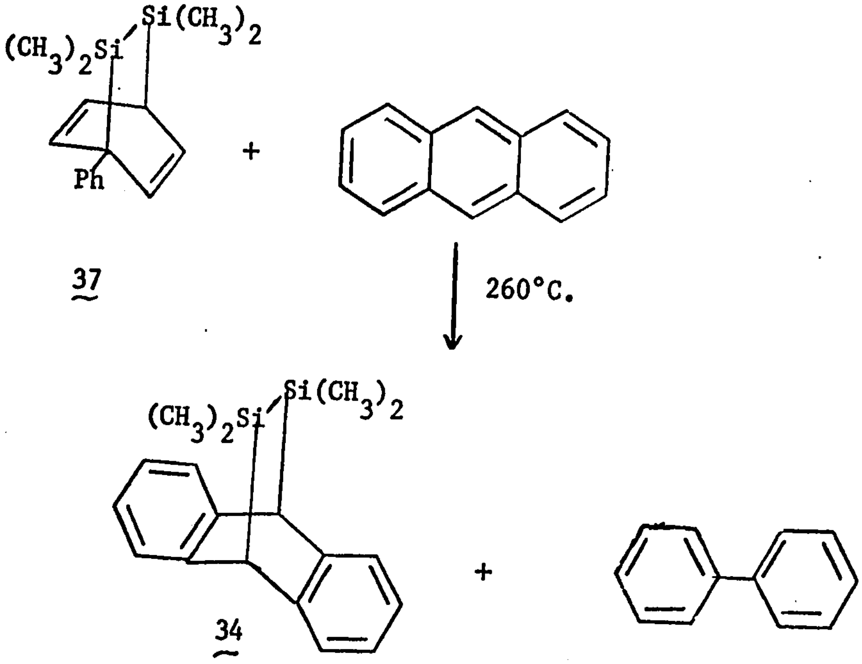
Since the Diels-Alder reaction is reversible, if tetramethyldisilene is formed via a retro-Diels-Alder then it should be trapped via a Diels-Alder reaction. To be a suitable diene two criteria had to be met. First the diene must be stable at the temperatures required for the decomposition of the tetramethyldisilene adducts, and second the product formed after reaction with the diene must be stable at these same temperatures.

Since it was known that the anthracene-tetramethyldisilene adduct, 34, is stable up to about 500°C. and that anthracene reacts as a diene, anthracene appeared to be a good choice for a trap. When 34 was heated to 500°C. for 3 hr. in the presence of 7 equivalents of 9-deuteroanthracene, the resulting white solid gave a mass spectrum and NMR spectrum which indicated a nearly statistical incorporation of one deuterium atom into 34.

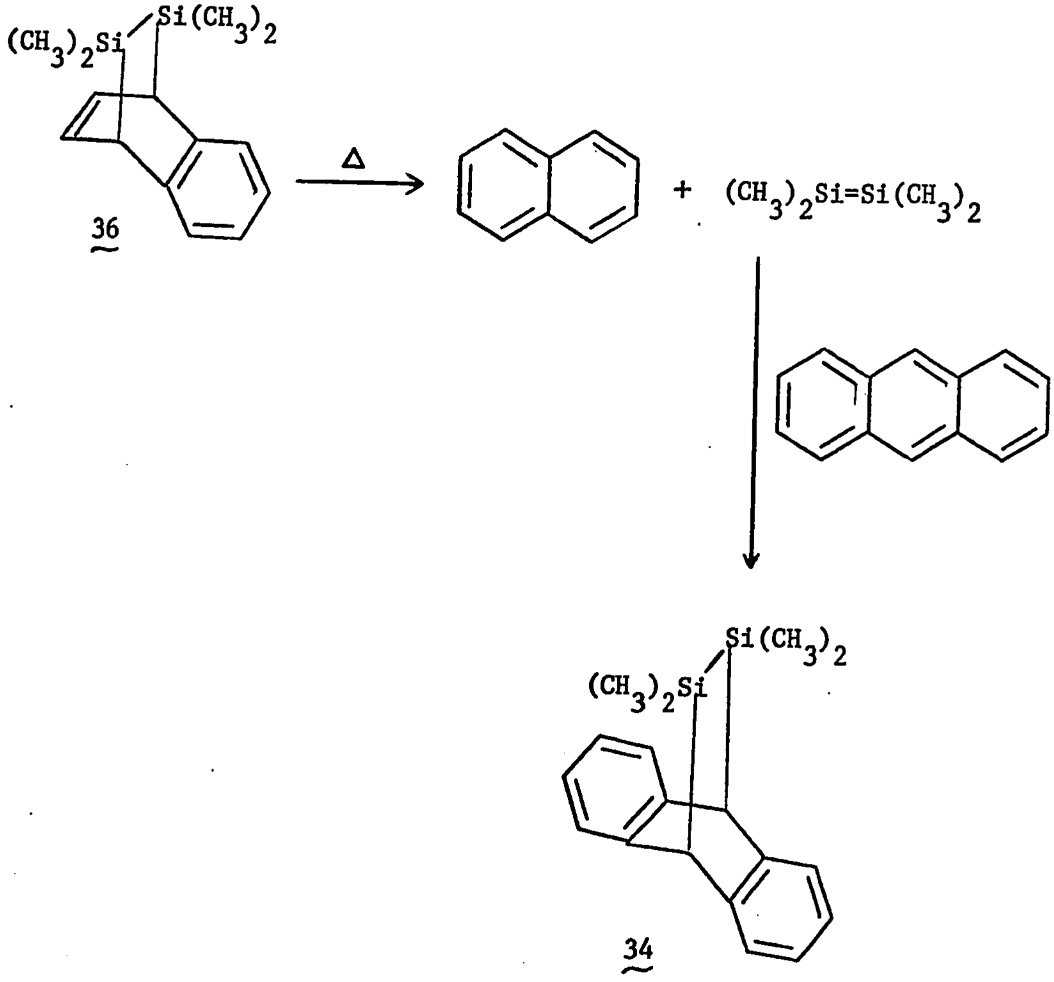


When the naphthalene-tetramethyldisilene adduct, 36, was heated to 380°C. in the presence of an equimolar amount of anthracene, a nearly quantitative yield of 34 was obtained. Heating the biphenyl-tetramethyldisilene adduct, 37, with anthracene at 260°C. also gave a nearly quantitative yield of 34.

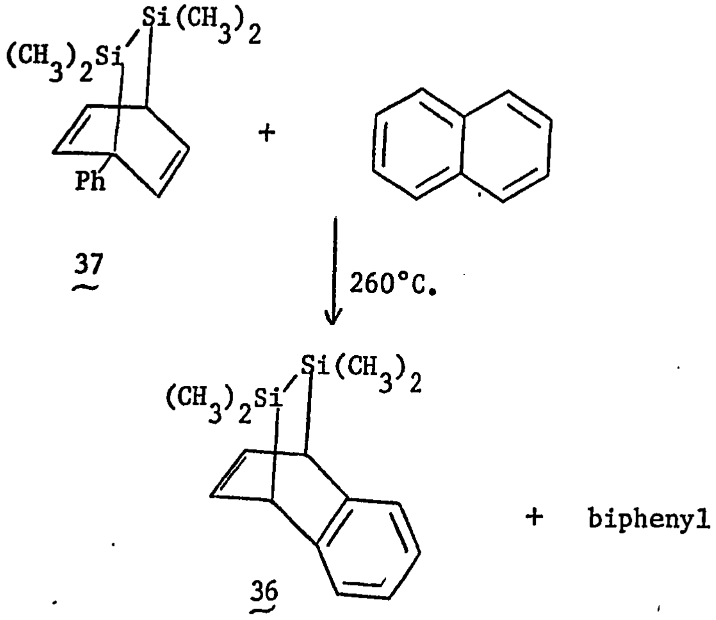




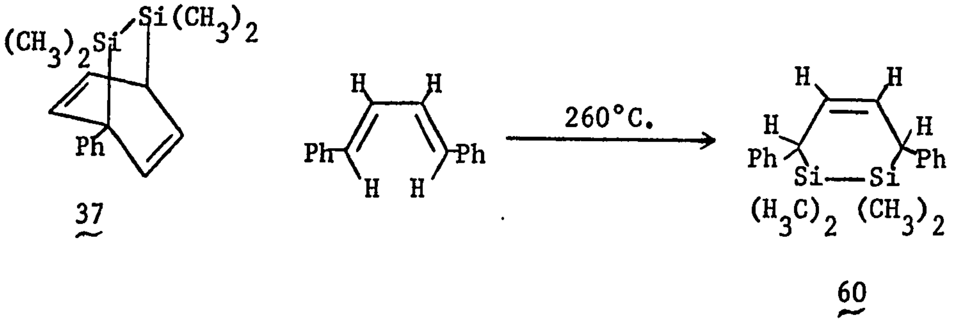
In order to determine whether this was a bimolecular reaction between the adduct and anthracene or whether it was an unimolecular decomposition of the adduct to form "free" tetramethyldisilene, followed by the reaction of the tetramethyldisilene with the anthracene, 1 equivalent of the naphthalene-tetramethyldisilene adduct, 36, was heated to 335°C. for 15 min. in the presence of from one to ten equivalents of anthracene and found in all cases to give a 15% yield of 34. This indicated that the decomposition was indeed unimolecular and thereby provided further evidence for the existence of tetramethyldisilene as a discrete intermediate.



The biphenyl-tetramethyldisilene adduct, 37, was found to react with two other dienes. Heating a mixture of 37 and naphthalene to 260°C. for 24 hr. yielded the naphthalene-tetramethyldisilene adduct, 36, in nearly quantitative yields.



Similarly heating 37 at 260°C. with a slight excess of *trans, trans*-1,4-diphenyl-1,3-butadiene gave a 29% yield of 3,6-diphenyl-4,4,5,5-tetramethyl-4,5-disila-1-cyclohexene, 60. Only one isomer of 60 was formed; this isomer was presumably the *cis*-isomer. Compound 60 gave an NMR spectrum which showed a multiplet at τ=2.5-3.0,

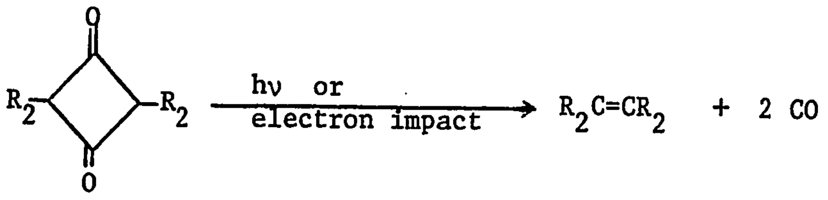


a doublet at τ=4.0, a doublet at τ=6.9, and two singlets at τ=9.9 and τ=10.1. These peaks had relative intensities of 10:2:2:6:6. The mass spectrum showed a parent peak at m/e 322 and a major fragmentation peak at m/e 116, $[(CH_3)_2Si{=}Si(CH_3)_2]^{+\cdot}$.

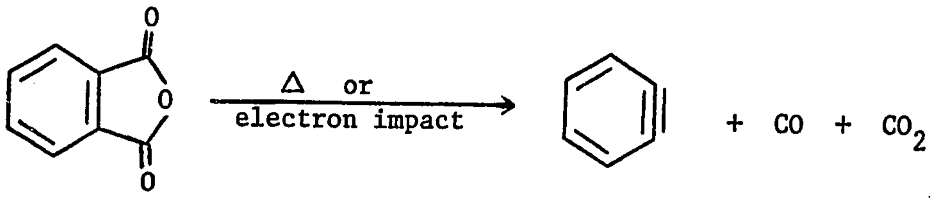
These reactions with dienes are good evidence that the silicon-silicon bond has remained in tact during the thermal dissociation of the 7,8-disilabicyclo[2.2.2]octa-2,5-dienes..

ANALOGY BETWEEN ELECTRON IMPACT AND THERMALLY INDUCED DECOMPOSITION

In the last decade there has been a great deal of interest in the analogy between electron impact fragmentation and the fragmentation induced by photolysis or thermolysis.[88] Turro and co-workers[89] reported in 1965 the striking similarity between the low voltage (10 eV) mass spectral fragmentation and photochemical decomposition of cyclobuta-1,3-dienes.

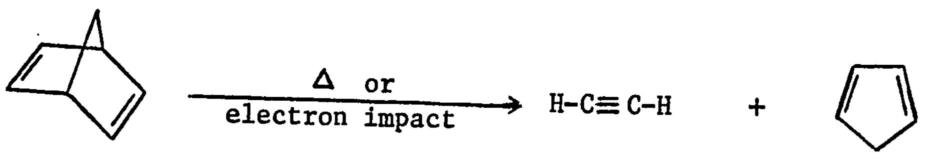


The analogy between electron impact and thermally induced decomposition of aromatic anhydrides was studied simultaneously by three separate groups.[90-94]

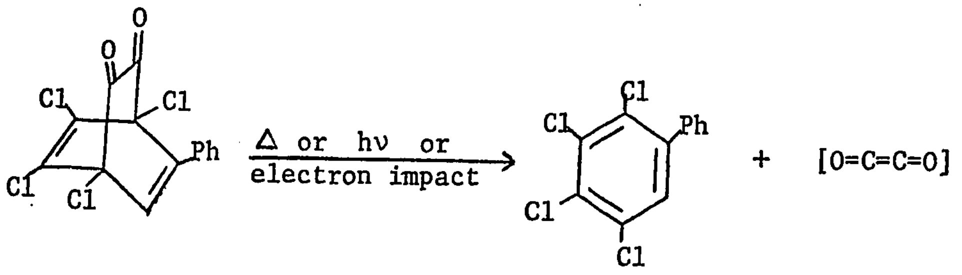


Similar analogies have been reported for tetracyclone,[95] indanetrione,[96] dibenzothiophene-5,5-dioxide,[97] and 1,1,4,4-tetramethyltetralin-2,3-dione.[98]

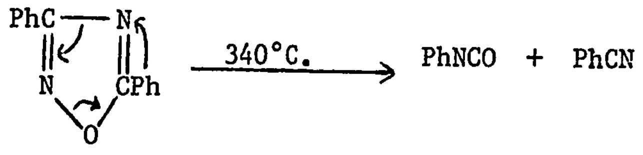
Numerous examples of analogous electron impact and thermally induced retro-diene reactions have been reported.[99-101] Strating, Zwanenburg, Wagenaar, and Udding[52] have used this analogy as a major



part of their argument for the formation of bis-carbon monoxide from the pyrolysis and photolysis of bicyclo[2.2.2]octadienes.



Cotter and Knight[102] have shown that while a good correlation exists between the electron impact fragmentation and thermal fragmentation of 3,5-diphenyl-1,2,4-oxadiazole, 61, no correlation exists in the case of 2,5-diphenyl-1,3,4-oxadiazole, 62. This brings up the question of when can these analogies be drawn. If one could predict when mass spectrometric fragmentation and thermolytic fragmentation are the same, and when mass spectrometric and photolytic



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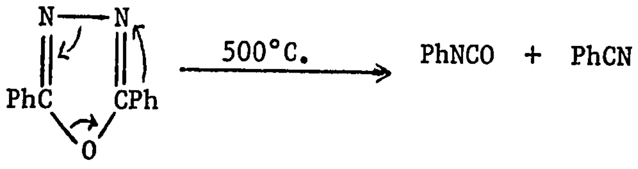

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fragmentation are the same, then the mass spectrometer would become a powerful tool for studying the thermolysis and photolysis of organic compounds.

In 1968 Daugherty[103] published the first semi-quantitative approach to this problem. He stated that two questions had to be answered before the relationship between mass spectrometric, thermolytic, and photolytic fragmentation could be examined. First, what is the electronic state for the ions produced by electron impact; second, what is the relationship between the reactivity of radical-cations and even-electron systems. To help answer the first question, Daugherty put all 50-70 eV induced mass spectrometric fragmentation reactions into three classes. Reactions which occur from low-lying doublet or singlet states belong in class I, those which occur from excited electronic states belong in class II, and those which occur from indeterminant electronic states belong in class III. Since the known lifetimes of excited doublet states are approximately 10^{-8} sec., and the existence of significant metastable ions in a 50-70 eV mass spectra has been shown to bracket the rate constant for formation of the daughter ion between 10^4 and 10^6 sec.$^{-1}$,[104] compounds which give rise to significant metastables for the decomposition of their molecular ions belong in class I. Likewise, compounds which do not give rise to metastables for the decomposition of their molecular ions belong in class II.

Daugherty[103] then pointed out that reactions of class I should yield to a perturbation molecular orbital (PMO) treatment for thermal reactions, while those in class II should yield to MO treatments of excited state reactions. After a detailed PMO treatment of electrocyclic reactions of ground state radical-cations, Daugherty stated that mass spectrometric class I electrocyclic reactions should be directly analogous to thermal processes. The rules for analogy between other types of mass spectrometric, thermal and photo reactions tend to be much more complex. Two warnings must be made before stating conclusively that an electrocyclic class I reaction observed in the mass spectrometer will also occur thermally. The first is that low probability processes in mass spectra may not occur thermally, and the second is that the observed mass spectrometric reaction may occur from a rearranged molecular ion which is not available thermally.

A detailed mass spectral study of the 7,8-disilabicyclo[2.2.2]-octa-2,5-dienes 34, 36, and 37 was undertaken. At 70 eV all three compounds showed a base peak at m/e 116 and a significant peak for the appropriate aromatic residue. An exact mass on the m/e 116 peak showed it to have a molecular formula of $C_4H_{12}Si_2$ (calculated for $C_4H_{12}Si_2$: 116.0478, found: 116.0478). All three compounds also gave a metastable peak for the $p^{+\cdot}\rightarrow 116^{+\cdot}$ transition. To show that this is, in fact, a low energy transition, mass spectra were taken at 10, 15, and 20, as well as at 70 eV. These results are shown in tables II, III, IV.

Beside showing that this reaction was indeed a low energy (high probability) transition, these results also indicate that the ease of reaction increased as one went from the anthracene to the naphthalene to the biphenyl adduct. As was discussed earlier this is consistent with the formation of the aromatic residue in the rate determining step.

That the $C_4H_{12}Si_2$ fragment was indeed tetramethyldisilene and that the molecular ion had not undergone a rearrangement before loss of the $C_4H_{12}Si_2$ fragment, could not be determined on the basis of these mass spectral studies. However, the trapping experiments with dienes indicated that any rearrangement which may occur does so after the formation of the tetramethyldisilene.

We have shown that a high probability, class I, electrocyclic decomposition of 7,8-disilabicyclo[2.2.2]octa-2,5-dienes occurs on electron impact. This information is strong evidence that the same decomposition occurs thermally, since this analogy has often been observed experimentally and has a good theoretical backing.[103]

Ionization Potential	Percent of the Total Ion Current			
	$P^{+\cdot}$	Anthracene$^{+\cdot}$	$[(CH_3)_2Si{=}Si(CH_3)_2]^{+\cdot}$	Other
10 eV	89.4	0.5	10.1	---
15 eV	39.5	4.7	53.5	2.3
20 eV	31.0	4.4	57.5	7.1
70 eV	13.6	4.2	51.2	31.0

TABLE II: Effect of Varying the Ionization Potential of the Mass Spectrum on 34

Ionization Potential	Percent of the Total Ion Current			
	$P^{+\cdot}$	Naphthalene$^{+\cdot}$	$[(CH_3)_2Si{=}Si(CH_3)_2]^{+\cdot}$	Other
10 eV	38.8	0.8	60.4	---
15 eV	21.7	1.4	74.2	2.7
20 eV	17.7	2.8	59.6	19.9
70 eV	8.0	3.6	43.8	44.6

TABLE III: Effect of Varying the Ionization Potential on the Mass Spectrum on 36

Ionization Potential	Percent of the Total Ion Current			
	$P^{+\cdot}$	$\text{Biphenyl}^{+\cdot}$	$[(CH_3)_2Si{=}Si(CH_3)_2]^{+\cdot}$	Other
10 eV	23.6	---	76.4	---
15 eV	8.0	3.5	80.5	8.0
20 eV	4.1	3.7	68.1	24.1
70 eV	2.5	2.0	32.3	63.2

TABLE IV: Effect of Varying the Ionization Potential on the Mass Spectrum on **37**

SUMMARY AND CONCLUSIONS

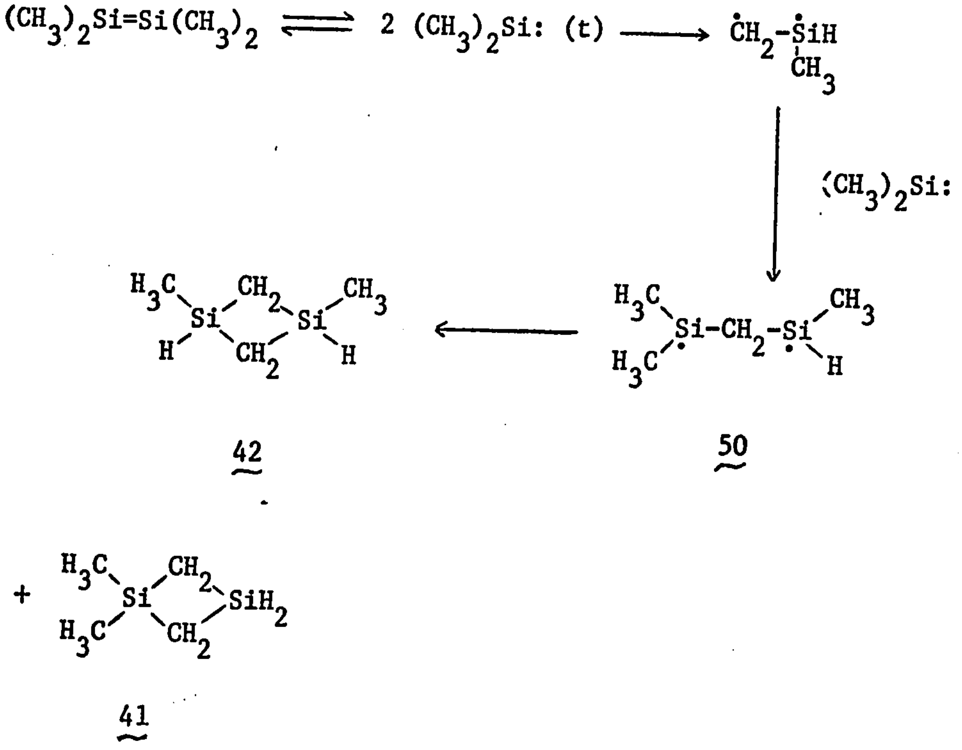
We have shown that 7,8-disilabicyclo[2.2.2]octa-2,5-dienes can be prepared by reaction of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, **20**, with aromatic radical-anions. These adducts once formed were found to thermally dissociate at temperatures between 250°-500°C. The order of thermal stability increased from the biphenyl to the naphthalene to the anthracene adduct, which is consistent with thermal dissociation via a retro-diene reaction. Flow pyrolysis of these adducts gave 1,1-dimethyl-1,3-disilacyclobutane, **41**, and 1,3-dimethyl-1,3-disilacyclobutane, **42**, as the major volatile products.

When the naphthalene-tetramethyldisilene adduct, **36**, was decomposed in the presence of silicon hydrides a complex series of reactions occurred. Apparently one of the major initial products was 1,1,2,2-tetramethyldisilane, **43**, Thermal dissociation in the presence of dienes resulted in the transfer of the tetramethyldisilene bridge intact. The rate of this transfer appeared to be independent of the concentration of the diene. It was also found that these adducts undergo a facile electron impact induced retro-diene reaction to give the radical-cation of tetramethyldisilene.

The observation that all of the observed reactions of a given adduct were initiated at the same temperature, eg. the neat decomposition, reaction with silicon hydrides, and the reaction with anthracene of the naphthalene-tetramethyldisilene adduct, **36**, all started to occur at 360°C., indicated that dissociation to a common intermediate may have been involved.

This was supported by the observation that the tetramethyldisilene bridge transfer from naphthalene to anthracene occurred at the same rate in the presence of from one to ten equivalents of anthracene. That the rate of transfer appeared to be independent of the anthracene concentration indicated that a bimolecular reaction was not involved in the rate determining step. Tetramethyldisilene appeared to be the most likely intermediate since bridge transfer was quantitative and there was a good analogy with electron impact.

As we have shown previously the reaction with silicon hydrides and the flow pyrolysis can also be readily rationalized as occurring via tetramethyldisilene. However, it is also possible to rationalize some of these results in terms of the dissociation of tetramethyldisilene to give triplet dimethylsilylene. For example, the major products from the flow pyrolysis could be formed by the route shown below.



Singlet dimethylsilylene cannot be involved since it is known to polymerize readily to polydimethylsilylene[53] and to readily react with silicon hydrides by insertion into the silicon hydride bond, not by hydrogen abstraction.[82]

$$(CH_3)_2Si:\ (s)\ +\ R_3SiH \longrightarrow R_3SiSi(CH_3)_2H^{*}$$

Regardless of the exact fate of tetramethyldisilene, it must initially be formed in a singlet state by a concerted thermally initiated retro-diene reaction. Once formed it may be regarded as having a silicon-silicon pπ-pπ double bond unless steric repulsion of the vincinal methyl groups is greater than the π-bond energy.

---

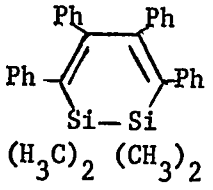
* No 1,1,2,2-tetramethyldisilane, 43, was found.

CHAPTER 4: MASS SPECTRA

In this thesis we have used mass spectral fragmentation extensively as an aid in structural identification, since most of the experiments were done with small amounts of material and many of the reaction mixtures were quite complex. In the latter case a gas chromatograph directly coupled to a rapid scan mass spectrometer was found to be very useful.

It was felt that the importance of mass spectrometry warranted the detailed presentation of the mass spectra of some compounds prepared in this thesis.

The mass spectrum of the disilacyclohexadiene, 21, (figure 2) shows an extremely complex fragmentation pattern. The lower mass ions are those which one would expect from this compound: the $(CH_3Si)^+$ peak at m/e 43, the $[(CH_3)_2Si]^+$ peak at m/e 58, the $[(CH_3)_2SiH]^+$ peak at m/e 59, the $[(CH_3)_3Si]^+$ peak at m/e 73, the $(PhSi)^+$ peak at m/e 105, and the $[(CH_3)_2SiPh]^+$ peak at m/e 135.



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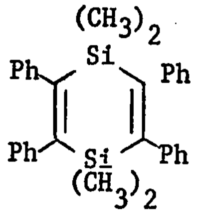


23

Johnson, Gohlke, and Nasutavins[65] have reported that 23 gives a major fragment at m/e 221. They gave three possible structures for this ion. In our case these would be 61, 62, and 63. We feel that structure 61 is the most likely possibility since it could be aromatic, which would account for its stability.

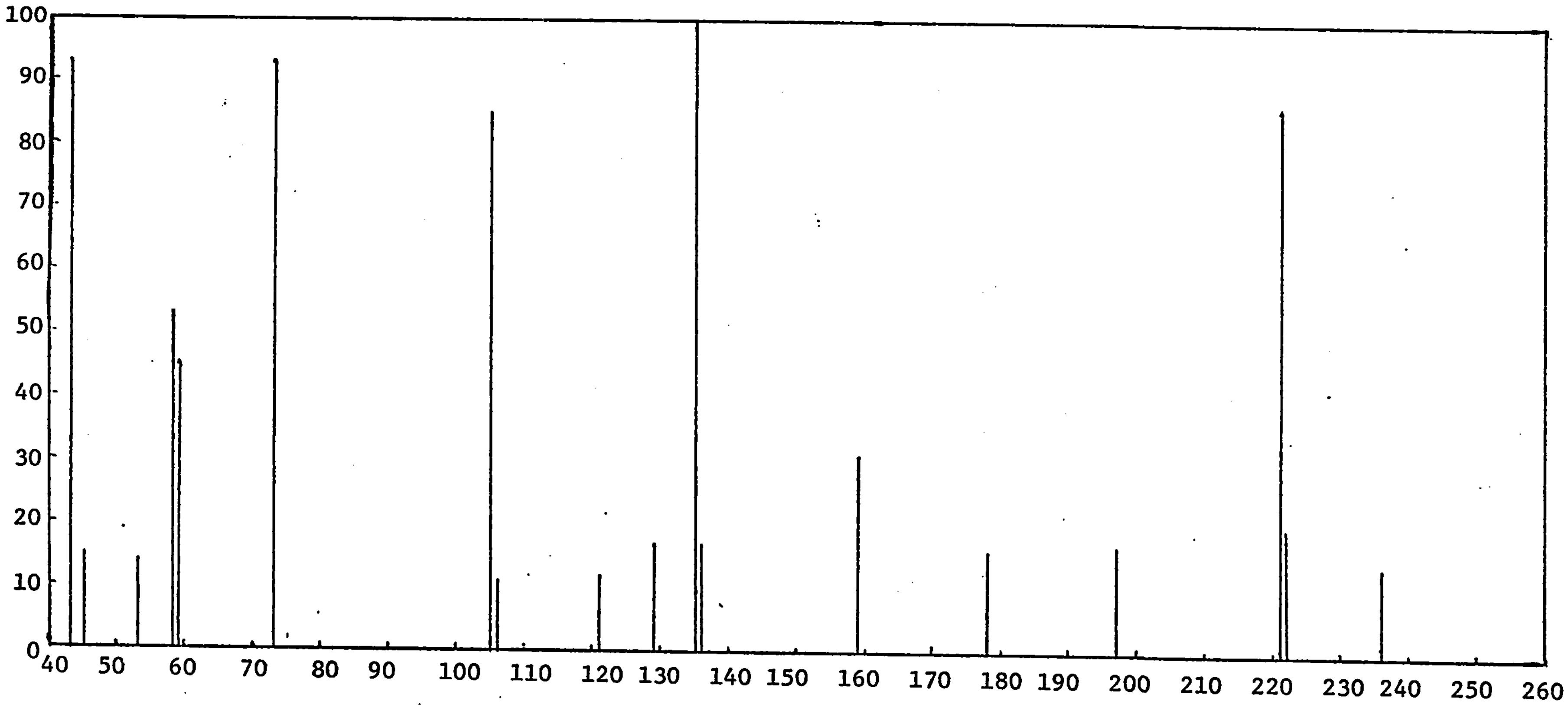


Figure 2: The 70 eV Mass Spectrum of Compound 21

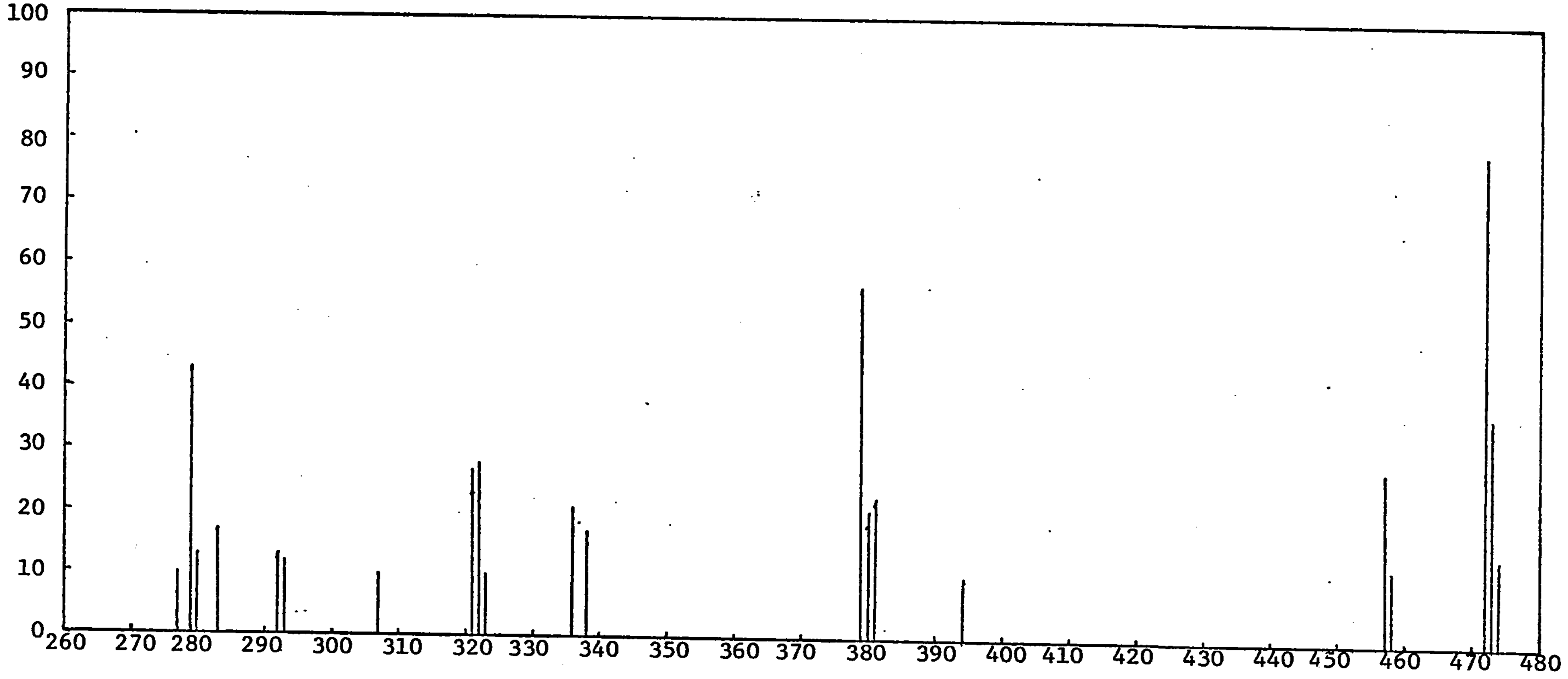
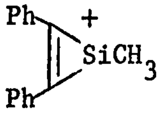


Figure 2 (continued)



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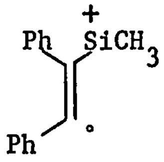

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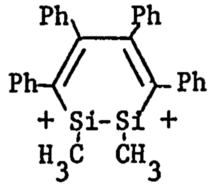


63

A major path of fragmentation is the initial loss of a methyl radical to give the m/e 457 peak, followed by the loss of C_6H_6 to give the m/e 379 peak. This latter transition is accompanied by a large metastable peak ($379^2/457=314.8$; found 314.8). An exact mass indicated that the m/e 379 peak had the composition $C_{25}H_{23}Si_2$ (calculated: 374.1338; measured: 374.1341). We have been unable to assign a probable structure to the peak; however, extensive rearrangement must have taken place prior to its formation.

The mass spectra of the 7,8-disilabicyclo[2.2.2]octa-2,5-dienes: 34, 36, and 37; (figures 3, 4, and 5 respectively) have very simple fragmentation patterns. All three compounds have a base peak at m/e 116, $[(CH_3)_2Si{=}Si(CH_3)_2]^{+\cdot}$, and a peak at m/e 73, $(CH_3)_3Si^+$. These two peaks are the only major fragmentation peaks in these spectra. The spectrum of 34 showed a small peak for the anthracene radical-cation at m/e 178. Likewise 36's spectrum showed a small peak at m/e 128 for the naphthalene radical-cation, and 37's spectrum showed a small peak at m/e 154 for the biphenyl radical-cation. All three spectra have metastable peaks for the parent to m/e 116 transition ($116^2/294=47.4$, found: 47.4; $116^2/244=55.2$, found: 55.2; and $116^2/270=49.8$, found: 49.8).

The mass spectra of 1,1-dimethyl-1,3-disilacyclobutane and 1,3-dimethyl-1,3-disilacyclobutane, 41 and 42, (figures 6 and 7 respectively) are virtually identical. They give a large parent ion and a major peak resulting from the loss of a methyl radical (m/e 101). They also showed peaks at m/e 115 and m/e 114; resulting from the

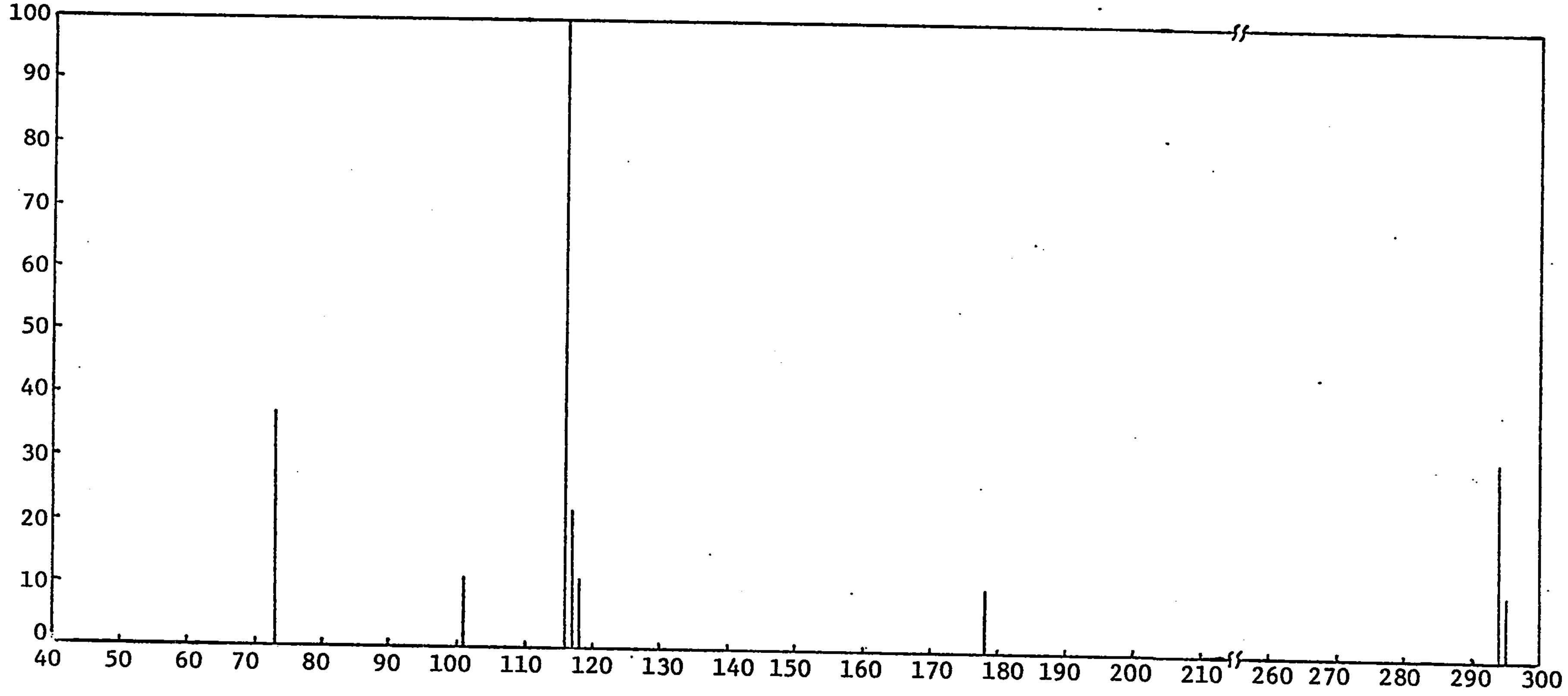


Figure 3: The 70 eV Mass Spectrum of Compound 34

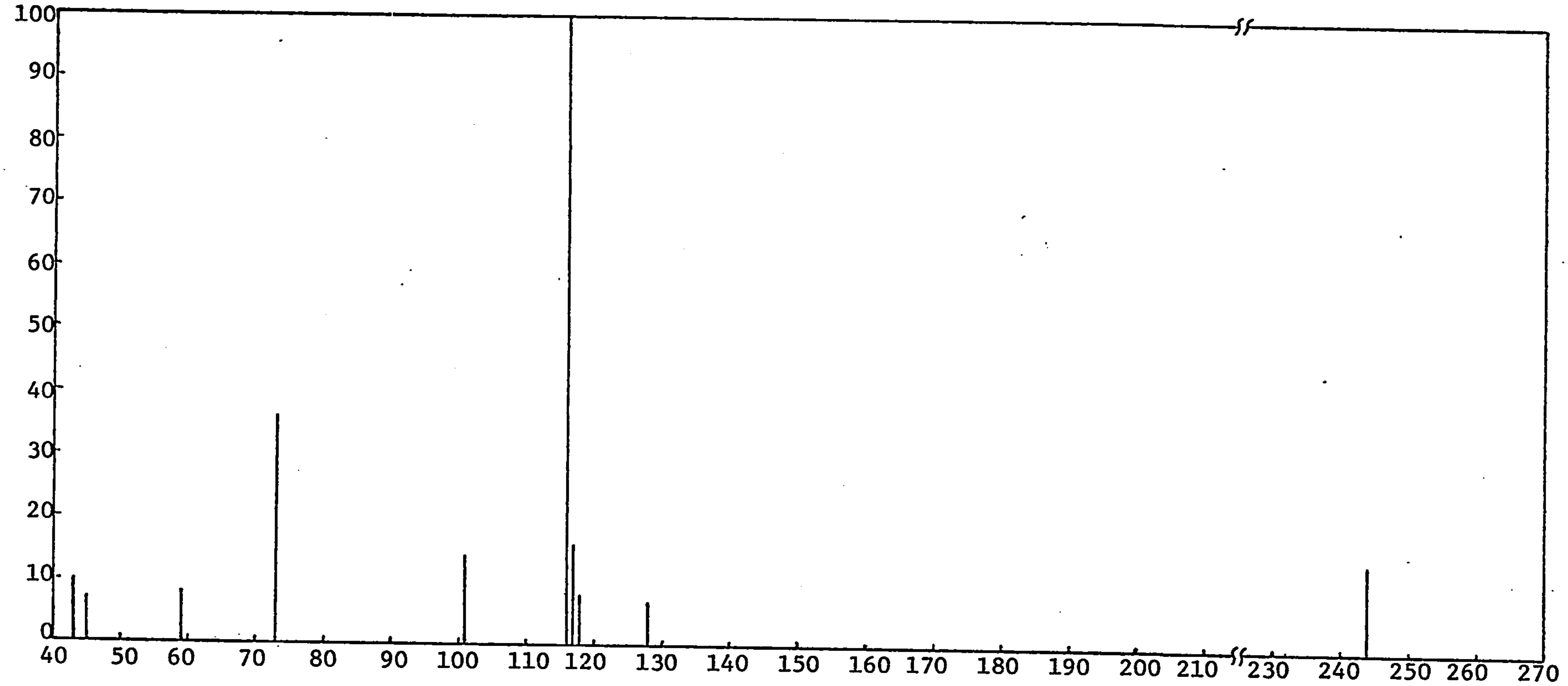


Figure 4: The 70 eV Mass Spectrum of Compound 36

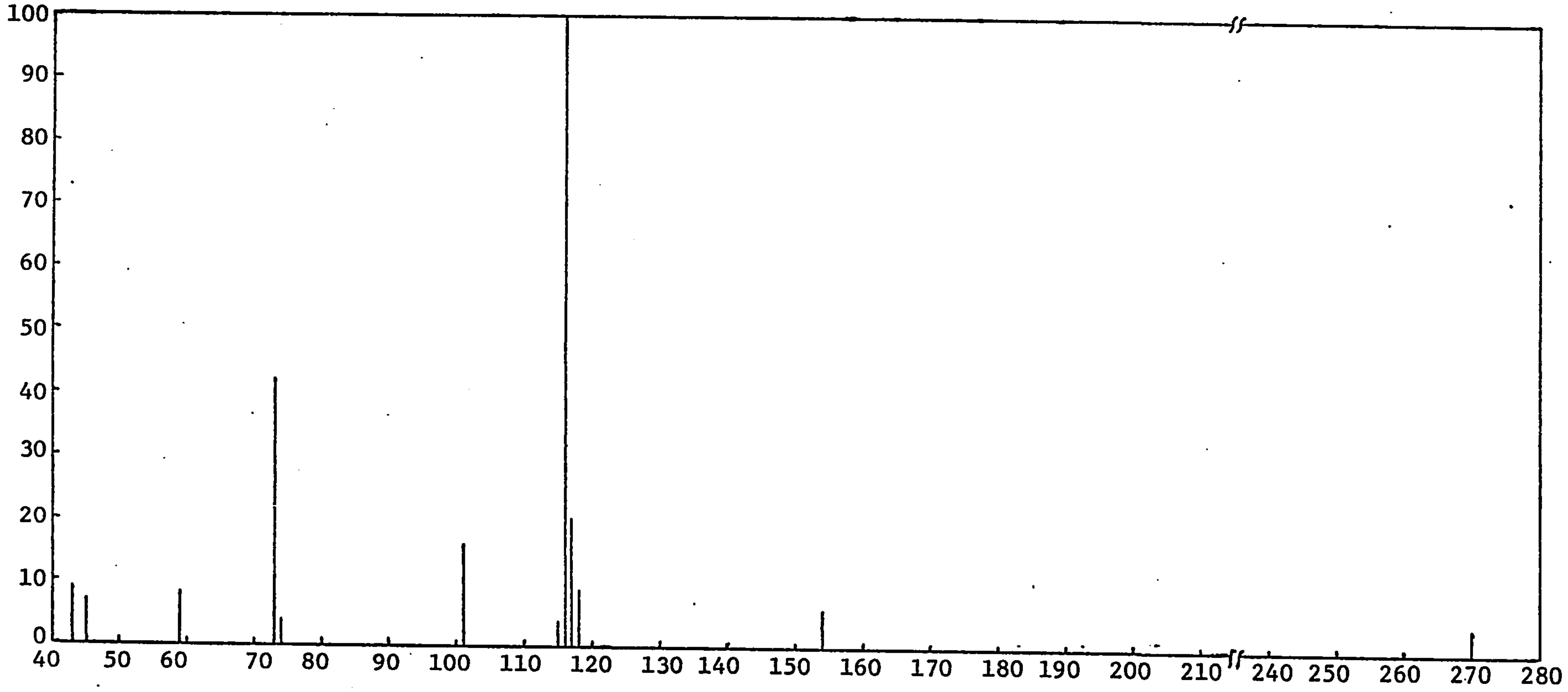


Figure 5: The 70 eV Mass Spectrum of Compound 37

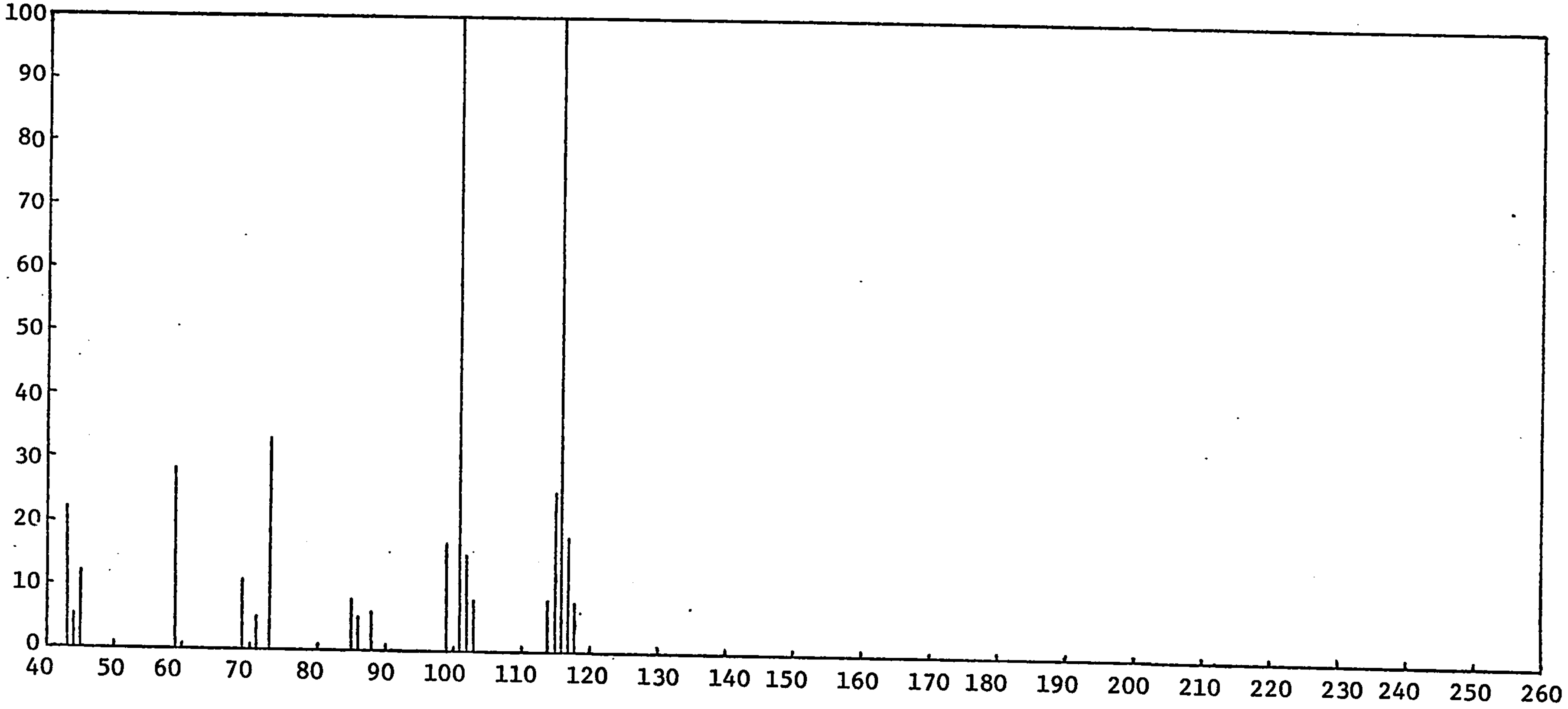


Figure 6: The 70 eV Mass Spectrum of Compound 41

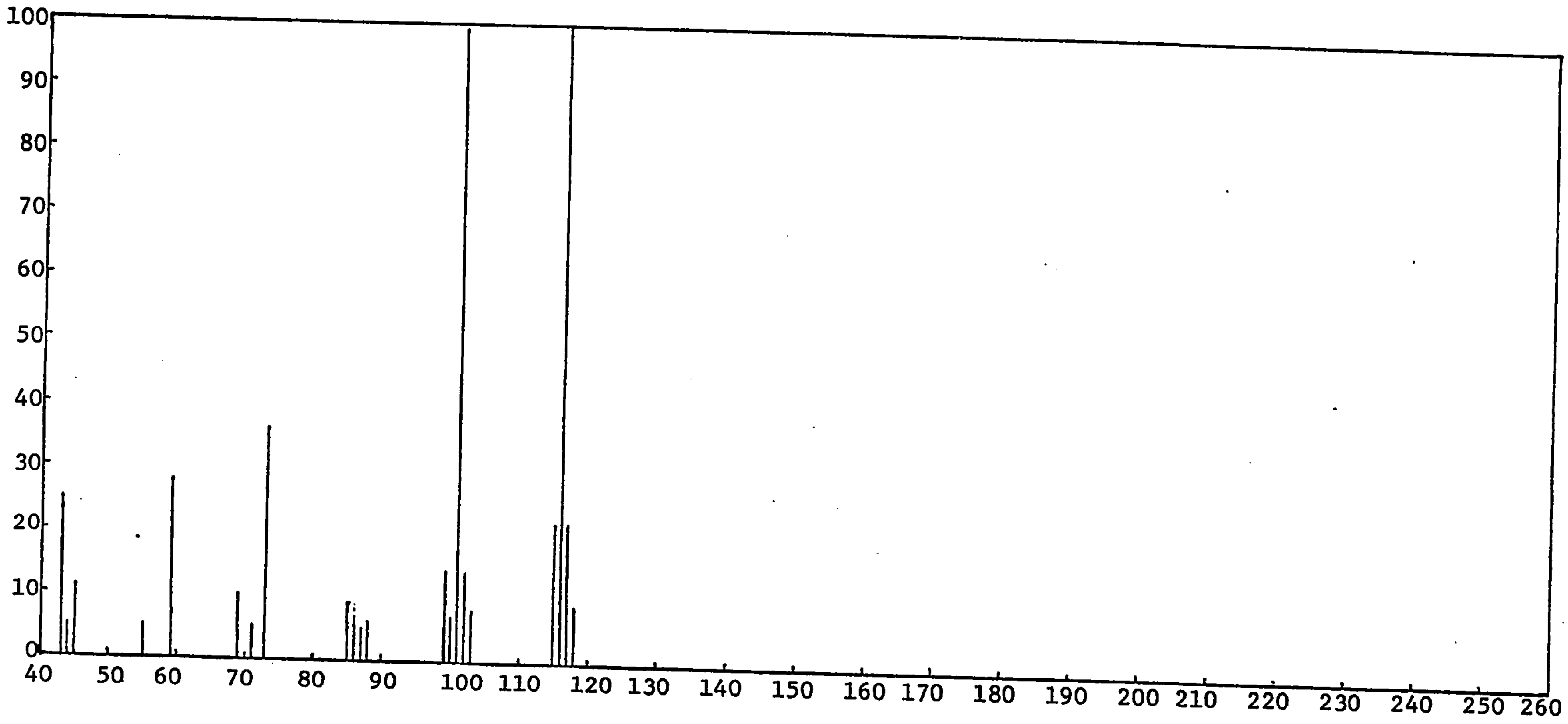


Figure 7: The 70 eV Mass Spectrum of Compound 42

loss of one and two hydrogens respectively.

The mass spectrum of 1,1,1,2-tetramethyldisilane, 44, (figure 8) showed only one major peak at m/e 73, $(CH_3)_3Si^+$, which results from the cleavage of the silicon-silicon bond. Other than this peak it showed a small parent peak at m/e 118; a parent peak minus a methyl radical at m/e 103; a $(CH_3)_2SiH^+$ peak at m/e 59; a $CH_3SiH_2^+$ peak at m/e 45; and a CH_3Si^+ peak at m/e 43.

The mass spectrum of 1,1,2,2-tetramethyldisilane, 43, (figure 9) is more complex than that of 44. Its base peak at m/e 59, $(CH_3)_2SiH^+$, results from the cleavage of the silicon-silicon bond. This spectrum also had major peaks at m/e 43, CH_3Si^+; m/e 53, $[(CH_3)_2Si]^{+\cdot}$; m/e 73, $(CH_3)_3Si^+$; m/e 103, $[(CH_3)_2SiHSiH(CH_3)]^+$; and m/e 118, parent$^{+\cdot}$.

The mass spectrum of 2,5-disilahexane, 47, (figure 10) is quite different from any we have previously observed. The base peak at m/e 72 probably arises from an electron impact induced dehydrosilation. The only other major fragment is the $CH_3SiH_2^+$

$$[CH_3SiH_2CH_2CH_2SiH_2CH_3]^{+\cdot} \longrightarrow \underset{m/e\ 72}{[CH_2{=}CHSiH_2CH_3]^{+\cdot}} + CH_3SiH_3$$

fragment at m/e 45. The compound showed only a weak parent peak at m/e 118.

1,1,1-Triethyl-2,2-dimethyldisilane, 57, (figure 11) fragments on electron impact by first cleaving the silicon-silicon bond to give $(C_2H_5)_3Si^+$ at m/e 115. This fragment then loses C_2H_4 to give the base peak at m/e 87, $(C_2H_5)_2SiH^+$. Another loss of C_2H_4 from the m/e 87 peak gives the m/e 59 peak, $C_2H_5SiH_2^+$. All three of these transitions are supported by the appropriate metastable peaks ($115^2/174=76.0$, found: 76.0; $87^2/115=65.8$, found: 65.8; and $59^2/87=40.0$, found: 40.0).

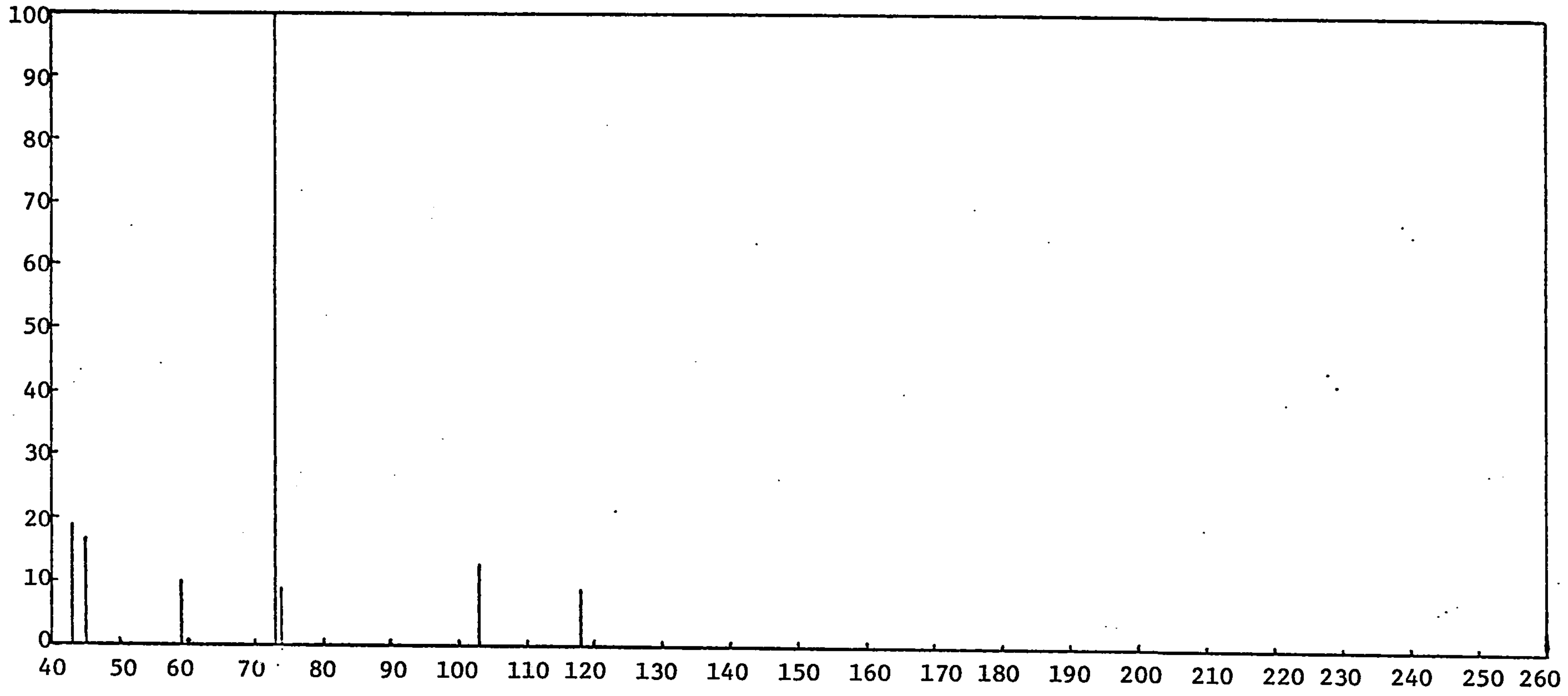


Figure 8: The 70 eV Mass Spectrum of Compound 44

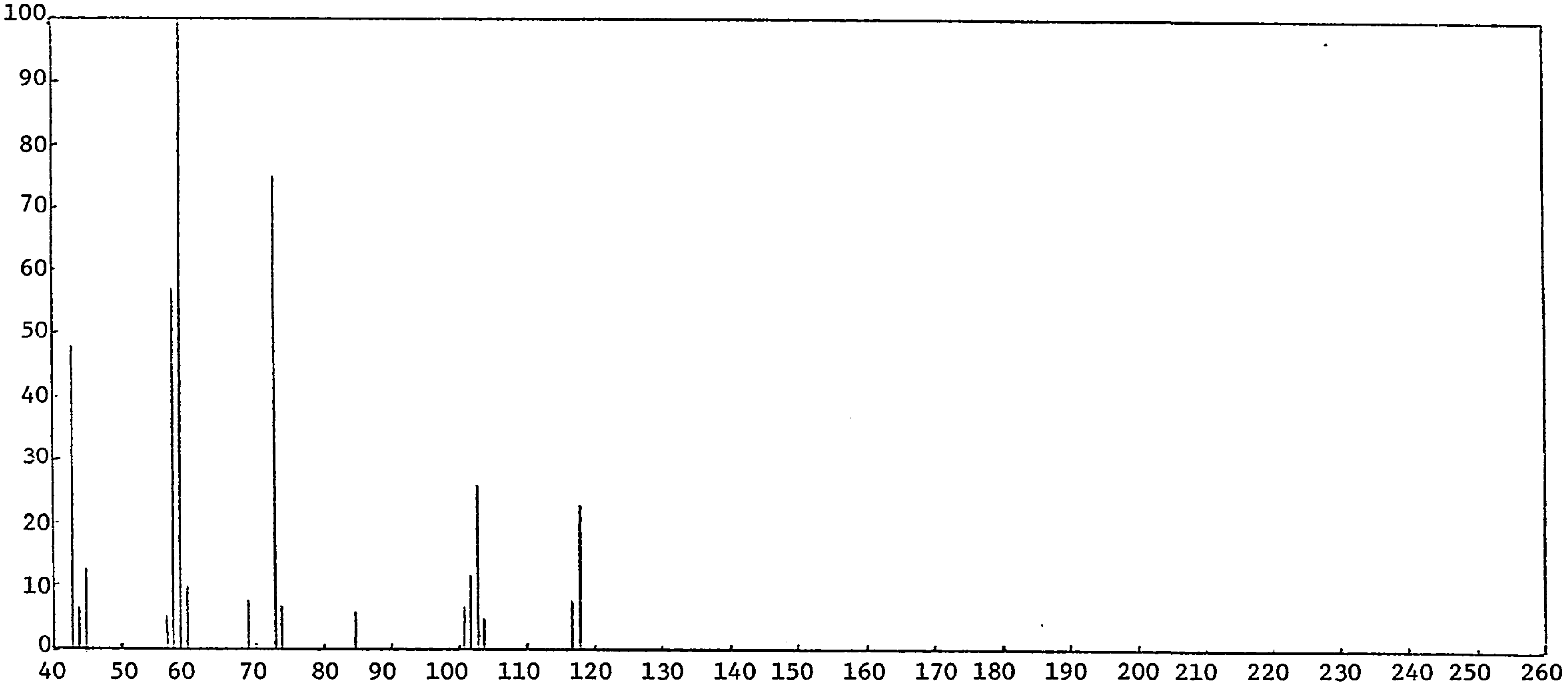


Figure 9: The 70 eV Mass Spectrum of Compound 43

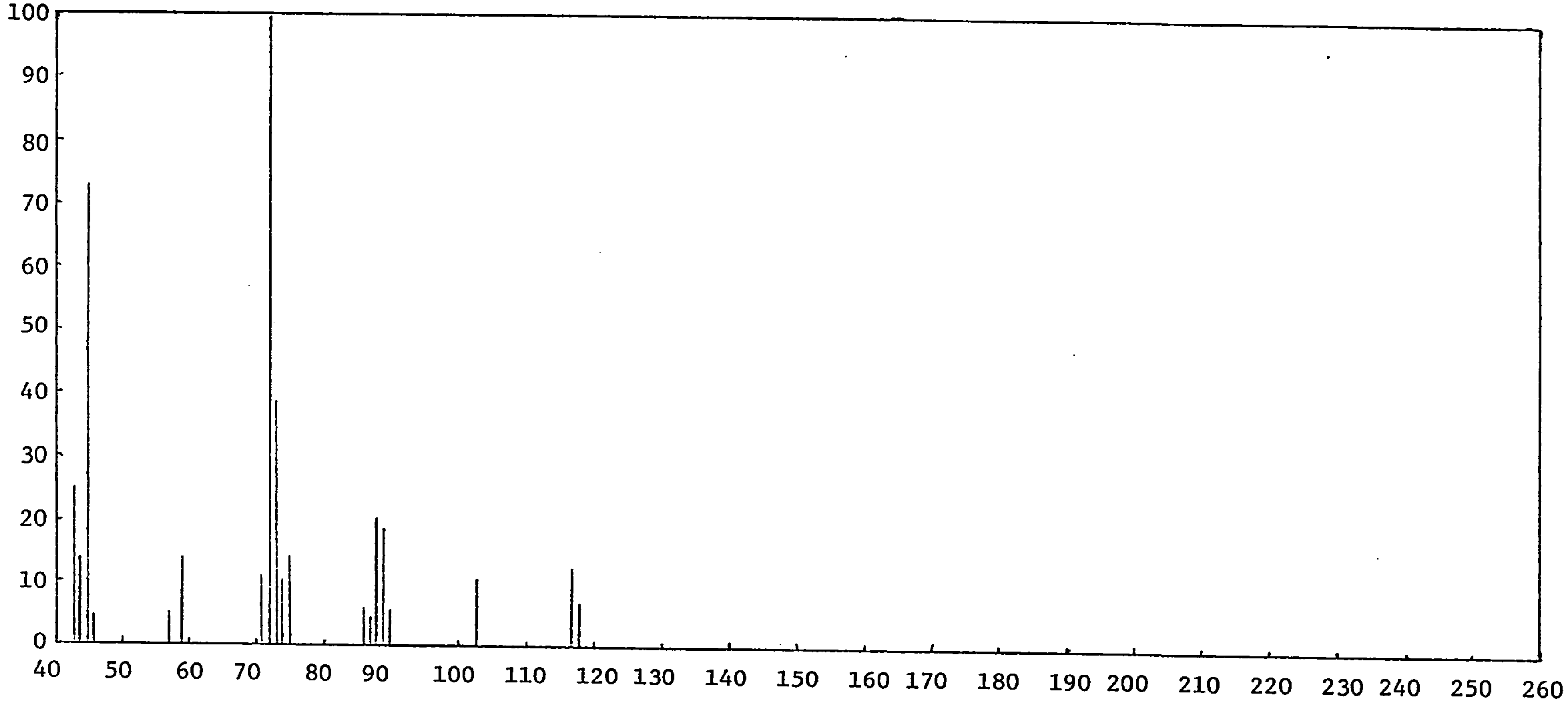


Figure 10: The 70 eV Mass Spectrum of Compound 47

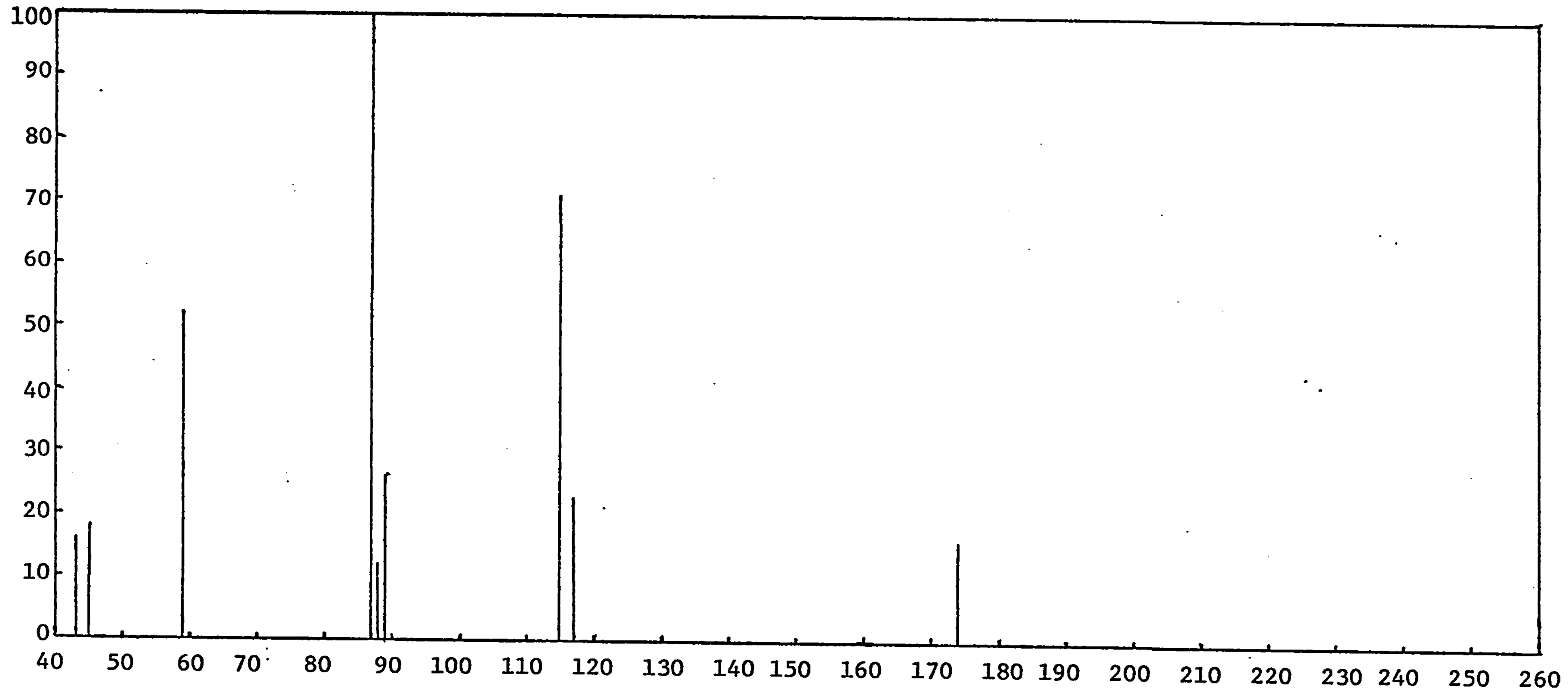
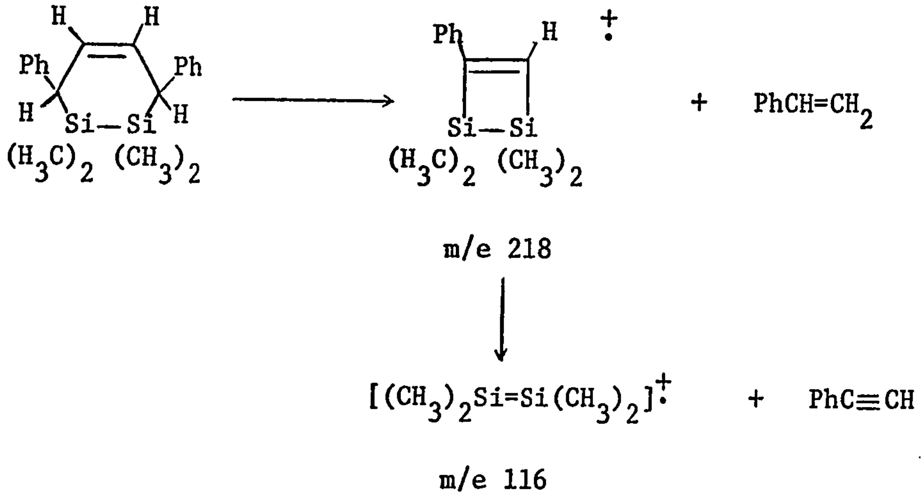


Figure 11: The 70 eV Mass Spectrum of Compound 57

$$\begin{tikzcd} {[(C_2H_5)_3SiSi(CH_3)_2H]^{+\cdot}} \arrow[r] & \underset{m/e\ 115}{(C_2H_5)_3Si^+} \arrow[d, "-C_2H_5"] & + \quad \cdot Si(CH_3)_2H \\ \underset{m/e\ 59}{C_2H_5SiH_2^+} & \underset{m/e\ 87}{(C_2H_5)_2SiH^+} \arrow[l, "-C_2H_5"'] & \end{tikzcd}$$

The mass spectrum of the disilacyclohexene, 60, (figure 12) showed only two major fragments: the peak at m/e 73 for $(CH_3)_3Si^+$ and the peak at m/e 116 for $[(CH_3)_2Si{=}Si(CH_3)_2]^{+\cdot}$. Whether the m/e 116 fragment is formed via a retro-diene reaction or via some other route is not known, since there were no metastable peaks to indicate the pathway for its formation. There is, however, a metastable peak for the fragmentation of m/e 322 (the parent ion) to give m/e 218 ($218^2/322=147.7$; found: 147.7). The exact mass of the m/e 218 peak showed it to have the composition $C_{12}H_{18}Si_2$ (calculated: 218.0947; found: 218.0958). A possible structure for this ion is indicated in the reaction sequence below. We have also indicated in



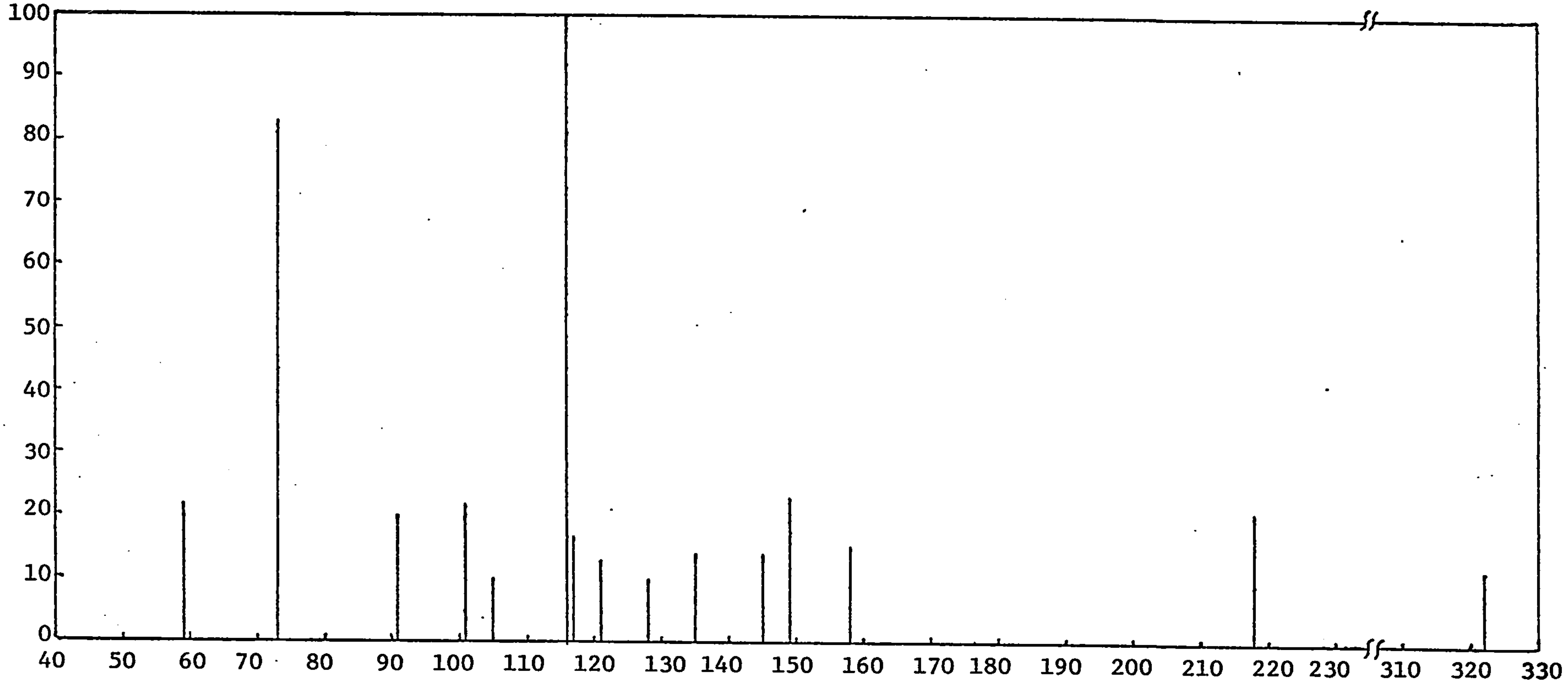


Figure 12: The 70 eV Mass Spectrum of Compound 60

This reaction sequence that the m/e 116 ion could arise via this route as opposed to its formation via a retro-diene reaction of the parent ion.

With the notable exception of the disilacyclohexadiene, 21, the interpretation of the mass spectra of organo-silicon compounds which we have taken have been straight forward and a valuable aid in structure elucidation.

CHAPTER 5: EXPERIMENTAL

INSTRUMENTS AND SPECIAL EQUIPMENT

NMR Spectrometry: All NMR spectra were taken on Varian Associates A-60 or HA-100 nuclear magnetic resonance spectrometers. τ values are reported from external TMS.

Infrared Spectrometry: All infrared spectra were taken on a Perkin-Elmer 421 infrared spectrometer.

Mass Spectrometry: Heated inlet samples were run on a GEC/AEI MS-2 mass spectromter. GC-MS runs were performed on a GEC/AEI MS-12 mass spectrometer coupled to a Varian Hi-Fi Aerograph gas chromatograph equipped with a temperature programmer. For direct probe spectra a GEC/AEI MS-12 mass spectrometer was used, and for exact mass measurements a double-focusing GEC/AEI MS-9 mass spectrometer was used. An ionization potential of 70 eV was used unless otherwise specified.

Gas Chromatography: A Varian Aerograph A-90-P3 gas chromatograph equipped with a Varian temperature programmer and Honeywell recorder was used. Unless otherwise specified a 20 foot by 1/8 inch stainless steel column packed with 5% GESF-96 on acid washed, silylated chromasorb G was used with a helium flow rate of 40-50 ml/min.

Microanalysis: Microanalyses were performed by the University of Alberta Dept. of Chemistry microanalytical lab and by Galbraith Laboratories.

Pyrolysis: Small scale tube pyrolysis (<1 gm.) were performed in the oven shown in figure 13. Larger scale tube pyrolyses (<5 gm.) were performed using the oven shown in figure 14. An iron-constantan thermocouple with 0°C. lead was used to determine the oven temperature. The flow pyrolyses experiments were done using the apparatus shown in figure 15. The oven used for the flow experiments was a Lindberg Hevi-Duty furnace.

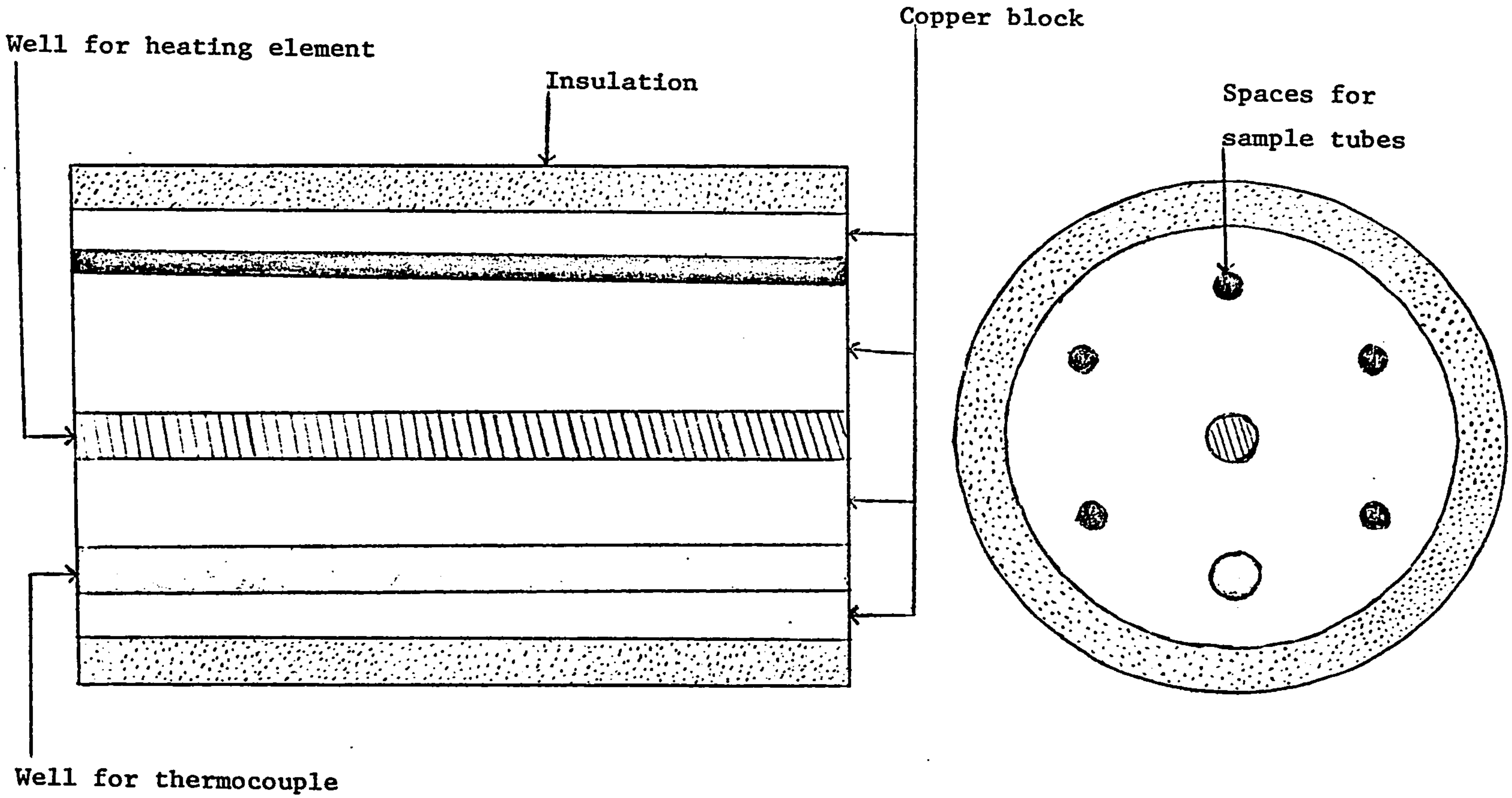


Figure 13: Oven for Small Scale Tube Pyrolysis

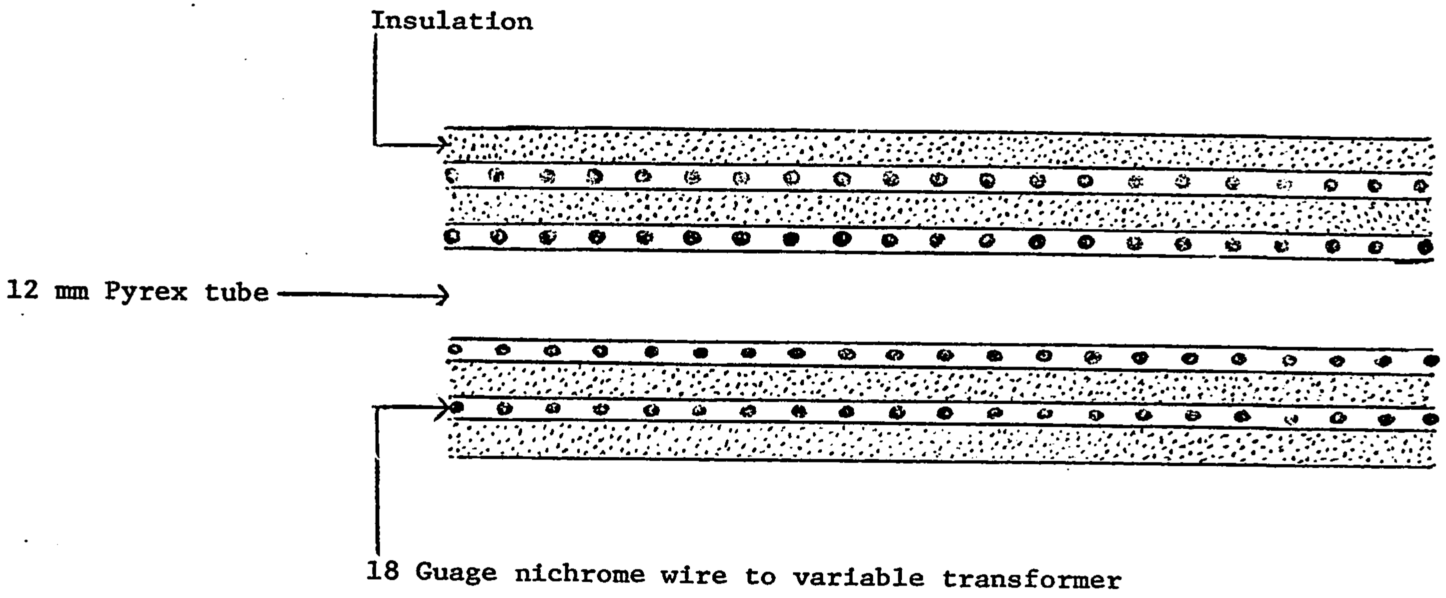


Figure 14: Oven for Large Scale Tube Pyrolysis

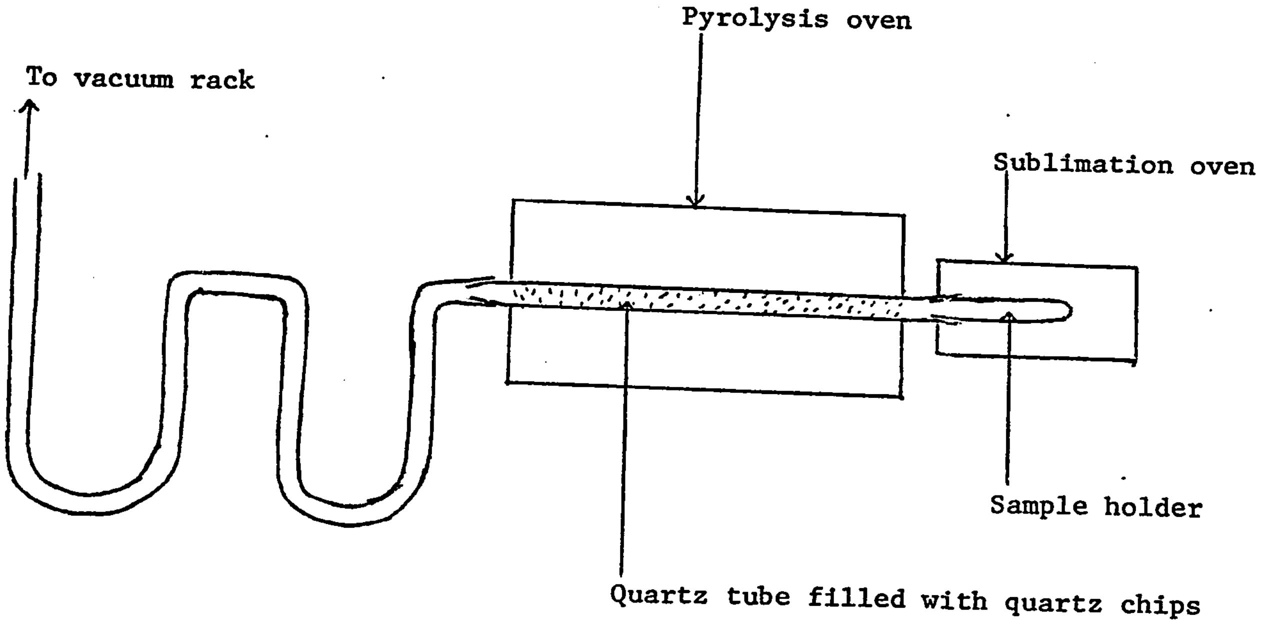


Figure 15: Apparatus for Flow Pyrolysis

PREPARATIONS AND ATTEMPTED PREPARATIONS

General: All reactions were done under dry nitrogen unless otherwise specified. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were freshly distilled from calcium hydride and shaken with Linde 4A molecular sieves before use. Freshly opened Mallinckrodt anhydrous diethyl ether was used without further purification. The hexamethyldisilane was purchased from Pierce Chemical Co.

All of the following compounds were prepared following reported procedures and all gave spectral data and melting points (or boiling points) which were in agreement with the reported data: 1,1,2,2-tetramethyldisilane, **43**;[75] pentamethylchlorodisilane;[105] 1,1,3,3-tetramethyl-1,3-disilacyclobutane, **2**;[74] 1,2,3,4-tetraphenyl-5,5-dimethyl-5-sila-1,3-cyclopentadiene, **19**;[53] and hexaethyldisilane.[106]

1,1,2,2-Tetramethyl-1,2-dichlorodisilane, 20: The tetramethyldichlorodisilane, **20**, was prepared from hexamethyldisilane following the method of Sakurai, Tominaga, Watanabi, and Kumada.[86] The final purification was done by distillation on an annular teflon spinning band column. The fraction b.p. 140-144°C./700 Torr was used in later preparations (lit. b.p. 148°C./760 Torr).[86] A NMR spectrum showed only one peak at τ=10.2. However, gas chromatography showed a small impurity (<5%) whose retention time was identical to an authentic sample of pentamethylchlorodisilane.

1,2,3,4-Tetraphenyl-5,5,6,6-tetramethyl-5,6-disila-1,3-cyclohexadiene, 21: To 0.80 g. (0.114 g-atom) of freshly cut and cleaned lithium wire in 120 ml. of anhydrous diethyl ether was added 18.0 g. (0.101 mole) of diphenylacetylene. This mixture was stirred for 16 hr., then 450 ml. of anhydrous THF were added with mechanical stirring, followed by the dropwise addition of 9.36 g. (0.0502 mole) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, **20**, in 60 ml. of THF. The solution was refluxed for 2.5 hr., then 250 ml. of water were slowly added. The organic layer was spearated and dried over anhydrous sodium sulfate. The volatile material was removed on a rotary evaporator to give a yellow oil, which was dissolved in heptane. On cooling this heptane solution, 6.3 g. (24% yield) of compound 21 were obtained. Further cooling of the heptane solution gave a mixture containing 2.7 g. (11% yield) of compound 21 and 2.7 g. (13% yield) of 1,2,3,4-tetraphenyl-5,5-dimethyl-5-sila-1,3-cyclopentadiene, 19.

Compound 21 was a yellow crystalline solid, m.p. 168.5-170°C. on recrystallization from heptane. Its NMR spectrum in carbon tetrachloride showed peaks at τ=2.7-3.3 (multiplet) and τ=9.8 (singlet) which integrated in the ratios of 20:12. Its mass spectrum had a parent peak at m/e 472 and major fragmentation peaks at m/e 457, 379, 279, 221, 135, 105, 73, 59, 58, and 43. Its infrared spectrum in carbon tetrachloride had absorptions at 3080, 3060, 3020, 2960, 2895, 1598, 1575, 1489, 1442, 1405, 1255, 1242, 1085, 1072, 1030, 975, 911, 891, 850, 708, 700, 677, 667, 648, 621, and 599 cm^{-1}. Anal. calc. for $C_{32}H_{32}Si_2$: C, 81.30; H, 6.82. Found: C, 81.30; H, 6.75.

Compound 19 showed an identical NMR spectrum and mass spectrum to those of an authentic sample. It also reacted with dimethylacetylene dicarboxylate to give a compound which was identical to that reported by Gilman, Cottis, and Atwell.[53]

2,3-Bis-(methylcarboxylate)-7,7,8,8-tetramethyl-1,4,5,6-tetraphenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene, (an attempted preparation): A mixture of 1.0 g. (2.12 mmole) of compound 21 and 1.0 ml. (4.52 mmole) of dimethylacetylene dicarboxylate was heated to 160°C. for 5 hr. On cooling, 1.0 g. of crystals was formed which was identical in every respect to compound 21.

1,2,3,4,5,6-Hexaphenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene, (an attempted preparation): A mixture of 100 mg. (0.212 mmole) of compound 21 and 75 mg. (0.42 mmole) of diphenylacetylene was heated to 200°C. for 21 hr. A NMR spectrum and a mass spectrum indicated that no reaction had occurred.

1,2,3,4,5-Pentaphenyl-6,7,7,8,8-pentamethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene, (an attempted preparation): A mixture of 500 mg.

(1.60 mmole) of compound 21 and 0.20 ml. (1.62 mmole) of 1-phenylpropyne was degassed and sealed under vacuum in a glass tube. This was heated to 200°C. for 23 hr., then cooled. A NMR spectrum showed only peaks due to starting materials.

5:6-Benzo-1,2,3,4-tetraphenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene, (an attempted preparation): To a refluxing mixture of 1.1 g. (2.33 mmole) of compound 21 in 15 ml. of THF, 1.20 g. (8.77 mmole) of anthranilic acid in 25 ml. of THF and 1.50 g. (12.8 mmole) of isoamyl nitrite in 15 ml. of THF added dropwise simultaneously from two addition funnels. The addition took 2.5 hr., after which the resulting red-brown solution was evaporated to dryness on a rotary evaporator. Most of the brown-black solid obtained could not be redissolved in organic solvents. The portion which did dissolve was recrystallized from Skelly B to give 0.2 g. of pure 21.

2:3,5:6-Dibenzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]-octa-2,5-diene, 34:

First Preparation: To 71.4 g. (0.40 mole) of anthracene in 450 ml. of THF was added 18.4 g. (0.80 g-atom) of finely cut sodium. This mixture was refluxed for 4 hr. then cooled to room temperature. After which 75.0 g. (0.40 mole) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, 20, was slowly added. After addition was complete, methanol was added to destroy any remaining sodium. This was followed by addition of diethyl ether and water. The organic layer was separated, washed, and dried over anhydrous sodium sulfate. The volatile material was removed on a rotary evaporator to give a yellow oil which was dissolved in ethanol and cooled to give yellow crystals. Three recrystallizations from ethanol/chloroform gave 1.8 g. (2% yield) of compound 34, m.p. 161-163°C. The spectral data was identical to that reported in the third preparation.

Second Preparation: A mixture of 11.0 g. (0.478 g-atom) of finely cut sodium and 42.7 g. (0.240 mole) of anthracene was refluxed for 4 hr. in 300 ml. of THF, then the mixture was cooled to

-78°C. and 45.0 g. (0.242 mole) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, 20, in 250 ml. of THF was added. The reaction mixture was then added and the organic layer was spearated, washed, and dried over anhydrous magnesium sulfate. The volatile material was removed on a rotary evaporator, then carbon tetrachloride was added and the solution filtered to give 3.4 g. of solid, whose NMR spectrum was identical to that of anthracene. The carbon tetrachloride was then removed to give a yellow syrup. Attempts at crystallizing this syrup from ethanol/chloroform and from pentane failed. Chromatography of this syrup on a silica gel column eluted with benzene gave a crystalline solid as the first fraction. Recrystallization from pentane yielded 1.0 g. (1% yield) of 35. Later fractions from the silica gel column gave NMR spectra which indicated that they were complex mixtures.

Compound 35 had a m.p. of 158-159°C. Its NMR spectrum showed absorptions in deuterochloroform at τ=2.9 (singlet), τ=6.1 (singlet), τ=9.7 (singlet), and τ=10.2 (singlet), which had a relative integration of 8:2:12:12 respectively. The infrared spectrum in carbon tetrachloride had absorptions at 3070, 3025, 2950, 2895, 2840, 1680, 1605, 1490, 1480, 1450, 1400, 1286, 1272, 1250, 1173, 1100, 1043, 942, and 897 cm^{-1}. Its mass spectrum showed peaks at m/e 45, 59, 73, 115, 116, 131, 145, 147, 174, 175, 176, 178, 189, 203, 233, 248, 353, and 426. An exact mass on the m/e 426 peak was measured to be 426.1680 (calculated for $C_{22}H_{30}Si_4O$: 426.1686).

Third Preparation: After 35.6 g. (0.20 mole) of anthracene was added to 5.9 g. (0.24 g-atom) of 28% lithium dispersion in 250 ml. of DME, the mixture was stirred for 3 hr. at room temperature, then cooled to -78°C. After which 18.7 g. (0.10 mole) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, 20, were added over a 1.5 hr. period. The mixture was poured onto ice and concentrated hydrochloric acid, then diethyl ether was added. The organic layer was separated and dried over anhydrous sodium sulfate. The volatile material was removed on a rotary evaporator. Carbon tetrachloride was added to the residue and the excess anthracene was filtered off. Cooling gave 8.0 g. (27% yield) of compound 34. Further purification was obtained by recrystallization from ethanol/chloroform followed by sublimation at 155°C./0.01 Torr.

Compound 34 is a white crystalline solid, m.p. 162-164°C. Its NMR spectrum in carbon tetrachloride shows three singlets at τ=3.0, τ=6.3, and τ=10.3, which integrate in the ratio of 8:2:12 respectively. Its infrared spectrum in carbon tetrachloride shows bands at 3083, 3025, 3012, 2955, 2920, 2900, 2850, 1478, 1466, 1450, 1402, 1283, 1246, 1240, 1202, 1060, 1029, 935, 895, 879, and 858 cm^{-1}. Its mass spectrum shows a parent peak at m/e 294 and fragmentation peaks at m/e 178, 116, 101, and 73. Compound 34 can be stored in a stoppered vial in the dark indefinitely. *Anal.* Calc. for $C_{18}H_{22}Si_2$: C, 73.40; H, 7153. Found: C, 73.04; H, 7.53.

2:3-Benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene, 36: After 30.0 g. (0.244 mole) of naphthalene was added to 7.0 g. (0.357 g-atom) of 28% lithium dispersion in 300 ml. of DME, the mixture was stirred for 3 hr. at room temperature. After cooling to -78°C., 20.0 g. (0.108 mole) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, 20, in 100 ml. of DME was slowly added. The resulting mixture was poured onto ice and concentrated hydrochloric acid. Diethyl ether was added and the organic layer was separated, washed, and dried over anhydrous sodium sulfate. The volatile material was removed on a rotary evaporator, leaving 49.3 g. of yellow oil. This oil was placed in a sublimator under a reduced pressure of 0.1 Torr. Heating to 60-70°C. gave 19.6 g. of crystalline material which was a mixture of naphthalene and 2,2,3,3,5,5,6,6-octamethyl-1,4-dioxohexasilane. Both of these compounds gave NMR spectra and gass chromatographic retention times identical with those of authentic samples. On raising the temperature on the sublimator to 80-90°C., 11.0 g. (42% yield) of compound 36 was obtained. Further purification was obtained by recrystallization from carbon tetrachloride.

Compound 36 is a white crystaliine solid, m.p. 64-66°C. Its NMR spectrum in deuterochloroform has a singlet at τ=2.9, a double-doublet at τ=3.9, a double-doublet at τ=6.6, a singlet at τ=9.8 and a singlet at τ=10.0. Its infrared spectrum in carbon tetrachloride has peaks at 3055, 3030, 3000, 2945, 2910, 2895, 1462, 1445, 1243, 1238, 1208, 1175, 1128, 1052, 995, 978, and 895 cm^{-1}. Its mass spectrum showed a parent peak at m/e 244 and major fragmentation peaks at m/e 128, 116, 101, 73, 59, 45, and 43. *Anal.* Calc. for $C_{14}H_{20}Si_2$: C, 68.78; H, 8.24. Found: C, 68.97; H, 8.29.

After 36 had been stored for 2 weeks in a stoppered vial in the dark, a mass spectrum showed a large new peak at m/e 260. An exact mass measurement on this peak gave 260.1055 (calculated for $C_{14}H_{20}Si_2O$: 260.1052).

1-Phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene, 37:

First Attempted Preparation: A mixture of 1.54 g. (0.220 g-atom) of freshly cut and cleaned lithium wire, 15.4 g. (0.100 mole) of biphenyl, and 150 ml. of THF was stirred for 3 hr. at room temperature to give a dark green-blue solution. The temperature of this solution was lowered to -78°C. and 18.6 g. (0.100 mole) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, 20, in 150 ml. of THF was rapidly added. The reaction mixture was then poured onto ice and dilute hydrochloric acid, and then ether and benzene were added. The organic layer was spearated, washed, and dried over anhydrous sodium sulfate. The volatile material was removed on a rotary evaporator to give 27.5 g. of a thick paste. A NMR spectrum of this paste in deuterochloroform showed a complex absorption at τ=2.3-3.0 and at τ=9.5-10.1. The absence of peaks in the τ=4.0-7.0 region indicated that the desired compound had not been formed and therefore, this reaction was abandoned.

Second Attempted Preparation: A mixture of 30.8 g. (0.200 mole) of biphenyl, 5.9 g. (0.24 g-atom) of 28% lithium dispersion, and 250 ml. of DME was stirred at room temperature for 3 hr. then cooled to -78°C. To this, 18.7 g. (0.100 mole) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, 20, was added over a 1 hr. period. Then the reaction mixture was poured onto ice and concentrated hydrochloric acid. The organic layer was separated, washed, and dried over anhydrous sodium sulfate. The volatile material was removed on a rotary evaporator to give a yellow solid, which was placed in a sublimator. A white solid (mostly biphenyl based on g.l.c. and NMR) was sublimed off, leaving a yellow oil. This oil was dissolved in carbon tetrachloride and cooled, but it yielded no crystalline material. Likewise, dissolving it in hexane gave no crystalline material. No further attempts at purification were made.

Third Preparation: A mixture of 25.2 g. (0.164 mole) of biphenyl and 1.5 g. (0.214 g-atom) of freshly cut and cleaned lithium wire was stirred in 150 ml. of anhydrous diethyl ether and 75 ml. of THF overnight at which time all of the lithium had disappeared. Then 15.0 g. (0.0805 mole) of the dichlorodisilane, 20, in 75 ml. of THF was added at -78°C. The reaction micture was poured onto ice and concentrated hydrochloric acid. The organic layer was separated, washed, and dried over anhydrous sodium sulfate. The volatile material was removed on a rotary evaporator leaving a yellow solid, which was placed in a sublimator. After which 10.6 g. of white solid (mostly biphenyl based on g.l.c.) was sublimed from the mixture at 50-80°C./0.1 Torr. The residue was dissolved in carbon tetrachloride and cooled to give white crystals which were washed with cold heptane to obtain 2.73 g. (13% yield) of compound 37.

The product, 37, was a white crystalline solid, m.p. 118-121°C. Its NMR spectrum in deuterochloroform showed a multiplet at τ=2.5-2.8, a multiplet at τ=3.7-4.1, a triple-triplet at τ=6.9, a singlet at τ=9.7, and a singlet at τ=10.0, which integrate in the ratio of

5:4:1:6:6. Its infrared spectrum in carbon tetrachloride had peaks at 3085, 3055, 3035, 3018, 2959, 2925, 2892, 2865, 2850, 1792, 1580, 1545, 1479, 1472, 1463, 1425, 1383, 1256, 1240, 1230, 1225, 1206, 1165, 1052, 1015, 945, 908, 903, 879, 868, 835, and 812 cm^{-1}. The mass spectrum gave a parent peak at m/e 270 and major fragmentation peaks at m/e 211, 116, 101, 73, 59, 45, and 43. An exact mass on the m/e 270 peak gave 270.1258 (calculated for $C_{16}H_{22}Si_2$: 270.1260). Anal. Calc. for $C_{16}H_{22}Si_2$: C, 71.04; H, 8.20. Found: C, 70.72; H, 7.88.

7,7,8,8-Tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene, (an attempted preparation): A mixture of 6.9 g. (0.0885 mole) of benzene, 6.5 g. (0.260 g-atom) of 28% lithium dispersion, and 16.4 g. (0.0885 mole) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, 20, was stirred for eleven days, then added to ice and concentrated hydrochloric acid. Ether was added and the organic layer was separated, washed, and dried over anhydrous sodium sulfate. The volatile material was then removed on the rotary evaporator to give an oil whose NMR spectrum showed only absorptions in the silicon-methyl region (no olefinic or bridgehead protons were present).

1,4-Diphenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (an attempted preparation): A mixture of 66 g. (0.287 mole) of p-terphenyl, 7.2 g. (0.288 g-atom) of 28% lithium dispersion, and 200 ml. of THF was stirred at room temperature for 2 hr., then cooled to -78°C. After which 20 g. (0.108 mole) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, 20, in 100 ml. of THF was added.. The reaction mixture was then poured onto ice and concentrated hydrochloric acid. The organic layer was separated, washed, and dried over anhydrous sodium sulfate. The volatile material was removed on a rotary evaporator to give a yellow paste. Addition of hexane and filtering gave 23.2 g. of p-terphenyl, m.p. 208-210°C. Cooling the hexane solution gave a yellow oil. Likewise, no crystalline material could be obtained by dissolving the oil in either carbon tetrachloride or ethanol and cooling. A NMR spectrum indicated that this yellow oil was a complex mixture.

1,3-Dimethyl-1,3-disilacyclobutane, 42: A few pieces of magnesium turnings were covered with 1 ml. of THF then 4 drops of methyl iodide and a few drops of a solution, containing 50 g. (0.309 mole) of methyl-(chloromethyl)-dichlorodilane in 60 ml. of THF, were added. As soon as the reaction had started the remainder of the methyl-(chloromethyl)-dichlorosilane solution was added. To this mixture 13 g. (0.535 g-atom) of magnesium turnings was slowly added at such a rate as to keep the reaction mixture's temperature below 50°C. (this required occassional cooling in a cold water bath). After addition of the magnesium was finished, the reaction mixture was stirred for 2 hr., followed by addition of hexane. The solid precipitate which had formed was filtered off. The THF and hexane were distilled from the reaction mixture and the 32.6 g. of remaining oil was slowly added to 3.9 g. (0.103 mole) of lithium aluminum hydride in 150 ml. of anhydrous diethyl ether. The mixture was stirred for an hour, then added to ice and concentrated hydrochloric acid. The organic layer was separated, washed, and dried over anhydrous sodium sulfate. The diethyl ether was distilled off leaving an oil from which 500 mg. of 1,3-dimethyl-1,3-disilacyclobutane, 42, was obtained by preparative gas chromatography. The infrared spectrum was in agreement with that published in the literature.[74] The NMR spectrum in carbon tetrachloride showed a multiplet at τ=5.1-5.5, a doublet at τ=9.6, and a triplet at τ=9.8, which had intensity ratios of 2:6:4. Its mass spectrum showed a parent peak at m/e 116 and major fragmentation peaks at m/e 115, 101, 99, 73, and 59.

2,2,4-Trichloro-4-methyl-2,4-disilapentane: After 5.0 g. (0.208 g-atom) of magnesium turnings was covered with THF, several drops of methyl iodide followed by several drops of dimethyl-(chloromethyl)-chlorosilane were added. After reaction had begun, 80 g. (0.540 mole) of methyltrichlorosilane was added. Then 20 g. (0.141 mole) of dimethyl-(chloromethyl)-chlorosilane in 100 ml. of THF was slowly added over a one hour period with vigorous stirring. After the addition was complete, the reaction mixture was heated to

70°C. and stirred for 4 hr. After cooling, 100 ml. of pentane were added and the solid precipitate was filtered off. Fractional distillation gave 16.0 g. (52% yield) of pure 2,2,4-trichloro-4-methyl-2,4-disilapentane.

This product was a colorless liquid, b.p. 182-185°C. (literature b.p. 186°C.).[107] A neat NMR spectrum showed three singlets at τ=9.1, τ=9.2, and τ=9.5 with relative intensities of 2:3:6 respectively. The mass spectrum did not show a parent peak at m/e 220, but gave a major fragmentation peak at m/e 205, which had an isotope pattern consistent with the presence of three chlorines. An exact mass on the m/e 205 peak gave 204.9229 (calculated for $C_3H_4Si_2Cl_3$: 204.9231). Other major fragmentation peaks were at m/e 185, 93, 65, 55, 43, and 41.

2-Methyl-2,4-disilapentane, 46: After 14 g. (0.0637 mole) of 2,2,4-trichloro-4-methyl-2,4-disilapentane was slowly added to 3.6 g. (0.0973 mole) of lithium aluminum hydride in 100 ml. of anhydrous diethyl ether, the reaction mixture was refluxed for 5 hr. After cooling, the reaction mixture was poured onto a mixture of ice and concentrated hydrochloric acid. The organic layer was spearated, washed, and dried over anhydrous sodium sulfate. Fractional distillation gave 3.0 g. (40% yields) of 2-methyl-2,4-disilapentane, 46.

Compound 46 was a colorless liquid, b.p. 86-87°C. (literature b.p. 88.5°C.).[108] Its NMR spectrum in deuterochloroform had a multiplet at τ=5.9-6.4, a multiplet at τ=9.8-10.0, and a quartet at τ=10.1-10.4, which had relative intensities of 3:9:2 respectively. The gas phase infrared spectrum showed absorptions at 2970, 2915, 2135, 1263, 1052, 962, 885, 841, 800, and 769 cm^{-1}. The mass spectrum was identical to that reported by Fritz, Grobe and Kummer.[25] Anal. Calc. for $C_4H_{14}Si_2$: C, 40.60; H, 11.92. Found: C, 40.50; H, 12.00.

2,5-Disilahexane, 47: A mixture of 0.5 ml. of methyldichlorosilane, 0.25 ml. of methylvinyldichlorosilane and 2 drops of chloroplatinic acid solution ($7x10^{-3}$M in ethanol) was heated to reflux. Then the remaining 9.0 g. (0.0789 mole) of methyldichlorosilane and

10.0 g. (0.0714 mole) of methylvinyldichlorosilane were slowly added to the refluxing mixture. After three days the reaction mixture was cooled and the unreacted starting materials distilled from the mixture. The remaining 4.0 g. of residue was slowly added to 2.0 g. (0.0527 mole) of lithium aluminum hydride in 50 ml. of anhydrous diethyl ether, and the resulting mixture was poured onto ice and concentrated hydrochloric acid. The organic layer was separated off, washed, and dried over anhydrous sodium sulfate. Distillation yielded 80 mg. of impure product. Final purification was done by preparative g.l.c.

Compound 47 was a clear, colorless liquid whose NMR spectrum in carbon tetrachloride showed a multiplet at τ=6.2-6.5, a triplet at τ=9.2-9.4, and a triplet at τ=9.8-10.0, with relative intensities of 4:4:6 respectively. Its gas phase infrared spectrum showed absorptions at 2975, 2910, 2895, 2140, 1416, 1265, 1258, 1142, 1065, 952, and 897 cm^{-1}. Its mass spectrum showed a parent peak at m/e 118 as well as peaks at m/e 117, 103, 89, 88, 75, 73, 72, 59, 45, 44, and 43.

Bis-(trimethylsilyl)-mercury: Sodium amalgam was prepared by slowly adding 2.5 g. of finely cut sodium to 500 g. of mercury with rapid stirring.

A mixture of 100 g. (0.0218 g-atom of sodium) of sodium amalgam, 4.7 g. (0.0436 mole) of trimethylchlorosilane, and 20 ml. of cyclohexane was placed in a flask under dry nitrogen and shaken for 10 days. The reaction mixture was then filtered in a Schlenk tube to give a yellow-green solution, which was placed into a sublimation apparatus and the cyclohexane was removed under reduced pressure. The resulting yellow solid was sublimed to give 1.87 g. (50% yield) of bis-(trimethylsilyl)-mercury.

1,1,1,2-Tetramethyldisilane, 44: A mixture of 1.87 g. (6.09 mmole) of bis-(trimethylsilyl)-mercury and 1.5 g. (13.2 mmoles) of methyldichlorosilane was degassed and sealed in a pyrex tube. This tube was heated to 120°C. for 48 hr. The tube was then opened after cooling in liquid nitrogen. The organic liquid was decanted off of the 1.06 g. (98% yield) of mercury. The organic product was dissolved in 5 ml. of anhydrous diethyl ether and slowly added to 0.6 g. (12.8 mmole) of lithium aluminum hydride in 25 ml. of anhydrous diethyl ether, which was then refluxed for 4 hr. The reaction mixture was then poured onto ice and concentrated hydrochloric acid. The organic layer was separated, washed, and dried over anhydrous sodium sulfate. Most of the ether was distilled off and 50 mg. of the desired 1,1,1,2-tetramethyldisilane, 44, were obtained from the residue by preparative g.l.c. The only other product which was identified was hexamethyldisilane.

Compound 44 was a clear, colorless liquid whose NMR spectrum in carbon tetrachloride showed a multiplet at τ=6.3-6.7 and a multiplet at τ=9.7-9.9, with relative intensities of 2:12. Its gas phase infrared spectrum had absorptions at 2960, 2900, 2115, 1255, 937, 832, 750, and 700 cm^{-1}. The mass spectrum had a parent peak at m/e 118 and fragmentation peaks at m/e 103, 73, 59, 45, and 43.

The hexamethyldisilane was found to have identical g.l.c. retention time ans mass spectral fragmentation pattern to an authentic sample.

2,2-Dimethyl-2,4-disilabutane, 45: After 15 g. (0.123 mole) of chloromethyltrimethylsilane was slowly added to 4.0 g. (0.165 g-atom) of magnesium turnings in 100 ml. of anhydrous diethyl ether, the reaction mixture was refluxed for 0.5 hr. After cooling, the Grignard solution was slowly added to 100 g. (0.595 mole) of tetrachlorosilane in 200 ml. of anhydrous diethyl ether. After addition was complete, 100 ml. of pentane was added and the mixture was filtered. The pentane, ether, and excess tetrachlorosilane were distilled off. Then the residue was diluted with 50 ml. of anhydrous diethyl ether and slowly added to 7.0 g. (0.184 mole) of lithium aluminum hydride in 100 ml. of anhydrous diethyl ether. The reaction mixture was refluxed overnight, then poured onto an ice and concentrated hydrochloric acid mixture. The organic layer was separated, washed, and dried over anhydrous sodium sulfate. Fractional distillation gave 2.6 g. (18% yield) of 2,2-dimethyl-2,4-disilabutane, 45.

Compound 45 was a clear, colorless liquid, b.p. 77.5°C. Its NMR spectrum in carbon tetrachloride showed a triplet at τ=6.4-6.6, a singlet at τ=10.0, and a quartet at τ=10.1-10.5, with relative intensities of 3:2:9. The gas phase infrared spectrum had absorptions at 2960, 2900, 2150, 1420, 1256, 1140, 1051, 946, 848, 783, 762, and 758 cm^{-1}. Its mass spectrum was identical to that reported by Fritz, Grobe, and Kummer.[25]

1,1-Dimethyl-1,3-disilacyclobutane, 41, (an attempted preparation): Several drops of methyl iodide were added to 2 magnesium turnings covered by 1 ml. of THF. After the reaction had started, 10.2 g. (0.0653 mole) of bis-(chloromethyl)-dimethylsilane and 11.0 g. (0.0654 mole) of tetrachlorosilane in 100 ml. of THF were added. To this mixture 3.5 g. (0.144 g-atom) of magnesium turnings was added over a 6 hr. period. The resulting mixture was stirred for another 2 hr., then 100 ml. of pentane was added and the mixture filtered. The pentane and THF were distilled off and 50 ml. of anhydrous diethyl ether was added to the residue. This ether solution was then slowly added to 3.0 g. (0.0789 mole) of lithium aluminum hydride in 50 ml. of anhydrous diethyl ether. After being stirred overnight the reaction mixture was poured onto ice and concentrated hydrochloric acid. The organic layer was separated, washed, and dried over anhydrous sodium sulfate. The ether was distilled off leaving a very complex mixture of products. A g.l.c. trace showed 11 major volatile compounds, none of whose mass spectral fragmentation patterns could correspond to 1,1-dimethyl-1,3-disilacyclobutane, 41, (mass spectra were obtained by a g.l.c. directly coupled to the mass spectrometer).

Triphenylsilane: After 30 g. (0.102 mole) of triphenylchlorosilane in 200 ml. of anhydrous diethyl ether was slowly added to 5 g. (0.131 mole) of lithium aluminum hydride in 200 ml. of anhydrous diethyl ether, the mixture was stirred for 15 min. then the excess lithium aluminum hydride was destroyed with ethyl acetate. The resulting solution was added to dilute hydrochloric acid and ice.

The organic layer was separated, washed, and dried over anhydrous sodium sulfate. The volatile material was removed on a rotary evaporator, and the residue was dissolved in ethanol. Cooling yielded 28 g. (100% yield) of triphenylsilane, m.p. 28-30°C. Recrystallization from pentane raised the melting point to 35-36°C. (literature m.p. 36-37°C.).[109] Its NMR spectrum in carbon tetrachloride showed a multiplet at τ=2.3-2.8 and a singlet at τ=4.5, whose relative intensities were 15:1 respectively.

Pentamethyldisilane: After 10 g. (0.0603 mole) of pentamethylchlorosilane was slowly added to 1.1 g. (0.0289 mole) of lithium aluminum hydride in 50 ml. of anhydrous diethyl ether, the mixture was refluxed for 5 hr., then poured onto ice and concentrated hydrochloric acid. The organic layer was separated, washed, and dried over magnesium sulfate. Fractional distillation gave 3.9 g. (49% yield) of pure pentamethyldisilane, b.p. 97-99°C. (literature b.p. 98.5-98.7°C.).[75] A NMR spectrum and infrared spectrum were identical to those reported in the literature.[75]

9-Deuteroanthracene: A mixture of 5.0 g. (0.0194 mole) of 9-bromoanthracene, 1.0 g. (0.0417 g-atom) of magnesium turnings, and 100 ml. of THF was refluxed for 4 hr. The Grignard solution thus formed was added to 50 ml. of deuterium oxide; followed by addition of 100 ml. of diethyl ether. The organic layer was separated, washed, and dried over anhydrous sodium sulfate. The volatile material was removed on a rotary evaporator, and the residue was dissolved in ethanol. Cooling yielded 1.0 g. (28% yield) of 9-deuteroanthracene, m.p. 205-218°C. It was further purified by sublimation before use, m.p. 217-218°C. (literature m.p. 218-219°C.).[110] A mass spectrum showed it to be 62.6% deuterated.

Reaction of 1,1,2,2-tetramethyl-1,2-dichlorodisilane, 20, with zinc: A mixture of 1.0 g. (5.38 mole) of 20, 0.50 g. (7.69 g-atom) of zinc, and 5 ml. of benzene was stirred for 24 hr. A g.l.c. trace indicated that no reaction had occurred.

PYROLYSIS EXPERIMENTS

Neat tube pyrolysis of the anthracene-tetramethyldisilene adduct, 34: After 70 mg. of 34 was sealed in an evacuated pyrex tube, it was heated to 500°C. for 12 hr. On cooling to room temperature, the tube was opened and its contents dissolved in deuterochloroform. An NMR spectrum showed the characteristic multiplet of anthracene at τ=1.0-2.7 and a complex of peaks at τ=9.0-10.3. The only peak on the g.l.c. trace (besides solvent) was that due to anthracene.

Neat tube pyrolysis of the naphthalene-tetramethyldisilene adduct, 36: After 520 mg. of 36 was sealed in an evacuated pyrex tube, it was heated to 350°C. for 24 hr. The tube was opened at room temperature and a g.l.c. trace indicated that the only volatile product was naphthalene. A NMR spectrum indicated that 70% decomposition had occurred and that the only aromatic product had the characteristic multiplet of naphthalene. The reaction mixture was placed on an alumina column and eluted with cyclohexane. In this manner, 168 mg. (88% yield) of naphthalene was obtained, m.p. 74-77°C. No separation of the silicon containing compounds was obtained.

In a second pyrolysis, 50 mg. of 36 was sealed in an evacuated tube and heated to 390°C. for 3 hr. The tube was cooled in a liquid nitrogen bath before opening. The contents of the tube were dissolved in toluene. A g.l.c. trace showed that a trace of trimethylsilane was formed. This was identified by its g.l.c. retention time and its mass spectral fragmentation pattern obtained by a g.l.c. directly coupled to the mass spectrometer. A NMR spectrum in carbon tetrachloride showed no starting material. It gave a multiplet at τ=2.1-2.7 which was characteristic of naphthalene and a complex absorption at τ=9.4-10.4. The infrared spectrum in carbon tetrachloride showed a weak, broad absorption at 2100 cm^{-1}.

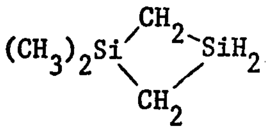
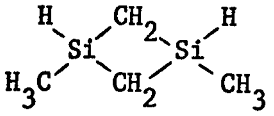
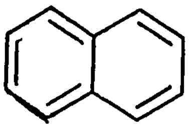
Neat tube pyrolysis of the biphenyl-tetramethyldisilene adduct, 37: After 150 mg. of 37 was heated at 235°C. in an evacuated sealed tube for 23 hr., the tube was cooled in a liquid nitrogen bath before opening. A g.l.c. trace showed biphenyl and a trace of trimethylsilane as the only volatile products. Both were identified by comparing g.l.c. retention times and mass spectral fragmentation patterns with those of authentic samples. A NMR spectrum in deuterochloroform indicated that a 67% decomposition of 37 had occurred. An infrared spectrum in carbon tetrachloride showed a weak absorption at 2125 cm^{-1}.

Neat flow pyrolysis of the naphthalene-tetramethyldisilene adduct, 36: Using the apparatus shown in figure 15, 227.0 mg. of 36 was sublimed into the 490-510°C. furnace at 0.01 Torr. over a 4 hr. period. The products were collected in a liquid nitrogen trap at the exit port of the furnace. After the sublimation was complete, the liquid nitrogen trap was allowed to warm to room temperature and the material within, which was volatile at 0.01 Torr., was distilled into a flask containing 414.1 mg. of cyclopentane in a liquid nitrogen bath. A g.l.c. trace showed six products. Five of these were identified by comparison of g.l.c. retention time and mass spectral fragmentation patterns with those of authentic compounds. These products were trimethylsilane; 2,2-dimethyl-2,4-disilabutane, 45; 2-methyl-2,4-disilapentane, 46; 1,3-dimethyl-1,3-disilacyclobutane, 42; and naphthalene.

By preparative g.l.c., 7.7 mg. of the sixth product, 41, was collected. Its NMR spectrum in dichloromethane showed a quintuplet at τ=5.5-5.7, a singlet at τ=9.7, and a triplet at τ=9.8, whose relative intensities were 2:6:4 respectively. Its gas phase infrared spectrum had absorptions at 2960, 2905, 2142, 1359, 1260, 963, 958, 888, 844, 837, and 820 cm^{-1}. Its mass spectrum showed an intense parent peak at m/e 116 and major fragmentation peaks at m/e 101, 73, 59, and 43. When chlorine gas was passed over a cyclopentane solution of 41, an exothermic reaction occurred with the evolution of gas. Adding methyl lithium to this reaction mixture caused a white precipitate to form. A g.l.c. trace showed that a product had been formed whose g.l.c. retention time and mass spectral fragmentation were identical to those of an authentic sample of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, 2.

Approximate yields of the six products were determined by comparing the g.l.c. peak areas of the reaction mixture with the g.l.c. peak areas of standard solutions of each of the compounds. Table V gives the results.

TABLE V: Products from Flow Pyrolysis of 36

Peak	Compound	% yield
1	$(CH_3)_3SiH$	3
2	$(CH_3)_3SiCH_2SiH_3$ 45	0.5
3	$(CH_3)_2SiHCH_2SiH_2CH_3$ 46	2
4	 41	30
5		10
6		7*

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* The naphthalene was not quantitatively distilled into the cyclopentane, as crystals of it were found through out the vacuum line.

Neat flow pyrolysis of the biphenyl-tetramethyldisilene adduct, 37: Using the apparatus shown in figure 15, 200 mg. of 37 were slowly distilled into a 450°C. furnace at 0.01 Torr. Then using exactly the same procedure as used on compound 36, a cyclopentane solution containing the products volatile at 0.01 Torr. was obtained. A g.l.c. trace showed the same silicon containing products in the same relative amounts as were obtained for compound 36. In addition a small amount of biphenyl was identified by its g.l.c. retention time.

The pyrolysis of 36 in the presence of triphenylsilane: A mixture of 100 mg. (0.427 mmole) of 36 and 600 mg. (2.31 mmole) of triphenylsilane was sealed in a tube under vacuum and heated to 390°C. for 3 hr. The tube was then cooled in a liquid nitrogen bath, opened and the contents dissolved in toluene. Dimethylsilane; 1,1,2,2-tetramethyldisilane, 43; and naphthalene were identidied as three of the products by their g.l.c. retention times and mass spectral fragmentation, which were both identical to those of authentic samples. All other reaction products were less volatile than these three and because of the high (>160°C.) column temperatures required, only poor quality mass spectra could be obtained. For this reason none of the less volatile products were identified.

The pyrolysis of 36 in the presence of phenyldimethylsilane, 56: A mixture of 200 mg. (0.819 mmole) of 36 and 1 ml. (6.54 mmole) of 56 was degassed and sealed in a pyrex tube, which was then heated to 400°C. for 17 hr. After cooling in a liquid nitrogen bath, the tube was opened, and a g.l.c. trace was run. There were 17 peaks in the g.l.c. trace. Of these the following six compounds were identified by comparison of their g.l.c. retention times and mass spectral fragmentation with those of authentic samples: dimethylsilane; trimethylsilane; 1,1,2,2-tetramethyldisilane, 43; phenyldimethylsilane, 56; naphthalene; and diphenyldimethylsilane.

The neat pyrolysis of 56: After 1 ml. of 56 was degassed and sealed in a pyrex tube, it was heated to 400°C. for 17 hr. After cooling in a liquid nitrogen bath, the tube was opened, and a g.l.c.

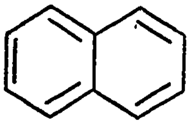
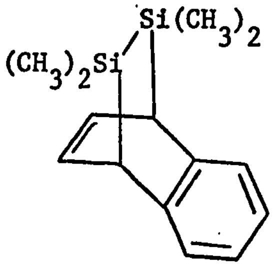
trace was run. There were 16 peaks in the g.l.c. trace which were the same as those in the previous experiment except that no naphthalene was present and the relative amount of **43** was significantly less.

The pyrolysis of 36 in the presence of triethylsilane: A mixture of 44.0 mg. (0.180 mmole) of **36** and 78.9 mg. (0.493 mmole) of triethylsilane was degassed and sealed in a pyrex tube, which was then heated to 350°C. for 1 hr. After cooling in a liquid nitrogen bath, the tube was opened and a series of g.l.c. traces were taken showing a complex mixture with approximately 50 different peaks. The following compounds were identified by comparison of retention times and mass spectral fragmentation patterns with authentic samples: dimethylsilane; trimethylsilane; 1,1,2,2-tetramethyldisilane, **43**; pentamethyldisilane; triethylsilane; naphthalene; and **36**.

The major silicon containing product, **57**, gave a mass spectrum with a parent peak at m/e 174 and major fragments at m/e 115, 87, and 59. By preparative g.l.c., 20 mg. of **57** were collected from this and two other similar reactions. It was a clear colorless liquid whose NMR spectrum in carbon tetrachloride showed a heptet at τ=6.2-6.6, a multiplet at τ=8.9-9.7, and a doublet at τ=9.9-10.0, with relative intensities of 1:15:6 respectively. On this basis, **57** was assigned the structure of 1,1,1-triethyl-2,2-dimethyldisilane. The effluent from one of the smaller g.l.c. peaks had a mass spectrum which showed a parent ion at m/e 232 and major fragments at m/e 217, 193, 189, 117, 115, 87, 73, and 45. This spectrum was consistent with the structure 1,1,1-triethyl-2,2,3,3-tetramethyltrisilane. No other effluent from the g.l.c. gave a mass spectrum which could be consistent with that structure. No hexaethyldisilane was found.

Percentage yields based on the amount of **36** present before reaction were obtained by comparing g.l.c. peak areas with the peak areas of standard solutions. These results are shown in table VI.

TABLE VI: Reaction of 36 with Triethylsilane

Compound	% Yield
$(CH_3)_2SiH_2$	---*
$(CH_3)_3SiH$	2
$(CH_3)_2SiHSi(CH_3)_2H$	7
$(CH_3)_3Si\text{-}Si(CH_3)_2H$	trace
$(C_2H_5)_3Si\text{-}Si(CH_3)_2H$	17**
	28
$(C_2H_5)_3Si\text{-}Si(CH_3)_2Si(CH_3)_2H$	3**
	63

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* No quantitative measurement of the amount of dimethylsilane formed was made, due to its high volatility, b.p. -20°C.

** A standard solution of pentamethyldisilane was used to determine these yields.

Two tubes each containing 200 mg. (0.819 mmole) of 36 and 800 mg. (6.89 mmole) of triethylsilane were heated to 400°C. One tube was removed from the furnace after 0.5 hr. and the other was removed after 3 hr. The ratio of 43 to 57 was 1:0.87 after 0.5 hr. and 1:1.71 after 3 hr.

The pyrolysis of 1,1,2,2-tetramethyldisilane, 43, in the presence of triethylsilane: A mixture of 366.6 mg. (3.11 mmole) of 43 and 755.4 mg. (6.52 mmole) of triethylsilane was degassed and sealed in a pyrex tube. The mixture was heated to 400°C. for 3 hr. then cooled in a liquid nitrogen bath and opened. A g.l.c. trace indicated that two major products had been formed: dimethylsilane and 1,1,1-triethyl-2,2-dimethyldisilane, 57.

The neat pyrolysis of hexaethyldisilane: After 0.2 ml. (0.727 mmole) of hexaethyldisilane was degassed and sealed in a pyrex tube, it was heated to 360°C. for 5 hr. then cooled to room temperature and opened. A g.l.c. trace showed only a trace of remaining hexaethyldisilane and a complex mixture of products. The major product was identified as triethylsilane by comparison of its g.l.c. retention time and its mass spectral fragmentation with those of an authentic sample.

The pyrolysis of 36 in the presence of toluene: A mixutre of 200 mg. (0.819 mmole) of 36 and 800 mg. (8.70 mmole) of toluene was degassed and sealed in a pyrex tube. The mixture was heated to 390°C. for 3 hr. It was then cooled in a liquid nitrogen bath and opened. A g.l.c. trace showed the only volatile products to be naphthalene and a trace of trimethylsilane. No 43 or bibenzyl were formed.

The pyrolysis of 36 in the presence of diphenylmethane: A mixture of (0.410 mmole) of 36 and 400 mg. (2.38 mmole) of diphenylmethane was degassed and sealed in a pyrex yube. The mixture was heated to 390°C. for 3 hr., then cooled in a liquid nitrogen bath and opened. A g.l.c. trace showed the only volatile products to be naphthalene and a trace of trimethylsilane.

The pyrolysis of 34 in the presence of 9-deuteroanthracene: A mixture of 30 mg. (0.103 mmole) of 34 and 200 mg. (1.12 mmole) of 9-deuteroanthracene (62.6% deuterated) was sealed in a pyrex tube and heated to 450-480°C. for 3 hr. A mass spectrum of the mixture showed that 34 had 14.3% excess d_1.

The tube was resealed and heated to 480-510°C. for 2 hr. Another mass spectrum indicated that 34 had 48.8% excess d_1. Complete equilibrium would give 57.3% excess d_1. There was no evidence in the mass spectrum of dideuteration.

The pyrolysis of 36 in the presence of anthracene: A mixture of 50 mg. (0.205 mmole) of 36 and 36.5 mg. (0.205 mmole) of anthracene was sealed in a pyrex tube and heated to 380°C. for 1.5 hr. After the tube was opened, a NMR spectrum was taken. The spectrum showed only peaks due to a 1:1 mixture of naphthalene and 34. The mixture was then placed in a sublimator and the naphthalene was sublimed off at 60°C./0.1 Torr. The temperature was then raised to 160°C. and 53.3 mg. (90% yield) of a solid, m.p. 161-164°C., was collected. This solid gave a NMR spectrum and mass spectrum which were identical to those of an authentic sample of 34.

Four tubes each containing 50 mg. (0.205 mmole) of 36; as well as 36.5 mg. (0.205 mmole), 73.0 mg. (0.410 mmole), 182.5 mg. (1.025 mmole), and 365.0 mg. (2.05 mmole) respectively of anthracene were heated to 335°C. for 15 min. NMR spectra of each of these samples showed that the ratio of 36 to 34 was 6.5:1 or 15% decomposition of 36.

The pyrolysis of 37 in the presence of anthracene: A mixture of 100 mg. (0.370 mmole) of 37 and 200 mg. (1.12 mmole) of anthracene was sealed in a pyrex tube and heated to 260-270°C. for 24 hr. Then the tube was opened and a NMR spectrum was taken. It showed only two peaks with chemical shifts outside the aromatic region of the spectrum. These peaks had identical chemical shifts and relative intensities (2:12) as the NMR spectrum of an authentic sample of 34. A mass spectrum showed only peaks due to anthracene, biphenyl, and 34.

The pyrolysis of 37 in the presence of naphthalene: A mixture of 100 mg. (0.370 mmole) of 37 and 200 mg. (1.56 mmole) of naphthalene was sealed in a pyrex tube and heated to 260-27-°C. for 24 hr. A g.l.c. trace showed only peaks for naphthalene, biphenyl, and 36. Likewise, a NMR spectrum and mass spectrum of the mixture showed only peaks due to these three compounds.

The pyrolysis of 37 in the presence of 1,4-diphenyl-1,3-butadiene: A mixture of 440 mg. (1.63 mmole) of 37 and 400 mg. (1.94 mmole) of 1,4-diphenyl-1,3-butadiene was sealed in a pyrex tube and heated to 260-270°C. for 24 hr. The tube was then opened and its contents dissolved in carbon tetrachloride. Cooling yielded 150 mg. (29% yield) of 60. The carbon tetrachloride was then removed on a rotary evaporator, and the remaining mixture was dissolved in Skelly B. Cooling gave 94 mg. (38% yield) of biphenyl.

Compound 60 was a white crystalline solid, m.p. 154.5-156.0°C., whose NMR spectrum in deuterochloroform showed a multiplet at τ=2.5-3.0, a doublet at τ=4.0, a doublet at τ=6.9, a singlet at τ=9.9, and a singlet at τ=10.1. These peaks had the relative intensities of 10:2:2:6:6. Its mass spectrum had a parent peak at m/e 322 and major fragmentation peaks at m/e 218, 149, 116, 101, 91, 73, and 59. An exact mass on the m/e 322 peak was measured at 322.1570 (calculated for $C_{20}H_{26}Si_2$: 322.1573). *Anal.* Calc. for $C_{20}H_{26}Si_2$: C, 74.46; H, 8.12. Found: C, 74.49; H, 8.04.

APPENDIX I: PYROLYSIS AND PHOTOLYSIS OF 1,2,3,4-TETRAPHENYL-5,5,6,6-TETRAMETHYL-5,6-DISILA-1,3-CYCLOHEXADIENE

INTRODUCTION

In recent years there has been considerable interest in the pyrolysis of alkyl-substituted polysilanes. On the other hand there have been no reports in the literature on the photolysis of these compounds.

The first alkyl-substituted polysilane, whose thermal decomposition was studied, was hexamethyldisilane. In 1958 Shiina and Kumada[81] reported that hexamethyldisilane decomposed at 600°C. to give 2,2,4-trimethyl-2,4-disilapentane, 61, and a small amount of trimethylsilane.

$$(CH_3)_3Si\text{-}Si(CH_3)_3 \xrightarrow{600°C.} \underset{\underset{\sim}{61}}{(CH_3)_3SiCH_2Si(CH_3)_2H} + (CH_3)_3SiH$$

Later Davidson and co-workers[111-112] studied the decomposition at low pressure and found instead of 61, the rather complex mixture shown below.

$$(CH_3)_3Si\text{-}Si(CH_3)_3 \xrightarrow[0.2\ Torr.]{500°C.} (CH_3)_3SiH + (CH_3)_4Si$$

$$+ (CH_3)_5Si_2CH_2Si(CH_3)_3$$

$$+ (CH_3)_5Si_2CH_2Si_2(CH_3)_5$$

Sakurai, Hosomi, and Kumada[113] then reinvestigated the reaction. This time they heated the hexamethyldisilane to 400°C. for 3 hrs. in a sealed tube and again found only compound 61 and a trace of trimethylsilane.

Eaborn and Semmie[114] showed that at high pressures a radical chain reaction occurred which led to the products observed by Kumada, but at low pressures the chain propagating step was so slow that radical recombinations occurred giving the complex mixture observed by Davidson and Stephenson.[112]

$$(CH_3)_3Si\text{-}Si(CH_3)_3 \longrightarrow 2\ (CH_3)_3Si\cdot$$

$$(CH_3)_3Si\cdot + (CH_3)_3Si\text{-}Si(CH_3)_3 \longrightarrow (CH_3)_3SiH + (CH_3)_3Si\text{-}Si(CH_3)_2CH_2\cdot$$

$$(CH_3)_3Si\text{-}Si(CH_3)_2CH_2\circ \longrightarrow (CH_3)_3SiCH_2\dot{S}i(CH_3)_2$$

$$(CH_3)_3SiCH_2\dot{S}i(CH_3)_2 + (CH_3)_3Si\text{-}Si(CH_3)_3 \longrightarrow (CH_3)_3SiCH_2Si(CH_3)_2H + (CH_3)_3Si\text{-}Si(CH_3)_2CH_2\cdot$$

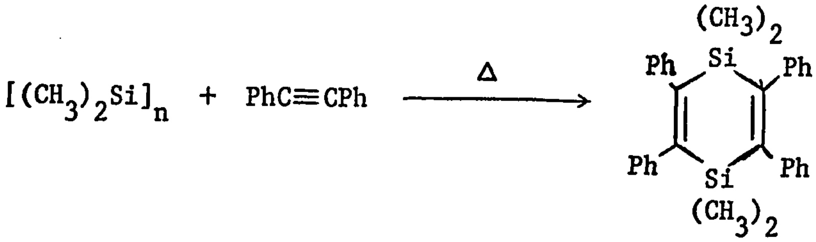
$$2\ (CH_3)_3SiCH_2\dot{S}i(CH_3)_2 \longrightarrow [(CH_3)_3SiCH_2Si(CH_3)_2]_2$$

The next compound to have its thermal decomposition studied was linear poly-dimethylsilylene. This polymer was first synthesized in 1949 by Burkhard,[115] by treating dimethyldichlorosilane with molten sodium. It is a white solid which is insoluble in hydrocarbon solvents and ignites spontaneously when heated to 200°C. in air.

$$(CH_3)_2SiCl_2 + Na \longrightarrow [(CH_3)_2Si]_n + NaCl$$

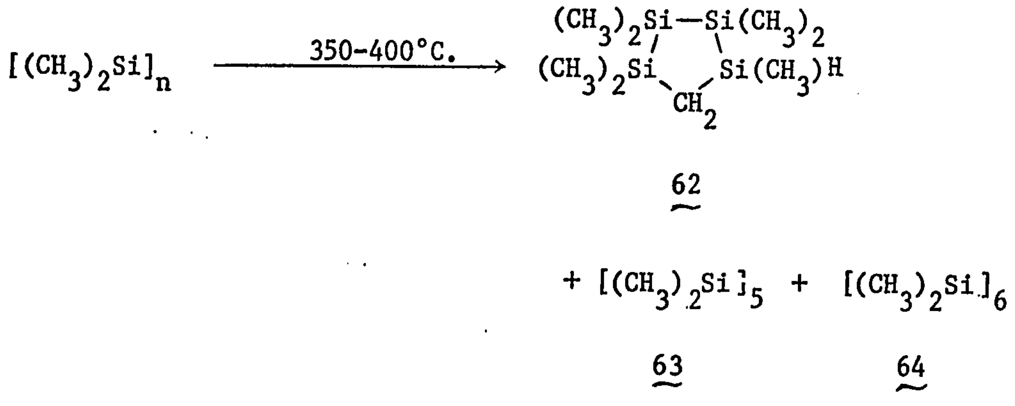
Vol'pin and co-workers[63] showed that when linear polydimethylsilylene was pyrolyzed in the presence of diphenylacetylene, a reaction occurred to give a compound which they identified as

1,2-diphenyl-3,3-dimethyl-3-silacyclopropene, 24, but which was later shown to be 1,2,4,5-tetraphenyl-3,3,6,6-tetramethyl-3,6-disila-1,4-cyclohexadiene, 23.[64-66] This was taken as evidence that linear poly-dimethylsilylene decomposed with the elimination of dimethylsilylene. Whether or not this reaction is a good test for the presence of dimethylsilylene is still in doubt, since the mechanism for the formation of compound 23 is still being elucidated.[115] Nefedov, Garzo, Szekely, and Shiryaev[18] found that if linear poly-dimethylsilylene was placed in an oven at 160°C. or over, which was directly coupled to a g.l.c., a number of lower molecular weight cyclic polymers would be formed. They did not, however, identify any of these compounds.



23

Carberry and West[117] also found that the neat decomposition of this polymer led to lower molecular weight compounds of which they identified three; 62, 63, and 64. Compound 62 is interesting in that it shows a thermally induced rearrangement similar to that of hexamethyldisilane.



62

63

64

+ others containing Si-H and Si-CH_2-Si bonds

In 1963, Urenovitch and MacDiarmid[118] studied the thermal decomposition of polysilyl cyanides. They found that pentamethylcyanodisilane, 65, decomposed at 175°C. to give trimethylcyanosilane and higher molecular weight polysilanes. Heptamethylcyanotrisilane, 66, was found to decompose similarly, but at a higher temperature. A trace of trimethylsilane was found in the products, and it was felt

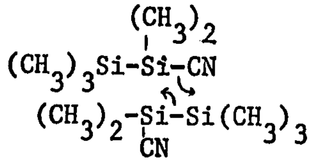
$$\underset{65}{(CH_3)_3Si\text{-}Si(CH_3)_2CN} \xrightarrow[7\ \text{hrs.}]{175°\text{C.}} \underset{74\%}{(CH_3)_3SiCN} + (CH_3)_3Si[Si(CH_3)_2]_nCN$$

$$\underset{66}{(CH_3)_3Si\text{-}Si(CH_3)_2Si(CH_3)_2CN} \xrightarrow[60\ \text{hrs.}]{195°\text{C.}} (CH_3)_3SiCN$$

$$+ (CH_3)_3Si[Si(CH_3)_2]_nCN$$

$$+ \underset{\text{trace}}{(CH_3)_3SiH}$$

that this was due to the formation of trimethylsilyl free radicals. Two possible mechanisms were given for the formation of the observed products.



$$(CH_3)_3Si-\overset{(CH_3)_2}{Si}-CN$$
$$(CH_3)_2-\underset{CN}{Si}-Si(CH_3)_3$$

mechanism 1

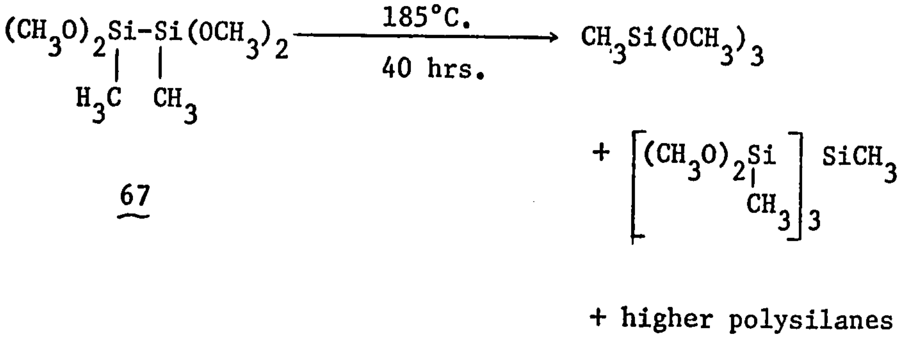
$$(CH_3)_3Si-Si(CH_3)_2CN \longrightarrow (CH_3)_3Si\cdot + \cdot Si(CH_3)_2CN$$

$$(CH_3)_3Si\cdot + (CH_3)_3Si-Si(CH_3)_2CN \longrightarrow (CH_3)_3Si-\dot{Si}(CH_3)_2 + (CH_3)_3SiCN$$

$$(CH_3)_3Si-\dot{Si}(CH_3)_2 + (CH_3)_2\dot{Si}CN \longrightarrow (CH_3)_3Si-Si(CH_3)_2Si(CH_3)_2CN$$

mechanism 2

The thermal decomposition of methoxy-substituted polysilanes has been studied in detail by Atwell and co-workers. In a preliminary report Atwell and Weyenberg[120] described the decomposition of 1,1,2,2-tetramethoxy-1,2-dimethyldisilane, 67, and 1,1,2,2-tetramethyl-1,2-dimethoxydisilane, 68. The former compound, 67, decomposed at 185°C. to give methyltrimethoxysilane, tris-(methyldimethoxysilyl)-methylsilane, and "higher polysilanes". Compound 68 decomposed at 225°C.



$$(CH_3O)_2\underset{H_3C}{Si}-\underset{CH_3}{Si}(OCH_3)_2 \xrightarrow[40\text{ hrs.}]{185°C.} CH_3Si(OCH_3)_3 + \left[(CH_3O)_2\underset{CH_3}{Si}\right]_3 SiCH_3$$

67

\+ higher polysilanes

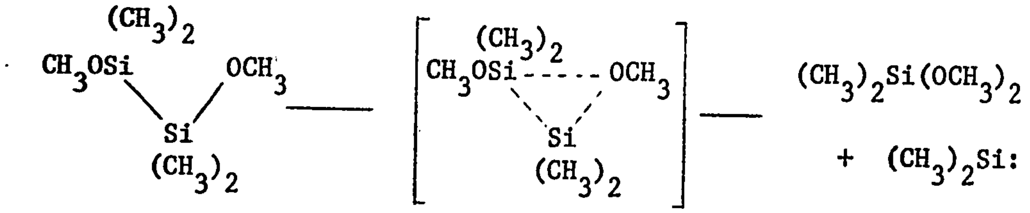
to give dimethyldimethoxysilane and higher molecular weight polysilanes.

$$CH_3O[Si(CH_3)_2]_2OCH_3 \xrightarrow{225°C.} (CH_3)_2Si(OCH_3)_2$$

68

$$+ \quad CH_3O[Si(CH_3)_2]_nOCH_3$$

In a more detailed study, Atwell and Weyenberg[116] found that the decomposition of 1,2-dimethoxytetramethyldisilane gives as a primary product dimethylsilylene, which can then insert into any available Si-O bond or react with appropriate traps, eg. PhC≡CPh. They proposed the following mechanism for decomposition:



They found that the dimethoxy derivatives of the trisilanes also thermally decomposed in a similar manner, but at a higher temperature. Most of this work is covered in a recent review on divalent silicon by Atwell and Weyenberg.[49]

Sakurai, Hosomi, and Kumada[85] have studied the thermal decomposition of pentamethyldisilane and 1,1,1,2,2,3,3-heptamethyltrisilane, 69. They found that heating either of these compounds to 300°C. gave a series of polysilanes as shown in the equations below.

$$(CH_3)_3Si\text{-}Si(CH_3)_2H \xrightarrow[15\ hrs.]{300°C.} CH_3[(CH_3)_2Si]_nH$$

$$n=0,1,2,3,4,5,6,7$$

$$(CH_3)_3Si\text{-}Si(CH_3)_2Si(CH_3)_2H \xrightarrow[15\ hrs.]{300°C.} CH_3[(CH_3)_2Si]_nH$$

69

$$n=0,1,2,3,4,5,6,7$$

A mechanism involving the elimination of dimethylsilylene followed by insertion into the silicon-hydrogen bond was proposed. This

$$(CH_3)_3Si\text{-}Si(CH_3)_2H \longrightarrow (CH_3)_3SiH \quad + \quad (CH_3)_2Si:$$

$$(CH_3)_2Si: \quad + \quad CH_3[(CH_3)_2Si]_nH \longrightarrow CH_3[(CH_3)_2Si]_{n+1}H$$

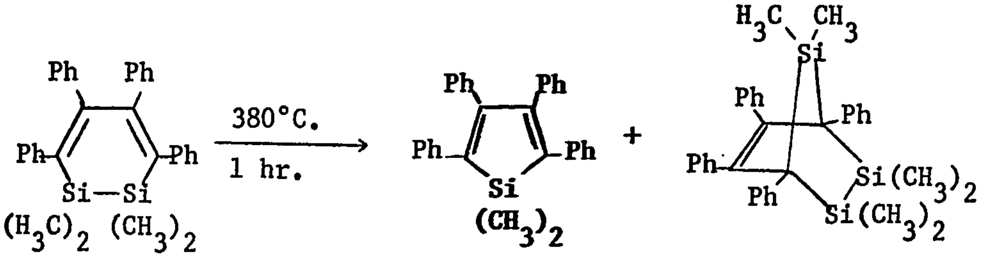
type of insertion has previously been shown by Skell and Goldstein[78] to occur when dimethylsilylene is generated in the presence of silicon hydrides.

During the attempted Diels-Alder reactions of 1,2,3,4-tetraphenyl-5,5,6,6-tetramethyl-5,6-disila-1,3-cyclohexadiene, 21, and various dienophiles, it was observed that 21 decomposed upon heating or exposure to ultra-violet light. The following appendix describes the results obtained during a preliminary study of the thermal and photo decomposition of 21.

RESULTS AND DISCUSSION

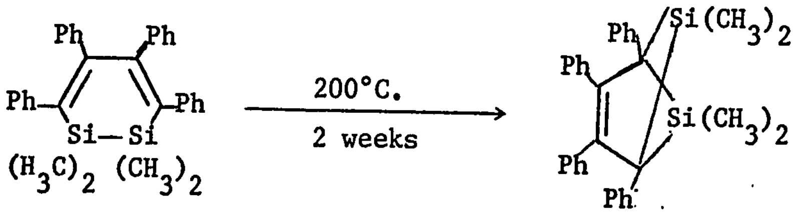
When 21 was heated to 300°C. for 19 hrs., a NMR spectrum of the pyrolysis product showed that a complex mixture of compounds was present. Fractional crystallization gave a 33% recovery of 21 and a 14% yield of 1,2,3,4-tetraphenyl-5,5-dimethyl-5-silacyclopentadiene, 19.

When the temperature was raised to 375°C. for 0.5 hrs., the reaction mixture was greatly simplified. Attempts to separate this mixture failed. No separation was obtained by column chromatography on a silica gel column or by fractional crystallization. The products were too involatile to make use of g.l.c. The NMR spectrum of the mixture had a multiplet at τ=2.5-3.4 and singlets at τ=9.5, τ=9.8, τ=9.9, τ=10.0, and τ=10.1 with relative integrations of 40:6:6:3:3:6. Subtracting out the absorptions due to compound 19, left a multiplet at τ=2.5-3.4 and singlets at τ=9.8, τ=9.9, τ=10.0, and τ=10.1 with relative integrations of 20:6:3:3:6. The mass spectrum of the mixture was in agreement with the presence of two major compounds: one with a parent mass of m/e 414 (compound 19) and the other with a parent mass of m/e 530 (compound 70). It was also found that when the mixture was exposed for a while to air that m/e 530 peak decreased in size and was replaced by a peak at m/e 546. This behavior is similar to the oxidation of other cyclic compounds containing a silicon-silicon bond. All of these data are consistent with the pyrolysis mixture being composed of 19 and a second compound, 70, whose structure is shown below.



21 19 70

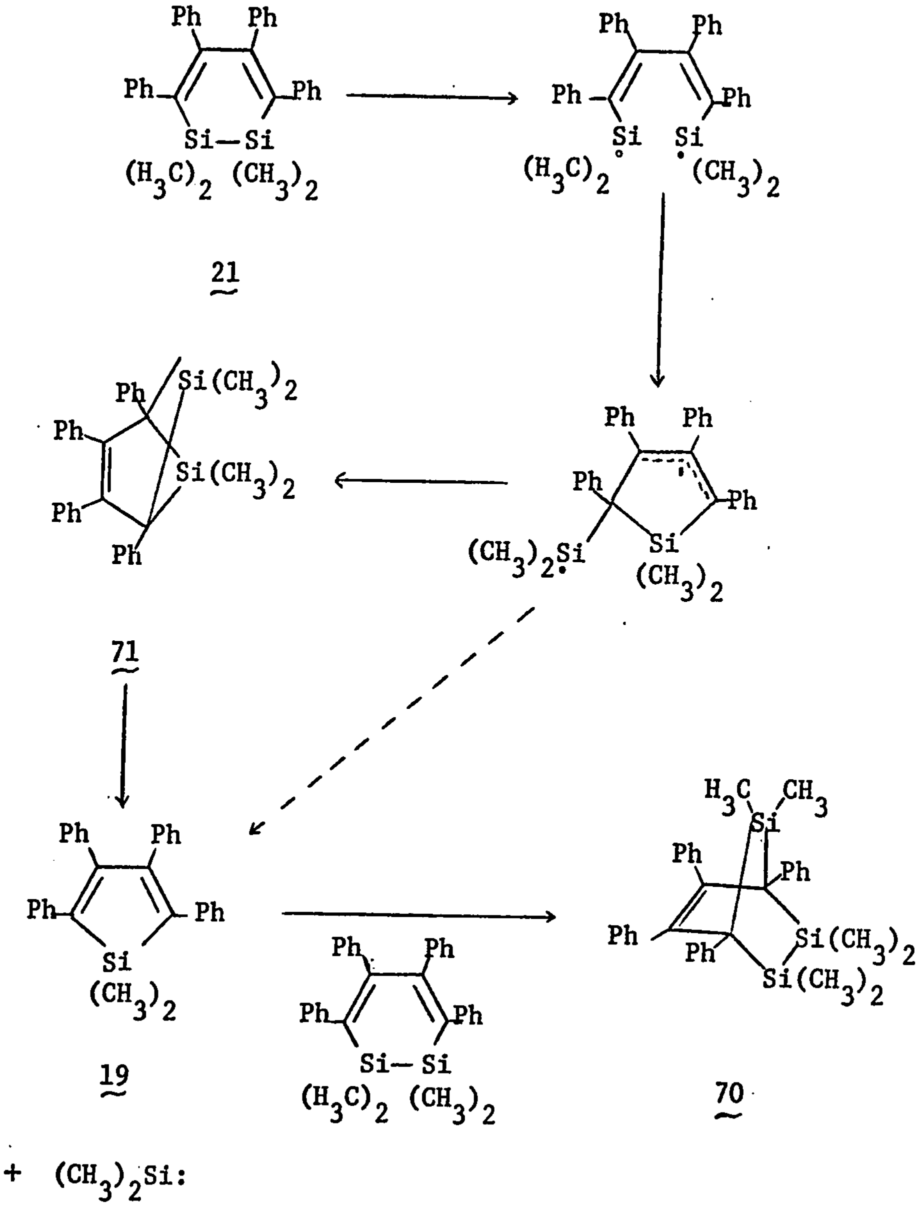
Heating 21 at 200°C. for 2 weeks gave a mixture which appeared to contain approximately equal amounts of starting material, 21, and of a new compound, 71. Heating the mixture to higher temperatures resulted in a loss of 71 with the subsequent formation of 19. Subtracting the NMR absorptions due to 21, meant that the NMR spectrum of 71 had a multiplet at τ=2.8-3.7, a singlet at τ=9.3, and a singlet at τ=9.4 with the relative integration of 20:6:6. The mass spectra of the mixture had no new peaks not present in the mass spectrum of 21; however, the relative heights of the peaks were quite different. Of particular interest was the fact that the parent peak at m/e 472 in the mixture was relatively much higher than in compound 21. A 10 eV mass spectrum of the mixture gave m/e 472 as the highest peak (100%) with the next highest being m/e 414 at only 5%. At this electron impact energy one would expect to see all of the parent peaks present, and very little fragmentation. Since m/e 472 was the only peak of any size at 10 Ev, one may conclude that both compounds 21 and 71 have a mass of 472. A structure for 71 which is consistent with this information is shown in the reaction below. Unfortunately, efforts to isolate 71 were unsuccessful.



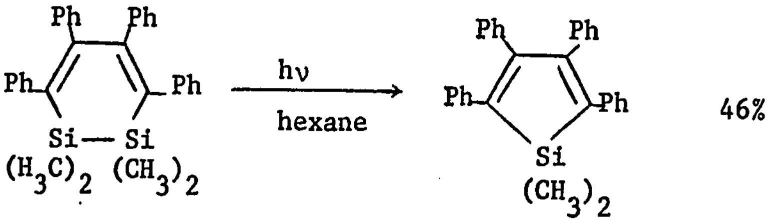
21

71

A possible mechanistic scheme for the thermolysis of 21 is shown below.

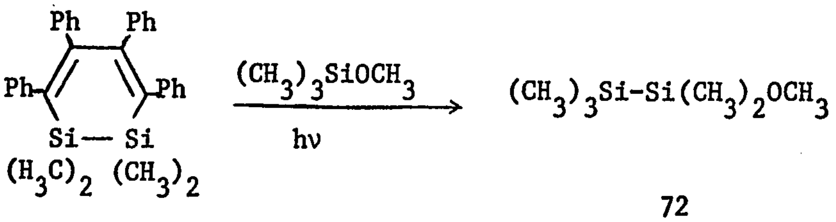


A mass spectrum of a sample of 21 stored for several weeks in the presence of light showed a large new peak at m/e 414. When a solution of 21 in hexane was irradiated for 24 hrs. with a Hanovia 30620 lamp, a 46% yield of 19 was isolated from the foul smelling solution obtained as a product.



21 19

When the reaction was repeated using trimethylmethoxysilane as a solvent, a 10% yield of pentamethylmethoxydisilane, 72, was obtained. Since methoxysilanes can be used as traps for dimethylsilylene,[49] the results indicate that dimethylsilylene may be eliminated during the photolysis of 21.



72

21

EXPERIMENTAL

General: Pyrolysis reactions were done in 6 mm x 10 cm pyrex tubes using the oven shown in figure 13. Photolysis was done using a Hanovia 30620 lamp. All NMR spectra were taken on a Varian Associates A60 nuclear magnetic resonance spectrometer. τ values were measured from external TMS. All g.l.c. traces were taken on a Varian Aerograph A-90-P3 gas chromatograph equipped with a 20 foot by 1/8 inch stainless steel column packed with 5% GESF-96 on acid washed, silylated chromasorb G, using a helium flow rate of 50-50 ml./min. Mass spectra were done on either a GEC/AEI MS-12 or MS-9 mass spectrometer.

Pentamethylmethoxydisilane, 72: a mixture of 3.9 g. (0.0295 mole) of pentamethyldisilane and 6 ml. (0.148 mole) of methanol was stirred in an ice bath, as 6 μl. of 1.6N methyl lithium was added. The reaction vessel was then warmed to 40°C. in an oil bath. After 24 hr. the reaction vessel was cooled and 50 μl. of acetic acid was added. Distillation gave 2.2 g. (46% yield) of pure **72**, b.p. 126-128°C. (literature b.p. 124-130°C.).[120] The NMR spectrum was in agreement with that reported in literature.[120] The neat infrared spectrum showed absorptions at 2950, 2892, 2822, 1438, 1394, 1245, 1186, 1087, 875, 833, 801, 769, 748, 742, 738, 719, 690, 646, and 612 cm^{-1}.

The neat pyrolysis of 21 at 300°C.: After 200 mg. of **21** was sealed in an evacuated pyrex tube, it was heated to 300°C. for 19 hr. A NMR spectrum of the resulting mixture was very complex. The mixture was dissolved in hexane and cooled to give 65 mg. (32% recovery) of starting material, **21**. The hexane was then removed on a rotary evaporator, and the residue was dissolved in ethyl acetate. Cooling gave 28 mg. (16% yield) of **19**, m.p. 169-178°C. This product had identical NMR and mass spectra to those of an authentic sample of **19**.

The neat pyrolysis of 21 at 375°C.: After 194 mg. of **21** was sealed in a pyrex tube, it was heated to 375°C. for 0.5 hr. A NMR spectrum in carbon tetrachloride showed a multiplet at τ=2.5-3.4 and singlets at τ=9.5, 9.8, 9.9, 10.0, and 10.1, whose relative intensities were 40:6:6:3:3:6. The mass spectrum had major peaks at m/e 43, 58, 59, 73, 105, 135, 221, 321, 414, 472, and 530. After the mixture had been exposed to air for one week a mass spectrum showed a new peak at m/e 546 with a decrease in the relative size of the m/e 530 peak.

Attempts to separate the mixture by fractional crystallization from carbon tetrachloride, hexane, and ethanol all failed to give any separation. The mixture was then placed on a silica gel column and eluted with benzene. The only detectable material to come out of the column was a substance which gave a very complex NMR spectrum.

The neat pyrolysis of 21 at 200°C.: After 100 mg. of 21 was sealed in a pyrex tube, it was heated to 200-210°C. for 2 weeks. A NMR spectrum in carbon tetrachloride of the mixture showed a multiplet at τ=2.8-3.7 and singlets at τ=9.3, 9.4, and 9.8. A mass spectrum of the mixture showed no peaks not present in the spectrum of 21; however, the relative intensities of the peaks were different. A mass spectrum at 10 eV showed only two major peaks at m/e 472 (100%) and m/e 414 (5%). Attempts to separate the mixture by fractional crystallization from either carbon tetrachloride, chloroform, pentane, or ethanol were unsuccessful. When the mixture was heated to 300°C. for 20 hr., its NMR spectrum became much more complex and a mass spectrum showed a major peak at m/e 414.

Photolysis of 21 in hexane: After 0.411 g. (0.870 mmole) of 21 was dissolved in 100 ml. of hexane and the solution was placed in a 3 cm quartz cell, the solution was degassed 4 times and then kept under dry nitrogen. After 24 hr. of irradiation the hexane was removed on a rotary evaporator leaving a foul smelling oil. This oil was redissolved in a small amount of hexane and cooled to give 0.1153 g. (46% yield) of yellow crystalline solid, whose NMR spectrum and mass spectrum were identical to spectra of authentic 19. Further crystallization from ethanol gave 0.1579 g. of a solid whose NMR and mass spectra were both very complex and suggestive of a mixture.

Photolysis of 21 in trimethylmethoxysilane: A mixture of 200 mg. (0.466 mmole) of 21 and 2.59 g. (24.9 mmole) of trimethylmethoxysilane was degassed and sealed in a 10 mm pyrex tube. After 24 hr. of irradiation the tube was opened and a g.l.c. trace taken. The only volatile product was pentamethylmethoxydisilane, 72, which was formed in a 10% yield. Compound 72 was identified by comparison of its g.l.c. retention time and its mass spectral fragmentation pattern with those of an authentic sample of 72.

APPENDIX 2: THE CLEAVAGE OF CERTAIN CARBON-SILICON BONDS BY LITHIUM ALUMINUM HYDRIDE IN THF

INTRODUCTION

Lithium aluminum hydride is widely used in organosilicon chemistry to form silicon hydrides by the reduction of Si-X bonds, where X is a good leaving group (ie. X= halogen or oxygen).[38] At the time the work reported in this appendix was done, the cleavage of silicon-carbon bonds by inorganic hydrides was not thought of as a general class of reaction, although there were a few isolated reports of this type of reaction.

In 1957 Kaesz and Stone[121] attempted the preparation of chloromethylsilane, dichloromethylsilane, and trichloromethylsilane by the lithium aluminum hydride reduction of the respective silicon chlorides. Chloromethyltrichlorosilane was reduced smoothly with no evidence of silicon-carbon bond cleavage. The di- and trichloromethyltrichlorosilanes both produced considerable amounts of silane

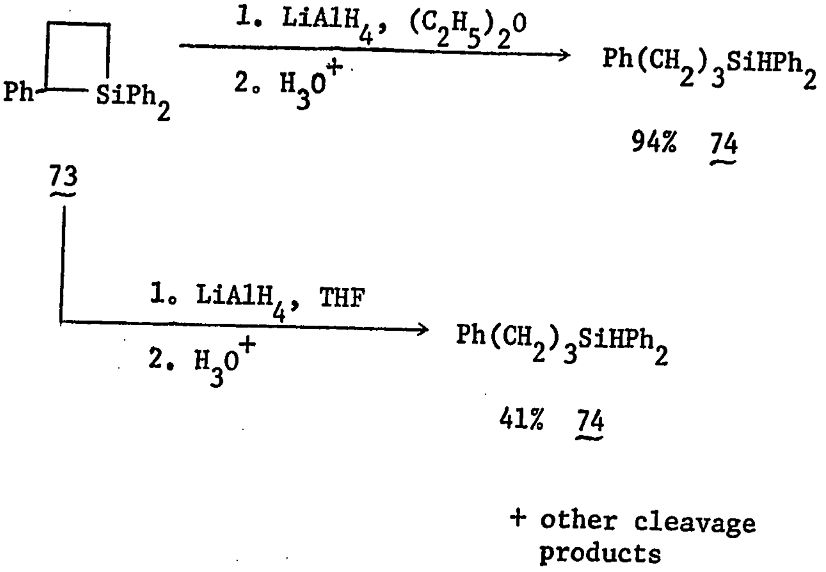
$$ClCH_2SiCl_3 \xrightarrow[(C_4H_9)_2O]{LiAlH_4} ClCH_2SiH_3$$

$$Cl_2CHSiCl_3 \xrightarrow[(C_4H_9)_2O]{LiAlH_4} Cl_2CHSiH_3 + SiH_4$$

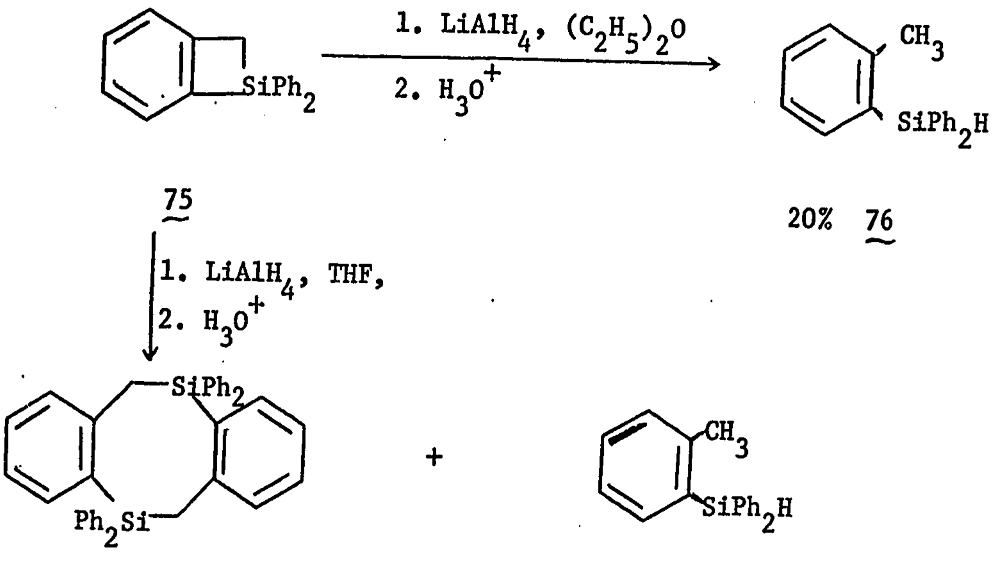
$$Cl_3CSiCl_3 \xrightarrow[(C_4H_9)_2O]{LiAlH_4} Cl_3CSiH_3 + SiH_4$$

during their respective reductions. The trichloromethylsilane was never isolated due to explosions which occurred during work-up. This production of silane was the first reported evidence that inorganic hydrides could cleave silicon-carbon bonds.

Gilman and Atwell[122-123] reported a study of the reactions of small ring compounds containing silicon. They found that when 1,1,2-triphenyl-1-silacyclobutane, 73, was treated with lithium aluminum hydride in diethyl ether, an almost quantitative yield of 1,1,4-triphenyl-1-silabutane, 74, was formed.[122] When THF was substituted for the diethyl ether the yield of 74 was decreased due to unspecified, "secondary cleavages".



Reaction of 2:3-benzo-1,1-diphenyl-1-sila-2-cyclobutene, 75, with lithium aluminum hydride in diethyl ether gave a 20% yield of *o*-tolyldiphenylsilane, 76; but when THF was substituted for the diethyl ether, a 12% yield of 2:3,6:7-dibenzo-1,1,5,5-tetraphenyl-1,5-disila-2,6-cyclooctadiene, 77, was produced as well as 76.[123]



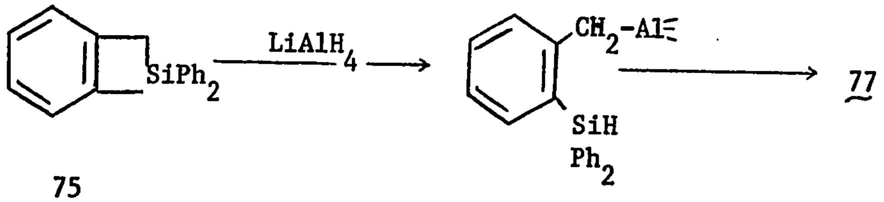
75

20% 76

12% 77

26% 76

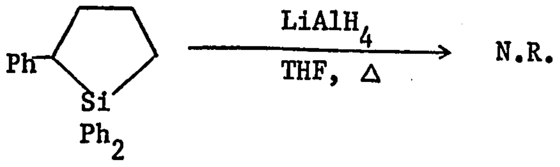
It was postulated that the formation of 77 was due to a coupling reaction of the intermediate aluminum compound.



77

75

When Gilman and Atwell[122] attempted the cleavage of 1,1,2-triphenyl-1-silacyclopentane, 78, they observed no reaction even in refluxing THF. They therefore concluded that the cleavage of 73 and 75 was associated with the strain of the four-membered ring.



78

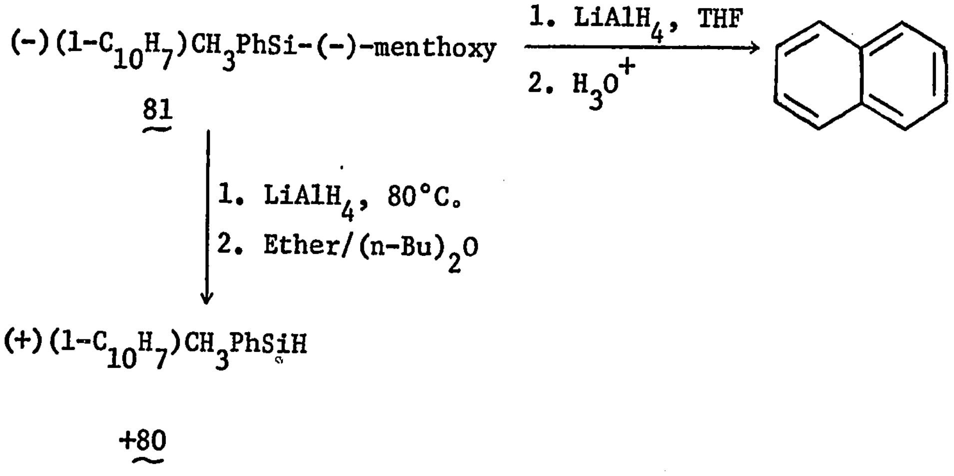
Ruhlmann and Heine[124] have reported the cleavage of carbon-silicon bonds in benzyltriphenylsilane, 79, by sodium hydride in cyclohexane at 200°C. and 100-200 atm. of hydrogen.

$$\underset{79}{Ph_3SiCH_2Ph} \xrightarrow[2.\ H_3O^+]{1.\ NaH,\ 200°C.,\ H_2} Ph_4Si + Ph_3SiH + Ph_2SiH_2 + C_6H_5CH_3 + C_6H_6 + \text{resins}$$

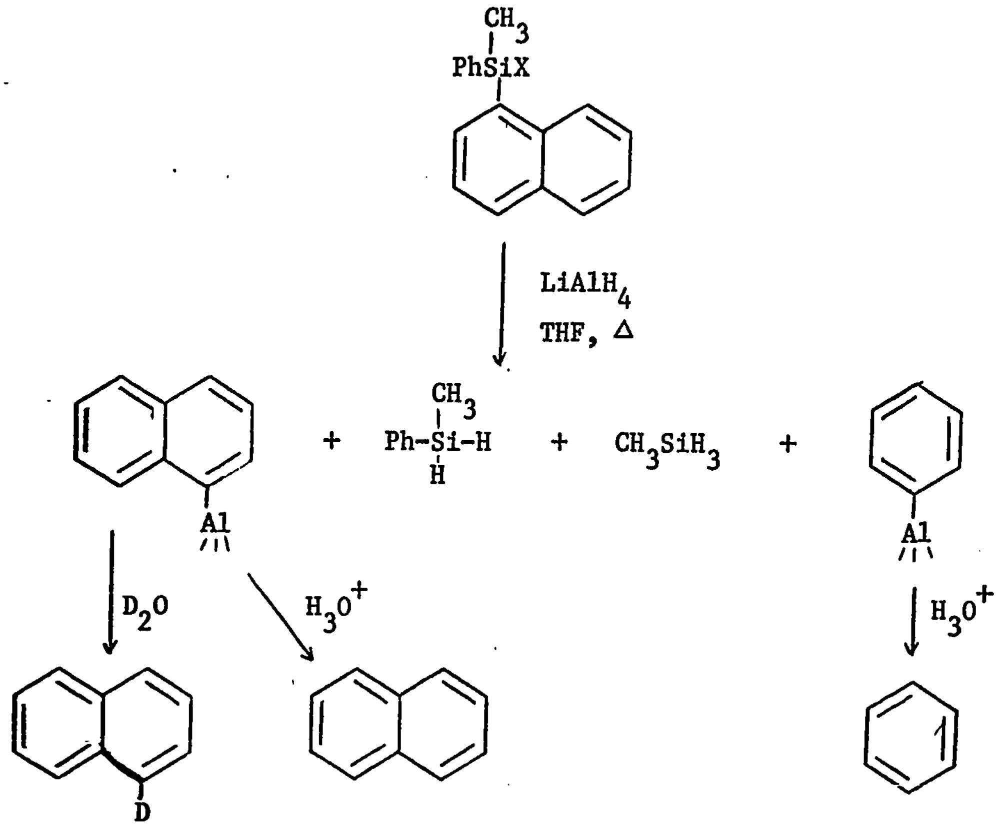
RESULTS AND DISCUSSION

In the reported preparation of (+)-methyl-1-naphthylphenylsilane, +80,[125] the diastereomer, (-)-methyl-1-naphthylphenyl-(-)-menthoxysilane, 81, is reduced with lithium aluminum hydride in a mixture of diethyl ether and di-n-butyl ether at 80°C. We felt that refluxing THF (b.p. 65°C.) might make a good substitute for the above solvent system; however, when this substitution was made, a virtually quantitative yield of naphthalene was obtained following the usual work-up.

The racemic silane, ±80, was treated with lithium aluminum hydride in refluxing THF, and it was found to give methylsilane and phenylmethylsilane as the only volatile products. Hydrolysis of the pot residue yielded benzene, (57%), and naphthalene, (98%), as products. The complete absence of benzene and naphthalene in the volatile material prior to hydrolysis, suggests that they are present in the reaction mixture as organoaluminum derivatives.



In order to test for the presence of an organometallic compound in the pot residue, deuterium oxide was used during the work-up and the resulting naphthalene's mass spectrum indicated that it was primarily $C_{10}H_7D$.



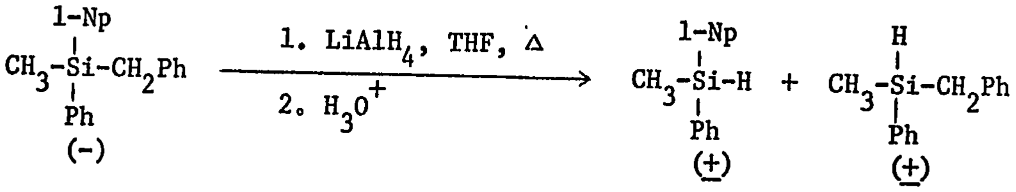
When benzyltriphenylsilane, 79, was treated with lithium aluminum hydride in refluxing THF, the benzyl group was readily cleaved to give triphenylsilane. However, when benzyltrimethylsilane

$$\underset{79}{Ph_3SiCH_2Ph} \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4,\ THF,\ \Delta} Ph_3SiH$$

was refluxed for 18 hrs. with lithium aluminum hydride in THF, only a trace of trimethylsilane was found in the cold trap and 95% of the benzyltrimethylsilane was recovered. Naphthyltrimethylsilane was also unreactive under similar conditions.

In an attempt to determine the stereochemistry of this reaction, (-)-methyl-1-naphthylphenylbenzylsilane, 82, was treated with lithium aluminum hydride in refluxing THF. Work-up gave racemic methyl-1-naphthylphenylsilane and racemic methylphenylbenzylsilane in a 9:1

ratio. However, it was subsequently shown that silicon hydrides undergo a facile hydrogen-hydrogen exchange with racemization in THF.[126]



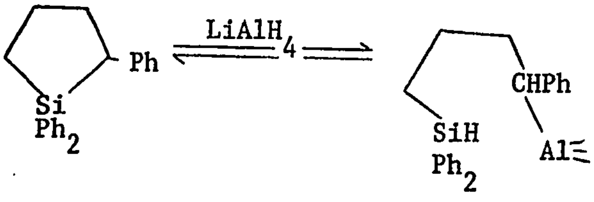
$$\underset{(-)}{\mathrm{CH_3}-\overset{\text{1-Np}}{\underset{\text{Ph}}{\mathrm{Si}}}-\mathrm{CH_2Ph}} \xrightarrow[\text{2. } H_3O^+]{\text{1. } LiAlH_4\text{, THF, }\Delta} \underset{(\pm)}{\mathrm{CH_3}-\overset{\text{1-Np}}{\underset{\text{Ph}}{\mathrm{Si}}}-\mathrm{H}} + \underset{(\pm)}{\mathrm{CH_3}-\overset{\text{H}}{\underset{\text{Ph}}{\mathrm{Si}}}-\mathrm{CH_2Ph}}$$

82

In order to test its generality the reaction was tried on organogermanium and organotin compounds. Benzyltriphenylgermane did not react with lithium aluminum hydride in refluxing THF. Benzyltriphenyltin reacted rapidly at room temperature giving, after work-up, tetraphenyltin and an infusable mixture of tin oxides. Hexaphenylditin has been reported to give similar results when treated with lithium aluminum hydride under more vigorous conditions.[127]

It is known that nucleophilic reagents in polar solvents cleave carbon-silicon bonds in the following order: $Bz>Ph>>CH_3$.[38] They also cleave carbon-tin bonds faster than carbon-silicon bonds, which in turn are cleaved faster than carbon-germanium bonds.[128] These results suggest that in a polar ether lithium aluminum hydride reacts as a typical nucleophile towards the cleavage of carbon-group IV bonds.

Since the reaction involved the formation of an organoaluminum compound as well as a silicon hydride, there is the possibility of recombination. Thus in the work of Gilman and Atwell[3] the failure to observe cleavage in the case of 1,1,2-triphenyl-1-silacyclopentane, 78, probably was due to the position of the equilibrium, in the reaction shown below, lying far to the left.



78

The reaction offers some possible synthetic advantages in the cleavage of silicon-carbon bonds in compounds containing reactive functional groups. But, more important, if such cleavage reactions are to be avoided during the reduction of organosilicon compounds, THF and presumably other polar solvents should not be used.

EXPERIMENTAL

General: All reactions were carried out under an atmosphere of dry nitrogen. The THF used was freshly distilled from lithium aluminum hydride, and the *n*-butyl ether was distilled from calcium hydride before use. Lithium aluminum hydride from both Metal Hydrides Inc. and from Reasearch Organic/Inorganic Chemical Co. was used. Mass spectra, NMR spectra and infrared spectra were determined on Metropolitan-Vickers MS-9, Varian Associates A-60, and Perkin-Elmer 421 spectrometers respectively. The NMR spectra were calibrated against external TMS.

Methyl-1-naphthylphenylsilane, 80: (±)-, (+)-, and (-)-**80** were readily prepared by lithium aluminum hydride reduction of (±)-methyl-1-naphthylphenylmethoxysilane and of the separated (-)-menthoxy diasteriomers respectively, following the procedures of Sommer and co-workers.[125]

Reaction of (-)-methyl-1-naphthylphenyl-(-)-menthoxysilane with lithium aluminum hydride in THF: A mixture of 80 gms. (0.20 moles) of (-)-methyl-1-naphthylphenyl-(-)-menthoxysilane and 13 gms. (0.34 moles) of lithium aluminum hydride in 300 ml. of THF was refluxed for 18 hrs. Following acid work-up, the resultant syrup was dissolved in ethanol and 24.5 gms. (97% yield) of naphthalene crystallized out. The naphthalene was identical in all respects to an authentic sample.

Reaction of (+)-methyl-1-naphthylphenylsilane with lithium aluminum hydride in THF: A mixture of 9.8 gms. (0.04 moles) of (±)-**80** and 2.6 gms. (0.067 moles) of lithium aluminum hydride was refluxed for 18 hrs. in 60 ml. of THF, in a reaction vessel connected via a reflux condenser to a -80°C. cold trap.

A mass spectrum of the volatile material in the cold trap was identical to that reported for methylsilane.[15] A NMR spectrum in carbon tetrachloride of the liquid in the cold trap was the same as that from a mixture of THF and methylsilane[129] and an infrared spectrum showed a strong absorption at 2170 cm^{-1} from the Si-H of the methylsilane.

The volatile material was removed from the reaction mixture under reduced pressure. A g.l.c. trace of the distllate showed only peaks for THF and for phenylmethylsilane, identified by comparison of g.l.c. retention time, NMR and infrared spectra with results from an authentic sample.

Finally the non-volatile residue was worked up with ethyl acetate followed by dilute hydrochloric acid. A g.l.c. trace of the resultant organic material showed benzene and naphthalene in a relative ratio of 0.58:1. Finally, 4.9 gms. (98% yield) of naphthalene was isolated when the other volatile materials were removed.

Reaction of (+)-methyl-1-naphthylphenylmethoxysilane with lithium aluminum hydride in THF: When (±)-methyl-1-naphthylphenylmethoxysilane and an excess of lithium aluminum hydride in THF were refluxed for 18 hrs. and then worked up with ethyl acetate, followed by deuterium oxide, the major product obtained was naphthalene-d_1 (73%) identified by its mass spectrum. The 27% of undeuterated naphthalene probably arose from either moisture in the ethyl acetate or proton abstraction from the acetate by some of the strong bases present.

Reaction of triphenylbenzylsilane with lithium aluminum hydride in THF: A mixture of 3.5 gms. (0.01 moles) of triphenylbenzylsilane and 0.57 gms. (0.015 moles) of lithium aluminum hydride in 50 ml. THF was refluxed for 7 hrs. and then worked-up as above. Recrystallization of the product from ethanol-water gave 1.65 gms. (62% yield) of triphenylsilane, identical in all respects to an authentic sample. A NMR spectrum of the oil obtained by evaporating the mother liquor showed, in addition to a multiplet at τ=2.5, a singlet at τ=4.54 from the Si-H of triphenylsilane, and a weak singlet at τ=5.14, probably from the Si-H of diphenylsilane.

Attempted reaction of 1-trimethylsilylnaphthalene with lithium aluminum hydride in THF: A mixture of 8.0 gms. (0.04 moles) of 1-trimethylsilylnaphthalene and 2.6 gms. (0.068 moles) of lithium aluminum hydride in 60 ml. of THF was refluxed for 18 hrs.

Following the usual work-up NMR examination of the reaction product showed it to be 1-trimethylsilylnaphthalene. The absence of naphthalene was confirmed by a g.l.c. trace.

Reaction of trimethylbenzylsilane with lithium aluminum hydride in THF: A mixture of 2.0 gms. (0.012 moles) of trimethylbenzylsilane and 0.73 gms. (0.019 moles) of lithium aluminum hydride in 12 ml. of THF was refluxed for 18 hrs. in a reaction vessel, connected via a condenser to a -80°C. cold trap.

A mass spectrum of the material in the cold trap was identical to that of an authentic sample of trimethylsilane. However, work-up as above gave 1.9 gms. (95%) of recovered trimethylbenzylsilane.

Reaction of triphenylbenzylgermane with lithium aluminum hydride in THF: A mixture of 0.2 gms. (0.00052 moles) of triphenylbenzylgermane and 0.12 gms. (0.0031 moles) of lithium aluminum hydride in 5 ml. of THF was refluxed for 4.5 hrs. Following the usual work-up, recrystallization from ethanol gave 0.2 gms. (100%) of recovered triphenylbenzylgermane.

Reaction of triphenylbenzyltin with lithium aluminum hydride in THF: A mixture of 0.75 gms. (0.0017 moles) of triphenylbenzyltin and 0.09 gms. (0.0024 moles) of lithium aluminum hydride in THF was stirred at room temperature for 24 hrs. An excess of ethyl acetate was added and the mixture was then stirred for 6 hrs. before the addition of dilute hydrochloric acid and diethyl ether. Filtration gave 0.25 gms. of an infusable white solid (found: 28.1% C, 2.03% H) from which a small amount of tetraphenyltin, m.p. 226-227°C., were distilled, when the solid was heated to 320-330°C. An additional 0.1 gm. of tetraphenyltin was obtained by crystallization of the ether soluble material.

Reaction of (-)-methyl-1-naphthylphenylbenzylsilane with lithium aluminum hydride in THF: A solution of 0.30 gms. (0.0009 moles) of (-)-methyl-1-naphthylphenylbenzylsilane,[130] $[\alpha]_D^{25} = -6.45°$ (c 2.7, cyclohexane) and 0.052 gms. (0.0013 moles) of lithium aluminum hydride in 4 ml. of THF, was refluxed for 9.5 hrs. Work-up with ethyl acetate, followed by dilute hydrochloric acid and diethyl ether, gave 0.22 gms. of an oil, $[\alpha]_D^{25} = -4.7°$ (c 15, cyclohexane). A NMR spectrum of the oil indicated that it contained approximately 45% of methyl-1-naphthylphenylbenzylsilane, and 10% of benzylmethylphenylsilane. Chromatography of 0.15 gms. of the oil on 100 gms. of silica gel, eluted with cyclohexane-benzene, gave approximately 54 mg. (36%) of (±)-methyl-1-naphthylphenylsilane, 6 mg. (4%) of (±)-benzylmethylphenylsilane, and 89 mg. (60%) of recovered (-)-methyl-1-naphthylphenylbenzylsilane, $[\alpha]_D^{25} = -5.1°$ (c 2.7, cyclohexane).

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