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Gas phase thermal interconversions of silacyclobutanes, alkylsilylenes, and silacyclopropanes

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GAS PHASE THERMAL INTERCONVERSIONS OF SILACYCLOBUTANES,
ALKYLSILYLENES, AND SILACYCLOPROPANES

Iowa State University

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Gas phase thermal interconversions
of silacyclobutanes, alkylsilylenes,
and silacyclopropanes

by

Nolan Tillman

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

Department: Chemistry
Major: Organic Chemistry

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In Charge of ~~Major~~ Work

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For the Major ~~Department~~

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Iowa State University
Ames, Iowa

1986

TABLE OF CONTENTS

	Page
INTRODUCTION	1
HISTORICAL	2
Thermal Decomposition of Silacyclobutanes	2
C-H Insertion and Elimination Reactions Involving Silylenes	10
Thermal Reactions Involving Silacyclopropanes	34
RESULTS AND DISCUSSION	52
Pyrolysis of 1-Hydridosilacyclobutanes	52
Thermal Reactions of Alkylsilylenes	85
CONCLUSION	127
EXPERIMENTAL	135
General Procedures for Flash Vacuum Pyrolyses	135
General Procedures for Flow Pyrolyses	137
Instrumentation	137
Procedures and Results	139
BIBLIOGRAPHY	198
ACKNOWLEDGEMENTS	206

INTRODUCTION

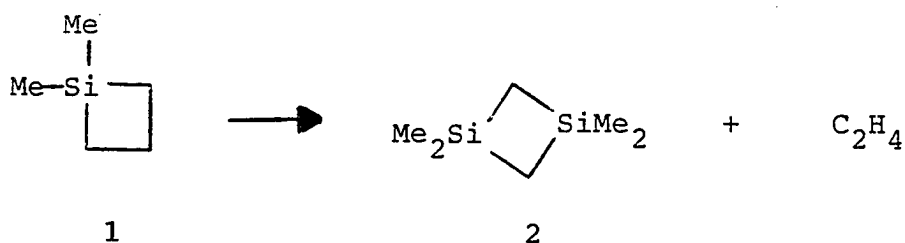
In the recent development of the chemistry of organo-silicon reactive intermediates, silacyclobutanes have played a key role in the development of the chemistry of silenes (silicon-carbon double bonded intermediates). Most silacyclobutanes cleanly afford silenes and ethene as nearly exclusive products upon thermolysis. 1-Hydrido-1-silacyclobutanes are unique in that propene is formed as a significant product upon thermal decomposition. This dissertation will present the results of an investigation into the mechanism of this reaction, employing labelled 1-deuteriosilacyclobutanes, and of a related study of alkyl-silylenes suggested by work with silacyclobutanes.

A comprehensive Historical section is first presented, summarizing key points of the current knowledge of silacyclobutanes, silylenes, and silacyclopropanes which are pertinent to the results of this research. Further information and references may be found in the relevant reviews cited in the text.

HISTORICAL

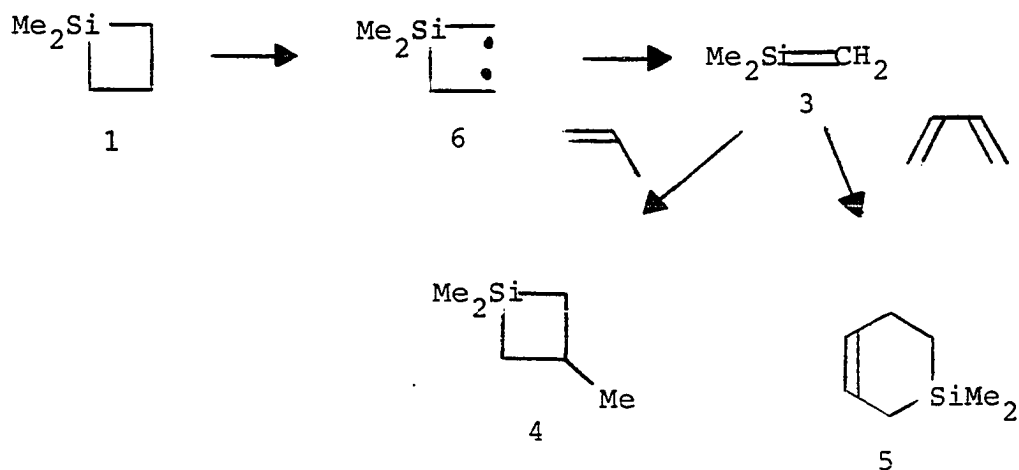
Thermal Decomposition of Silacyclobutanes

Silacyclobutanes have been known since 1954 when Sommer and Baum reported the first confirmable preparation of 1,1-dimethylsilacyclobutane **1** (1). Thermal gas phase decompositions of silacyclobutanes have only been investigated since the middle 1960s when it was first reported that **1** affords ethene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane **2** as exclusive products upon gas phase pyrolysis (2, 3, 4a).



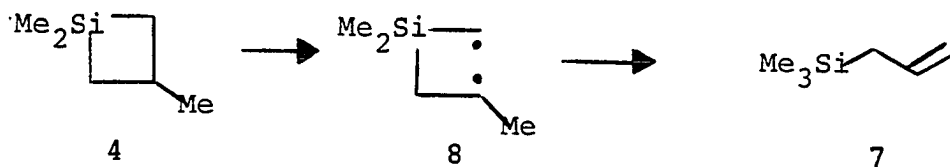
The elucidation of the mechanism of this decomposition has played a pivotal role in recent organosilicon chemistry, since it was through pyrolysis of **1** that proof of the existence of silene **3** as a discrete reactive intermediate was established (4). Vacuum pyrolysis of **1** cleanly afforded 1,1,3,3-tetramethyl-1,2-disilacyclobutane **2** (silene **3** dimer) and ethene in a first order process with

very similar Arrhenius parameters ($k = 10^{15.6} \exp[-62300 \text{ kcal/RT}]$) as those known for the cyclobutane thermolysis ($k = 10^{15.68} \exp[-61000/\text{RT}]$) (5). The rate of decomposition observed was inhibited by the addition of excess ethene or propene (with formation in the latter case of 1,1,3-trimethylsilacyclobutane 4). Trapping experiments were consistent with the formation of silene 3, including copyrolysis of 1 with 1,3-butadiene, which afforded 1,1-dimethyl-1-silacyclohex-3-ene 5, the 4 + 2 adduct of silene 3 and butadiene.



These results, although virtually demanding of silene intermediacy, do not establish the site of initial bond rupture or indicate whether a diradical (e.g., 6) is involved. The first clue indicating that 6 was the init-

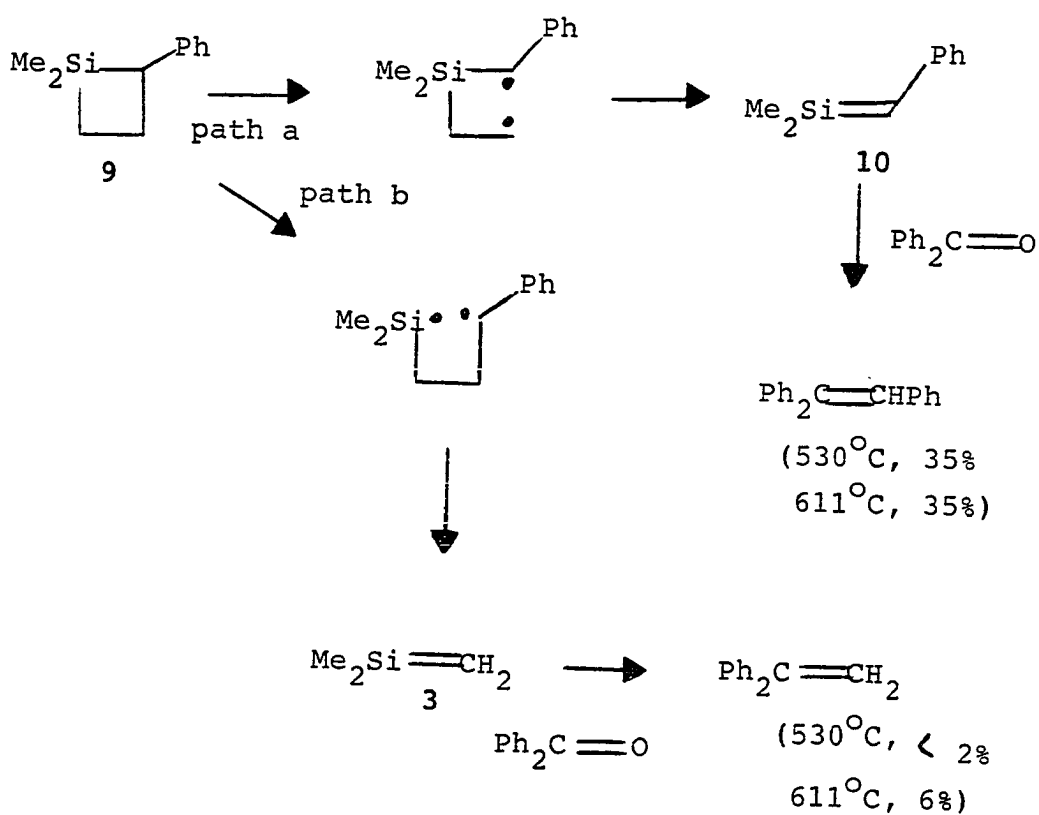
ially formed intermediate, and that silacyclobutanes decompose via initial β -C-C bond scission, and not initial α -Si-C bond breakage, was provided by the pyrolysis of 1,1,3-trimethylsilacyclobutane 4 (6). The product, 1-allyl-1,1,1-trimethylsilane 7, is easily rationalized as the product of intramolecular disproportionation of diradical 8.



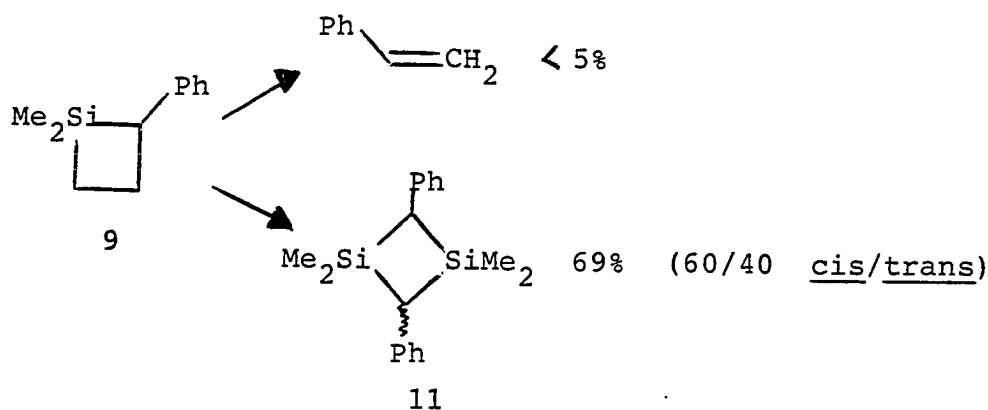
Several groups studying the pyrolysis of unsymmetrical 1,1,2-trisubstituted-1-silacyclobutanes independently provided conclusive evidence that the β -C-C bond is the site of initial bond breakage. Golino et al. studied the gas phase pyrolysis of 1,1-dimethyl-2-phenyl-1-silacyclobutane 9 between 530-600°C (7). The ratio of 1,1-dimethyl-2-phenylsilene 10 dimers or trapping products (various trapping agents were used, including benzophenone, illustrated below in Scheme 1) to products derived from 1,1-dimethylsilene 3 was interpreted as a measure of the rela-

tive extent of C-C bond scission (path a) vs. Si-C bond scission (path b), and found to vary from > 30/1 at 530°C to > 6/1 at 611°C. The pyrolysis of 9 was also studied by Valkovitch et al. (8). At 500°C (nitrogen flow pyrolysis) a 69% yield of 1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane 11 was obtained (based on recovered 9), along with ethene. Styrene (< 5% yield) was noted as a product in one run.

Scheme 1



Scheme 1 (continued)



A similar picture emerged in the work of Barton et al., who analyzed the products from the nitrogen flow pyrolysis of 1,1,2-trimethyl-1-silacyclobutane, concluding that at 520°C 75.2% of the disilanyl products resulted from initial C-C bond homolysis (9). The relative yield of disilane products resulting from Si-C bond homolysis rose from 24.8% at 520°C to 44.9% at 680°C .

Despite this consistent and straightforward picture which emerged from these studies of silacyclobutanes, 1-hydridosilacyclobutanes, in particular the parent system, silacyclobutane **12** itself, have proved more problematic. Although matrix isolation of 1,1-dimethylsilene **3** from 1,1-dimethylsilacyclobutane **1** has been accomplished on numerous occasions, efforts to isolate the corresponding unsubstituted silene **13** from **12** have consistently failed (4b, 10). Although Sommer reported the chemical trapping of **13** with

some traps (benzophenone and hexamethylcyclotrisiloxane), other traps failed, and in the absence of trapping agent no dimers of 13 could be found; only an intractable silicon containing polymer was formed (11).

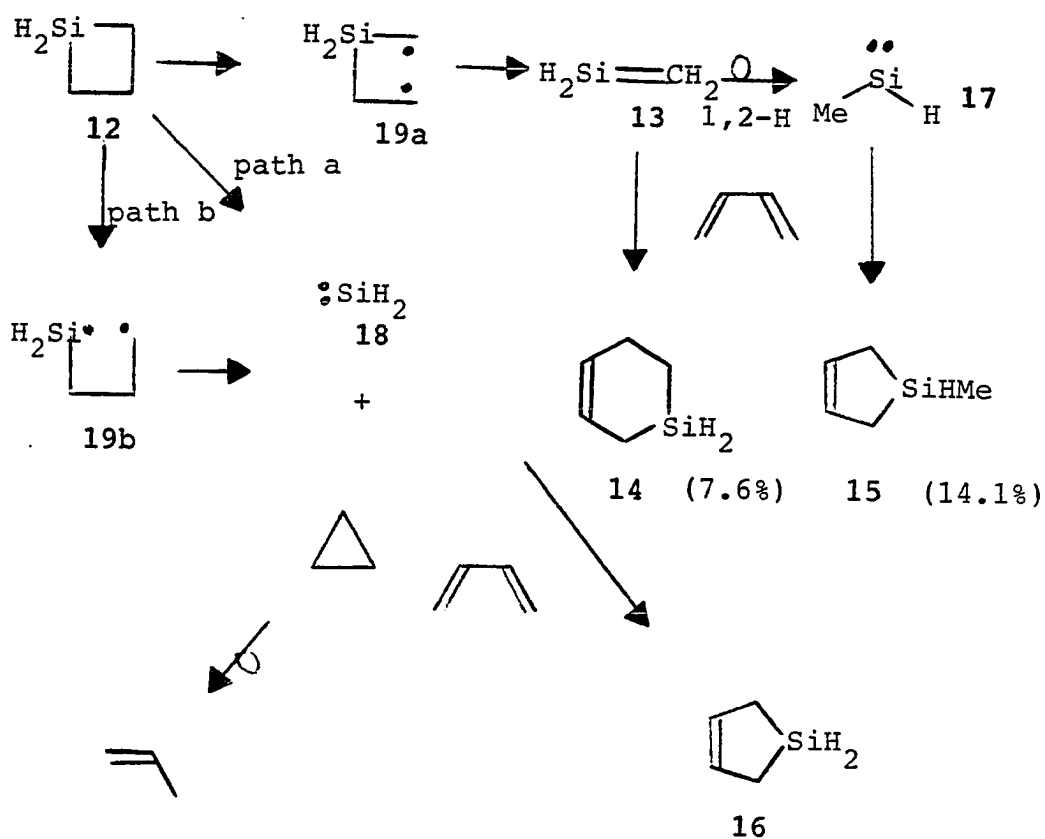
Renewed interest in the pyrolysis of 12 was triggered by a report of Conlin and Gill, who in 1983 published results for the low pressure copyrolysis of 12 and 1,3-butadiene (12). The major process of decomposition was the expected one of C-C bond homolysis and formation of silene 13 via diradical 19a, but in addition to 1-silacyclohex-3-ene 14 (the 4 + 2 cycloaddition product of butadiene and silene 13), 1-methyl-1-silacyclopent-3-ene 15 and 1-silacyclopent-3-ene 16 were obtained (Scheme 2). Since silacyclopentenes are formed as adducts of silylenes and butadiene, 15 was taken as evidence for the intermediacy of methylsilylene 17 which was postulated to be formed via a 1,2-hydrogen shift in silene 13. Conlin also reported the formation of cyclopropane (or propene resulting from its isomerization at higher temperatures); its presence along with 16 constituted evidence for a competitive decomposition of 12 to silylene 18. Based upon thermodynamic considerations a stepwise process of initial Si-C bond homolysis and subsequent elimination of silylene 18 from diradical 19b was favored over a direct chelotropic

extrusion of 18.

Conlin's principle interest in studying the pyrolysis of 12 was to demonstrate the conversion of 13 to 17 via a 1,2-hydrogen shift (a topic which has sparked a good deal of controversy and served as a remarkably interesting test of both experimental capabilities and the accuracy of current calculational methods in organosilicon chemistry [13]). Of more interest to this investigation, however, is the origin of silylene 18 from silacyclobutane 12. Neither a concerted elimination of 18 (path a, Scheme 2) nor the diradical mechanism favored by Conlin and Gill (path b) seemed adequate in the light of several relevant considerations: (a) Davidson et al. found that no cyclopropane was actually formed, only propene, even under conditions where cyclopropane is stable; (b) the decomposition of 1,1-dimethylsilacyclobutane 1 is a very clean reaction affording only ethene and silene, and no propene is formed whatsoever; (c) silicon-carbon bond energies are little affected by substituents on silicon (D of $H_2Si-CH_3 = 88.3$ kcal/mol, and D of $Me_3Si-CH_3 = 89.4$ kcal/mol) (4a, 14, 15).

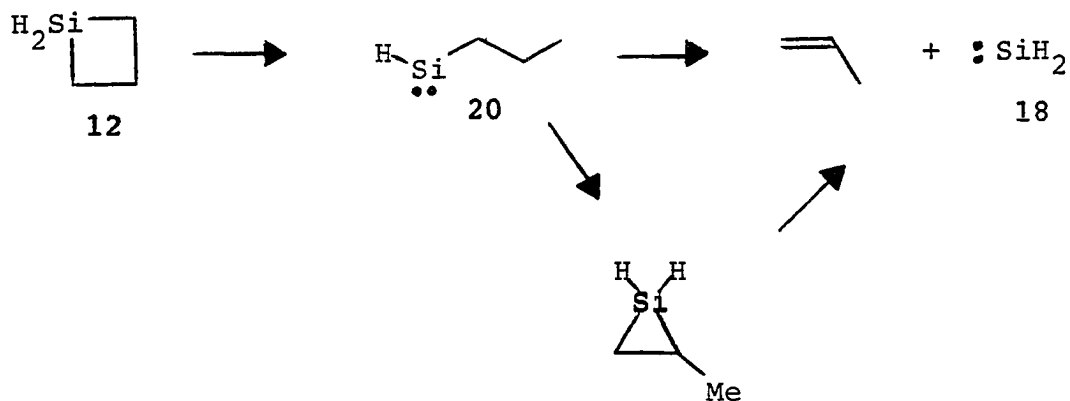
Thus there appeared to be no reason, considering these factors, that silacyclobutane 12 should afford propene, when 1,1-dimethylsilacyclobutane 1 does not. A mechanism which explains the unique involvement of hydrogen on

Scheme 2



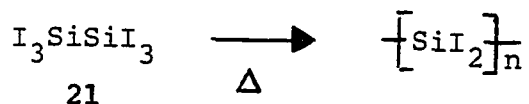
silicon was sought. It was hypothesized that 12 decomposed to silylene 18 and propene via initial α -elimination of a methyl group to form propylsilylene 20 which then undergoes further decomposition to propene and silylene 18. As will be discussed in the next section of this Historical, this hypothesis had precedent in the known decomposition of

alkylsilylenes to olefins, and it had been observed that alkyl elimination in silanes could occur, yielding silylenes. It was to test this proposition that this dissertation research was originally undertaken.

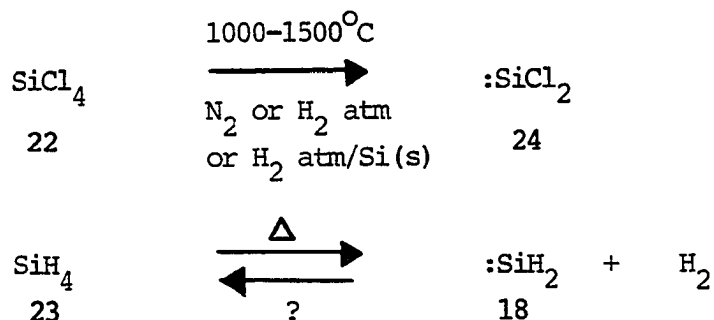


C-H Insertion and Elimination Reactions Involving Silylenes

Since the discovery by Friedel and Ladenburg in 1880 that the thermal decomposition of hexaiododisilane 21 afforded a polymer of diiodosilylene, α -elimination has become by far the most important thermal method for the generation of silylenes (divalent silicon analogues of carbenes) (16-22). Typical precursors employed include both disilanes (as in the experiment of Ladenburg) and mono-silanes.



In the case of monosilanes, silylenes were first confirmed as intermediates in the thermal decomposition of tetrahalosilanes, and since the 1930s numerous thermal reactions at high temperature of tetrahalosilanes which probably involve dihalosilylenes have been discovered (19-21). These include the formation of dichlorosilylene 24 in the pyrolysis of silicon tetrachloride 22 in a nitrogen or hydrogen atmosphere or in a hydrogen atmosphere over a silicon surface (19). Silane 23 itself has similarly been determined, despite a great deal of initial controversy, to thermally decompose via an initial unimolecular elimination of dihydrogen with formation of silylene 18 ($\log A = 13.3$, $E^a = 53$ kcal/mol) (16-19, 23, 24). Although the reverse reaction, silylene insertion into the dihydrogen bond, has not been experimentally confirmed, it has been calculated to have an activation energy of 6.3 ± 1 kcal/mol and experimentally estimated to be 5.5 ± 1 kcal/mol (25, 26).

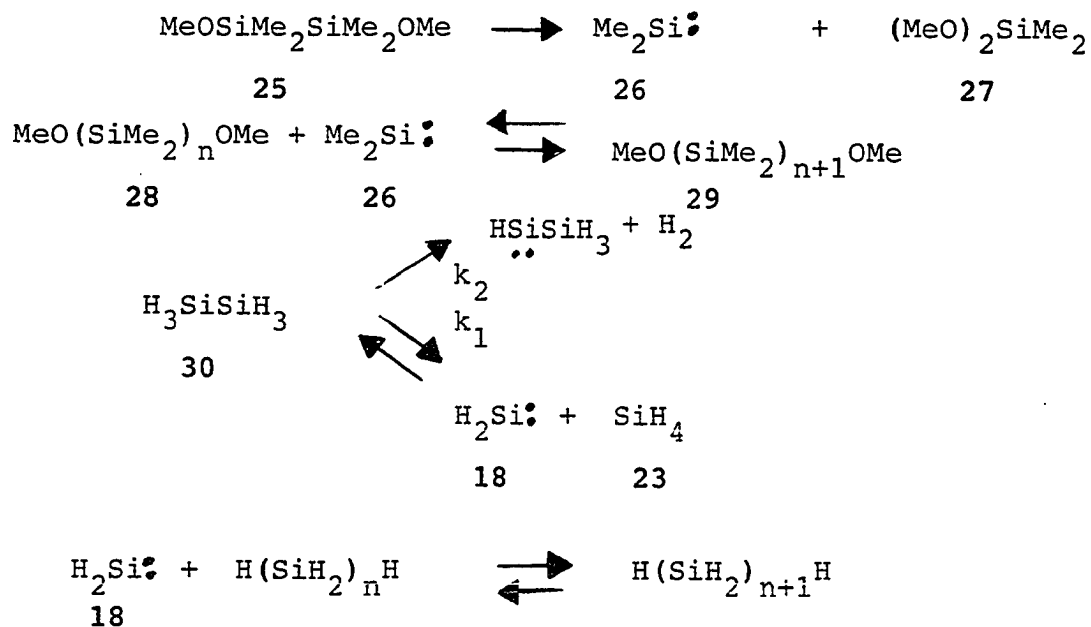


Much lower temperatures may be achieved in the pyrolysis of suitable disilanes, the decomposition of which has become the method of choice for the thermal generation of silylenes. For example, Atwell and Weyenberg found that the pyrolysis of methoxydisilanes cleanly affords silylenes at very convenient temperatures ($> 200^\circ\text{C}$ in sealed tubes). The thermolysis of 1,2-dimethoxytetramethyldisilane 25 proceeded at 225°C in a sealed tube, affording dimethylsilylene 26 and dimethyldimethoxyoxysilane 27 in a reaction which was determined to be unimolecular and reversible (19, 27, 28). Insertion of 26 into Si-O bonds resulted in the formation of α,ω -dimethoxypolysilanes 28 and 29.

Hydridodisilanes behave similarly, and it is well established for example that disilane 30 decomposes thermally to silylene 18 and silane 23 in a reversible reaction, with silylene insertion into the Si-H bonds forming

trisilane and higher molecular weight polysilanes 31 (24, 26, 29-32). Insertion into Si-H bonds is a general reaction of silylenes, widely employed as a characteristic trap (16, 19, 32). More recent work has indicated that in the disilane pyrolysis, elimination of molecular hydrogen is competitive with silane elimination ($k_1/k_2 \approx 3.0/1.0$, Scheme 3), although still a minor process (33).

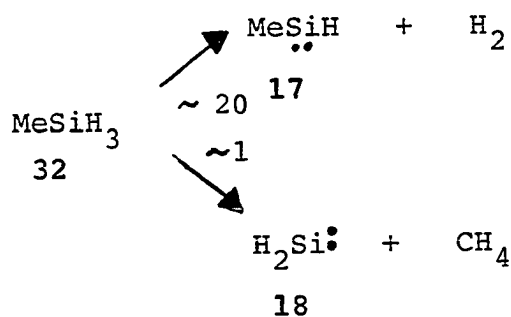
Scheme 3

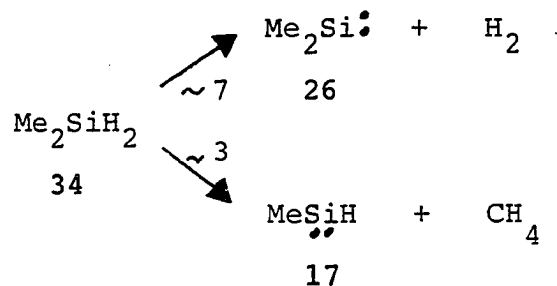


Despite the wide variety of silylene-forming reactions by alpha-elimination processes known, silylene formation via elimination of the elements of carbon and hydrogen (alkyl elimination) has remained a rare process, first

noted by Davidson and Ring in the low pressure pyrolysis ($\leq 10^{-1}$ torr, 930-1000 K) of methylsilane 32. The major primary reaction was found to be unimolecular dihydrogen elimination (also found by Neudorfl and Strausz) which produces methylsilylene 17, however also detected was a small amount of methane ($< 5\%$), attributed to a unimolecular process of alkyl elimination which yields methane and silylene 18 (34, 35).

Whereas methane formation accounts for less than 1/20 of the methylsilane 32 decomposition, methane elimination becomes more significant in the pyrolysis of dimethylsilane 34. Rickborn et al. found that under stirred-flow pyrolysis conditions (843-992 K) methane was detected in the reaction products (36). Its unimolecular formation was calculated to constitute ca. 30% of the primary process dimethylsilane decomposition at 1200 K.





Arrhenius parameters for dihydrogen and methane elimination from silane 23, methylsilane 32, and dimethylsilane 34 have been collected for comparison and are presented in Table 1.

In what may be an apparent example of an "intramolecular" C-H elimination Barton, Burns, and Burns found that copyrolysis of methylsilylene 17 generator 1,1,1,2-tetramethyldisilane 35 with acetylenes afforded products indicative of vinylsilylene formation, presumably arising via intermediate silacyclopropenes (Scheme 4) (39). Copyrolysis of 35 with acetylene afforded 1-ethynyl-1-methyl-1-vinylsilane 36. This was rationalized as the result of addition of 17 to acetylene (an excellent silylene trap), yielding silacyclopropene 37, which rearranges to vinylmethylsilylene 38. Reaction of 38 with another molecule of acetylene produces silacyclopropene 39

Table 1. Monosilane pyrolysis Arrhenius parameters

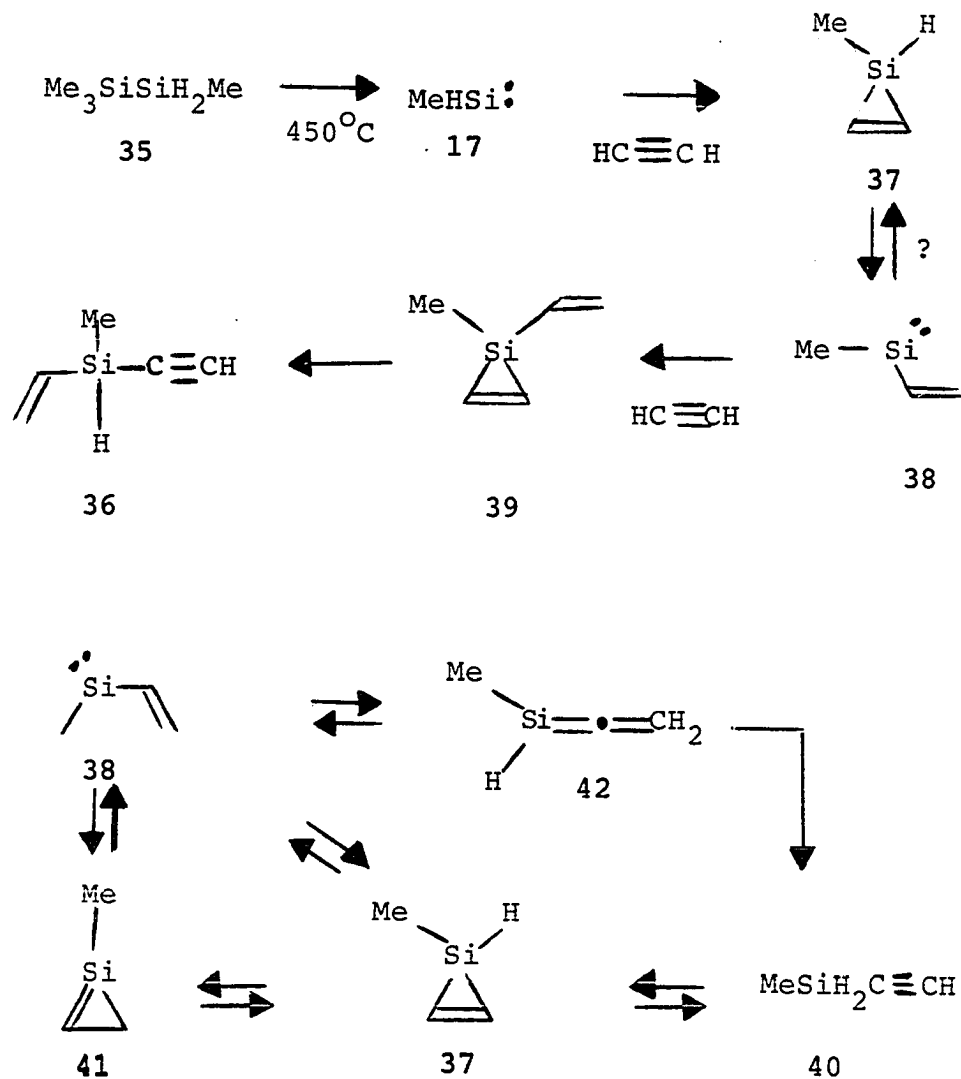
Reaction	Log A	E _a (kcal/mol)	Ref.
$\text{SiH}_4 \longrightarrow \text{H}_2\text{Si:} + \text{H}_2$	13.2	53.6	25, 38 ^a
	13.8	55.1	38
	13.3	52.7	37
$\text{MeSiH}_3 \longrightarrow \text{MeHSi:} + \text{H}_2$	14.1	64.8	34
	14.9	63.2	35
	15.2	64.8	37
$\text{MeSiH}_3 \longrightarrow \text{H}_2\text{Si:} + \text{CH}_4$	13.6	69.3	34
	14.7	66.7	37
$\text{Me}_2\text{SiH}_2 \longrightarrow \text{Me}_2\text{Si:} + \text{H}_2$	14.3	68.0	35
$\text{Me}_2\text{SiH}_2 \longrightarrow \text{MeHSi:} + \text{CH}_4$	14.8	73.0	36
	15.0	72.0	37

^aData are from ref. 25 as recalculated in ref. 38.

which rearranges to the observed product 36.

That the reaction of 37 to 38 may be reversible was suggested by earlier results of Barton and coworkers, who found that 38 rearranged to 1-methylethynylsilane 40 in the absence of acetylene (Scheme 4) (40). This could occur through direct C-H insertion to form silacycloprop-2-ene 37, although an alternative explanation was advanced in which 38 undergoes intramolecular π -addition forming silacycloprop-1-ene 41 which rearranges by formal 1,3-hydrogen

Scheme 4



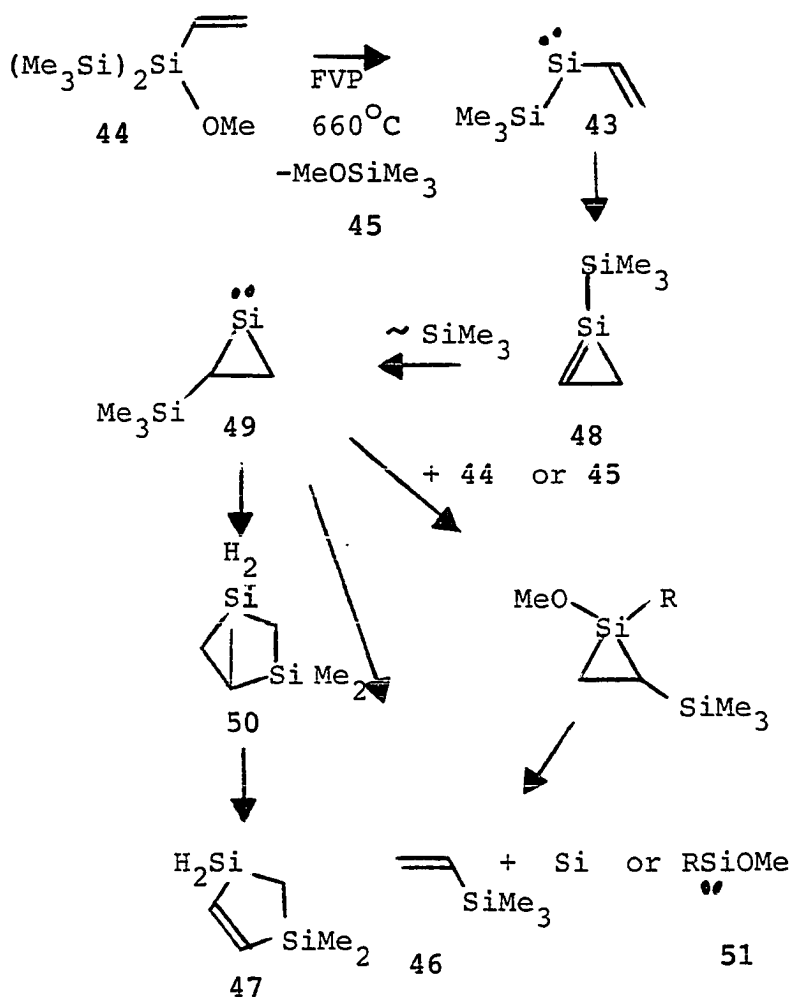
shift to 37. Although unprecedented, it was also recognized that sila-allene 42, formed by C-H insertion (1,2-H shift) in 38 could provide still another route for the conversion of 38 to 41. Clearly, the possible intercon-

versions of vinylsilylenes, silacyclopropenes, and sila-allenes presents a complicated and experimentally difficult question to resolve.

Whether vinylsilylenes rearrange to silacycloprop-2-enes (e.g. 38 to 37) directly via C-H insertion or via the intermediacy of silacycloprop-1-enes (intramolecular π -addition followed by hydrogen atom shift) is an interesting question which has probably not been completely decided. The π -addition route is likely a very high energy process, since calculations by Gordon et al. indicate that silacycloprop-1-ene lies approximately 49 kcal/mol above silacycloprop-2-ene on the C_2H_4Si energy surface, and some 51 kcal/mol above vinylsilylene (41). Yet experimental evidence has been accumulated which tends to support the intramolecular π -addition mechanism. Barton and Burns found that trimethylsilylvinylsilylene 43, prepared in the flash vacuum pyrolysis of disilane precursor 44, afforded methoxytrimethylsilane 45, vinyltrimethylsilane 46, and 1,1-dimethyl-1,4-disilacyclopent-2-ene 47 as the observed products (Scheme 5) (42). Their formation was rationalized as the result of an initial intramolecular π -addition of 43, which produces silacycloprop-1-ene 48, and isomerization of silene 48 to silylene 49, which either extrudes a silicon atom (to give the observed vinyltrimethylsilane

46) or undergoes γ -C-H insertion to disilahousane 50. Carbon-carbon bond homolysis then easily converts 50 to the product 47. Gaspar has pointed out that rather than extruding a silicon atom, 49 may trap a methoxysilane (e.g., unreacted 44 or methoxytrimethylsilane 45) and the intermediate silacyclopropane ejects methoxysilylene 51 (18).

Scheme 5

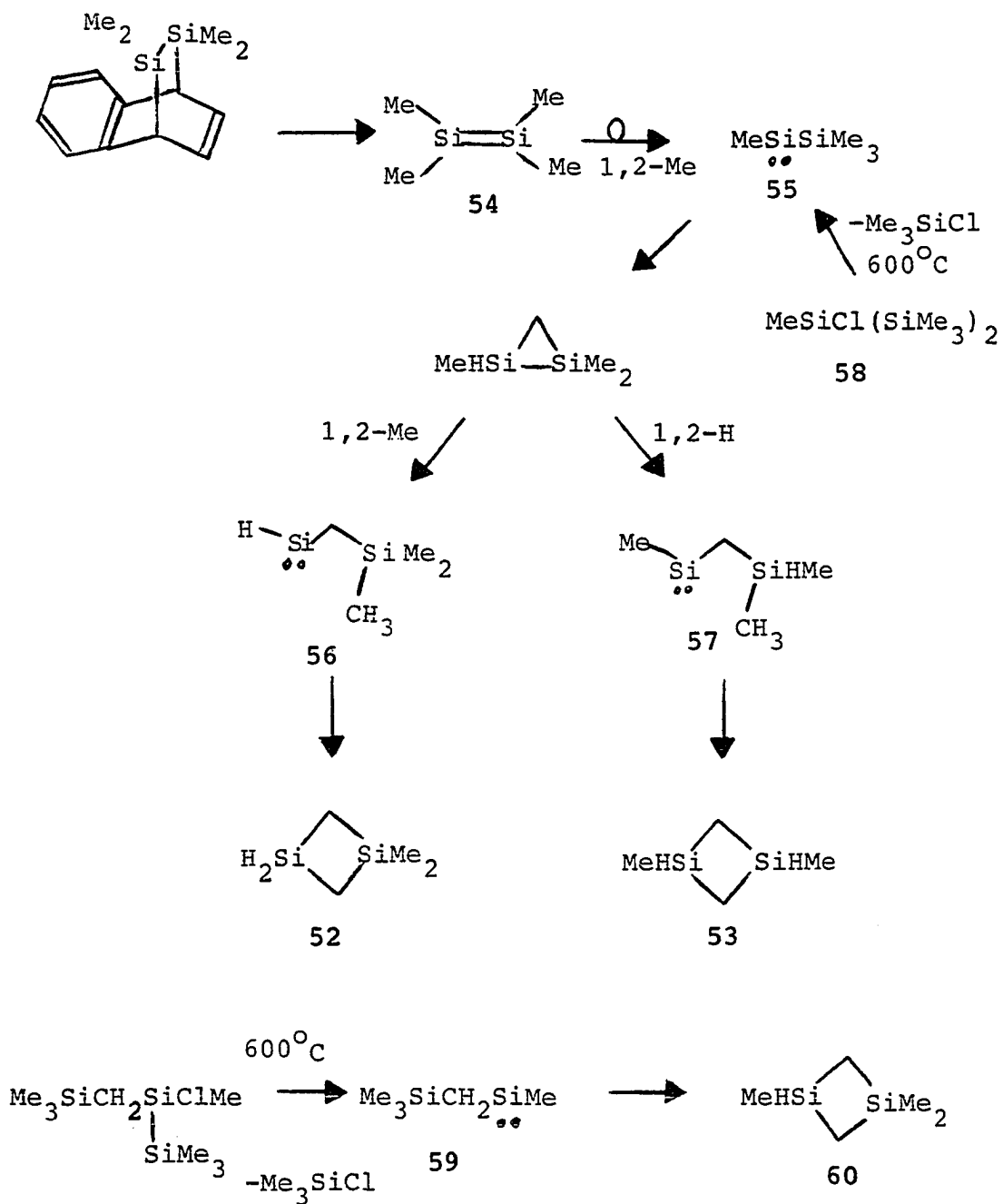


A number of other examples of intramolecular C-H insertion reactions of silylenes are at present known. The earliest suggestion of an intramolecular C-H insertion came from the work of Wulff, Goure, and Barton, who provided convincing evidence that disilacyclobutanes 52 and 53, the ultimate products from the gas phase thermal rearrangement of tetramethyldisilene 54, were formed (in 30% and 10% yields, respectively) via a mechanism involving silylenes 55-57 and several key C-H insertion reactions (Scheme 6) (43). This mechanism was put forth as an alternative to a proposal by Roark and Peddle, who originally discovered the rearrangement, which invoked several diradical intermediates (44).

The proposed mechanism was tested by direct generation of silylene 55 (from bis(trimethylsilyl)-chloromethylsilane 58) which gave 52 and 53 in remarkably similar yields (28% and 15% respectively), trapping experiments, and by direct generation of silylene 59, an analogue of silylenes 56 and 57, which afforded the expected 1,1,3-trimethyldisilacyclobutane 60 in good yield (Scheme 6).

The "Barton mechanism" (Scheme 6) for the tetramethyldisilene 54 rearrangement provided the earliest (and still one of the most spectacular) examples of a number of thermal organosilicon reactive intermediate rearrangements

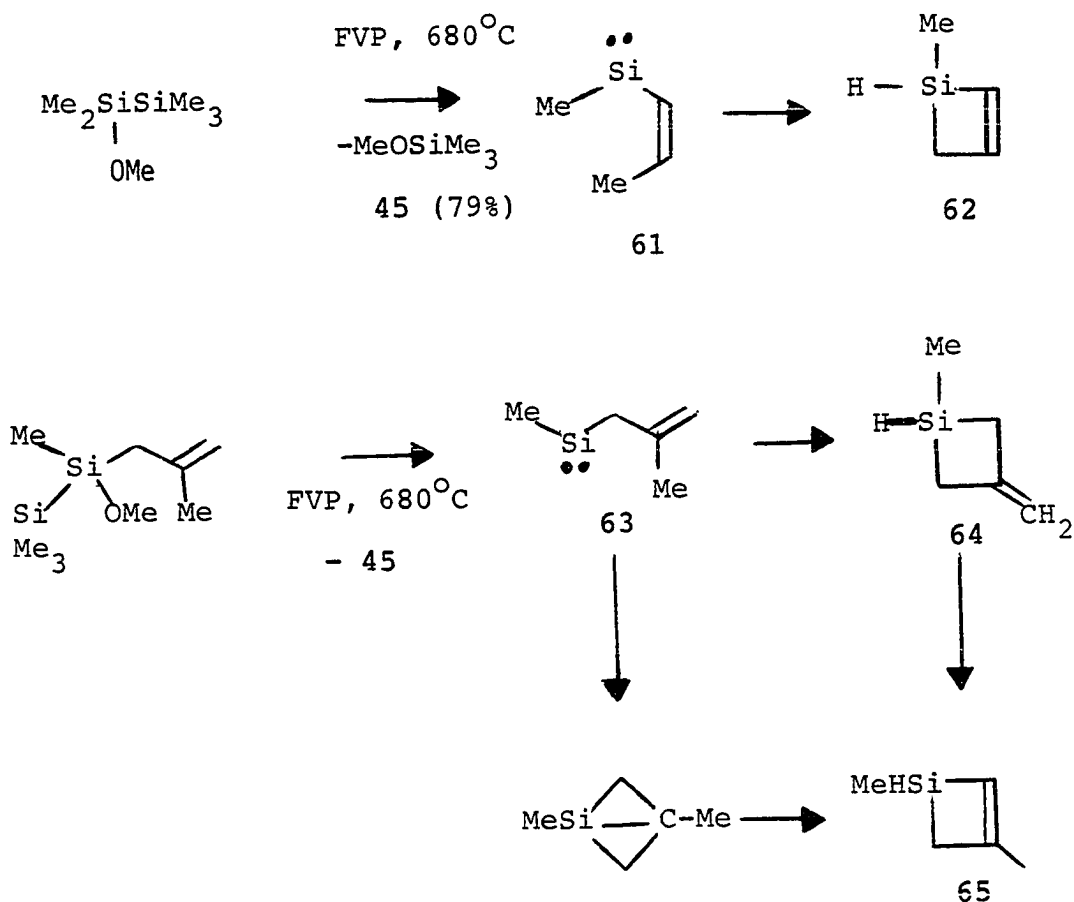
Scheme 6



which were to follow in subsequent years. It incorporated a number of suggestions which were at the time quite revolutionary including the key features of a 1,2-methyl shift in a disilene, and silylene C-H insertion. As the number of similar rearrangements known grew, a very rich and lively field of organosilicon chemistry evolved.

There are a number of examples of intramolecular silylene insertions into allylic C-H bonds. Methyl-1-(1-propenyl)silylene 61 cleanly affords 1-methyl-1-silacyclobut-2-ene 62 in 37% yield (Scheme 7) (45). Allylic C-H insertion (with silacyclobutane ring formation) is apparently favored over intramolecular π -addition in the rearrangement of methallylmethylsilylene 63; the products observed were methylenesilacyclobutane 64 (41%) and 1,3-dimethyl-1-silacyclobut-2-ene 65 (20%) (Scheme 7) (45). Of two possible mechanistic routes, initial π -addition or C-H insertion, to the ultimate silacyclobutene product, it is possible that C-H insertion is exclusive since 64 rearranged to 65 (which itself is stable) under the reaction conditions employed. Pyrolysis of 64 gave a product mixture consisting of a 1.0/0.55 ratio of 64/65.

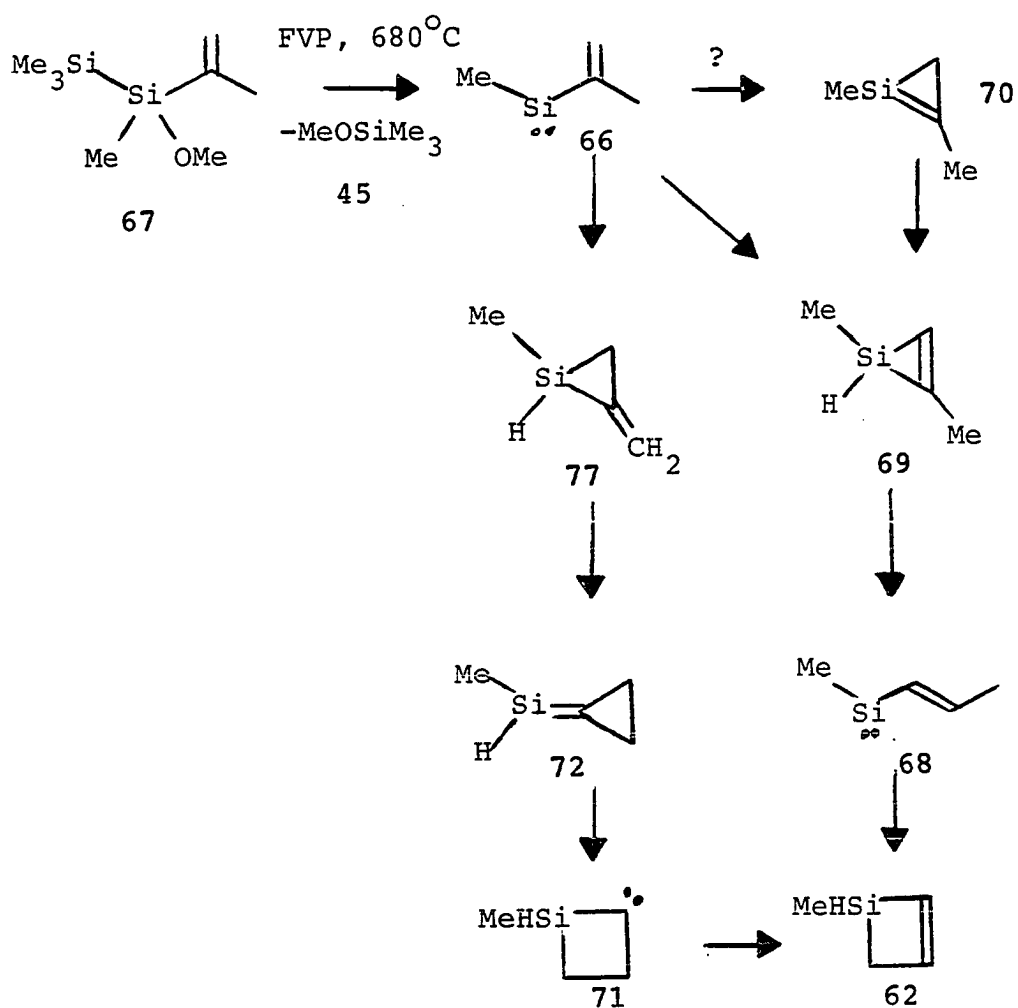
Scheme 7



At least one C-H insertion is involved in the rearrangement of 2-propenylmethylsilylene 66, formed in the flash vacuum pyrolysis of 67 (45). Several mechanistic routes were proposed by the authors (Burns and Barton) to explain the formation of 1-methyl-1-silacyclobut-2-ene 62 as the exclusive product (16%). Favored by the authors was

the rearrangement of 2-propenylsilylene 66 to 1-propenylsilylene 68 through the intermediacy of silacycloprop-2-ene 69; once again, however, it remains ambiguous whether a silacycloprop-1-ene 70 is involved in the process (Scheme 8).

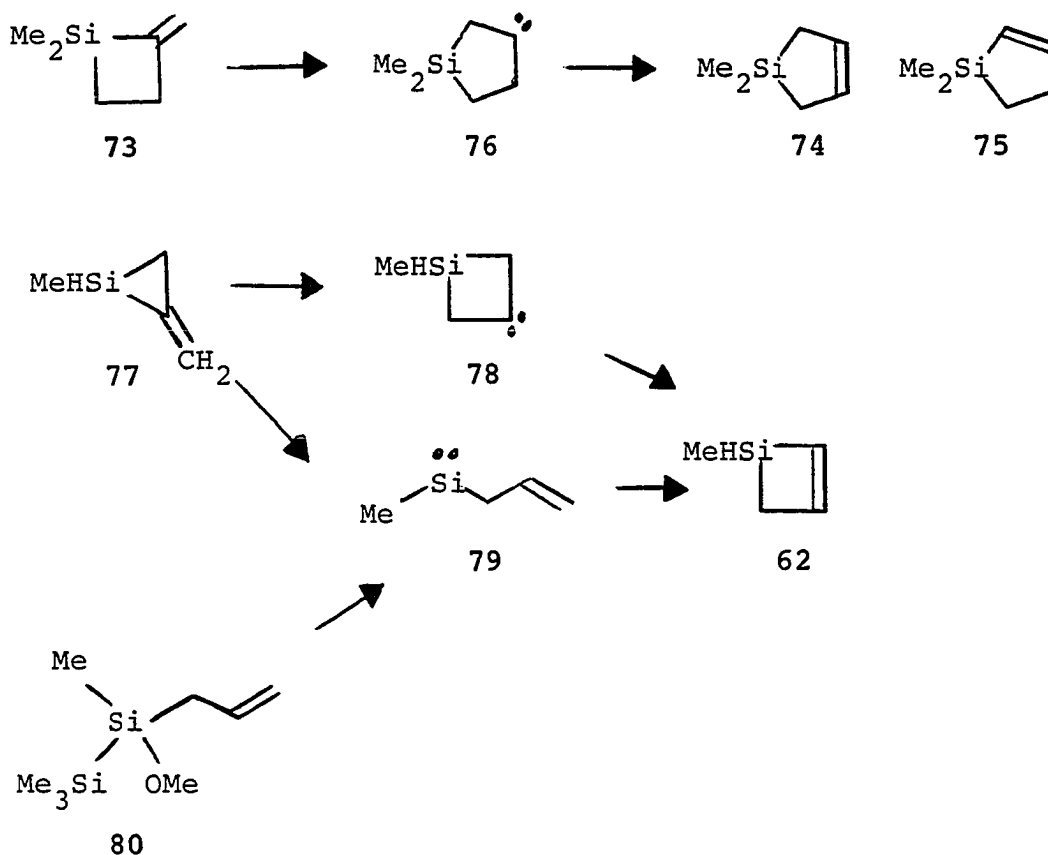
Scheme 8



An alternative mechanism involving insertion into an allylic C-H bond in 66 and rearrangement to carbene 71 (perhaps through a "methylene silacyclopropane rearrangement" to silene 72, Scheme 8) would be a high energy process and at the time an unprecedented possibility, not favored by the authors. A different carbene mechanism is however suggested by recent work of Conlin et al., who found that methylene silacyclobutane 73 efficiently yielded a mixture of silacyclopentenes 74 and 75 (Scheme 9); a novel 1,2-silicon shift affording carbene 76 was proposed as the pathway (46). In this light, it is not unreasonable to propose C-H insertion by 66 with formation of methylene-silacyclopropane 77 and a direct isomerization of 77 to carbene 78. Another alternative is via isomerization of 77 to methylallylsilylene 79. Silylene 79 is known from the FVP of disilane 80 to yield 1-methylsilacyclobut-2-ene 62 in comparable yield (Scheme 9) (45).

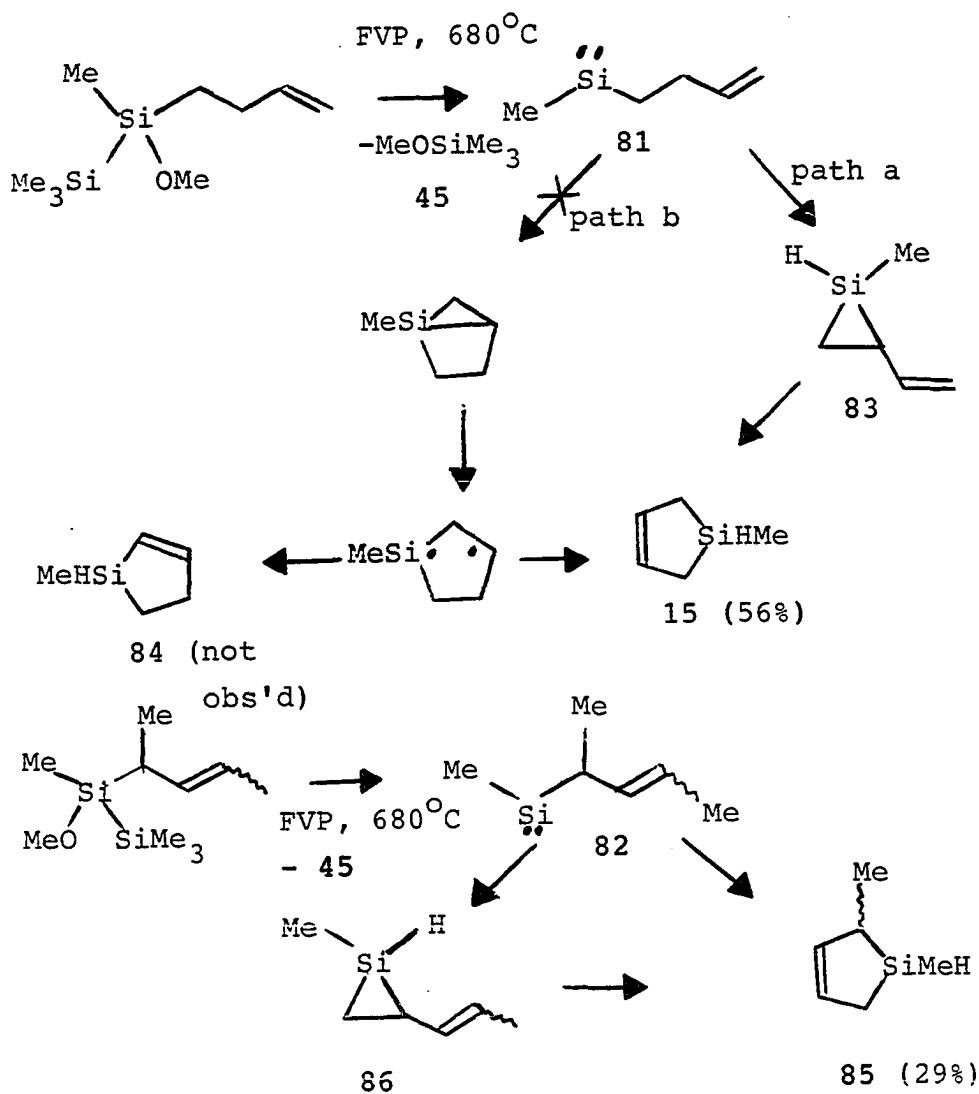
Two examples of silylenes which may undergo thermal intramolecular C-H insertion are methylbut-3-enylsilylene 81 and methyl-4-(pent-2-enyl)silylene 82 (Scheme 10) (47). Under the reaction conditions employed 81 afforded silacyclopent-3-ene 15 exclusively; the mechanism favored was initial allylic β -C-H insertion and vinylsilacyclopropane rearrangement of intermediate 83 (path a). A key result,

Scheme 9



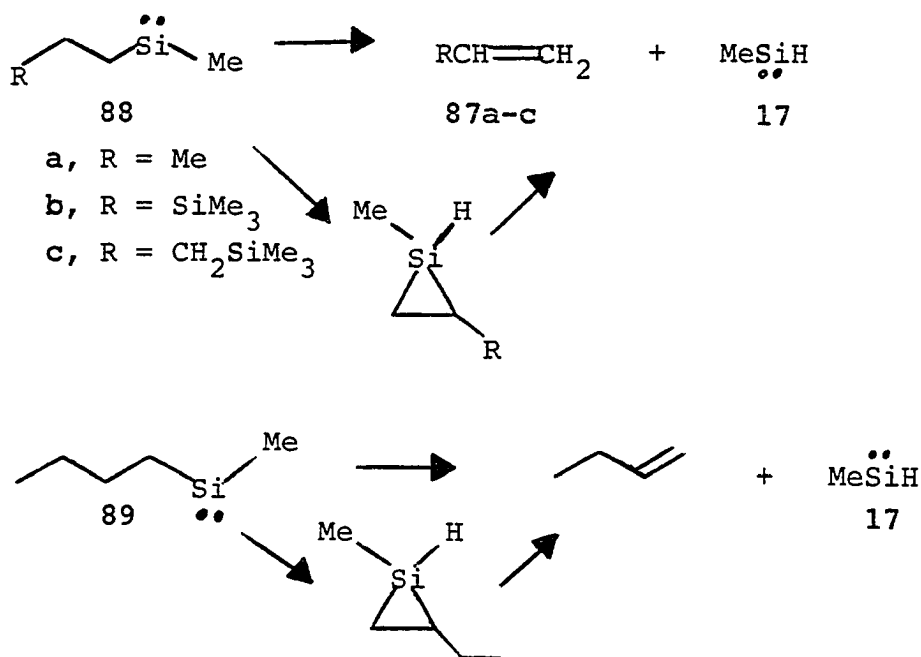
that there was none of the isomeric silacyclopent-2-ene 84 formed under these conditions suggested that an alternative intramolecular π -addition process (path b) did not occur. Formation of 1,2-dimethyl-1-silacyclopent-3-ene 85 from 82 was interpreted by the authors as the result of allylic C-H insertion; nevertheless this is not demanded as β -C-H insertion and rearrangement of vinylsilacyclopropane 86 is consistent with the result.

Scheme 10



Silylenes containing a saturated alkyl chain with hydrogens invariably decompose to the corresponding alkenes and smaller silylenes as the major process. For example, Guselnikov et al. reported the formation of 1-alkenes 87a-c from the decomposition of alkylsilylenes 88a-c (generated

in the gas phase from the reaction of the corresponding 1,1-dichlorosilanes with sodium-potassium vapor at 300°C) (48, 49). Similarly, Barton and Burns reported the formation of 1-butene from methylbutylsilylene 89 (47). Both authors proposed silacyclopropanes as intermediates.

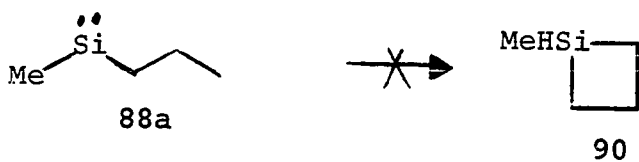


Gusel'nikov et al. also considered the possibility of C-H insertion and silacyclobutane formation by such alkylsilylenes (49). Despite a careful search for 1-methylsilacyclobutane 90 in the pyrolysis products of methylpropylsilylene 88a, under conditions where it was expected to be stable, it proved impossible to detect its presence at all (Scheme 11). Ethene (the major product of silacyclobutane

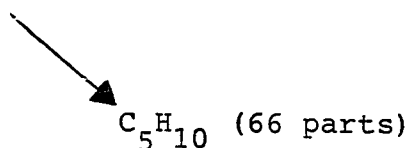
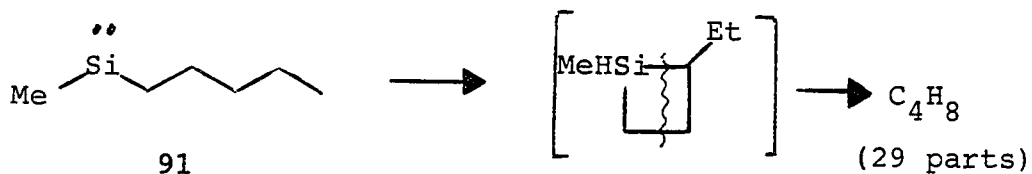
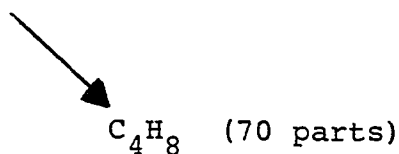
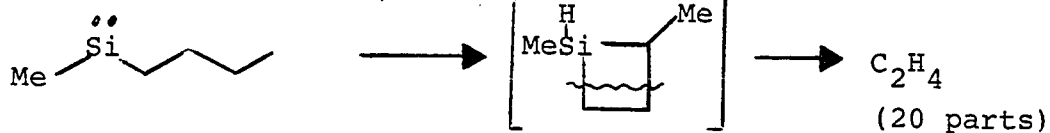
decomposition) was present in only a very small amount (< 6%). This was in conflict with results of Lopatnikova, who found that methylalkylsilylenes (generated in his experiments under comparable conditions via alkali metal vapor reduction at 340°C of the corresponding 1,1-dichlorosilanes) yielded significant amounts of alkenes of reduced carbon chain length (50). These were postulated as being formed through the intermediacy of silacyclobutanes (Scheme 11), although the silacyclobutanes themselves could not be detected. Thus, methylbutylsilylene 89 yielded 20 parts ethene in addition to 70 parts butene in his experiments. However, despite this result, it was reported in the same paper that that methylpentylsilylene 91 did not afford ethene; butene was found instead. Formally this may be explained as the result of γ -C-H insertion followed by decomposition of the intermediate silacyclobutane via either Si-C bond homolysis or initial cleavage of the less substituted C-C bond. It is difficult to see why this silylene should differ so from the results claimed by the author for silylene 89. It is well established in the literature that silacyclobutanes decompose predominantly by homolysis of the β -C-C bond; and there is no apparent reason why homolysis of the the more substituted silacyclobutane bond would not be favored in this case.

Scheme 11

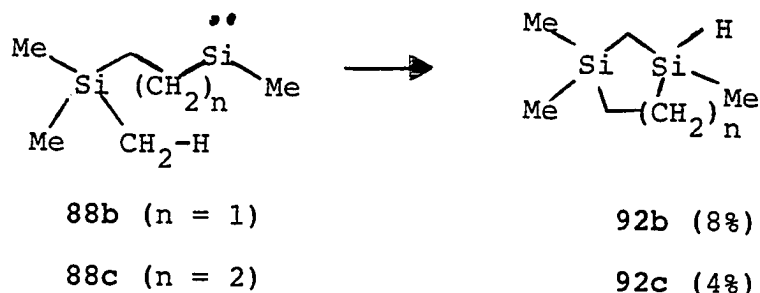
Gusel'nikov (Ref. 49):



Lopatnikova (Ref. 50):



Quite interestingly, although no silacyclobutanes were apparently formed from the reaction of trimethylsilylalkylsilylenes 88b and 88c, these silylenes did undergo δ - or ϵ -C-H insertion to form cyclic disilacyclopentane 92b or disilacyclohexane 92c, although as a minor process (Scheme 12) (49).

Scheme 12

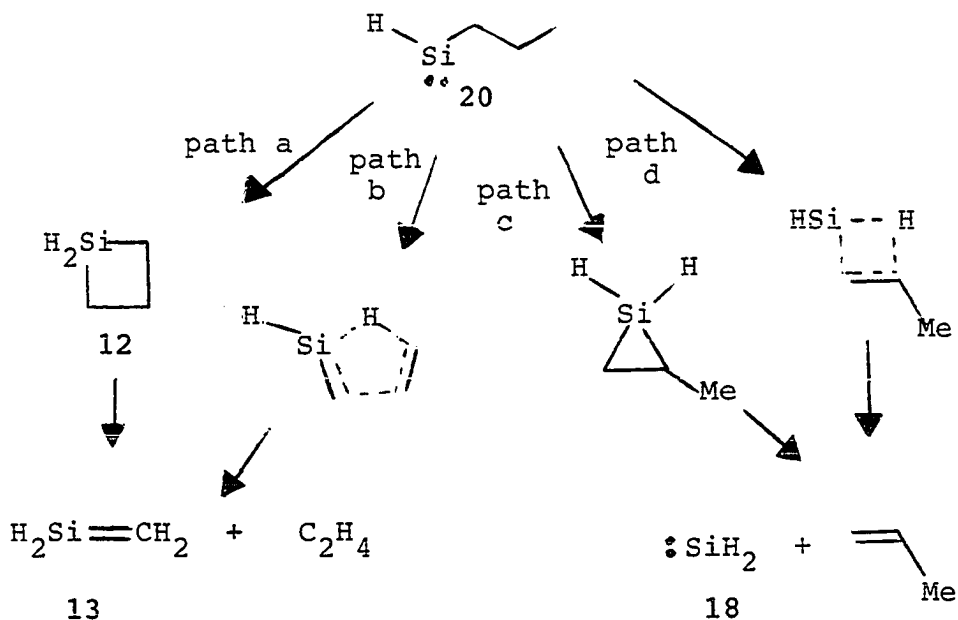
The shock induced pyrolyses of ethylsilane 93 and propylsilane 94, which decompose to ethylsilylene and propylsilylene 20, have been studied (51, 52). Ethylsilylene and propylsilylene 20 were found to yield the expected alkenes ethene and propene, respectively, as the major products and Arrhenius parameters were determined. However, it was reported that propylsilylene 20 decomposed not only to propene, but also to ethene, both products being formed with about the same activation energy (ca. 31 kcal/mol) (37, 52). This result agrees with Lopatnikova, but is at odds with Gusel'nikov's results (vide supra) (49, 50). The formation of ethene was rationalized as the result of intermediate silacyclobutane formation (path a, Scheme 13), the observed activation energy being consistent with an estimate based upon the sum of silacyclobutane ring

strain (16.8 kcal/mol was used, although other values of 22.7 and 25.9 kcal/mol have been obtained [53]) and the estimated C-H insertion activation energy for silylene insertion into the C-H bond of methane (ca. 17 kcal/mol). However the authors failed to observe any silacyclobutane. Silacyclopropane formation (path c) would be expected to involve considerably more ring strain than silacyclobutane ring formation, resulting in a considerably higher activation energy (\geq 44 kcal/mol was estimated, assuming, as with silacyclobutane formation, that the transition state incorporates most of the strain energy of the developing ring) than the measured activation energy (ca. 31 kcal/mol). Therefore, an alternative possibility, decomposition of propylsilylene to propene and silylene via a direct, concerted (four-center) elimination of silylene was proposed (path d) (52, 54). It should be pointed out that although these authors have at times favored the 4-center concerted process for this reaction, they have at other times seemed to favor the silacyclopropane intermediate (36). A similar concerted process forming ethene and silene 13 (path b, Scheme 13) was suggested (though not favored) as an alternative to path a (52).

It is evident that at this point considerable uncertainty existed both regarding the products formed from the

alkylsilylene decomposition, and the mechanism(s) involved. Are ethene and propene both formed from n-propylsilylene 20, or solely propene? Does the major path of alkylsilylene decomposition proceed via silacyclopropane intermediacy, or is it rather a direct and concerted process? One of the goals of this dissertation research has been to gather additional evidence regarding the identity of the true products by generating appropriate silylenes from alternative precursors and to acquire direct evidence regarding silacyclopropane intermediacy.

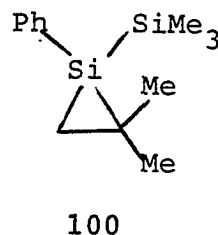
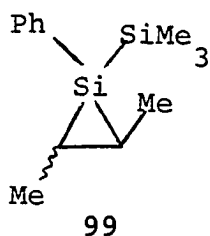
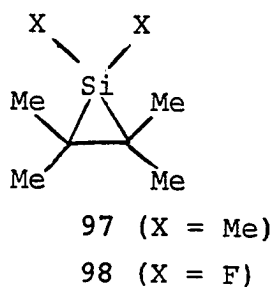
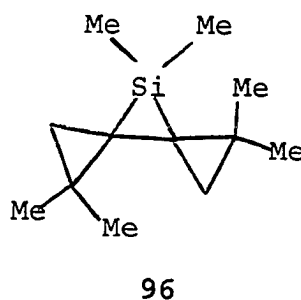
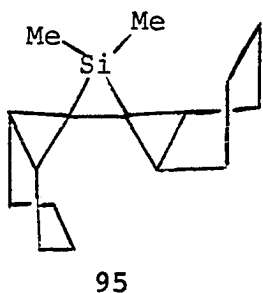
Scheme 13



Thermal Reactions Involving Silacyclopropanes

As a class of compounds, silacyclopropanes (siliranes) have proved remarkably more difficult to isolate and appear to be considerably more reactive than would be expected from a comparison with other silacarbo-cycles, e.g., the silacyclobutanes (55). Although silacyclobutanes and disilacyclobutanes have long been known and four atom rings containing silicon (4c) possess considerable thermodynamic stability, silacyclopropanes are known chiefly as reactive intermediates. Only a few completely isolable silacyclopropanes have been prepared including bis(cyclopropylidene)siliranes 95 and 96, which are apparently stabilized by overlap of the cyclopropyl Walsh orbitals with orbitals (possibly the d orbitals) on silicon (56-59). Concentrated solutions (with spectroscopic characterization) of other silacyclopropanes have also been prepared, for example compounds 97-100 (60-62).

Silacyclopropanes are quite reactive compounds and will react with virtually any electrophilic or nucleophilic reagent. They are also subject to radical attack. Cleavage generally occurs at the ring Si-C bonds to give 1,3-addition products. Silacyclopropanes are attacked by such reagents as oxygen, water, alcohols, amines, hydrogen



sulfide, amides, organolithium reagents, lithium metal, strong acids, and carboxylic acids. As a measure of their reactivity, 96 reacts with the enol form of cyclohexanone at 65°C to form a silyl enol ether, and 97 reacts with CCl_4 in THF solution at room temperature in a vigorously exothermic reaction to give products indicative of radical ($\text{Cl}\cdot$ or $\cdot\text{CCl}_3$) attack on silicon (55, 63).

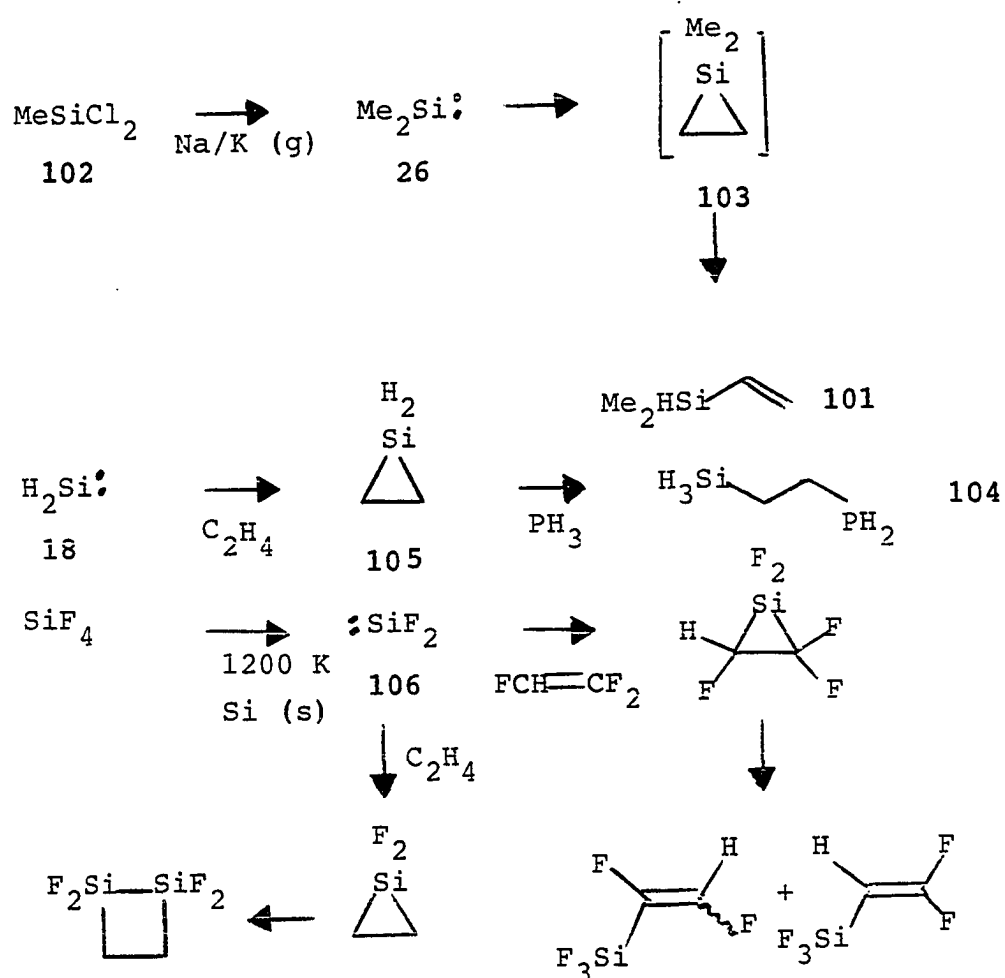
The formation of silacyclopropanes from the addition of silylenes to olefins seems a logical process for sila-

cyclopropane formation. In 1964 Skell and Goldstein reported the formation of vinyl dimethylsilane 101 from the reaction of dimethylsilylene 26 (generated in the gas phase from the reduction of dichlorodimethylsilane 102 with sodium-potassium vapor) with ethene; the observed product was rationalized as the result of isomerization of 1,1-dimethylsilacyclopropane 103 (64). The reaction of nucleogenic silylene 18 ($^{31}\text{SiH}_2$) with ethene has been reported, based upon the observation of a silacyclopropane/phosphine adduct 104 which could be formed from silacyclopropane 105 (65). Other silylene additions to ethene have been reported, including the reaction of difluorosilylene 106; the intermediate silacyclopropane can also insert another molecule of difluorosilylene to form an unusual 1,2-disilacyclobutane (61, 66-68). Addition of 106 to 1,2,2-trifluoroethene generates fluorinated silaethenes which can be rationalized as resulting from silacyclopropane intermediacy (66, 67). These results are summarized in Scheme 14.

Since these early reports of silacyclopropane formation the extreme thermal instability of silacyclopropanes has become known. Seyferth and Annarelli have found that hexamethylsilirane 97 thermally extrudes dimethylsilylene 26 at less than 100°C (69, 70). Given this apparent rever-

sibility of the addition of silylenes to C=C double bonds, detection of silacyclopropane formation using high temperature methods of silylene generation is only possible where the silacyclopropane may react to form stable products as an alternative to silylene elimination (several examples

Scheme 14

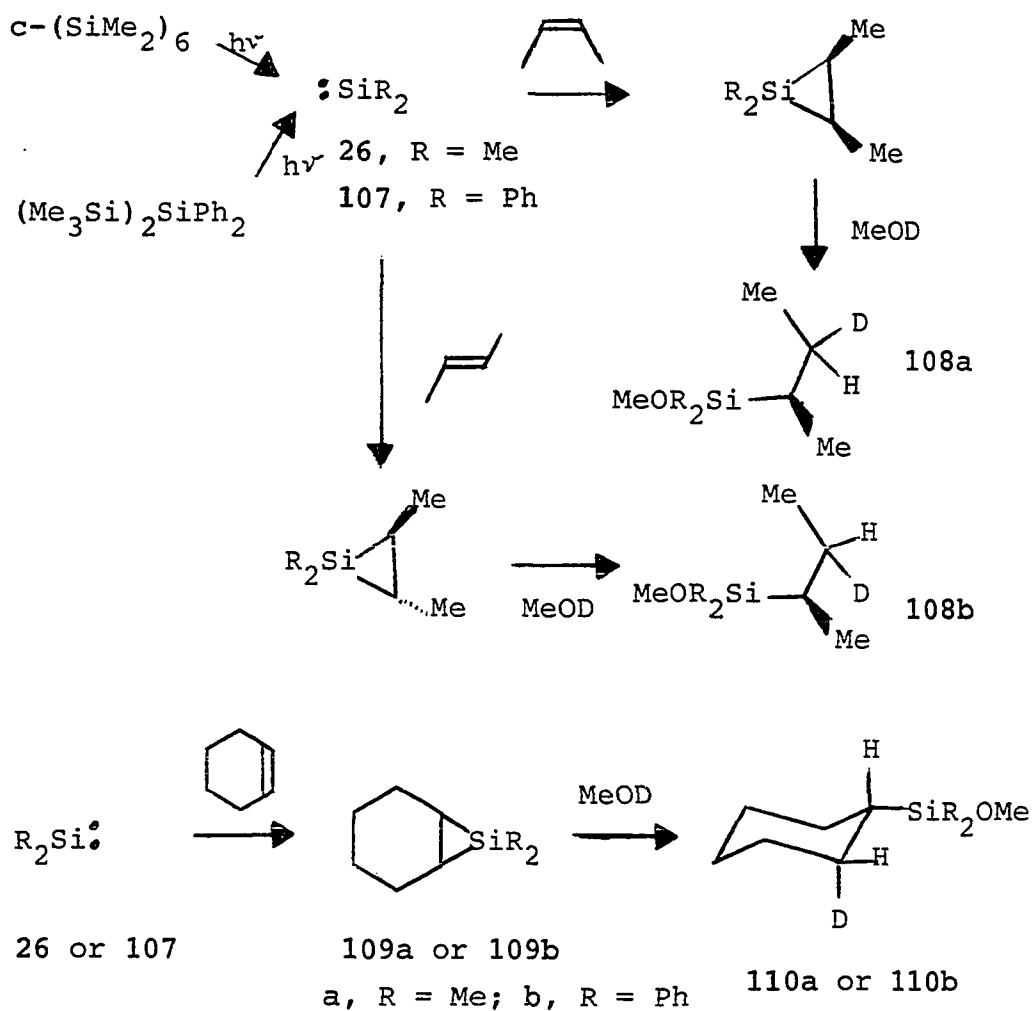


have already been presented). Atwell and Weyenberg's assertion (26) that silylene addition to double bonds could not compete with insertion into Si-O bonds may very well be true; it is possible however that it occurs but simply goes undetected. Such important problems as the stereo-specificity of silylene addition to olefins have thus only recently been investigated employing photolytic generation of silylenes or dimethylsilylene 26 production from the thermal decomposition, under relatively mild conditions, of hexamethylsilirane 97.

The stereochemistry of silylene addition to olefins has been investigated by Tortorelli and Jones who found that either dimethyl- or diphenylsilylene (26 or 107), photochemically generated from polysilane precursors in solutions of Z- or E-2-butene and methanol-d afforded deuterated s-butylmethoxysilanes, 108 (Scheme 15) (71). The β hydrogens in 108 are diastereotopic, and it was found that Z- or E-2-butene gave, respectively, diastereomers 108a and 108b. Since absolute configurations could not be determined, this experiment does not tell by itself whether the addition is cis or trans, but it does imply that both the silylene addition and the methanolysis must be stereospecific. The addition followed by methanolysis of 26 or 107 also occurred stereospecifically to cyclopentene and

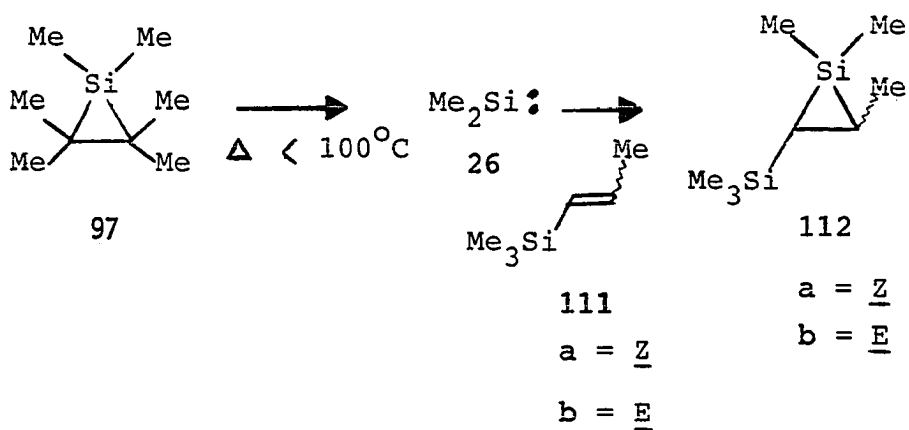
cyclohexene, implying that the addition reaction must be cis. Trapping of the siliranes 109a and 109b formed from cyclohexene in methanol-d and NMR analysis of the products 110a and 110b revealed the deuterium to be incorporated in

Scheme 15

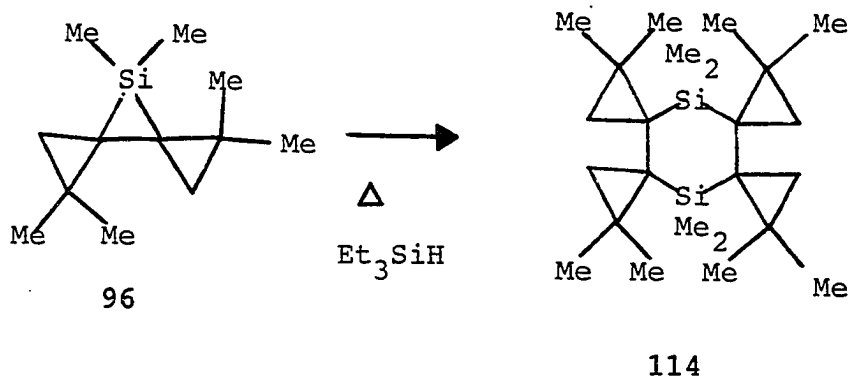
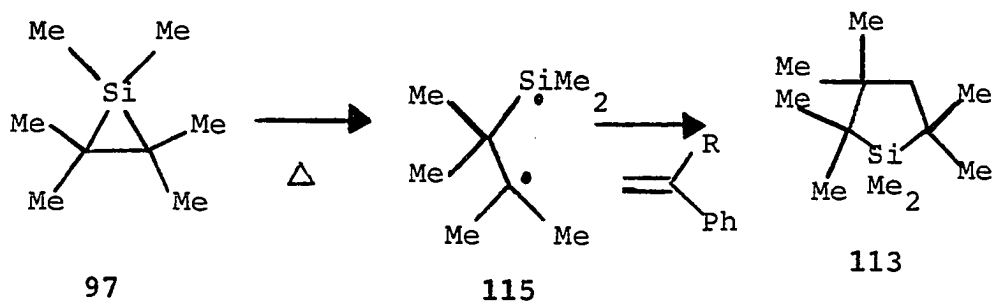


the axial position. Assuming that the bulky silyl group preferentially occupies an equatorial position, then the methanolysis of silacyclopropanes 109 must also be cis, i.e., the C-D bond is formed cis to the Si-C bond formed (Scheme 15).

These elegant experiments of Tortorelli and Jones using photolytically generated silylenes have been substantiated by Seyferth and coworkers, who found that hexamethylsilirane 97 thermally transferred dimethylsilylene 26 at less than 100°C stereospecifically to various olefins, resulting in the formation of new siliranes (72). Thermolysis of 97 in excess Z- or E-1-propenyltrimethylsilane 111 was found to afford silacyclopropanes 112 a or b which NMR analysis indicated were formed with stereospecific retention of the Z- or E-relationship of the trimethylsilyl and methyl groups.



The thermal decomposition of silacyclopropanes has been studied in less detail and remains more ambiguous. Although hexamethylsilirane 97 decomposes with apparent extrusion of dimethylsilylene 26 and in many experiments gives as sole reported products compounds indicating transfer of 26, other experiments suggest that the Si-C bond may undergo homolytic cleavage. The earliest confirmed example of this may be found in the work of Skell and Goldstein, who found that the ultimate product of the dimethylsilylene 26 addition to ethene was vinyl dimethylsilane 101; its formation may be rationalized as the result of initial Si-C bond homolysis followed by 1,2-H atom shift (Scheme 14, vide supra) (64). More suggestive is a result of Seyferth and Annarelli, who found that hexamethylsilirane 97 when thermalized in the presence of styrenes afforded not the anticipated silirane products; rather sole formation (in > 50% yields) of silacyclopentanes 113 was observed (70). Furthermore, thermolysis of spirocyclic silirane 96 did not transfer dimethylsilylene in trapping experiments using triethylsilane; only dimerization of starting material (structure 114 was suggested for the dimer, but without spectral proof) was found to occur (69). The mechanism of these processes is unproven; they may be the result of a direct reaction of the Si-C bond, or diradicals (e.g., 115)



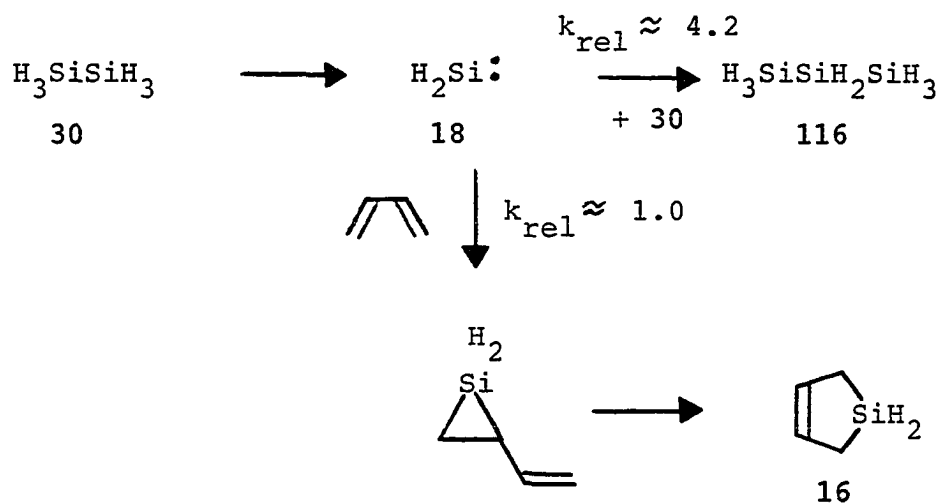
may be involved.

Seyferth and Annarelli have suggested that extrusion of dimethylsilylene from 97 may proceed via diradical 115 (70); this should be viewed in the light of the principle of microscopic reversibility and the observed stereospecific (and possibly concerted) cis addition of silylenes to olefins. If the addition of silylenes to C=C double bonds proceeds exclusively by a concerted process, then so must the reverse reaction also occur. One possibility is

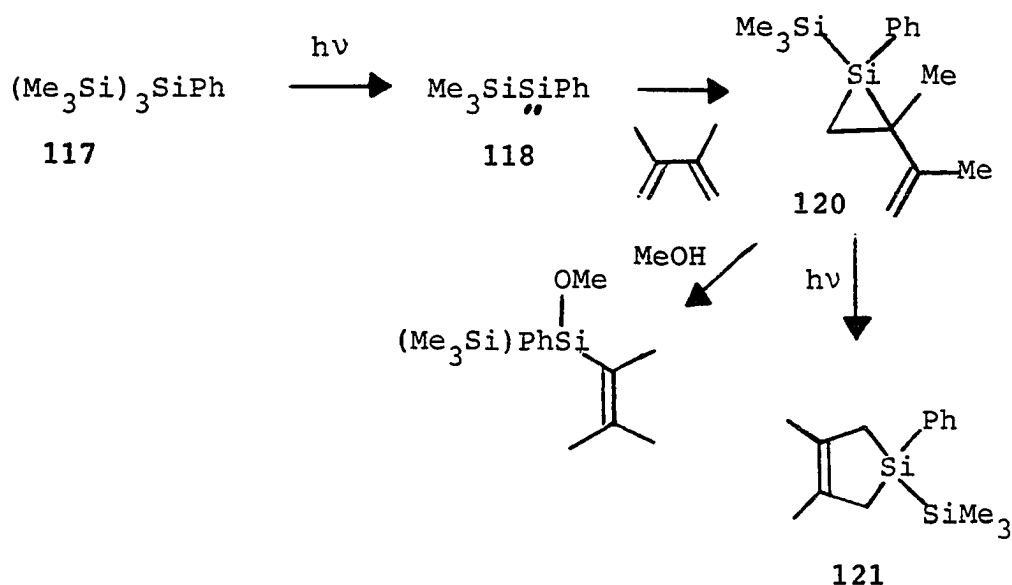
that diradical 115 is formed in the stereospecific addition of dimethylsilylene 26 to C=C double bonds, with ring closure proceeding substantially more rapidly than bond rotation in 115. However the reaction of 97 with styrenes implies the existence of a biradical which, if formed, persists in solution long enough to allow significant reaction with the styrenes (73). Clearly many details of this energy surface have yet to be elaborated both experimentally and through calculations.

A special case of silacyclopropane formation from the silylene/olefin reaction is the addition of silylenes to conjugated 1,3-dienes. The initially formed vinylsilacyclopropanes have occasionally been trapped or spectroscopically observed, although they tend to undergo facile isomerization to silacyclopentenes. Due to the thermal stability of silacyclopentenes silylenes are effectively and irreversibly trapped by 1,3-dienes at most temperatures employed, and the reaction of silylenes with conjugated dienes can be detected even in the presence of excellent silylene traps including methoxysilanes and hydridosilanes. Consequently trapping with 1,3-butadienes has become a widely employed and characteristic test for silylene intermediacy. As an example, Jenkins et al. reported that silylene 18 may be trapped by 1,3-butadiene to form sila-

cyclopent-3-ene 16; the relative rate of trisilane 116 formation via insertion of 18 into disilane 30 employed as the silylene precursor to addition to 1,3-butadiene was estimated to be ca. 4.2/1.0 (74).

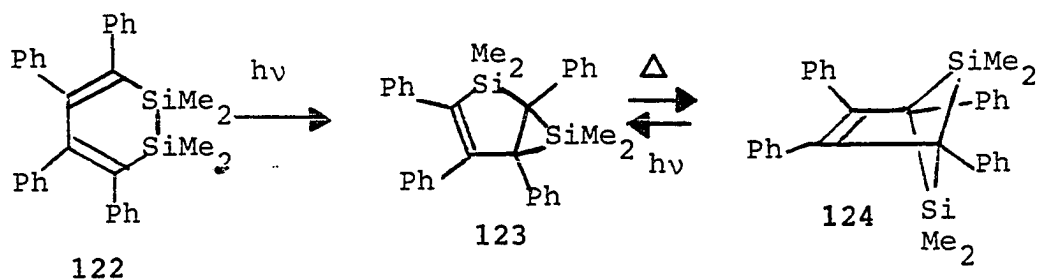


Chemical trapping of intermediate vinylsilacyclopropanes has been accomplished by Ishikawa et al., who photolyzed 2-phenylnonamethyltrisilane 117 to generate silylene 118 in the presence of 2,3-dimethyl-1,3-butadiene 119 (62). Addition of methanol resulted in the production of methoxydisilanes which indicated the intermediacy of vinylsilacyclopropane 120. Compound 120 was subject to further photolysis and formation of silacyclopent-3-ene 121.

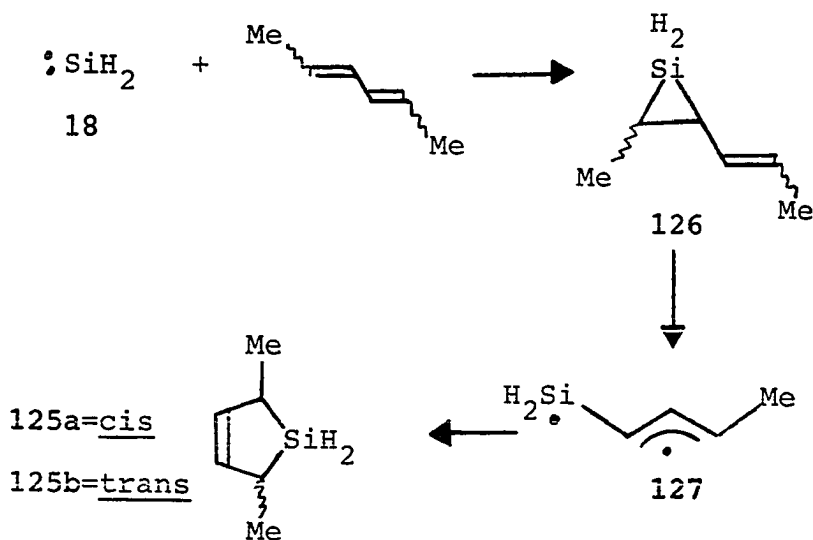


Direct spectroscopic detection of a vinylsilacyclopropane was reported by Nakadaira et al., who observed that photolysis of disilacyclohexadiene 122 afforded a stable intermediate vinylsilacyclopropane 123, observable by NMR, which thermally converted to bicyclic 124. Photolysis of 124 regenerated 123 (Scheme 16) (75).

Scheme 16



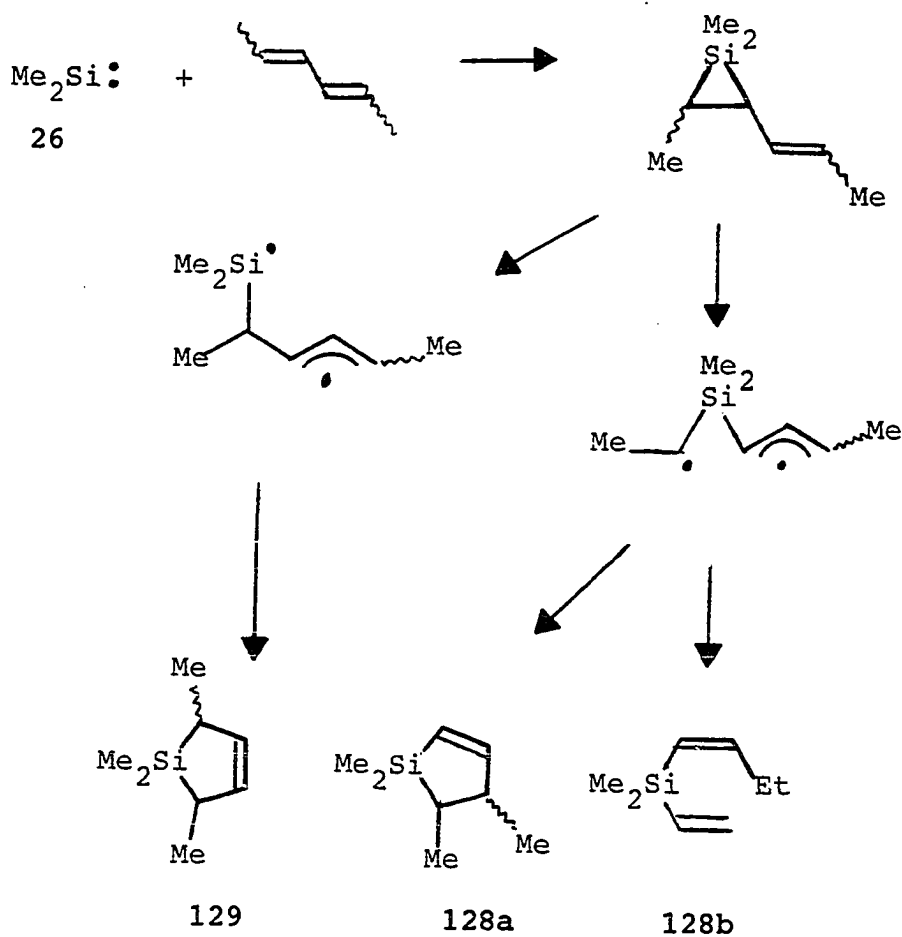
The thermal vinylsilacyclopropane rearrangement probably does not involve a concerted 1,3-Si shift. Thus Lei et al. found that the addition of silylene 18 (generated in a flow pyrolysis of disilane 30) to 2,4-hexadienes was not a stereospecific process; a 2/1 ratio of silacyclopentenes 125a-b was obtained from cis/trans 2,4-hexadiene and a 6/1 ratio was obtained from the trans/trans isomer (76). This was rationalized as the result of silylene π -addition which forms silirane 126 which undergoes Si-C bond homolysis. The resulting diradical 127 then closes to products 125.



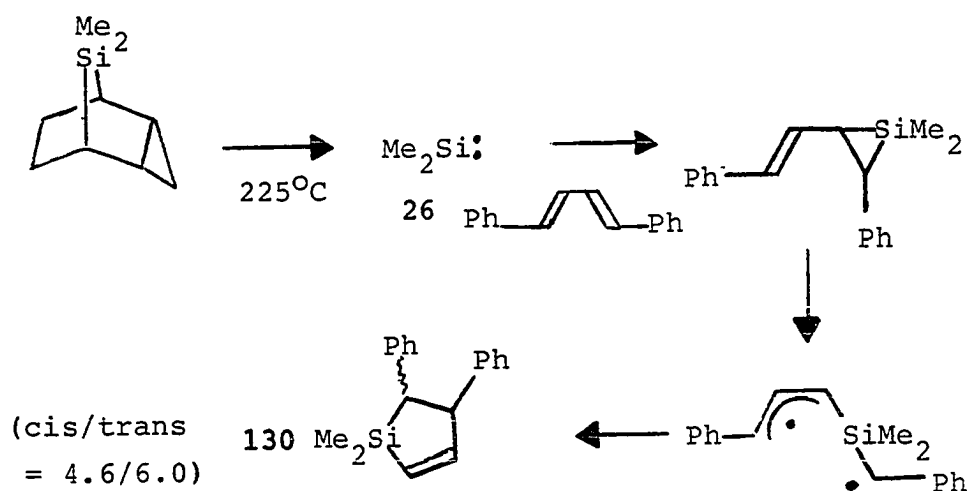
Products from C-C bond homolysis of vinylsilacyclopropanes and rearrangement have also been observed. Lei et al. found that addition of dimethylsilylene 26 to 2,4-hexadienes afforded products 128a-b, rationalized as the

result of vinylsilacyclopropane C-C bond cleavage, in addition to silacyclopent-3-ene 129 resulting from Si-C bond cleavage (76). The ratio of products 128/129 was 4/1 when the diene employed was trans/trans 2,4-hexadiene, and 14/1 when cis/trans isomer was used (Scheme 17).

Scheme 17



Cyclic 1,3-dienes acting as silylene traps afford similar results. For example, in the case of cyclopentadienes, the intermediate silacyclopropanes undergo virtually exclusive C-C bond scission, forming silacyclohexadienes (77). Presumably the relief of ring strain provides a driving force for ring expansion. Cleavage of the C-C bond can also be exclusive where the 1,3-diene is substituted so as to stabilize the resulting diradical. Sakurai and coworkers found that the addition of dimethylsilylene 26 to 1,4-diphenyl-1,3-butadiene afforded only 1,1-dimethyl-4,5-diphenyl-1-silacyclopent-2-ene 130 (78).



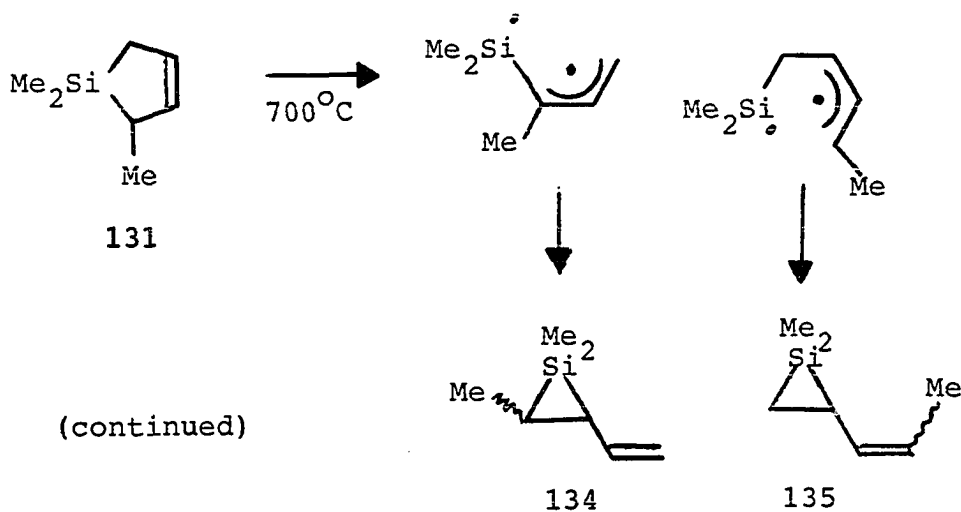
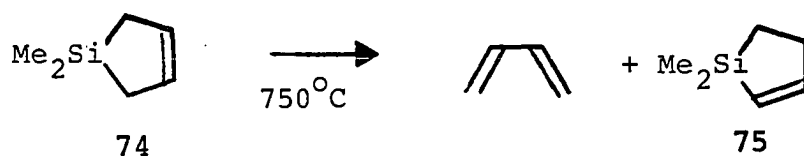
Homolysis of the C-C bond also provides a rationale for the observation that at higher temperatures both silacyclopent-2-ene and silacyclopent-3-enes are observed from trapping of silylenes with 1,3-butadiene (see for example,

Conlin and Wood [79]). At 750°C Lei and Gaspar found that 1,1-dimethyl-1-silacyclopent-3-ene 74 was converted to the isomeric 1,1-dimethylsilacyclopent-2-ene 75 in 16% yield (Scheme 18) (80). Extrusion of dimethylsilylene also occurred and 1,3-butadiene was obtained in 53% yield. The unsymmetrical 1,1,2-trimethylsilacyclopent-3-ene 131, in addition to dimethylsilylene extrusion, also formed, upon pyrolysis, products 132 and 133 which demand a formal C-C bond shift in the presumed silacyclopropane intermediates 134 and 135, perhaps through diradicals 136 and 137. The product 138 of an ene-reaction of vinylsilacyclopropane 134 was also found. By itself, this reaction does not demand the involvement of the diradical intermediates suggested by Gaspar and shown below (Scheme 18), but it is demanded by the principle of microscopic reversibility if it is true, as is believed (vide supra), that the rearrangement of the corresponding vinylsilacyclopropanes to the same product silacyclopentenes is a stepwise process through biradical intermediates.

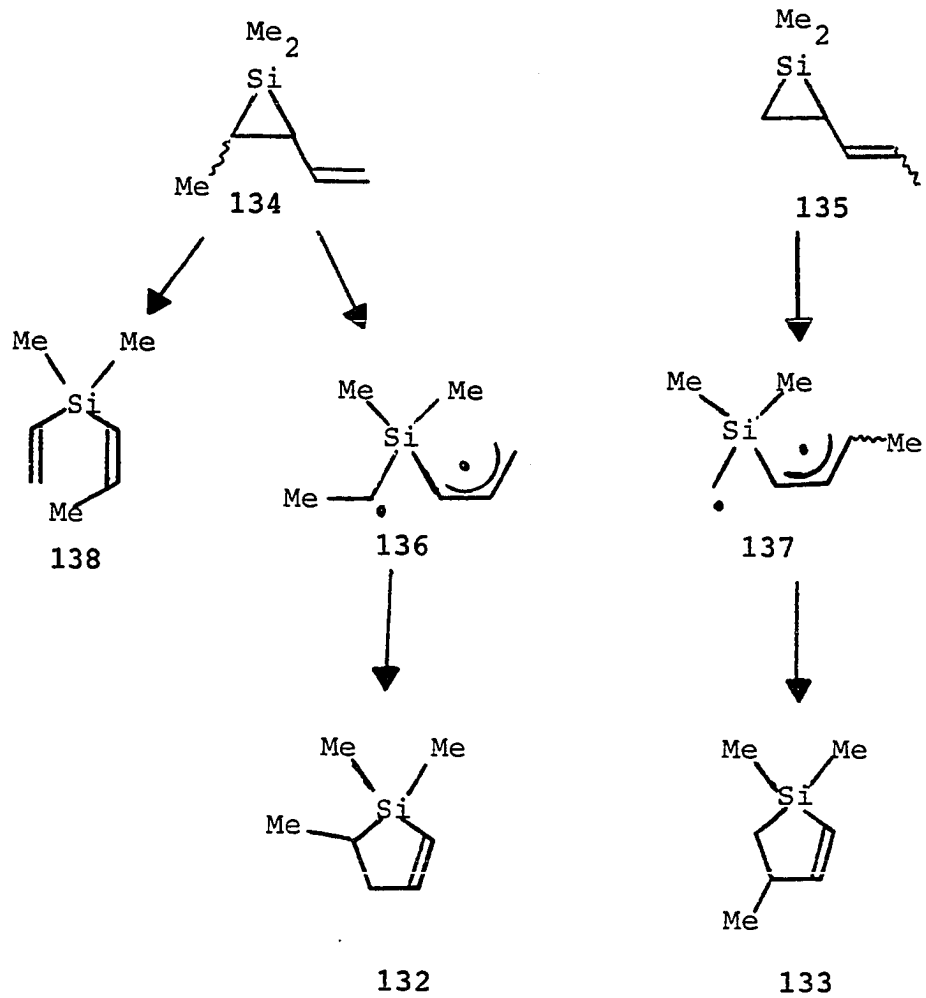
In summary, it is clear that despite the difficulty in their synthesis and isolation, silacyclopropanes are viable intermediates, the existence of which is supported by an overwhelming amount of evidence. Silylenes add to C=C double bonds stereospecifically in what is undoubtedly a

cis and possibly a concerted manner. By microscopic reversibility then, silacyclopropanes may extrude silylenes by a concerted reductive elimination. Silacyclopropanes also undergo competitive Si-C and C-C bond homolysis, and although all the factors which control the relative rates of silylene extrusion, and Si-C or C-C bond homolysis are not clear, such factors as ring strain or incorporation of stabilizing substituents at the ring carbons are clearly important.

Scheme 18



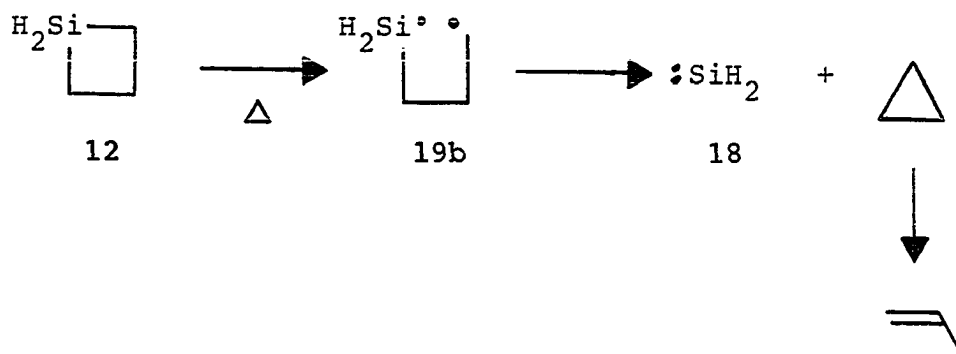
Scheme 18 (continued)



RESULTS AND DISCUSSION

Pyrolysis of 1-Hydridosilacyclobutanes

As discussed in the Historical section the pyrolysis of silacyclobutanes is a generally clean reaction with β -C-C bond homolysis the predominant initial decomposition step leading to silene and ethene formation. However the decomposition of the parent system, silacyclobutane 12 is anomalous in that propene is also formed in a competitive process. To explain this Conlin and Gill proposed initial Si-C bond breakage and decomposition of the resulting di-radical 19b to cyclopropane and silylene 18 (Scheme 19) (12). This was favored on thermodynamic grounds over a chelotropic extrusion of silylene 18 and cyclopropane.

Scheme 19

In contradiction to Conlin and Gill's report of cyclopropane formation in the silacyclobutane 12 pyrolysis, Davidson et al. have found that cyclopropane is not formed in the silacyclobutane pyrolysis (14). This was subsequently confirmed by Conlin and Kwak for the pyrolysis of 1-methylsilacyclobutane, where the formation of propene, but not cyclopropane, was reported (81). The formation only of propene, under conditions where cyclopropane is stable, casts doubt on the validity of the proposed mechanism of Scheme 19. In addition to this, the rationalization of Conlin and Gill seems unreasonable in the light of known substituent effects on Si-C bond dissociation energies, which indicate that hydrogen substitution on silicon should have an insufficient effect to explain why silylene 18 and propene should be eliminated from 12 when propene and dimethylsilylene 26 are not formed from dimethylsilacyclobutane 1. Based upon this, an alternative mechanism was suggested to account for the unique involvement of the silyl hydride in this reaction: α -elimination of a methyl group from silacyclobutane 12 to form propylsilylene 20, which subsequently decays to silylene 18 and propene (Scheme 20). This suggestion has precedent in the literature, where elimination of methane from silanes to form silylenes is a known process (34). The decomposition of

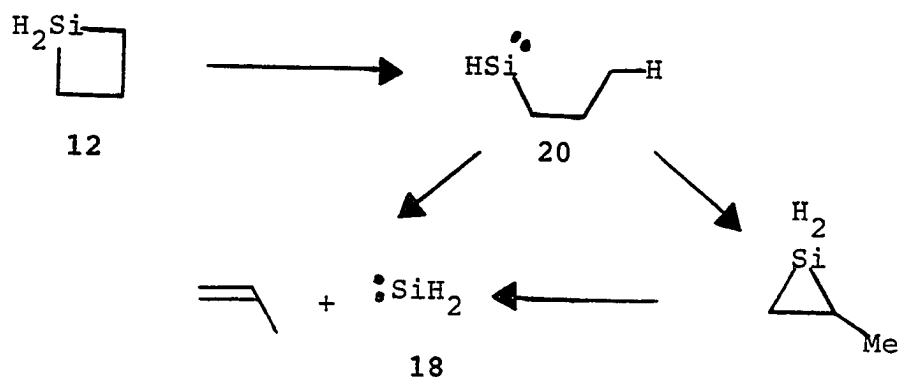
alkyl silylenes to alkenes and silylenes is also a known process, usually rationalized as proceeding through sila-cyclopropane intermediates (47, 49, 50), although a direct, concerted decomposition has also been suggested (52, 54).

Investigation of the kinetics of silacyclobutane 12 decomposition at the University of Leicester, England, by Davidson et al. determined the Arrhenius parameters for propene formation, with the results $\log A = 14.4$, $E_a = 57.8$ kcal/mol (14). These numbers appear to be in accord with the proposed mechanism of Scheme 20 if it is assumed that most of the silacyclobutane ring strain (values from 16.8 to 25.9 kcal/mol have been found [53]) is released in the transition state of the initial, rate determining α -elimination. With this assumption, a reduction in the activation energy by 15 kcal/mol relative to dimethylsilane (which eliminates methane with an activation energy of 73 kcal/mol, Table 1), a reasonable analogy to silacyclobutane, is not unexpected.

If the mechanism presented in Scheme 20 is valid, then pyrolysis of 1-deuterated silacyclobutanes would provide an appropriate test of the mechanism.

Silacyclobutane 12 and the dideuterated analogue 1,1-dideuterio-1-silacyclobutane 12-d₂ were easily prepared by the method of Iaane, reduction of 1,1-dichloro-1-sila-

Scheme 20



cyclobutane with LiAlH_4 or LiAlD_4 (82). Compound 12- d_2 was prepared in this fashion with quantitative deuteration, with no silyl hydride observed by ^1H NMR.

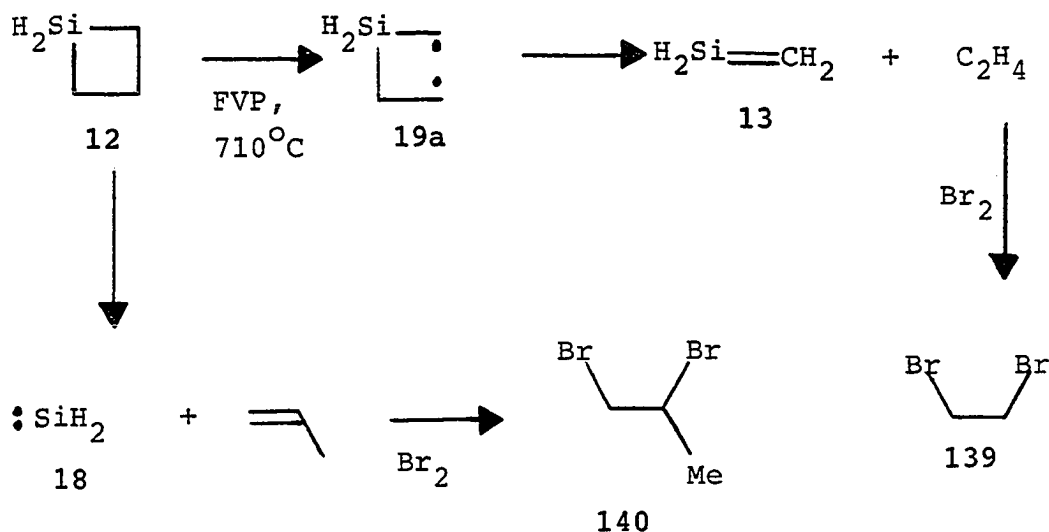
FVP of undeuterated 12 at 710°C resulted in formation of an effervescent pyrolysate, with most of the mass recovered boiling off upon warming to room temperature at 1 atm. With this procedure, only a 15% ultimate mass recovery was obtained, containing mostly recovered 12 (8% GLC yield).

A convenient method was devised for analyzing the volatile gases formed in this and similar pyrolyses. The FVP was performed and the products were trapped in the usual fashion in a liquid nitrogen cooled trap at -196°C . A second trap consisting of a 50 or 100 mL gas collection flask equipped with a greaseless vacuum stopcock was placed between the initial trap and the vacuum source. After

pyrolysis, the two traps were isolated from the hot zone and the vacuum source, and the products were warmed to room temperature under high vacuum, and then condensed into the gas bulb at -196°C . Gases formed and collected in this fashion could be analyzed directly by sampling through a septum. The sampled gases were chromatographically analyzable on either a 6' Unibeads 2S column or a 30' 23% SP-1700 on Chromosorb-P-AW column. Analysis of the samples by MS could be obtained using the Unibeads column attached to a Finnegan 4023 Gas Chromatograph-Mass Spectrometer (GCMS). Alternatively, bromine could be placed in the gas bulb prior to gas collection and the volatile alkenes determined by analysis of the dibromoalkanes formed.

In this fashion, when the pyrolysis of 12 was repeated and the gases were collected and brominated, 1,2-dibromoethane 139 and 1,2-dibromopropane 140 were found in 41-47% and 11-13% yields, respectively. This indicates that ca. 80% of the decomposition proceeds via the usual process of silacyclobutane decomposition, initial β -C-C bond homolysis forming diradical 19a which decays to silene and ethene. The propene pathway accounts for ca. 20% of the decomposition (Scheme 21).

Scheme 21



FVP of 12-d₂ at 710°C afforded an effervescent pyrolystate upon warming to room temperature at 1 atm pressure; the pyrolystate after gas liberation (38-43% mass recovery in two runs) consisted predominantly of unreacted 12-d₂. Isolation of the recovered starting material by preparative GLC and analysis by ¹H NMR and ²H NMR showed no scrambling of deuterium onto the carbons of the silacyclobutane ring. A small but variable silyl hydride formation was detected by ¹H NMR, amounting to 0.14-0.16H for two runs (loss of deuterium with a corresponding 7-8% silyl hydride formation).

When the volatile gases formed were collected and ana-

lyzed by GC and GCMS, ethene and propene were found in approximate relative amounts of 86 parts and 14 parts respectively. The mass spectra indicated minimal deuteration of the ethene. The propene was much more highly deuterated.

Table 2 presents the results of the GCMS analysis of the propene and ethene formed from the pyrolysis of $12-d_2$. Run at the same time and conditions were samples of authentic, undeuterated ethene and propene. The per cent composition of d_0 , d_1 and d_2 species were calculated by the method of Biemann (83). Using this method, the measured relative intensities of the undeuterated ethene and propene M , $M+1$, and $M+2$ peaks were used to calculate corrected ion intensities for the ethene and propene mass spectra, which represent the contributions to these ion intensities by the d_0 , d_1 and d_2 species. The mol % d_0 , d_1 or d_2 species is easily calculated as the percent of the corrected ion intensity of the M , $M+1$ or $M+2$ species to the total corrected ion intensity.

As an example of the use of this method, consider the deuterated ethene in Table 2. The $M+$ ion intensity for ethene from $12-d_2$ was 100.00 (arbitrary units); the measured $M+1$ intensity was 15.87. Since there is no $M-1$ peak in the reference undeuterated ethene, the value of

Table 2. Deuterium incorporation in ethylene and propylene from FVP of 12-d₂

Compound	Ion	Ion Intensity ^{a,b}	Corrected intensity ^c	Mol % deuterated species ^c
ethene (M = 28)	M-2	2.76	--	--
	M-1	1.38	--	--
	M	100.00	100.00	86 (d ₀)
	M+1	15.87	13.63	12 (d ₁)
	M+2	3.12	2.74	2 (d ₂)
propene (M = 42)	M-2	3.89	--	--
	M-1	8.06	--	--
	M	48.06	30 ^d	19 (d ₀)
	M+1	100.00	99 ^d	62 (d ₁)
	M+2	34.72	30 ^d	19 (d ₂)
	M+3	4.72	--	--

^a18 eV scan obtained on Finnegan GC-MS with 6' Unibeads 2S column.

^bMeasured ion intensity of deuterated sample propene and ethene.

^cCalculated by the method of Biemann (83). Reference spectra: ethene, M-2 = 2.41, M-1 = 0.00, M = 100.00, M+1 = 2.24, M+2 = 0.02; propene, M-2 = 3.98, M-1 = 17.60, M = 100.00, M+1 = 4.52, M+2 = 0.08.

^dEstimated as described in text.

100.00 must be due exclusively to d₀ ethene. The M+1 peak from undeuterated ethene is 2.24 units, thus d₀ contributes 2.24 units to the measured M+1 peak in the deuterated sample, and d₁ must then contribute 15.87 - 2.24 = 13.63 units, which is the corrected ion intensity for the M+1

peak. In the same fashion, the contributions of d_0 and d_1 ethene are subtracted from the M+2 peak to obtain the corrected M+2 intensity, 2.74. The per cent d_0 , d_1 and d_2 are found to be $100.00/116.37 = 86\%$, $13.63/116.37 = 12\%$, and $2.74/116.37 = 2\%$.

This calculation works well for ethene in this example because there is no M-1 peak in the reference, undeuterated ethene. This is not the case for propene, which shows a sizable (17.60 relative %) M-1 peak, and therefore the measured M+ ion cannot be taken as a straightforward quantification of the amount of d_0 propene in the sample. Since the major species in the deuterated sample is clearly d_1 propene, the M+ ion intensity includes a contribution from d_1 propene. Since there are five hydrogens in d_1 propene and only one deuterium, an approximate estimate of this contribution may be made by assuming that H loss will significantly exceed D loss and simply taking the relative M-1 ion intensity from undeuterated propene as the contribution of d_1 to M+. This gives $30 = 48 - 18$ as a rough estimate of the amount of d_0 species present in the deuterated sample. Continuing the calculation in the normal fashion gives an estimate of 19% d_0 , 62% d_1 , and 19% d_2 as the composition of the sample.

Regardless of the uncertainty in the exact numbers, it

is clear that d_1 propene is the major species of propene formed in the pyrolysis of 12- d_2 . This experiment constituted the first experimental test of the mechanism proposed in Scheme 20 and the result is consistent with initial formation of propylsilylene 20 by α -elimination and hydrogen (or deuterium) transfer, and inconsistent with either a direct chelotropic extrusion of silylene 18 or the diradical mechanism favored by Conlin and Gill (12) (Scheme 19), both of which processes would predict the formation of mostly d_0 propene.

In order to confirm the analysis of deuterated propene in the product mixture, and to provide a method of determining the location of deuterium in the propene formed from 12- d_2 , the pyrolysis was repeated and the product gases trapped in bromine. The 1,2-dibromoethane 139 (55%) and 1,2-dibromopropane 140 (10%) formed were analyzed by mass spectral, ^1H NMR, and ^2H NMR methods. The experiment was repeated twice (Runs 1 and 2). Yield and mass spectral data are presented in Table 3, and the data for integration of the ^2H NMR of the dibromopropane 140 spectra are presented in Table 4. The ^2H NMR spectrum of the dibromopropane 140 from Run 1 is reproduced in Fig. 1. Runs 1 and 2 in Table 3 correspond to Runs 1 and 2 in Table 4.

The mass spectral results (Table 3) for the brominated

olefins are in approximate agreement with the results estimated by examining the gases directly. The dibromoethane 139 formed shows somewhat more d_1 species (14-21%, average 18%) than found previously for ethene (12%). Nevertheless, agreement is found in that d_0 is by a large measure the major species present in both experiments. Similarly, d_1 dibromopropane 140 is in both cases found to be the major species detected (53-62%, average 58%) vs. 62% from the direct analysis of propene.

There is a significant variation in the amount of d_2 dibromopropane 140 in the two runs (10% and 25%, Table 3), although the average, 18% d_2 , is close to the estimate found previously for the d_2 propene (19%) by direct GC-MS examination of the gases formed. The cause for this variance is not known, although one factor may be that the method of calculation employed tends to be increasingly less accurate for d_n species as n increases (83). In addition, different instruments were employed for each run. Run 1 was analyzed by GC-MS (Finnegan Model 4023 GC-MS), integrating the ion intensities over the entire chromatographic peak area, and Run 2 was analyzed as neat samples (isolated by preparative GLC) on a Kratos MS-50, which became available during the course of this research.

Table 3. Yield and percent deuterium incorporation for 1,2-dibromoethane 139 and 1,2-dibromopropane 140 formed from flash-vacuum pyrolysate of 1,2-d₂

Run ^a	Compound	Yield (%)	Ion	Ion Intensity ^b	Corrected intensity ^c	Mol % deuterated species ^c
1	139 (M = 186)	-- ^d	M-1	1.50	--	--
			M	51.27	51.27	78 (d0)
			M+1	16.53	13.78	21 (d1)
			M+2	100.00	1.08	1 (d2)
			M+3	27.09	--	--
			M+4	53.00	--	--
			M+5	13.65	--	--
	M+6	3.04	--	--		
	140 (M = 200)	-- ^d	M-1	--	--	--
			M	1.18	1.18	19 (d0)
			M+1	3.33	3.32	53 (d1)
			M+2	3.89	1.55	25 (d2)
			M+3	6.72	0.16	3 (d3)
			M+4	4.15	0.00	0
M+5			3.39	--	--	
M+6	1.39	--	--			

^aRun 1, Finnegan 4023 GC-MS, 20 eV; run 2, Kratos MS-50 Mass Spectrometer, neat samples, 26 eV.

^bMeasured ion intensity of deuterated samples.

^cCalculated by the method of Biemann (83). The following reference spectra were used. Run 1: undeuterated 139, M-1 1.67, M 52.22, M+1 2.80, M+2 100.00, M+3 1.85, M+4 48.27, M+5 0.97; undeuterated 140, M-1 0.05, M 6.25, M+1 0.08, M+2 12.20, M+3 0.38, M+4 5.68, M+5 0.11. Run 2: undeuterated 139, M-1 5, M 265, M+1 15, M+2 515, M+3 15, M+4 251, M+5 6; undeuterated 140, M-2 16, M-1 3, M 203, M+1 10, M+2 394, M+3 15, M+4 191, M+5 7.

^dYield not obtained.

Table 3. (continued)

Run	Compound	Yield (%)	Ion	Ion intensity	Corrected intensity	Mol % deuterated species
2	139 (M = 186)	55	M-1	4	--	--
			M	169	169	81 (d0)
			M+1	40	29	14 (d1)
			M+2	333	3	1 (d2)
			M+3	74	7	3 (d3)
			M+4	167	--	--
			M+5	36	--	--
	140 (M = 200)	10	M-2	16	--	--
			M-1	3	--	--
			M	43 ^e	43	26 (d0)
			M+1	105	103	62 (d1)
			M+2	105	17	10 (d2)
			M+3	206	2	1 (d3)
			M+4	100	--	--
M+5	103	--	--			
M+6	38	--	--			

^e Measured mass m/e 199.88362 (C₃H₆⁷⁹Br₂).

Isolation of the dibromopropane 140 from 12-d₂ by preparative GLC gave a sample, the ²H NMR of which clearly shows that the deuterium incorporated is scrambled throughout the molecule. The integrated intensities for the deuterium signals from Runs 1 and 2 are presented in Table 4. From this data it is apparent that the deuterium in the 140 is ca. 21% incorporated at C₁, 17% at C₂, and 63% at C₃, where the carbons are numbered according to the usual IUPAC

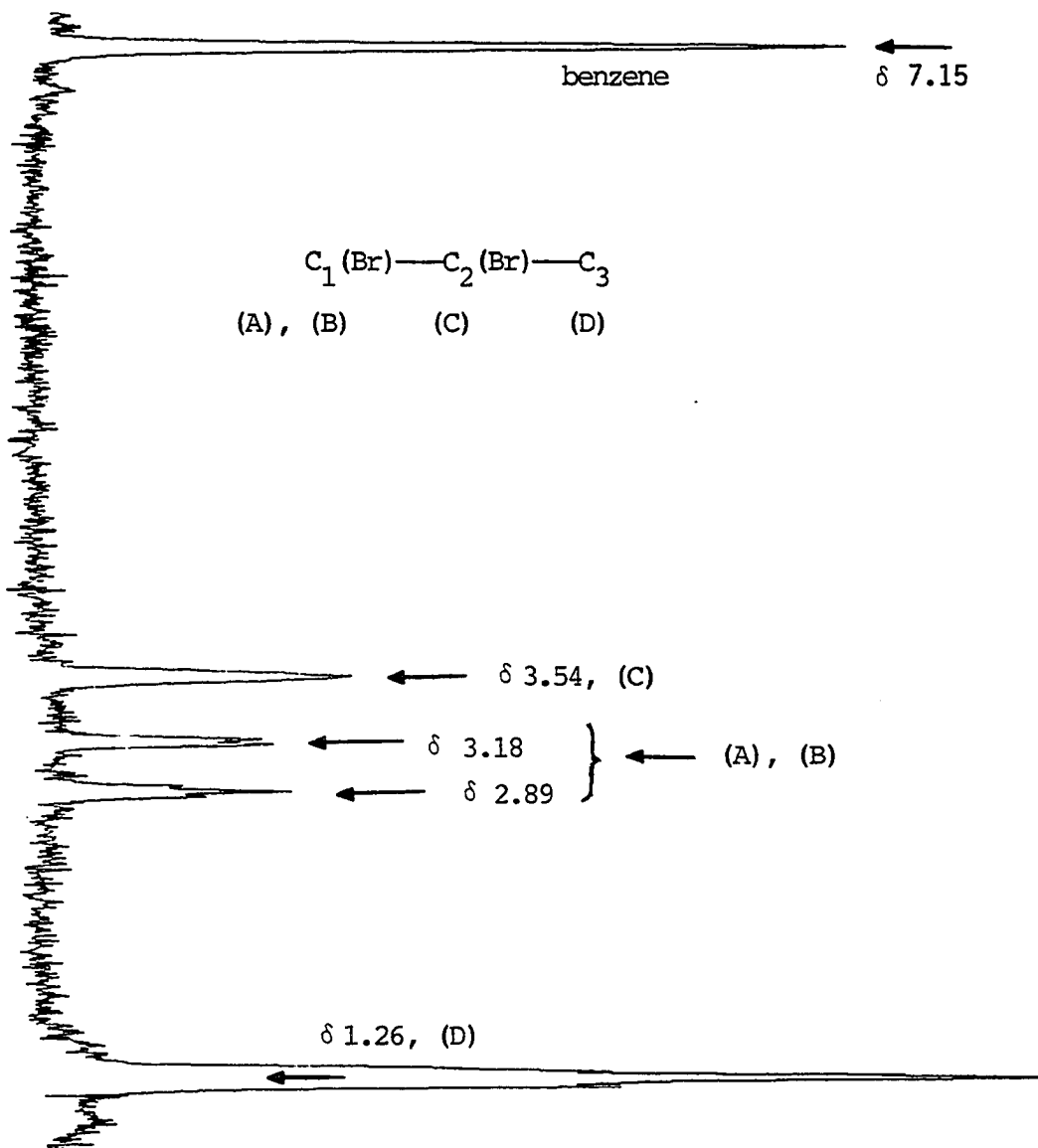


Figure 1. ^2H NMR of 1,2-dibromopropane 140 from bromination of the pyrolysis products from the FVP of 12-d_2 (benzene solution, 46 MHz; insert indicates assignment of the resonances for 140; the peak at δ 7.15 is natural abundance deuterated benzene)

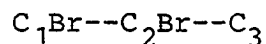
Table 4. Deuterium distribution in 1,2-dibromopropane 140 from pyrolysis of 1,2-d₂

Run ^a	Shift, ppm, (δ scale) ^b	Carbon ^c	Relative intensity ^d
1	2.89	1	11.4
	3.18	1	10.7
	3.51	2	17.1
	1.26	3	62.1
2	2.88	1	10.9
	3.17	1	9.5
	3.52	2	16.8
	1.25	3	62.9

^a²H NMR spectra determined on a Bruker WM-300 spectrometer (46 MHz) in benzene solution.

^bChemical shifts referenced to natural abundance deuterium in benzene solvent.

^cSignal assigned for deuterium substituted on C₁, C₂, or C₃. The two sites on C₁ are diastereotopic. The numbering is according to the scheme:



^dRelative signal intensity normalized to 100 total.

nomenclature. Completely random distribution of the deuterium predicts 34% incorporation at C₁, 17% at C₂, and 50% at C₃. Hence there is some favoring of incorporation of deuterium at C₂ (corresponding to the methine position in

the propene formed) and at C₃ (the allylic position in propene).

To sum up the results from FVP of silacyclobutane 12 and 12-d₂, pyrolysis of 12 at 710°C afforded as products propene and ethene in an approximately 1/4 ratio, with nearly complete decomposition and 8% starting material recovery. The use of dideuterated 12-d₂ afforded labelled ethene and propene (in a 1.0/5.5 ratio determined for one run from the yields of dibromides formed upon bromination). The ethene and propene were both labelled, average values being for the ethene 82% d₀ and 16% d₁, and for the propene, 21% d₀, 59% d₁, and 18% d₂. The propene was determined to have the deuterium label positionally scrambled, although incorporation at the allylic position was somewhat favored. Recovery of the starting material showed the pyrolysis proceeded with ca. 7-8% deuterium exchange in the labelled silacyclobutane via silyl hydride formation; no incorporation of deuterium onto the carbons of the silacyclobutane ring was found by ²H NMR.

To test the effect of a single deuterium substituted on silicon 1-methyl-1-deuterio-1-silacyclobutane 90-d₁ (prepared in an analogous fashion to 12-d₂ by LiAlD₄ reduction of 1-chloro-1-methyl-1-silacyclobutane) was pyrolyzed at 710°C. Ethene and propene were both formed,

although the relative amount of propene formed was significantly less than in the case of 12 or 12-d₂. Analysis of the gases by GC-MS indicated that both the ethene and propene were deuterated, deuteration of the ethene being minimal (< 10% d₁), while most of the propene was deuterated (> 50% d₁). Unfortunately the propene peak was significantly contaminated by impurities and reliable numbers for deuterium incorporation could not be directly obtained.

However bromination of the products from the pyrolysis provided the needed information. Dibromoethane 139 (29%) and dibromopropane 140 (1%) were both detected in the product mixture. The mass spectral results and calculated deuterium incorporation are presented in Table 5. These results show that there is very little d₁ dibromoethane 139 (6%), and the remainder is exclusively d₀. The dibromopropane 140 is exclusively d₁ (68%) and d₀ (32%) with no d₂ detectable.

²H NMR of the dibromopropane from 90-d₁ (Fig. 2) showed very little scrambling. A single sizable peak was found at δ 1.26, the chemical shift of the methyl resonance (benzene solution) in 140. Small peaks may be present at ca. δ 3.0, 3.3, and 3.6 which correspond to the expected positions of the other resonances in the NMR of 140, however, this is uncertain due to the fact that only a few

Table 5. Percent deuterium incorporation in 1,2-dibromoethane 139 and 1,2-dibromopropane 140 from flash-vacuum pyrolysate of 90-d₁

Compound	Ion	Ion intensity ^a	Corrected intensity ^b	Mol % deuterated species ^b
139 ^c (M = 186)	M-2	7	--	--
	M-1	3	--	--
	M	147	147	94 (d0)
	M+1	16	10	6 (d1)
	M+2	278	0	0 (d2)
	M+3	27	9	--
	M+4	127	--	--
140 ^d (M = 200)	M-2	1	--	--
	M-1	1	--	--
	M	10	10	32 (d0)
	M+1	22	21	68 (d1)
	M+2	20	0	0 (d2)
	M+3	41	--	--
	M+4	12	--	--
	M+5	20	--	--
M+6	2	--	--	

^aMeasured intensity determined on a Kratos MS-50 Mass Spectrometer, neat samples.

^bCalculated by the method of Biemann (83) using the following reference spectra determined for undeuterated 139 and 140: 139, M-1 1, M 171, M+1 7, M+2 330, M+3 9, M+4 160; 140, M-1 0, M 35, M+1 2, M+2 69, M+3 2, M+4 33, M+5 1.

^c21 eV scan.

^d25 eV scan.

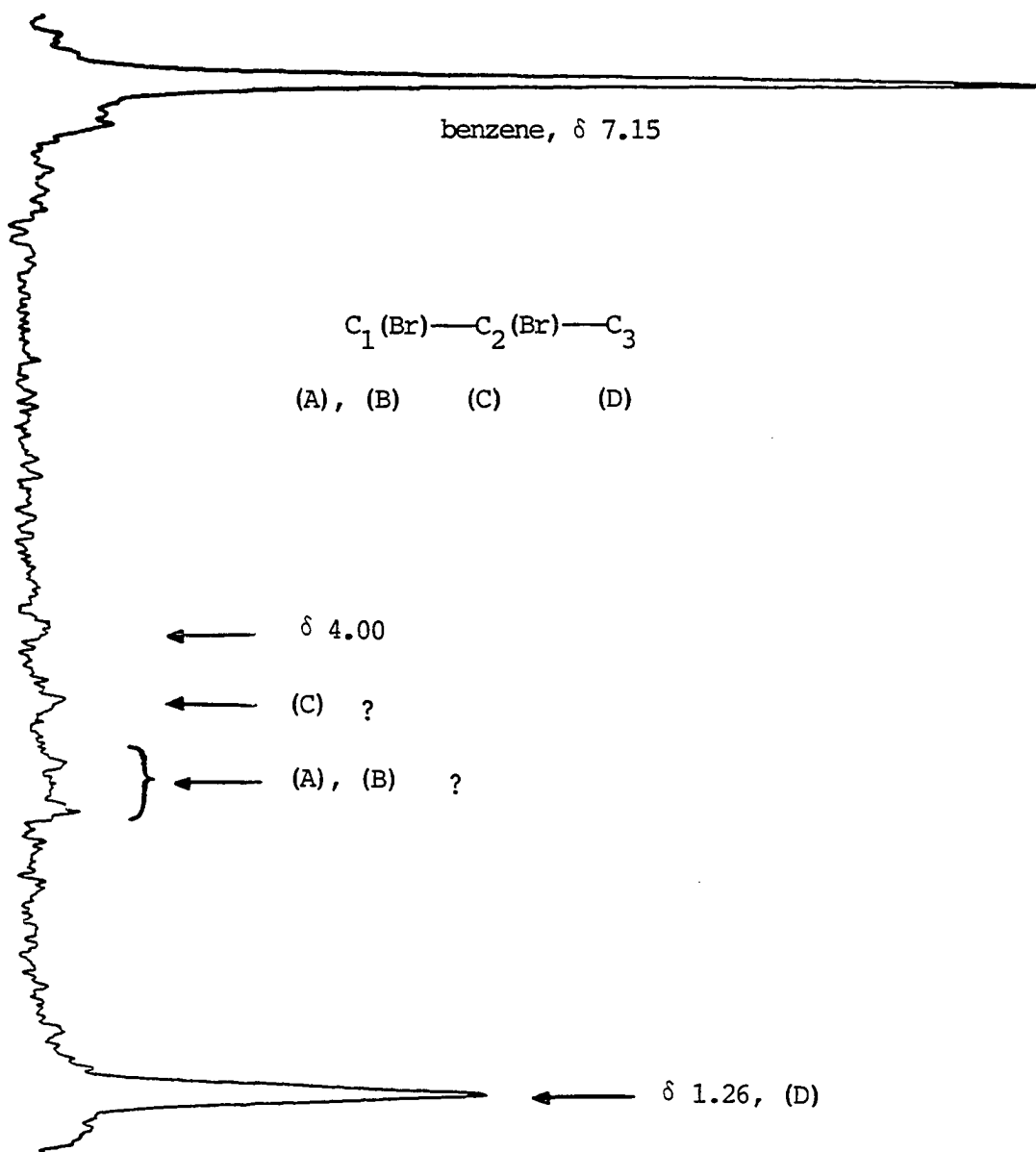
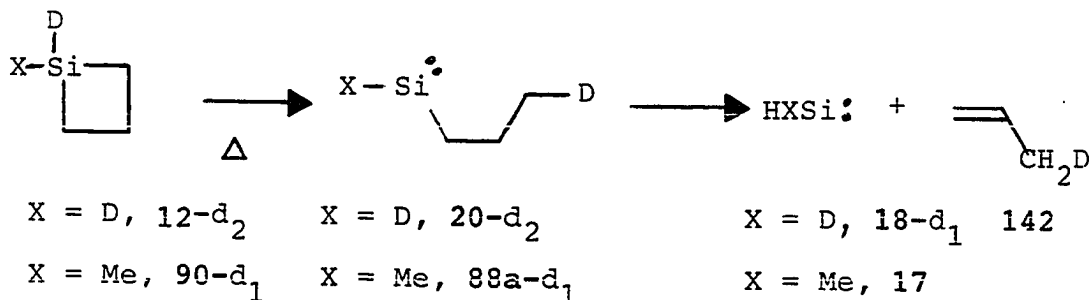


Figure 2. ^2H NMR of 1,2-dibromopropane 140 from bromination of the flash-vacuum pyrolysate of 90- d_1 (benzene solvent, 46 MHz; insert shows assignment of resonances of 140; the peak at δ 7.15 is natural abundance deuterated benzene)

milligrams of sample could be isolated for spectral analysis due to the low yield of propene formed, resulting in a poor signal to noise ratio.

Thus the only species of deuteriopropene detected in the pyrolysis of 90-d₁ is 3-deuteriopropene 142. This is consistent with the mechanism of Scheme 22, where initial deuterium transfer should form propylsilylenes 20 and 88a initially deuterated in the C₃ position. In the absence of complete label scrambling enhanced incorporation of deuterium onto the allylic position of the propene formed would be expected, and this has been found to be the case for both 12-d₂ and 90-d₁.

Scheme 22



As a control experiment, 3-deuteriopropene 142 was prepared in 27% yield by quenching allyl Grignard reagent with D₂O. When the propene 142 evolved was bubbled through liquid bromine, 1,2-dibromo-3-deuteriopropene (35% yield)

140-d₁ was formed with 96% incorporation of a single deuterium label, the remainder being composed of undeuterated species. When the 142 thus prepared was pyrolyzed at 720°C and the products were brominated, the 140 obtained was 93% mono- and 7% nondeuterated. There was no scrambling of the label position detectable.

If the incorporation of deuterium into the propene evolved from 1-deuterio-1-silacyclobutanes is due exclusively to the mechanisms outlined in Schemes 20 and 22 then silylene 18 formed in the decomposition of 12-d₂ should be deuterated in a fashion complimentary to that observed for the propene. This question was addressed by copyrolyzing 12-d₂ with 2,3-dimethyl-1,3-butadiene 119. Information about silylene 18 could thus be gained by consideration of the trapping adduct formed.

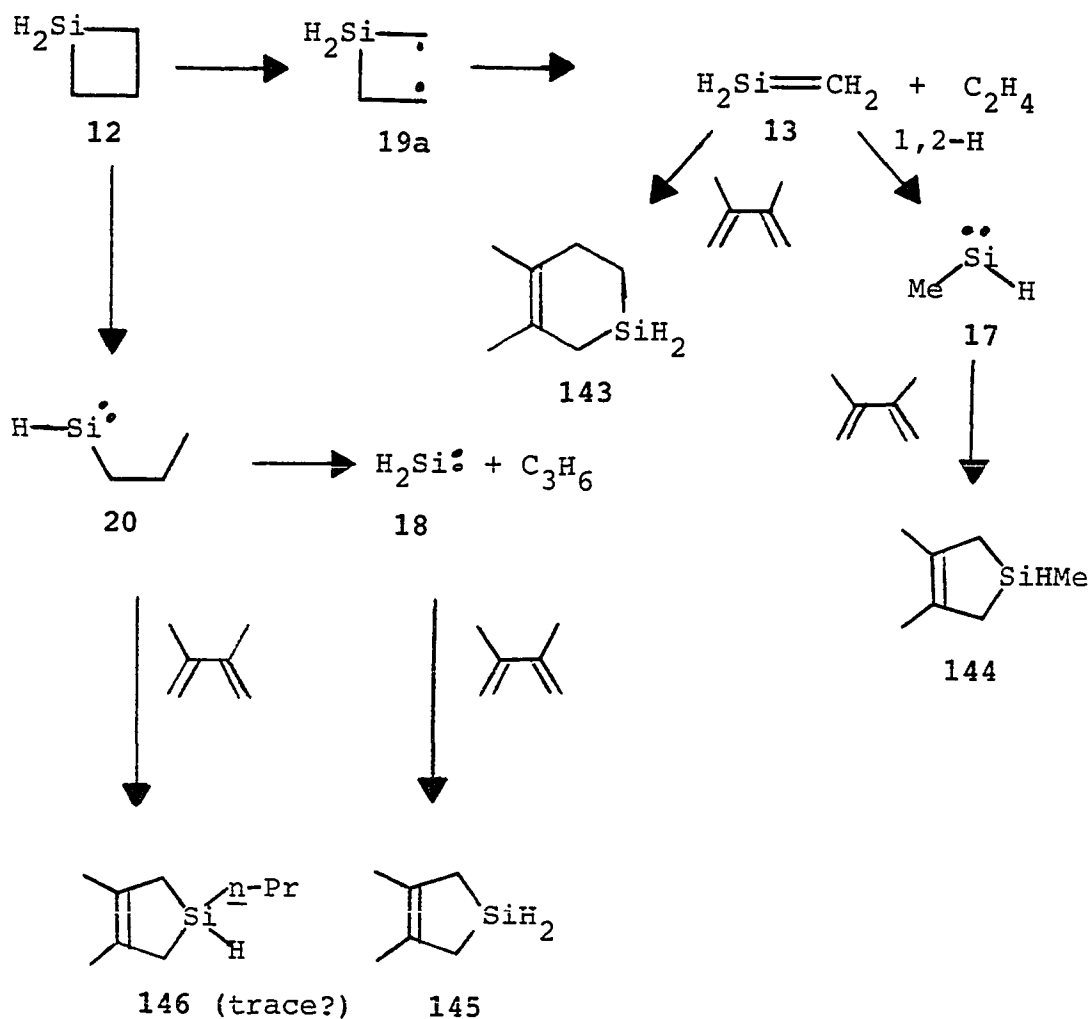
Undeuterated 12 was first copyrolyzed with 119 to establish the identities and characterize the products formed in the pyrolysis. Compound 12 was copyrolyzed with a 4- to 6-fold molar excess of 2,3-dimethyl-1,3-butadiene 119 in a nitrogen flow. A total of three runs were performed over the temperature range 520°C to 570°C. The major products were identified by their spectral characteristics as 3,4-dimethyl-1-silacyclohex-3-ene 143, 1,3,4-trimethyl-1-silacyclopent-3-ene 144, and 3,4-dimethyl-1-

silacyclopent-3-ene 145 (Scheme 23). The yields obtained for the various products are included in Table 6. The identities of products 144 and 145 were confirmed by independent synthesis. It was of interest to see whether any propylsilylene 20 could be trapped in this experiment. A careful search revealed only a trace of a compound whose GCMS matched that of an independently synthesized sample of 1-n-propyl-3,4-dimethyl-1-silacyclopent-3-ene 146, which would be the trapping adduct of 20 and 119. Its formation in at most trace amounts is not particularly surprising since other work with alkylsilylenes (vide infra) has generally found that under these conditions alkyl silylenes decompose to alkenes and smaller silylenes more rapidly than they undergo trapping reactions with butadienes. Since the propene-forming path in the pyrolysis of 12 makes up only ca. 20% of the decomposition, it is reasonable to anticipate trapping of 20 in only trace amounts.

Compound 12-d₂ was copyrolyzed with 119 under conditions comparable to those already described for undeuterated 12. The major silicon-containing products were deuterated analogues of 143-145. The yields for a total of three runs are included Table 6.

The deuterated products 143-145 from the copyrolysis of 12-d₂ and 119 were extensively analyzed by MS, ²H NMR,

Scheme 23



^1H NMR, and IR methods to determine deuterium incorporation and distribution.

The mass spectral ion intensities were measured at 12 eV by GCMS. The data from these analyses and the percent deuterium calculations are presented in Table 7. These

Table 6. Product yields from copyrolysis of 12 and 12-d with 2,3-dimethylbutadiene 119^a

Run	Cpd. ^c	Molar excess 119	T, °C	M.R., % ^d	Yield, % (GLC) ^b		
					143	144	145
1 ^e	12	6.0	520	54	6	5	1
2 ^e	12	4.2	540	59	12	6	2
3 ^e	12	6.0	570	61	2	4	0.5
4 ^f	12-d ₂	6.1	520	81	15	7	1
5	12-d ₂	6.2	530	77	21	9	2
6 ^f	12-d ₂	4.7	540	73	12	8	2
7 ^g	12-d ₂	6.0	570	46	1	2	0.3

^aNitrogen flow pyrolysis.

^bAbsolute yields determined by GLC against mesityl bromide internal standard.

^c12 or 12-d₂.

^dMass recovery.

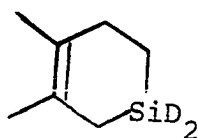
^eNo starting material 12 was recovered.

^f3% unreacted 12-d₂ was recovered.

^gNo unreacted 12-d₂ remained.

calculations are reasonably accurate for compound 143, however large M-1 peaks in the reference spectra for undeuterated silacyclopentenes 144 and 145 (ca. 8%) introduce an element of uncertainty into the calculated values of deuterium incorporation for these compounds.

The mass spectral results of Table 7 indicate that compound 143 is formed from 12-d₂ as $\geq 95\%$ 143-d₂. This is corroborated by ¹H NMR and IR data which both show only a trace of silyl hydride formation ($\leq 0.06\text{H}$ in the NMR). ²H NMR indicated that deuterium was present only as silyl deuteride. These data are all consistent with the assignment of structure 143a as the nearly exclusive silacyclohex-3-ene product formed.



143a

Product 144 was formed in this copyrolysis with extensive deuterium incorporation; the major species formed (48 mol %) is apparently doubly deuterated. Formation of 144-d₂ is consistent with formation of silylene 17-d₂ by a

Table 7. Percent deuterium incorporation in products 143, 144, and 145 from copyrolysis of 12-d₂ with excess 2,3-dimethyl-1,3-butadiene 119^a

Cpd. ^b	Ion	Ion intensity ^c	Ref. ion intensity ^d	Corr. intensity ^e	Mol % deuterated species ^e
143 (M = 126)	M-2	0.2	0.2	--	--
	M-1	0.3	0.3	--	--
	M	1.4	100.0	1.4	1 (d0)
	M+1	5.0	12.4	5.0	5 (d1)
	M+2	100.0	4.1	99.8	94 (d2)
	M+3	13.5	0.4	0.9	--
	M+4	4.1	0.1	--	--
144 (M = 126)	M-2	1	1	--	--
	M-1	9	8	--	--
	M	36	100	36	19 (d0)
	M+1	67	15	62	33 (d1)
	M+2	100	5	89	48 (d2)
	M+3	13	--	--	--
	M+4	1	--	--	--
145 (M = 112)	M-2	5	1	--	--
	M-1	4	8	--	--
	M	53	100	53	30 (d0)
	M+1	100	15	92	53 (d1)
	M+2	46	5	29	17 (d2)
M+3	7	0	--	--	

^aData obtained from Run 4, Table 6.

^bDeuterated 143, 144, or 145.

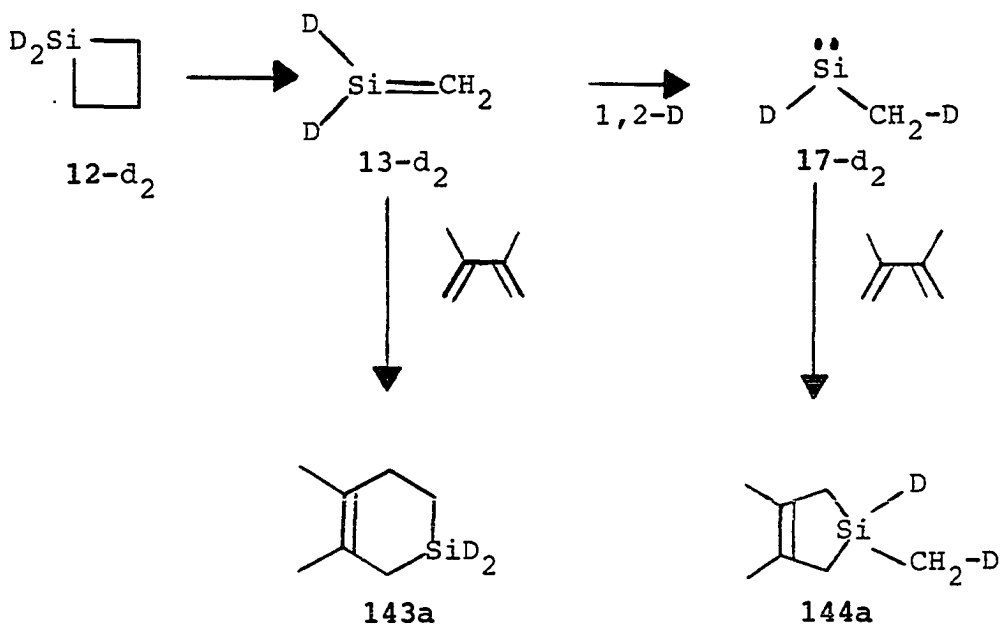
^cMeasured ion intensity on Finnegan 4023 GC-MS of deuterated samples.

^dMeasured ion intensity on Finnegan 4023 GC-MS of authentic undeuterated samples.

^eCalculated by the method of Biemann (83) using reference spectra for undeuterated samples.

1,2-D shift (Scheme 24). If trapped without subsequent scrambling or deuterium loss, then dideuterated silacyclopentene 144a would be the exclusive product formed. However the data in Table 7 make it clear that extensive deuterium loss has in fact occurred, with d_1 product (33%) and d_0 product (18%) also present.

Scheme 24



The deuterated 144 also showed IR and NMR spectra which indicated loss of deuterium and formation of silyl hydride. The IR spectrum showed a very strong silyl hydride band, and the ¹H NMR spectrum showed a silyl

hydride resonance which integrated as 0.25H. The silicon methyl, normally a clean doublet in undeuterated 144, was split into a complex multiplet, and integrated as 2.6H. The ^2H NMR results correlate with this data. Resonances corresponding to silyl deuteride (1.00D, integration in arbitrary units) and to deuterium substituted on the silicon methyl (0.79D) were found, and none others. The integrated ^1H and ^2H NMR signal intensities for the deuterated 144 are represented in Fig. 3.

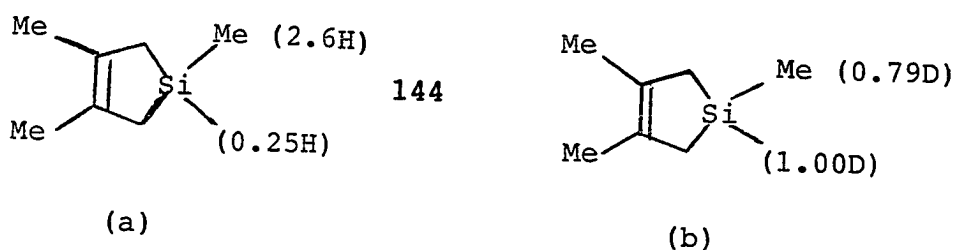
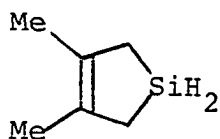


Figure 3. (a) ^1H and (b) ^2H NMR integrals of deuterated 144 formed in the copyrolysis of 1,2- d_2 and 2,3-dimethyl-1,3-butadiene 119 (the deuterium NMR intensities are in arbitrary units; the proton NMR integrals are relative to the 6H vinyl methyl resonance)

The MS and ^2H NMR data combined indicate that structure 144a (Scheme 24) is the major deuterated species of 144 formed in this copyrolysis. This is consistent with the 1,2-H (or D) shift interconverting silene 13 and

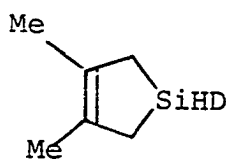
methylsilylene 17 which has been proposed by Conlin and Gill and others (12, 13). However the extensive deuterium loss raises the question of whether methylsilylene 17-d₂ or product 144a undergoes secondary reactions in this pyrolysis, and whether an alternative mechanism for methylsilylene 17 formation must be sought (84). Resolution of these experimentally difficult questions was not undertaken in this dissertation research.

More pertinent to this investigation was the nature of the deuterated 3,4-dimethyl-1-silacyclopent-3-ene 145 obtained. The mass spectral data indicate that the 145 is predominantly d₁ (53 mol %), with lesser amounts of d₀ (30 mol %) and d₂ (17 mol %). ²H NMR results showed only a silyl deuteride resonance. The IR spectrum of the product showed both an SiD (s) and an SiH (vs) band, and the ¹H NMR showed a significant (1.2H) silyl hydride resonance. Therefore silacyclopentene 145 is formed as only three deuterated isomers 145a (d₀), 145b (d₁) and 145c (d₂).



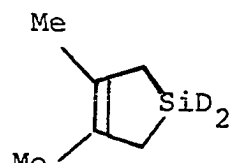
145a

(30 mol %)



145b

(53 mol %)



145c

(17 mol %)

If deuterated silylene 18 and deuterated propene are formed in the same decomposition process of 12-d₂, then the deuteration of silylene 18 (or its trapping adduct 145) should compliment the deuteration observed in the propene. One would expect similar relative amounts of d₁ silylene 18 to be formed as d₁ propene. The results have indicated this to be the case, although the variation in the conditions employed must be kept in mind (FVP at 710°C conditions were used to characterize the propene, while the trapping experiments were done in a nitrogen flow system at ca. 540°C). Found were 59 mol % d₁ propene and 53 mol % monodeuterated 145b. Similarly, d₀ propene should correspond with d₂ silylene 18, and d₂ propene with d₀ silylene. Observed were 21 mol % d₀ propene vs. 17 mol % 145c (d₂), and 18 mol % d₂ propene vs. 30 mol % 145a (d₀).

It appears that the low yields of silylene 18 adduct 145 formed in this experiment are at least partly due to the thermal instability of silacyclopentenes under these conditions. When an authentic, independently prepared sample of 1,1-dideuterio-1-silacyclopent-3-ene 145c was copyrolyzed with a 10.7-fold molar excess of 119, the silacyclopentene was recovered in only 18% yield. There was little loss of the deuterium label. Unpyrolyzed 145c was determined to be 95% d₂ by mass spectral determination, and

the pyrolyzed 145c was found to be 91% d_2 . These results are summarized in Table 8. The pyrolyzed 145c was also examined by ^2H NMR and no scrambling of the label position could be detected.

In summary, the pyrolysis of 1-deuterated silacyclobutanes 12- d_2 and 90- d_1 has clearly shown that predominantly deuterated propene is formed in the decompositions. The observed deuteration of the propene (favoring incorporation onto the allylic position of the propene) occurring without detectable incorporation of deuterium onto the ring carbons of the starting silacyclobutane is most economically rationalized by suggesting that deuterio- (or hydrido-) silacyclobutanes decompose to propene predominantly via initial, irreversible propylsilylene formation, followed by rapid decomposition of the propylsilylene to propene. This interpretation is strengthened by the comparable deuteration observed (by analysis of the trapping adduct 145) in the silylene 18 formed in the pyrolysis of 12- d_2 .

The d_2 propene observed in the FVP of 12- d_2 and the incorporation of deuterium onto C_1 and C_2 of the propene formed suggested a scrambling process in deuterated propylsilylene 20- d_2 was occurring prior to propene formation. Since hydridosilacyclopropanes have been suggested as

Table 8. Deuterium incorporation in unpyrolyzed and pyrolyzed 145c

Com- pound ^a	Ion (M = 112)	Ion intensity ^b	Corrected ion intensity ^c	Mol % deuterated species ^c
145c un- pyrolyzed	M-2	1	--	--
	M-1	0	--	--
	M	10	10	1 (d0)
	M+1	37	36	3 (d1)
	M+2	1015	1015	95 (d2)
	M+3	121	4	0
	M+4	39	--	--
	M+5	3	--	--
145c, pyr- olyzed	M-2	10	--	--
	M-1	3	--	--
	M	36,9 ^d	45 ^e	4 (d0)
	M+1	56	51	4 (d1)
	M+2	1112	1103	91 (d2)
	M+3	144	15	1 (d3)
	M+4	44	--	--
	M+5	4	--	--

^aCompound 145c before and after nitrogen flow copyrolysis with excess 2,3-dimethylbutadiene 119 (see text).

^bObserved ion intensity measured on a Kratos MS-50 Mass Spectrometer, 10.3 eV, neat samples (arbitrary units).

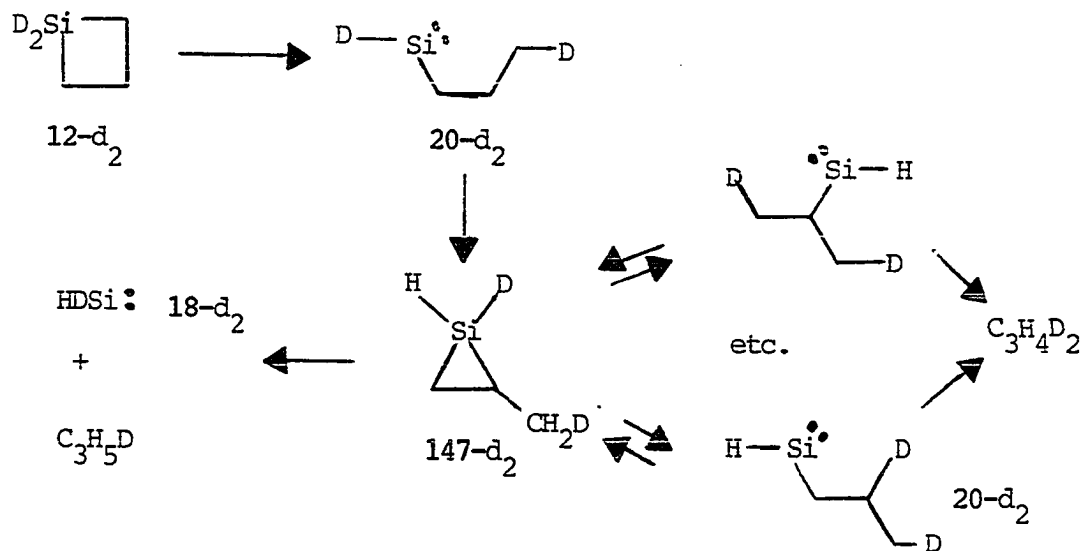
^cCalculated by the method of Biemann (83) using the following reference spectrum for undeuterated 145 determined at the same time and conditions: M-2 13, M-1 4, M 409, M+1 47, M+2 15, M+3 1, M+4 0, M+5 0.

^dTwo ions were found; the ion for 145-d₀ was not identified.

^eThe total intensity for the ions at M = 112 was used (see note d), hence these calculated values represent the maximum amount of 145-d₁.

likely intermediates in the known decomposition of alkylsilylenes to alkenes and silylenes (see Historical section), it was hypothesized that such intermediates (e.g., 147-d₂, Scheme 25) might be involved in the observed scrambling. Since relief of ring strain provides enough lowering of the activation energy for alkyl elimination to become significant for hydridosilacyclobutanes, a similar silacyclopropane to alkylsilylene reaction should be even more favored. Thus, a reversible alkylsilylene-silacyclopropane isomerization could explain the observed deuterium scrambling and formation of d₂ propene. These considerations are summed up in Scheme 25, in which, for clarity, only a few of the possible intermediates are shown.

Scheme 25



Subsequently, as will be described in the next section, alkylsilylenes were independently generated in pyrolysis experiments to probe in a less ambiguous fashion the questions of scrambling, silacyclopropane formation, and the possibility of a reversible silacyclopropane-alkylsilylene isomerization suggested by this work with silacyclobutanes.

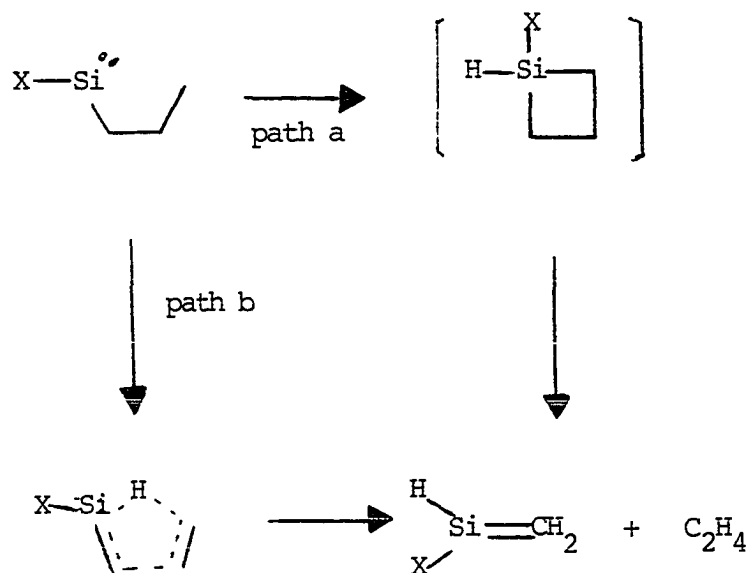
Thermal Reactions Of Alkylsilylenes

In the preceding section it was shown that propylsilylenes are formed in the initial step of the pathway of thermal decomposition of hydridosilacyclobutanes to propene. The pyrolysis of 1,1-dideuterio-1-silacyclobutane $12-d_2$ afforded largely monodeuterated propene, however some doubly labelled propene was also observed. The d_2 propene was postulated to arise as a consequence of a reversible silylene-silacyclopropane equilibrium (Scheme 25).

Furthermore the lack of any scrambling of deuterium onto the carbons of the silacyclobutane ring when $12-d_2$ was recovered after pyrolysis suggests that the initial formation of 20 is not reversible. This conclusion conflicts however with research by other workers (37, 50) who have suggested the possibility of ethene formation from propylsilylene (an observation which is subject to controversy

[49], see Historical section) which could occur through γ -C-H insertion and silacyclobutane formation (path a, Scheme 26). The analogous process is well known for 1,3-disilacyclobutane formation, as originally noted in the rearrangement of tetramethyldisilene 54(43), and γ -C-H insertion into an allylic C-H bond with 3-methylene-1-silacyclobutane ring formation has been discovered in the reaction of silylene 63 (Historical section) (45). It has also been suggested that propylsilylene could afford ethene via a concerted process (path b, Scheme 26) (52).

Scheme 26

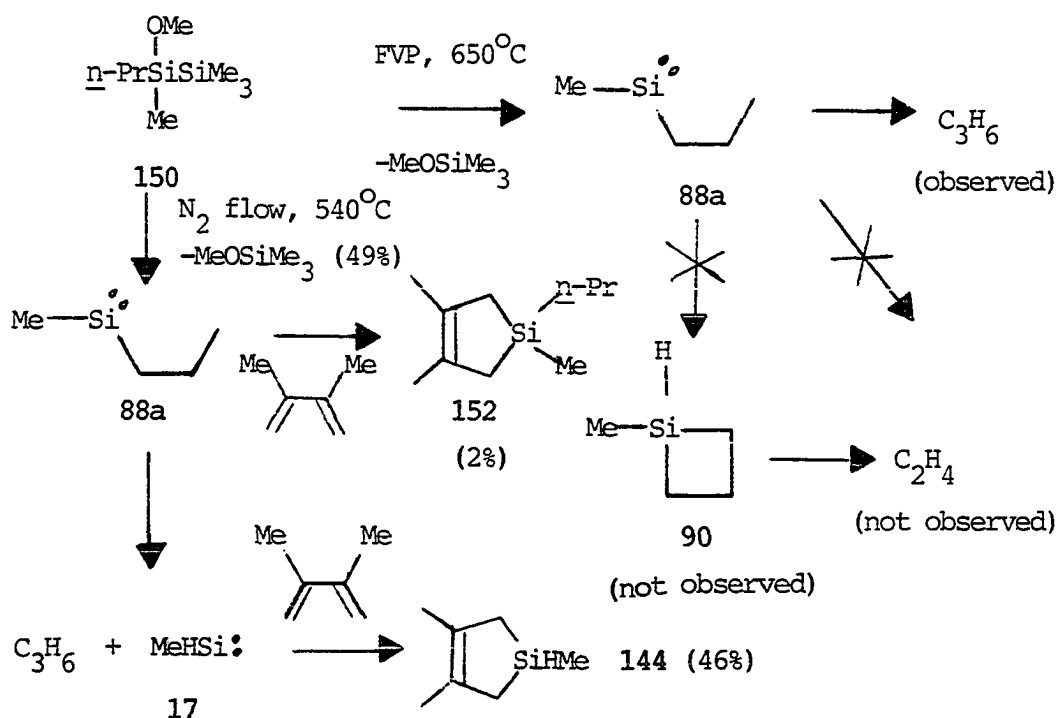


In order to clarify some of these questions the direct generation of alkylsilylenes was undertaken. First to be studied was methylpropylsilylene 88a, generated from 1-methoxy-1-n-propyl-1,2,2,2-tetramethyldisilane 150. Synthesized in 30% yield from 1,1-dichloro-1,2,2,2-tetramethyldisilane 151 (85), 150 was subjected to FVP at 650°C. The collected pyrolysate was degassed and the gases collected at -196°C; the remaining liquid pyrolysate and the gases were analyzed separately. The liquid fraction (24% mass recovery) was found to contain a single major component, the expected methoxytrimethylsilane 45, as well as numerous trace compounds. A thorough search by GC-MS failed to disclose any 1-methyl-1-silacyclobutane 90. Admittedly, a small amount of 90 could have gone undetected, since silacyclobutanes would be expected to decompose extensively at these temperatures (12 was recovered in only 8% yield at 710°C). More conclusive is the fact that when the gaseous fraction was analyzed by GC-MS, the major product was propene, with ethene, the principal silacyclobutane decomposition product, present in only trace amounts (< 1% of propene, uncorrected). We therefore failed to observe any evidence of either path a or path b (Scheme 26) occurring.

Copolyrolysis of 150 with a 5.4-fold molar excess of

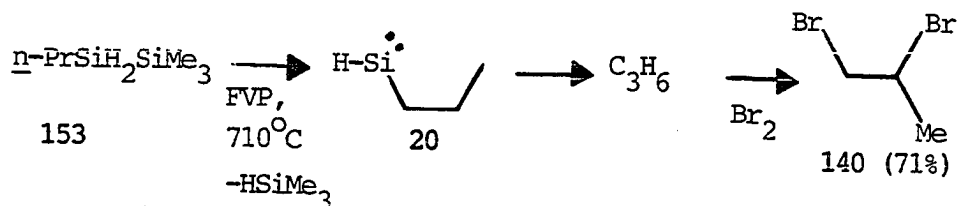
2,3-dimethyl-1,3-butadiene at 540°C resulted in the first trapping of an alkylsilylene, although the rapidity of the decomposition of 88a to propene and methylsilylene 17 is illustrated by the low yield of adduct 152, 2%. The following products were characterized: methoxytrimethylsilane 45 (49%), 1,3,4-trimethyl-1-silacyclopent-3-ene 144 (46%), 1-*n*-propyl-1,3,4-trimethyl-1-silacyclopent-3-ene 152 (2%), and unreacted 150 (4%) (Scheme 27). The identification of compound 152 was confirmed by independent synthesis.

Scheme 27



The FVP of 1-n-propyl-2,2,2-trimethyldisilane 153 also afforded propene, but no ethene. Compound 153 was prepared in 6% overall yield from 1,1,1-trichloro-2,2,2-trimethyldisilane 154 (86) by reaction of 154 with propyl Grignard reagent and reduction of the intermediate 1-n-propyl-1,1-dichloro-2,2,2-trimethyldisilane 155 with LiAlH_4 ; despite numerous efforts better overall yields proved unobtainable.

The FVP of 153 at 710°C afforded an effervescent pyrolysate containing propene as the major identifiable species. Analysis by gas chromatography indicated that ethene was present in only trace (< 3% of propene) quantities. Repetition of the pyrolysis and trapping of the alkenes formed in bromine afforded a 71% yield of 1,2-dibromopropane 140.



1,1-Dideuterio-1-n-propyl-2,2,2-trimethyldisilane 153- d_2 was prepared in the same fashion as 153 except with reduction of 155 with LiAlD_4 . To see whether deuterated propylsilylene 20 would scramble deuterium, 153- d_2 was pyr-

olyzed under FVP conditions at 710°C. Analysis of the gaseous products by GC and GC-MS showed the major characterizable product to be deuterated propene, estimated to be ca. 24% d₀, 65% d₁, and 11% d₂. A cautionary note, however, is in order regarding the accuracy of this estimate; the facile loss of hydrogen in the mass spectrum of propene renders the calculation of deuterium incorporation innaccurate, as discussed above regarding the FVP of 12-d₂. Only a trace of ethene (< 1% of propene) was detected, which was apparently highly deuterated (> 50% d₁). At 700°C the sample was completely decomposed.

Pyrolysis of 153-d₂ under FVP conditions at 710°C and bromination of the alkenes formed gave deuterated 1,2-dibromopropane 140 in 83% yield. Two independent experiments both determined the 140 formed to be a mixture of d₀ (38-40%) and d₁ (60-62%) with no d₂ present (Table 9). Furthermore the deuterium was almost completely scrambled in the 140 as determined by ²H NMR (Fig. 4). Integration of the signals gave relative intensities of 29% at C₁, 22% at C₂, and 49% at C₃; complete randomization would afford intensities of 34% at C₁, 17% at C₂, and 50% at C₃.

When the pyrolysis of 153-d₂ was repeated at a lower temperature (500°C) a 70% yield of deuterated trimethylsilane 156-d₁ and a 19% yield of recovered 153-d₂ was

obtained. ^2H NMR of both products indicated that there was no positional scrambling of deuterium (notably incorporation of deuterium onto the propyl chain in 153) for either compound; only silyl deuterides were detected. ^1H NMR indicated a small amount of deuterium loss and silyl hydride formation for both compounds ($\leq 0.1\text{H}$, or ca. 5% and 10% silyl hydride formation in the recovered, deuterated 153 and 156, respectively).

The minimal deuterium exchange and lack of scrambling seen in the recovered starting material 153- d_2 , and the nearly quantitative deuteration (as silyl deuteride) of the trimethylsilane indicates that propylsilylene is formed as monodeuterated 20- d_1 and that the scrambling and labelling results obtained could be due to a reaction of the propylsilylene intermediate formed. This experiment rules out prior scrambling in the starting material or transfer of deuterium from trimethylsilane 156 to the propene.

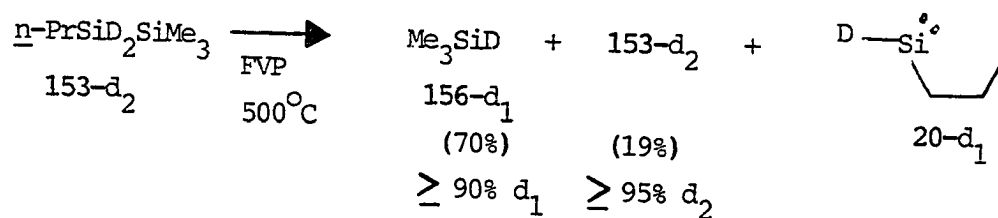


Table 9. Percent deuterium incorporation in 1,2-dibromopropane 140 from FVP of 1-n-propyl-1,1-dideuterio-2,2,2-trimethyldisilane 153-d₂

Run	Yield of 140	Ion (M = 200)	Ion intensity ^a	Corr. ion intensity ^b	Mol % deuterated species
1 ^c	83	M-2	0	--	--
		M-1	1	--	--
		M	61	61	38 (d0)
		M+1	100	98	62 (d1)
		M+2	124	1	0 (d2)
		M+3	194	--	--
		M+4	71	--	--
		M+5	95	--	--
		M+6	11	--	--
		M+7	1	--	--
2 ^d	-- ^e	M-1	50	--	--
		M	988	988	40 (d0)
		M+1	1541	1477	60 (d1)
		M+2	1983	0	0 (d2)
		M+3	2982	--	--
		M+4	1250	--	--
		M+5	1466	--	--
		M+6	185	--	--

^aMeasured ion intensity, deuterated sample, arbitrary units.

^bCalculated by the method of Biemann (83) using the following reference spectra for undeuterated 140: Run 1, M-2 1, M-1 6, M 725, M+1 28, M+2 1,413, M+3 50, M+4 685, M+5 23, M+6 1; run 2, M-1 823, M 47,783, M+1 3,106, M+2 97,049, M+3 3,439, M+4 48,498, M+5 987, M+6 66.

^cSample and reference spectra determined on a Kratos MS-50 Mass Spectrometer, neat samples.

^dSample and reference spectra determined on a Finnegan 4023 GCMS.

^eNot determined.

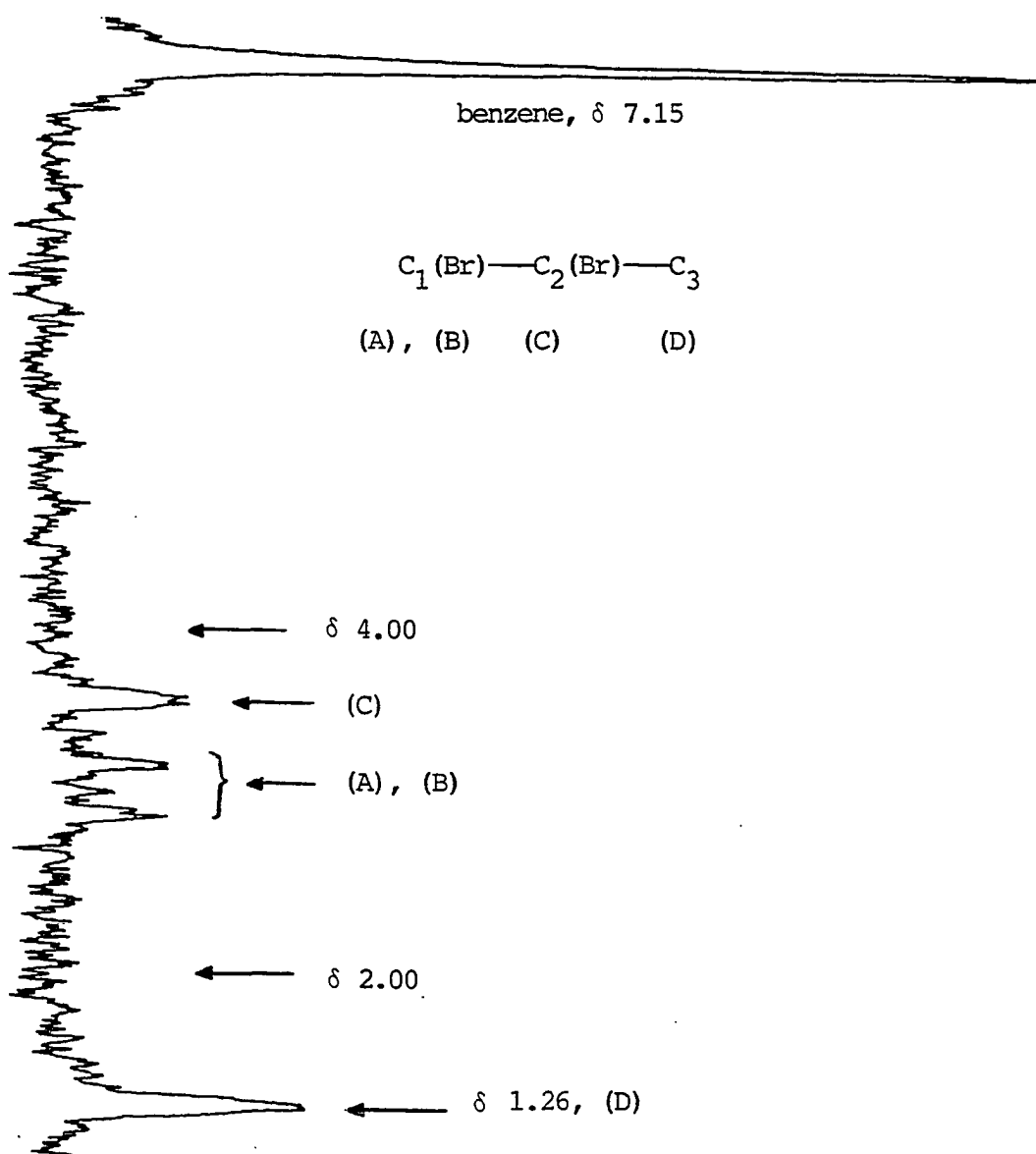
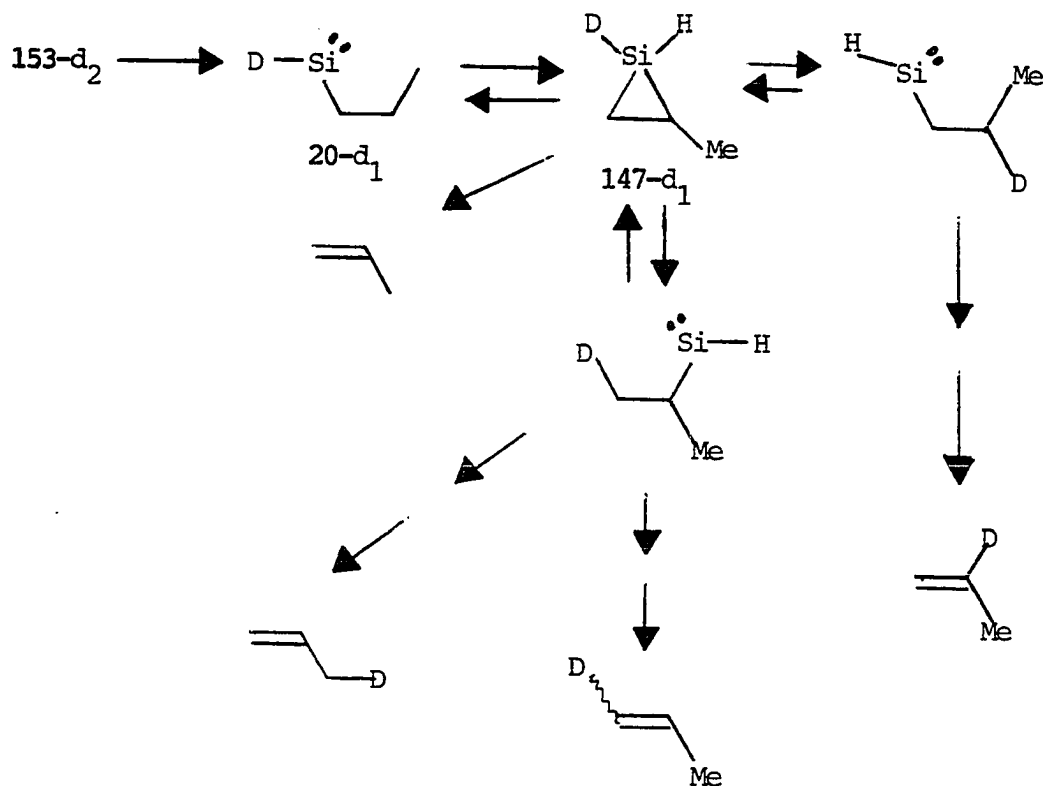


Figure 4. ^2H NMR of 1,2-dibromopropane 140 from bromination of flash-vacuum pyrolysate of 153- d_2 (benzene solution, 46 MHz; insert shows the assignment of resonances; the peak at δ 7.15 is natural abundance deuterated benzene)

The significant deuterium incorporation in the propene formed in the pyrolysis of 153-d₂ and nearly random scrambling observed are consistent with the proposed alkylsilylene-silacyclopropane isomerization (Scheme 28). Also interesting is the lack of significant d₂ propene. It would be expected that if deuterium incorporation were the result of a bimolecular radical or silylene process, then such a process would result not only in the formation of d₁ propene, but also d₂ propene in significant amounts. As d₁ propene was formed, it would compete with d₀ propene in any such reaction resulting in d₂ product. The results of Table 9 clearly indicate that such a statistical randomization of the label is not occurring; therefore a unimolecular scrambling process is implied. This question of possible bimolecular reactions will be discussed in more detail later in this section.

Another consequence of the proposed alkylsilylene-silacyclopropane isomerization is the prediction that alkylsilylenes should form alkenes with formally "migrated" double bonds. This has not previously been reported in the literature. For example, Gusel'nikov et al. (49) and Barton and Burns (47) both reported only the formation of 1-alkenes from alkylsilylene decompositions. Therefore the pyrolysis of 1-n-butyl-1-methoxy-1,2,2,2-tetramethyl-

Scheme 28



disilane 157 (47) was reexamined.

The FVP of 157 (47) was performed at 708°C and the gaseous products collected and analyzed by GC and GCMS. Three different butenes were found with retention times and mass spectra corresponding to 1-butene (49 parts), E-2-butene (31 parts), and Z-2-butene (20 parts), as well as the expected methoxytrimethylsilane 45 (17 parts, uncorrected), and a compound tentatively identified only by MS as methylsilane (24 parts, uncorrected). Propene and

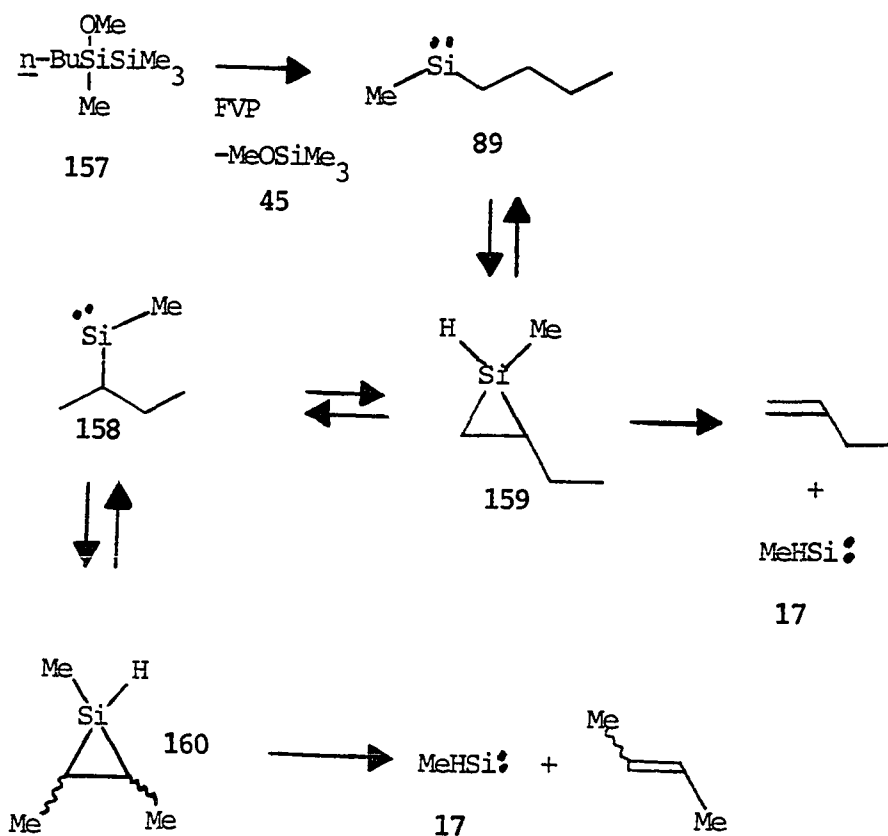
ethene were found in only trace (< 1 part each) amounts. The relative yields of butenes have been corrected using literature TC response factors (87). Repetition of the experiment at 560°C showed 1-butene (36 parts), E-2-butene (41 parts), Z-2-butene (23 parts), the compound identified as methylsilane (24 parts), and methoxytrimethylsilane (84 parts) were the sole products obtained.

Additional confirmation of the product butene identities was provided by bromination of the alkenes. FVP of 157 at 703°C and bromination of the pyrolysate yielded 1,2-dibromobutane (21%) and 2,3-dibromobutane (two isomers, presumably meso and dl forms, in 26% and 19% yields). It was not determined which isomer was dl and which was meso.

These results may be rationalized as the result of initial methylbutylsilylene 89 formation and equilibration of isomeric silylenes 89 and 158 with silacyclopropanes 159 and 160 (Scheme 29).

Extending the alkyl chain by two carbons resulted not only in the formation of 1- and 2-hexenes, but also of 3-hexenes. FVP of 1-hexyl-1-methoxy-1,2,2,2-tetramethyl-disilane 161 at 605°C yielded a very clean pyrolysate containing only four product peaks by capillary GLC; no unreacted 161 remained. The products were identified by isolation by preparative GLC and their spectral charac-

Scheme 29



teristics as methoxytrimethylsilane 45 (83%), 1-hexene (45%), Z-2-hexene (18%), and a mixture of E-2-hexene and 3-hexenes (33%). This mixture was characterized by MS, ¹H NMR and ¹³C NMR. The ¹H NMR (Fig. 5) in benzene-d₆ solution contained a total of eight peaks in the methyl region, including a triplet at δ 0.85 (J = 7.3 Hz) which is the C₆ methyl of E-2-hexene. Irradiation of the spectrum at δ 1.98 (insert, Fig. 5) collapses the eight peaks to

five; the triplet remains (labelled "a", Fig. 5, insert) and the remaining peaks simplify to two peaks at δ 0.90 and 0.93 ("b" and "c", Fig. 5, insert). The resonance at δ 0.93 matches the chemical shift of an available sample of E-3-hexene. The remaining peak in the decoupled spectrum was presumed to belong to Z-3-hexene. Additional confirmation of the structural assignments was provided by a ^{13}C NMR spectrum of the mixture, which showed resonances assignable to each isomer (E-2-, E-3- and Z-3-hexenes), matched against literature values (for Z-3-hexene) or values of available samples (E-2-hexene and E-3-hexene). Integration of the ^1H NMR spectrum indicated that the E-2-hexene/3-hexene (both isomers) ratio was 2.6/1.0, and the E-3-hexene/Z-3-hexene ratio was 2.1/1.0.

It is noteworthy that in our hands hexenes (along with the other expected decomposition product, methoxytrimethylsilane) are the exclusive products of thermal decomposition of 161. No evidence of any silacyclobutanes, silacyclopentanes, of silacyclohexanes, indicating competitive intramolecular γ -, δ -, or ϵ -C-H insertion was found.

If deuteration of the alkenes formed from alkylsilylenes and formal migration of the double bond produced are both the result of a silylene-silacyclopropane isomerization, then pyrolysis of a labelled alkylsilylene with an

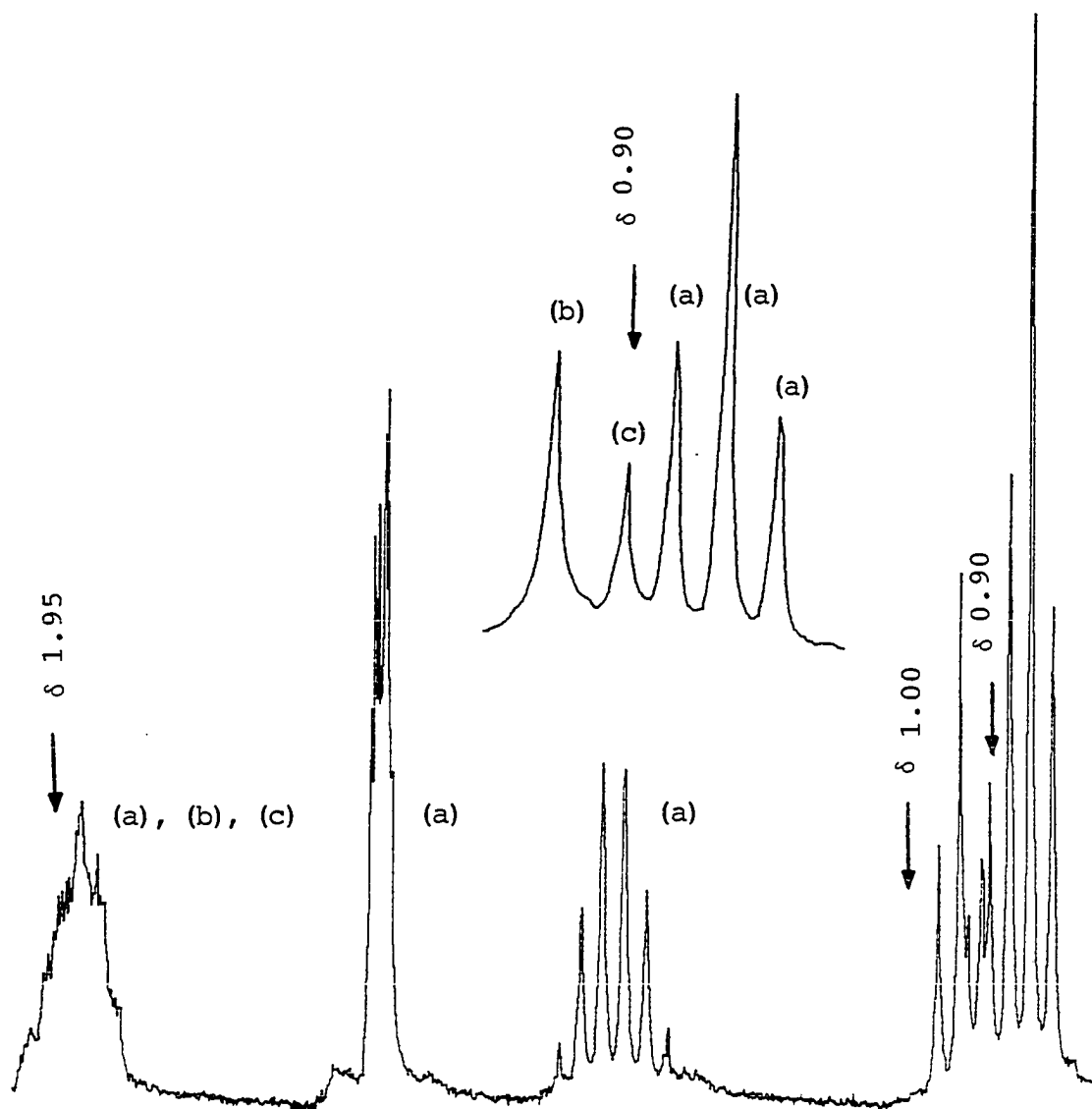


Figure 5. Alkyl region of the ^1H NMR spectrum of the mixture of E-2-hexene and 3-hexenes obtained upon flash-vacuum pyrolysis of 161 (benzene- d_6 solution, 300 MHz; peaks are labelled as assigned to (a) E-2-hexene, (b) E-3-hexene, and (c) Z-3-hexene; insert shows expansion of the methyl region, decoupled by irradiation of the spectrum at δ 1.98)

extended carbon chain should show increasing deuteration with double bond migration. To test this hypothesis, 1,1,1-trideuterio-n-hexylsilane 162-d₃ was synthesized and pyrolyzed.

However, the pyrolysis of undeuterated 162 (88) (synthesized by reduction of n-hexyl-1,1,1-trichlorosilane [89] with LiAlH₄) was conducted first to establish the product identities. An effervescent pyrolysate was obtained. After liberation of the gases upon warming at 1 atm pressure, the remaining liquid was found to contain three hexene peaks and recovered 162. The identity of the hexene peaks was established by GLC retention times compared with authentic samples, GC-MS, and ¹H NMR spectra of samples isolated by preparative GLC. Found were 1-hexene (17%), Z-2-hexene (4%), and a mixture of E-2-hexene and 3-hexenes (11%) in a ratio estimated by ¹H NMR analysis (similar to that presented previously in detail for the pyrolysis of 161) to be 1.2/1.0 Z-2-hexene/3-hexene. Unreacted 162 was recovered in 4% yield from FVP at 735°C (Scheme 30).

The yields of hexenes from 162 were considerably lower than those found for the FVP of 161; this was determined to probably be the result of secondary decomposition of the alkenes. When the pyrolysis was repeated and the gaseous products were collected and analyzed by GLC and GCMS a

number of lighter alkenes were determined to be present. Found were the following compounds, with relative yields in parentheses: ethene (1.03), propene (0.82), 1-butene (0.20), 1-pentene (0.30), butadiene (< 0.10), 1-hexene (1.00), Z-2-hexene (0.21), and the E-2- and 3-hexene mixture (0.45). These identifications are based on MS spectra and GC retention times on two different columns. The relative amounts have been corrected using available or estimated TC response factors (87). 1-Pentene was also identified by ^1H NMR as a product in the copyrolysis of 162 with 1,3-butadiene (vide infra).

In this pyrolysis, although some 1-butene was detected, GLC and GCMS analysis failed to detect significant amounts of 2-butene (GLC analysis could not absolutely rule out the presence of 2-butene, due to low sample concentration, however the presence of 2-butene could be determined to be less than 8% of the amount of 1-butene). The fact that, although a mixture of isomeric hexenes are obtained in the pyrolysis, 2-butenes are not formed in a similar amount constitutes evidence against the possibility that the alkene isomerization observed in this pyrolysis is the result of bimolecular processes, e.g., radical or silylene chain processes. If, for example, 162 decomposed initially solely to 1-hexene which was isomerized by

bimolecular processes, such a process would also occur to a comparable degree with 1-butene.

To determine whether the lighter alkenes and low hexene yields are the result of secondary decomposition, a mixed hexene solution similar in composition to the product hexene mixture was prepared, consisting of 44% 1-hexene, 17% Z-2-hexene, 28% E-2-hexene, and 12% 3-hexene (Z and E isomers) and pyrolyzed at 735°C under FVP conditions. The pyrolysis products were collected as a gaseous sample; the products, identified by GLC and GC-MS, with corrected relative amounts in parentheses, were: ethene (0.40), propene (0.38), 1-butene (0.20), butadiene (0.30), 1-hexene (1.00), and the remaining hexenes. The peak areas of the hexenes by capillary GLC were little changed by pyrolysis. After pyrolysis, the relative hexene peak areas were found to be 1-hexene (42%), Z-2-hexene (16%), and the mixture of E-2- and 3-hexenes (42%), as compared with 44%, 17%, and 40% respectively in the unpyrolyzed starting sample. Only trace amounts of Z- and E-2-butene, four pentene isomers, and two pentadiene isomers were also found by GC-MS. The amounts of these trace products were, however, too small to be detected by routine GLC using TC detection. The relative yields of light alkenes to 1-hexene proved variable, possibly the result of the relative involatility

of hexene, which may have resulted in incomplete collection of sample; repetition of the experiment afforded relative yields of ethene (0.85), propene (0.45), 1-butene (0.20), butadiene (0.45), and 1-hexene (1.00), which are closer to the amounts observed in the pyrolysis of 162.

When pure 1-hexene, or a 69.5/30.5 mixture of Z-2-hexene/E-2-hexene were pyrolyzed, no isomerization of the starting materials was detected, although effervescent pyrolysates, indicating decomposition to lighter gases, were observed. FVP of 1-hexene at 735°C afforded a 64% mass recovery with a 52% yield of unchanged 1-hexene, and FVP of a 69.5/30.5 ratio of Z-2-hexene/E-2-hexene gave yields of 21% E-2-hexene and 13% Z-2-hexene.

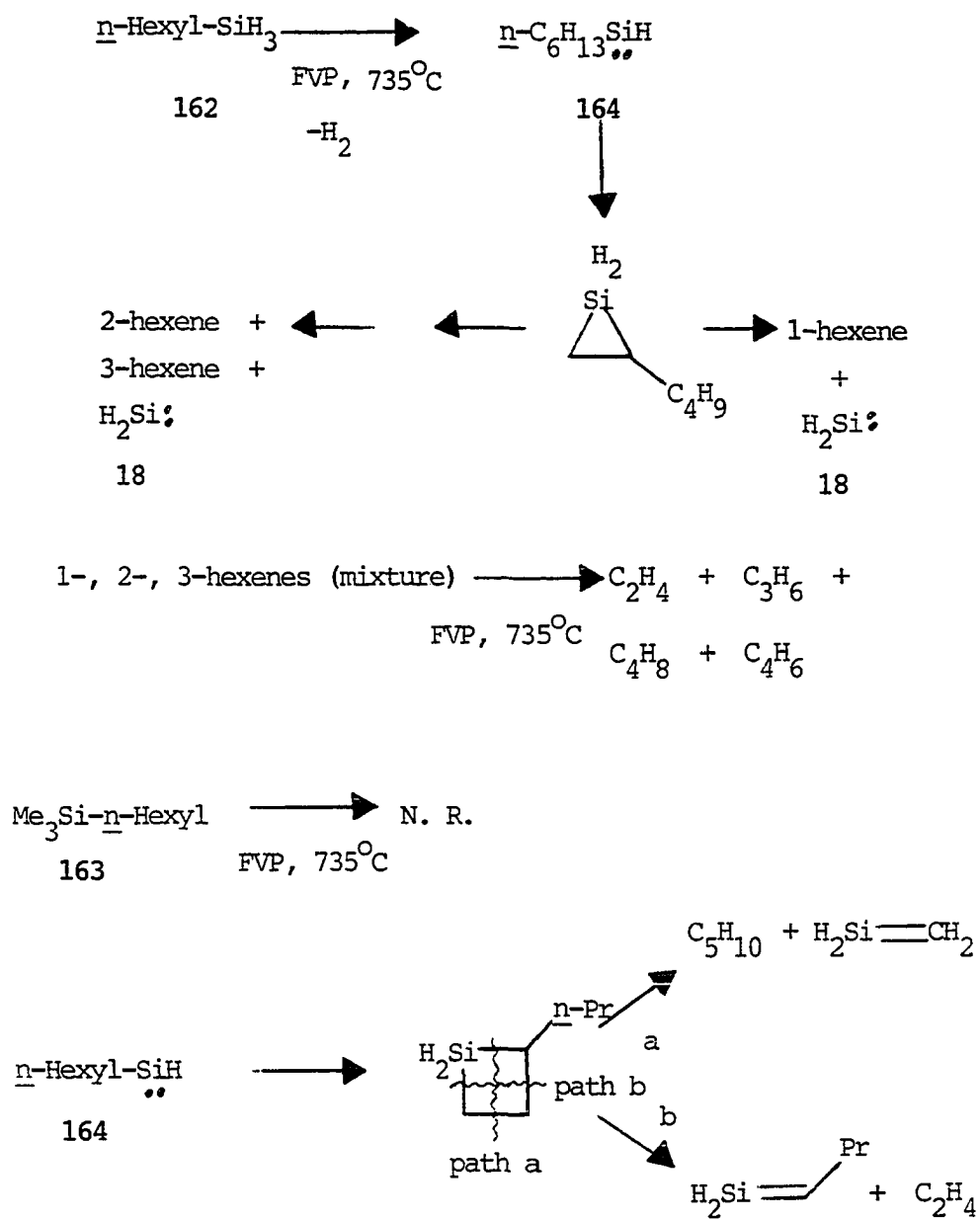
In order to test for products arising from Si-C or C-C bond cleavage in alkylsilanes under these conditions, 1,1,1-trimethyl-1-n-hexylsilane 163 (90) was subjected to FVP at 740°C, resulting in a 72% mass recovery of a pyrolysate consisting exclusively of unchanged 163 by GLC and ¹H NMR analysis. Thus, none of the products found in the pyrolysis of 162 can be accounted for by fragmentation in the starting material alkyl chain.

These results for the pyrolysis of 162 and the associated control experiments are summarized in Scheme 30. Elimination of dihydrogen from 162 forms hexylsilylene 164

which then decomposes to 1-, 2- and 3-hexenes. At the temperatures employed (735°C) these hexenes are subject to secondary decomposition to lighter alkenes. The pyrolysis of 163 indicated that no C-C or Si-C bond homolysis was occurring. Pent-1-ene was tentatively identified in the pyrolysate of 162 on the basis of MS and and GLC retention times; the formation of this product does not appear to be the result of secondary hexene decomposition. The mechanism of pentene formation is unknown; it would not be expected to be the result of γ -C-H insertion and silacyclobutane formation, since, if this occurs, pentene formation (path a, Scheme 30) would not be expected to be competitive with ethene (and 2-n-propyl-1-silene) formation via cleavage of the more substituted C-C bond in the silacyclobutane intermediate (path b, Scheme 30). A concerted decomposition (as in path b, Scheme 26) could explain the formation of pentene, but this suggestion must be rejected on the grounds that at very similar temperatures the pyrolysis of 150 and 153 afforded no ethene.

Having investigated the pyrolysis of undeuterated 162 in considerable detail, the pyrolysis of deuterated 162-d₃ was undertaken. For two runs at 740°C, product yields were: 1-hexene (13-18%), Z-2-hexene (3-4%), and a mixture of E-2-hexene and 3-hexenes (ca. 1.7/1.0 E-2-/3-hexene,

Scheme 30



9-12%). Unreacted, deuterated 162 was recovered in 4-7% yield.

The products and unreacted, deuterated 162 were separated by preparative GLC and spectral data were obtained. The unreacted 162 recovered showed ca. 13% deuterium loss and silyl hydride formation (0.39H) by ^1H NMR integration. Because of facile H or D loss from 162 in the mass spectrum, mass spectral results for deuterium incorporation could only be obtained by measuring ion intensities of resolved parent ions for d_3 and d_2 162 at high resolution ($R_s = 75,000$). The relative intensities for d_3 species and d_2 species were found to be 15.5 ± 1.0 and 8.5 ± 1.0 , respectively. Reliable quantitation for d_1 and d_0 could not be obtained because only very small ions which were shoulders on larger peaks could be observed. ^2H NMR revealed no scrambling of deuterium onto the carbons of the alkyl chain; all deuterium was present as silyl deuteride.

^2H NMR and mass spectra of the product hexene peaks were obtained. Table 10 records the MS results, and Table 11 reports the integrated ^2H NMR signal intensities for 1-hexene and Z-2-hexene. ^2H NMR data of the mixture of E-2-hexene and 3-hexene are given in the Experimental.

It is clear from Table 10 that increasing deuteration with formal double bond migration is in fact observed, as

predicted. Thus 1-hexene from 162-d₃ is 28% monodeuterated and 66% nondeuterated, whereas the Z-2-hexene is 58% monodeuterated and 39% undeuterated. The mixture of E-2- and 3-hexenes shows approximately the same amount of deuteration (35% d₀ and 61% d₁) as the Z-2-hexene. In all compounds, d₂ hexene formation is nearly insignificant.

The ²H NMR of the 1-hexene and Z-2-hexene revealed complex and extensive scrambling of deuterium in both products (Table 11). At most positions, the incorporation of deuterium is nearly statistical, however an enhanced signal at C₂ of 1-hexene, some 300% larger than would be anticipated from merely random scrambling, is quite apparent. The effect is still apparent in the Z-2-hexene, where the C₂ and C₃ positions (which are unfortunately unresolvable in the spectrum) still show a ca. 50% signal enhancement over what would be expected from random incorporation. This could be the result of the proposed silylene-silacyclopropane isomerization, if a kinetic effect favors incorporation at C₂. Such a mechanism is diagrammed in Scheme 31, where the C-D (or C-H) elimination of the silacyclopropane intermediates occurs with the silylene moiety favoring the less hindered site, i.e., k₋₃ > k₄.

Table 10. Percent deuterium incorporation in hexenes from FVP of 162-d₃

Compound	Ion (M=84)	Actual ion intensity ^a	Corrected ion intensity ^b	Mol % deuterated species
1-hexene	M-2	--	--	--
	M-1	--	--	--
	M	844	844	66 (d0)
	M+1	423	363	28 (d1)
	M+2	87	59	5 (d2)
	M+3	14	10	1 (d3)
<u>Z</u> -2-hex-ene	M-2	--	--	--
	M-1	--	--	--
	M	899	899	39 (d0)
	M+1	1396	1332	58 (d1)
	M+2	166	70	3 (d2)
	M+3	17	10	0 (d3)
isomeric mixture ^c	M-2	--	--	--
	M-1	--	--	--
	M	1565	1565	35 (d0)
	M+1	2856	2745	61 (d1)
	M+2	358	161	4 (d2)
	M+3	49	33	1 (d3)

^a Measured ion intensities of deuterated hexene determined on a Kratos MS-50 Mass Spectrometer, 20 eV, neat samples.

^b Calculated by the method of Biemann (83) using the following reference spectrum (of undeuterated Z-2-hexene) for all samples, 20 eV: M-2 0, M-1 0, M 4896, M+1 346, M+2 9, M+3 0.

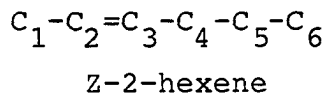
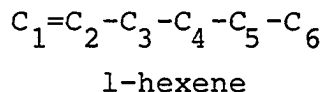
^c Mixture of E-2-hexene and 3-hexenes as described in text.

Table 11. Deuterium distribution in 1-hexene and \underline{Z} -2-hexene from pyrolysis of 162-d₃ determined by $\underline{2}$ H NMR

Compound	Signal (ppm, δ) ^a	Assign- ment ^b	Signal intensity ^c	% deuter- erium at C _n ^d	Theory ^e
1-hexene	4.9-5.2	1	125.3	16	17
	5.5-6.0	2	200.0	26	8
	1.8-2.1	3	171.0	22	17
	1.1-1.5	4, 5 ^f	228.6	30	34
	0.7-0.9	6	42.9	6	25
\underline{Z} -2-hex- ene	1.4-1.7	1	722	27	25
	5.3-5.7	2, 3 ^f	719	27	17
	1.8-2.1	4	331	13	17
	1.2-1.4	5	521	20	17
	0.7-0.9	6	350	13	25

^aChemical shift of signal, benzene solution, Bruker WM-300 NMR Spectrometer (46 MHz), deuterated benzene (natural abundance) internal standard.

^bSignals assigned to deuterium substituted on carbons C_n numbered according IUPAC nomenclature:



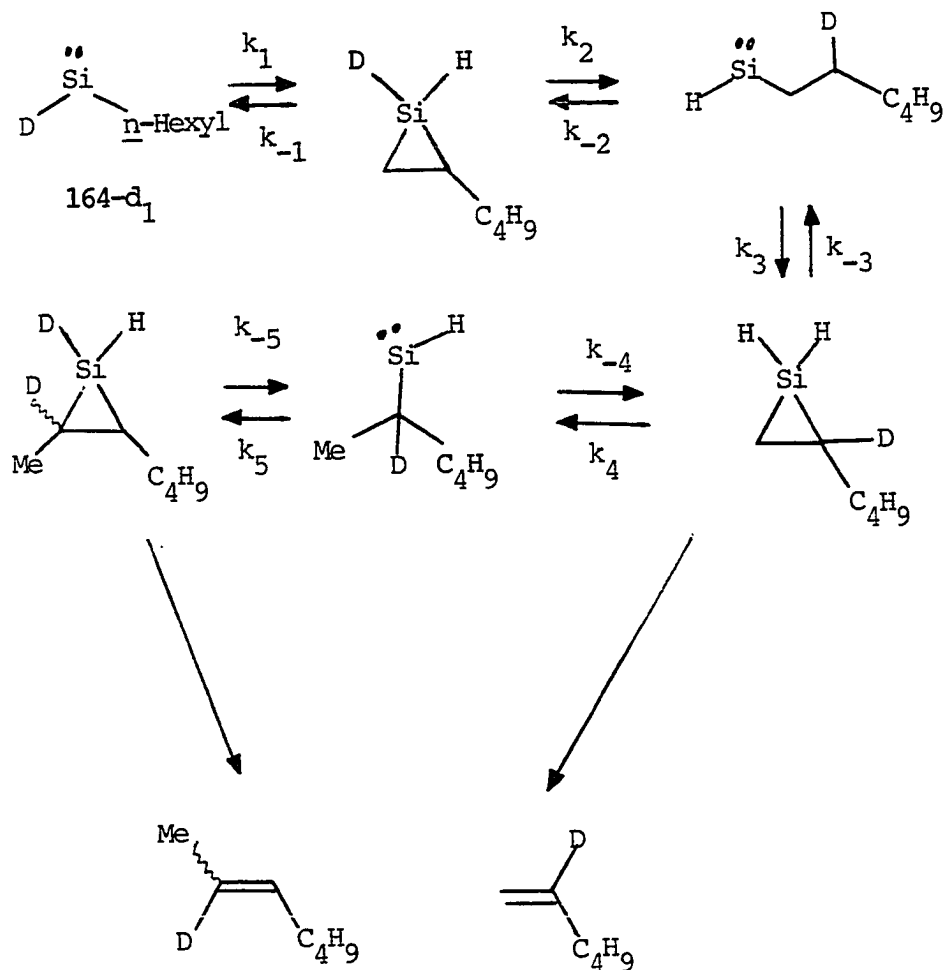
^cIntegrated signal intensity.

^dPercent signal intensity at C_n as percent of total spectrum intensity; for example, at C₁ of 1-hexene the signal intensity is 125.3, or 16.3% of the total integrated spectrum intensity (767.8).

^eCalculated intensity for each signal assuming completely random scrambling of incorporated deuterium in the compound.

^fSignals overlap.

Scheme 31



A number of control experiments were performed to test whether the rearrangement and scrambling phenomena observed in the pyrolysis of alkylsilylenes were in fact the result of a unimolecular silylene process, or the result of complicating bimolecular radical or silylene chains. Although Davidson and Ring (34) found that under low pressure pyro-

lysis conditions (0.01-0.1 torr) radical contribution to the methylsilane 32 pyrolysis was insignificant, at higher pressures (40-400 torr) the decompositions of methylsilane 32 and dimethylsilane 34 were believed by Neudorfl and Strausz (35) to have a radical component, which could be suppressed by the addition of ca. 10% ethene. Rickborn et al. (36) also found the decomposition of 34 at shock temperatures (> 1150 K) to be up to 85% the result of unquenched radical and silylene chains.

Therefore the pyrolysis of 162 was undertaken under a variety of conditions to test the effect of added radical and silylene scavenging reagents. For this work, gas flow pyrolysis conditions (1 atm pressure, 575-590°C with gas flow 35 mL/min) were employed. This procedure allowed copyrolysis of 162 with other reagents to be conveniently performed via either coaddition or changing of the carrier gas. The relative yield of 1-hexene to rearranged, isomeric 2- and 3-hexenes can be taken as a measure of the effect of the additive or carrier gas. Bimolecular silylene or radical processes should be detectable by the suppression of 2- and 3- hexene formation in copyrolyses with scavengers.

The results of these experiments are presented in Table 12. Pyrolysis under inert gas flow conditions

(nitrogen carrier gas) resulted in a relative increase in yields of 2- and 3-hexenes as compared with FVP conditions. A 20-35% combined yield of 2- and 3-hexenes was observed, compared with only a 6-7% yield of 1-hexene. This contrasts with the FVP results (vide supra) which produced more 1-hexene (17%) than 2- and 3-hexenes (15% combined).

Changing the carrier gas to ethene resulted in a considerable change in relative yields; under these conditions 2- and 3-hexene formation (13-25%) still predominated over 1-hexene formation (5-11%), but it is clear that the relative yield of the 2- and 3-isomers is diminished compared with nitrogen gas flow conditions. Ethene gas flow pyrolysis also resulted in the production of a new product, identified by MS and ^1H NMR as diethylsilane 165, formed in minor amounts (in undetermined yield, but estimated by uncorrected FID response to be < 5%). There were no other major products. The formation of 165 may be rationalized as the result of either a radical or a silylene process. A radical mechanism (Scheme 32a), which deserves consideration since ethene is known as an excellent scavenger of silyl radicals (91), could occur via initial formation of radical 166 by Si-C bond homolysis, which adds to ethene to form radical 167, which rearranges to ethylsilyl radical 168 by hydrogen abstraction followed by

Table 12. Pyrolyses of hexylsilane 162 under nitrogen, ethene, and butadiene flow conditions

Run	Carrier gas ^b	Diluent or additive ^c	Temp., °C	Yields, % ^a				Mass recovery, %
				A	B	C	D	
1	N ₂	I (9.2)	580	6	6	14	28	65
2	N ₂	I (9.9)	585	7	9	20 ^d	19	67
3	N ₂	I (6.9)	590	7	12	23	4	56
4	N ₂	II (8.9)	585	5	7	18	-- ^e	56
5	C ₂ H ₄	I (8.7)	575	7	4	9	27	67
6	C ₂ H ₄	I (8.0)	580	8	4	10	34	64
7	C ₂ H ₄	II (11.6)	580	11	7	18	-- ^e	77
8	C ₄ H ₆	--	585	9	3	5	29	--
9	C ₄ H ₆	III	585	18 ^f	3 ^f	6 ^f	29	--

^aYields are absolute as percent of 162 used, except Run 9, note (f). A = 1-hexene, B = Z-2-hexene, C = mixture of E-2-hexene and 3-hexenes (see text), D = unreacted 162.

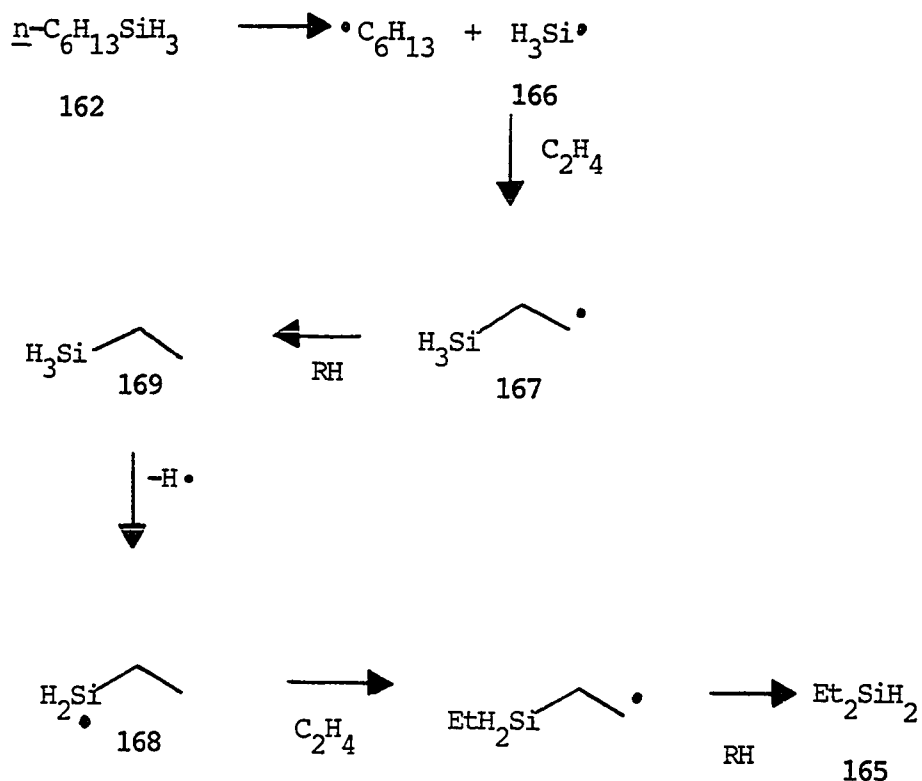
^bNitrogen (N₂), ethene (C₂H₄) or 1,3-butadiene (C₄H₆) carrier gas.

^cSample dissolved in diluent for nitrogen or ethene flow pyrolyses, I = cyclohexane, II = toluene (molar excess of diluent in parentheses). Butadiene pyrolyses used no diluent. Run 9, III = 26 mol % 1-hexene added.

^dFound by ¹H NMR to be a 1.1/1.0 ratio of E-2-hexene/3-hexenes.

^eIndeterminable because toluene and 162 coeluted on capillary GLC column used for yield determinations.

^fYields reported as percent of 162 plus added 1-hexene.

Scheme 32a

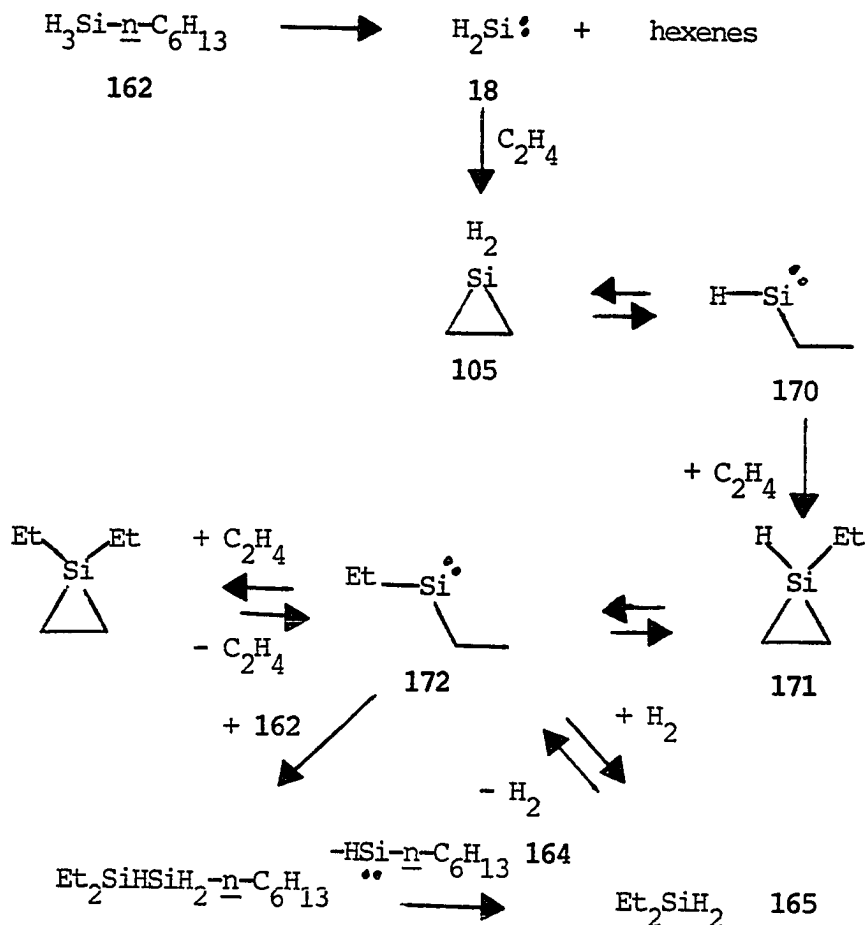
hydrogen loss in the resulting ethylsilane 169. Continuation of this process by addition of a second molecule of ethene to radical 168 leads to the observed 165.

Although they reported that radical chains were involved in the pyrolysis of methylsilane (35), Neudorfl and Strausz found that silyl radical formation occurred via Si-H and not Si-C bond homolysis. In their experiments, pyrolysis of 32 with added ethene resulted in methylethyl-

silane formation. No ethylsilane was reported. Based on these literature results, copyrolysis of 162 with ethene should afford hexylethylsilane, which was not found. An alternative silylene mechanism to explain the formation of 165 is presented in Scheme 32b. Silylene 18, formed from the decomposition of 162, may add to ethene; the initially formed silacyclopropane 105 isomerizes to ethylsilylene 170. Addition of a second molecule of ethene to silylene 170 is followed by rearrangement of the silacyclopropane 171 formed to diethylsilylene 172. The product 165 is finally formed either by insertion by 172 into an Si-H bond of unreacted 162 followed by elimination of hexylsilylene 164, or by insertion of silylene 172 into dihydrogen. Insertion of silylene 172 into an Si-H bond is perhaps to be favored over insertion into the dihydrogen bond, since the latter reaction is experimentally unproven to date, although it has been calculated that the insertion of silylene 18 into dihydrogen has an energy of activation of only ca. 6 kcal/mol (25).

Although published after these results were obtained, a scheme similar to Scheme 32b has been proposed by Erwin et al. to explain the formation of di-n-propyl- and iso-propyl-n-propylsilane as products in silane-propene copyrolysis

Scheme 32b



experiments (54). Furthermore, based upon the lack of any characteristic radical fragmentation or coupling products, the authors have concluded that radical processes are not important in the silane pyrolysis in the presence of olefins. Their results are in essential agreement with these dissertation results.

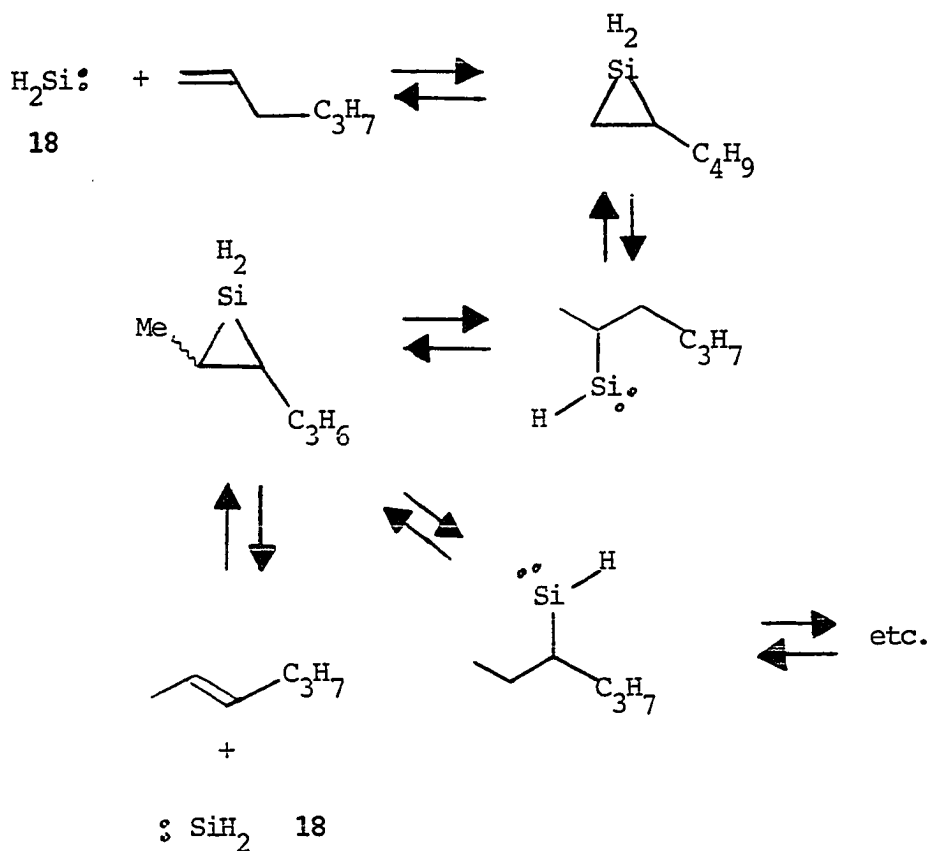
Also apparent from Table 12 is the lack of any significant effect of toluene addition (a radical chain inhibitor [36, 92], used as a diluent in place of cyclohexane) on either the nitrogen or the ethene flow pyrolysis yields.

The copyrolysis of n-butyldimethylsilane 174 (93) with 1-hexene provided a model system to test for radical processes. If radicals are formed in the pyrolysis of 162 by Si-H, S-C, or C-C bond homolysis, they should also occur, without silylene formation, in the pyrolysis of 174. When 174 (1.54 mmol) was copyrolyzed with 1-hexene (1.74 mmol) under nitrogen flow conditions at 575°C no isomerization of the 1-hexene was detected. Compound 174 was recovered unchanged in 57% yield, and 1-hexene was recovered in 42% yield.

The effect of possible bimolecular silylene chains was investigated by pyrolyzing 162 in a stream of butadiene carrier gas, an excellent silylene trap, at 585°C (Table 12, Run 8). A dramatic change in relative yields was found compared with the nitrogen flow and ethene flow yields; the relative yields of 1-hexene (9%) and 2- and 3-hexenes (8% combined) approach the FVP value for 162 (17% and 15% respectively, vide supra). Therefore it appears that under gas flow conditions in the absence of silylene trapping

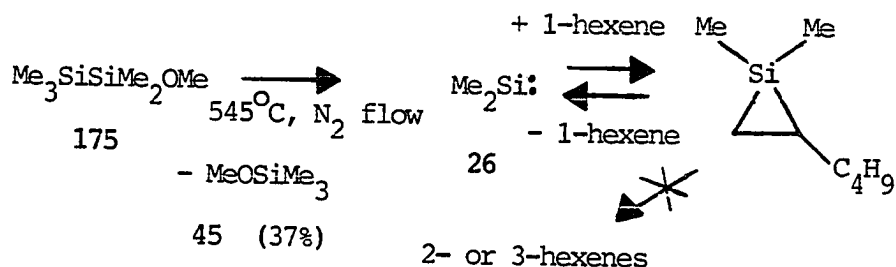
agents bimolecular silylene-alkene reactions do in fact occur, resulting in olefin isomerization. Since silylenes are known to react with alkenes to form silacyclopropanes (see Historical section), this process may be written as occurring through reversible silylene-alkene reaction coupled with the alkylsilylene-silacyclopropane isomerization (Scheme 33).

Scheme 33



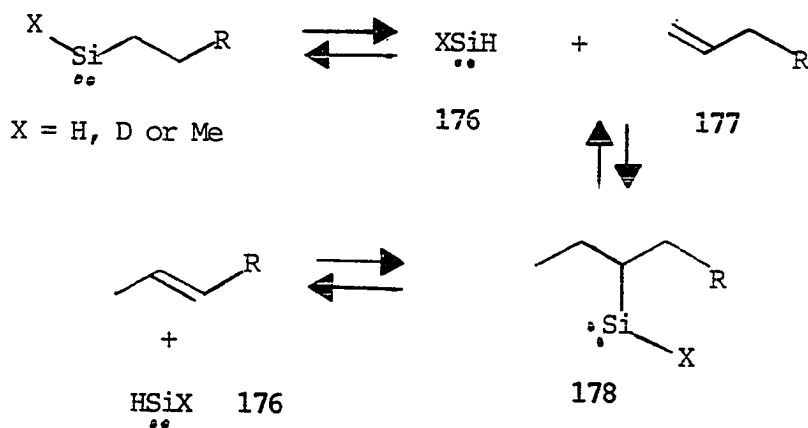
Also found in the copyrolysis of 162 and butadiene was a product identified by MS and ^1H NMR as 1-pentene. The mass spectrum and capillary GLC retention time matched that of a product also tentatively identified in the FVP of 162 as 1-pentene (vide supra).

As a control experiment, dimethylsilylene 26 generator methoxypentamethyldisilane 175 (0.899 mol) was copyrolyzed with 1-hexene (1.02 mol) at 545°C . Recovered in 46% yield was 1-hexene, with GLC analysis showing that isomeric 2- and 3-hexenes, if formed, were present in < 3% yield. Also produced was methoxytrimethylsilane 45 in 37% yield. Starting material 175 was recovered in 21% yield. Therefore it is apparent that any isomerization of alkenes arising from bimolecular silylene reactions is unique to hydrido-silylenes. If dimethylsilylene 26 reacts with 1-hexene under these conditions, the silacyclopropane formed must merely revert to 26 and 1-hexene, without isomerization of the hexene.



As discussed in the Historical section, Erwin et al. have suggested, on the basis of thermodynamic considerations, that the decomposition of alkylsilylenes to alkenes proceeds in a concerted fashion, and that no silacyclopropane may be involved (54). This proposed mechanism, if true, would explain our results, including deuterium scrambling and isomeric alkene formation, according to the process diagrammed in Scheme 34. Direct decomposition of an alkylsilylene (X = H, D or Me) forms silylene 176 and 1-alkene 177. Scrambling and double bond isomerization could occur by the reverse of this process, "hydrosilation" of the initially formed alkene 177 by silylene 176, which could occur with incorporation of silicon on C₂ of the alkene forming species such as alkylsilylene 178.

Scheme 34



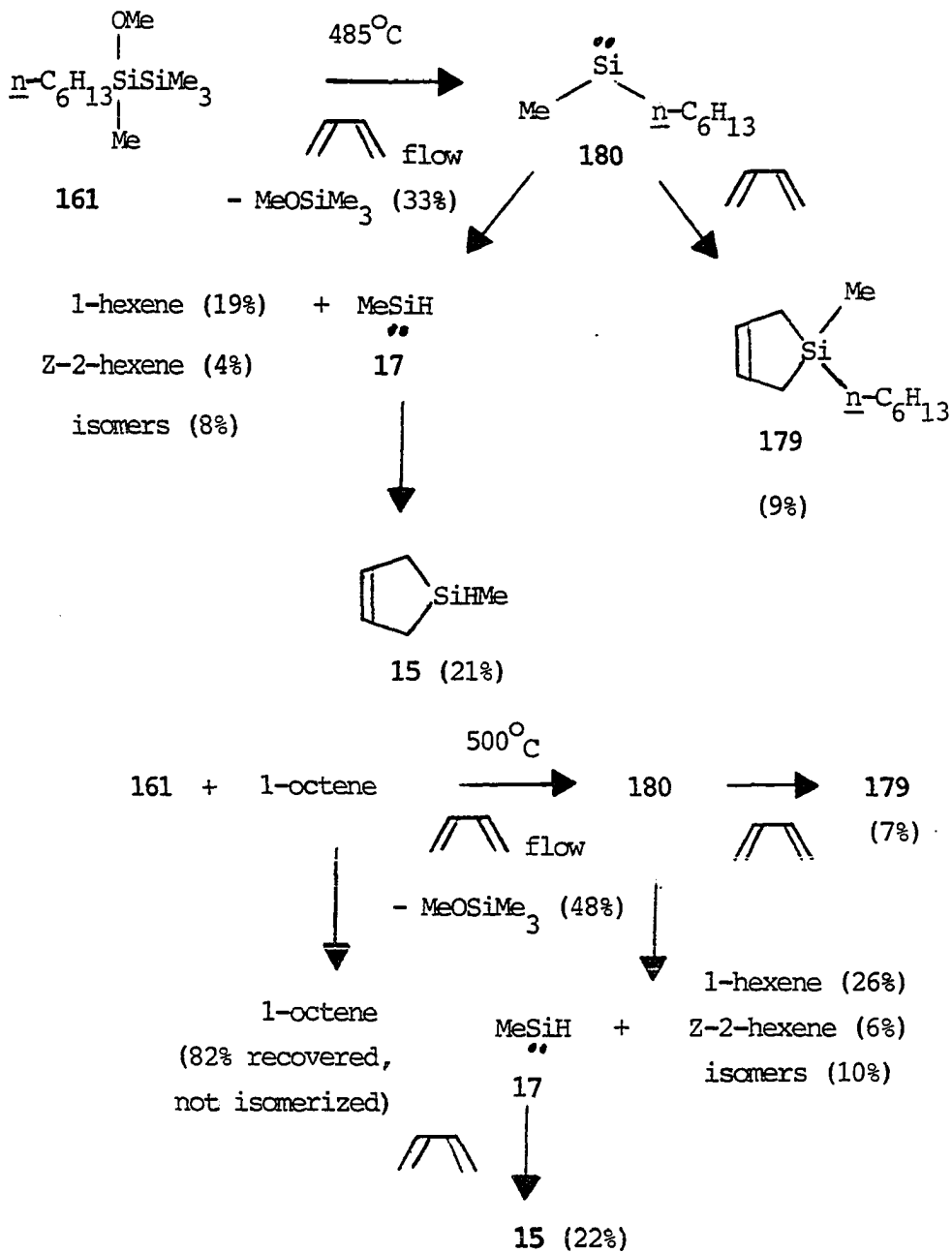
Whether the mechanism of Scheme 34 is exclusively responsible for the scrambling and isomerization reactions discussed in this section can be tested by demonstrating that olefin isomerization occurs under conditions where bimolecular reactions have been completely suppressed. The copyrolysis of 162 in butadiene appears to meet this condition. When 162 was spiked with 26 mol % 1-hexene and pyrolyzed in a stream of butadiene at 585°C (Table 12, Run 9), a 40% decrease in the ratio of total 2- and 3-hexene yields to the 1-hexene yield was observed (based on total moles of 162 and 1-hexene used). If hexylsilylene 164 formed 1-hexene exclusively and the isomeric hexenes arose entirely via bimolecular chain processes (Scheme 34), then the added 1-hexene would be indistinguishable from the hexene formed from 164, and the yield ratio would be expected to change very little. In a qualitative sense, this does not appear to be the case.

A more unambiguous test was provided by the copyrolysis of 1-hexyl-1-methoxy-1,2,2,2-tetramethyldisilane 161 with butadiene and added 1-octene. The results are summarized in Scheme 35. Without 1-octene added, copyrolysis of 161 in a stream of 1,3-butadiene (485°C) afforded as products methoxytrimethylsilane 45 (33%), 1-methyl-1-silacyclopent-3-ene 15 (methylsilylene 17 adduct, 21%), 179, the trapping

product of hexylmethylsilylene 180 (9%), as well as the hexene products 1-hexene (19%), Z-2-hexene (4%), and a mixture of E-2-hexene/3-hexenes in a 4/1 ratio (8%). Compound 161 was recovered in 28% yield. When the pyrolysis of 161 in butadiene was repeated (1.44 mol, 500°C) with 1-octene (0.77 mol) added, the relative yields of products derived from 161 were insignificantly changed, and the 1-octene was recovered without isomerization. ¹H NMR analysis of the 1-octene, isolated by preparative GLC, and a thorough analysis of the pyrolysate by GC-MS failed to disclose the presence any isomers of 1-octene. It was also established that pyrolysis of 1-octene under these conditions in a stream of butadiene did not result in any isomerization or fragmentation to hexene. This result demands that there must be a unimolecular pathway for the formation of 2- and 3-hexenes from 161.

In summary, the research described in this section has demonstrated that the pyrolysis of alkyl silylenes (of carbon chain length C_n), generated from a variety of precursors, affords mixtures of isomeric C_n-alkenes. Deuterium incorporation and scrambling in the alkenes occurs when 1-deuterioalkylsilylenes are generated. These phenomena are postulated to arise from a process which occurs even under conditions where radical or silylene chain reac-

Scheme 35



tions are suppressed. Hence a unimolecular rearrangement is demanded, which is most economically explained as the result of a silylene-silacyclopropane isomerization reaction (Scheme 36). The product alkenes could either be formed directly from alkylsilylenes (path a, dashed arrows Scheme 36), or from silacyclopropane intermediates (path b). The data in this dissertation do not allow a distinction to be made between these pathways, although the latter route is favored based upon the literature, which has conclusively demonstrated that silacyclopropanes thermally decompose at low temperatures to silylenes and alkenes.

These results have also found additional evidence that under some gas phase pyrolysis conditions the decomposition of silacyclopropanes to alkenes and smaller silylenes is reversible, i.e., that silylenes react with olefins more readily than has been believed in the past. It appears from this work that 1-hydridosilylenes may react with alkenes resulting in positional double bond isomerization of the olefin. However, in this research this problem was not directly addressed, and further research involving copyrolyses of hydridosilylene generators and alkenes is therefore suggested.

The decomposition of alkylsilylenes via β -C-H

insertion appears to occur exclusively in preference to γ -, δ -, or ϵ -C-H insertion (paths c, d, and e, Scheme 36), which would produce silacyclobutanes, silacyclopentanes, or silacyclohexanes, respectively, none of which appeared to have ever been formed by alkylsilylenes in this research.

Finally, the data produced by the generation of alkylsilylenes has allowed no additional conclusions to be made regarding the controversial and interesting question (12, 13) of the silylene-silene isomerization via 1,2-H shift (which may be regarded as an " α -C-H insertion," path f).

CONCLUSION

A thorough study of 1,1-dideuterio-1-silacyclobutane 12-d₂ and 1-deuterio-1-methyl-1-silacyclobutane 90-d₁ has established that such silacyclobutanes thermally yield propene via an initial C-D, α -elimination (1,2-deuterium shift). Propene is formed from either 12-d₂ or 90-d₁ under FVP conditions (at ca. 700°C) with predominant incorporation of deuterium (e.g., 21% d₀, 59% d₁, and 18% d₂ from 12-d₂). Trapping experiments verified that the silylene 18 (H₂Si:) produced in the propene-forming pathway is deuterated in a complimentary fashion (30% d₀, 53% d₁, and 17% d₂) to the propene. Positional scrambling of the label in the propene was also observed.

When alkylsilylenes were independently generated from known thermal silylene precursors, 1-deuterioalkylsilylenes afforded deuterated alkenes, and alkylsilylenes with C₄ or longer carbon chains yielded isomeric n-alkene product mixtures. A unimolecular silylene rearrangement process was implicated based upon the results of pyrolyzing n-hexylsilane 162 under varied nitrogen, ethene, and butadiene gas flow conditions, and the results from the copyrolysis of 1-methoxy-1-n-hexyl-1,2,2,2-tetramethyldisilane 161 with 1,3-butadiene. The results were found to be in

accord with a proposed alkylsilylene-silacyclopropane isomerization, occurring through a reversible β -C-H silylene insertion reaction. This β -insertion reaction was found to be exclusive in preference to other insertion reactions, since no products which would indicate γ -, δ -, or ϵ -insertion could be detected.

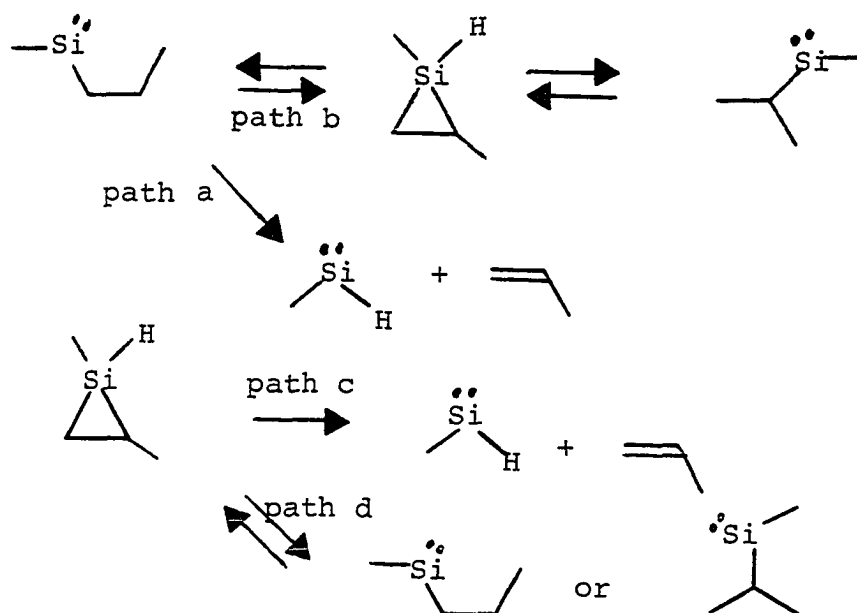
A consideration of the results from the pyrolyses of deuterated silacyclobutanes vs. the results from the pyrolysis of known silylene precursors however points to an unresolved dilemma in this research. The pyrolysis of 12-d₂ resulted in the formation of ca. 18% d₂ propene vs. 59% d₁ propene. This is clearly at odds with what would be predicted based upon the result that 1-deuterio-1-n-propyl-silylene 20-d₁, generated under comparable conditions from the disilane precursor 1-n-propyl-1,1,-dideuterio-2,2,2-trimethyldisilane 153-d₂, afforded 60-62% d₁ propene and 38-40% d₀ propene. Complete consistency of these results would demand the conclusion that either 12-d₂ should form more d₂ than d₁ propene, or 153-d₂ should have produced a much lower ratio of d₁ to d₀ propene. In a similar fashion, although various alkylsilylenes yielded a distribution of n-alkene products, the propene formed in the pyrolysis of 90-d₁ contained deuterium only in the 3-position. A similar double bond isomerization should have

yielded 1-deuteriopropene.

Thus it appears that comparable alkylsilylene intermediates, generated under the similar conditions of temperature and pressure, are giving rise to different product distributions when generated from different precursors. The suggestion therefore deserves consideration that alkylsilylenes produced in the pyrolysis of hydrido-silacyclobutanes vs. alkylsilylenes produced in the pyrolysis of hydrido- or methoxydisilanes may react from energetically different states. Two suggestions seem reasonable: (a) that an alkylsilylene may decompose via competitive pathways either directly to an alkene and a simpler silylene (path a, Scheme 37), or through a silacyclopropane intermediate (path b), the partitioning between the two pathways being dependent upon the internal energy (electronic or vibrational) of the silylene, and (b) that the silacyclopropane intermediate will either decompose to a silylene and an alkene (path c) or isomerize to an alkylsilylene (path d), with the relative rates of the two processes being dependent upon the internal energy of the silacyclopropane. In either case, the differences in the product yields must be related to the initially formed state of the alkylsilylene involved.

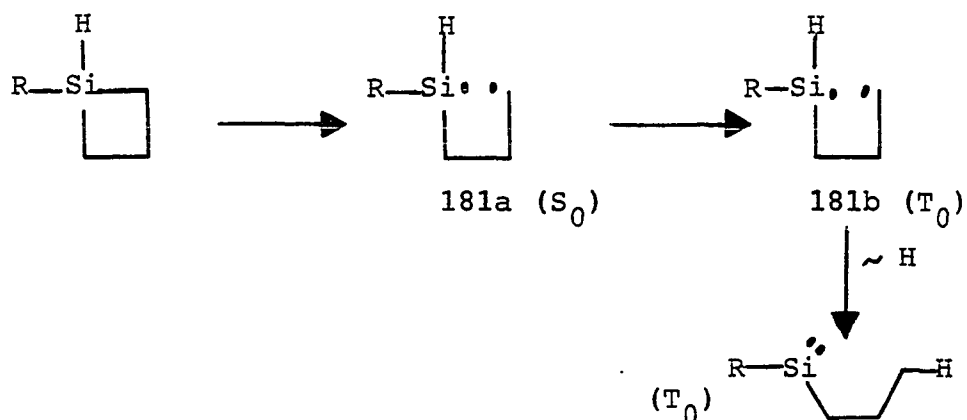
Experimental work and theoretical calculations have

Scheme 37



found the first excited singlet state (1B_1) of silylene 18 to lie some 44-50 kcal/mol above the singlet ground state, which is unlikely to be significantly changed by mere substitution of a propyl group (94). Clearly the energetic requirements for formation of this state are too high. The lowest triplet state, on the other hand, lies in a much more accessible range (15-20 kcal/mol) (94, 95). The initial thermal formation of a triplet silylene from a disilanyl precursor is spin-forbidden, although it could be envisaged as resulting from a stepwise decomposition of a hydridosilacyclobutane (Scheme 38).

Scheme 38

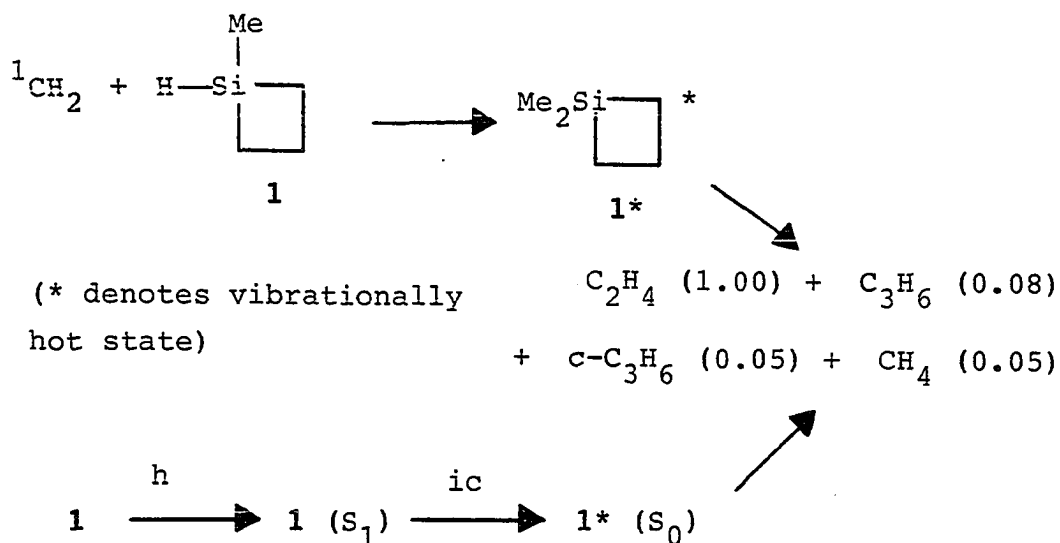


However nothing is now known regarding the relative energetics of such 1,4-silicon-carbon diradicals as 181a and 181b. This mechanism is also in conflict with the fact that silylene-forming eliminations are generally molecular in nature, including the elimination of methane from methylsilane (see Historical section) which appears to occur as a concerted, single step process (34).

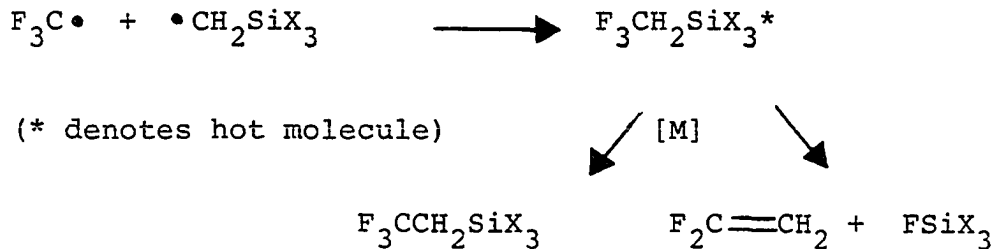
Another possibility is that an alkylsilylene formed from either hydrosilacyclobutane decomposition or one from a disilanyl precursor might be formed as a vibrationally excited, "hot" silylene showing distinctive reactivity patterns. Hot intermediates have been proposed to explain apparently anomalous results in the case of 1,4-diradicals (96, 97), thermal decompositions of strained ring systems (98-101), and the photolysis of cyclobutanones (102), to

name just a few examples. In organosilicon chemistry, dimethylsilacyclobutane **1** formed by chemical activation by insertion of singlet methylene into the Si-H bond of 1-methyl-1-silacyclobutane **90** shows, in common with the normal pyrolysis of **1**, predominant ethene formation, but, in addition, an approximately 15% yield of other products, including propene, cyclopropane, and methane, is also formed. The product distribution in this experiment is strikingly similar to that observed in the direct photolysis of **1**, and therefore both chemical activation and photolysis were postulated to result in a common, vibrationally excited intermediate **1*** (Scheme 39) (103).

Scheme 39



Another example from organosilicon chemistry may be found in the decomposition of hot β -trifluoromethylsilanes $F_3CCH_2SiX_3$ ($X = Me$ or F) formed from the radical recombination of trifluoromethyl and α -silyl radicals (104-106).



A legitimate criticism of this suggestion of a hot silylene is that well-documented cases of hot molecule reactions typically involve formation of the excited species in exothermic processes, usually driven by ring strain relief, chemical activation (as in the insertion of methylene into the Si-H bond of 90 cited above, which is exothermic by ca. 118 kcal/mol), or by internal conversion of a higher energy, photolytically generated intermediate ($S_1 \rightarrow S_0$). All of the silylene-forming reactions discussed in this dissertation are by contrast clearly endothermic.

Therefore further research is in order to explore this question, concentrating on more quantitative investigation of product distributions (including deuterium incorporation) of alkylsilylenes as they are affected by bath

gas pressure (which leads to cooling of hot species by collisional deactivation). For example, if a hot silylene is formed in the decomposition of 1,1-dideuterio-1-silacyclobutane 12, this should be revealed by investigation of the deuterium incorporation in the propene formed as a function of bath gas pressure. Generation of chemically activated 1-deuterio-1-methylsilacyclobutane 90-d₁, and of alkylsilylenes by photolysis or chemical activation, should also lead to interesting extensions of this work.

EXPERIMENTAL

General Procedures for Flash Vacuum Pyrolyses (FVP)

Flash vacuum pyrolyses (FVP) were performed by slowly distilling compounds through a heated, seasoned horizontal quartz pyrolysis tube (16 mm I. D.) packed with quartz chips, and collecting the products in a trap cooled by liquid nitrogen. The tube was evacuated by a Varian oil diffusion pump to ca. 10^{-5} mm Hg. Vacuums were measured by an ion gauge placed behind a liquid nitrogen cooled trap. The pyrolysis of some compounds, especially hydridosilanes, was accompanied by the formation of noncondensables, e.g., dihydrogen. Unless otherwise specified, vacuums quoted represent vacuums measured during the pyrolysis by the ion gauge. The rate of pyrolysis was controlled by attenuating the rate of distillation by either cooling the distilling flask with a $\text{CO}_2(\text{s})/\text{i-PrOH}$ cooling bath or by partially closing a sequence of two greaseless vacuum stopcocks (J. Young and Co.) placed between the distilling flask and the entrance to the hot zone. The rate of pyrolysis was modulated in this fashion to maintain a constant pressure (measured at the ion gauge), typically 10^{-4} to 10^{-3} mm Hg. The rate of distillation of compounds being pyrolyzed was on the order of 0.1 g per hour. In the course of this

work, a 0-10 mm Hg Baratron vacuum gauge was installed to measure the pressure in the reaction zone, placed either immediately before or after the hot zone. Where available, pressures so measured were used to monitor the rate of distillation of the compound being pyrolyzed, and are quoted as "reaction zone pressures", which typically fell in the range 0.050-0.15 mm Hg. The installed gauge was found to show a random variation in the reading of $\pm 2 \times 10^{-3}$ mm Hg. The pyrolysis tube was heated with a Lindberg oven. The reaction zone was approximately 200 mm in length. Temperatures were measured at the center, and were controlled by an Omega CN 300 temperature controller.

Where gaseous products were formed in FVP experiments, the products were collected after emerging from the hot zone, and upon completion of the pyrolysis, distilled into a second trap constructed of a 50 or 100 mL volume round bottom flask attached to a greaseless vacuum stopcock (J. Young and Co.). The gases could be sampled via a gas-tight syringe through a septum, and analyzed by gas chromatography or GCMS (see "Instrumentation", below, this section). If bromine was added to the gas bulb before the products were transferred to it, this setup provided a good method for trapping the volatile alkenes and characterizing them by the dibromides formed.

General Procedures for Flow Pyrolyses

Flow pyrolyses were conducted in a vertical quartz pyrolysis tube packed with seasoned quartz chips. Samples were added to the top of the tube by syringe and the pyrolysate was swept through the quartz tube with a gas flow, typically at a flow rate of 35 mL/min. The products were collected in a dry ice/iso-propanol cooled trap. Temperatures were measured and controlled by an Omega CN 300 temperature controller.

Instrumentation

All proton NMR (^1H NMR) spectra were recorded on a Nicolet Model NT-300 spectrometer (at 300 MHz). Proton chemical shifts are reported as parts-per-million (δ scale) using residual protons from either chloroform-d (δ 7.25) or benzene-d₆ (δ 7.15) as internal standards. ^{13}C NMR spectra were obtained on the NT-300 spectrometer (at 75 MHz), and chemical shifts are reported as parts-per-million (δ scale) using either solvent chloroform-d (δ 77.00) or benzene-d₆ (δ 128.00) as internal standards. ^2H NMR spectra were recorded on a Bruker WM-300 spectrometer (at 46 MHz) in benzene solution, with chemical shifts reported as parts-per-million (δ scale) using natural abundance deuterium in benzene as internal standard (δ 7.15).

Capillary gas chromatographic analyses were performed on either a Hewlett Packard 5890 or 5790 model gas chromatograph using either a 12 m or a 30 m RSL-150 column. Preparative GLC was performed on either a Varian model 920 or 1700 gas chromatograph. Column size and packing will be reported as used.

Chromatography of gas samples was performed using a Fisher Series 4800 gas chromatograph with thermal conductivity (TC) detection. Columns employed were either a 1/8" X 30' 23% SP-1700 on Chromosorb-P-AW column or a 1/8" X 6' Unibeads 2S column. GCMS of gas samples was performed on a Finnegan Model 4023 Gas Chromatograph-Mass Spectrometer using the Unibeads 2S column, unless otherwise specified.

Gas chromatograph mass spectra (GCMS) were recorded on either a Finnegan Model 4023 Gas Chromatograph/Mass Spectrometer or a Hewlett Packard 5970 Mass Selective Detector attached to a a Hewlett Packard 5890 Gas Chromatograph. Exact mass measurements were obtained on either an AEI MS-902 or a Kratos MS-50 Mass Spectrometer. Unless otherwise stated, all measurements were at 70 eV.

Quantitative mass spectra for deuterium analyses were obtained on either the Finnegan 4023 GCMS or a Kratos MS-50 Mass Spectrometer (neat samples), and were recorded at low eV. Corrected ion intensities and percent deuterium values

were calculated by the method of Biemann (83).

Infrared spectra (IR) were recorded on either a Beckmann IR 4250 or an IBM IR 98 (FTIR). Gas chromatograph infrared spectra (GCIR) were obtained on the IBM IR 98 Spectrometer attached to a Hewlett Packard 5880 Gas Chromatograph equipped with a 30 m capillary column. All bands are reported in reciprocal centimeters (cm^{-1}).

Boiling points are reported uncorrected. Elemental Analyses were performed by either MicAnal (Tucson AZ) or Galbraith Laboratories (Knoxville TN).

Unless otherwise specified, all GC yields were calculated using predetermined response factors and are absolute.

Procedures and Results

Synthesis of 1-silacyclobutane, 12 The synthesis of 12 was conducted by a modification of the procedure of Laane (82). 1,1-Dichlorosilacyclobutane (7.1 g, 0.050 mol) was added dropwise via syringe to a stirring slurry of LiAlH_4 (1.13 g, 0.030 mol) in dibutyl ether (50 mL) at -23°C under a nitrogen atmosphere. After the addition the solution was gradually warmed to room temperature and stirred overnight. The product and solvent were then trap-to-trap distilled from 25°C to -78°C under vacuum

(increased gradually from 50 mm Hg to full oil pump vacuum). Final distillation through a 5" X 1/2" fractionating column packed with glass helices afforded 2.4 g (0.032 mol, 67%) of 12, bp. 43-45°C. Final purification was achieved by preparative GLC (20' 20% SE-30 on Chromosorb W, 60°C isothermal).

Synthesis of 1,1-dideuterio-1-silacyclobutane, 12-d₂

Compound 12-d₂ (82) was prepared according to the procedure described for 12, except that LiAlD₄ was used in place of LiAlH₄. In a typical preparation, 4.0 g (0.028 mol) of 1,1-dichloro-1-silacyclobutane was reduced with 1.0 g LiAlD₄ in 50 mL of dibutyl ether and 1.3 g (0.017 mol, 61%) of 12-d₂ were obtained. Final purification was obtained by preparative GLC. ¹H NMR analysis of the product obtained indicated that quantitative deuteration was obtained: ¹H NMR (C₆D₆) δ 1.02 (t, J = 8 Hz, 4.0H), 2.12 (pentet, J = 8 Hz, 2.0H). Only a very small silyl hydride could be detected at δ 4.66 (m, ~0.01H). MS 76 (1.9), 75 (5.0), 74 (65.1), 73 (19.3), 72 (22.6), 71 (10.9), 70 (7.5), 47 (12.2), 46 (100.0), 45 (87.8), 44 (69.7), 43 (27.9), 42 (17.0). ²H NMR (C₆H₆) showed only a silyl deuteride at δ 4.67.

FVP of 1-silacyclobutane, 12 A total of 0.4352 g (6.04 mmol) of 12 were slowly distilled through a horizontal quartz-packed pyrolysis tube at 710°C at 5×10^{-4} mm Hg, and the products collected at -196°C. Warming the pyrolysate to 25°C was accompanied by considerable effervescence. After liberation of the gases, the remaining pyrolysate (0.0690 g, 15% mass recovery) was analyzed by GC and GCMS, containing mostly unreacted 12 (8%), identified by ^1H NMR after isolation by preparative GLC (20' 20% SE-30 on Chromosorb W, 60°C isothermal).

FVP of 1-silacyclobutane 12 and trapping of products in bromine The pyrolysis of 12 was repeated as described above. The pyrolysate, initially trapped in a liquid nitrogen cooled trap, was distilled under vacuum into a gas bulb cooled to -196°C fitted with a greaseless vacuum stopcock containing a 2-fold molar excess of bromine. After standing overnight the bromine solution was dissolved in 50 mL methylene chloride and washed with saturated sodium sulfite in 1/1 methanol/water until the bromine color was removed, then twice with 100 mL water. After drying (MgSO_4) the solvent was removed by rotary evaporation and the yellow residue extracted into 1.5 mL hexane. Analysis by capillary GLC indicated the formation of 1,2-dibromoethane (139) (Run 1 47%, Run 2 41%) and 1,2-

dibromopropane (140) (Run 1 11%, Run 2 13%).

FVP of 1,1-dideuterio-1-silacyclobutane, 12-d₂

Flash vacuum pyrolyses of 12-d₂ were conducted by slowly distilling the compound (typical scale: 0.2545 g, 3.44 mmol) through a horizontal quartz-packed pyrolysis tube at 710°C and collecting the products at -196°C. During the pyrolysis the vacuum rose from an initial value of 2×10^{-5} mm Hg, indicating the formation of non-condensables (e.g., dihydrogen), and the rate of distillation was controlled by cooling the sample of 12-d₂ with a dry ice/i-PrOH bath to maintain a constant pressure (measured at the ion gauge) of 10^{-4} to 10^{-3} mm Hg. Warming of the collected pyrolysate to room temperature resulted in considerable effervescence. After liberation of the gases, the remaining liquid, representing 38% and 43% mass recovery in two runs, was analyzed by capillary GLC and GCMS, and found to consist of a single major component (> 90%), identified as recovered starting material. The recovered, deuterated 12 was isolated by preparative GLC (20' 20% SE-30 on Chromosorb W, 60°C isothermal). Analysis by ²H NMR showed only a silyl deuteride resonance at δ 4.67 (C₆H₆). Analysis by ¹H NMR showed some silyl hydride formation, with integration values of 0.14 H and 0.16H for the two runs, representing 7% and 8% deuterium exchange (as silyl hydride formation)

respectively.

The pyrolysis was repeated as described above, however the gases were collected and analyzed. GC and GCMS of the gaseous sample (18 eV) identified ethene as the major component, along with propene in lesser amounts. Observed ion intensities for the ethene and propene, and calculated deuterium incorporations for the ethene and propene are presented in Table 2. The calculation of the % deuterium incorporation, discussed in the Results and Discussion section, was performed by the method of Biemann (83). GLC of the gas sample, using literature TC response factors (87), afforded an estimate of the relative yields of propene and ethene as 86 mol % ethene and 14 mol % propene.

GCMS of the gases also detected another major component, base peak $m/e = 46$, possibly deuterated methylsilane, MS (18 eV) 50 (2.9), 49 (18.8), 48 (51.1), 47 (72.4), 46 (100.0), 45 (43.7), 44 (11.9), 31 (16.5). Found in minor amounts were what may be deuterated silane 23, MS (18 eV) 35 (2.6), 34 (40.0), 33 (45.3), 32 (100.0), 31 (68.4), 30 (19.8), and deuterated dimethylsilane 34, MS (18 eV) 65 (3.9), 64 (19.6), 63 (60.9), 62 (96.2), 61 (100.0), 60 (75.1), 59 (25.0), 49 (14.5), 48 (40.0), 47 (59.2), 46 (75.2), 45 (41.9).

FVP of 1,1-dideuterio-1-silacyclobutane 12-d₂ and trapping of products in bromine. The FVP of 12-d₂ (0.6008 g, 8.12 mmol) was repeated at 710°C as described above and the products were trapped at -196°C. The pyrolysate was distilled into a gas collection flask at -196°C which contained excess bromine (3.3 g, 21 mmol). After warming to room temperature and sitting overnight, the contents were extracted into methylene chloride (50 mL) and washed with saturated sodium sulfite in 1/1 methanol/water until the bromine color disappeared, and then washed twice with 100 mL of water. After drying (MgSO₄) the solvent was removed by rotary evaporation to leave a yellow oil which was extracted into 1.5 mL hexane. The solution was analyzed by capillary GLC and GCMS, and the products were isolated by preparative GLC (15' 15% SE-30 on Chromosorb W, 100°C isothermal). Only two significant products were detected, identified as 1,2-dibromoethane 139 (55%) and 1,2-dibromopropane 140 (10%) by comparison of GC, GCMS, and ¹H NMR spectra with authentic samples. Deuterium incorporation was determined by measurement of mass spectral ion intensities and calculated by the method of Biemann (83). Mass spectral data along with per cent deuterium incorporation results and yield data are summarized in Table 3.

Spectral characteristics for the 1,2-dibromopropane 140 formed were as follows: ^1H NMR (C_6D_6) δ 1.27-1.37 (m, 3H), 2.92 (t, $J = 10$ Hz, 1H), 3.22 (d of d $J = 10$ Hz, $J' = 4$ Hz, 1H), 3.54-3.66 (m, 1H). This matched an authentic sample of undeuterated 1,2-dibromopropane with the exception of the multiplet centered at δ 1.32 which was a doublet ($J = 6.5$ Hz) in the undeuterated sample. ^2H NMR (C_6H_6) δ 1.26 (m, deuteriums on methyl group), 2.89 (m) and 3.18 (m) (both diastereotopic methylene deuteriums), 3.54 (m, methine deuterium). Relative integration of the deuterium signals and distribution of deuterium in the dibromopropane are shown in Table 4. The results of two runs are shown. Run 1 and Run 2 of Tables 3 and 4 correspond. The deuterium spectrum of the dibromopropane formed (Run 1) is reproduced in Fig. 1.

Synthesis of 1-deuterio-1-methyl-1-silacyclobutane

90-d₁ Compound 90-d₁ was prepared by a method similar to that described for 1,1-dideuteriosilacyclobutane 12-d₂ (107). In a typical procedure 4.0 g of 1-chloro-1-methyl-1-silacyclobutane (0.033 mol) was added dropwise via syringe to a stirring slurry of LiAlD_4 (0.50 g, 0.012 mol) in 35 mL dry dibutyl ether at -23°C under nitrogen atmosphere. After stirring for 1 h at -23°C the solution was warmed to room temperature and stirred overnight. Trap-to-trap dis-

tillation (25°C to -78°C under vacuum) afforded a solution of 90-d₁ in Bu₂O free of LiAlD₄. Fractional distillation at 1 atm pressure through a 6" X 1/2" column packed with glass helices yielded 2.0 g (0.023 mol, 69%) product, bpt. 64-5°C. Final purification was achieved by preparative GLC (10' 10% SE-30 on Chromosorb W, 60°C isothermal). The following spectral characteristics were recorded: ¹H NMR (C₆D₆) δ 0.15 (s, 3H), 0.80-1.00 (m, 2H), 1.06-1.22 (m, 2H), 1.96-2.27 (m, 2H), (there was no trace of silyl hydride by ¹H NMR); IR (neat) 2970 (s), 2930 (s), 2860 (w), 2120 (vw) (residual SiH), 1540 (s) (Si-D), 1390 (w), 1245 (m), 1115 (m), 865 (m), 780 (m) cm⁻¹; MS 87 (25), 60 (12), 59 (100), 58 (45), 46 (16), 45 (51), 43 (71), 41 (12).

FVP of 1-deuterio-1-methyl-1-silacyclobutane 90-d1

Compound 90-d₁ (0.081 g, 0.931 mmol) was distilled through a horizontal quartz-packed pyrolysis tube at 710°C at a pressure of 5 X 10⁻⁴ mm Hg. The pyrolysate was collected in a liquid nitrogen cooled trap and then distilled under vacuum into a gas collection flask. Analysis by GCMS (70 eV) indicated the presence of deuterated ethene (< 10% deuteration), MS 30 (0.8), 29 (10.7), 28 (100.0), 27 (67.0), 26 (66.9), 25 (10.0), 24 (2.7); reference (un-deuterated) ethene, run at the same time and conditions, MS 30 (0.0), 29 (2.0), 28 (100.0), 27 (46.9), 26 (48.2), 25

(7.2), 24 (1.9). Also detected in a much smaller amount was deuterated propene, MS (70 eV) 44 (3.3), 43 (48.0), 42 (100.0), 41 (76.5), 40 (45.8), 39 (62.5), 38 (18.0), 37 (10.6), 36 (1.9); reference propene run at the same time and conditions had the following MS: 43 (2.6), 42 (69.3), 41 (100.0), 40 (25.7), 39 (72.2), 38 (18.0), 37 (10.9), 28 (3.9), 27 (40.7), 26 (10.4). The deuterated propene peak in the GCMS was contaminated with unidentified impurities, therefore the mass spectral ion intensities of the propene in this experiment are admittedly uncertain, and the deuteration results obtained by bromination (vide infra) provide better quantitation.

FVP of 1-deuterio-1-methylsilacyclobutane 90-d₁ and trapping of products in bromine Compound 90-d₁ (0.7241 g, 8.33 mmol) was slowly distilled through a horizontal quartz-packed pyrolysis tube at 710°C, pressure 5 X 10⁻⁴ mm Hg, and the products initially trapped in a liquid nitrogen cooled trap. The pyrolysate was distilled under vacuum into a gas collection flask containing excess bromine (2.0 g, 12.5 mmol). After warming to 25°C the products were allowed to sit 2 h, then dissolved in 50 mL methylene chloride and washed with saturated sodium sulfite in 1/1 methanol/water until the bromine color was removed. The organic phase was washed with 3 X 75 mL water, dried

(MgSO_4), and the solvent removed by rotary evaporation to leave a yellow oil which was extracted into 1 mL of hexane. Analysis by capillary GLC and GCMS was used to identify 1,2-dibromoethane 139 (29%) and 1,2-dibromopropane (140 1%). The 140 formed was isolated by preparative GLC. The ^2H NMR (Fig. 2) of the 140 showed a single peak at δ 1.26 (s). Very small resonances at ca. δ 3.0, 3.3, and 3.6 may be present (integrating to \leq 15% of the methyl deuteride resonance at δ 1.26) which may belong to the 140, however, the sample obtained was too dilute (only milligram quantities of 140 could be isolated) to allow any definite assignment of these faint signals, even after a 10,000 scan accumulation. The mass spectra of the 139 and 140 formed was obtained at low eV (21-25 eV), and ion intensities, corrected ion intensities, and percent deuterium results are presented in Table 5.

Preparation of 3-deuteriopropene, 142 A total of 19.5 g (0.161 mol) of allyl bromide in 200 mL dry ether were dropwise added under nitrogen at a rate sufficient to maintain a gentle reflux to a stirring slurry of Mg (5.0 g, 0.21 mol) in which the reaction had been initiated with a crystal of iodine and 0.5 g (0.004 mol) of allyl bromide. After the addition was complete the solution was refluxed an additional 2 h. After cooling to room temperature the

Grignard reagent was quenched by a dropwise addition of D_2O . The gas thus liberated was passed through an ethylene glycol/dry ice cooled condenser and a calcium sulfate drying tube and was frozen in a liquid nitrogen cooled trap. The trap containing the frozen propene was isolated from the reaction setup, evacuated to less than 1 mm Hg, and the gas formed was condensed into a steel gas cylinder at $-196^\circ C$, keeping the trap cooled to $-78^\circ C$ to minimize contamination by trace ether or other impurities. Obtained was 1.7 g (23%) propene.

Preparation of 1,2-dibromo-3-deuteriopropene 140-d1

The preparation of 3-deuteriopropene was repeated as described above, except that the propene generated was passed through liquid bromine (10 mL) instead of the $-196^\circ C$ trap. The bromine solution containing the product was extracted into pentane and washed with saturated sodium sulfite in 1/1 methanol/water until the bromine color was removed. The organic phase was washed twice with 100 mL water, dried ($MgSO_4$) and rotary evaporated to leave 6.1 g (0.030 mol, 35%) of nearly pure product, characterized as 1,2-dibromo-3-deuteriopropene by its spectral characteristics. An analytical sample was isolated by preparative GLC (15' 15% SE-30 on Chromosorb W, 100 C isothermal). 2H NMR (C_6D_6) δ 1.31 (d of t where triplet is 1:1:1, $J_{H-H} = 6.5$ Hz,

$J_{\text{D-H}} = 2.0 \text{ Hz}$, 2H), 2.96 (app. t, $J = 10.0 \text{ Hz}$, 1H), 3.25 (d of d, $J = 10.0 \text{ Hz}$, $J' = 4.4 \text{ Hz}$, 1H), 3.61 (m, app. sextet, 1H); ^{13}C NMR (C_6D_6) δ 23.70 (t, $J_{\text{D-C}} = 19.3 \text{ Hz}$), 37.78, 45.93; ^2H NMR (C_6H_6) δ 1.30 (m). The following mass spectral ion intensities were used to calculate percent deuterium incorporation (Finnegan 4023 GCMS, 18 eV): 200 (2.28) (M+), 201 (51.26), 202 (6.11), 203 (100.00), 204 (5.46), 205 (46.97), 206 (1.63); reference (undeuterated) 1,2-dibromopropane, MS 200 (M+) (52.46), 201 (2.79), 202 (100.00), 203 (4.24), 204 (47.94), 205 (1.89), 206 (0.27). A calculation of percent deuterium incorporation by the method of Biemann (83) gives 96% d_1 and 4% d_0 .

Pyrolysis of 3-deuteriopropene 142 Compound 142

(50 mL at STP) was passed through a horizontal quartz packed pyrolysis tube at 10^{-3} mm Hg at 720°C and the products were collected in a liquid nitrogen cooled trap. The product was distilled into a gas collection flask containing 0.25 mL of bromine at -196°C . After warming to room temperature the products were extracted into methylene chloride, washed with saturated sodium sulfite in 1/1 methanol/water until the bromine color was removed, then washed with water, dried, and rotary evaporated. A yellow oil remained which contained 1,2-dibromopropane as the major product. A sample isolated by preparative GLC had ^1H

NMR, ^{13}C NMR, and ^2H NMR spectral characteristics identical with 1,2-dibromo-3-deuteriopropene prepared by direct bromination of 3-deuteriopropene. The following mass spectral ion intensities were obtained (Finnegan GCMS, 18 eV): 200 (3.82), 201 (52.70), 202 (8.10), 203 (100.00), 204 (5.44), 205 (49.46), 206 (2.32); reference (undeuterated) 1,2-dibromopropene 200 (52.67) (M+), 201 (0.69), 202 (100.00), 203 (2.10), 204 (48.54), 205 (1.73), 206 (0.15). A calculation of percent deuterium incorporation by the method of Biemann (83) indicates the product is 93% d_1 and 7% d_0 . Considering the percent deuteration of dibromopropene prepared directly from 3-deuteriopropene, there is a 97% retention of the deuterium label in the pyrolyzed 3-deuteriopropene.

Copyrolysis of 1-silacyclobutane 12 with 2,3-dimethylbutadiene 119 Compound 12, dissolved in a 4- to 6-fold molar excess of 2,3-dimethylbutadiene, was dropwise added via syringe to a vertical quartz-packed pyrolysis tube swept with a nitrogen flow of 35 mL/min. In three runs, over the temperature range 520-570 $^{\circ}\text{C}$, no 12 was recovered. Mass recoveries ranged from 54-61%.

Capillary GLC, GCMS, and ^1H NMR of samples isolated by preparative GLC (20' 20 % SE-30 on Chromosorb W, 50 $^{\circ}\text{C}$ initial, 4 $^{\circ}$ ramp) identified 3 major products: 3,4-di-

methyl-1-silacyclohex-3-ene 143, 1,3,4-trimethyl-1-silacyclopent-3-ene 144, and 3,4-dimethyl-1-silacyclopent-3-ene 145. Yields for these products are included in Table 6. All efforts at preparative GLC failed to achieve highly purified samples of 144 and 145, and ^1H NMR identification was made by comparison of the spectra with those of authentic samples of 144 and 145 obtained by independent synthesis (vide infra). A fourth product was detected by GCMS in only trace amounts, the mass spectrum of which matched that of a sample of 3,4-dimethyl-1-n-propyl-1-silacyclopent-3-ene 146, obtained by independent synthesis (vide infra).

Compound 143 was identified by its spectral characteristics: ^1H NMR (C_6D_6) δ 0.72 (m, 2H, collapses to t, $J = 3.5$ Hz, with hv at δ 1.98, and to t, $J = 6.8$ Hz, with hv at δ 3.89), 1.28 (broad s, 2H), 1.59 (s, 3H), 1.64 (s, 3H), 1.98 (t, $J = 6.8$ Hz, 2H, collapses to s with hv at 0.72), 3.89 (app. pentet, collapses to t, $J = 3.5$ Hz, with hv at 1.28, and to t, $J = 3.0$ Hz, with hv at 0.72); ^{13}C NMR (C_6D_6) δ 3.95, 13.36, 20.90, 22.39, 29.83, 124.82, 129.96; IR (neat) 2930, 2905, 2850, 2140 (vs) (Si-H), 945 (vs), 855 (s) cm^{-1} ; MS 126 (M⁺) (72), 125 (15), 111 (72), 98 (53), 97 (85), 85 (32), 84 (78), 83 (100), 71 (33), 70 (49), 69 (37), 67 (44), 59 (37), 58 (32), 55 (59), 53 (38); calc'd

for $C_7H_{14}Si$ m/e 126.0865, measured m/e 126.0865. Anal.
Calc'd for $C_7H_{14}Si$: C, 66.58; H, 11.17. Found: C, 66.41;
H, 11.36.

Synthesis of 1,3,4-trimethyl-1-silacyclopent-3-ene,
144 1-Chloro-1,3,4-trimethyl-1-silacyclopent-3-ene 182
was prepared as an intermediate by copolymerizing 19.3 g of a
solution of mixed chloromethyldisilanes (high boiling
residue from the direct synthesis of methylchlorosilanes,
supplied by Dow Corning Co., consisting of approximately
15% 1,2-dichlorotetramethyldisilane, 30% 1,1,2-trichloro-
trimethyldisilane, and 30% 1,1,2,2-tetrachlorodimethyl-
disilane by uncorrected GCMS response) dissolved in 35.6 g
(0.434 mol) of 2,3-dimethylbutadiene by rapid dropwise
addition of the solution to a vertical quartz-packed pyro-
lysis tube at 625°C swept with nitrogen flow at 50 mL/min.
The products were collected at -78°C and distilled at 1 atm
pressure to remove volatiles. Vacuum distillation (60 mm
Hg through a 4" X 1/2" glass helices fractionating column)
afforded a continuous fraction boiling from 83-96°C, 8.4 g.
Capillary GLC analysis showed the distillate to contain 4.2
g of the desired 182 (0.026 mol). Preparative GLC afforded
an analytical sample of 182, with the following spectral
characteristics: 1H NMR ($CDCl_3$) δ 0.58 (s, 3H), 1.58 (d,
J = 14 Hz, 2H), 1.67 (d, J = 14 Hz, 2H), 1.71 (s, 6H,

overlaps with smaller peak of d at 1.67); ^{13}C NMR (CDCl_3) δ 1.21, 18.91, 27.48, 129.72; IR (neat) 2980, 2915, 2880, 1440, 1390, 1255 (s), 1175 (s), 805 (s), 785 (s) cm^{-1} ; MS 162 (36), 160 (100) (M^+), 147 (34), 145 (97), 124 (48), 118 (35), 109 (64), 105 (30), 79 (29), 59 (42); calc'd for $\text{C}_7\text{H}_{13}\text{ClSi}$ m/e 160.04751, measured m/e 160.04747.

Compound 144 was obtained by adding 2.0 g of this distillate containing 182 (1.0 g, 6.2 mmol) dropwise to a stirring slurry of LiAlH_4 (0.25 g, 6.4 mmol) in 4 mL THF at -23°C . After warming to 25°C and stirring overnight, the solution was trap-to-trap distilled (25°C to -78°C) under vacuum to remove it from the LiAlH_4 and the resulting solution contained 0.281 g of 144, (2.23 mmol, 36% based on 182). Final purification was achieved by preparative GLC. The following spectral characteristics were found: ^1H NMR (C_6D_6) δ 0.06 (d, $J = 3.5$ Hz, 3H), 1.28 (d, $J = 18$ Hz, 2H), 1.57 (d, $J = 18$ Hz, 2H), 1.66 (s, 6H, partially overlaps smaller peak of d at 1.57), 4.35 (m, 1H); ^{13}C NMR (C_6D_6) δ -4.15, 19.90, 23.72, 131.34; IR (neat) 2978, 2876, 2131 (s) (Si-H), 1443, 1250, 1175, 889, 829, 806, 748 cm^{-1} ; MS 126 (48) (M^+), 125 (15), 111 (100), 109 (32), 85 (23), 84 (27), 83 (44), 71 (19), 69 (24), 67 (17), 59 (40), 58 (31), 55 (18); calc'd for $\text{C}_7\text{H}_{14}\text{Si}$ m/e 126.08648, measured m/e 126.08628. Anal. Calc'd for $\text{C}_7\text{H}_{14}\text{Si}$: C, 66.58; H, 11.17.

Found: C, 66.65; H, 11.51.

Preparation of 3,4-dimethyl-1-silacyclopent-3-ene, 145

A solution containing 1,1-dichloro-3,4-dimethyl-1-silacyclopent-3-ene 183 was prepared by dropwise addition of 16.4 g of hexachlorodisilane (0.61 mol) dissolved in 30.4 g (0.37 mol) 2,3-dimethylbutadiene 119 to a vertical quartz-packed pyrolysis tube at 610°C swept with a nitrogen flow of 60 mL/min. The products were collected in a -78°C trap and distilled at 1 atm pressure to remove unreacted butadiene and other volatile products. Vacuum distillation at 30 mm Hg through a 4" X 1/2" fractionating column packed with glass helices yielded a continuous fraction with the boiling range 82-90°C, 8.9 g, of approximately 85% pure product (by capillary GLC, uncorrected FID response). An analytical sample of 183 was obtained by preparative GLC (14' 15% SE-30 on Chromosorb W, 100°C initial, 8°/min ramp). Spectral characteristics found were: ^1H NMR (C_6D_6) δ 1.36 (s, 6H), 1.55 (s, 4H); ^{13}C NMR (C_6D_6) δ 18.49, 29.08, 129.28; IR (neat) 2980, 2905 (s), 2845, 1445 (s), 1390 (s), 1370, 1165 (vs), 1105, 970, 780 (vs), 760 (vs), 745 (vs), 685 cm^{-1} ; MS 182 (10), 180 (15) (M^+), 167 (9), 165 (14), 144 (13), 140 (7), 138 (10), 129 (13), 82 (50), 81 (14), 67 (100), 65 (23), 63 (44), 54 (24), 53 (20); calc'd for $\text{C}_6\text{H}_{10}\text{Cl}_2\text{Si}$ m/e 179.99289, measured m/e 179.99290.

This solution of 183 (1.0 g) was then added dropwise (neat) to a stirring slurry of LiAlH_4 (0.15 g, 3.95 mmol) in 5 mls THF under nitrogen atmosphere at -23°C . After the addition, the solution was warmed to room temperature and stirred overnight. The solution was trap-to-trap distilled under vacuum from 25°C to a -78°C trap. Analysis by capillary GLC showed the distilled solution to contain 0.407 g of 145 (3.64 mmol, 53% based on hexachloro-disilane). Final purification was achieved by preparative GLC (14' 15% SE-30, 70°C initial, $8^\circ/\text{min}$ ramp). Compound 145 had the following spectral characteristics: ^1H NMR (C_6D_6) δ 1.43 (broad s, 4H), 1.59 (s, 6H), 4.04 (pentet, $J = 3.7$ Hz, collapses to s with hv at 1.43); ^{13}C NMR (C_6D_6) δ 19.11, 19.16, 131.00; IR (neat) 2950, 2900 (s), 2880 (s), 2850 (s), 2850, 2130 (vs) (Si-H), 1435, 1165 (s), 940 (vs), 895, 805 (vs), 790 (vs) cm^{-1} ; MS 112 (81) (M^+), 111 (40), 97 (100), 95 (46), 84 (38), 83 (43), 71 (34), 70 (54), 69 (48), 67 (39), 55 (81), 53 (35); calc'd for $\text{C}_6\text{H}_{12}\text{Si}$ m/e 112.07083, measured m/e 112.07116. Anal. Calc'd for $\text{C}_6\text{H}_{12}\text{Si}$: C, 64.20; H, 10.79. Found: C, 63.92; H, 11.03.

Synthesis of 3,4-dimethyl-1-n-propyl-1-silacyclopent-3-ene, 146 1-Chloro-1-n-propyl-3,4-dimethyl-1-silacyclopent-3-ene 184 was first prepared by adding 1.75 g (14.2 mmol) of n-propyl bromide dropwise as a neat solution

via syringe over 20 min to a stirring slurry of 0.50 g (72 mmol) Li in 25 mL ether under argon atmosphere with wire whip stirring. After the addition the solution was stirred an additional 0.5 h, and the anion was transferred dropwise over 30 min via canula to a stirring solution of 2.57 g of approximately 85% pure 1,1-dichloro-3,4-dimethyl-1-silacyclopent-3-ene 183, the preparation of which is described in the synthesis of 145 (vide supra), in 50 mL ether at -78°C . After the transfer the solution was warmed to 25°C and stirred overnight. Precipitated salts were filtered through celite/sintered glass and the ether removed by distillation. The residue was trap-to-trap distilled, under vacuum with gentle heating, to a -78°C trap. The distillate was found to contain 0.503 g of 184 by capillary GLC yield (2.67 mmol, 15% overall yield from hexachloro-disilane). Final purification of the 184 was achieved by preparative GLC (12' 12% QF-1-0065 on Chromosorb W, 160°C isothermal) to afford 0.262 g pure 184; ^1H NMR (C_6D_6) δ 0.79 (t, $J = 8$ Hz, collapses to s with hv at 1.39, 2H), 0.87 (t, $J = 7.3$ Hz, collapses to s with hv at 1.39, 3H), 1.39 (m, app. sextet, $J = 8$ Hz, 2H, overlaps s at 1.45), 1.45 (broad s, 2H, overlaps 1.39), 1.58 (s, 6H, overlaps 1.62), 1.62 (broad s, 2H); ^{13}C NMR (C_6D_6) δ 17.20, 17.47, 18.95, 19.54, 26.59, 129.96; MS 190 (20), 188 (56) (M^+),

147 (37), 146 (32), 145 (100), 131 (20), 110 (24), 109 (27), 63 (35); calc'd for $C_9H_{17}ClSi$ m/e 188.07881, measured m/e 188.07887.

Compound 184 (0.261 g, 1.38 mmol) was dropwise added neat via syringe to a stirring slurry of $LiAlH_4$ (0.082 g, 2.2 mmol) in 2 mL THF under nitrogen at $-23^\circ C$. The solution was warmed to $25^\circ C$ and stirred overnight. Trap-to-trap distillation ($25^\circ C$ to $-78^\circ C$) under vacuum gave a solution containing 0.141 g product 146 (0.91 mmol, 66% GLC yield). Final purification was achieved by preparative GLC (14' 15% SE-30 of Chromosorb W, 60° initial, $4^\circ/min$ ramp). Compound 146 had the following spectral characteristics: 1H NMR (C_6D_6) δ 0.61 (t of d, collapses to t, $J = 7.8$ Hz, with hv at 4.31, and to d, $J = 3.0$ Hz, with hv at 1.40, 2H), 0.93 (t, $J = 7.3$ Hz, collapses to s with hv at 1.40, 3H), 1.25-1.45 (overlapping multiplets, including half of AB pattern characteristic of silacyclopentene allylic ring protons, and the two methylene protons of the propyl group, 4H), 1.56 (d of broadened peaks, other half of AB pattern, $J = 18$ Hz, collapses to s with hv at 1.40, peaks sharpen with hv at 4.31, 2H), 4.31 (m, app. septet, $J = 3.2$ Hz, collapses to pentet, $J = 3.2$ Hz, with hv at 0.61, and to broad s with hv at 1.40, 1H); ^{13}C NMR (C_6D_6) δ 14.92, 17.84, 18.45, 19.33, 21.73, 130.08; IR (neat) 2960 (s), 2905 (s),

2865 (s), 2110 (s) (Si-H), 1165 (s), 845 (s) cm^{-1} ; MS 154 (57) (M⁺), 112 (39), 111 (100), 109 (25), 97 (37), 69 (21), 67 (23); calc'd for $\text{C}_9\text{H}_{18}\text{Si}$ m/e 154.1178, measured m/e 154.1183. Anal. Calc'd for $\text{C}_9\text{H}_{18}\text{Si}$: C, 70.05; H, 11.76. Found: C, 69.95; H, 11.91.

Copyrolysis of 1,1-dideuterio-1-silacyclobutane 12-d₂
with 2,3-dimethyl-1,3-butadiene 119 The procedure followed as closely as possible that described for the copyrolysis of 12 with 2,3-dimethyl-1,3-butadiene. Compound 12-d₂, dissolved in a 4.7- to 6.2-fold molar excess of the butadiene, was added dropwise via syringe drive to a vertical quartz-packed pyrolysis tube swept with a nitrogen flow of 35 mL/min and the products were collected at -78°C. The pyrolysis was repeated three times over the temperature range 520-540°C, and once at 570°C. Capillary GLC and GCMS indicated the formation of the same products as described in the copyrolysis of 12, although deuterated. Products were isolated by preparative GLC (15' 15% SE-30 on Chromosorb W, 50°C initial, 4°C/min ramp) and identified on the basis of their ¹H NMR, IR, and mass spectral characteristics as deuterated 3,4-dimethyl-1-silacyclohex-3-ene 143, deuterated 1,3,4-trimethyl-1-silacyclopent-3-ene 144, and deuterated 3,4-dimethyl-1-silacyclopent-3-ene 145. Yield data for the products characterized are included in Table

6. Compounds 144 and 145 could not be totally purified by preparative GLC, and impurities in the NMR could not be avoided, although the spectra are clearly distinguishable. Unreacted 12-d₂ was found in only small ($\leq 3\%$) amounts. At higher temperature, as is apparent from Run 7, Table 6 (570°C), the yields of all products dropped precipitously.

Spectral data were obtained from Run 4 (Table 6), unless otherwise noted. ¹H NMR chemical shifts were matched against authentic standards. Mass spectral data (obtained by GCMS because of the difficulty of obtaining adequately pure neat samples of 144 and 145 by preparative GLC) for compounds 143, 144, and 145 and percent deuterium calculations are reported in Table 7.

Recovered starting material (12-d₂) had the following MS data: MS 76 (1.7), 75 (4.6), 74 (49.8), 72 (17.4), 71 (9.7), 70 (8.6), 46 (100.0), 45 (94.0).

Compounds 143-145 had the following spectral properties. For deuterated 143: ¹H NMR (C₆D₆) δ 0.69 (t, J = 6.7 Hz, collapses to s with hv at 1.99, 2H), 1.27 (s, 2H), 1.59 (s, 3H), 1.65 (s, 3H), 1.99 (t, J = 6.7 Hz, collapses to s with hv at 0.69, 2H), a small silyl hydride was found at δ 3.87 (broad s, 0.06 H); ²H NMR (C₆H₆) δ 3.89 (s), no other resonances were found; IR (GC-FTIR) (Run 5, Table 6) 2940 (s), 2865 (m), 2140 (vw) (residual Si-H), 1560 (vs)

(Si-D) cm^{-1} . For deuterated 144: ^1H NMR (C_6D_6) δ 0.07 (m, 2.6H), 1.29 (d, $J = 18$ Hz, 2.0H), 1.58 (d, $J = 18$ Hz, integral undetermined due to unknown impurity), 1.67 (s, 6H), 4.36 (m, apparent sextet, $J = 3.3$ Hz, 0.25H); ^2H NMR (C_6H_6) δ 0.05 (apparent 1:2:1 t, $J_{\text{H-D}} = 2.0$ Hz, 0.79D), 4.37 (s, 1.00D); IR (GC-FTIR) (Run 5, Table 6) 2915 (vs), 2130 (s) (Si-H), 1560 (vs) (Si-D), 1180 (s), 890, 800 (vs) cm^{-1} . The ^1H and ^2H NMR integration data for compound 144 are diagrammed in Fig. 3. For 145 (deuterated): ^1H NMR (C_6D_6) δ 1.43 (s, 4.0H), 1.59 (s 6.0H), 4.04 (pent, $J = 3.8$ Hz, 1.2H); ^2H NMR (C_6H_6) δ 4.04 (Si-D), (no other resonances were found); IR (GC-FTIR) (Run 5, Table 6) 2915 (s), 2130 (vs) (Si-H), 1560 (s) (Si-D) cm^{-1} .

Mass spectra of deuterated samples 143, 144, and 145 were determined at low eV (12 eV, Finnegan 4023 GCMS) and compared with reference spectra of authentic undeuterated compounds determined at the same time and conditions. These results are presented in Table 7. Corrected ion intensities and percent deuterium results were calculated by the method of Biemann (83). For compounds 144 and 145 the large M-1 ion in the reference sample diminishes the accuracy of these calculations and therefore the results quoted are at best close estimates of the true deuterium incorporation.

Synthesis of 1,1-dideuterio-3,4-dimethyl-1-silacyclopent-3-ene, 145c Compound 145c was prepared by the method described for the preparation of 145 (using the 85% pure 183) in 43% overall yield (by GLC) from hexachloro-disilane. Final purification was obtained on a 8' 15% SE-30 on Chromosorb W column, 70°C isothermal. Spectral characteristics were: $^1\text{H NMR}$ (C_6D_6) δ 1.42 (s, 4H), 1.64 (s, 6H), (no Si-H was found); IR (neat) 2985 (m), 2915 (s), 2885 (s), 2860 (s), 2860 (m), 2140 (vw) (residual Si-H), 1560 (vs) (Si-D), 1445 (m), 1175 (s), 765 (s), 735 (s), 680 (vs), cm^{-1} , (the very weak band at 2140 cm^{-1} indicates only a trace of Si-H); MS (10.3 eV, Kratos MS-50, neat sample) 116 (3.8), 115 (11.9), 114 (100.0), 113 (3.6), 112 (1.0). Mass spectral measurements (Kratos MS 50, neat samples) and a calculation by the method of Biemann (83) indicated the product 145c was $\geq 95\%$ d_2 . The MS results with % deuterium calculations are included in Table 8.

Flow pyrolysis of 1,1-dideuterio-3,4-dimethyl-1-silacyclopent-3-ene 145c in excess 2,3-dimethyl-1,3-butadiene 119 A solution of 0.2075 g of 145c (1.82 mmol), dissolved in 1.5990 g (19.5 mmol) of 2,3-dimethyl-1,3-butadiene 119 was slowly added dropwise via syringe drive to a vertical quartz-packed pyrolysis tube at 535°C swept with a nitrogen gas flow of 35 mL/min. The products were col-

lected at -78°C with a 67% mass recovery. The major components of the pyrolysate were recovered starting material (18% GLC yield) and dimethylbutadiene 119 by capillary GLC and GC-MS analysis. Preparative GLC of the recovered, deuterated 145 (8' 15% SE-30 on Chromosorb W, 70°C isothermal) afforded a sample whose spectral characteristics were little changed from unpyrolyzed 145c: ^1H NMR (C_6D_6) δ 1.42 (s, 4H), 1.64 (s, 6H); ^2H NMR (C_6H_6) δ 4.0 (s), no other signals were found; IR (neat) 2985 (m), 2915 (s), 2885 (s), 2860 (m), 2140 (w) (Si-H), 1560 (vs) (Si-D), 1175 (s), 765 (s), 735 (s), 680 (vs) cm^{-1} , the band at 2140 cm^{-1} has increased somewhat in relative intensity relative to unpyrolyzed 145c. The mass spectrum was determined (10.3 eV, Kratos MS-50, neat sample) and ion intensities, corrected ion intensities, and percent deuterium incorporation calculated by the method of Biemann (83) are included in Table 8.

Synthesis of 1-n-propyl-1-methoxy-1,2,2,2-tetramethyl-
disilane, 150 Neat 1-bromopropane (3.26 g, 0.026 mol) was added dropwise via syringe over 20 min to a stirring slurry of 0.80 g (0.115 mol) lithium wire (cut into small pieces) in 40 mL dry ether stirred with a wire whip under argon. After the addition the anion was slowly transferred via canula to a vigorously stirred solution of 4.68 g

(0.025 mol) of 1,1-dichlorotetramethyldisilane 151 (85) in 100 mL ether chilled to -23°C . The solution was warmed to 25°C after the addition and stirred an additional 4 h. Then an equimolar solution (0.27 mol each) of pyridine/methanol was added at once, and stirring was continued for an additional 6 h. Filtration through celite/sintered glass, rotary evaporation of solvent, precipitation of the remaining salts by addition of pentane, and refiltration through celite/sintered glass was followed by rotary evaporation of solvent and vacuum distillation through a 4" X 1/2" fractionation column packed with glass helices to afford 1.50 g product (0.0080 mol, 30%), bp $105-110^{\circ}\text{C}$ at 85 mm Hg. Final purification was achieved by preparative GLC (15' 10% OV-101 on Chromosorb W, 130°C initial, $2^{\circ}/\text{min}$ program). Spectral characteristics found were: ^1H NMR (CDCl_3) δ 0.09 (s, 9H), 0.16 (s, 3H), 0.61-0.81 (m, 2H), 0.967 (t, $J = 7.2$ Hz, 3H), 1.40 (app. sextet, $J = 7.5$ hz, 2H), 3.41 (s, 3H); ^{13}C NMR (CDCl_3) δ -3.10, -1.58, 16.95, 18.16, 19.05, 51.32; IR (neat) 2963 (s), 2897 (s), 2872 (s), 2827 (s), 1456, 1406, 1246 (s), 1088 (s), 955, 866 (s), 756 (s) cm^{-1} ; MS 190 (3.2) (M^+), 175 (5.3), 161 (0.6), 148 (6.3), 147 (17.5), 135 (9.7), 134 (17.1), 133 (100.0), 117 (29.8), 89 (9.6), 75 (71.6), 73 (35.8), 59 (34.7); calc'd for $\text{C}_8\text{H}_{22}\text{OSi}_2$ m/e 190.12100, measured m/e 190.12093. Anal. Calc'd for

$C_8H_{22}OSi_2$: C, 50.45; H, 11.64. Found: C, 50.59; H, 11.93.

FVP of 1-n-propyl-1-methoxy-1,2,2,2-tetramethyl-
disilane, 150 Compound 150 (0.2993 g, 1.57 mmol) was distilled at room temperature through a horizontal quartz-packed pyrolysis tube at 10^{-3} mm Hg pressure heated to $650^{\circ}C$. The products were collected in a liquid nitrogen cooled trap. After the pyrolysis the products were isolated from the hot zone and the vacuum inlet and separated into a liquid fraction and a gaseous fraction by warming the initial trap to $-78^{\circ}C$ under vacuum and condensing the gases thus liberated into a 50 mL gas collection flask at $-196^{\circ}C$. The liquid remaining in the $-78^{\circ}C$ trap (24% mass recovery) consisted almost entirely of a single component (MeOSiMe₃ 45) by capillary GC and GCMS. A thorough search of the GCMS chromatogram failed to disclose the presence of any 1-methyl-1-silacyclobutane 90. Analysis of the gaseous fraction by GCMS (Finnegan 4023 GC/Mass Spectrometer) revealed the major component to be propene on the basis of its mass spectrum (18 eV): MS 44 (0.6), 43 (4.1), 42 (100), 41 (63.2), 40 (16.9), 39 (9.5), 28 (1.0), 27 (8.5), 26 (0.7). Also identified by GCMS were ethene, in only a trace ($\leq 1\%$ of propene) amount, MS 29 (2.6), 28 (100.0), 27 (3.8), a compound which may be methylsilane

(estimated as ca. 23% of propene by uncorrected GCMS total ion current), MS 47 (2.1), 46 (7.3), 45 (62.6), 44 (100.0), 43 (8.6), 31 (5.6), 30 (19.5), a small amount (\leq 10% of propene by uncorrected GCMS total ion current) of a compound which may be dimethylsilane, MS 61 (3.3), 60 (10.2), 59 (100.0), 58 (89.5), 57 (2.5), 47 (1.1), 46 (4.3), 45 (40.7), 44 (64.4), 43 (9.3), 31 (6.5), and a trace of trimethylsilane, MS 75 (2.8), 74 (6.3), 73 (74.2), 61 (3.3), 60 (8.3), 59 (100.0), 58 (31.8), 45 (3.7), 31 (3.6).

Copyrolysis of 1-n-propyl-1-methoxy-1,2,2,2-tetra-
methylsilane 150 and 2,3-dimethyl-1,3-butadiene 119 A
solution of 0.5264 g 150 (3.19 mmol) in 1.42 g 2,3-di-
methyl-1,3-butadiene 119 (17.3 mmol) was dropwise added via
syringe drive over 1 h to a seasoned vertical quartz-packed
pyrolysis tube at 540°C swept with a nitrogen flow of 35
mL/min. The products were collected in a dry ice/iso-
propanol cooled trap (74% mass recovery). The major
products were isolated by preparative GLC (12' 12% SE-30 on
Chromosorb W, 70°C initial, 10°/min program) and identified
as MeOSiMe₃ 45 (49%), 1,3,4-trimethyl-1-silacyclopent-3-ene
144 (46%, spectral data matches authentic sample indepen-
dently prepared, vide supra), 1-n-propyl-1,3,4-trimethyl-1-
silacyclopent-3-ene 152 (2%), and recovered 150 (4%).

Compound 152 could not be purified completely by preparative GLC, however ^1H NMR and ^{13}C NMR spectra contained all resonances found in a sample of 152 prepared by independent methods (vide infra), and the GCMS of this compound was found to match exactly.

Synthesis of 1-n-propyl-1,3,4-trimethyl-1-silacyclopent-3-ene, 152 1,1-Dichloro-1-methyl-1-n-propylsilane (108) (6.00 g, 0.038 mol) was stirred with 5.00 g 2,3-dimethyl-1,3-butadiene 119 in 30 mL dry HMPA and 1.0 g Mg turnings (0.041 mol) under nitrogen at 80°C for 5 days. The solution was then dissolved in pentane and washed with dilute HCl (aq.) to remove HMPA, then several times with water. After drying (MgSO_4) and filtering the solvent was removed by rotary evaporation to leave 1.25 g of a very heavy oil containing 0.319 g (5% yield) of product. No further attempt was made to maximize the yield. Preparative GLC (15'15% SE-30 on Chromosorb W, 70°C initial, $10^\circ/\text{min}$. ramp) afforded pure product. Spectral characteristics found were: ^1H NMR (C_6D_6) δ 0.09 (s, 3H), 0.58 (t, $J = 8.0$ Hz, 2H), 0.95 (t, $J = 7.3$ Hz, 3H), 1.23-1.46 (overlapping m, 6H, including an AB system, H_A at 1.29, H_B at 1.35, $J_{\text{AB}} = 18$ Hz apparently overlapping with 2H of the propyl group), 1.93 (s, 6H); ^{13}C NMR (C_6D_6) δ -2.43, 17.71, 18.02, 18.32, 19.42, 24.69, 130.75; IR (neat) 2961 (vs),

2922 (s), 2872 (s), 1443 (w), 1250 (m), 1175 (s), 825 (s), 816 (s), 775 (m) cm^{-1} ; MS 168 (M+) (39), 153 (3), 126 (29), 125 (100), 123 (23), 111 (43), 109 (14), 97 (20), 85 (17), 83 (22), 59 (67); calc'd for $\text{C}_{10}\text{H}_{20}\text{Si}$ m/e 168.13343, measured m/e 168.13316. Anal. Calc'd for $\text{C}_{10}\text{H}_{20}\text{Si}$: C, 71.34; H, 11.97. Found: C, 71.60; H, 11.78.

Preparation of 1,1,1-trimethyl-2-n-propyldisilane, 153

1,1-Dichloro-1-n-propyl-2,2,2-trimethyldisilane 155 was prepared from 1,1,1-trichlorotrimethyldisilane 154 (86) and 1-bromopropane by slowly adding 1-bromopropane (3.75 g, 0.0305 mol) dissolved in 60 mL dry ether to a stirring slurry of Mg (1.00 g, 0.0411 mol) and 0.25 g of 1-bromopropane (total moles 0.0325, 4.00 g) under N_2 atmosphere in which the Grignard reaction had been initiated with a crystal of iodine. The addition was done at a rate sufficient to maintain a gentle reflux. After the addition the solution was stirred at room temperature for 5 h. The Grignard was transferred via canula and dropwise added to a stirring solution of 154 (6.74 g, 0.0325 mmol) in 50 mL ether at -78°C . The solution was gradually warmed to 25°C by stopping the addition of dry ice to the iso-propanol/dry ice cooling bath. After stirring overnight at room temperature, 50 mL pentane were added and the solution was filtered through celite/sintered glass. The solvents were

removed by distillation and the product removed from the remaining salts by trap-to-trap distillation (25°C to -78°C under vacuum). Distillation through a 4" X 1/2" fractionating column packed with glass helices (considerable foaming of the distillate was noted) at 65 mm Hg afforded a continuous fraction, bp 110-115°C, 2.2 g (0.010 mol, 31%), of 155. An analytical sample isolated by preparative GLC (15' 15% SE-30 on Chromosorb W) gave satisfactory spectral properties: ^1H NMR (CDCl_3) δ 0.24 (s, 9H), 1.02 (t, $J = 7.3$ Hz, 3H), 1.15 (t, $J = 8$ Hz, 2H), 1.55 (m, app. sextet, $J = 7.5$ Hz, 2H); ^{13}C NMR (CDCl_3) δ -3.01, 16.14, 17.34, 24.67; MS 216 (0.8), 214 (1.2) (M+), 201 (0.3), 199 (0.4), 159 (1.2), 157 (1.8), 93 (3.0), 74 (9.0), 73 (100.0), 72 (2.2), 65 (2.0), 63 (2.8), 59 (7.4), 58 (2.1); calc'd for $\text{C}_6\text{H}_{16}\text{Cl}_2\text{Si}_2$ m/e 214.01677, measured m/e 214.01619. The procedure described above proved very difficult to reproduce and generally much lower yields were obtained.

A total of 1.10 g of compound 155 was added neat at a dropwise rate via syringe to a stirring slurry of 0.200 g LiAlH_4 in 3 mL THF under nitrogen atmosphere at -23°C. Trap-to-trap distillation (25°C to -78°C under vacuum, 0.25 torr) gave a solution containing 0.272 g of 153 by GLC yield (1.86 mmol, 36% from 155, 12% overall from 154). Final purification was accomplished by preparative GLC (15'

15% SE-30 on Chromosorb W, 70°C initial, 6°/min ramp).

Compound 153 had the following spectral characteristics:

^1H NMR (C_6D_6) δ 0.13 (s, 9H), 0.65-0.75 (m, collapses to t, 0.69, $J = 8$ Hz, with $h\nu$ at 3.63, 2H), 0.95 (t, $J = 7.3$ Hz, 3H), 1.44 (m, app. sextet, $J = 7.5$ Hz, 2H), 3.63 (t, $J = 4.5$ Hz, 2H, collapses to s with $h\nu$ at 0.69); ^{13}C NMR (C_6D_6) δ -0.76, 9.36, 17.55, 21.47; IR (neat) 2955 (s), 2925, 2895, 2870, 2095 (vs) (Si-H), 1240 (s), 925, 830 (s), 770 (s) cm^{-1} ; MS 146 (7) (M^+), 131 (1), 103 (7), 102 (3), 89 (7), 74 (12), 73 (100), 59 (11); calc'd for $\text{C}_6\text{H}_{18}\text{Si}_2$ m/e 146.09741, measured m/e 146.09492. Anal. Calc'd for $\text{C}_6\text{H}_{18}\text{Si}_2$: C, 49.23; H, 12.39. Found: C, 48.69; H, 12.74.

Synthesis of 1,1-dideuterio-1-n-propyltrimethyl-
disilane, 153-d₂ Compound 153-d₂ was prepared according to the procedure described above for 153 with LiAlD_4 used instead of LiAlH_4 . The yield was 11% (by GLC) overall from 1,1,1-trichlorotrimethyldisilane 154. A sample isolated by preparative GLC showed spectral properties consistent with quantitative deuteration: ^1H NMR (C_6D_6) δ 0.13 (s, 9H), 0.68 (t, $J = 8$ Hz, 2H), 0.94 (t, $J = 7.3$ Hz, 3H), 1.44 (m, app. sextet, $J = 7.5$ Hz), (no silyl hydride was detectable); IR (neat) 2950 (vs), 2920, 2885, 2860, 1530 (vs) (Si-D), 1240, 1060, 850, 825, 795, 730, 715, 680, 655 cm^{-1} ; MS 148 (4) (M^+), 105 (2), 104 (2), 103 (1), 102 (2), 91

(4), 90 (2), 75 (4), 74 (10), 73 (100), 72 (3), 71 (1), 69 (1), 60 (5), 59 (5), 58 (2). The ^1H NMR and IR results indicate that quantitative deuteration was obtained.

FVP of 1-n-propyl-2,2,2-trimethyldisilane, 153

Compound 153 (0.1020 g, 0.699 mmol) was slowly distilled through a seasoned horizontal quartz-packed pyrolysis tube at 710°C , 10^{-3} mm Hg pressure. The products were collected in a liquid nitrogen cooled trap and then distilled into a gas collection flask. The gases collected were analyzed by GLC on a 30' 23% SP-1700 on Chromosorb P-AW column at 60°C . Comparison of retention times with authentic samples of ethene and propene indicated the formation of propene, with ethene present in at most trace amounts ($\leq 3\%$ relative to propene).

The pyrolysis was repeated as described above, except that the gases formed were distilled into a gas collection bulb containing excess bromine. After warming to room temperature and standing overnight the bromine solution was dissolved in 50 mL pentane, washed with saturated sodium sulfite in 1/1 methanol/water until the bromine was removed, then three times with 75 mL water, dried, and rotary evaporated. The clear residue remaining was found to contain 1,2-dibromopropane in 71% GLC yield.

FVP of 1,1-dideuterio-1-n-propyltrimethyldisilane,

153-d₂ The pyrolysis of 153-d₂ was conducted as described for 153 at 710°C, pressure 3 X 10⁻³ mm Hg. Analysis of the gases formed by GCMS indicated the formation of primarily monodeuterated propene, MS (18eV) 45 (3.6), 44 (21.3), 43 (100.0), 42 (54.4), 41 (8.2), 40 (2.3). Undeuterated propene reference, run at same time and conditions had the following MS: 44 (0.08), 43 (4.5), 42 (100.0), 41 (17.6), 40 (4.0). If the contribution of the d₁ species to the M+ (m/e = 42) ion in the deuterated propene is estimated as 17.6 (from the M-1 intensity in the reference propene), a calculation by the method of Biemann (83) affords an estimate of the sample composition as 24% d₀, 65% d₁, and 11% d₂ propene. Also found was only a trace of ethene (< 1% relative to propene), apparently highly deuterated: MS 30 (23.4), 29 (96.5), 28 (100.0), 27 (10.8), 26 (7.4).

At 700°C, 153-d₂ is completely decomposed. The pyrolysis was repeated at 500°C, 6 X 10⁻⁵ mm Hg pressure (reaction zone pressure measured by a Baratron gauge was 0.1 mm Hg), and the products were collected in a liquid nitrogen cooled trap. An effervescent pyrolysate was obtained, which was immediately dissolved in decalin to facilitate recovery. Capillary GLC and GCMS indicated two

major components were present, identified as deuterated trimethylsilane (70%) and undecomposed starting material (19%). Spectral characteristics determined were: trimethylsilane, ^1H NMR (C_6D_6) δ 0.00 (s, 9.00 H), only a trace of silyl hydride at 4.19 (m, $\leq 0.10\text{H}$); ^2H NMR (C_6H_6) δ 4.19 (s) (no other signals were found). Recovered starting material (153-d₂) matched the ^1H NMR spectrum of unpyrolyzed material, except that a trace of silyl hydride appears to have been formed: δ 3.63 (m, $\leq 0.10\text{H}$). ^2H NMR of pyrolyzed 153-d₂ showed only a silyl deuteride at δ 3.63 (s).

FVP of 1,1-dideuterio-1-n-propyltrimethyldisilane, 153-d₂, and trapping of products in bromine The procedure described above for the FVP of 153-d₂ was repeated (with 0.0504 g 153-d₂, 0.340 mmol), and the products were distilled into a 50 mL round bottom flask equipped with a greaseless vacuum stopcock containing an excess of bromine. The products were worked up by extracting into methylene chloride, washing with sat'd sodium sulfite in 1/1 MeOH/water to remove the excess bromine, drying (MgSO_4), and removal of solvent by rotary evaporation. The residue contained 1,2-dibromopropane in 83% yield. The dibromopropane was isolated by preparative GLC (15' 20% QF-1-0065 on GasChrom Q, 120°C, isothermal). Per-

cent deuterium incorporation was calculated from mass spectral ion intensities; the data are presented in Table 9. The ^2H NMR (Fig. 4) showed the following signals, with integrated intensities in arbitrary units (C_6H_6): δ 1.06-1.40 (unresolved m, 100 counts, methyl group), 2.75-2.98 (m, 30 counts) and 3.05-3.26 (m, 29 counts) (diastereotopic methylene deuteriums), 3.41-3.73 (m, 45 counts, methine deuterium). From the integrated intensities the relative deuterium distribution may be estimated as 29% at C_1 , 22% at C_2 , and 49% at C_3 (numbering by IUPAC nomenclature).

FVP of 1-n-butyl-1-methoxy-1,2,2,2-tetramethyldisilane

157 Compound 157 (47) was slowly distilled through a horizontal quartz packed pyrolysis tube at 2×10^{-4} mm Hg at 708°C and the products were collected in a liquid nitrogen cooled trap. At the conclusion of the pyrolysis the products were distilled in vacuo into a 100 mL gas collection flask at -196°C . The gaseous products were characterized by gas chromatography and GCMS. Identifications were based on mass spectra at 18 eV, and the relative product abundances were determined by peak areas (triangulation) obtained on a Fischer Model 4800 Gas Chromatograph equipped with a 30' 23% SP-1700 on Chromosorb-P-AW column, and were adjusted using literature response factors (87) for the

butenes. The products were identified (with relative amounts in parentheses) as: 1-butene (49 parts), MS 57 (5.1), 56 (93.4), 55 (27.5), 42 (4.5), 41 (100.0), 40 (8.0), 39 (10.7); E-2-butene (31 parts), MS 57 (4.6), 56 (100.0), 55 (16.2), 42 (2.3), 41 (67.2), 40 (4.5), 39 (8.1); Z-2-butene (20 parts), MS 57 (4.9), 56 (100.0), 55 (16.8), 54 (12.8), 53 (4.2), 41 (66.8), 40 (5.3), 39 (14.4). The distinction between the butenes was made by comparison of the GLC retention times on the two columns employed with authentic samples of 1-butene and Z-2-butene. Also found in significant amounts was a gas identified as methylsilane 32 (approximately 24 parts, uncorrected) by its mass spectrum: MS 47 (2.3), 46 (7.6), 45 (66.6), 44 (100.0), 43 (10.3), 31 (5.5), 30 (18.0). Methoxytrimethylsilane 45, the expected elimination product of 157, was identified in the gas sample by its mass spectrum (approximately 17 parts, uncorrected). Found in only very small amounts were ethene (< 1 part), propene (< 1 part), and products affording mass spectra suggesting dimethylsilane 34 (< 2 parts) and trimethylsilane (< 2 parts). Repetition of the experiment at 560°C at 2×10^{-4} mm Hg (reaction zone pressure < 0.06 mm Hg) yielded the same products in similar relative yields: 1-butene (36 parts), E-2-butene (41 parts), Z-2-butene (23 parts), methylsilane (24 parts,

uncorrected), methoxytrimethylsilane 45 (84 parts, uncorrected).

Additional confirmation of the product identities was provided by bromination of the pyrolysate. The pyrolysis was repeated with 0.3398 g 157 (1.67 mmol) at 703°C, 4×10^{-5} mm Hg, the products collected at -196°C and distilled into a gas collection flask at -196°C containing 0.80 g (5.0 mmol) bromine. After warming and standing for several hours the bromine solution was dissolved in 50 mL methylene chloride, washed with sat'd sodium sulfite in 1/1 methanol/water until colorless, then twice with 75 mL water. After drying (MgSO_4) the organic phase was filtered and rotary evaporated to leave a yellow oil, which was extracted into ca. 1.5 mL hexane. Capillary GLC analysis showed there to be three major products present, which could be separated by preparative GLC into two peaks. The first peak ("A") was found to be a mixture of two products, identified as meso- and dl-2,3-dibromobutane. The major isomer (26% GLC yield) had the following spectral properties: ^1H NMR (C_6D_6) δ 1.40-1.49 (mult., 6H), 3.55-3.70 (mult., 2H); ^{13}C NMR (C_6D_6) δ 25.13, 54.16; MS 218 (0.3), 216 (0.6), 214 (0.3) (M+), 137 (42.5), 135 (42.4), 109 (6.4), 107 (7.3), 73 (12.9), 55 (100.0). The minor isomer (19% GLC yield) had the spectral properties: ^1H NMR (C_6D_6) δ

1.36 (d, $J = 6.7$ Hz, 6H), 3.80-3.91 (mult. 2H); ^{13}C NMR (C_6D_6) δ 20.80, 52.71; MS 218 (0.5), 216 (0.1), 214 (0.6) (M+), 137 (42.9), 135 (44.3), 109 (6.8), 107 (7.5), 55 (100.0). It was not determined which isomer was meso and which was dl, however presumably the major isomer is meso because it would be formed from E-2-butene, which was present in the gaseous samples in relatively larger amounts than the Z-isomer. The other peak ("B") was isolated by preparative GLC (same column and conditions) and identified as pure 1,2-dibromobutane (21% GLC yield) on the basis of the following spectral properties: ^1H NMR (C_6D_6) δ 0.71 (t, $J = 7.2$ Hz, 3H), 1.42 (app. sextet, $J = 7.5$ Hz, 1H), 1.65-1.80 (mult., 1H), 3.08 (apparent t, $J = 9.9$ Hz, 1H), 3.27 (d of d, $J = 10$ Hz, $J' = 4.6$ Hz, 1H), 3.58 (mult., 1H); ^{13}C NMR (C_6D_6) δ 10.97, 29.27, 35.81, 54.64; MS 218 (0.14), 216 (0.31), 214 (0.13) (M+), 137 (37.7), 135 (38.1), 55 (100.0). The ^1H and ^{13}C NMR and the mass spectrum of the 1,2-dibromobutane match those obtained for an authentic sample of the compound.

Synthesis of 1-n-hexyl-1-methoxy-1,2,2,2-tetramethyl-disilane 161 A 250 mL RB flask equipped with a magnetic stirrer, a condenser with a nitrogen gas inlet, a 125 mL pressure equilibrating addition funnel, and a septum inlet was charged with 1.2 g (0.049 mol) Mg, 5 mL THF, and 0.1 g

of 1-chlorohexane (109) and a crystal of iodine. The reaction initiated as the solution was brought to reflux. After initiation an additional 3.90 g chlorohexane (total moles 0.033) dissolved in 75 mL THF was added dropwise, and the solution was refluxed overnight. After cooling, the Grignard was transferred via canula to a stirring solution of 1,1-dichloro-1,2,2,2-tetramethyldisilane 151 (85) in 75 mL THF at -78°C under nitrogen in a 250 mL RB flask equipped with a condenser and an overhead stirrer. After the addition the solution was warmed to room temperature and stirred overnight. The solution was then refluxed an additional 24 h. After cooling to 0°C a solution of pyridine (2.55 mL, 0.033 mol) and methanol (1.50 mL, 0.059 mol) was added at once to the reaction mixture, and stirring continued an additional 3 h. An aqueous/pentane work up removed the THF. Rotary evaporation of the organic phase after drying (MgSO_4) left a residue weighing 5.6 g, which upon distillation (15 mm Hg) afforded 2.51 g product (0.0108 mol, 33%, bp $113-8^{\circ}\text{C}$). Preparative GLC (12' 15% SE-30, 70°C initial, $10^{\circ}\text{C}/\text{min}$ ramp) afforded pure 161, identified by its spectral characteristics: ^1H NMR (C_6D_6) δ 0.16 (s, 9H), 0.22 (s, 3H), 0.65-0.80 (mult., 2H), 0.90 (t, $J = 6.7$ Hz, 3H), 1.15-1.53 (overlapping mults., 8H), 3.31 (s, 3H); ^{13}C NMR (C_6D_6) δ -2.87, -1.41, 14.35, 16.78, 23.04,

23.86, 32.00, 33.66, 51.14; MS 232 (1.4) (M+), 217 (3.4), 147 (21.7), 135 (7.2), 134 (14.4), 133 (100.0), 117 (11.7), 89 (7.9), 75 (79.9), 74 (6.6), 73 (33.0), 59 (39.3); calc'd for $C_{11}H_{28}OSi_2$, m/e 232.16788, found m/e 232.1682. Anal. Calc'd for $C_{11}H_{28}OSi_2$: C, 56.82; H, 12.14. Found: C, 56.61; H, 12.40.

FVP of 1-n-hexyl-1-methoxy-1,2,2,2-tetramethyldisilane
161 Compound 161 (0.3230 g, 1.39 mmol) was slowly distilled (over 3.5 h) at 50°C through a horizontal, quartz-packed seasoned pyrolysis tube evacuated to 5×10^{-5} mm Hg at 605°C. The reaction zone pressure was ca. 0.05 mm Hg (measured at exit end by a Baratron vacuum guage). The products were collected in a liquid nitrogen cooled trap at -196°C. After warming to room temperature the pyrolysate (obtained in 68% mass recovery) contained only four major peaks by capillary GLC and GCMS, which were isolated by preparative GLC (25' 25% SE-30 on Chromosorb-W-AW, 50°C isothermal) and identified by their spectral characteristics compared with authentic samples. No unreacted 161 remained. Yields found were: methoxytrimethylsilane 45 (83%), 1-hexene (45%), Z-2-hexene (18%), and an isomeric hexene mixture (33%). Although 1- and Z-2-hexene were isolable in pure form, all efforts at purifying the third hexene peak failed. 1H NMR analysis of the mixture however

showed it to consist of a mixture of E-2-hexene, and Z- and E-3-hexene. The ^1H NMR spectrum (Fig. 5) in the alkyl region shows a clean sextet at δ 1.25-1.40, assigned to the C_5 methylene protons of E-2-hexene, and a multiplet at δ 1.55-1.60, assigned to the C_1 (vinyl methyl) protons of E-2-hexene. The region from δ 1.85-2.00 consists of overlapping allylic protons in both 2- and 3-hexenes. The region from δ 0.80-1.00 contains 8 peaks; irradiation at δ 1.34 collapses three of these to a singlet, assigned as the C_6 methyl triplet of E-2-hexene (δ 0.85, $J = 7.3$ Hz, matches authentic sample). Irradiation at δ 1.98 (Fig. 5, insert) collapses the eight peaks to five; the clean triplet at 0.85 remains and the remaining peaks simplify to two at δ 0.90 and 0.93 in an approximate relative intensity (by integration) of 1.0:2.1, respectively. The resonance at δ 0.93 was assigned to the equivalent C_1 and C_6 methyl protons of E-3-hexene by comparison of the chemical shift with an authentic sample. An authentic sample of Z-3-hexene was not available, however the δ 0.90 peak in the decoupled (hv at δ 1.98) spectrum was presumed to belong to Z-3-hexene; additional confirmation of this assignment was provided by ^{13}C NMR data. Peaks in the ^{13}C NMR of the mixture were assigned by comparison with available samples of E-2-hexene and E-3-hexene and literature values (110)

for those compounds and for Z-3-hexene. Peaks found were assigned (CDCl_3) to E-2-hexene (δ 13.62, 17.82, 22.75, 34.72, 124.71, 131.44), to E-3-hexene (δ 13.97, 25.55, 130.96), and to Z-3-hexene (δ 14.38, 20.43, the remaining resonance may be overlapped with either the 130.96 peak of E-3-hexene or the 131.44 peak of E-2-hexene; the literature shift is 131.25, vs. 131.24 for E-3-hexene [110a]).

Integration of the ^1H NMR and the decoupled ^1H NMR established that the mixed hexenes were approximately 2.6/1.0 E-2-hexene/3-hexene and 2.8/1.0 E-3-hexene/Z-3-hexene.

Preparation of n-hexyl-1,1,1-trichlorosilane A 250 mL 3-neck round bottom flask, to which was attached a reflux condenser with a nitrogen inlet, 250 mL addition funnel, and magnetic stirrer was dried and charged with Mg (11.0 g, 0.453 mol), ether (50 mL), 0.3 g 1-chlorohexane (109), and a crystal of iodine. After initiation of the reaction an additional 30.7 g (total moles 0.254 mol) of chlorohexane dissolved in 150 mL ether was added dropwise from the addition funnel at a rate sufficient to maintain a gentle reflux, heating as necessary. After the addition the solution was refluxed an additional 2.5 h and cooled to room temperature. The Grignard reagent was slowly transferred via canula to a stirring solution of SiCl_4 in 250 mL

ether at -78°C in a 500 mL 3-neck round bottom flask with overhead stirring. After the addition the solution was gradually warmed to room temperature and stirred overnight. Filtration through celite/sintered glass removed the precipitated salts, and fractional distillation through a 7" X 1" column packed with glass chips removed the ether. The residue was vacuum distilled through a 6" X 1/2" fractionation column at 20 mm Hg to afford 30.7 g product bp $94-97^{\circ}\text{C}$ (55% yield). n-Hexyltrichlorosilane (89) was identified by its spectral properties: ^1H NMR (CDCl_3) δ 0.86-0.92 (mult., 3H), 1.20-1.35 (overlapping multiplets, 4H), 1.35-1.47 (overlapping multiplets, 4H), 1.50-1.70 (mult., 2H); ^{13}C NMR (CDCl_3) δ 13.99, 22.27, 22.40, 24.40, 31.21, 31.48; MS 220 (2.0), 218 (2.2) (M^+), 191 (6.6), 189 (6.4), 177 (5.4), 175 (5.4), 163 (8.6), 161 (8.8), 137 (11.0), 135 (32.7), 133 (33.5), 57 (100.0), 56 (25.0), 55 (14.7).

Preparation of n-hexylsilane 162 n-Hexylsilane
162 (88) was prepared from n-hexyl-1,1,1-trichlorosilane (vide supra) by reduction with LiAlH_4 . n-Hexyl-1,1,1-trichlorosilane (6.0 g, 0.0273 mol) was added dropwise neat via syringe to a stirring slurry of LiAlH_4 (1.1 g, 0.029 mol) in 15 mL ether under nitrogen at -23°C and then stirred overnight after warming to room temperature. Trap-to-trap distillation (under vacuum, 1.5 mm Hg) removed the

solution from the LiAlH_4 and rotary evaporation removed the ether to leave nearly pure (> 96% by capillary GLC) 162 (1.53 g, 49%). Final purification was obtained by preparative GLC (12' 12% SE-30 on Chromosorb-W, 120°C isothermal). Satisfactory spectra were recorded: ^1H NMR (C_6D_6) 0.46-0.57 (mult. 2H), 0.87 (t, $J = 7$ Hz, 3H), 1.06-1.34 (overlapping multiplets, 8H), 3.64 (t, $J = 3.9$ Hz, 3H); ^{13}C NMR (C_6D_6) δ 6.13, 14.25, 22.89, 26.66, 31.79, 32.47; IR 2960 (s), 2925 (vs), 2860 (s), 2145 (vs) (Si-H), 1455 (m), 920 (vs), cm^{-1} ; MS 116 (0.8) (M^+), 115 (1.2), 114 (2.6), 88 (4.2), 87 (3.6), 86 (8.2), 73 (4.4), 60 (7.6), 59 (100.0), 58 (14.0), 57 (7.5), 56 (7.0).

Preparation of n-hexyl-1,1,1-trideuteriosilane, 162-d₃

Compound 162-d₃ was prepared using the same procedure as described above for the preparation of undeuterated 162 except that LiAlD_4 was used. To a stirring slurry of 1.3 g LiAlD_4 (0.032 mol) in 15 mL ether at -23°C under nitrogen was added dropwise 6.90 g (0.031 mol) of neat n-hexyl-1,1,1-trichlorosilane. After warming to room temperature, trap-to-trap distillation followed by rotary evaporation of the ether left 2.40 g (0.020 mol, 65%) of > 98% pure 162-d₃. Final purification was obtained by preparative GLC. Spectral analysis was consistent with quantitative deuteration: ^1H NMR (C_6D_6) δ 0.51 (t, $J = 7.5$ Hz, 3H), 0.87 (t,

$J = 7$ Hz, 3H), 1.09-1.32 (overlapping multiplets, 8H), there was no Si-H detectable; IR (neat) 2960 (s), 2920 (vs), 2860 (s), 1565 (vs) and 1555 (s) (Si-D), 1455 (w), 740 (s), 695 (s) cm^{-1} , there was no trace of any Si-H in the IR; MS 119 (0.7), 118 (0.2), 117 (0.7), 116 (2.3), 91 (4.7), 88 (3.3), 87 (4.3), 63 (7.6), 62 (100.0), 60 (10.0).

FVP of n-hexylsilane 162 Compound 162 was slowly distilled at room temperature through a horizontal quartz packed pyrolysis tube evacuated to 2×10^{-5} mm Hg at 735°C . During the pyrolysis the vacuum rose to 5×10^{-4} mm Hg, indicating the formation of noncondensables (e.g., dihydrogen).

The products were collected in a liquid nitrogen cooled trap. Upon warming to room temperature at 1 atm pressure considerable effervescence was noted. The products were dissolved in 1 mL pentane to facilitate recovery. The gaseous products were determined later in a separate experiment (vide infra).

The products were isolated by preparative GLC (25' 25% SE-30 on Chromosorb W-AW, 50°C isothermal for 20 min, then $10^{\circ}\text{C}/\text{min}$ program to 200°C). Yields were determined by capillary GLC. The products were identified by GCMS, ^1H NMR, and capillary and packed column retention times, as 1-hexene (17%), Z-2-hexene (4%), and an isomeric hexene

mixture (11%), determined by ^1H NMR to be a mixture of approximately 1.2/1.0 E-2-hexene/3-hexenes (the analysis was similar to that described above in the FVP of 161). Spectra and retention times were matched against authentic samples of 1-hexene, Z- and E-2-hexene, and E-3-hexene purchased from Aldrich. Starting material 162 was recovered in 4% GLC yield.

In a separate experiment the pyrolysis was repeated under the same conditions; measurement at the reaction zone using a Baratron Gauge determined the pressure to be 0.05-0.10 mm Hg. The products were collected in a liquid nitrogen cooled trap, and then distilled into a gas collection flask. Analysis of the gases was performed by GC and GCMS. Products identified on the basis of chromatographic properties and mass spectra, with relative amounts, corrected using literature response factors or response factors estimated by using close isomers (87), in parentheses, were: ethene (1.03), propene (0.82), 1-butene (0.20), 1-pentene (0.30), 1,3-butadiene (< 0.10), 1-hexene (1.00), Z-2-hexene (0.21), and the isomeric hexene mixture (0.45). Retention times and mass spectra were matched against authentic samples of ethene, propene, 1-butene, butadiene, and hexenes. The product 1-pentene was also identified in the copyrolysis of 162 with 1,3-butadiene by

^1H NMR (vide infra). Significantly, there was no 2-butene found by GCMS. GLC analysis (30' X 1/8" 23% SP-1700 on Chromosorb P-AW) showed that any 2-butene was present, if at all, in less than 8% of the 1-butene. A more accurate assesment cannot, however, be made from data obtained because of low sample concentration. Injection of the sample on a capillary GLC indicated that the gaseous sample was ca. 45% hexenes and 55% lighter gases.

Pyrolysis of a mixed hexene solution A solution of mixed hexenes consisting of 44% 1-hexene, 17% Z-2-hexene, 28% E-2-hexene, and 12% 3-hexene was prepared (the composition of the mixture was made to be similar to the product mixture obtained from the FVP of 162, and was characterized by GLC and ^1H NMR). Slow distillation through a horizontal seasoned quartz packed pyrolysis tube at 735°C was maintained with the pressure at ≤ 0.1 mm Hg in the reaction zone (4×10^{-5} at the Ion Gauge). The products were initially collected in a liquid nitrogen cooled trap and after the pyrolysis were distilled into a gas bulb for analysis. Analysis of the gases formed by GC and GCMS (in this experiment a cooled capillary column was used for GCMS) yielded the following identifications based on mass spectra and GC retention times (relative amounts in parentheses): ethene (0.40), propene (0.38), 1-butene (0.20),

1,3-butadiene (0.30), 1-hexene (1.00), and the remaining hexenes. Capillary GLC analysis showed the hexenes to consist of ca. 59% of the detectable gas present (by uncorrected FID response), with relative amounts of 1-hexene (1.00), Z-2-hexene (0.38), E-2- and 3-hexenes (1.01), compared with relative amounts of 1.00, 0.37, and 0.88 respectively found before pyrolysis. Hence the relative amounts of the hexenes, despite considerable decomposition, were little changed by pyrolysis. GCMS also indicated the presence of only traces of 2-butenes, four pentene isomers, and two pentadiene isomers, although these were formed in very minor amounts and could not be detected by routine GLC.

FVP of 1-hexene Pure 1-hexene (0.2266 g) was slowly distilled through a horizontal seasoned quartz-packed pyrolysis tube at 735°C, pressure < 0.1 mm Hg (at the reaction zone measured by a Baratron Gauge) and the products were collected in a liquid nitrogen cooled trap. Upon warming the pyrolysate showed effervescence. Analysis by capillary GLC showed only one major compound to be present, plus small amounts of more volatile gases, identified after isolation by preparative GLC and ¹H NMR and GCMS as unchanged 1-hexene in 52% yield. Mass recovery was 64%, and GCMS showed a complete absence of any other hexene

isomers.

FVP of 2-hexene A mixture of Z- and E-2-hexene (used as purchased from Aldrich, 0.2858 g) consisting of 69.5% Z-2-hexene and 30.5% E-2-hexene was slowly distilled through a horizontal quartz packed seasoned pyrolysis tube at 735 °C, reaction zone pressure 0.4 mm Hg (the pressure measured at the Ion Gauge was 7×10^{-5} mm Hg). The products were collected at -196 °C. Upon warming to room temperature, an effervescent pyrolysate was obtained, with a 48% mass recovery. Analysis by capillary GLC showed there to be only two major peaks corresponding to the 2-hexenes in 21% (Z-2-hexene) and 13% (E-2-hexene) yields (based on total moles of hexene used). Analysis by capillary GLC and ^1H NMR of unreacted starting material isolated by preparative GLC (25' 25% SE-30 on Chromosorb W, 50 °C isothermal) showed there to have been no 3-hexene or 1-hexene formed.

FVP of 1-n-hexyl-1,1,1-trimethylsilane 163

Compound 163 (90) (0.1234 g) was slowly distilled through a horizontal quartz-packed pyrolysis tube at 740 °C, reaction zone pressure 0.1 mm Hg, over 1.5 h and the products were collected in a liquid nitrogen trap. Upon warming, there was no effervescence noted, and the pyrolysate recovered (in 72% mass recovery) afforded a clean ^1H NMR of unreacted

163 and showed no other products by capillary GLC analysis. Only traces of gases (< 2% at most) were present.

FVP of n-hexyl-1,1,1-trideuteriosilane 162-d₃

Compound 163-d₃ was slowly distilled at 4×10^{-5} torr (Ion Gauge) through a horizontal quartz-packed, seasoned pyrolysis tube at 735°C. The products were collected at -196°C. Upon warming to room temperature at 1 atm considerable effervescence was noted. After extraction of the pyrolysate in pentane to facilitate handling and minimize loss, analysis by capillary GLC and GCMS indicated three hexene peaks were formed, which were isolated, along with the unreacted 162-d₃, by preparative GLC (25' 25% SE-30 on Chromosorb W-AW, 50°C, 20 min, then 10°C/min program). Identified on the basis of chromatographic properties, mass spectra, and ¹H NMR analysis were 1-hexene (13%), Z-2-hexene (3%), and a mixture of isomeric hexenes (9%). The mixture showed in the ¹H NMR (C₆D₆) a broad singlet at δ 1.59 assigned to E-2-hexene (a multiplet in undeuterated samples but perhaps broadened by deuterium substitution), a triplet at δ 0.94 ($J = 7.6$ Hz) assigned to E-3-hexene (matched authentic sample). Smaller peaks overlap in the methyl region of the ¹H NMR which presumably belong to Z-3-hexene. The characterization of the mixture is supported by ¹³C NMR (CDCl₃) which revealed resonances

assignable (on the basis of literature values [110] and available samples of E-2-hexene and E-3-hexene) to E-2-hexene (δ 13.61, 17.79, 22.76, 34.73, 124.70, and 131.44), to E-3-hexene (δ 13.96, 25.55, and 130.96), and to Z-3-hexene (14.37 and 20.43). The remaining vinyl carbon of Z-3-hexene could not be identified; it may overlap with the 130.96 of E-3-hexene (the literature shifts [110a] are 131.24 for Z-3-hexene vs. 131.25 for E-3-hexene). Integration of the ^1H NMR signals afforded an estimate of 1.7/1.0 as the ratio of E-2-hexene/3-hexenes. Neither the ^1H NMR or the ^{13}C NMR spectra provided any clear evidence of splitting by deuterium.

The pyrolysis was repeated to provide samples for ^2H NMR and mass spectrometric analysis of deuterium incorporation, with yields of 1-hexene (18%), Z-2-hexene (4%), the isomeric hexene mixture (12%), and unreacted 162- d_3 (7%) found. Mass spectrometric measurements, corrected ion intensities, and percent deuterium incorporation calculations for the hexene samples are presented in Table 10. Integrated ^2H NMR signal intensities for the 1-hexene and Z-2-hexene (which could be obtained in pure form) are presented in Table 11. The remaining isomeric hexene mixture showed the following ^2H NMR, with relative intensities (in arbitrary units) in parentheses: (C_6H_6) δ

0.6-1.1 (107), 1.2-1.4 (58), 1.4-1.7 (81), 1.7-2.2 (95),
5.2-5.6 (100).

The unreacted, isolated 162 was analyzed by ^1H NMR and found to be unchanged except for the appearance of a silyl hydride (0.39H, representing 13% deuterium loss). ^2H NMR of the unreacted starting material showed no incorporation of deuterium onto the carbon chain; only a silyl deuteride at δ 3.7 was present. Mass spectral determination of the deuteration by the method of Biemann (83) proved impossible due to the facile loss of H from undeuterated 162 in the MS, however the spectrum was obtained at high resolution ($R_s = 75,000$) and ions corresponding to 162- d_3 (m/e 119.1210, intensity 15.5 ± 1) and 162- d_2 (m/e 118.1147, intensity 8.5 ± 1) were found. Relatively small ions corresponding to d_1 and d_0 were detected but could not be reliably measured because they were found only as shoulders on much larger neighboring ions in the spectrum. These results suggest 12% replacement of deuterium with hydrogen and are consistent with the ^1H NMR results.

Flow pyrolyses of 162 in nitrogen, ethene, or 1,3-butadiene carrier gases As a general procedure, 162 was added dropwise (in cyclohexane or toluene diluents or neat, in the case of butadiene flow experiments) to a vertical quartz-packed pyrolysis tube packed with quartz chips swept

with a gas flow of 35 mL/min. The products were collected at -78°C in a dry ice/iso-propanol cooled trap. Analysis by capillary GLC and GCMS established that the same products were formed in these pyrolyses as characterized in the FVP of 162. Gaseous products were not efficiently trapped or analyzed for in this experiment. Conditions and yields are summarized in Table 12. Neither toluene nor cyclohexane, used as diluents in nitrogen and ethene flow pyrolyses, afforded appreciable background products at these temperatures. Yields were determined against anisole as internal standard added to the pyrolysate, using predetermined response factors, and are absolute.

Nitrogen flow pyrolyses In a typical run (Run 1, Table 12) 0.1159 g (1.00 mmol) of 162 was dissolved in cyclohexane (0.7696 g, 9.16 mmol) and added dropwise over 0.5 h to the pyrolysis tube at 585°C , with a 65% mass recovery. Isolation of the products (Run 2 Table 12, 25' 25% SE-30 on Chromosorb W, 50°C isothermal) along with capillary GLC and GCMS confirmed the identity of the products as 1-hexene, Z-2-hexene, and an isomeric mixture of ca. 1.1/1.0 E-2-hexene/3-hexene by integration of the ^1H NMR spectrum.

Ethene flow pyrolyses The pyrolysis was performed on a similar scale and under comparable

conditions as described in the nitrogen flow pyrolyses. Capillary GLC and GCMS indicated the formation of the same products as characterized in the FVP of 162, along with a new product (in undetermined yields, but estimated by capillary GC FID response as $\leq 5\%$) identified as diethylsilane 165 on the basis of its ^1H NMR and MS: ^1H NMR (C_6D_6) δ 0.52 (mult. of 9 peaks, 4H, collapses to q, $J = 7.8$ Hz, with $h\nu$ at 3.85), 0.94 (t, $J = 7.8$ Hz, 6H, collapses to s with $h\nu$ at 0.52), 3.85 (pent., $J = 3.5$ Hz, 2H, collapses to s with $h\nu$ at 0.52); MS 90 (0.3), 89 (1.1), 88 (8.9) (M^+), 87 (12.5), 86 (12.8), 59 (97.4), 58 (100.0), 43 (31.0). Notably, significant amounts of products resulting from hexylsilylene addition to ethylene were not found.

1,3-Butadiene flow pyrolyses Because of the presence of butadiene byproducts a more rapid addition of 162 was employed. Neat 162 (0.3131) was added over 15 min to the pyrolysis tube. Capillary GC, GCMS, and isolation of the products by preparative GLC (25' 25% SE-30 on Chromosorb W, 50°C , isothermal) and ^1H NMR confirmed the identities of 1-hexene, Z-2-hexene, and a mixture consisting of a 1.3/1.0 ratio of E-2-hexene/3-hexenes. Also identified by GCMS and ^1H NMR of an isolated sample (same column and conditions) was 1-pentene (yield undetermined but estimated as $\leq 4\%$). Yields of hexenes given in Table

12 were calculated after employing a correction necessitated by the formation of relatively small amounts of background products resulting from butadiene pyrolysis overlapping the 2- and 3-hexene peaks. This was done by subtracting from the measured peak areas an estimated background contribution referenced to a standard peak present in both the butadiene plus 162 and a sample of butadiene (no 162) pyrolysate. In a separate run (Run 9, Table 12) a small amount of 1-hexene was added (26 mol %); yields reported for Run 9 (except for unreacted 162) are based on total moles of 162 plus 1-hexene used.

Copyrolysis of 1-n-butyl-1,1-dimethylsilane 174 with 1-hexene A solution of 0.1787 g (1.54 mmol) of 174 (93) and 0.1458 g (1.74 mmol) of 1-hexene in cyclohexane diluent (1.178 g, 14.0 mmol) was dropwise added over 35 min to a vertical seasoned quartz chip packed pyrolysis tube at 575°C swept with a nitrogen flow of 35 mL/min. The products were collected in a dry ice/iso-propanol cooled bath, with a 60% mass recovery. Analysis by capillary GLC and GCMS revealed no detectable isomerization of the hexene. 1-Hexene was recovered in 42% yield; the 174 was recovered in 47% yield.

Copyrolysis of 1-hexene with 1-methoxypentamethyl-
disilane 175 A solution of 1-hexene (0.0853 g, 1.02
 mmol) and 175 (111) (0.1456 g, 0.899 mmol) in cyclohexane
 (0.8265 g) was slowly added via syringe drive over 1 h to a
 vertical quartz chip packed, seasoned pyrolysis tube at
 550°C swept with a nitrogen flow of 35 mL/min and the
 products were collected in a dry ice/iso-propanol cooled
 trap. GCMS and capillary GLC analysis of the pyrolysate
 showed that methoxytrimethylsilane 45 (37%), unreacted 175
 (21%), and 1-hexene (46%) were present. Yields of 45 and
 175 are based on starting moles of 175 used; the yield of
 1-hexene is based on the starting moles of 1-hexene.
 Capillary GLC analysis showed that 2- and 3-hexenes, if
 formed at all, are present in < 3% yield.

Copyrolysis of 1-n-hexyl-1-methoxy-1,2,2,2-tetra-
methyldisilane 161 and 1,3-butadiene Neat 161 (0.4845
 g, 2.09 mmol) was dropwise added over 20 min to a vertical
 quartz chip packed pyrolysis tube swept with a butadiene
 flow of 35 mL/min at 485°C. The products were collected
 at -78°C in a dry ice/iso-propanol cooled trap. The
 products were identified by capillary GLC and GCMS and were
 isolated by preparative GLC (25' 25% SE-30 on Chromosorb W,
 50°C isothermal). Products identified were methoxytri-
 methylsilane 45 (33%), 1-hexene (19%), Z-2-hexene (4%), and

a mixture of hexene isomers (8%) determined by ^1H NMR to be a ca. 4/1 mixture of E-2-hexene/3-hexenes, 1-methyl-1-silacyclopent-3-ene 15 (112) (21%), and 1-n-hexyl-1-methyl-1-silacyclopent-3-ene 179 (9%). Unreacted 161 was recovered in 28% yield. There was no evidence found for any isomerization of 161 based upon GCMS and ^1H NMR of the isolated, recovered starting material. Compound 179 had the following spectral characteristics: ^1H NMR (CDCl_3) δ 0.07 (s, 3H), 0.59 (t, $J = 8$ Hz, 2H), 0.82 (t, $J = 7$ Hz, 3H), 1.07-1.37 (overlapping multiplets, 12H), 5.79 (broad s, 2H); ^{13}C NMR (CDCl_3) δ -3.60, 14.08, 14.70, 16.61, 22.60, 24.11, 31.62, 33.03, 131.04; MS 182 (8.4) (M+), 167 (1.8), 154 (4.5), 139 (4.5), 100 (8.5), 99 (37.7), 98 (47.4), 97 (100.0), 95 (16.5), 83 (21.7), 72 (10.4), 71 (13.7); calc'd for $\text{C}_{11}\text{H}_{22}\text{Si}$ m/e 182.1492, found m/e 182.1491. GCMS afforded evidence of an isomer of 179: MS 182 (2.7), 167 (7.6), 154 (9.0), 99 (7.8), 98 (11.7), 97 (100), 95 (12.3), 83 (15.9), 71 (5.1), 69 (6.7), 55 (5.9). The yield of this product was too low to allow complete characterization.

Copyrolysis of 161, 1-octene, and 1,3-butadiene A mixture of 161 (0.3344 g, 1.44 mmol) and 1-octene (0.0867 g, 0.77 mmol) were dropwise added via syringe over 15 min to a vertical quartz chip packed pyrolysis tube at 500°C

swept with a flow of 1,3-butadiene of 35 mL/min. The products were collected at -78°C in a dry ice/iso-propanol cooled trap and were identified by capillary GLC and GCMS as being the same as found in the copyrolysis of 161 in 1,3-butadiene, above: methoxytrimethylsilane 45 (48%), 1-hexene (26%), Z-2-hexene (6%), E-2-hexene/3-hexene (mixture) 10%, 1-methyl-1-silacyclopent-3-ene 15 (112) (22%), 1-n-hexyl-1-methyl-1-silacyclopent-3-ene 179 (7%), and unreacted 161 (23%). A thorough search of the GCMS (including single ion chromatogram of the m/e ion 112), and isolation (by preparative GLC) and ^1H NMR analysis of the 1-octene recovered failed to disclose any isomerization of the 1-octene. The yield of recovered 1-octene was 82% (based on starting moles of 1-octene).

Copyrolysis of 1-octene with 1,3-butadiene Neat 1-octene (0.1787 g, 1.60 mmol) was added dropwise to a vertical quartz chip packed pyrolysis tube at 500°C swept with a butadiene gas flow of 35 mL/min. The products were collected in a -78°C cooled trap. Capillary GLC and GCMS analysis revealed no isomerization or fragmentation of the 1-octene to hexenes. The yield of 1-octene recovered was 64%.

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