1985

Mechanistic and synthetic aspects of acetylene-alkylidenecarbene rearrangements in the gas phase

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MECHANISTIC AND SYNTHETIC ASPECTS OF ACETYLENE - ALKYLIDENECARBENE REARRANGEMENTS IN THE GAS PHASE

Iowa State University PH.D. 1985

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Mechanistic and synthetic aspects of acetylene-alkylidenecarbene rearrangements in the gas phase

by

Brian Laue Groh

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

Department: Chemistry
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1985

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To my parents

INTRODUCTION

The chemistry of unsaturated carbenes constitutes a rather new area of research in organic chemistry. Much of the work that has appeared in the literature is summarized in three reviews by Stang (1-3).

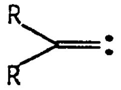
The majority of the research conducted on unsaturated carbenes has been carried out at low temperature in solution. The remainder of the research in this area has been done in the gas phase. Generation of unsaturated carbenes in the gas phase is accomplished by one of two methods. One involves the thermal decomposition of heterocycles which extrude unsaturated carbenes at elevated temperatures. The other entails a thermally induced 1,2-shift on an acetylene.

This work will attempt to examine the mechanistic and synthetic aspects of 1,2-silyl migrations on acetylenes. Whenever possible, a comparison will be made of the relative migratory aptitudes of silicon, as a dimethylsilyl or a trimethylsilyl substituent, and hydrogen on acetylenes. Finally, the trapping of unsaturated carbenes by insertion into C-H, O-H, and Si-H bonds will be examined for their synthetic utility and efficiency.

HISTORICAL SECTION

Nearly twenty years ago, unsaturated carbenes were recognized as viable intermediates in the pioneering works of Hartzler, Köbrich, Newman, and their co-workers. A summary of these early studies has been published (4). Although still in its infancy, chemistry of unsaturated carbenes has already been a subject of considerable investigation (1-3). To date, unsaturated carbenes remain characterized only by their chemical behavior. These unstable, reactive intermediates have neither been isolated nor observed spectroscopically. Further characterization of the nature of unsaturated carbenes and development of their chemistry remains a challenge.

An unsaturated carbene, **1**, is a reactive intermediate where the electron deficient carbon is an integral part of the unsaturated system. A standard nomenclature has not yet been generally applied to the naming of unsaturated carbenes. Currently, unsaturated carbenes are given trivial names or named as derivatives of alkylidenecarbenes, vinylidenes, and methylene carbenes. Within this dissertation, unsaturated carbenes will be named as derivatives of alkylidenecarbenes in accordance with the system suggested by Stang (1). For example, **2** would be named trimethylsilylphenylmethylidenecarbene.



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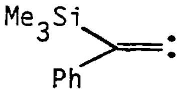
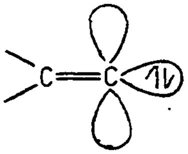
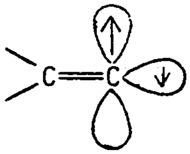


2

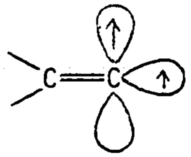
Unsaturated carbenes may exist in any of three possible low-energy states. A singlet (S_0) where the two unshared electrons are spin paired in a single orbital, **3**, a singlet (S_1) where the electrons are spin paired and in different orbitals, **4**, or the triplet (T_1) state where the electrons are of parallel spin and occupy different orbitals, **5**. These orbitals are derived from nonbonding π and σ orbitals on the valence carbon. While the π orbital retains its p character in both the singlet and triplet states, the hybridization of the σ orbital varies from mainly s character ($sp^{0.6}$) in the singlet state to mainly p character ($sp^{1.8}$) in the triplet state (5).



3 (S_0)



4 (S_1)



5 (T_1)

Numerous calculations have appeared over the last ten years regarding the relative energies of the S_0, S_1, and T_1 spin states. While the relative energies of the three states have generally been accepted to decrease in the order S_1, T_1, S_0, estimates of the relative energies have varied widely. The most recent and generally accepted values obtained by nonempirical calculations for the singlet and triplet spin states of methylidene, **6**, predict a singlet ground state, S_0, with a singlet-triplet energy difference of 42 kcal/mole (6). The next excited state, S_1, is an additional 13 kcal/mole higher in energy than the triplet state. The activation energy of the rearrangement of methylidenecarbene, **6**, to acetylene, **7**, has been estimated at 1-2 kcal/mole (6, 7). With such a low-energy barrier, it is of little surprise that the lifetime of carbene **6** has been calculated and experimentally verified to be approximately 10^{-10} to 10^{11} s (6, 8).

6 **7**

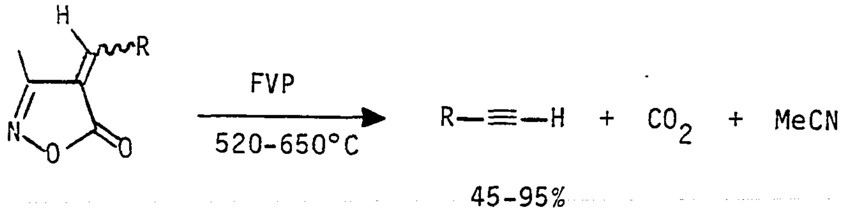
In contrast to the minimal barrier for the methylidenecarbene-acetylene rearrangement, the difluoromethylidenecarbene-difluoroacetylene rearrangement is predicted to have an activation energy of 36 kcal/mole (9). This barrier is consistent with the experimental observation that difluoromethylidenecarbene has been intermolecularly trapped with methanol, hydrogen sulfide, and alkanes, while methylidenecarbene has not (10, 11).

A theoretical investigation of the effects of other substituents upon methylidenecarbene has yielded some interesting results (12). Electronegative substituents such as NH_2, OH, F, CN, and Cl were found to destabilize alkylidenecarbenes, while electropositive substituents, for example, BeH, BH_2, CH_3, and SiH_3, result in stabilization of the carbene. Apeloig and Schreiber suggest that σ-inductive electron donation and hyperconjugation between the carbon and the substituent bonding electrons and the vacant 2p orbital of the carbene are the important stabilizing mechanisms for alkylidenecarbenes. They also concluded that two substituents have a substantially larger stabilizing (or destabilizing) effect than simply twice the effect of a single substituent. For example, boranylmethylidenecarbene is stabilized by 7.9 kcal/mole relative to methylidenecarbene, while bis(boranyl)methylidenecarbene is stabilized by 21.8 kcal/mole.

In view of the short lifetimes of alkylidenecarbenes and lack of suitable methods of generation, it is little wonder that direct verification of the singlet ground state of unsaturated carbenes has not been accomplished. In an attempt to resolve the issue, indirect evidence has been obtained using the technique, first proposed by Skell and Garner (13), of examining the stereochemistry of carbene addition to olefins (14, 15). A study undertaken by Stang and Mangum examined the addition of isopropylidenecarbene, generated from the reaction of 2,2-dimethylvinyltriflate with potassium _t_-butoxide, to several olefins (16). The results revealed that addition of isopropylidenecarbene to _cis_-2-butene was greater than 99.5% stereoselective, addition to _trans_-2-butene was 100% stereospecific, and addition to both _cis_- and _trans_-2-methoxy-2-butene was more than 98% stereoselective. These data, coupled with the belief that isopropylidenecarbene generated by this method is a free carbene (17), strongly suggest the carbene is reacting in the singlet (S_0) state. The question of whether isopropylidenecarbene was reacting in its ground state was probed by the addition of perfluorocyclobutane, an inert diluent, to facilitate intersystem crossing of the carbene to the possibly lower energy triplet state. The diluent had no effect on the stereochemistry of addition of isopropylidenecarbene to trans-2-butene, indicating that the singlet is truly the ground state in accord with theoretical calculations (6, 7). There is little doubt that alkylidenecarbenes possess and react in a singlet ground state that is separated by a large energy difference from the triplet state.

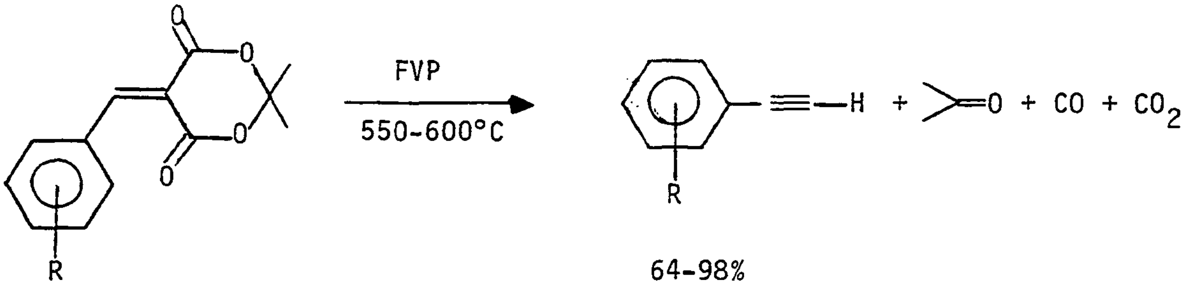
Since alkylidenecarbenes are electron deficient, they are expected to be electrophilic. This postulate was confirmed in a study by Stang and Mangum who examined the reactivity of isopropylidenecarbene with ring-substituted styrene derivatives (18). The carbene, obtained by base elimination of the appropriate triflate, gave a Hammett σ-ρ plot for addition to the styrenes with a ρ value of -0.75. The sign and magnitude are indicative of a mildly electrophilic carbene species comparable to dichloro- and difluorocarbene. In view of the electrophilic nature of unsaturated carbenes, addition to olefins has been postulated to be initiated by interaction between the vacant p orbital of the carbene and the π orbital of the olefin. This has been verified by the theoretical and experimental investigations of Apeloig and co-workers (19).

As has already been mentioned, the majority of research on alkylidenecarbenes has been carried out in solution. In addition, some work has been done and continues to be done in the gas phase where the unsaturated carbenes are produced free and unhindered. One of the few methods developed to produce alkylidenecarbenes in the gas phase involves thermal decomposition of isoxazolones. Good yields of arylacetylenes were obtained by Wentrup and Reichen in the flash vacuum pyrolysis (FVP) of isoxazolones **8** (20). The mechanism of the decomposition has not been described, but extrusion of carbon dioxide and acetonitrile accompany formation of the proposed arylmethylidenecarbenes. Based upon the low energy barrier to 1,2-hydrogen migration on alkylidenecarbenes (6, 7), the arylacetylenes obtained are the expected rearrangement products of the proposed intermediate β-hydrogen substituted alkylidenecarbenes.



8

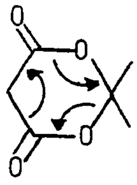
Wentrup and Winter have exploited the thermal decomposition of isoxazolones, **9**, in the synthesis of several chloro, methoxy, dimethylamino, and hydroxy substituted arylacetylenes. Pyrolyses of the isoxazolone derivatives were carried out at 520-620°C producing the corresponding acetylenes in 45-95% yield. Acetylenic derivatives of pyrroles, thiophenes, furans, indenes, and other cyclic compounds, whose preparation is difficult or impossible by other methods, were obtained in yields ranging from 65-95% (21).



9

R = H, p-Me, m-Me, p-MeO, o-MeO, p-Cl, p-CN, o-Ph

A similar pyrolytic route to unsaturated carbenes, concurrently developed by Brown and his colleagues, involves the FVP of 2,2-dimethyl-1,3-dioxan-4,6-dione (Meldrum's acid) derivatives such as **9**. Acetylenes are obtained in yields of 64-98%. Also produced in the thermal decomposition of the 1,3-dioxan-4,6-dione derivatives are acetone, carbon dioxide, and carbon monoxide. It is not clear whether acetone and carbon dioxide are formed by way of a concerted extrusion, **10**, or if they arise from diradical **11**, or possibly through the intermediacy of malonic anhydride, **12** (22). Carbon monoxide is produced by decarbonylation of intermediate methyleneketenes.



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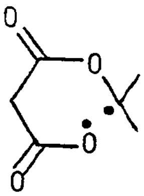

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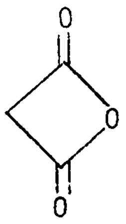
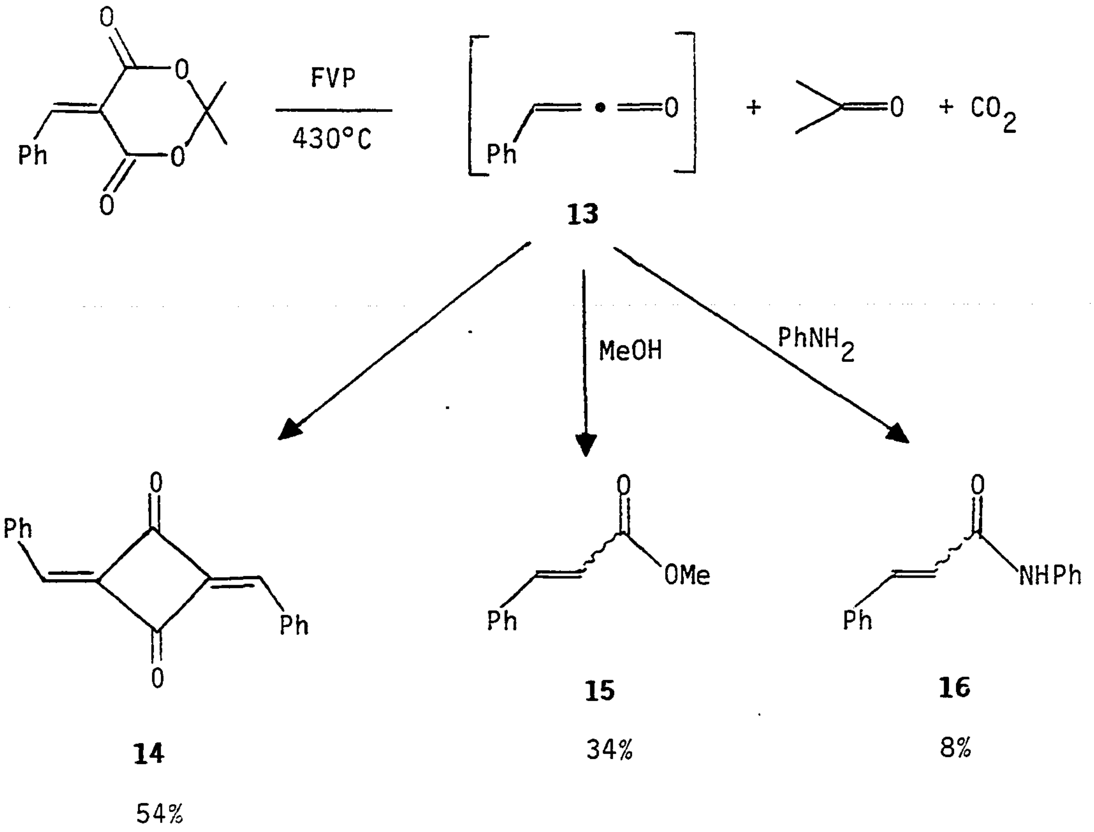
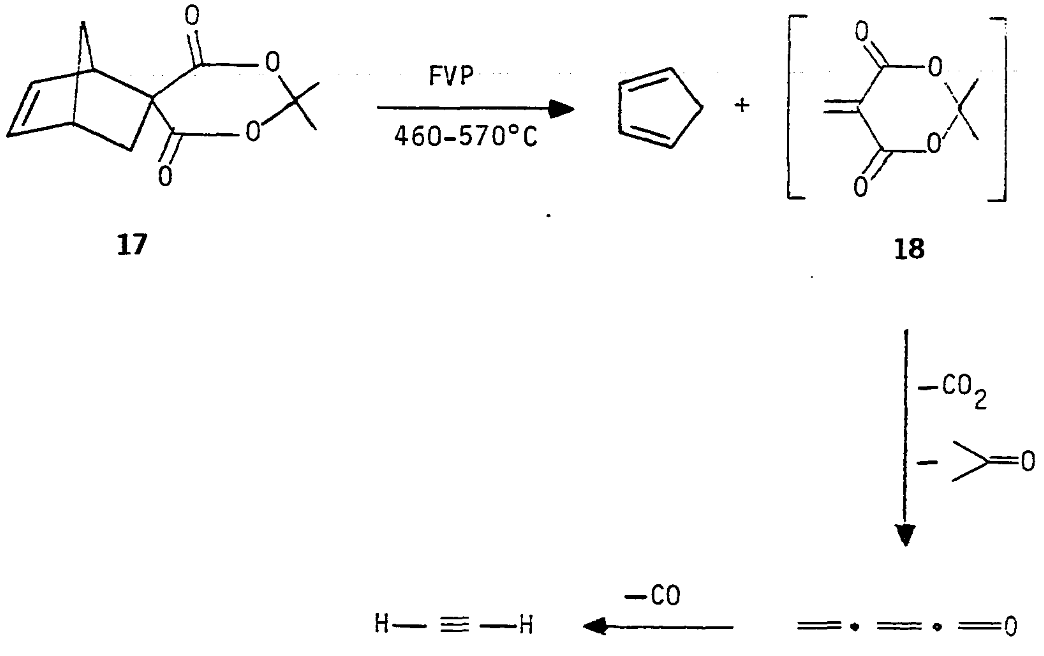


12

Proposed intermediacy of phenylmethyleneketene, **13**, was based on isolation of symmetrical cyclobutane-1,3-dione **14** and on trapping experiments with methanol and aniline which gave cinnamic ester **15** and amide **16** (23). In addition, Brown and co-workers have obtained an IR spectrum of the pyrolysate maintained at -196°C. A strong absorption band at 2090 cm^{-1} was attributed to the presence of intermediate 13.



Further spectroscopic evidence for the intermediacy of methyleneketenes in the FVP of Meldrum's acid derivatives was obtained by Brown et al. (24). Pyrolysis of **17**, used as a convenient source of the unstable methyleneketene precursor **18**, at 495°C gave cyclopentadiene, acetone, carbon dioxide, and methyleneketene. All were detected in the pyrolysis stream by direct introduction of the components to a mass spectrometer. The IR spectrum of the pyrolysate, collected and maintained at -196°C, was recorded. A strong absorption at 2100 cm^{-1} was attributed to the presence of methyleneketene. Pyrolysis of 17 at temperatures of 520°C or higher resulted in the formation of acetylene, presumably via methylidenecarbene, as determined by mass spectrometry. The amount of acetylene produced was found to increase rapidly with increasing temperature.



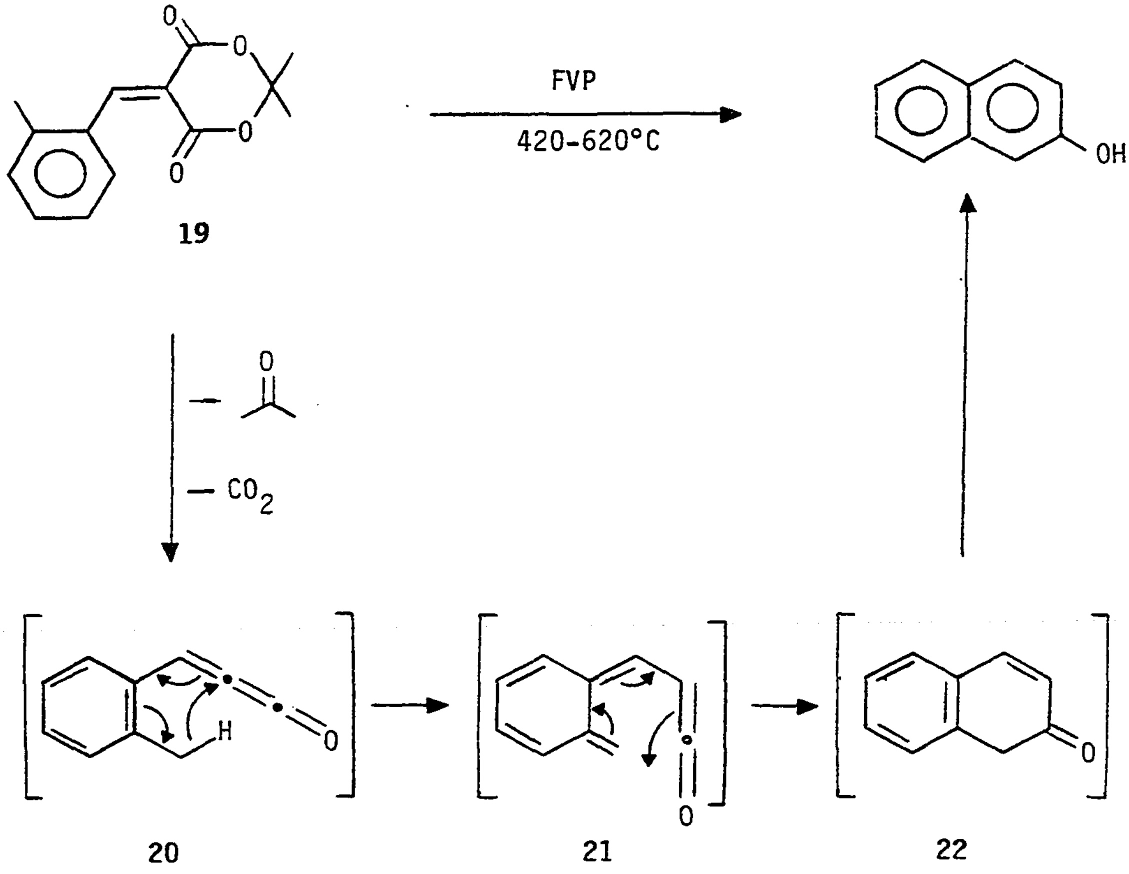
As has been demonstrated, intermediate arylmethyleneketenes resulting from pyrolysis of Meldrum's acid derivatives lose CO to give arylalkyidenecarbenes which subsequently rearrange to acetylenes. An exception to this was found when aryl-1,3-dioxan-4,6-dione derivatives with substituents bearing hydrogen in the ortho position of the ring were pyrolyzed (Scheme 1). Instead of ortho substituted acetylenes, 2-naphthols were obtained in near quantitative yields (25). Brown and McMullen have rationalized formation of 2-naphthol in the pyrolysis of **19** as shown in Scheme 1. Initial loss of acetone and carbon dioxide gives methyleneketene **20** which rearranges to vinyl ketene **21** via a 1,5-hydrogen migration. Subsequent cyclization produces the thermodynamically unstable ketone **22**. Finally, tautomerization of **22** yields 2-naphthol as the sole product. Pyrolysis of deuterium labeled **19** ($\underline{o}$-CHD_2) gave 2-naphthol labeled at positions adjacent to and including the hydroxyl group as expected from the proposed mechanism.

Baxter and collaborators have successfully utilized the methyleneketene to naphthol rearrangement in the synthesis of numerous, substituted naphthols (26). They also prepared several oxygen, nitrogen, and sulfur heterocycles in 54-92% yield as outlined in Scheme 2. All precursors were obtained in high yield from condensation of the requisite aldehydes with Meldrum's acid.

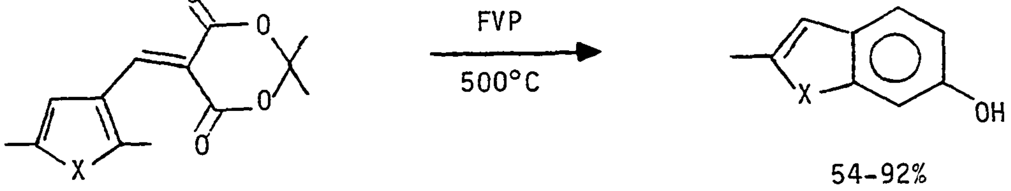
Brown and Jones have also used this strategy in a key step in the synthesis of the natural product ruscodibenzofuran (27). This rather novel synthesis offers no significant advantage over the route developed by Höberg and Hjalmarsson (28).

Another route affording alkylidenecarbenes via intermediate ketenes was recently developed by Besida and collaborators (29). The

Scheme 1



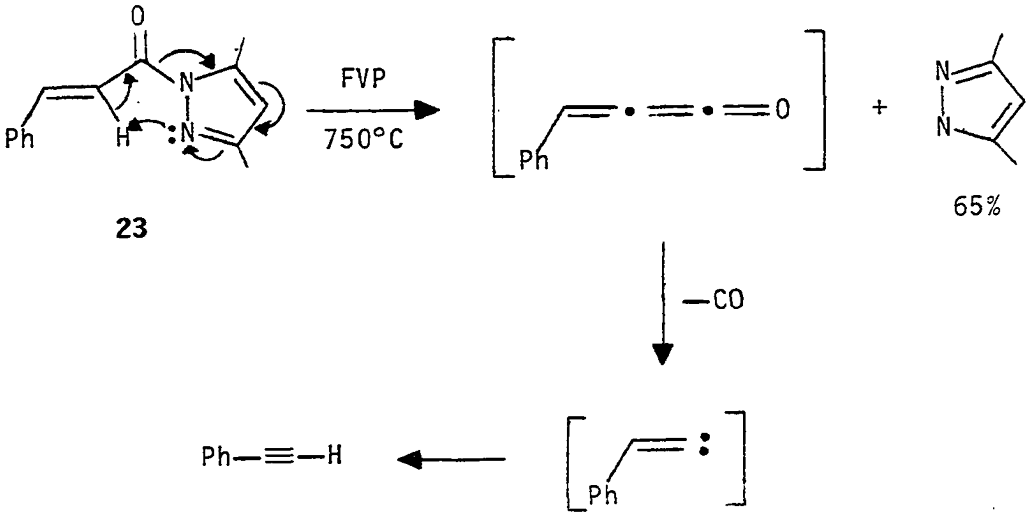
Scheme 2



X = S, NH, NMe, O

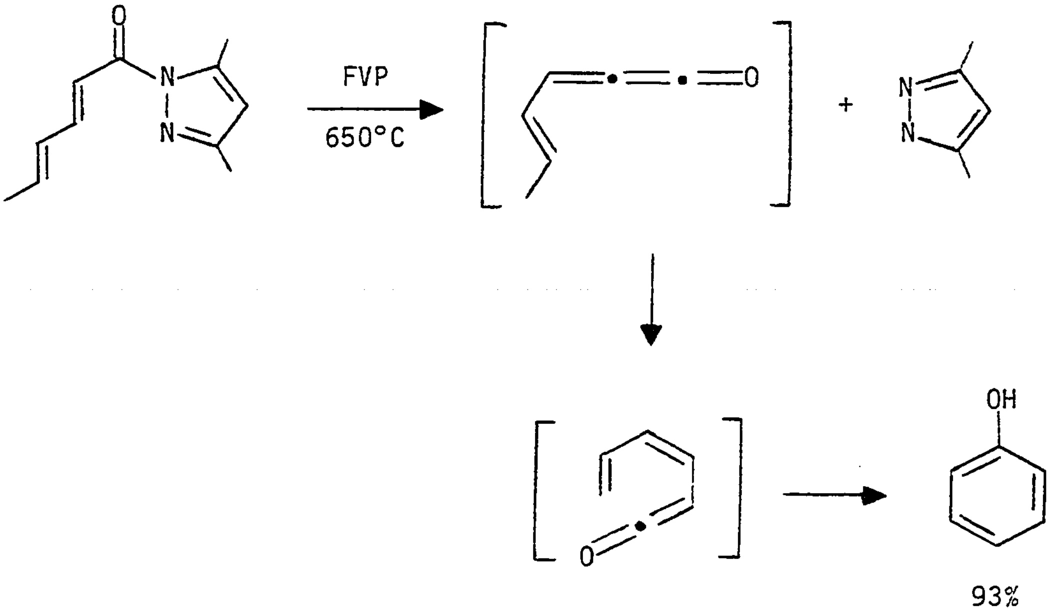
method involves the FVP of N-alkenoylpyrazoles. For example, FVP of 1-cinnamoyl-3,5-dimethylpyrazole, **23**, produced phenylacetylene in 93% yield along with a 65% yield of 3,5-dimethylpyrazole. The mechanism of this elimination was probed by placing a deuterium label geminal to the carbonyl group. Pyrolysis of deuterium labeled **23** revealed only 2% deuterium incorporation in phenylacetylene. The mechanism proposed is shown in Scheme 3. The advantage of this route lies in the mild and general methods used in preparation of the pyrazole derivatives from acid chlorides as compared to the conditions required for preparation of Meldrum's acid derivatives from the requisite aldehydes.

Scheme 3

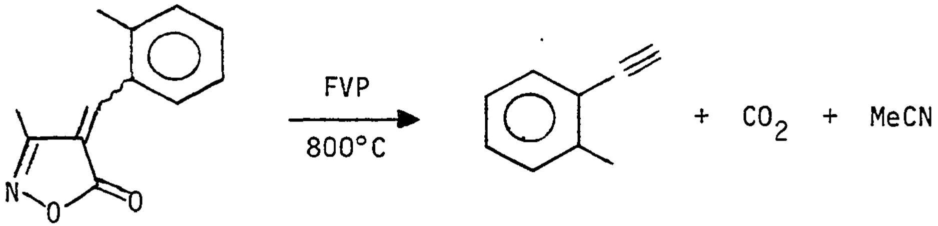


With intermediate methyleneketenes formed in the FVP of pyrazole derivatives, rearrangement to phenols is possible. This, indeed, occurs with appropriately substituted precursors as shown in Scheme 4. Several substituted phenols were prepared by Besida and co-workers utilizing this route (29). Though of slight general synthetic utility, this method would provide for a simple route to specifically labeled phenols.

Scheme 4



While FVP of 1,3-dioxan-4,6-dione, 3,5-dimethylpyrazole, and isoxazolone derivatives may result in formation of identical products, they may also give rise to distinctly different products. In contrast to the formation of 2-naphthol from the pyrolysis of Meldrum's acid derivative **19**, Wollweber, as cited in Briehl et al. (30), found that the FVP of isoxazolone derivative **24** at 800°C gave o-ethynyltoluene, **25**, in 95% yield. While the pyrolysis of isoxazolones directly yields alkylidenecarbenes, 1,3-dioxan-4,6-dione and 3,5-dimethylpyrazole derivatives decompose upon pyrolysis to produce intermediate methyleneketenes which fail to lose carbon monoxide but instead tautomerize and undergo subsequent rearrangements such as those shown in Schemes 1, 2, and 4.



24

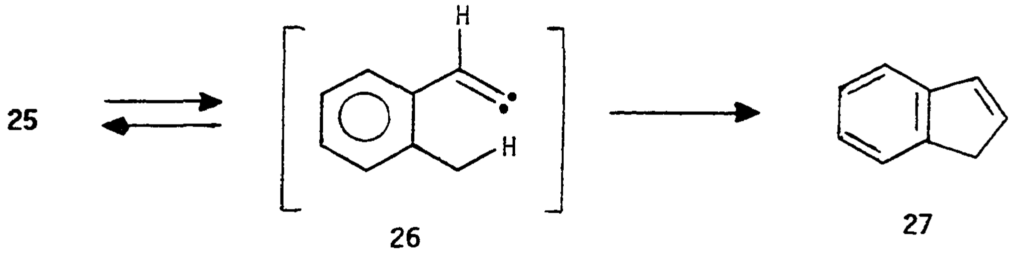
25 95%

Since β-hydrogen substituted alkylidenecarbenes readily isomerize to the corresponding acetylenes, it seems reasonable that FVP of acetylenes would provide a viable route to intermediate alkylidenecarbenes. This possibility was examined by Brown and co-workers in the FVP of o-ethynyltoluene, **25**, at 720°C which produced indene, **27**, in 79% yield (31). Isolation of indene was taken as evidence for the formation of carbene **26** which was subsequently trapped by C-H insertion into the o-methyl group (Scheme 5).

Further supportive evidence for the equilibrium of acetylenes and alkylidenecarbenes was obtained by Brown et al. in the pyrolysis of 2-ethynylbiphenyl, **28**, at 700°C (31). The authors mentioned that the formation of phenanthrene, **30**, could arise from insertion of carbene **29** into a C-H bond of the phenyl substituent by direct cyclization of

28 to a phenanthrene skeleton followed by hydrogen migration or even by isomerization of 1,2-benzazulene, **31**, to phenanthrene. However, they explained formation of **31** by π addition of carbene **29** to the adjacent phenyl substituent followed by ring expansion (path "B", Scheme 6).

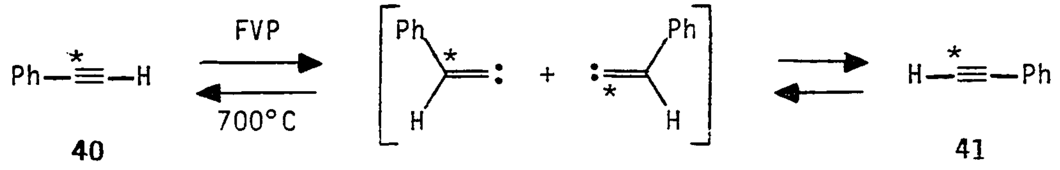
Scheme 5



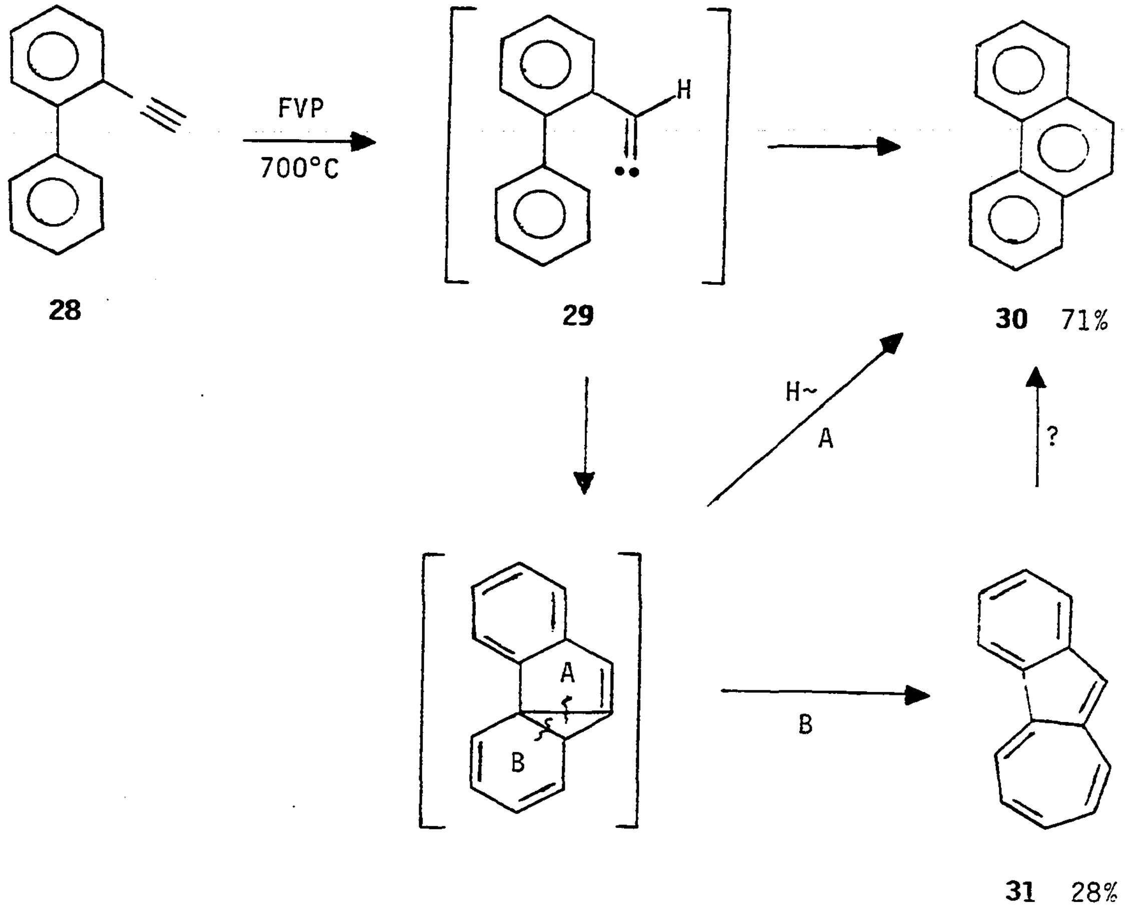
Additional examples of products arising from insertion of alkylidenecarbenes into C-H bonds, from the work of Brown and collaborators, are shown in Scheme 7 (32). Formation of acenaphthylene, **33**, and phenalene, **35**, support proposed formation of carbenes **32** and **34** by 1,2-hydrogen migration on the respective acetylenic frameworks. Formation of phenylindenes **38** and **39** from acetylene **36** indicates the possibility of a 1,2-phenyl migration resulting in formation of carbene **37**. The presence of 2-phenylindene was not unexpected based upon the known thermal interconversion of aryl substituted indenes.

The possibility of competitive 1,2-phenyl and 1,2-hydrogen migration was realized in an experiment by Brown and collaborators

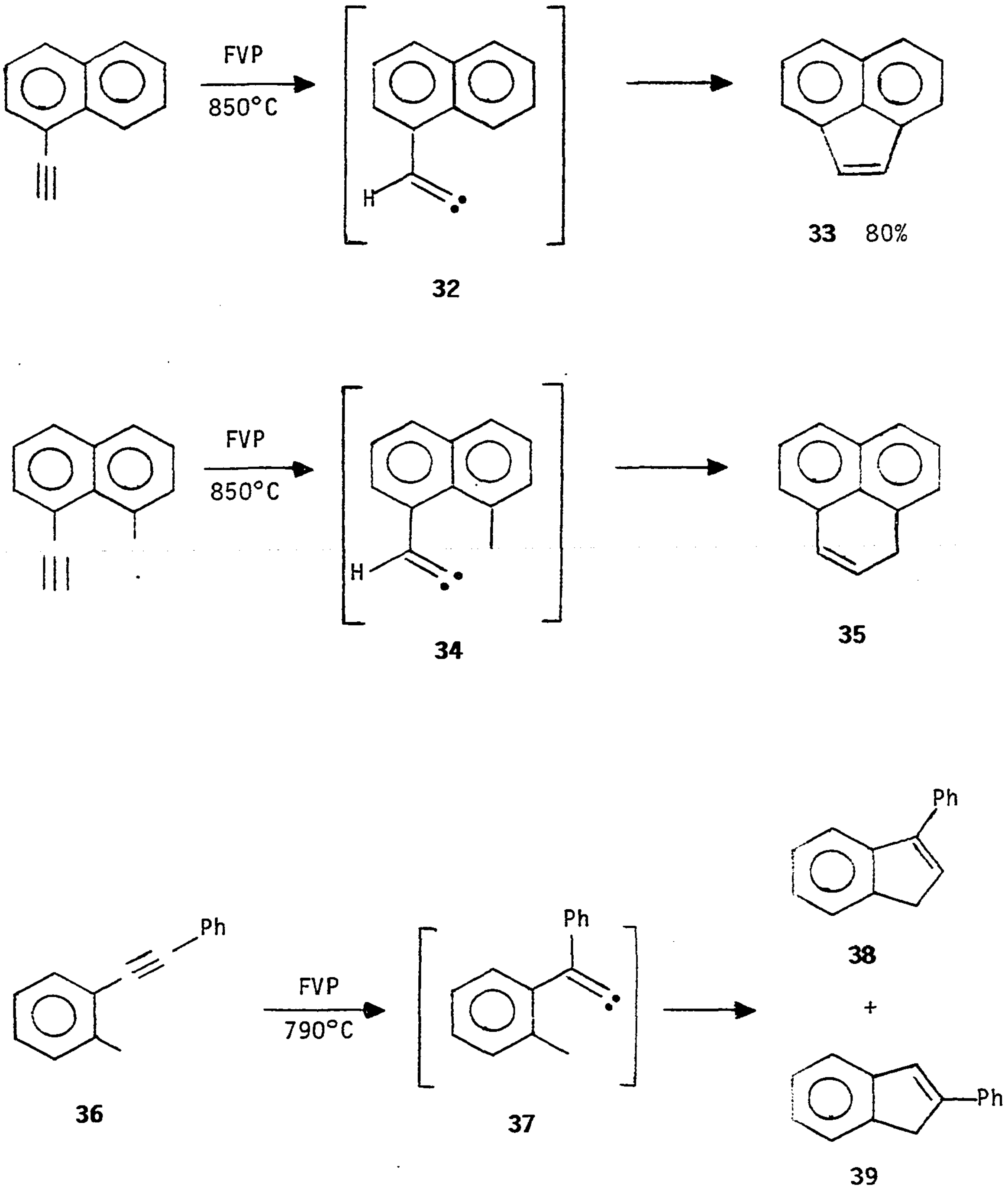
(31). Carbon-13 labeled phenylacetylene, **40**, was pyrolyzed at 700°C. Analysis of the pyrolysate revealed the presence of labeled acetylenes **40** and **41** in equal amounts. These results were explained by competitive hydrogen or phenyl migration.



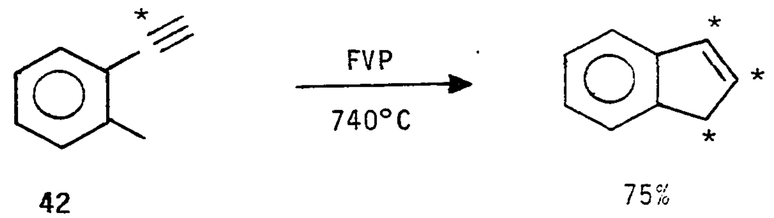
Scheme 6



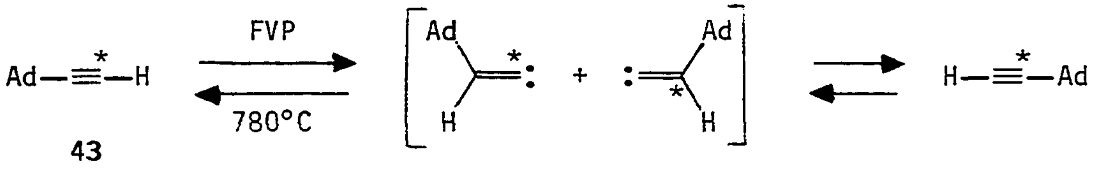
Scheme 7



As anticipated, labeled acetylene **42** gave indene with the carbon-13 label scrambled throughout the 1, 2, and 3 positions of the indenyl ring (32). The 2 position is presumably labeled through precyclization scrambling of the starting acetylene while the 1 and 3 positions are readily interconverted through successive 1,5-hydrogen shifts.

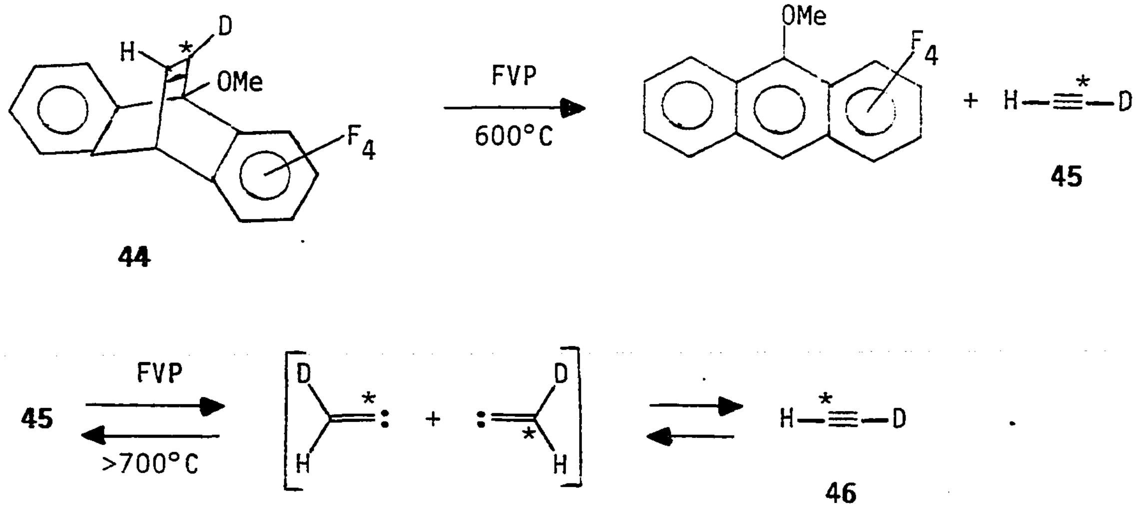


The competitive 1,2-migration of hydrogen and alkyl groups on acetylenes was also established by Brown and co-workers in the pyrolysis of carbon-14 labeled 1-adamantylacetylene, **43**. The label was found to be present in both acetylenic carbon positions in a ratio of 75:25 with the majority of the label unscrambled. Onset of scrambling was determined to occur at approximately 700°C.



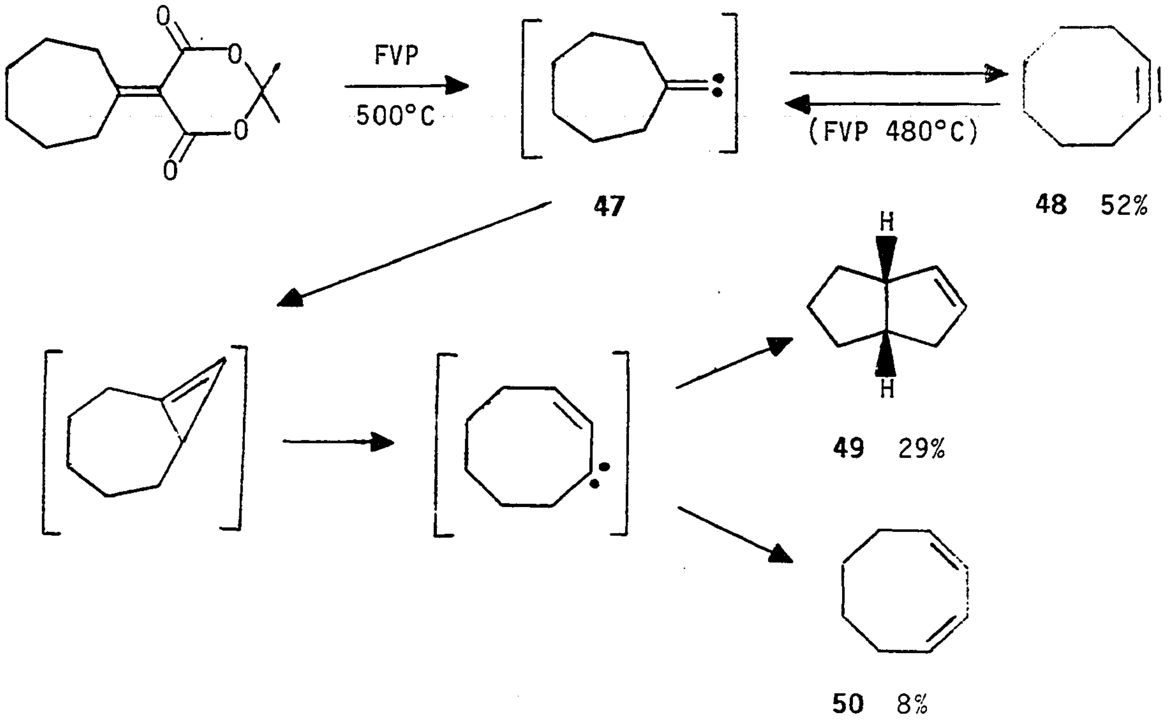
The thermal equilibrium of acetylenes and alkylidenecarbenes was most convincingly established in an elegant study by Brown and co-workers (33). The long and tedious synthesis of **44** ultimately led to doubly labeled acetylene **45**. Pyrolysis of **45** at 850°C gave a pyrolysate consisting of **45** and **46** in a 60:40 ratio. In addition, the authors established that scrambling does not occur below 700°C and no intermolecular hydrogen exchange takes place below 1050°C.

Scheme 8

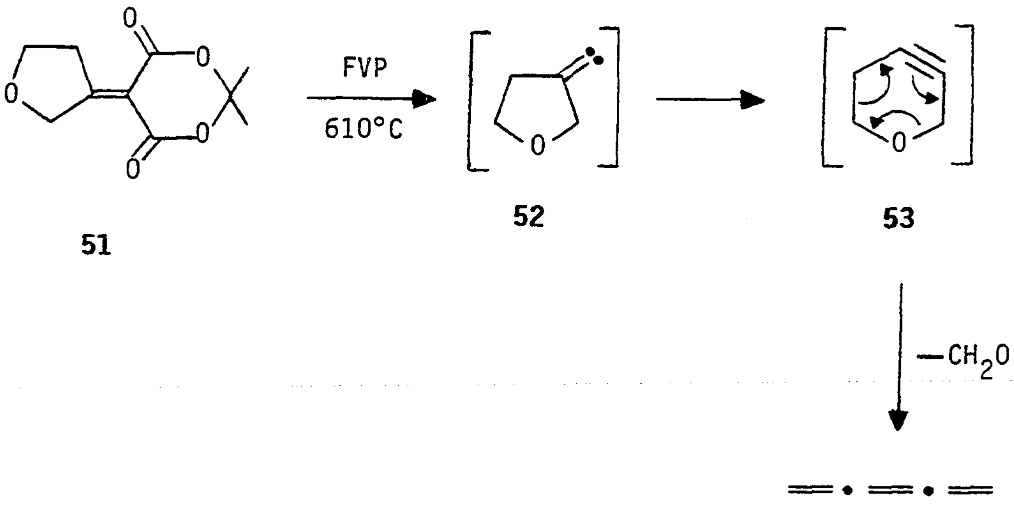


In an effort to exploit the reversible rearrangement of acetylenes to alkylidenecarbenes, Baxter and Brown prepared and pyrolyzed Meldrum's acid derivatives of four- to eight-membered cyclic ketones including tetrahydrofuran- and tetrahydrothiophen-3-ylidene derivatives (34). Products obtained from FVP of these cycloalkylidene derivatives were postulated to involve the formation of the expected cycloalkylidenecarbenes. A 1,2-alkyl shift would lead to the observed cycloalkynes. Insertion of the carbene into an adjacent C-H bond leads to the formation of a thermally unstable bicyclopropene which ring opens to a vinylcarbene leading to formation of the other observed products. A typical example of the sequence of these rearrangements is shown in Scheme 9. The 52% isolated yield of cyclooctyne, **48**, accompanied by the formation of **49** and **50** strongly implies the intermediacy of carbene **47**. Further evidence for the interconversion of acetylene **48** and carbene **47** was obtained upon pyrolysis of cyclooctyne at 480°C which gave **49** and **50** in addition to recovered **48**.

Scheme 9



Similarly, pyrolysis of tetrahydrofuran-3-ylidene, **51**, gave products rationalized by formation of carbene **52** which rearranges to give cycloalkyne **53** which in turn yields formaldehyde and butatriene by way of a retro-Diels-Alder fission. Flash vacuum pyrolysis of tetrahydrothiophen-3-ylidene gave analogous products.

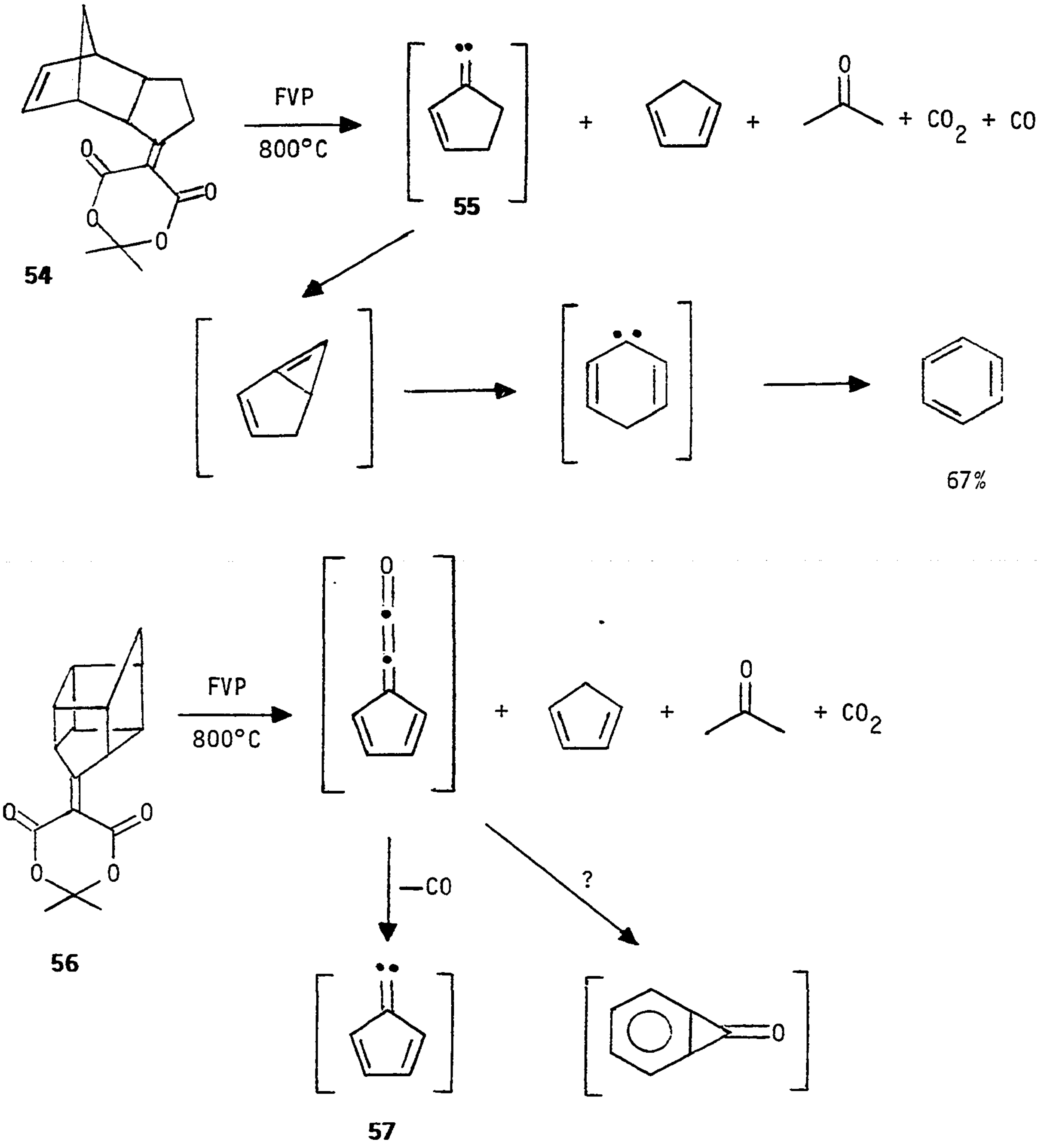


51 **52** **53**

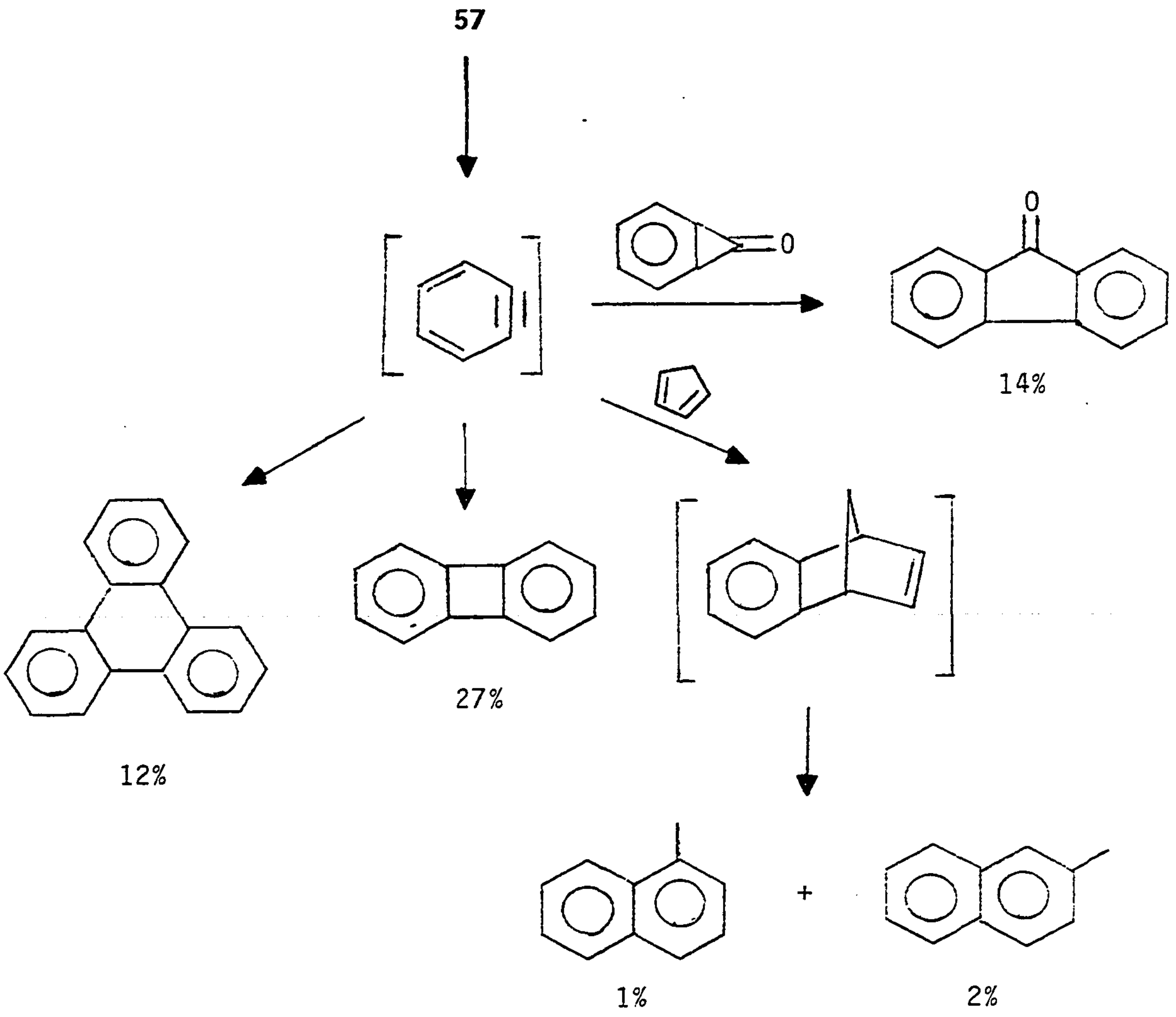
30%

Interesting extensions of this work by Armstrong and others resulted in formation of cyclopent-2-enylidenecarbene, **55**, and cyclopentadienylidenecarbene, **57** (35). Flash vacuum pyrolysis of **54** at 800°C gave quantitative yields of cyclopentadiene and acetone along with a 67% yield of benzene. Formation of benzene was postulated to involve carbene **55** as shown in Scheme 10. Pyrolysis of Meldrum's acid derivative **56** gave a complex mixture of products, some of which are shown in Scheme 10. The authors proposed that the products were derived from benzyne which was formed by isomerization of carbene **57**.

Scheme 10

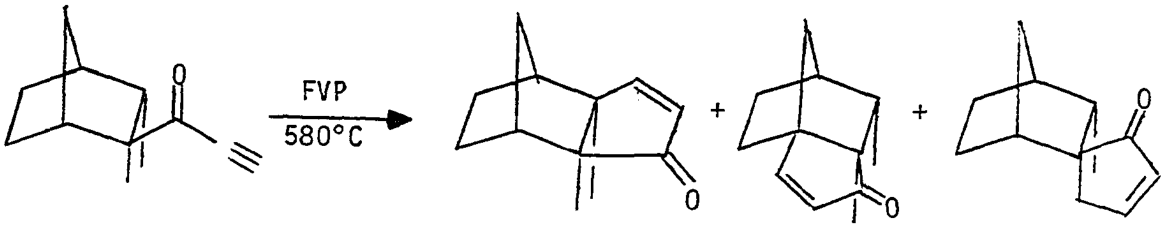


Scheme 10 (continued)



Dreiding's group has examined the regio- and stereospecificity of alkylidenecarbene cyclization of α-alkynones in the gas phase (36-38). Pyrolysis of α-alkynone **58** leads to the formation of transient carbene **59** which inserts into either of two different C-H bonds forming bicyclic or spiro ketones **60** or **61** (Scheme 11). Mass recovery varied from 90% for R = H, D, Me_3Si to 76% for R = CH_3. Temperature requirements necessary to attain complete cyclization of starting alkynone varied from 600°C for R = H to 700°C for R = Me_3Si. The most interesting observation was a greater than nine-fold preference for formation of bicyclic ketone **60** over the isomeric spiro ketone **61**. The selectivity was proposed to arise from a greater preference for secondary over primary C-H bond insertion. This premise was verified in subsequent experiments whereby numerous α-alkynones were pyrolyzed. All examples exhibited this same preference (37). As expected, tertiary C-H bond insertion was demonstrated to be favored over insertion into secondary and primary C-H bonds. One example of this is shown in Scheme 11 where the pyrolysis of α-alkynone **62** produced **63**, **64**, and **65** in ratios of 69:26:5. The specificity of the α-alkynone cyclization supports the postulate of a carbene intermediate since, for gas phase carbenes, preference of insertion into C-H bonds has already been established as tertiary > secondary > primary (39, 40).

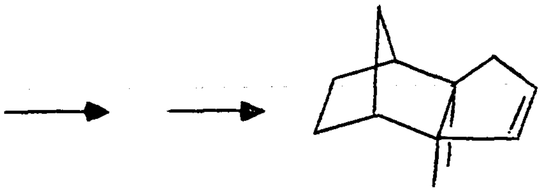
Application of the α-alkynone cyclization to the synthesis of (±) albene, **68**, revealed an interesting thirty-fold preference for formation of **66** over **67** even though both cyclizations involve carbene insertion into tertiary C-H bonds (38). The authors noted that the highly selective formation of **66** was the result of insertion into a C-H bond synperiplanar to the intermediate alkylidenecarbene. A synperiplanar arrangement of the alkylidenecarbene and the neighboring bridgehead C-H bond could not be attained disfavoring cyclization to give **67**. This observation implies an important conformational relationship between the reacting C-H bond and the alkylidenecarbene.



66 **67**

91 : 3 : 6

66



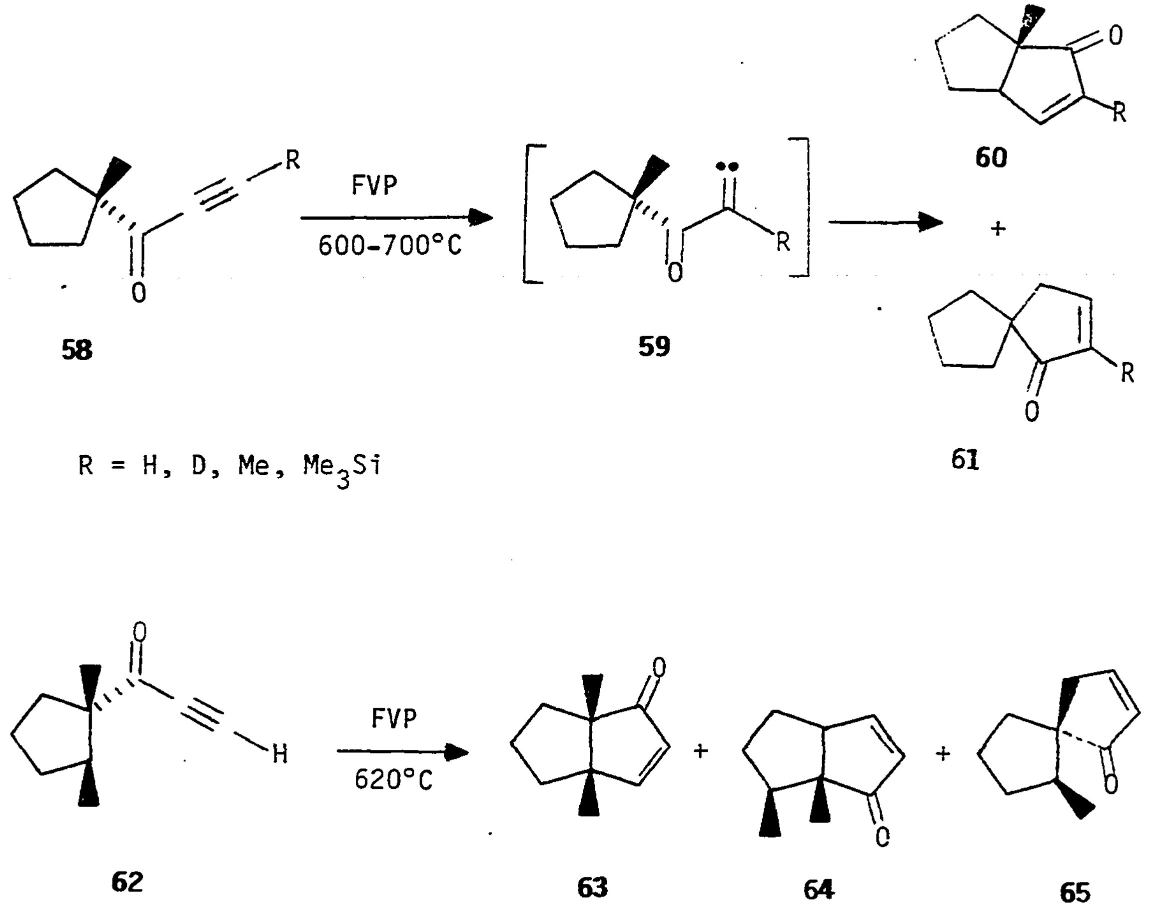
68

The α-alkynone cyclization has also been exploited in key steps in the total synthesis of (±)-modhephene and (±)-$\Delta^{9\,(12)}$-capnellene (41, 42).

As with unsymmetrically substituted acetylenes, there is the possibility of competitive 1,2-migration of substituents on α-alkynones. Although this premise has not been experimentally verified, theoretical calculations by Kaneti and co-workers suggest this is true (43). Comparisons were made for hydrogen, alkyl, formyl, and acyl migrations in the series propynal, butynal, and butynone.

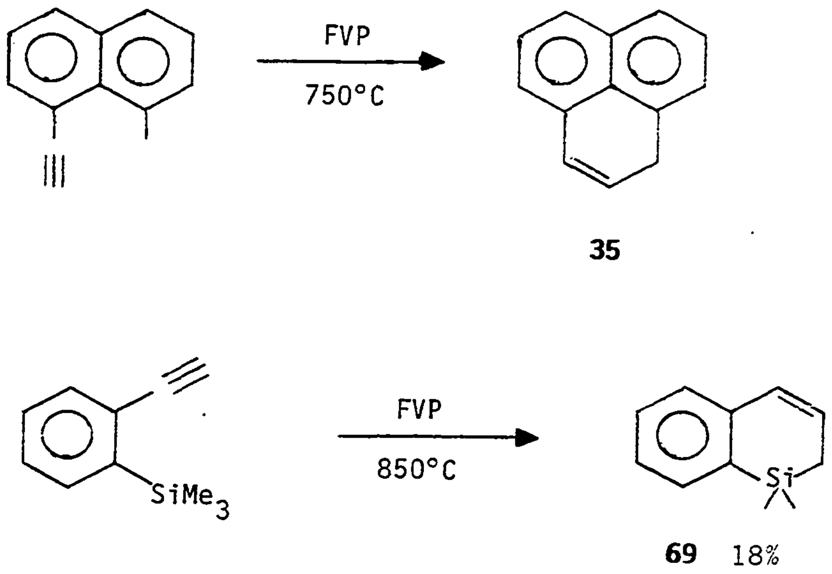
The differences predicted for the various pairs of substituents ranged from 3 kcal/mole for butynone to 10 kcal/mole for propynal. The authors found that the activation energy for a 1,2-shift of one substituent depended upon the other substituent on the acetylene. Their calculations permitted the conclusion that hydrogen and alkyl migration would compete favorably with formyl and acyl migration.

Scheme 11



The competitive formation of six-membered ring systems by intramolecular cyclization of alkylidenecarbenes is conspicuously absent though a possibility in many examples (36-38). Even when the formation of a five-membered ring was prohibited as in the pyrolysis of neopentylethynylketone, unless a C-C bond insertion is considered, no six-membered rings were formed. To date, only two examples of alkylidenecarbene trapping in the gas phase resulting in the formation of six-membered rings (Scheme 12) are known (32, 44). The yield of **35** was not specified but could not have exceeded 56%, and the yield of **69** was only 18%. It is apparent that alkylidenecarbenes, in the gas phase (37) as well in solution (45), show an important relationship in which a six-membered arrangement of reacting centers is highly preferred.

Scheme 12

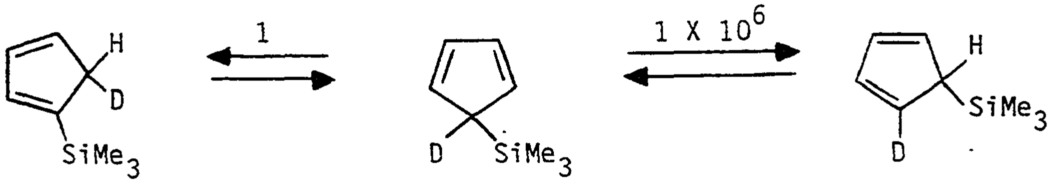


35

69 18%

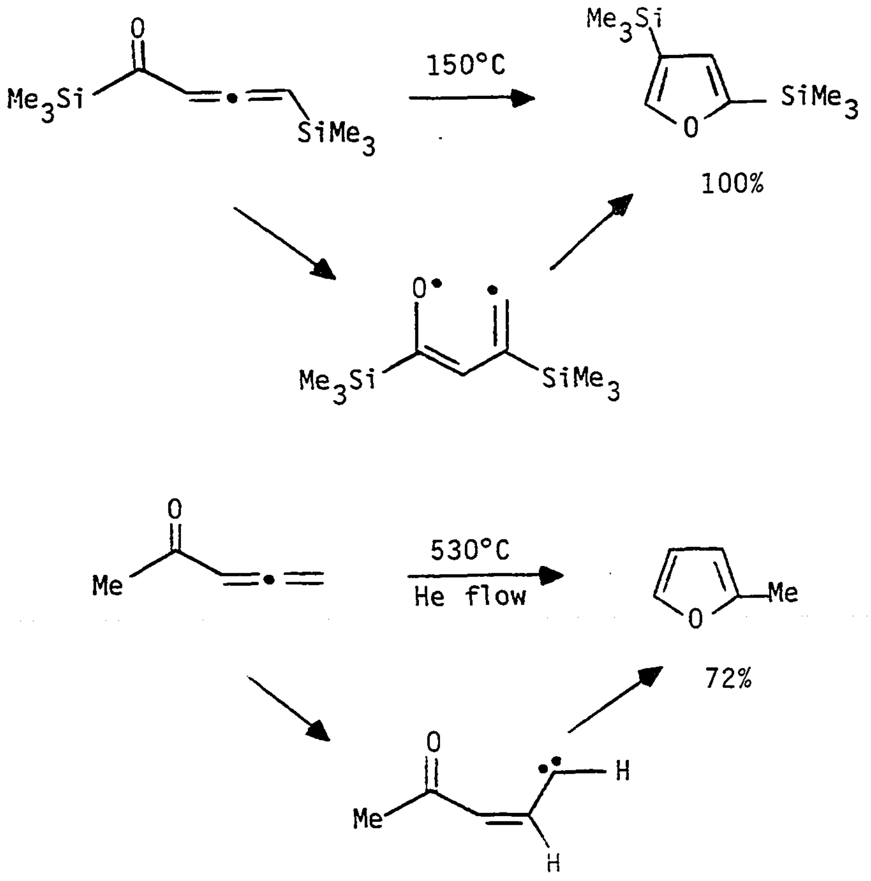
RESULTS AND DISCUSSION

The reason for using a silyl migrating group in these 1,2-shifts is a result of the general observation that silyl groups migrate more readily than does hydrogen (46). For example, trimethylsilyl has been shown to undergo a thermal 1,5-sigmatropic shift approximately one million times faster than does hydrogen (47).



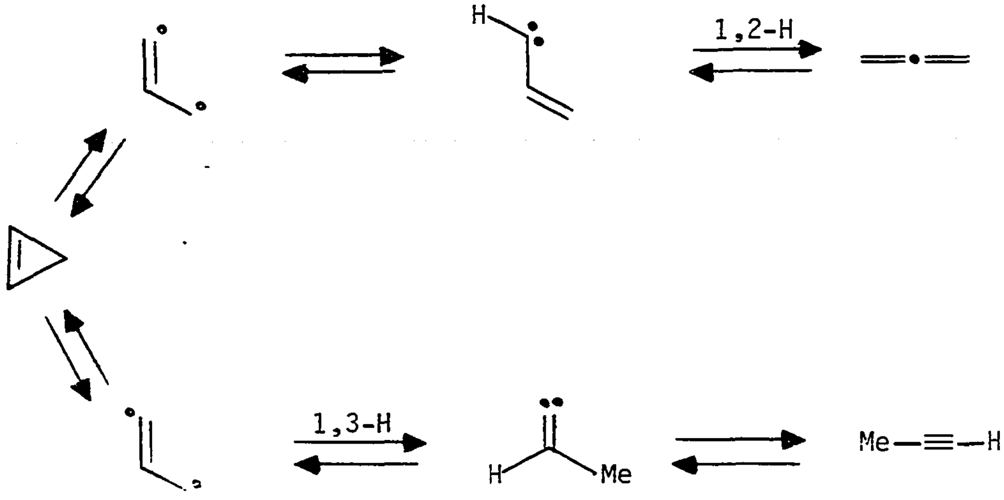
There is evidence which suggests 1,2-silyl migrations are more facile than the corresponding 1,2-hydrogen migrations. Barton and Hussmann found that trimethylsilyl 3-(trimethylsilyl)allenyl ketone readily cyclizes to 2,5-bis(trimethylsilyl)furan at 150°C (48). By comparison, methyl allenyl ketone cyclizes to 2-methylfuran at 530°C in a helium flow pyrolysis (49). Both cyclizations were proposed to be initiated by 1,2-shifts as is shown in Scheme 13. It seems reasonable, although it is not demanded, that both of these cyclizations proceed by 1,2-shifts, but the thermal requirement of the 1,2-hydrogen shift is much greater than the corresponding 1,2-silyl shift.

Scheme 13



The interconversion of allenyltrimethylsilane and trimethyl(propargyl)silane has been studied by Slutsky and Kwart (50). They proposed that this rearrangement occurs via a 1,3-silyl migration with inversion at silicon. More recently, Hopf and co-workers (51) have obtained data which suggest that the thermal interconversion of allene and propyne occurs through the intermediacy of cyclopropene. Although this interconversion has also been long assumed to occur via a single 1,3-hydrogen shift, it seems that a 1,2-hydrogen shift is required to involve cyclopropene as an intermediate. This postulate has been confirmed by the calculations of Honjou et al. (52) who have shown that the most favorable pathway for the interconversion of allene to propyne involves initial 1,2-hydrogen shifts and that cyclopropene is, indeed, an intermediate in this rearrangement. The scheme proposed by Honjou et al. is outlined in Scheme 14.

Scheme 14



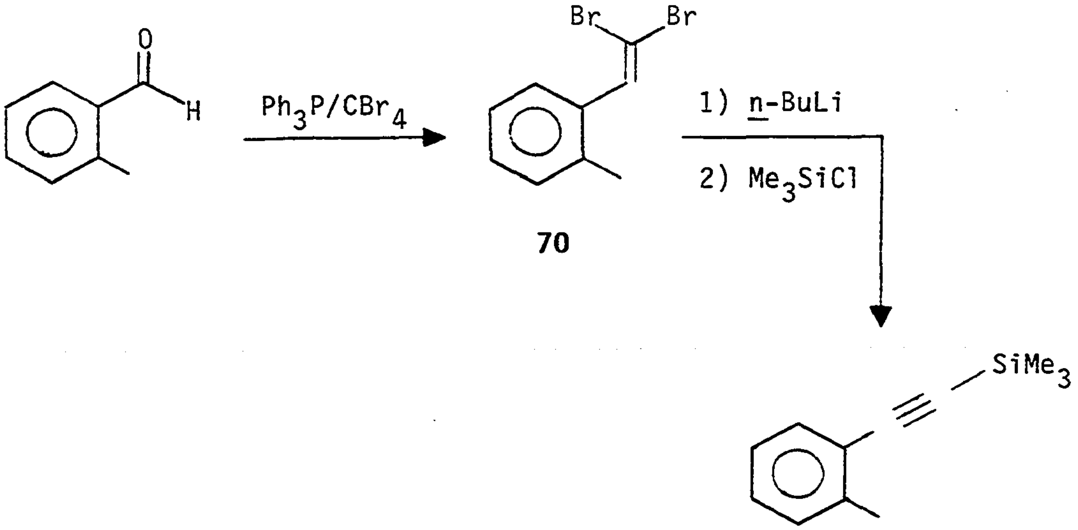
Despite all the examples of 1,2-hydrogen shifts on acetylenes already discussed (see Historical Section), the only example of a 1,2-silyl shift on an acetylene comes from the work of Karpf and Dreiding (36) and is shown in Scheme 11. In this single example, it was found that the thermal requirement of the 1,2-silyl shift was greater than that of the corresponding 1,2-hydrogen shift by about 100°C. The cause of this unexpected difference is not obvious, and no explanation was offered. No other 1,2-silyl migrations on acetylenes have appeared in the literature.

It must be kept in mind that while the 1,2-shifts referred to in this work consider only the hydrogen in terminal acetylenes or the silyl group in internal acetylenes as migrating groups, other 1,2-substituent migrations may be competitive as has been predicted by Kaneti et al. (43) and demonstrated by Brown et al. (33).

Formation of Carbocycles by the Pyrolysis of Acetylenes

Initial research in this area was prompted by the observations of Brown and co-workers (31) who found that FVP of o-ethynyltoluene, **25**, gave indene in high yield. It was hoped that substitution of the acetylenic hydrogen of **25** by a trimethylsilyl group would diminish the thermal requirements of this rearrangement. The large stabilizing effect predicted for silane substituted alkylidenecarbenes (12) may also facilitate intramolecular trapping of the carbene as well. In order to compare 1,2-silyl migrations with the analogous 1,2-hydrogen migrations observed by Brown and co-workers (31), the preparation of o-(trimethylsilylethynyl)toluene, **71**, was undertaken (Scheme 15). Reaction of commercially available o-tolualdehyde with the modified Wittig reagent prepared in situ from carbon tetrabromide and triphenylphosphine afforded gem-dibromide, **70**, in 86% yield. Treatment of **70** with two equivalents of n-butyllithium followed by quenching with chlorotrimethylsilane gave the desired acetylene in 93% yield. This approach to arylacetylenes proved to be quite general and was utilized to prepare many of the arylacetylenes examined throughout this work.

Scheme 15



70

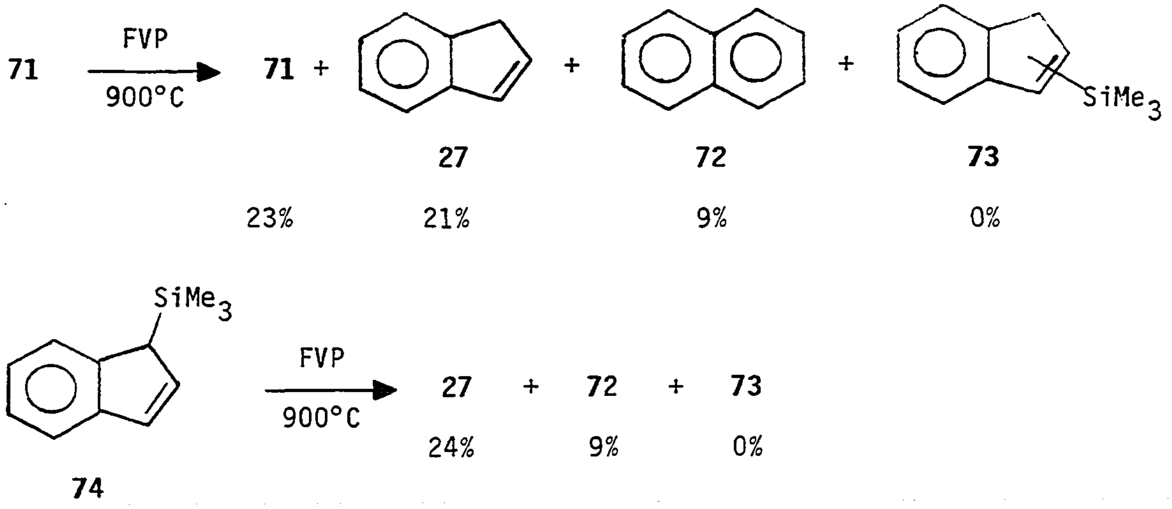
71

Only starting material was recovered from the flash vacuum pyrolysis of 71 at temperatures from 560°C to 800°C. At the disappointingly high temperature of 900°C, acetylene 71 produced indene, 27, and naphthalene, 72, in 21% and 9% yields, respectively, based on a 23% yield of recovered starting material (Scheme 16). No 3-trimethylsilylindene or the expected (53) 1- and 2-trimethylsilylindenes were present.

The presence of indene in the pyrolysate warranted examination of the thermal stability of the expected 1-, 2-, and 3-trimethylsilylindenes to the pyrolysis conditions. Since 1-trimethylsilylindene is the easiest of the isomers to prepare (54) and readily undergoes isomerization to the 2- and 3-isomers at 165°C (53), it was used instead of a mixture of the three isomers. Flash vacuum pyrolysis of 1-trimethylsilylindene, **74**, at 900°C led to the formation of indene and naphthalene in the yields shown in Scheme 16. No trace of starting material or other products retaining silicon were found. In both pyrolyses, small amounts of four or more inseparable isomers of molecular weight (MW) 130 were present in less than 1% yield each. These isomers are possibly formed along the pathway leading to the formation of naphthalene from **71**. While these data do not allow determination of the sequence of events leading to the loss of the silyl group, it is a reasonable assumption that indene and naphthalene are derived from silylindenes which are not stable under these conditions but decompose to give the observed products.

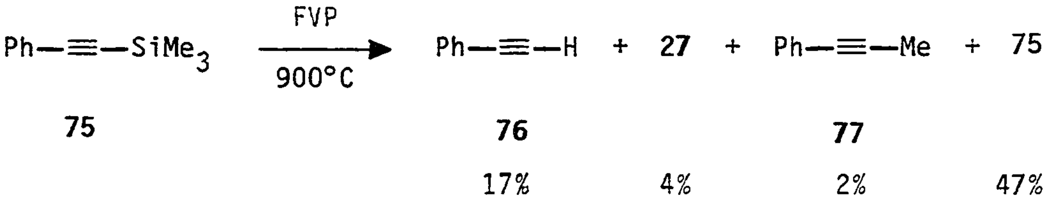
Indeed, the elements of dimethylsilylene are lost at 780°C in the FVP of 1-trimethylsilylindene, **74**, producing 1-, 2-, and 3-methylindenes in 11% combined yield at 63% completion (55). Subsequent rearrangement and decomposition of methylindenes gives rise to the formation of other isomers and also naphthalene by way of radical pathways (56). Loss of dimethylsilylene from other intermediate isomers of **71** would produce isomers of MW 130 which could conceivably become involved in the same pathways leading to the formation of naphthalene.

Scheme 16



Formation of indene from the FVP of **71** may be the result of the decomposition of **71** to o-ethynyltoluene which is known to cyclize to indene (31). As a test of this question, (trimethylsilyl)phenylacetylene, **75**, prepared from phenylacetylene following the procedure described by Eaborn and Walton (57), was pyrolyzed at 900°C (Scheme 17). The pyrolysate (70% mass recovery) was analyzed and found to contain phenylacetylene, **76**, indene, **27**, and 1-phenylpropyne, **77**, in 17%, 4%, and 2% yield, respectively, corrected for 47% yield of recovered **75**. The presence of phenylacetylene implies that formation of indene is possible in the pyrolysis of **71** via o-ethynyltoluene. However, absence of **25** in the pyrolysate of **71** (vide infra) and the low yield of phenylacetylene from **75** argues that initial loss of the silyl group is most likely a minor source of indene.

Scheme 17

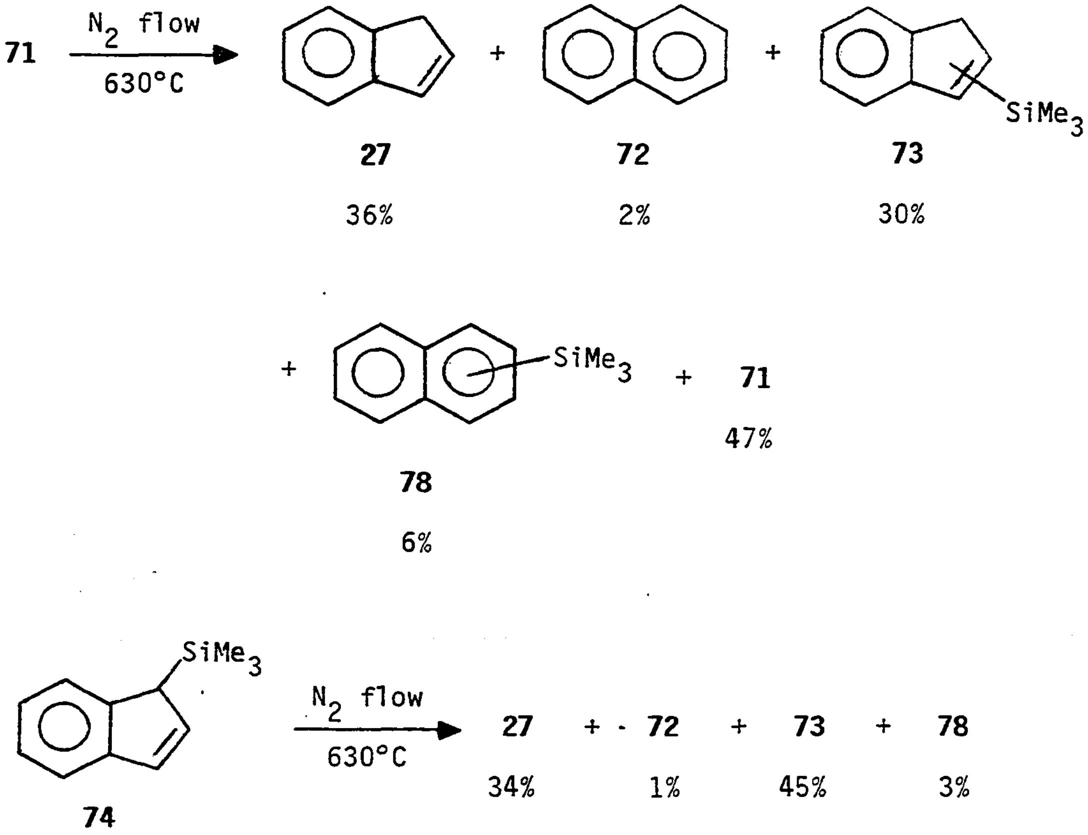


$$\underset{\textbf{75}}{\mathrm{Ph{-}{\equiv}{-}SiMe_3}} \xrightarrow[900°\mathrm{C}]{\mathrm{FVP}} \underset{\substack{\textbf{76}\\17\%}}{\mathrm{Ph{-}{\equiv}{-}H}} + \underset{4\%}{\textbf{27}} + \underset{\substack{\textbf{77}\\2\%}}{\mathrm{Ph{-}{\equiv}{-}Me}} + \underset{47\%}{75}$$

Interesting results were obtained from the nitrogen flow pyrolysis of o-(trimethylsilylethynyl)toluene at 630°C (Scheme 18). At 53% completion, the pyrolysate consisted of indene (36%), naphthalene (2%), MW 130 isomers (9% uncorrected), 1-, 2-, and 3-trimethylsilylindene (30% combined), and a trimethylsilyl substituted naphthalene (6% uncorrected). The presence of the three isomeric trimethylsilylindenes in good yield supports the earlier postulate of their intermediacy in the FVP of **71**. The formation of trimethylsilylnaphthalene, whose identity was based on GC/MS (gas chromatography/mass spectrometry) data, was surprising. No additional data have been accumulated which could offer a solution to the origin of **78**, and a discussion of its formation would be unprofitable.

These results necessitated the examination of the flow pyrolysis of the isomeric silylindenes, **73**. The products obtained from the flow pyrolysis of **74** are shown in Scheme 18 accompanied by their yields which are not corrected for recovered starting material.

Scheme 18



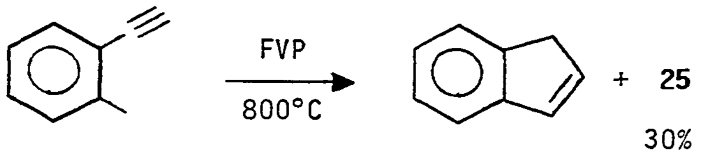
Based upon the data obtained from these pyrolyses, it seems that the mechanism proposed by Brown and co-workers (31), as shown in Scheme 5, is operative here as well. The difference lies in the subsequent loss of the silyl group and following reactions which are not understood.

As a direct comparison of the migratory aptitudes of silicon and hydrogen in these 1,2-shifts was desired, it was necessary to pyrolyze o-ethynyltoluene (Scheme 19) using the same pyrolysis apparatus used in the above studies. Pyrolysis of **25** at 800°C, 1 X 10^{-4} torr, led to the formation of indene in 86% yield based on a 30% yield of recovered **25**. Pyrolysis of **25** at 900°C, 1 X 10^{-4} torr, produced a pyrolysate (77% mass recovery) consisting of indene and acetylene **25** in a 9:1 ratio. These data also serve as a comparison of these conditions with those of Brown et al. who observed complete cyclization of o-ethynyltoluene to indene in 79% yield at 720°C, 0.05 torr (31).

The nitrogen flow pyrolysis of acetylene **25** was also examined (Scheme 19). At 630°C, indene was obtained in 43% yield as the only volatile product. The cyclization of acetylene **25** to indene is somewhat more facile than that of silyl derivative **71**. In addition to serving as a comparison with the pyrolyses of **71**, the absence of naphthalene in the pyrolyses of **25** suggests that neither **25** nor indene are significant sources of naphthalene in the pyrolysis of **71**.

As an additional example of a 1,2-silyl migration was sought, acetylene **79** was prepared employing the same sequence of reactions outlined in Scheme 15. Pyrolysis of **79** at 900°C, 1 X 10^{-4} torr, furnished a pyrolysate (58% mass recovery) consisting of phenanthrene and 9-trimethylsilylphenanthrene, **80**, in 19% and 10% yield, respectively, at 67% conversion (Scheme 20). The identity of these products was established by comparison of GC/MS data and GC retention times with authentic samples. In addition, a small amount (4%, uncorrected GC yield) of an isomer of **80** was obtained and has been speculated to be the anticipated trimethylsilylbenzazulene, **81**, based primarily upon GC/MS data. To again explain the formation of products not possessing silicon, the pyrolysis of 9-trimethylsilylphenanthrene, prepared from phenanthrene according to published procedures (58, 59), was investigated (Scheme 20). Flash vacuum pyrolysis of **80**, under the same conditions as **79**, afforded phenanthrene in 10% yield at 61% completion (52% mass recovery). No products resembling **81** were present. The formation of phenanthrene from pyrolysis of **80** identifies **80** as a source of **30**.

<u>Scheme 19</u>



25 **27**

86%

$$\mathbf{25} \xrightarrow[900°C]{FVP} \underset{75\%}{\mathbf{27}} + \underset{8\%}{\mathbf{25}}$$

$$\mathbf{25} \xrightarrow[630°C]{N_2\ flow} \underset{43\%}{\mathbf{27}}$$

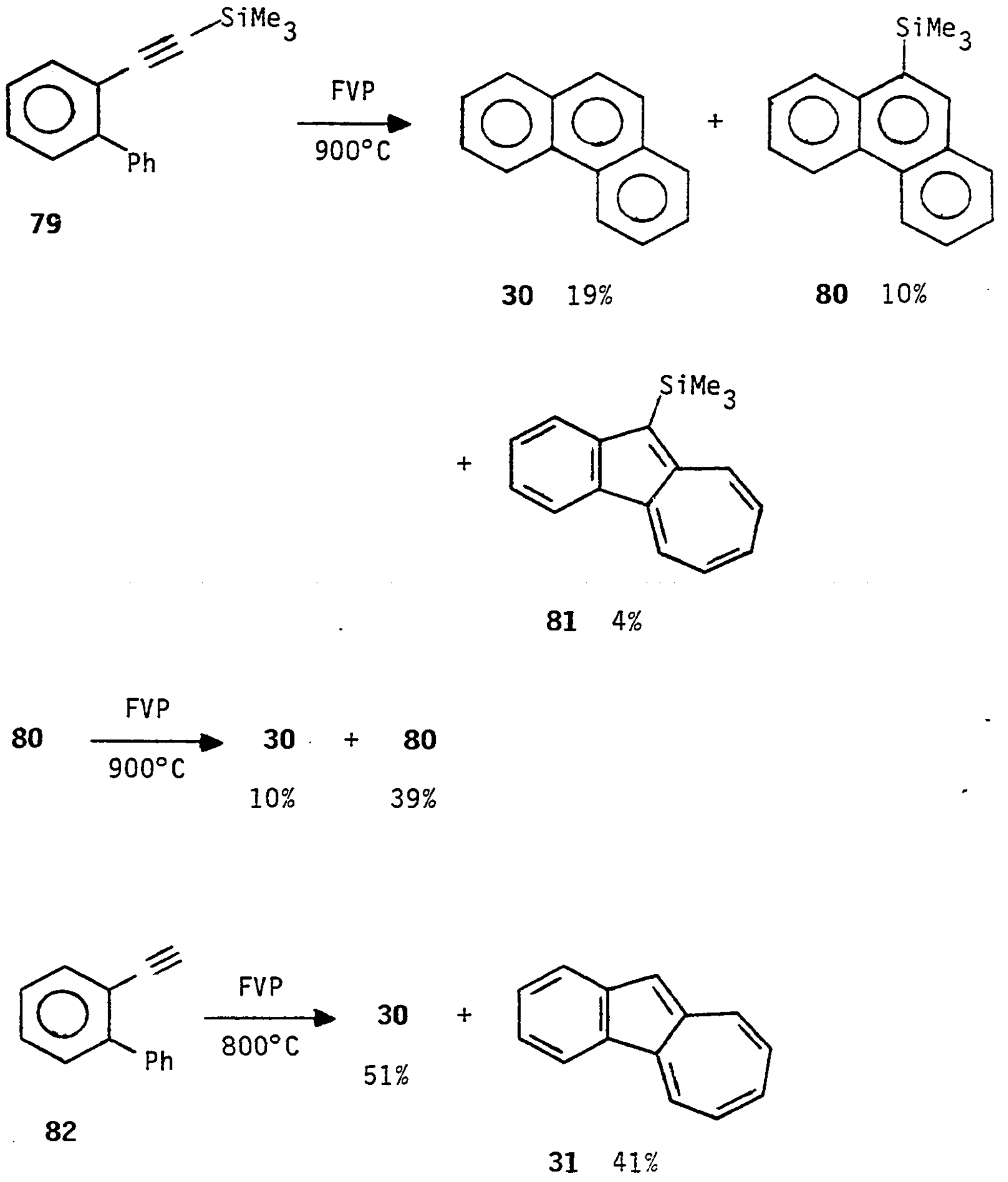
Comparison of the results of the FVP of **79** with those of o-ethynylbiphenyl, **82**, at 800°C, 1 X 10^{-4} torr, reveals that the cyclization of the hydrogen-substituted acetylene (Scheme 20) is more facile than the trimethylsilyl-substituted acetylene. Analysis of the pyrolysate (97% mass recovery) revealed the presence of phenanthrene and 1,2-benzazulene, **31**, in 51% and 41% yield, respectively, at 83% completion. The pyrolysis of **82** at 700°C, 0.2 torr, has previously been investigated by Brown et al. (31) who obtained **30** and **31** in 71% and 28% yield, respectively.

The nitrogen flow pyrolysis of acetylene **79** at 630°C furnished cyclic isomer **80** in 19% yield and the desilylated product, phenanthrene, in 32% yield based upon a 63% yield of recovered starting material. None of the expected 1,2-benzazulene derivative **81** was present. Pyrolysis of 9-trimethylsilylphenanthrene, **80**, at 630°C in a nitrogen flow led to the formation of phenanthrene in 24% yield at 54% conversion. The flow pyrolysis of o-ethynylbiphenyl, **82**, was also carried out at 630°C as a comparison with the pyrolysis of **79**. The results of these experiments appear in Scheme 21.

These cyclizations are fully consistent with the mechanisms proposed by Brown et al. (31) as shown in Scheme 6. The loss of the silyl group is most likely a secondary process and should have no effect on the proposed mechanism of formation of the initially formed polycyclic compounds.

In summary, the pyrolysis of trimethylsilyl-substituted acetylenes has afforded cyclic products consistent with an alkylidenecarbene intermediate. Loss of the trimethylsilyl group appears to occur after cyclization though loss prior to cyclization may be a minor, competitive process The more facile cyclization of hydrogen-substituted acetylenes is apparent as indicated by the relative amounts of recovered starting material in the pyrolysis of acetylenes

Scheme 20



79

30 19%

80 10%

81 4%

80 → **30** + **80**

10% 39%

82

30 51%

31 41%

and analogous silyl-substituted acetylenes. Cyclization of silyl-substituted acetylenes **71** and **79** requires approximately 100°C higher temperatures than terminal acetylenes **25** and **82**.

Scheme 21

$$\mathbf{79} \xrightarrow[630^\circ\mathrm{C}]{\mathrm{N_2\ flow}} \underset{32\%}{\mathbf{30}} + \underset{19\%}{\mathbf{80}} + \underset{63\%}{\mathbf{79}}$$

$$\mathbf{80} \xrightarrow[630^\circ\mathrm{C}]{\mathrm{N_2\ flow}} \underset{24\%}{\mathbf{30}} + \underset{46\%}{\mathbf{80}}$$

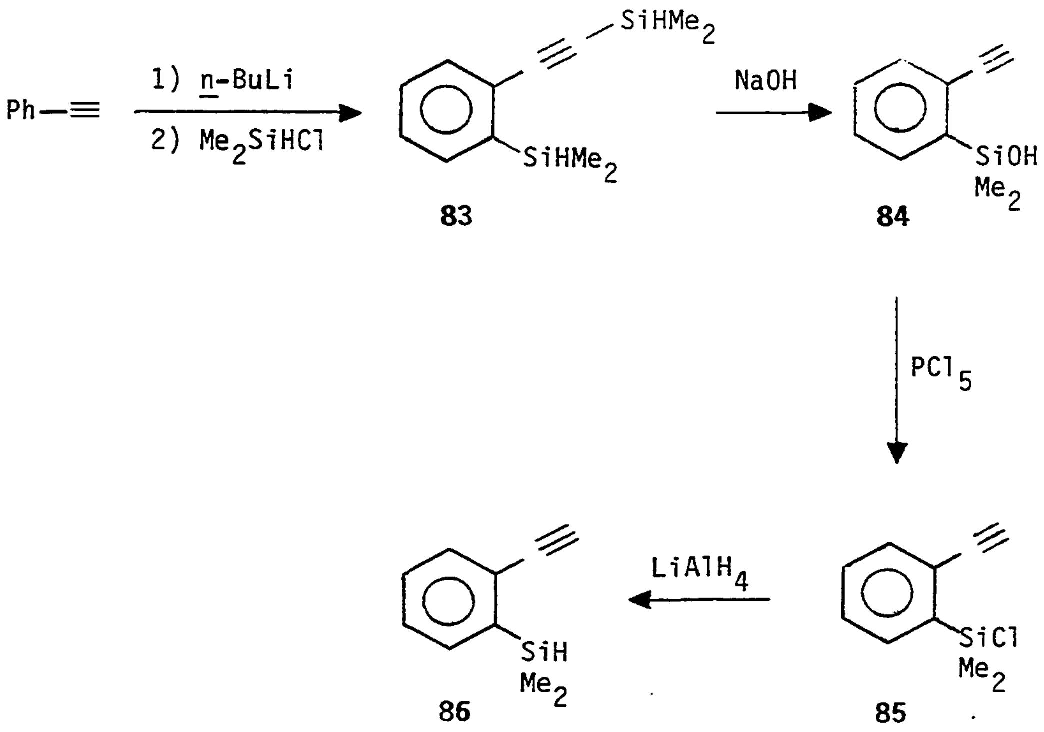
$$\mathbf{82} \xrightarrow[630^\circ\mathrm{C}]{\mathrm{N_2\ flow}} \underset{38\%}{\mathbf{30}} + \underset{1\%}{\mathbf{31}}$$

Formation of Silacycles by the Pyrolysis of β-Dimethylsilyl-Substituted Acetylenes

While the insertion of alkylidenecarbenes into C-H bonds in the gas phase has been well studied, insertion into other bonds has been little explored. Since silyl hydrides are known to be more efficient carbene traps than C-H bonds, synthesis of acetylenes with a dimethylsilyl group twice removed from the triple bond was initiated. Use of a dimethylsilyl group also takes advantage of the preference for alkylidenecarbenes to insert into a tertiary center (39, 40).

The initial effort to study alkylidenecarbene trapping by a silylhydride began with the synthesis of **86** (Scheme 22). Dimetalation of phenylacetylene with n-butyllithium was accomplished using the method described by Hommes and co-workers (60). Quenching of the dianion with dimethylchlorosilane gave dimethylsilyl(o-dimethylsilylphenyl)acetylene, **83**, in 70% yield. Cleavage of the acetylenic dimethylsilyl group with sodium hydroxide gave silanol **84** in 84% yield. This silanol was readily converted to silyl chloride **85** (62%) upon treatment with PCl_5. Reduction of **85** with lithium aluminum hydride afforded silyl hydride **86** in 76% yield.

Scheme 22



Flash vacuum pyrolysis of **86** at 800°C produced an 84% yield (86% mass recovery) of 1,1-dimethyl-1-silaindene, **87**, as the only product. Reduction of the pyrolysis temperature to 700°C afforded a 77% yield of **87** and an additional isomer in 17% yield. Attempted preparative GC resulted in near complete destruction of the isomer. All attempts at separation of the isomer from **87** failed. Based on GC/MS and GC/IR (gas chromatography/infrared spectrometry) data of the isomer and ^{1}H and ^{13}C NMR spectra of a mixture of the isomer with 87, the structure of 1,1-dimethyl-2-methylenebenzo-1-silacyclobutene, **88**, was assigned. The yield of **88** reached a maximum of 34% at 650°C, at which temperature 2% of the starting material remained and a 47% yield of **87** was formed. A summary of these experimental conditions and yields appears in Table 1.

Table 1. Yields[a] of products obtained from the FVP of **86** at 600°C to 800°C

t (°C)	**86**	**87**	**88**
800	0%	84%	0%
700	0%	77%	17%
650	2%	47%	34%
600	22%	42%	28%

[a] Not corrected for recovered **86**.

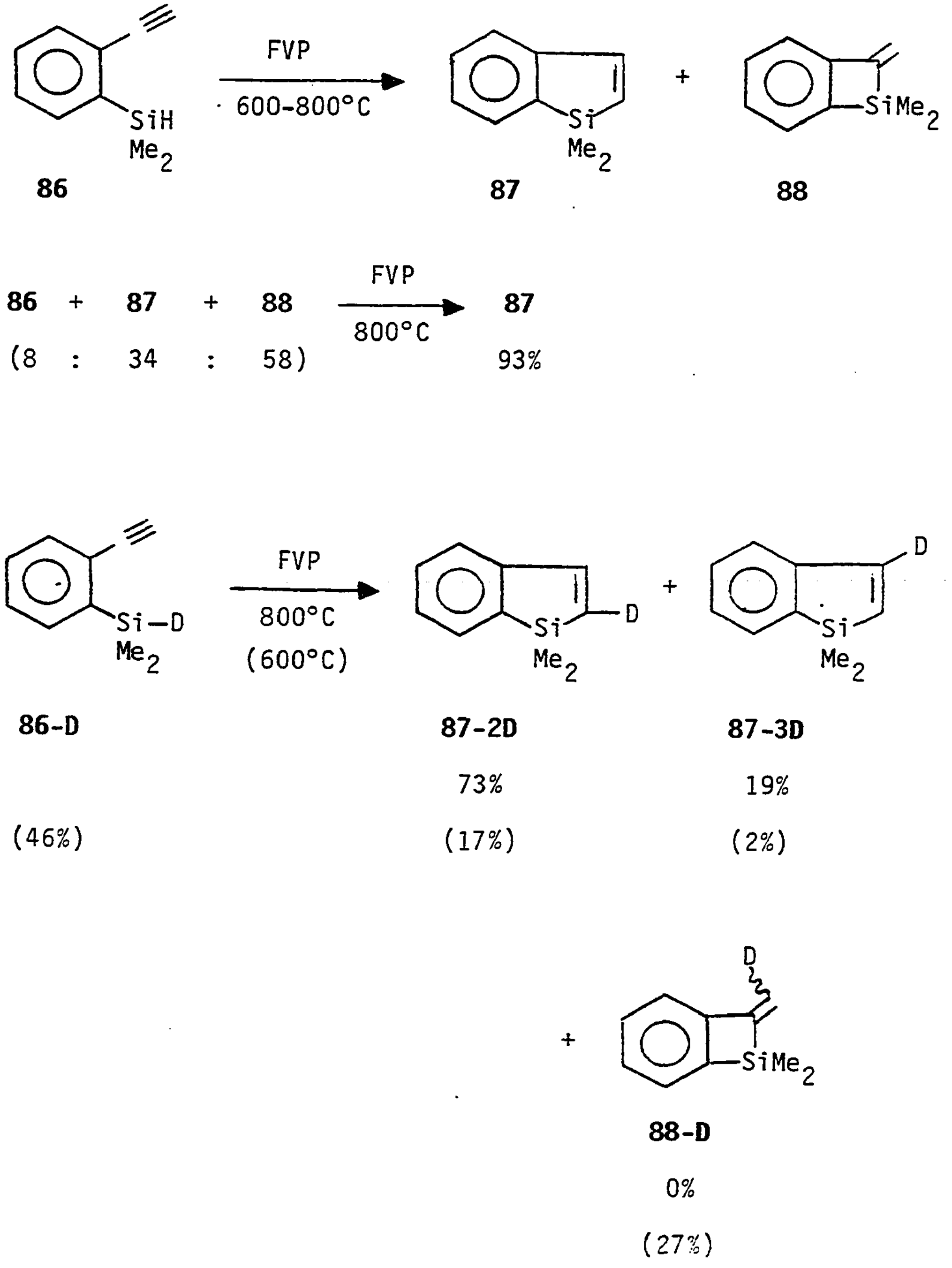
The all carbon analog of **88**, methylenebenzocyclobutene, was shown by Brown and co-workers to yield o-ethynyltoluene and indene upon FVP (31). However, methylenebenzocyclobutene was never obtained in the FVP of o-ethynyltoluene although hydrogen exchange of the deuterated o-methyl group and hydrogen of the acetylene function did occur.

The formation of **88** from the pyrolysis of **86** is consistent with the observations of Brown et al. and implies **88** as a source of **87**. Consequently, a mixture of **88** (58%), **87** (34%), and **86** (8%) was pyrolyzed at 800°C (Scheme 23). The pyrolysate was found to consist of only **87** obtained in 93% yield.

Since **88** is clearly a source of **87**, the question arose as to whether an intermediate alkylidenecarbene was involved in the formation of **87** or whether an alternate pathway involving **88** was solely responsible. An attempt was made to answer this question by a labeling experiment. Deuterated **86** (**86-D**) was prepared by reduction of silyl chloride **85** with $LiAlD_4$. Pyrolysis of **86-D** (Scheme 23) at 800°C afforded a mixture of **87-2D** (73%) and **87-3D** (19%). FVP of **86-D** at 600°C produced **88-D** (27%), **87-2D** (17%), and **87-3D** (2%), uncorrected for a 46% yield of recovered **86-D** which did not undergo scrambling.

Confirmation of the assigned positions of the deuterium label in **87-2D** and **87-3D** on the silaindenyl ring was made by NMR studies. The two vinyl protons of **87** appear as doublets at 6.26 and 7.32 ppm in the ^1H NMR spectrum. Irradiation of the silicon methyl resonance at 0.31 ppm resulted in an NOE enhancement of the absorption of 6.26 ppm. The ^{13}C NMR resonances at 132.28 and 149.18 ppm were assigned to C-2 and

Scheme 23


SiH
Me2
86
FVP
600-800°C
Si
Me2
87
+
SiMe2
88
86 + 87 + 88
(8 : 34 : 58)
FVP
800°C
87
93%
Si—D
Me2
86-D
(46%)
FVP
800°C
(600°C)
Si
Me2
D
87-2D
73%
(17%)
+
D
Si
Me2
87-3D
19%
(2%)
+
D
SiMe2
88-D
0%
(27%)

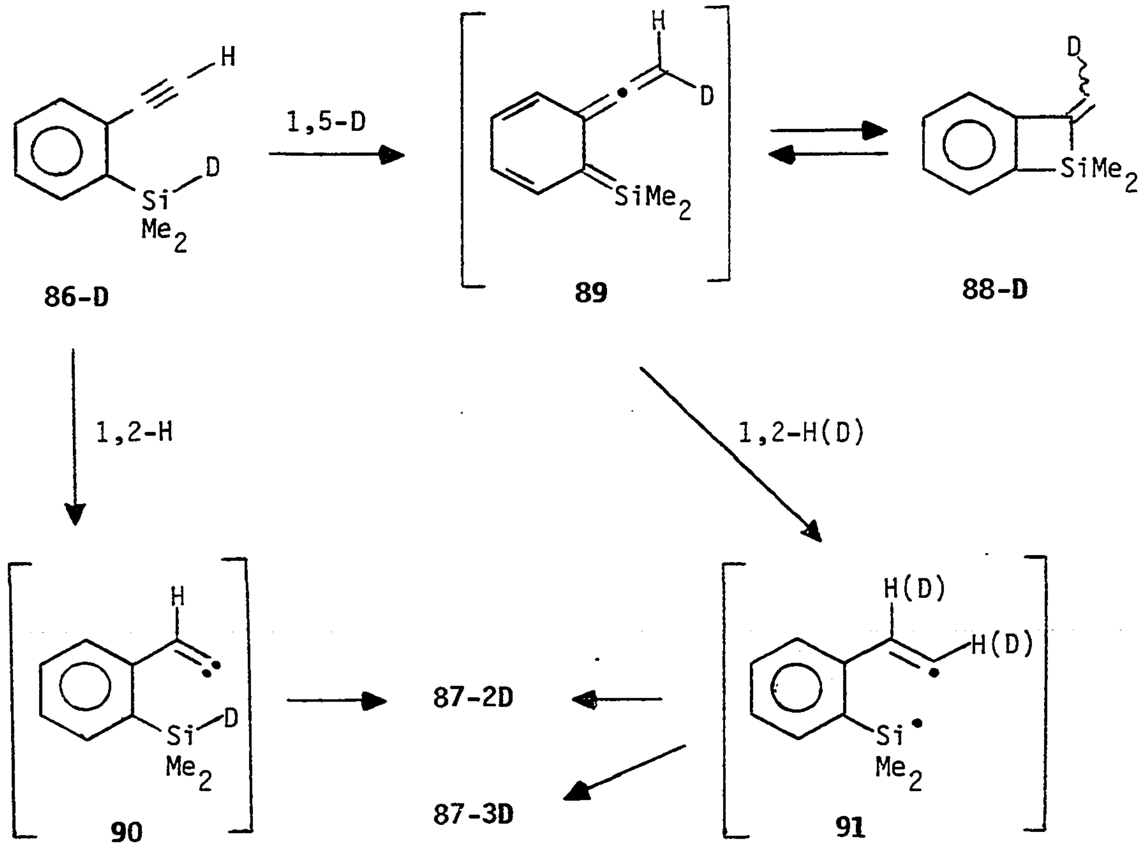
C-3, respectively, by decoupling experiments. A complete description of these experiments appears in the Experimental Section.

The results of the pyrolysis of **86-D** indicate two pathways leading to the formation of silaindene **87** (Scheme 24). One pathway involves a 1,2-hydrogen shift to give alkylidenecarbene **90** which undergoes Si-D insertion to afford only **87-2D** as the major product. The other pathway may begin with what appears to be a geometrically unfavorable 1,5-hydrogen shift. However, this 1,5-shift may well be facilitated by a low-energy bending mode available to acetylenes (61). Formation of **87-2D** and **87-3D** could then arise from a 1,2-hydrogen or deuterium migration on allene **89** to give diradical **91** which closes to give **87-2D** and **87-3D** in equal amounts neglecting isotope effects. A process similar to that proposed for the transformation of **89** to **91** was postulated to occur in the thermal interconversion of allene and propyne (51). While Brown and coworkers recognized the possibility of reversible formation of the all carbon analog of allene **89**, a pathway leading to indene not involving an alkylidenecarbene was not considered (31).

In order to obtain further information concerning the relative migratory aptitudes of hydrogen and silicon in acetylene-alkylidenecarbene isomerizations, the pyrolysis of silylacetylene **83** was examined (Scheme 25). FVP at 800°C produced a mixture of the anticipated 3-silylsilaindene **93** (62%), silaindene **87** (15%), and 2-silylsilaindene **97** in 4% yield. Formation of **87** can be readily accounted for since reductive elimination of silylenes from hydridovinylsilanes is a known process (62). This was experimentally verified by the copyrolysis of a mixture of **93** and **97** (94:6) at 800°C (Scheme 25). Silaindene **87** was formed in 15% yield along with a 68% combined yield of recovered **93** and **97** (93:7). Formation of **87** could also be the result of reductive elimination of dimethylsilylene from **83** to produce **86** and, ultimately, **87**. A comparable process has been found to occur in the elimination of silylene from ethynylsilane (63). Evidence for this competitive pathway leading to the formation of **87** was obtained in the FVP of **83** at 700°C. In addition to the expected products (**87**, **93**, and **97**), a trace amount (<1%) of **88** was obtained which presumably can only arise from acetylene **86**.

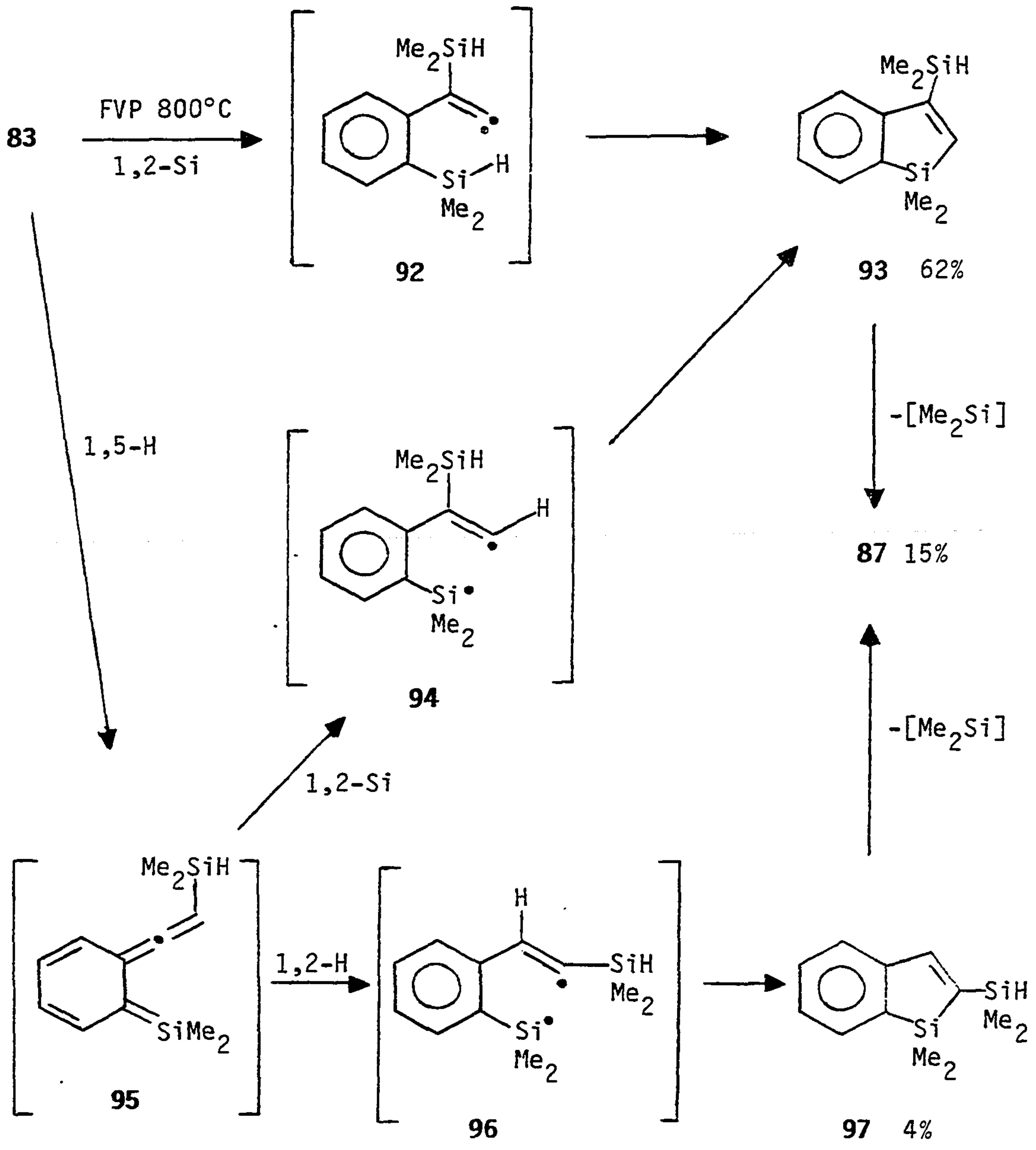
The presence of **97** indicates a pathway competitive with the formation of alkylidenecarbene **92** (Scheme 25). This other pathway may begin with a 1,5-hydrogen shift to form allene **95** which, when followed by a 1,2-hydrogen migration to produce diradical **96** and closure, would account for formation of **97**. Alternately, a 1,2-silyl migration on allene **95** would give diradical **94** which can close to give **93**. If 1,5-hydrogen migration is competitive with the 1,2-silyl migration of **83** and if the migratory aptitude of silicon in **95** is considerably greater than the competing 1,2-hydrogen migration, it is possible that this pathway contributes significantly to the production of **93**.

Scheme 24



Since it is possible that **93** is formed only via allene **95**, the fate of allene **95** was indirectly probed through the synthesis and FVP of the silyl-substituted methylenebenzocyclobutene **100** (Scheme 26). Synthesis was accomplished by reaction of benzocyclobutanone with the modified Wittig reagent prepared in situ from triphenylphosphine and carbon tetrabromide which produced dibromide **98** in 79% yield. Reduction of dibromide **98** cleanly afforded a 1:1 E/Z mixture of the

Scheme 25

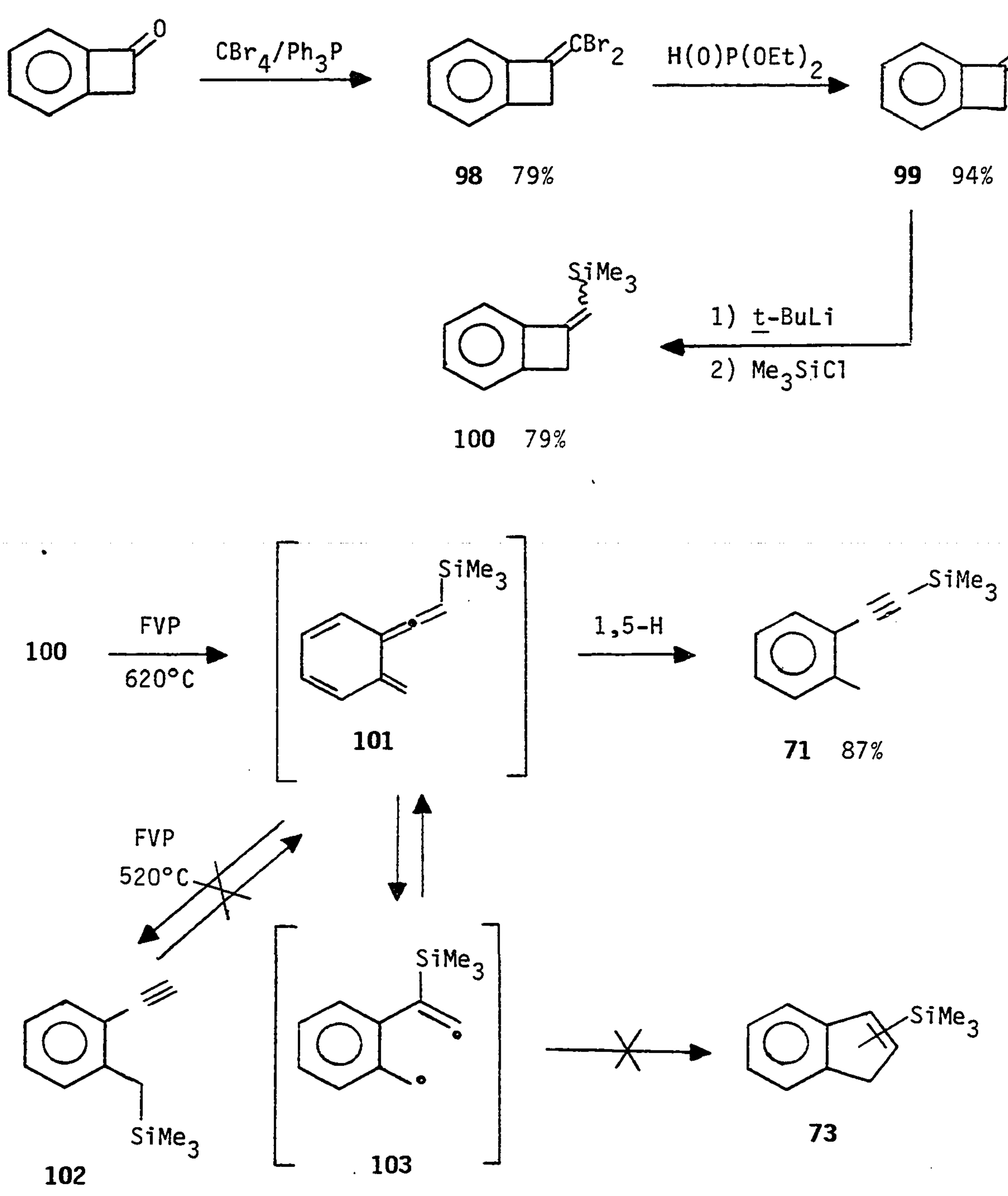

83
FVP 800°C
1,2-Si
Me2SiH
Si
H
Me2
92
Me2SiH
Si
Me2
93 62%
-[Me2Si]
87 15%
1,5-H
Me2SiH
H
Si
Me2
94
-[Me2Si]
1,2-Si
Me2SiH
SiMe2
95
1,2-H
H
SiH
Me2
Si
Me2
96
SiH
Me2
Si
Me2
97 4%

monobromide **99** in 94% yield. Metalation of **99** with t-butyllithium followed by quenching with chlorotrimethylsilane furnished a 1:1 mixture of E and Z isomers of **100**. Flash vacuum pyrolysis of **100** at 520°C to 620°C gave only acetylene **71**. At 620°C, conversion was complete, and acetylene **71** was exclusively obtained with an 87% mass recovery. Exclusive formation of acetylene **71** by a 1,5-hydrogen shift of the presumed intermediate allene **101** suggests that the pathway involving a 1,2-silyl shift on **95** to afford **93** is not of major significance. Rather, the formation of alkylidenecarbene **92** is likely the major source of **93**.

Pyrolysis of acetylene **102** investigated the possibility that allene **101** initially isomerized to acetylene **102** by a 1,5-silyl shift which in turn rearranged to the thermodynamically more stable acetylene **71** (Scheme 26). However, at 520°C, only unchanged **102** (87% mass recovery) was obtained though FVP of **100** at the same temperature gave a 35% yield of **71** and a 45% yield of recovered starting material.

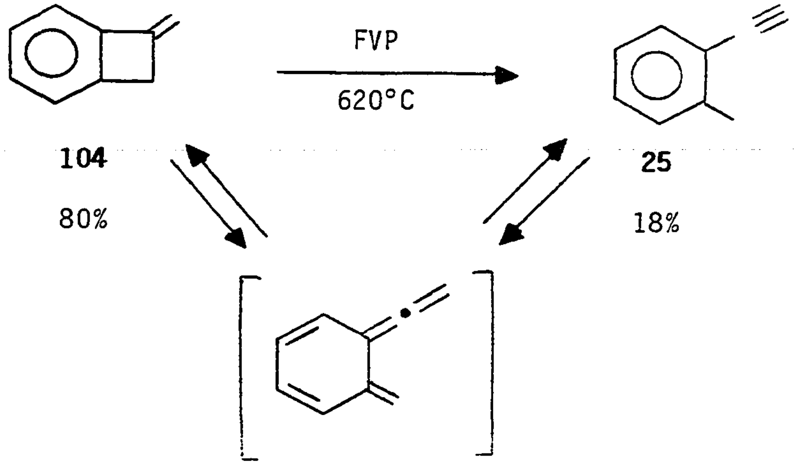
Conspicuously absent from the pyrolysis of **83**, even at 700°C which afforded a 30% yield of **93** and a 1% yield of **97** (based on 64% recovered **83**), is the silyl derivative of **88** formed by electrocyclic closure of allene **95**. This observation is not surprising based upon comparison of the pyrolyses of methylenebenzocyclobutene, **104**, at 620°C (Scheme 27) with that of **100** (Scheme 26) under identical conditions and the thermal requirement for isomerization of **88** to **87** (Scheme 23). It is apparent that the silyl substituent on **101** has facilitated the rearrangement of **101** to **71** relative to the rearrange-

Scheme 26


O
CBr4/Ph3P
CBr2
98 79%
H(O)P(OEt)2
Br
99 94%
1) t-BuLi
2) Me3SiCl
SiMe3
100 79%
100
FVP
620°C
SiMe3
101
1,5-H
SiMe3
71 87%
FVP
520°C
SiMe3
102
SiMe3
103
SiMe3
73

ment of **104** to **25**. This observation may be attributable to the silyl group of **101** becoming bonded to an sp center during the 1,5-hydrogen shift which causes a lowering of the activation energy of the 1,5-hydrogen shift while suppressing the 1,5-silyl shift. Though a 17% yield of **88** was obtained in the FVP of **86** at 700°C, extrapolation of the preceding rational to the FVP of **83** at 700°C suggests that the silyl derivative of **88** would not survive the pyrolysis.

Scheme 27



Since the identification of **97** was partially based on data obtained from **97** as a mixture with **93**, an attempt was made to prepare an authentic sample of **97** for spectral comparison with that obtained in the pyrolysis of **83**. Pyrolysis of disilylacetylene **105** should lead to carbene **107** which could cyclize by insertion into an aryl C-H bond to give **97**. However, FVP of **105** at 800°C afforded a 50% yield of **106** (corrected for 22% recovered **105**) as a result of reductive elimination of dimethylsilylene (Scheme 28). None of the desired silylsilaindene **97** was detected though a 3% yield of silaindene **87** was obtained. Silaindene **87** can arise from reductive elimination of dimethylsilylene from **97**, but acetylene **106** is also a likely source. Indeed, FVP (850°C) of **106** gave **87** in 14% yield at 29% conversion. Similarly, Karpf and Dreiding obtained 1-indenone in 22% yield from the pyrolysis of ethynyl phenyl ketone **108** (36).

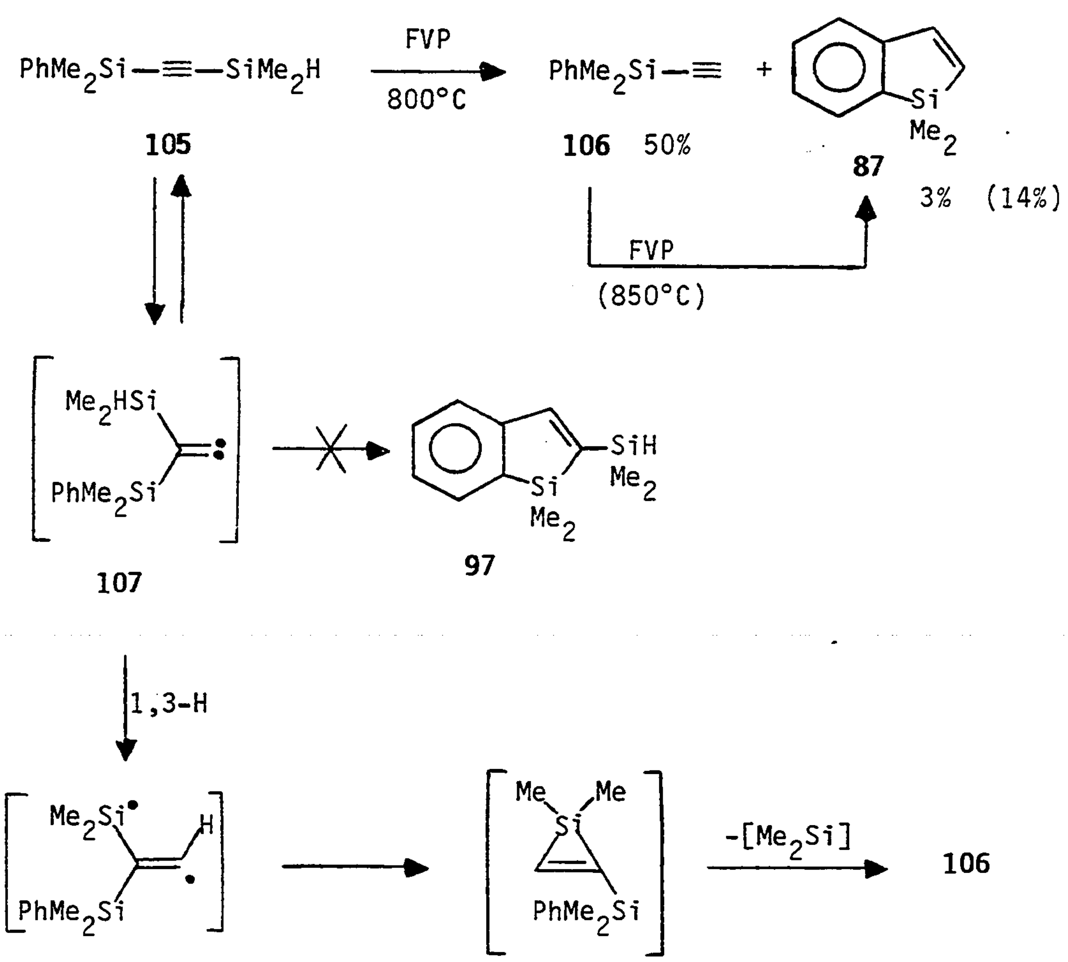
A possible explanation for the facile elimination of dimethylsilylene from **105** is outlined in Scheme 28. Carbene **107** may undergo a 1,3-hydrogen shift analogous to that proposed in the conversion of propyne to cyclopropene (52). The resulting diradical could close to a silacyclopropene which would extrude dimethylsilylene and result in the formation of acetylene **106**.

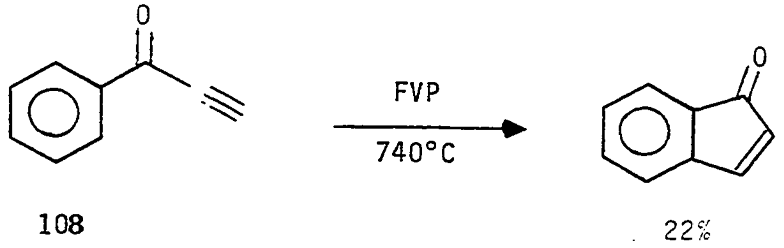
The observation that dimethylsilylene may be readily extruded from hydridodimethylethynylsilanes also fortifies the earlier postulate that reductive elimination of dimethylsilylene from **83** can occur and probably contributes to the formation of **87**.

Extensions of this new route to silacycles were sought in its application to simple alkynes. Cyclization of propargyloxysilanes would provide a simple route to unsubstituted oxasilacyclopentene, a potential precursor of silafuran.

Flash vacuum pyrolysis of the model system, dimethyl(propynyloxy)silane, **109**, at 700°C afforded a 32% yield of 3,3-dimethyl-4-oxa-3-silacyclopentene, **110**, (Scheme 29). Unfortunately,

Scheme 28

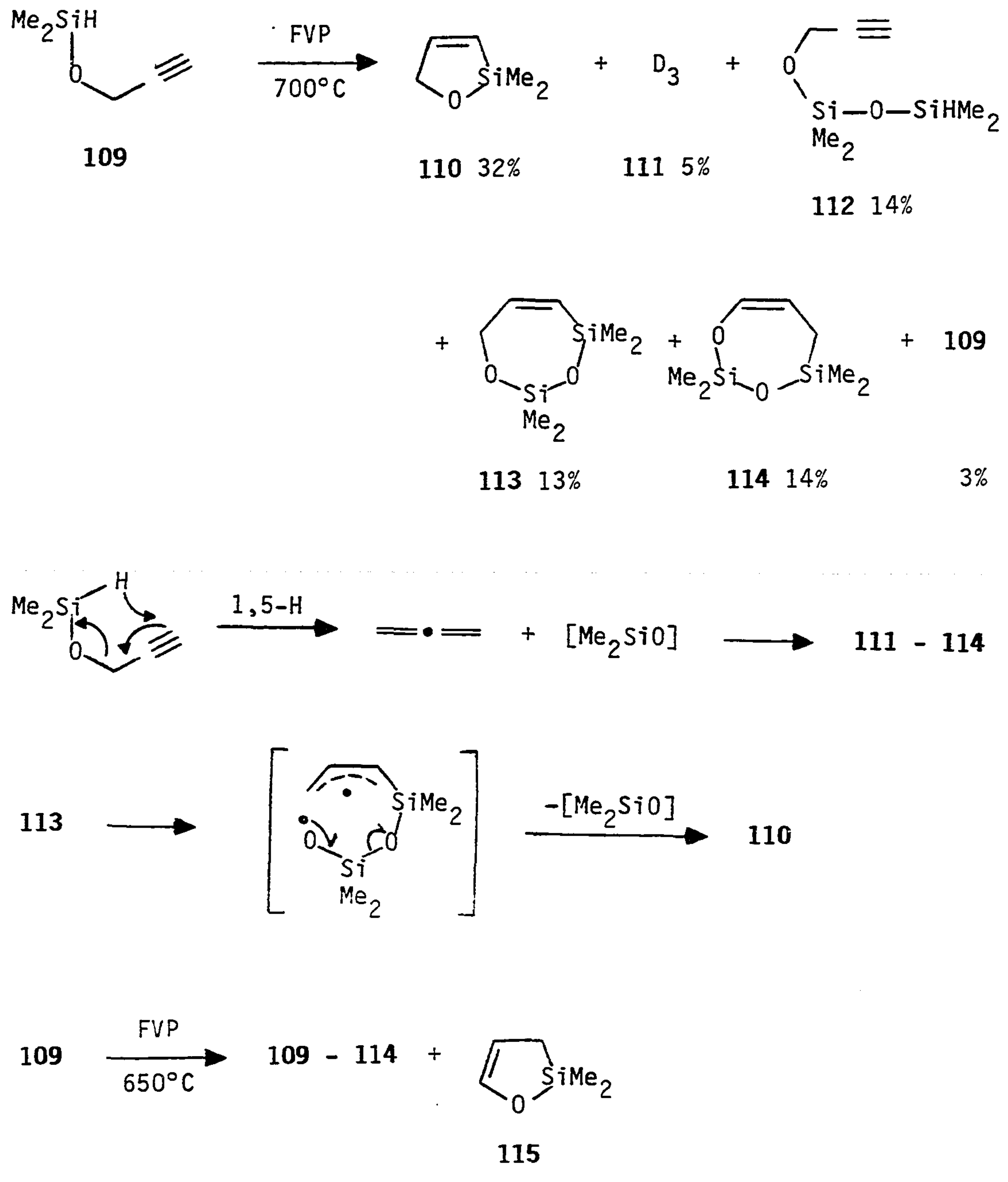

PhMe$_2$Si—≡—SiMe$_2$H
105
FVP
800°C
PhMe$_2$Si—≡
106 50%
+
Si
Me$_2$
87
3% (14%)
FVP
(850°C)
Me$_2$HSi
PhMe$_2$Si
107
SiH
Me$_2$
Si
Me$_2$
97
1,3-H
Me$_2$Si
H
PhMe$_2$Si
Me
Me
Si
PhMe$_2$Si
-[Me$_2$Si]
106


O
108
FVP
740°C
O
22%

four other products identified as hexamethylcyclotrisiloxane (D_3), **111**, 3-hydrido-1-propynyloxy-1,1,3,3-tetramethyldisiloxane, **112**, 3,3,5,5-tetramethyl-4,6-dioxa-3,5-disilacycloheptene, **113**, and 4,4,6,6-tetramethyl-3,5-dioxa-5,6-disilacycloheptene, **114**, were obtained in 5%, 14%, 14%, and 13% yield, respectively. These latter products presumably arise from trapping of dimethylsilanone by **109** and **110**. The elimination of dimethylsilanone probably proceeds via retro-ene fragmentation analogous to that which occurs in the thermal decomposition of 3-butyn-1-ol to allene and formaldehyde (64). Presence of allene in the pyrolysate (identified by IR, NMR, and GC/MS) is supportive of the mechanism postulated for the formation of dimethylsilanone (Scheme 29). While the formation of **112** and **113** are obviously the result of silanone addition to starting material and **110** (trimerization of silanone gives D_3), the formation of **114** was perplexing.

Since the thermal stability of the products was in question, each was pyrolyzed at 700°C. Only **110** was recovered from its pyrolysis, and pyrolysis of **112** afforded trivial amounts (3% each uncorrected for a 67% yield of recovered **112**) of **113** and **114**. Pyrolysis of **114** gave only a 2% yield of **110** and a 1% yield of D_3 uncorrected for recovered starting material (79%). Cycloheptene **113** proved to be the least stable to pyrolysis at 700°C affording a 21% yield of silacyclopentene **110**, 6% D_3, and 5% **114** uncorrected for recovered **113** (63%). The significant yield of **110** may be the result of cyclization of the diradical remaining after the elements of dimethylsilanone were

Scheme 29


Me2SiH
O
109
FVP
700°C
SiMe2
O
110 32%
D3
111 5%
O
Si—O—SiHMe2
Me2
112 14%
SiMe2
O
O
Si
Me2
113 13%
O
Me2Si
O
SiMe2
114 14%
109
3%
Me2Si
H
O
1,5-H
[Me2SiO]
111 - 114
113
SiMe2
O
O
Si
Me2
-[Me2SiO]
110
109
FVP
650°C
109 - 114
SiMe2
O
115

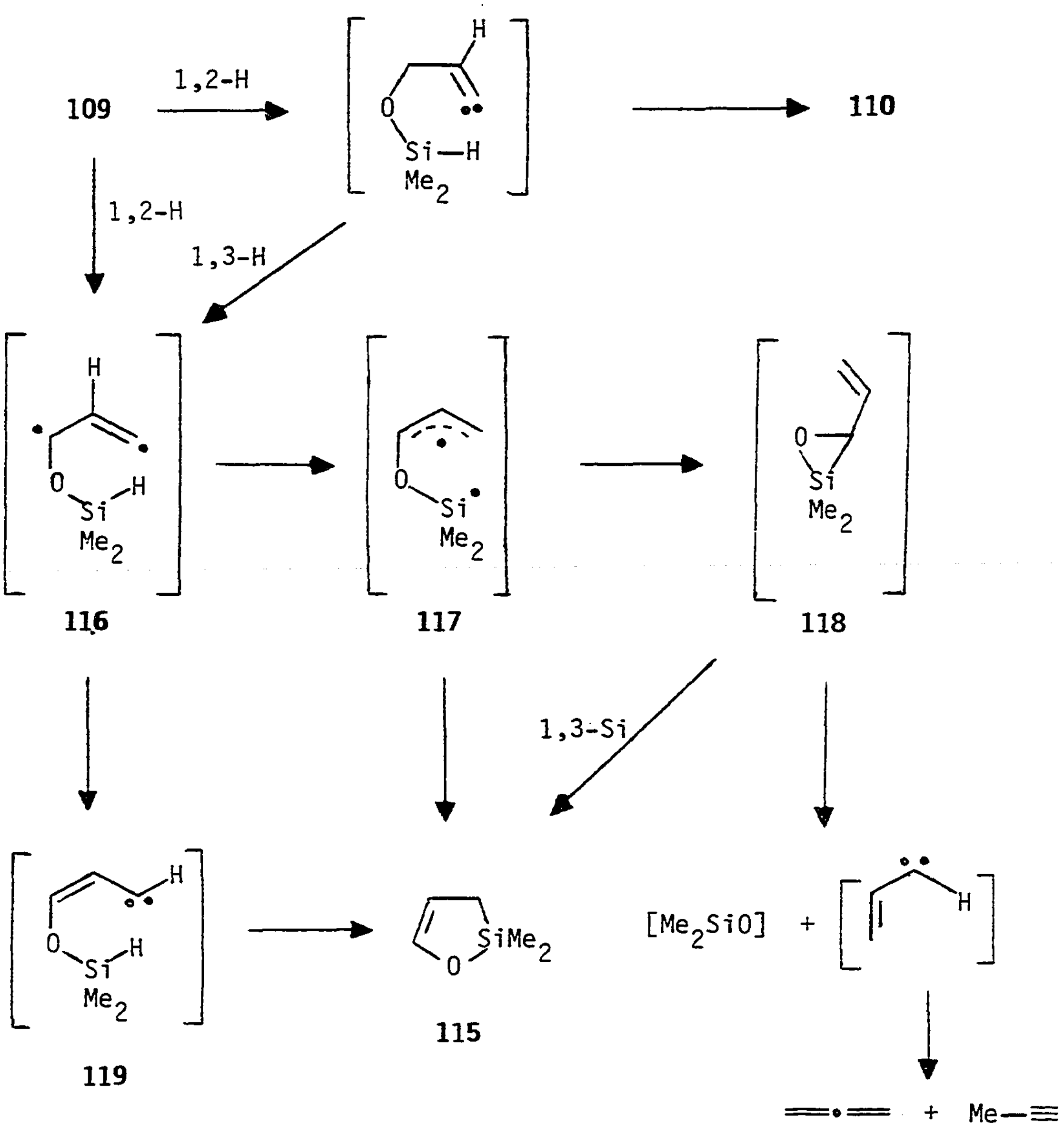
extruded from **113** (Scheme 29). Thermal extrusion of dimethylsilanone from cyclic siloxanes is well precedented and has recently been reviewed by Hussmann (65). Since only a small amount of **114** was produced in any of these pyrolyses, it appears that there is an additional source of **114**.

In search of a possible intermediate responsible for the presence of **114**, the pyrolysis of **109** was carried out at 650°C (Scheme 29). At 69% completion, D_3 (6%), **112** (20%), **113** (9%), and **114** (7%) were formed along with a 27% combined yield of **110** and its isomer (in a 1.87:1.00 ratio), 4,4-dimethyl-2-oxa-4-silacyclopentene, **115**. Silacycle **115** is a likely source of **114**. The absence of **115** in the pyrolysate obtained from FVP of **109** at 700°C suggests that **115** may be an additional source of **110**. However, FVP of a mixture of **110** and **115** (1.51:1.00) at 700°C afforded a pyrolysate (84.4% mass recovery) comprised of **110** and **115** (56.6% and 30.9% yield, respectively) in a 1.81:1.00 ratio as determined by ^{1}H NMR. Though **115** appears to isomerize to **110**, the change is scarcely larger than that which could be explained by selective destruction of **115**.

Formation of **115** is postulated to involve an alkylidenecarbene produced by an initial 1,2-hydrogen shift on acetylene **109**. A subsequent 1,3-hydrogen shift gives diradical **116** which abstracts a hydrogen from silicon to give **117** (Scheme 30). Diradical **117** can then close to give **115** directly or give silaepoxide **118** which would be expected to isomerize to **115** via a 1,3-silyl migration. Silaepoxide **118** could also extrude dimethylsilanone by α-elimination to afford vinylcarbene which has been shown to yield propyne (66) and allene after isomerization (51) of the intermediate cyclopropene (67). The contribution of this pathway to the formation of allene is probably slight since the isomerization of propyne to allene would not be expected to be complete under these conditions (51), and no propyne (nor any cyclopropene) was present in the pyrolysate. Another possibility which should be considered involves the transformation of diradical **116** into carbene **119** (analogous to that which has been proposed (52) to occur in the interconversion of allene, cyclopropene, and propyne) which can then cyclize by intramolecular Si-H insertion in **119** to yield silacycle **115**.

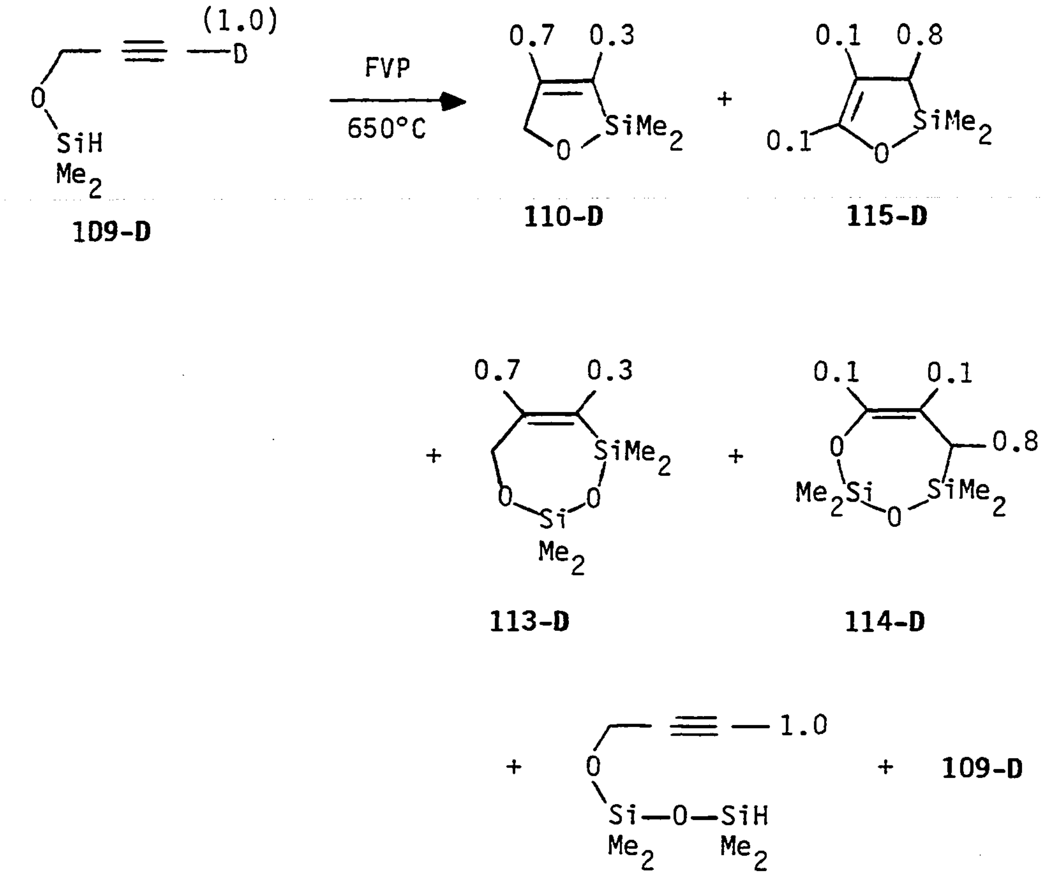
FVP of **109**, in which was incorporated a deuterium label on the acetylenic carbon to the extent of 79% (**109-D**), at 650°C gave the expected products with no scrambling of the label in recovered starting material or in **112-D** (Scheme 31). The remaining products all showed some degree of scrambling of the deuterium label, though in **114-D** and **115-D** the extent of scrambling was within experimental error (± 0.1 D). Deuterium incorporation in both vinyl positions of **110-D** and **113-D** indicates two pathways leading to their formation. Trapping of the expected alkylidenecarbene of **109** by the silylhydride functionality accounts for the majority of **110-D** (with the deuterium label beta to silicon) that is formed with the remainder possibly originating from isomerization of **115-D** to **110-D**. It is possible that cyclization is initiated by silyl radical formation. Addition of the silyl radical to the triple bond followed by hydrogen abstraction

Scheme 30



would lead to **110-D** labeled with deuterium alpha to silicon. In view of the formation of **115** and its isomerization to **110** and the results of the labeling study, this latter pathway could be of only minor significance. The positions and ratios of the deuterium label in products **113-D** and **114-D** strongly suggest their origins are **110-D** and **115-D**, respectively.

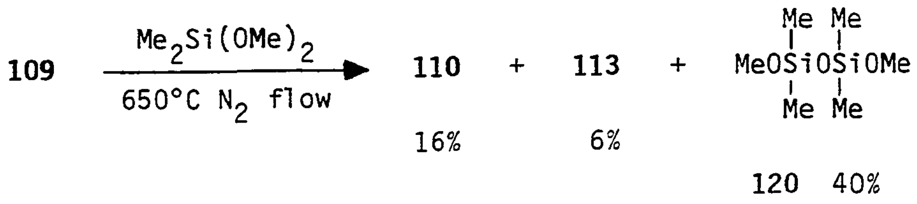
Scheme 31



109-D **110-D** **115-D** **113-D** **114-D** **112-D** **109-D**

Though FVP of **109** is the only known route to **110**, this rearrangement has limited synthetic utility due to the formation of undesirable silanone insertion products. If trapping of silanone by starting material and products could be eliminated, the yield of **110** could reach 71% based upon the yields of the observed products and recovered **109**. To prevent the formation of undesirable silanone trapped products, **109** was copyrolyzed with dimethoxydimethylsilane, an efficient silanone trap, at 600°C in a nitrogen flow (Scheme 32). The pyrolysate consisted of disiloxane **120** (40%, corrected for a small amount formed in the pyrolysis of dimethoxydimethylsilane alone), **110** (16%), and **113** (6%). While the formation of **120** substantiates the intermediacy of dimethylsilanone (Scheme 29), the copyrolysis failed to improve the yield of **110**.

Scheme 32



$$109 \xrightarrow[650°C\ N_2\ \text{flow}]{Me_2Si(OMe)_2} 110 + 113 + MeOSi(Me)_2OSi(Me)_2OMe$$

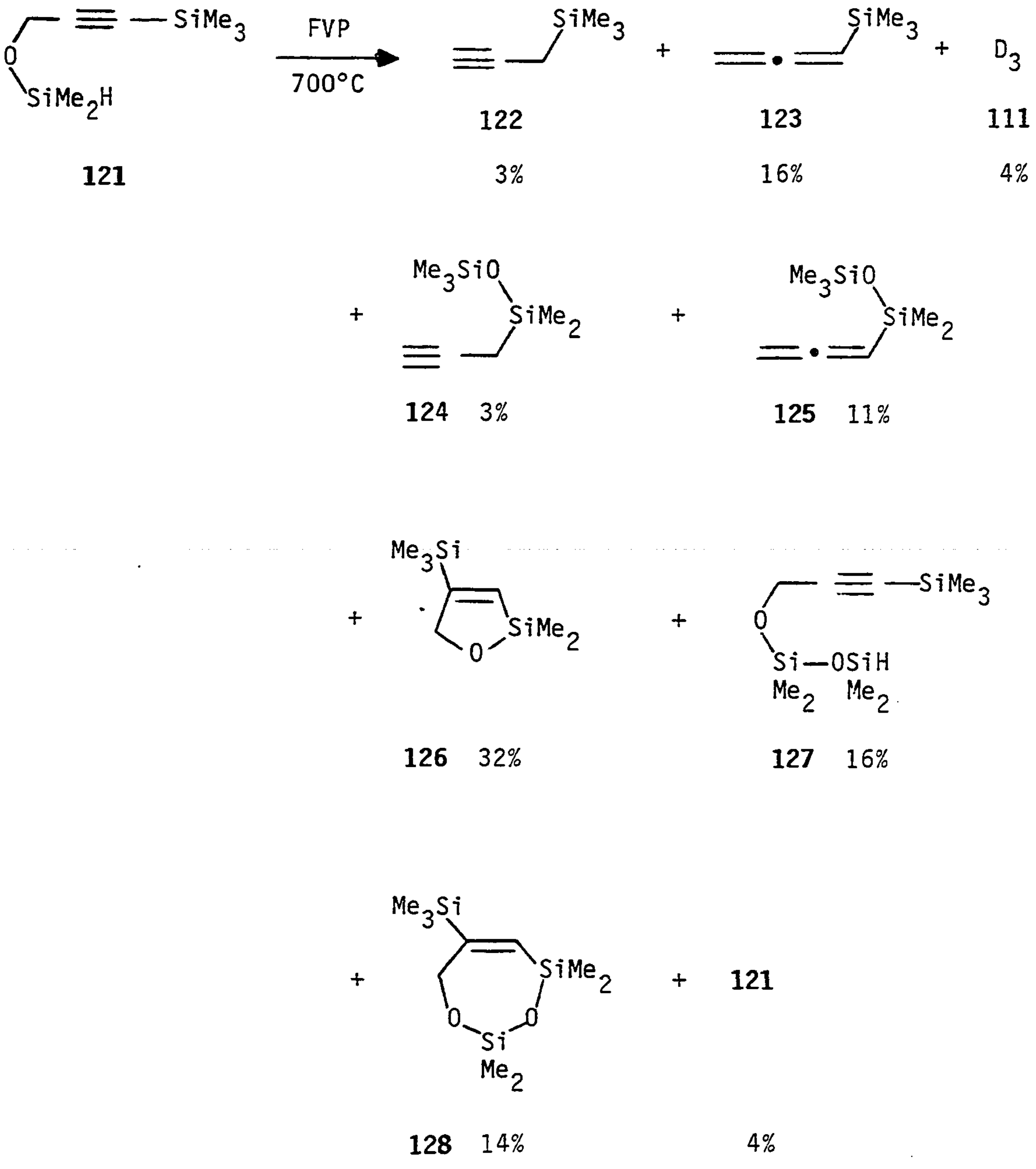
In order to compare the migratory aptitudes of silicon and hydrogen on simple alkynes, silylacetylene **121** was prepared. Flash vacuum pyrolysis of **121** at 700°C (96% conversion) gave products **122**-**128** in the yields shown in Scheme 33. All of these products except **124** and **125** are analogous to those obtained from FVP of **109** (Scheme

29). In this last comparison, the migratory aptitude of silicon appears to be nearly identical to that of hydrogen.

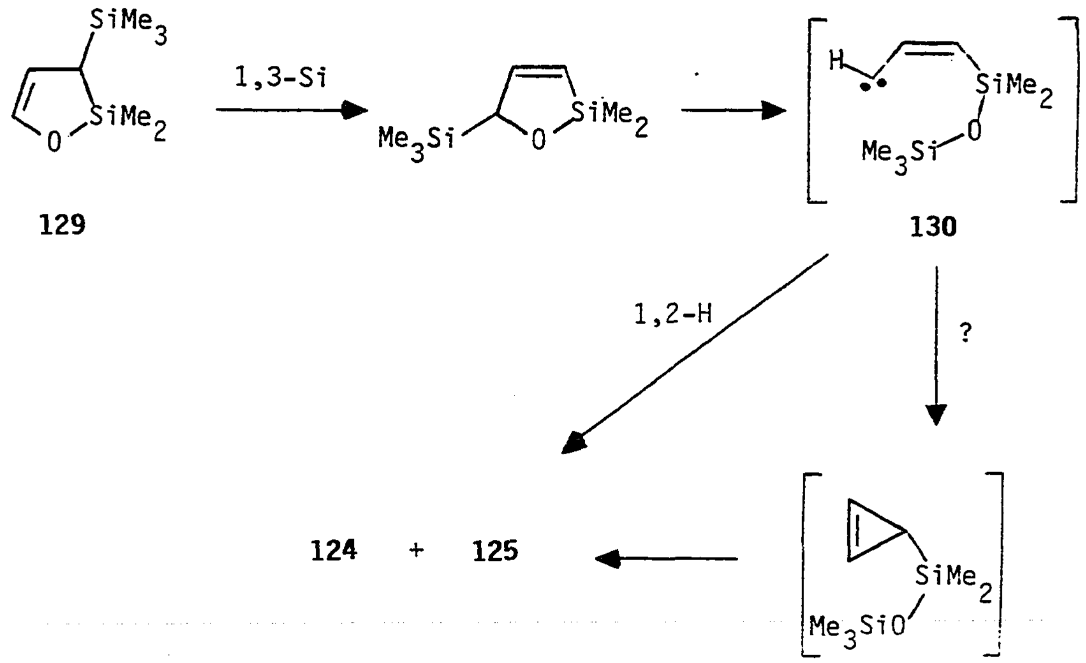
Notably absent from the pyrolysate are the trimethylsilyl analogs of **114** and **115**. Silacyclopentene **129**, the silyl substituted analogue of **114**, would not be expected to survive the pyrolysis. A facile 1,3-silyl migration followed by α-elimination would afford carbene **130** which probably led to the formation of **124** and **125** (Scheme 33). Apparently, these rearrangements are rapid enough to prevent the addition of dimethylsilanone to, or the isolation of, **129**. The presence of acetylenes **122** and **124**, whose origins are presumably allenes **123** and **125**, was predictable based on the known, facile interconversion of silylallenes and silylacetylenes (50).

It can be concluded that alkylidenecarbene cyclization has provided a convenient synthetic route to unsaturated silacycles difficult to prepare by other methods. As expected, the trapping of alkylidenecarbenes by Si-H bond insertion appears to be more efficient than insertion into C-H bonds. Deuterium labeling studies have revealed the presence of alternate modes of cyclization competitive with alkylidenecarbene trapping. Finally, a comparison of terminal and silyl-substituted acetylenes has shown that in these examples the thermal requirements of the cyclizaion of silyl acetylenes are greater than or, at best, comparable to those of terminal acetylenes.

Scheme 33


SiMe3
SiMe2H
FVP
700°C
SiMe3
SiMe3
D3
121
122
3%
123
16%
111
4%
Me3SiO
SiMe2
Me3SiO
SiMe2
124 3%
125 11%
Me3Si
SiMe2
O
O
SiMe3
Si—OSiH
Me2 Me2
126 32%
127 16%
Me3Si
SiMe2
O
O
Si
Me2
121
128 14%
4%

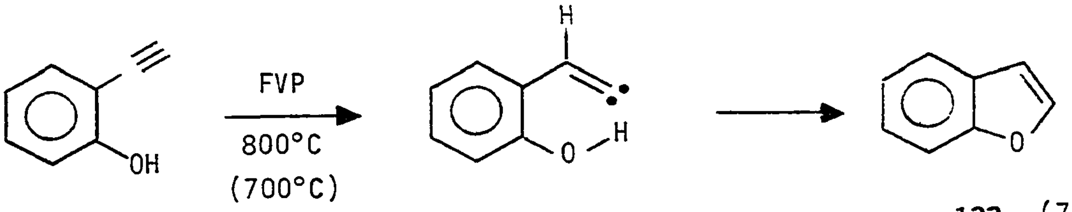
Scheme 33 (continued)



Application of Acetylene Cyclization to the Synthesis of Furan and Pyran Derivatives

The gas-phase cyclization of alkylidene carbenes lends itself to the formation of five-membered rings. This feature should allow and facilitate the preparation of furan derivatives. Slight modification of the starting acetylenes may permit the preparation of pyran derivatives as well. Furthermore, the use of silyl-substituted acetylenes would yield products bearing a synthetically useful silyl group. This feature is especially attractive since it could lead to substitution at an sp^2 center beta to oxygen, a synthetically challenging task by conventional methods.

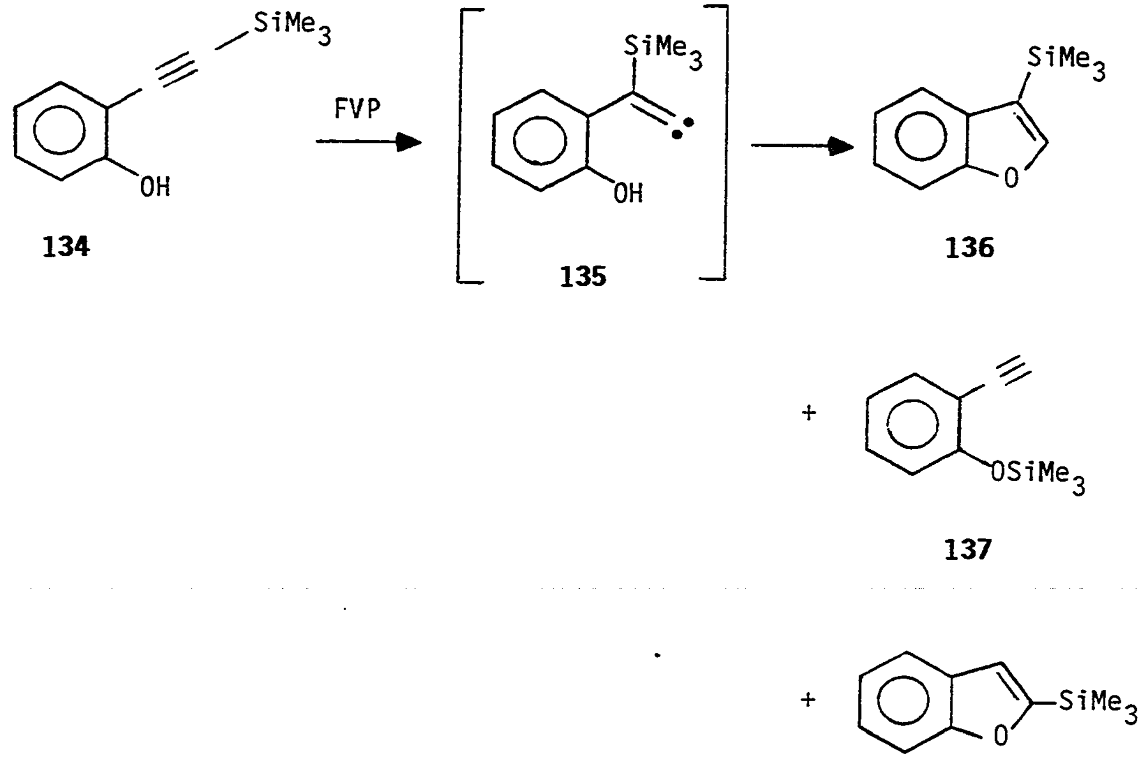
The formation of benzofuran has recently been reported by Bloch and Orvane who found that FVP of o-hydroxyphenylacetylene at 800°C produced benzofuran quantitatively (68). The product was proposed to arise solely from trapping of alkylidenecarbene **132**, formed by a 1,2-hydrogen shift on acetylene **131**, by insertion into the O-H bond.



131 **132** **133** (71%)

Extension of this cyclization to o-(trimethylsilylethynyl)phenol, **134**, would yield the unknown 3-trimethylsilylbenzofuran, **136**. The flash vacuum pyrolysis of **134** (Scheme 34) at 750°C (91% mass recovery) afforded not only the desired 3-trimethylsilylbenzofuran as the major product but also silyl ether **137** and 2-trimethylsilylbenzofuran, **138**, in 36%, 34%, and 30% relative yields. The pyrolysis was very clean, and the absolute yields were identical to the values obtained after correction of the relative yields of **136**, **137**, and **138** for the mass recovery.

Scheme 34



134

135

136

137

138

In an attempt to determine the origins of **137** and **138**, the pyrolyses of **134**, **136**, **137**, and **138** were each examined at several different temperatures. These results, and those of additional pyrolyses, are summarized in Table 2.

Table 2. Relative yields of products obtained from the FVP of **134**, **136**, **137**, and **138**

Compound pyrolyzed		% Relative yield			
	t (°C)	**134**	**136**	**137**	**138**
134	480	84.9	3.1	11.9	
	540	40.8	18.4	40.8	
	650		31.1	50.1	18.8
	700		35.0	37.4	27.6
	700[a]		36.3	43.4	20.3
	750		35.9	34.4	29.7
	750[b]		35.3	37.0	27.6
	750[c]		27.4	36.1	36.5
	800		34.9	36.7	28.4
136	700		100.0		
	800		68.9	20.7	10.4
137	540			100.0	
	700			60.6	39.4
	750		11.8	49.8	38.4
	800		20	49	31
138	700			64.9	35.1
	750		8.6	46.7	44.7
	800		21.9	45.1	32.9

[a] The pyrolysis was carried out at 1 X 10^{-5} torr.

[b] The sample was pyrolyzed through an acid washed pyrolysis tube.

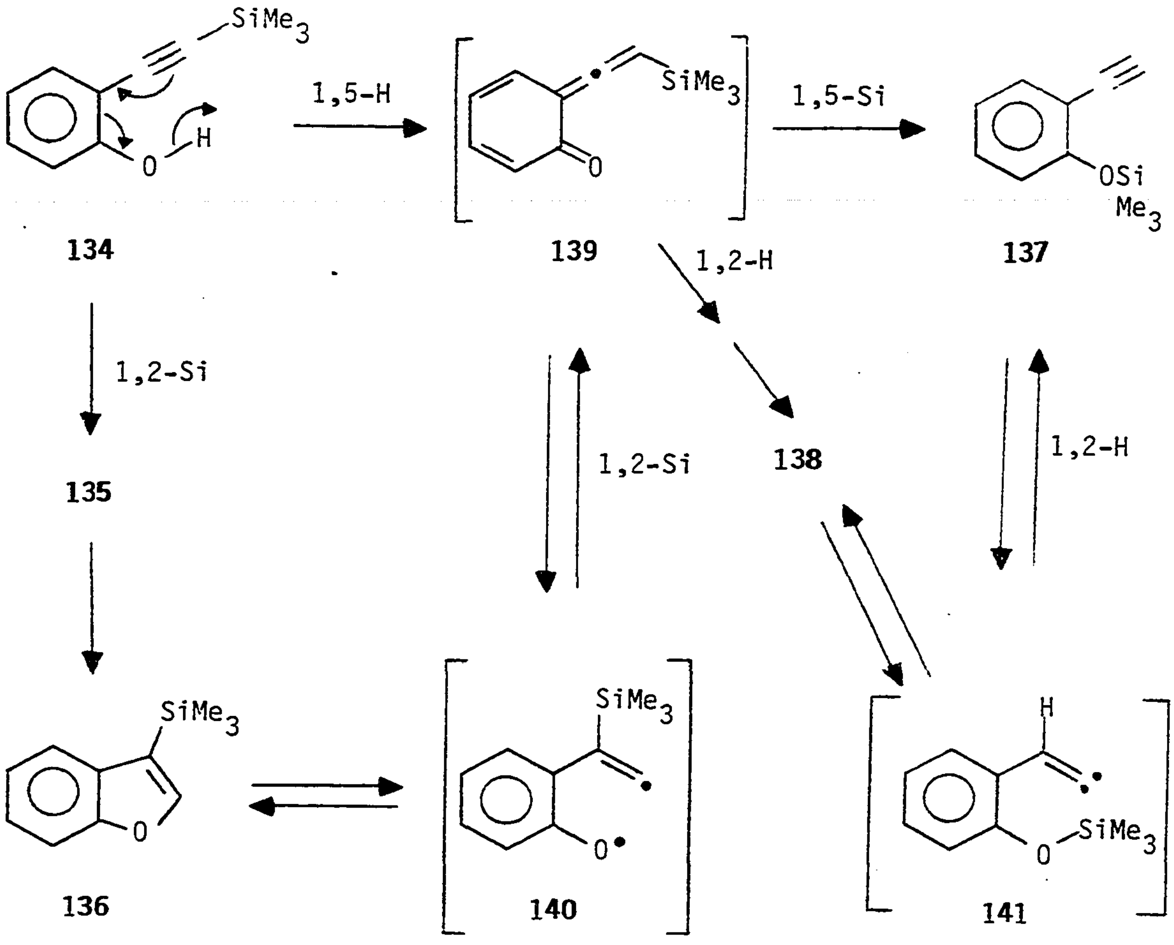
[c] The sample was pyrolyzed through a base washed pyrolysis tube.

It is apparent that products **137** and **138** did not simply arise from isomerization of 3-trimethylsilylbenzofuran since **136** was unaffected by FVP at 700°C. Even at 800°C, **137** and **138** were formed in 21% and 10% yields, respectively. Even though **136** can intersect the energy surface of **137** and **138**, it is not their only source. Benzofuran **138** is apparently not a primary product since pyrolysis of **134** at 540°C gives only **136** and **137** in 18% and 41% yields. Also, pryolysis of **134** under high vacuum favored the formation of **137** at the expense of **138** which supports the belief that the formation of **138** is the result of a secondary process. Flash vacuum pyrolysis of **137** at 700°C provided only **137** and **138** (61:39), while FVP of **138** at 700°C produced a pyrolysate comprised of only **138** and 137 (35:65). These results demonstrate the suspected interconversion of **138** and **137**.

There is an alternate pathway, not involving carbene **135**, leading to the formation of silyl ether **137** which equilibrates with benzofuran **138**. This second route, shown in Scheme 35, is initiated by a 1,5-hydrogen migration from oxygen to carbon producing allene **139**. A subsequent 1,5-silyl shift gives silyl ether **137**. Interconversion of **137** and **138** may involve a reversible 1,2-hydrogen shift on 137 producing carbene **141** which then inserts into the Si-O bond to yield **138**. The reverse of this isomerization probably proceeds via an unprecedented gas-phase α-elimination involving a silyl migration from carbon to oxygen in **138** to give alkylidenecarbene **141** and, ultimately, **137** after a 1,2-hydrogen shift.

Intermediate allenyl ketone **139** introduces a second possible pathway leading to the formation of 3-trimethylsilylbenzofuran (Scheme 35). A 1,2-silyl shift on **139** will result in the generation of diradical **140** which can cyclize to give **136**. At 800°C, benzofuran **136** may enter this energy surface by homolytic C-O bond cleavage. A subsequent 1,2-silyl migration produces allene **139**, a proposed common intermediate of **137** and **138**. This also suggests that allene **139** may be the sole intermediate responsible for the formation of **136**, **137**, and **141**. Finally, it is also possible that at high temperatures where **136**, **137**, and **141** are all interconvertible, a 1,5-hydrogen shift on **139** leads to **134** which can return to **139** or give **136** via alkylidenecarbene **135**.

Scheme 35



A direct comparison of the FVP of **134** with that of terminal acetylene **131** was desired. Pyrolysis of **131** at 700°C gave only **133**, benzofuran (71%). Pyrolysis at 650°C and 540°C produced benzofuran along with starting material in 93:7 and 29:71 ratios, respectively. Acetylene **134** is estimated, by extrapolation, to be completely consumed during FVP at 600°C. The thermal requirement for the cyclization of **131** to **133** is about 50°C greater than is required for the complete conversion of **134** to **136**–**138**.

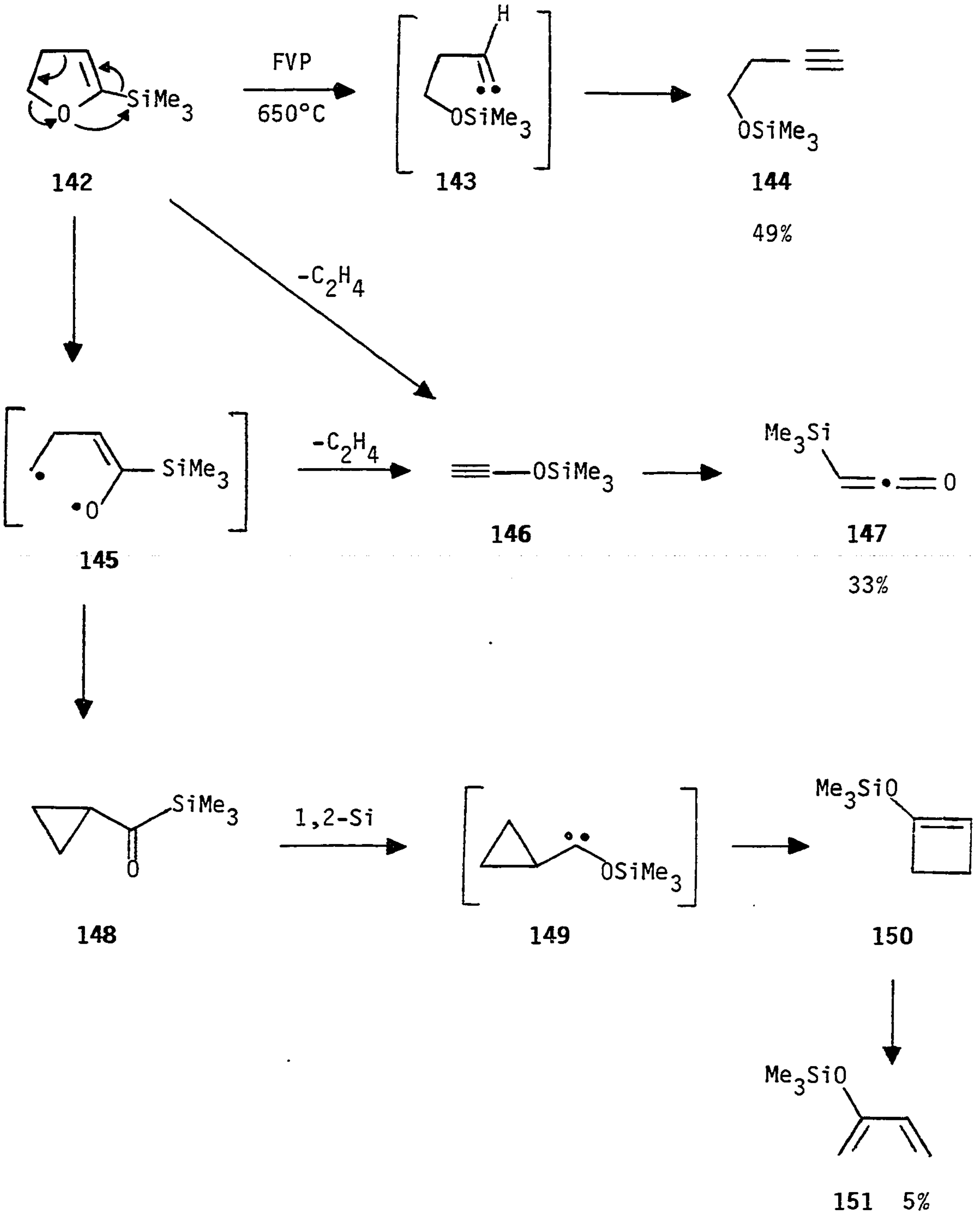
The possibility that 2-trimethylsilylbenzofuran was undergoing α-elimination to yield carbene **141** would represent the first example of a silicon mediated gas-phase reductive elimination resulting in the formation of an alkylidenecarbene. Supportive evidence for this proposed elimination was sought through the pyrolysis of the model compound, 2-trimethylsilyl-4,5-dihydrofuran, **142**. Analogous to the mechanism proposed for the isomerization of **138** to **137**, **142** should rearrange to carbene **143** which will produce 4-trimethylsiloxy-1-butyne, **144**, by way of a 1,2-hydrogen shift (Scheme 36).

Indeed, acetylene **144** is produced in 49% yield from the FVP of **142** at 650°C. Also produced in the pyrolysis are ketene **147** (33%) and siloxydiene **151** (5%). Both **147** and **151** may originate from diradical **145**, produced by C-O bond homolysis of **142**. The stepwise extrusion of ethylene from **145** could lead to siloxyacetylene **146** which is known (69) to thermally isomerize to **147**. It is also possible that acetylene **146** is produced by the concerted extrusion of ethylene from **142**. Alternatively, **145** could close to cyclopropyl ketone **148**, which is a major process in the thermolysis (70) and FVP, vide infra, of 2,3-dihydrofuran. Silyl ketone **148** is not observed but can undergo a 1,2-silyl shift to oxygen to form a carbene which would be expected to ring expand (71) and open to diene **151**.

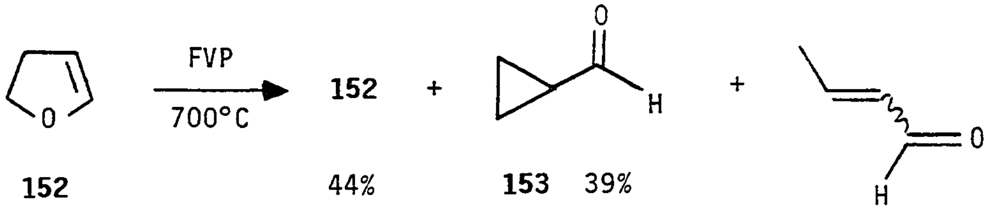
The flow pyrolysis of 2,3-dihydrofuran, **152**, has been shown to produce cyclopropane carboxaldehyde, **153**, and cis- and trans-crotonaldehyde, **154** (70). However, the sharp contrast of these results with those of the FVP of the silyl derivative **142** necessitated comparison of the FVP of **142** and **152**. At 600°C, a 4% yield of **153**, uncorrected for 83% recovered **152**, was obtained. FVP of 2,3-dihydrofuran at 700°C afforded a 44% yield of recovered starting material along with **153** (39%) and a 1:1 mixture (26%) of cis- and trans-crotonaldehyde (Scheme 37). While the products from the FVP of **152** are the same as those previously found in the flow pyrolysis of **152**, this comparison revealed the fact that the rearrangement of **142** is considerably more facile than that of **152**.

The possibility that the formation of the products shown in Scheme 34 was the result of base or acid catalysis was examined by pyrolysis of **134** at 750°C through base and acid washed pyrolysis tubes. No effect was observed for the acid treated case, and only a small change was observed in the base treated experiment. These observations suggest acid and base catalysis do not play a significant role in the rearrangements of **134** and its isomers **136**-**138**. These results appear in Table 2.

Scheme 36


SiMe$_3$
FVP
650°C
H
OSiMe$_3$
OSiMe$_3$
142
143
144
49%
-C$_2$H$_4$
SiMe$_3$
-C$_2$H$_4$
OSiMe$_3$
Me$_3$Si
O
145
146
147
33%
SiMe$_3$
O
1,2-Si
OSiMe$_3$
Me$_3$SiO
148
149
150
Me$_3$SiO
151
5%

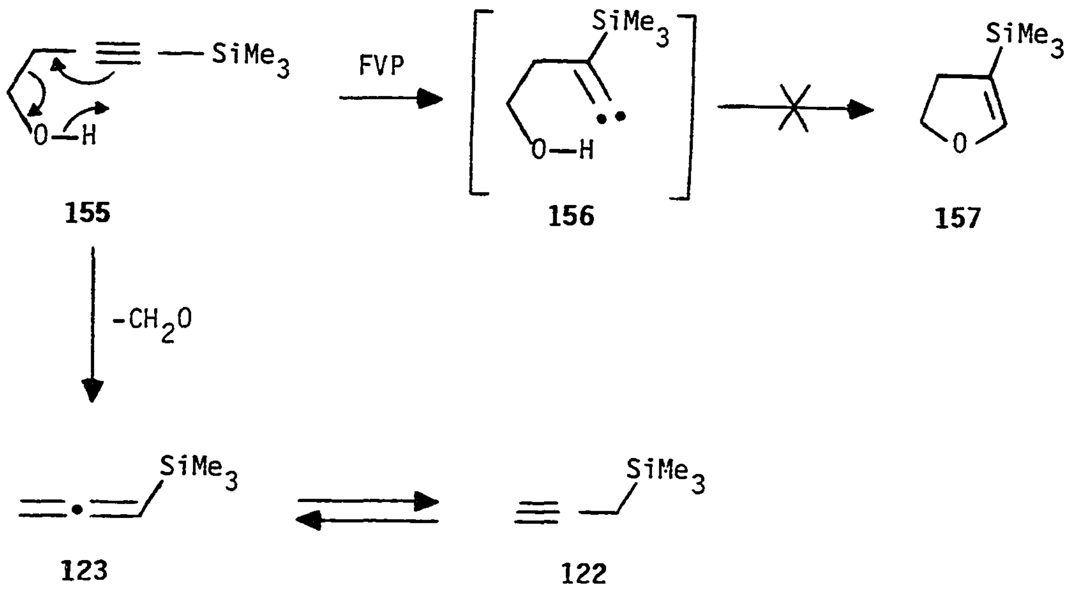
Scheme 37



152 44% **153** 39% **154** 26%

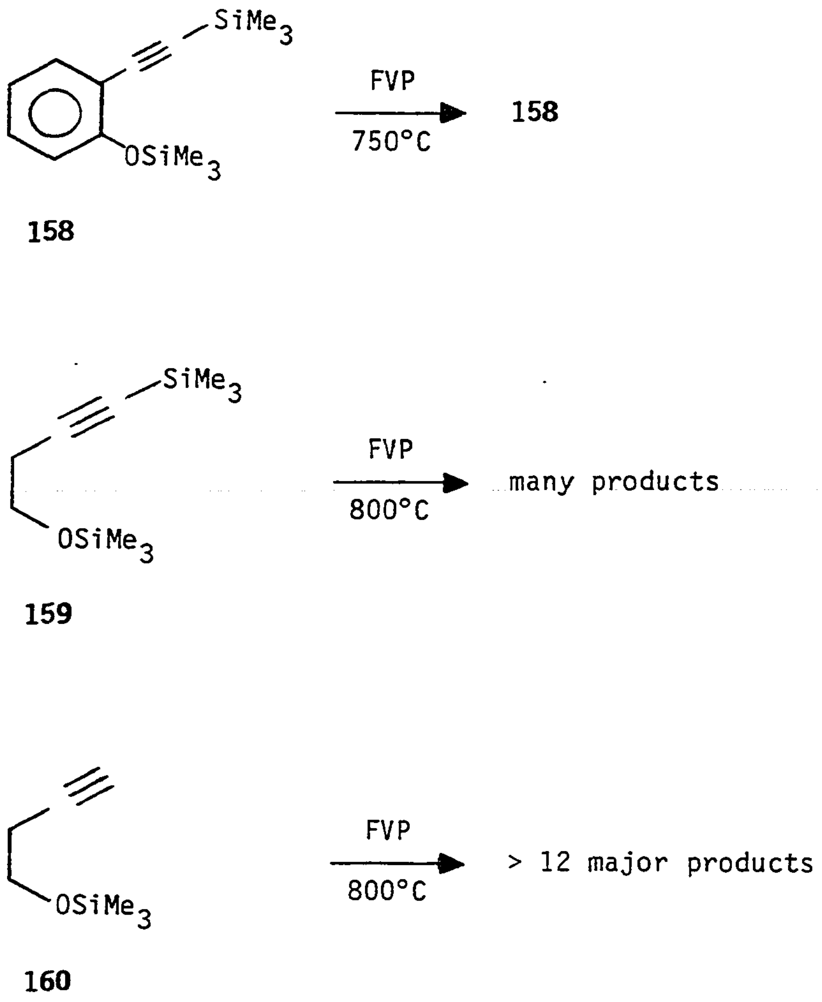
It was of interest to determine whether cyclization of silylacetylene **155** to dihydrofuran **157** via carbene **156** would be possible. Though a competitive fragmentation may exist as is known in the pyrolysis of 3-butyn-1-ol (72), the low temperature at which **134** is consumed suggests that cyclization of **155** may be a favorably competitive process. The pyrolysis of **155** was investigated at 600°C, 650°C, and 700°C. Silylallene **123** and its acetylenic isomer **122** were the only identifiable products formed, presumably via retro-ene fragmentation (Scheme 38). Analysis of the pyrolysate by ^{1}H NMR and GC/MS proved that none of the desired furan derivative **157** was obtained though traces of other unidentifiable products were present. At 700°C, the only products obtained were **123** (80%) and **122** (16%) accompanied by an undetermined amount of formaldehyde (identified as paraformaldehyde). As expected (72), the FVP of 3-butyn-1-ol at 700°C gave allene and formaldehyde.

Scheme 38



Substitution of the hydroxy hydrogen in **134**, **155**, and 3-butyn-1-ol with a trimethylsilyl group, giving acetylenes **158-160**, appears to effectively suppress the facile thermally induced 1,5-shift analogous to that which occurs in the parent acetylenes. Unfortunately, it does not facilitate the cyclization of an alkylidenecarbene intermediate. Pyrolysis of acetylene **158**, **159**, and **160** (Scheme 39) failed to produce the desired furan derivatives. Instead, the acetylenes decomposed or were recovered unchanged. The failure of the expected carbenes to insert into the Si-O bond of acetylenes **158**, **159**, and **160** is disappointing and does not support the mechanism proposed to account for the interconversion of acetylene **134** and benzofuran **138**. However, these systems are distinctly different and may not be satisfactory model systems for such a comparison.

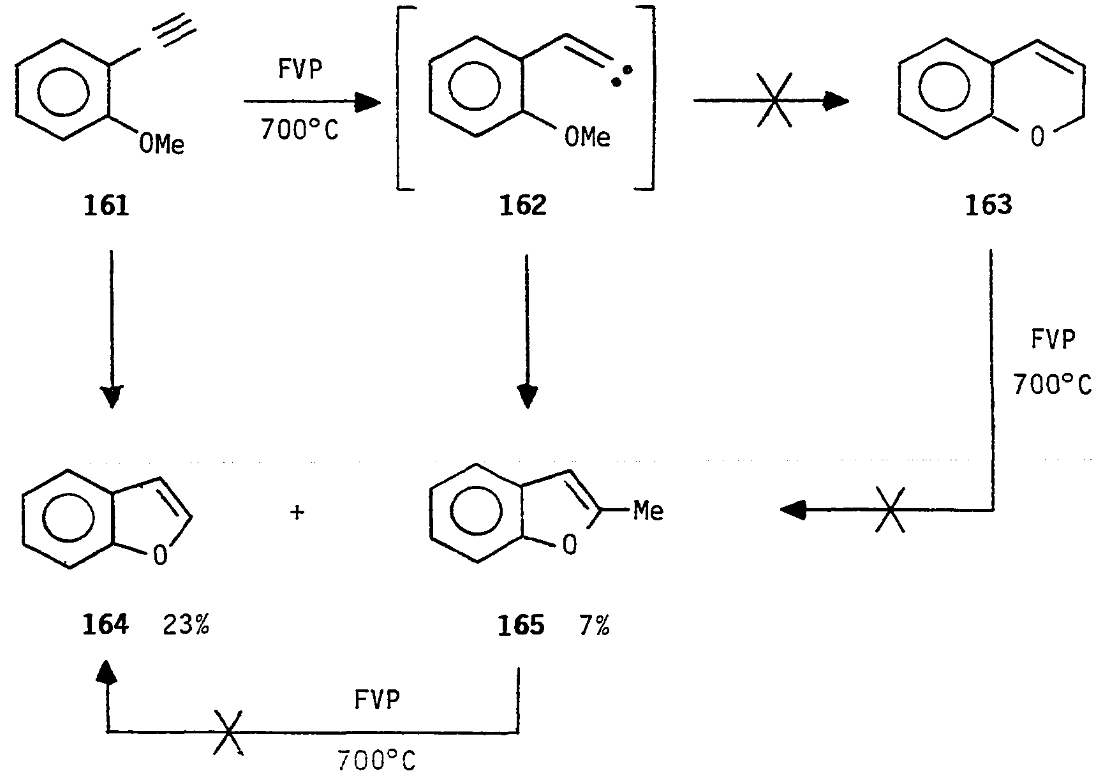
Scheme 39



While it has been shown that formation of six-membered rings in the gas-phase cyclization of alkylidenecarbenes is unfavorable (36, 37), a detailed study has not appeared in the literature. The only requirement for such a study is to eliminate the competitive formation of five-membered rings by carbene insertion into various R-H bonds. Anisole **161** effectively fills these requirements by blocking the five position without the use of bulky substituents. This is also a potential route for the preparation of 1,2-benzopyrans. Surprisingly, FVP of **161** at 700°C failed to produce any of the desired 1,2-benzopyran as anticipated by intramolecular C-H insertion into the o-methoxy substituent. Instead, a 23% yield of benzofuran, **164**, along with a 7% yield of 2-methylbenzofuran, **165**, was obtained (Scheme 40). The possibility that benzopyran **163** was produced but rearranged to the two benzofurans obtained was examined. FVP of **163** at 700°C afforded eight minor products in less than 16% combined yield at 23% completion. Analysis of the pyrolysate by GC/MS revealed that neither **164** nor **165** were present, ruling out **163** as their source. Since **165** was a potential source of benzofuran, **165** was pyrolyzed at 700°C. No decomposition occurred, and 96% of the starting material was recovered.

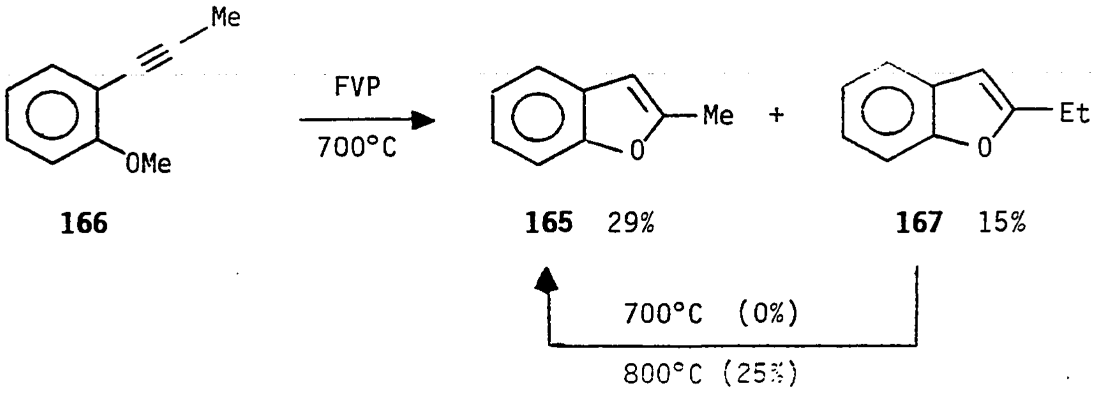
Similar results were obtained in the FVP of o-(1-propynyl)-anisole, **166**, at 700°C (Scheme 41). Again, no 1,2-benzopyrans were obtained though 2-methyl- and 2-ethylbenzofuran were produced in 29% and 15% yield, respectively. Pyrolysis of **166** at 650°C and 750°C failed to provide any additional information. While **167** resisted decomposition to **165** at 700°C, a 25% yield was obtained at 800°C. This suggests that the initially formed **157**, while still thermally activated, may be a source of **165** in the pyrolysis of anisole **166** via C-C bond homolysis and loss of methyl radical.

Scheme 40



Since 2-methylbenzofuran is not a source of benzofuran in the pyrolysis of anisole **161**, there must exist at least two competitive pathways leading to the formation of the observed products. One probable route involves initial loss of methyl radical from **161** followed by radical cyclization to form **164** as shown in Scheme 42. Similarly, anisole has been shown to give a 52% yield of phenol by loss of methyl radical in a flow pyrolysis at 640°C (73). A similar process can be invoked to explain the formation of 2-methylbenzofuran in the FVP of o-(1-propynyl)anisole, **166**. While the C-O insertion of alkylidenecarbene **162** to yield **165** (Scheme 40) is possible, an alternate pathway is likely. Benzofuran **165**, formed in the FVP of **161**, may arise by initial 1,5-methyl migration from oxygen to form allenyl ketone **170** (Scheme 42). A 1,2-hydrogen shift concomitant with aromatization and subsequent closure of diradical **171** would produce **165**.

Scheme 41



The decomposition of anisoles **161** and **166** appear to involve radical processes initiated by homolytic cleavages which may also explain the formation of 2-ethylbenzofuran. Formation of radical **174** by hydrogen abstraction followed by methyl radical migration and subsequent cyclization will lead to the production of **167** (Scheme 42). This could even result in a self-propagating process.

An additional pathway leading to **167** not directly involving radical intermediates is shown in Scheme 42. Isomerization of acetylene **166** to the corresponding allene **177** followed by concomitant cyclization and methyl migration would also yield benzofuran **167**.

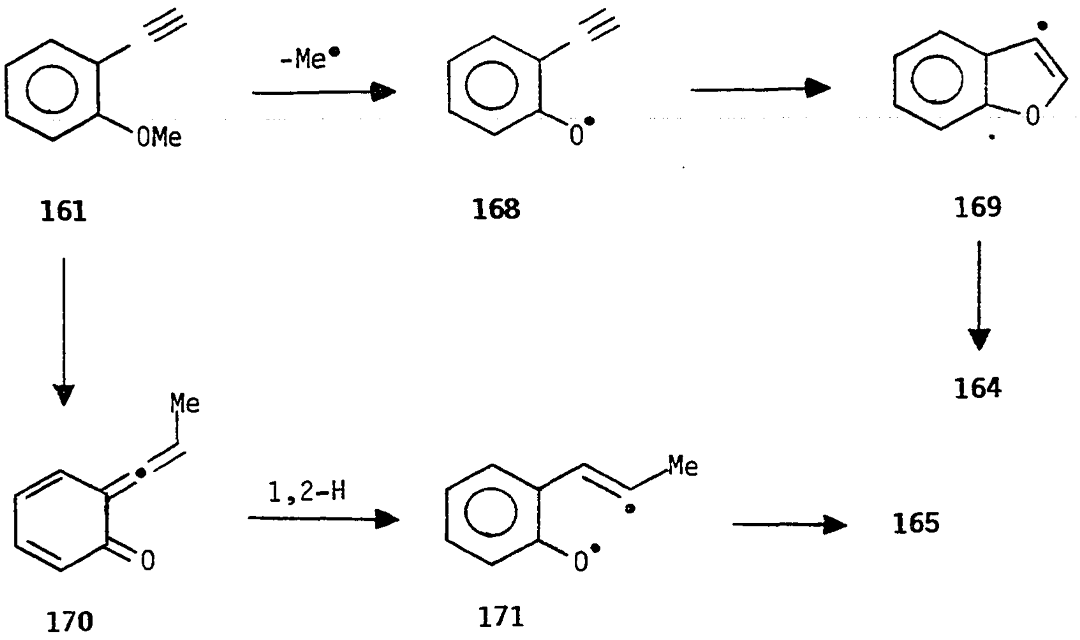
In order to compare the migratory aptitude of silicon relative to hydrogen and the effects of silyl substitution upon the chemistry of the thermal rearrangements of ortho acetylenic anisoles, the FVP of silyl substituted anisole **178** was examined (Scheme 43). Surprisingly, 2-ethylbenzofuran (45%) was the major product at 750°C and 99% conversion. Also produced was 2-methylbenzofuran (4%) whose origin is likely 2-ethylbenzofuran as was previously demonstrated. The unexpected formation of **167** corresponds to the remarkable loss of dimethylsilylene from acetylene **178**. It seems unlikely that initial reductive elimination of dimethylsilylene from **178** occurs since the product, **166**, has been shown (Scheme 41) to give 2-ethylbenzofuran as a minor product and 2-methylbenzofuran as the major product. This possibility is further diminished by the fact that (trimethylsilyl)-phenylacetylene **97** does not decompose significantly at 900°C, at which temperature only a 2% yield of 1-phenylpropyne is produced (Scheme 19). It also appears that O-Me homolysis may not be the initial step, as is postulated for anisoles **161** and **166**, since 2-trimethylsilylbenzofuran, **138**, and isomers **136** and **137** should be present in the pyrolysate. Examination of the pyrolysis of **178** at 700°C and 650°C failed to yield any additional information. Again, 2-ethylbenzofuran was the major product obtained (37% at 700°C and 20% at 650°C) along with recovered starting material and small amounts of **165**.

The possibility that **178** isomerized to carbene **179** and then inserted into the O-Me bond to give benzofuran **180** as the precursor of **167** was considered. Unfortunately, attempts to synthesize **180** to test this postulate failed. However, this possibility seems unlikely since furan **181** partially decomposes at 800°C to give only acetylenic and allenic products retaining the trimethylsilyl group in the yields shown in Scheme 44. The proposed mechanisms which give rise to the observed products are shown in Scheme 45. Ring opening of **181** leads to diradical **185**. This diradical can be transformed to either **186** or **188** by 1,2-silyl shifts. A 1,5-silyl shift on **186** would produce cis-**184** which must then isomerize to yield a mixture of both isomers. A 1,3-silyl shift on **188** would produce an equal mixture of cis- and trans-**184** as was obtained. Alternatively, **185** could isomerize to carbene **187** which may undergo a hydrogen migration to yield **189**. Ketene **189** could then undergo loss of carbon monoxide under the conditions of this pyrolysis to give **182** and **183**. It has been shown that furan also extrudes carbon monoxide during FVP to produce propyne and allene (74).

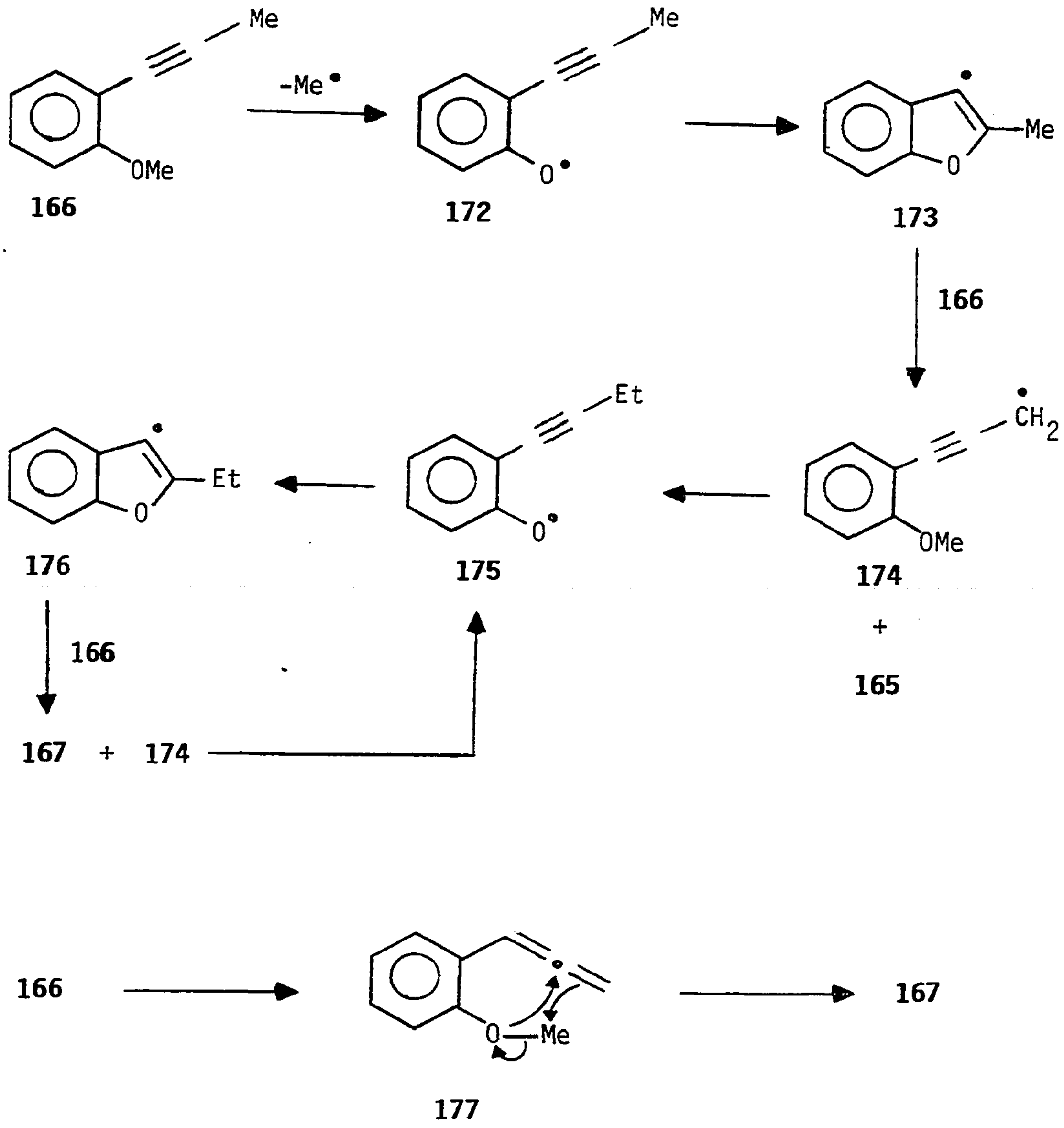
Still in search of clues to the mode of decomposition of anisole **178**, the FVP of acyclic enyne **190** was examined (Scheme 46). Quite surprisingly, dimethylsilylene was not extruded from **190**; rather, loss of carbon monoxide occurred resulting in the formation of allene **182** (30%) and acetylene **183** (2%). The only other product found was cis-siloxyenyne **184** (7%), produced by isomerization of starting material. Both products may be explained by an initial 1,5-sigmatropic methyl migration producing allene **186**, as suggested for the isomerization of **161** to **170** in Scheme 42. A 1,5-silyl migration on allene **186** would give <u>cis</u>-**184**. Alternatively, a 1,2-silyl migration on allene **186** will produce diradical **185** which ultimately gives allene **182** as shown in the sequence of rearrangements in Scheme 45. However, if diradical **185** is involved, furan **181** would be an expected product though none is formed. An alternative mechanism is postulated in Scheme 46 which does not involve diradical **185**. Instead, α-pyran **191** derived from C-H insertion of the expected alkylidenecarbene of **190** may be involved. Carbon oxygen bond homolysis of **191** produces diradical **192** and, subsequently, diene **193**. A 1,5-sigmatropic hydrogen shift gives ketene **194** which can decarbonylate to give allene **182** and acetylene **183** via vinylcarbene **195**.

The decarbonylation of **190** is not dependent upon, though possibly facilitated by, the presence of a silyl substituent. The FVP of the parent methoxyenyne, **196**, at 650°C gave 1-butyne and 1,2-butadiene as major products in addition to a 32% yield of recovered **196** (Scheme 47). Thus, 1,5-methyl migration on this framework appears to be a general process. This process may also be involved in the pyrolysis of anisole **178**. It seems probable that allenyl ketone **197** (Scheme 47) could eliminate dimethylsilylene to give acetylene **166**, a proven source of 2-ethylbenzofuran. However, the low yield of 2-methylbenzofuran, **165**, from the FVP of **178** makes this a bothersome explanation since **165** is the major product of FVP of **166**. Also, acetylene **198** should have been obtained from **197** via a 1,5-silyl shift. No **198** was found in the pyrolysate of **178** though acetylene **198** is stable to FVP at 700°C. Even the pyrolysis of **198** at 800°C leaves approximately 70% of the starting material unchanged (83% mass recovery) though ten other minor products are formed in minimal quantities.

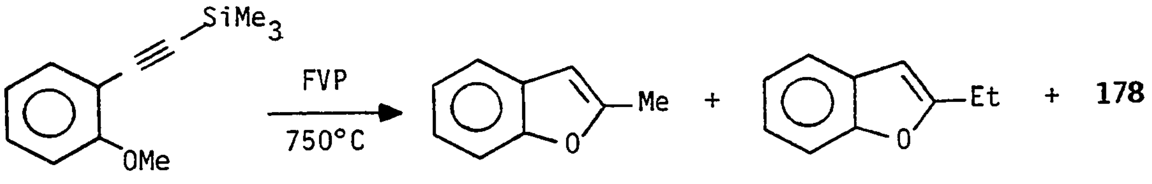
Scheme 42



Scheme 42 (continued)



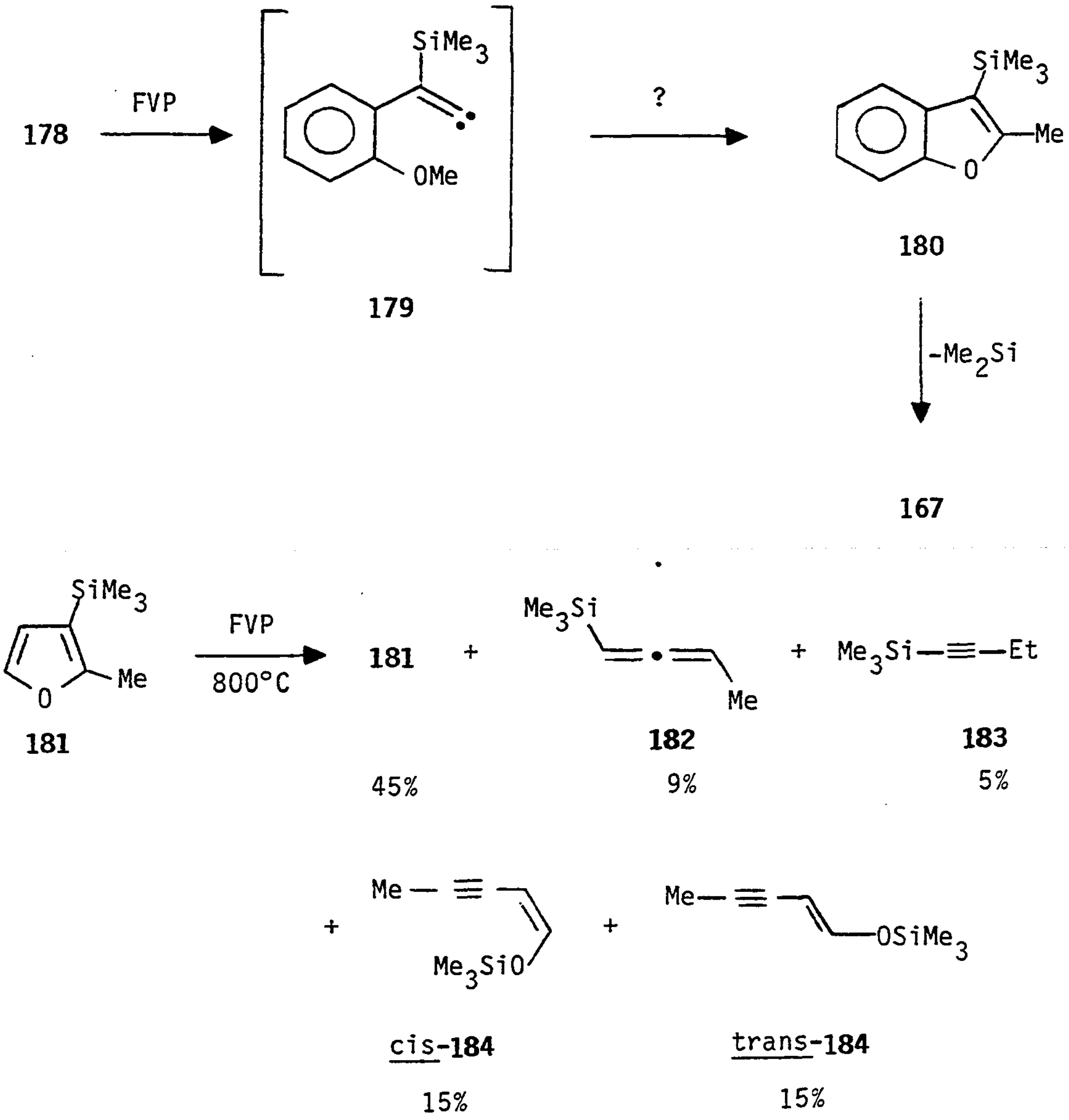
Scheme 43



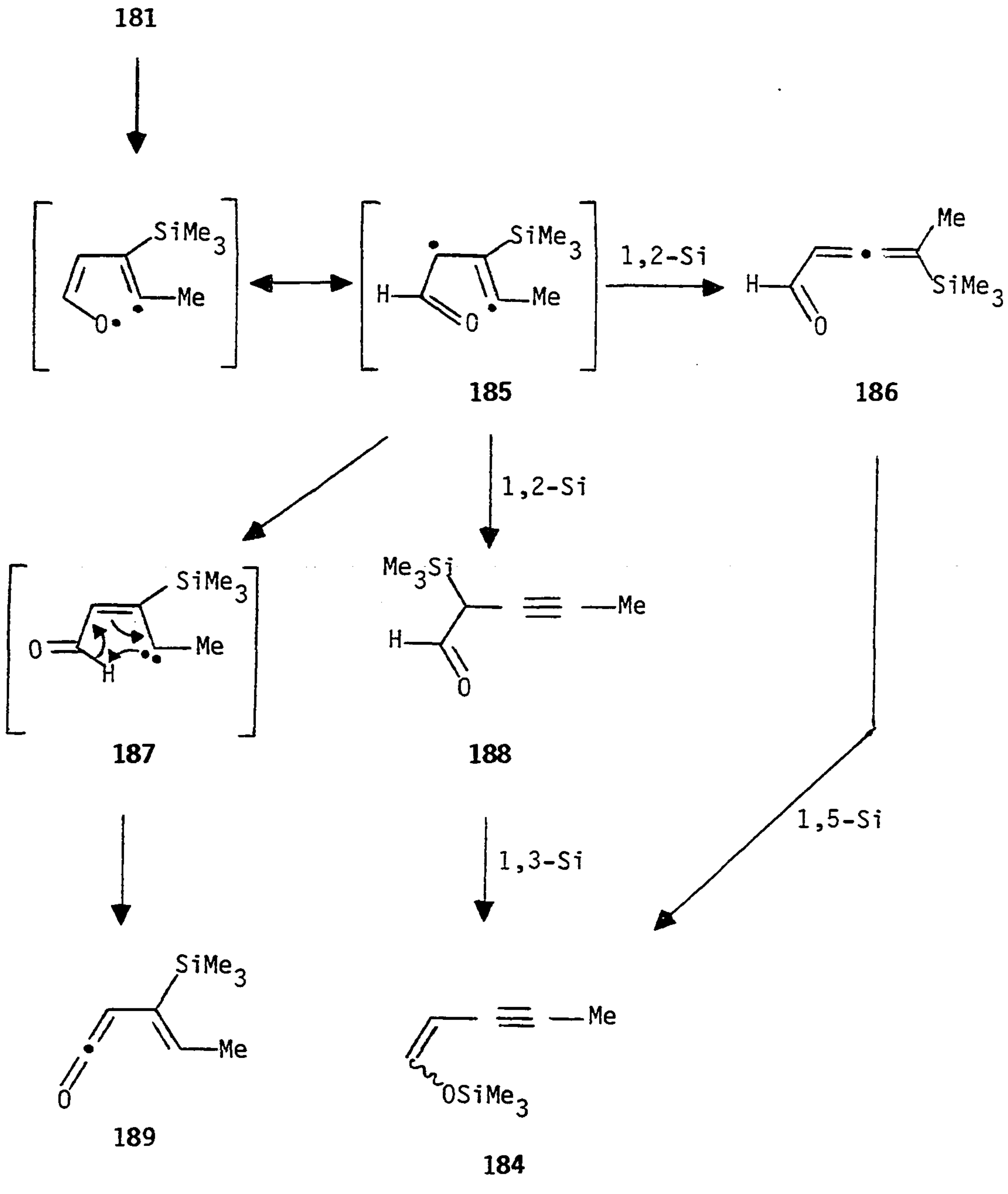
178 **165** 4% **167** 45% 1%

A detailed examination of the pyrolysis of o-(trimethylsilyl)-phenylacetylene described by Vuper (44), who found that 1,2-dihydrosilanaphthalene **69** was produced in 18% yield along with four unidentified isomers, suggests that a 1,5-methyl migration seems to occur on this analogous framework as well. Pyrolysis of o-(trimethylsilyl)phenylacetylene at 850°C and 90% completion produced indene (4%), silaindene **87** (6%), 1,2-dihydrosilanaphthalene **69** (20%), silaindenes **202** (3%), **203** (5%), and **208** (10%), 1,4-dihydrosilanaphthalene **211** (4%), and one remaining unidentified isomer in 1% yield. It seems reasonable that silaindenes **202** and **203** were produced by an initial 1,5-methyl migration on **199** which gives **201** as shown in Scheme 48. Either 1,2-hydrogen or 1,2-methyl shifts then result in the formation of the isomeric silaindenes. A 1,5-hydrogen shift would afford acetylene **204** which can undergo a 1,2-methyl shift to give carbene **205**. Intermediate carbene **205** could be responsible for the formation of silaindene **203** by a silyl hydride insertion or may give

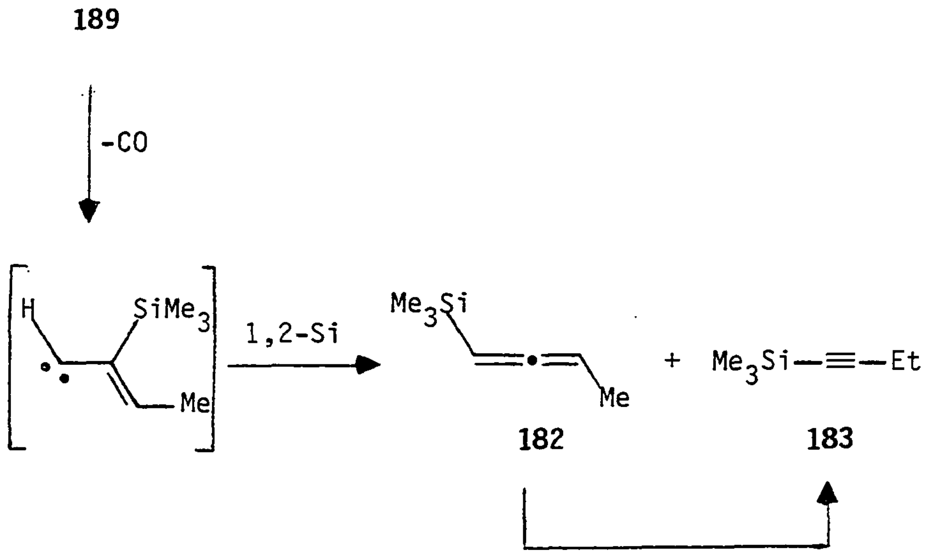
Scheme 44


178
FVP
SiMe3
OMe
179
?
SiMe3
Me
O
180
-Me2Si
167
SiMe3
Me
O
181
FVP
800°C
181
45%
Me3Si
Me
182
9%
Me3Si—≡—Et
183
5%
Me—≡
Me3SiO
cis-184
15%
Me—≡
OSiMe3
trans-184
15%

Scheme 45

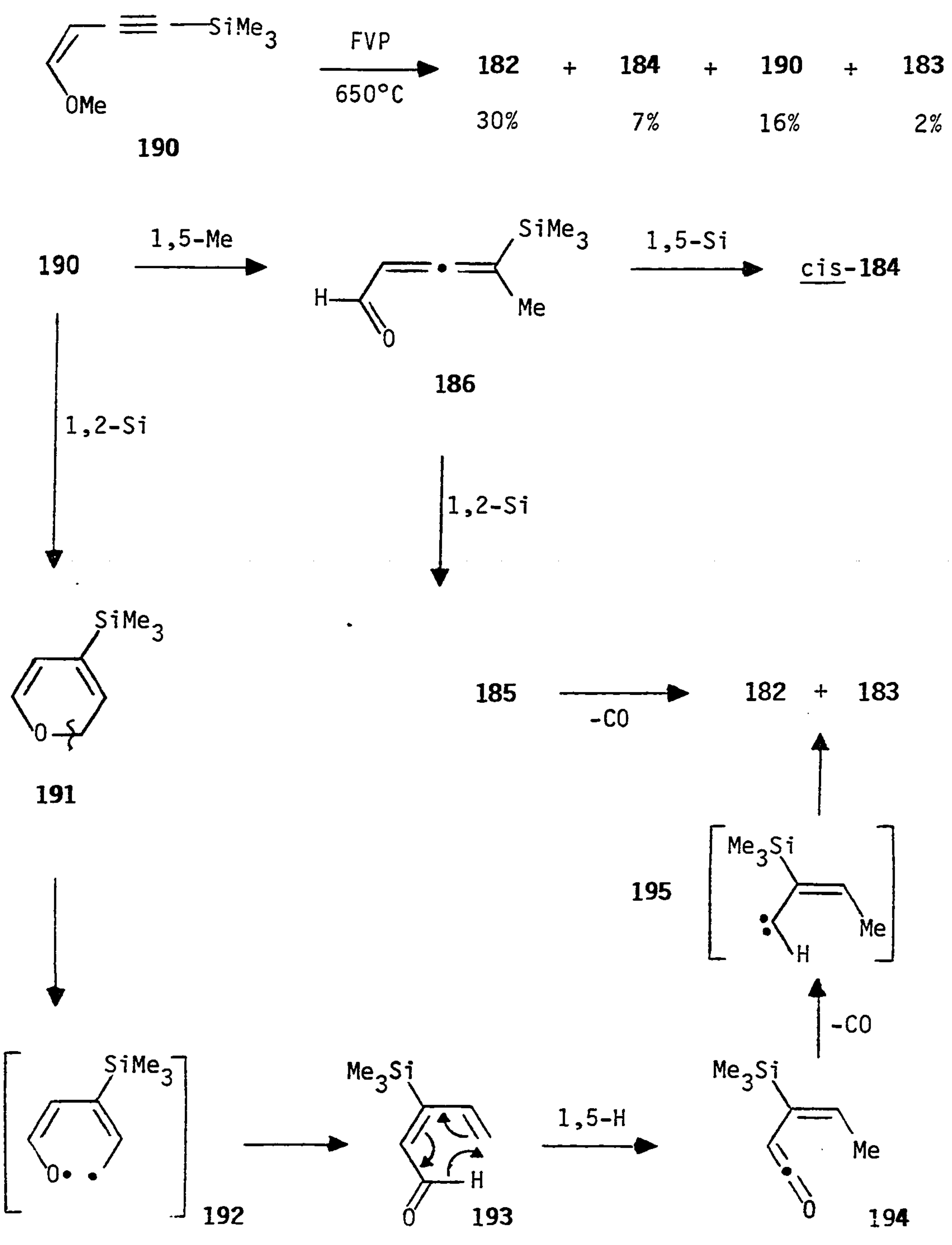

181
SiMe3
Me
O•
SiMe3
H
O
Me
185
1,2-Si
Me
H
O
SiMe3
186
1,2-Si
SiMe3
O
H
Me
187
Me3Si
Me
H
O
188
1,3-Si
1,5-Si
SiMe3
Me
O
189
Me
OSiMe3
184

Scheme 45 (continued)



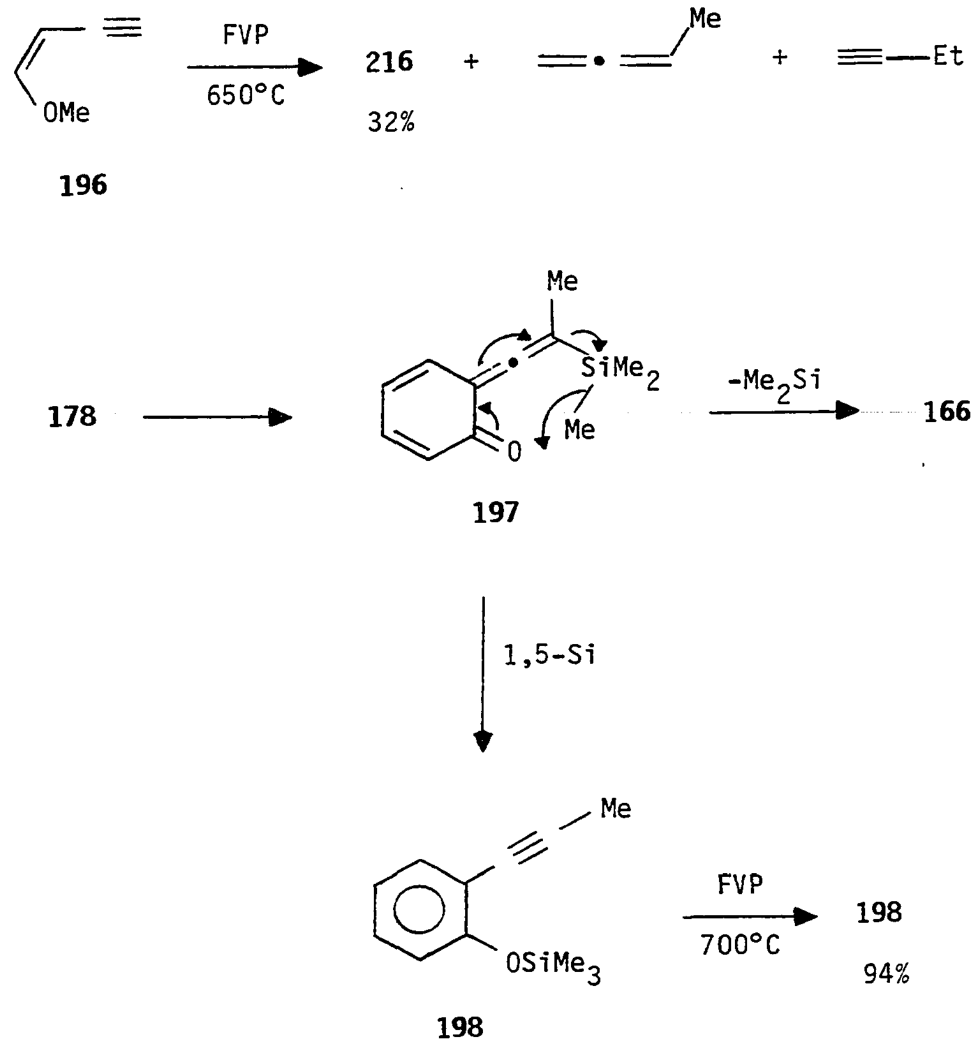
rise to silaindene **208** by a 1,3-hydrogen shift on **205** which forms diradical **206** and carbene **207**. Trapping of carbene **207** by the neighboring silylhydride group gives **208**. A 1,2-aryl shift on carbene **207** gives aryl allene **209** which can undergo a 1,5-hydrogen migration to give **210** which will cyclize affording 1,2-dihydronaphthalene **69**. An o-methylarylallene analogous to **209** has previously been shown to undergo such a rearrangement (75). It seems that the formation of 1,4-dihydronaphthalene **211** can readily be accounted for by radical induced isomerization of the double bond of **69** as is shown at the end of Scheme 48. The origins of indene and silaindene **87** are uncertain though these products may arise from extrusion of dimethylsilylene

Scheme 46

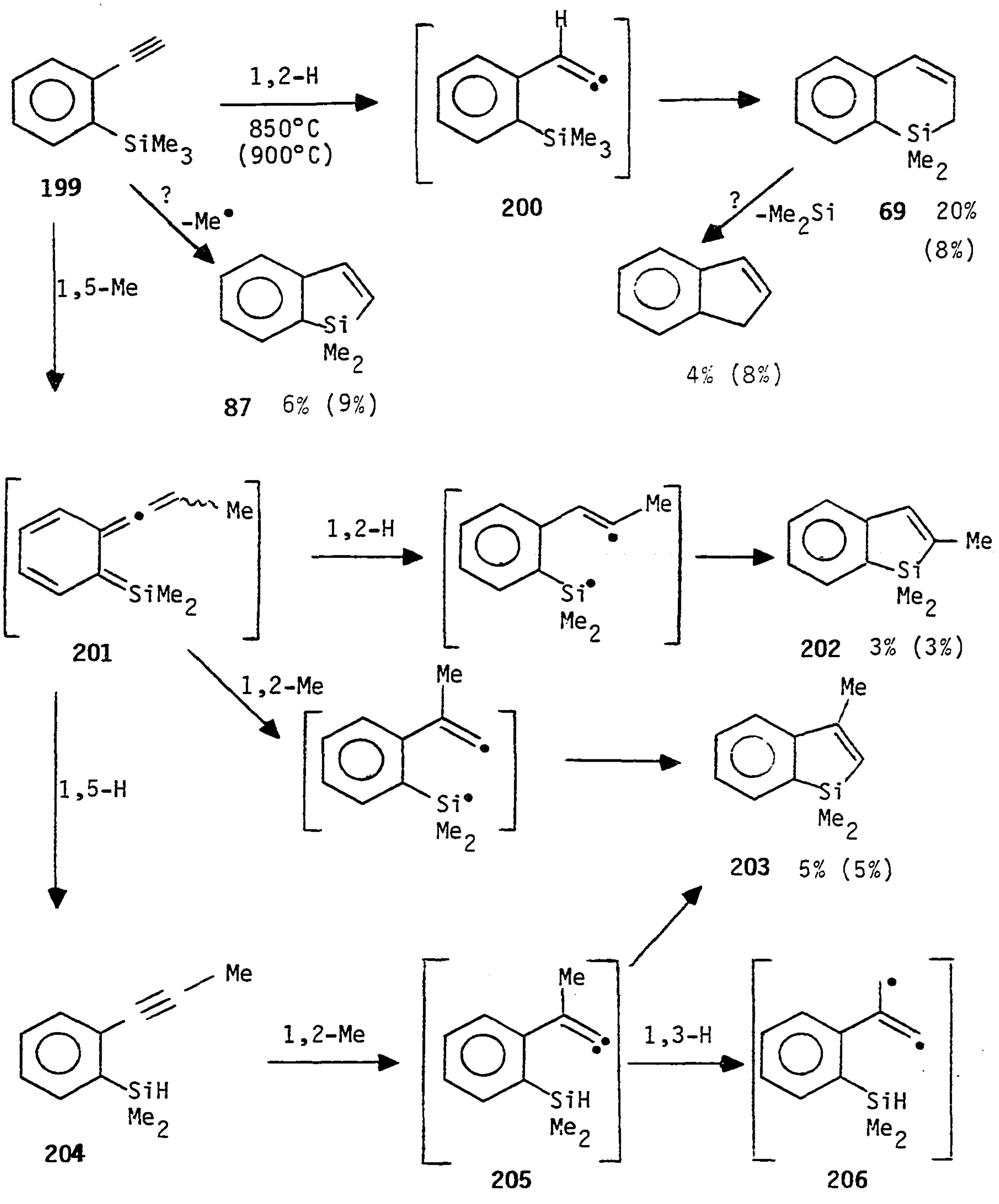

SiMe3
OMe
190
FVP
650°C
182 + 184 + 190 + 183
30% 7% 16% 2%
190
1,5-Me
SiMe3
H
O
Me
186
1,5-Si
cis-184
1,2-Si
1,2-Si
SiMe3
O
191
185
-CO
182 + 183
195
Me3Si
H
Me
SiMe3
O
192
Me3Si
H
O
193
1,5-H
Me3Si
Me
O
194
-CO

from **69** and loss of methyl radical from **199**. Cyclization of the resulting fragments leads to the formation of the respective products.

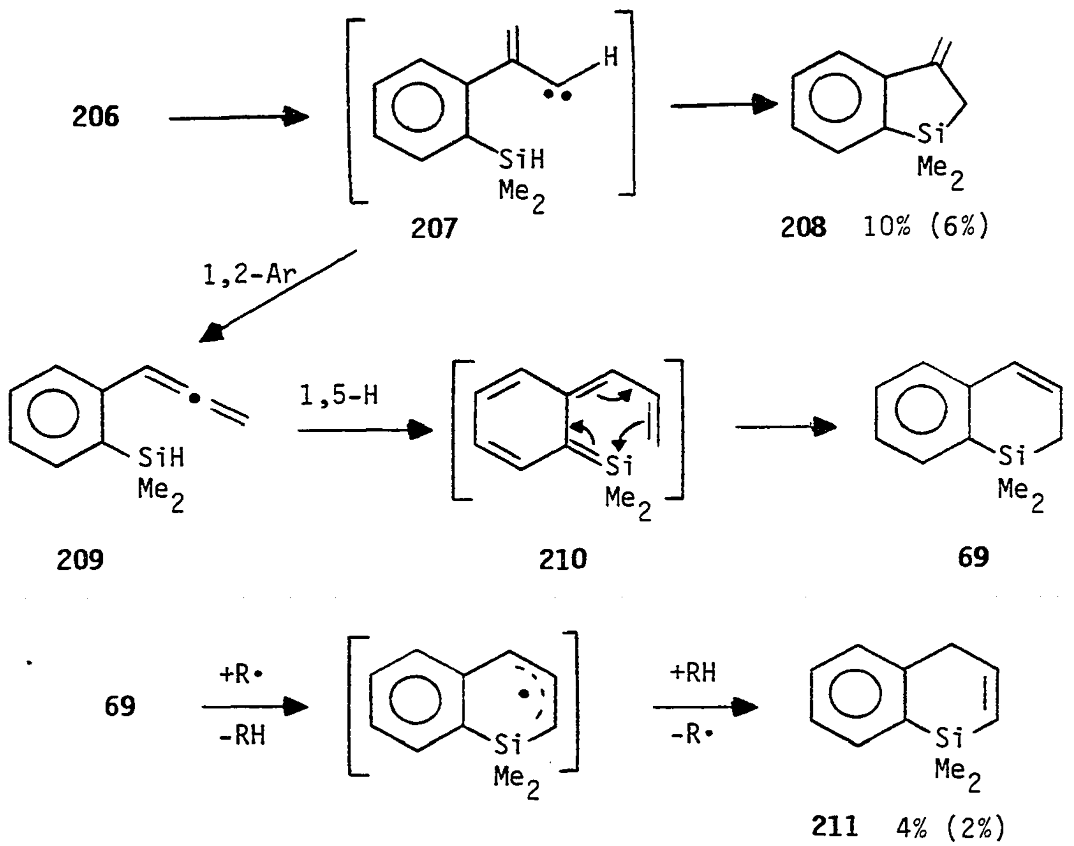
Scheme 47



Scheme 48


SiMe3
199
1,2-H
850°C
(900°C)
H
SiMe3
200
Si
Me2
69 20%
(8%)
?
-Me•
1,5-Me
Si
Me2
87 6% (9%)
?
-Me2Si
4% (8%)
Me
SiMe2
201
1,2-H
Me
Si•
Me2
Me
Si
Me2
202 3% (3%)
1,2-Me
Me
Si•
Me2
Me
Si
Me2
203 5% (5%)
1,5-H
Me
SiH
Me2
204
1,2-Me
Me
SiH
Me2
205
1,3-H
SiH
Me2
206

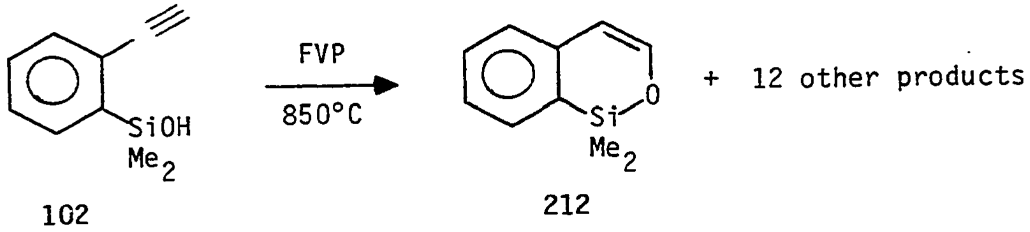
Scheme 48 (continued)



In a final attempt to gain some understanding of the processes involved in the conversion of anisole **178** to 2-ethylbenzofuran, **167**, the carbon-13 content of the methoxy group was enriched to 25%. Pyrolysis of labeled **178** gave 2-ethylbenzofuran with the label incorporated only in the methyl group with the same degree of carbon-13 enrichment as the starting material. The small amount of 2-methylbenzofuran which was formed showed no enhancement of the ^{13}C resonances in the NMR spectrum. Recovered **178** showed no scrambling of the label among the methyl groups. If o-(1-propynyl)anisole is involved in the formation of 2-ethylbenzofuran from **178**, it is probably not derived via the mechanism shown in Scheme 47. The mechanisms suggested for formation of 2-ethylbenzofuran are all consistent with the position of the label.

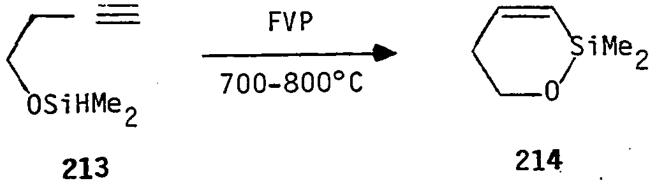
With the exception of the FVP of o-(trimethylsilyl)phenylacetylene, attempts to form six-membered rings by the methods described above have failed. By design, these products must arise from C-H bond insertion. Since the O-H bond has been shown by Bloch and Orvane (68) to be an efficient trap for alkylidenecarbenes in the gas phase, formation of a six-membered ring may be more feasible if insertion into an O-H bond were permitted. Such an example was investigated in the pyrolysis of silanol **102** (Scheme 49). The pyrolysis of **102** was examined over the temperature range of 650°C to 850°C. At the low temperature of 650°C, only slight conversion was noticed. The complexity of the pyrolysate steadily increased with increasing temperature. At 850°C, more than fourteen products (including two isomers of **102**) were present along with starting material as the major volatile product. GC/MS and ^{1}H NMR data suggested that the desired benzosilapyran **212** was present, but because of the complex nature of the pyrolysate, the pyrolysis of **102** was not further examined.

Scheme 49



Similarly, the insertion of an alkylidenecarbene into an Si-H bond resulting in the formation of a six-membered ring was investigated. Pyrolysis of acetylene **213** (Scheme 50) at 700°C produced at best a trace of the desired product, **214**, whose identity was based upon GC/MS and ^{1}H NMR data. The remainder of the pyrolysate consisted only of **213**. While attempting to increase the percent conversion by pyrolyzing **213** at higher temperatures, major decomposition was noted. At 800°C, numerous products were produced in only trace amounts.

Scheme 50



While these experiments failed to provide an efficient route to the desired products, a number of interesting, thermally induced rearrangements were observed. In an attempt to form 3-trimethylsilylbenzofuran, it was realized that alkylidenecarbenes can be thermally generated in the gas phase by α-elimination of a siloxane from α-silyl vinyl ethers. A second example of this method of alkylidenecarbene formation was revealed in the FVP of 2-trimethylsilyl-4,5-dihydrofuran. During the attempted formation of pyran derivatives, the surprising loss of dimethylsilylene from a silyl substituted anisole and the unexpected extrusion of carbon monoxide from its acyclic analogue occurred instead.

Generation of Alkylidenecarbenes by α-Elimination of Siloxanes in the Pyrolysis of α-Silyl Vinyl Ethers

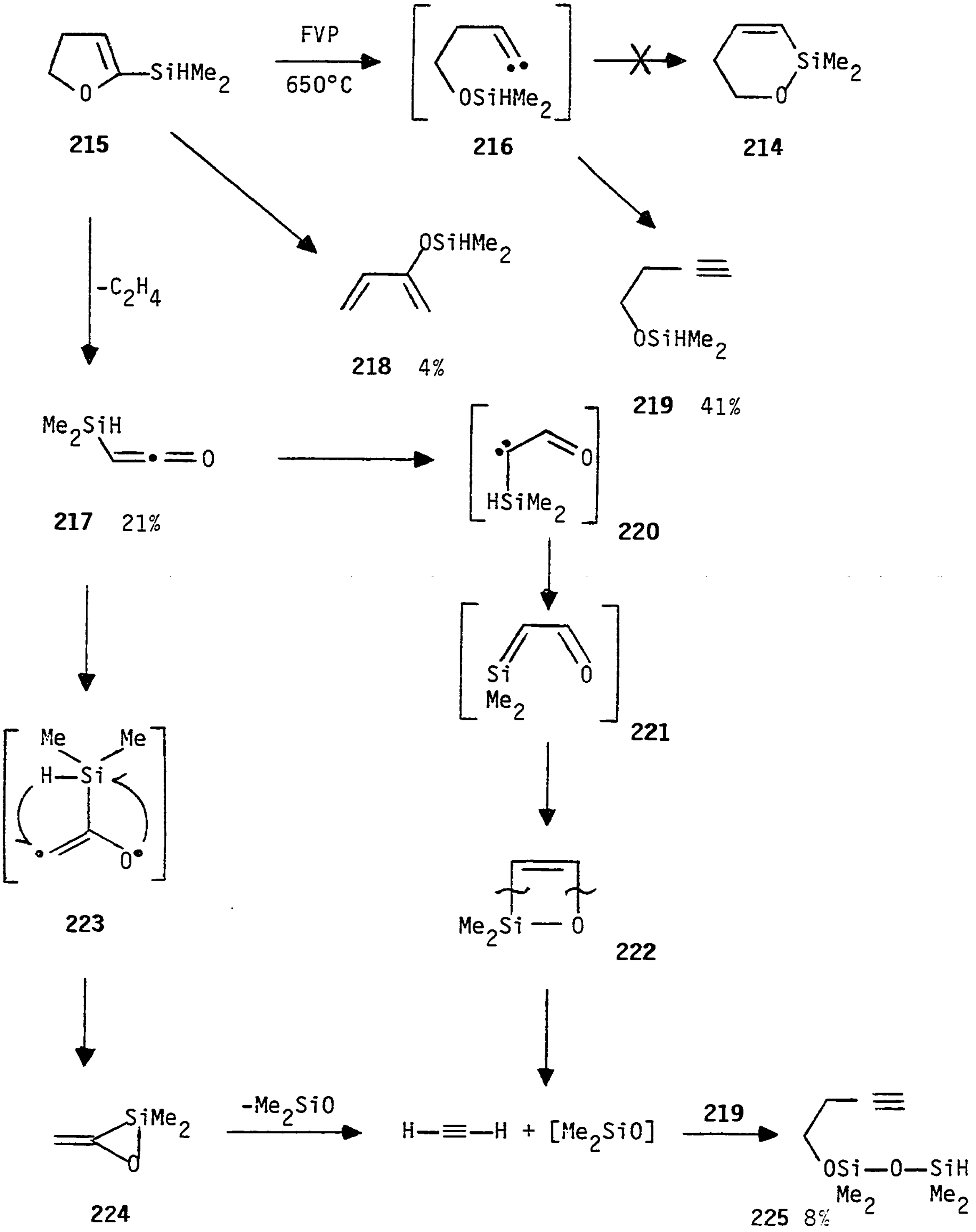
The surprising formation of alkylidenecarbenes in the FVP of α-silyl vinyl ethers **138** and **142** has revealed a new method of alkylidenecarbene generation in the gas phase. Some initial investigations into the utility of this transformation are described herein.

While the FVP of acetylene **213** failed to produce a significant yield of dihydrosilapyran **214** (Scheme 50), it was of interest to see if α-elimination on silyldihydrofuran **215** would allow intramolecular trapping of carbene **216**. The results of the pyrolysis of **215** at 650°C (Scheme 51) were strikingly similar to those obtained from FVP of **142** (Scheme 36). A 1,2-hydrogen shift on carbene **216** to afford acetylene

219 (41%) was completely favored over Si-H bond insertion leading to **214.** Also formed in the pyrolysis of **215** were dimethylsilylketene (21%), **217**, siloxydiene **218** (4%), and disiloxane **225** (8%). Both **217** and **218** are analogues of **147** and **151** which were formed in the FVP of **142** (Scheme 36). The formation of **225** was totally unexpected. Its origin may involve either of two possible pathways. One involves a 1,2-silyl shift to give diradical **223** which, in turn, gives silaepoxide **224.** Extrusion of methylidenecarbene, which produces acetylene, is concomitant with the formation of dimethylsilanone which is subsequently trapped by **219** to yield disiloxane **225.** Alternatively, a 1,2-hydrogen shift on **217** would lead to carbene **220** which could undergo a silylhydride migration to yield silene **221.** Subsequent electrocyclic ring closure gives silaoxete **222.** Silacycle **222** would be expected to thermally extrude the elements of dimethylsilanone. This latter rearrangement and decomposition has precedent in the work of Sekiguchi and Ando (76) who prepared and examined the chemistry of the first stable silaoxete which is shown in Scheme 52.

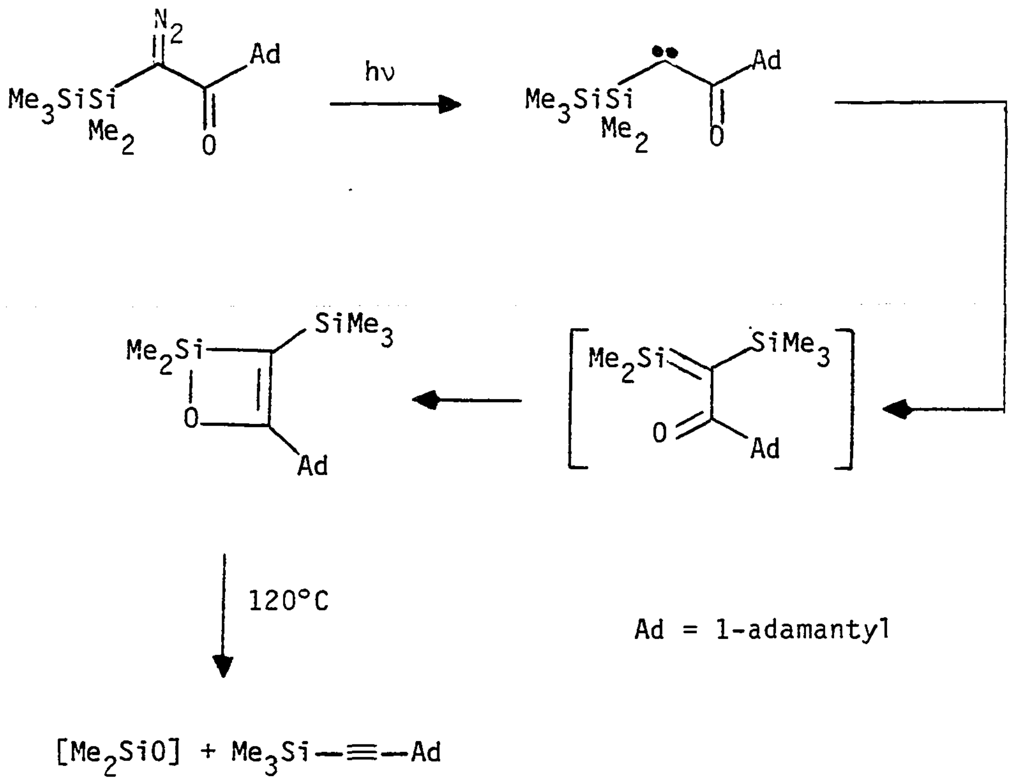
Acetylene was never identified as a product of the pyrolysis of **215** nor was the pyrolysis of the unstable ketene **217** examined to provide support for the mechanism proposed for the formation of dimethylsilanone. However, indirect evidence was obtained which supports this mechanism. Copyrolysis of a mixture of **215** and **226** (73.3:26.7), obtained as an inseparable mixture of the two constituents during several attempts to prepare pure **215**, produced acetylene **227** which was not found in the pyrolysis of **214** alone

Scheme 51


SiHMe2
O
215
FVP
650°C
OSiHMe2
216
SiMe2
O
214
-C2H4
OSiHMe2
218 4%
OSiHMe2
219 41%
Me2SiH
O
217 21%
O
HSiMe2
220
Si
Me2
O
221
Me
Me
H—Si
O
223
Me2Si — O
222
SiMe2
O
224
-Me2SiO
H—≡—H + [Me2SiO]
219
OSi—O—SiH
Me2
Me2
225 8%

(Scheme 53). Dimethylsilylacetylene, **227**, presumably arises by either mechanism proposed for the conversion of dimethylsilylketene, **217**, to acetylene and dimethylsilanone (Scheme 51). The estimated yield of **227** is probably low due to the problems inherent in measuring the yields of volatile compounds.

Scheme 52

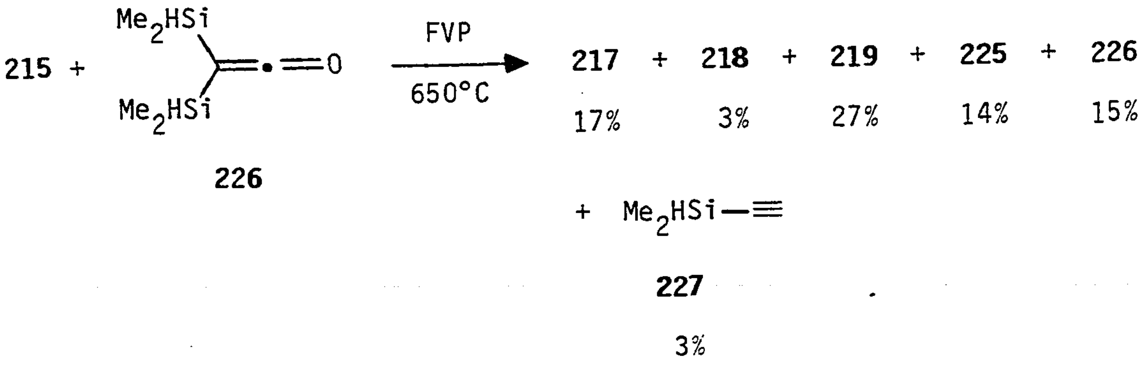


$[Me_2SiO] + Me_3Si—\equiv—Ad$

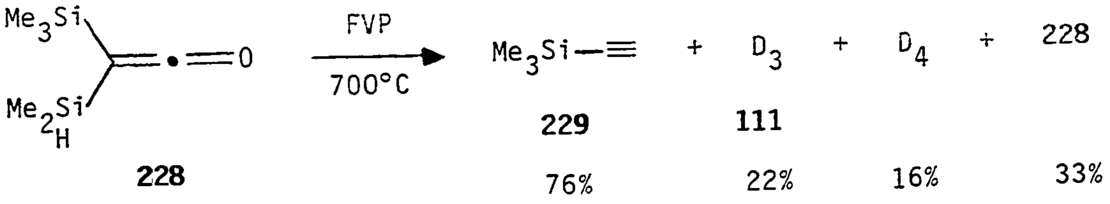
Ad = 1-adamantyl

To unambiguously demonstrate the route of decomposition of hydridosilylketenes, ketene **228** was pyrolyzed at 700°C. As expected, trimethylsilylacetylene was obtained as the major product (76%) along with D_3 (22%) and D_4 (16%) at 67% completion (Scheme 54). This experiment clearly demonstrates the decomposition of hydridosilylketenes to acetylenes and the elements of dimethylsilanone and supports the mechanisms proposed to account for the formation of 225 in Scheme 51.

Scheme 53



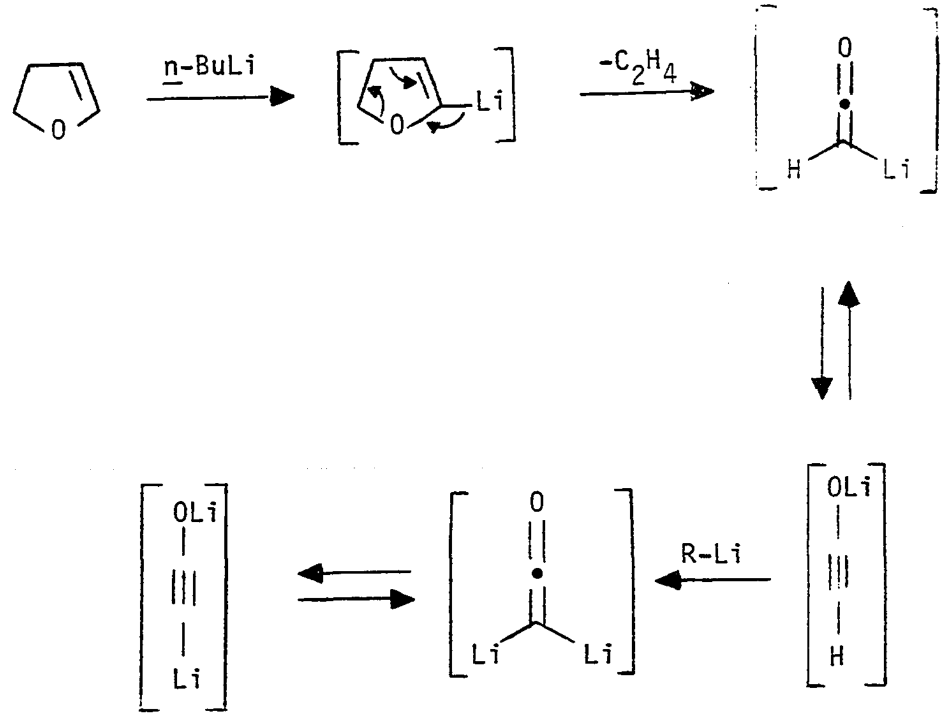
Scheme 54



While assessing the methods available for the synthesis of a silylketene to execute the previous experiment, it was realized that very few methods were available. All of these possible routes were quite involved and required several steps. The serendipitous formation of bis(dimethylsilyl)ketene in the synthesis of 2-dimethylsilyl-4,5-dihydrofuran is quite remarkable, unprecedented, and potentially offers a new and general route for the synthesis of ketenes. This novel route to dilithioketene is quite attractive in view of its simplicity and the use of inexpensive, commercially available starting materials. The only other synthesis of dilithioketene was accomplished in good yield by Hoppe and Schöllkopf (77). Their method requires the three step synthesis of 3-phenylisoxazole and the use of lithium tetramethylpiperidide, an expensive base, to effect the formation of the dilithioketene. Subsequently, numerous attempts were made to optimize the yield of the ketene product obtained by the metalation of 2,3-dihydrofuran.

The conversion of 2-lithio-4,5-dihydrofuran to dilithioketene presumably occurs by rearrangement and extrusion of ethylene to initially produce lithioketene as shown in Scheme 55. The lithioketene produced is then metalated by additional alkyllithium present in the reaction mixture to afford dilithioketene. It must be kept in mind that the lithioketene formed may be in equilibrium with its lithium alkynolate isomer which may also be metalated. Likewise, dilithioiketene could be in equilibrium with its dilithioalkynolate isomer. While only ketene products were obtained, the workup procedure employed could cause isomerization of initially formed silyl(siloxy)acetylenes to the ketene products obtained from the reaction. The use of other electrophiles and alternate workup procedures should aid in the elucidation of this intriguing rearrangement.

Scheme 55



In an attempt to drive the reaction to favor the formation of the ketene product, it was found that heating the reaction mixture at 35-45°C for two hours completely destroyed the desired product though the dihydrofuran product was still present. However, after initial formation of the 2-lithio-4,5-dihydrofuran with one equivalent of n-butyllithium, extended reaction times at room temperature favored the formation of the ketene product. After reaction of n-butyllithium with 2,3-dihydrofuran at 25°C for 24 hours followed by quenching the reaction with chlorodimethylsilane, a mixture of **226** and **215** were obtained in 28% and 19% yield, respectively. Extending the reaction time to 48 hours favored the formation of **226** over **215** (76:24), but the yield of bis(dimethylsilyl)ketene dropped to 21%.

Two equivalents of n-butyllithium are required for optimal yields, but because n-butyllithium will react with THF under these conditions, both equivalents cannot be added simultaneously. Consequently, after reaction of 2,3-dihydrofuran with one equivalent of alkyllithium for 24 hours, a second equivalent of n-butyllithium was added and allowed to react for an additional 10 hours. The reaction was then quenched with chlorotrimethylsilane which produced bis(dimethylsilyl)ketene in 33% yield and 2-trimethylsilyl-4,5-dihydrofuran in 38% yield.

Even though the addition of an equivalent of TMEDA had no effect on the ratios of products formed, changing the solvent to ether did. Twenty-four hours after metalation of 2,3-dihydrofuran in ether, the reaction was quenched with chlorotrimethylsilane to produce only 2-trimethylsilyl-4,5-dihydrofuran in 51% yield.

It was hoped that changing the counter ion from lithium to potassium would favor the formation of the ketene dianion. Therefore, metalation was also attempted using n-butyllithium (one equivalent) and potassium t-butoxide (one equivalent) in a mixture of THF and hexane (4:3) at -23°C. Unfortunately, only the dihydrofuran derivative was formed after quenching with chlorotrimethylsilane at

-23°C. Allowing the reaction to warm to room temperature resulted in the destruction of both the dihydrofuran and ketene products. Reaction of 2,3-dihydrofuran with n-butyllithium (one equivalent) and potassium t-butoxide (one equivalent) in hexane for two hours at -23°C and one hour at 25°C afforded 2-trimethylsilyl-4,5-dihydrofuran and bis(trimethylsilyl)ketene in 17% and 13% yield, respectively, after reaction with chlorotrimethylsilane.

Optimization of the reaction conditions and the use of different electrophiles may yet provide a simple and efficient route to the synthesis of ketenes. This intriguing reaction is certainly deserving of further investigation.

While continuing to investigate the application of α-elimination of a siloxane to afford alkylidenecarbenes, the pyrolysis of dimethylsilylfuran **230** was also examined (Scheme 56). It was hoped that carbene **231** would be formed with the desired stereochemistry which, in equilibration with siloxyenyne **232**, could be trapped to yield the known (78) silapyran **234** by a simple and efficient route.

The FVP of **230** did produce silapyran **234** but only in 15% yield. A 15% yield of recovered starting material was also realized. While **231** may be the source of **234**, the formation of **234** may also arise from homolytic C-O bond cleavage to produce diradical **236** which can isomerize to carbene **237**. A hydrogen migration from silicon would yield silene **238** which would be expected to rapidly cyclize to **234**. Either mechanism is possible though the latter may also explain the formation of the decarbonylated products which were formed. The formation of the isomeric decarbonylation products **245**, **247**, **256**, and **257** most likely results from the facile decarbonylation of ketenes **240** and **241** since the thermal decarbonylation of aldehydes (79) is generally more complex than decarbonylation of ketenes (23). However, the formation of the decarbonylated products from intermediate aldehydes such as **239** cannot be ruled out at this time.

Two other isomers of starting material were produced in 8% (**235**) and 7% (unidentified) yield. Of the two isomers, only **235** was separable from **230** and **234** permitting complete spectral analysis. Quite unexpected and puzzling was the presence of **235**. Its formation is rationalized by the mechanism shown in Scheme 56. Hydrogen migration on siloxyenyne **232** will give the zwitterionic allene **233** which then could cyclize to form silacycle **235**.

While the formation of allenes and acetylenes could be anticipated based on the known decomposition of furan to propyne and allene (74), the formation of silacyclobutene **247** was totally unexpected. The formation of **247** can be explained by Si-H bond insertion of carbene **244** formed by decarbonylation of **230** as shown in Scheme 56. Also possible is a 1,4-silylhydride migration on carbene **244** to give 1,1-dimethyl-1-sila-1,3-butadiene, **246**, which would close to **247**. An alternative and likely mechanism involves a silylhydride migration on carbene **253**, which is most likely entailed in the interconversion of **245**, **256**, and **257**, to give silabutadiene **246** which closes to **247** as shown in Scheme 57. Carbene **255** is probably found on this same energy surface and could be trapped by the neighboring silylhydride group to also give **247**.

The interconversion of **245**, **256**, and **257** is outlined in Scheme 57 and is based upon the mechanism proposed by Honjou et al. (52) for the interconversion of allene, cyclopropene, and propyne. This scheme has been simplified by giving preference to initial 1,2-silyl migrations as opposed to possible 1,2-hydrogen migrations (such as the isomerization of **245** to **251**) in keeping with the belief that silyl migrates faster than hydrogen. Also omitted is the possibility of 1,2-silyl migration on diradicals such as **248** which would form **245** or **257**. These migrations are predicted to be high energy processes for hydrogen (52) though they may occur with silyl groups. Since the energy surface of the interconversion of **242**, **245**, **256**, and **257** has not been investigated, alternate pathways involving 1,2-silyl shifts certainly cannot yet be excluded.

To determine whether or not silacyclobutene **247** could be formed during the interconversion of silanes **245**, **256**, and **257**, the flash vacuum pyrolysis of dimethyl(propargyl)silane was examined. At 700°C, the major constituents of the pyrolysis were **245** (9%), **247** (20%), **256** (10%), and **257** (3%). Though this experiment does not exclude other possible sources of **247** in the FVP of **230**, it does prove that **247** does arise from the isomerization of **257** and potentially from isomers **245** and **256**.

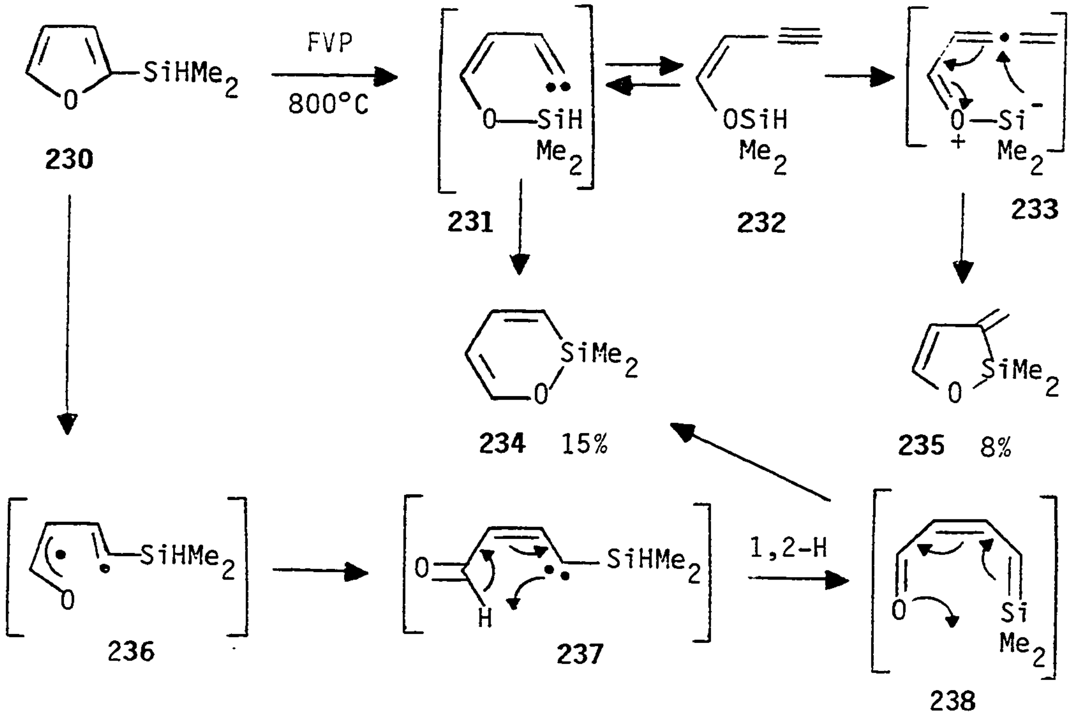
It is apparent from the literature that silicon plays an important role in the isomerization of silyl substituted allenes and propynes. An activation energy (E_a) of 50 kcal/mole was experimentally determined for the allenyltrimethylsilane to trimethyl(propargyl)silane rearrangement (50). This compares favorably with the experimentally derived values of 64 kcal/mole E_a for the allene to propyne rearrangement (80) and 63 kcal/mole E_a determined for the 1,2-butadiene to 2-butene rearrangement (81). This dramatic difference is probably due to the ability of silicon to undergo 1,2-shifts, such as the conversion of **245** to **251** (Scheme 57), or 1,3-shifts, such as the conversion of **255** to **252**, with greater ease than does hydrogen or methyl. Some experimental basis for this postulate may lie in the fact that acetylene **256** is formed at higher temperatures than at which the interconversion of **245** and **256** begins. The controlling factor here may be the higher energy requirements of the 1,3-hydrogen shift in going from **250** to **254** as compared to the corresponding silyl shift leading to **255** from **252**.

It is also of interest to note that pyrolysis of 1-methylcyclopropene at 490°C (81) in a static reactor led to the formation of 2-butyne (93%), 1,3-butadiene (5%), and 1,2-butadiene (2%). The products were proposed to arise from 1-methylcyclopropene by ring carbon-carbon bond homolysis followed by successive 1,2-hydrogen shifts. No carbenes were proposed to be involved in these rearrangements.

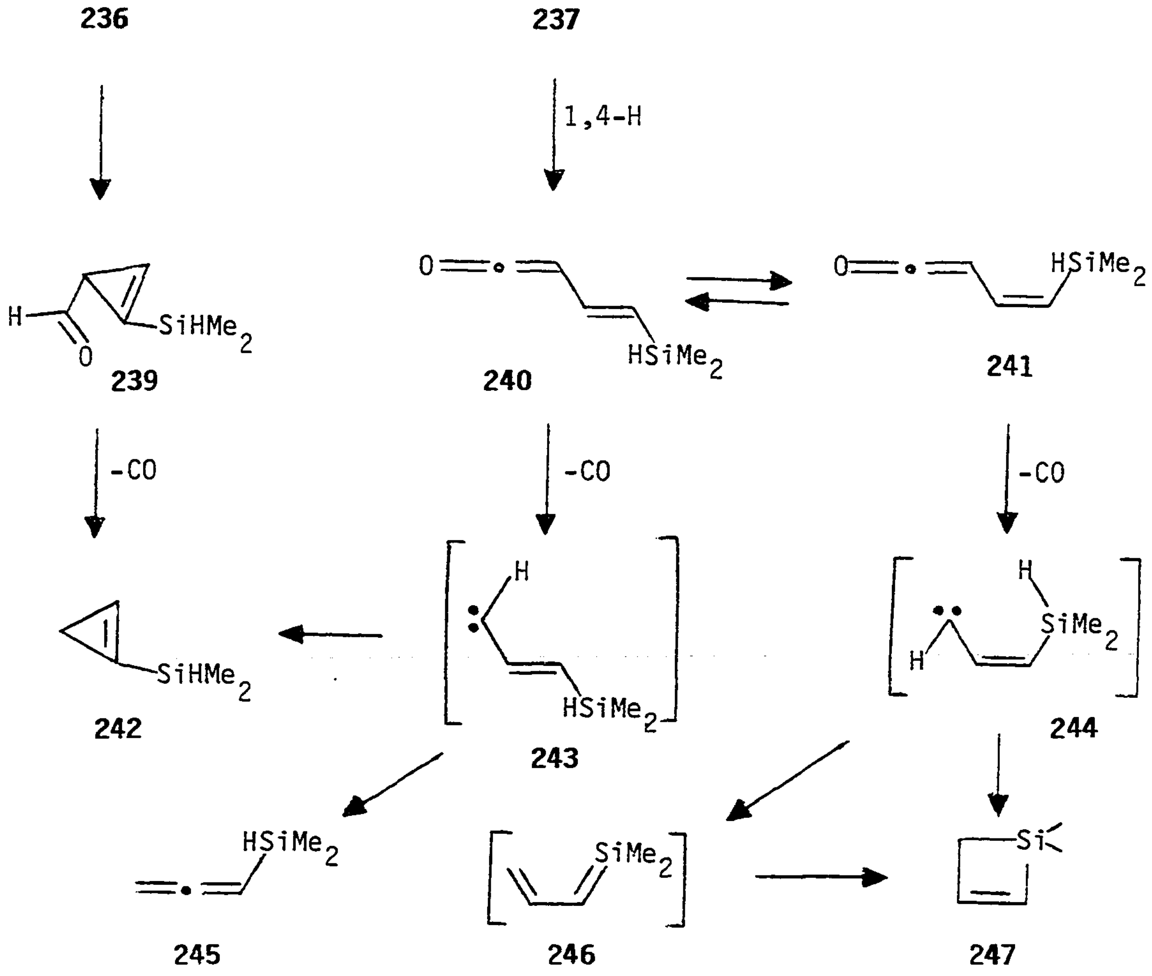
Finally, the pyrolysis of 2-trimethylsilylfuran was examined at 800°C (Scheme 58). Identified in the pyrolysate were silylallene **137** and silylacetylenes **136** and **258**. Also evident by ^{1}H NMR and GC/MS analysis were siloxyenynes **259**. The formation of siloxyenynes **259** is supportive of the intermediacy of an alkylidenecarbene. Since decarbonylation was competitive with enyne formation, this rearrangement was not synthetically useful, and its complete analysis was not pursued.

The considerable reluctance of dimethylsilyl- and trimethylsilylfuran to undergo rearrangement, with respect to silyldihydrofuran **142**, is probably a consequence of the resonance energy (16 kcal/mole) inherent in the furan ring system (82). The weaker C-O bond of the dihydrofurans which competitively undergo bond homolysis to yield products other than the acetylenes and products derived from the formation of these acetylenes may also be a factor.

Scheme 56

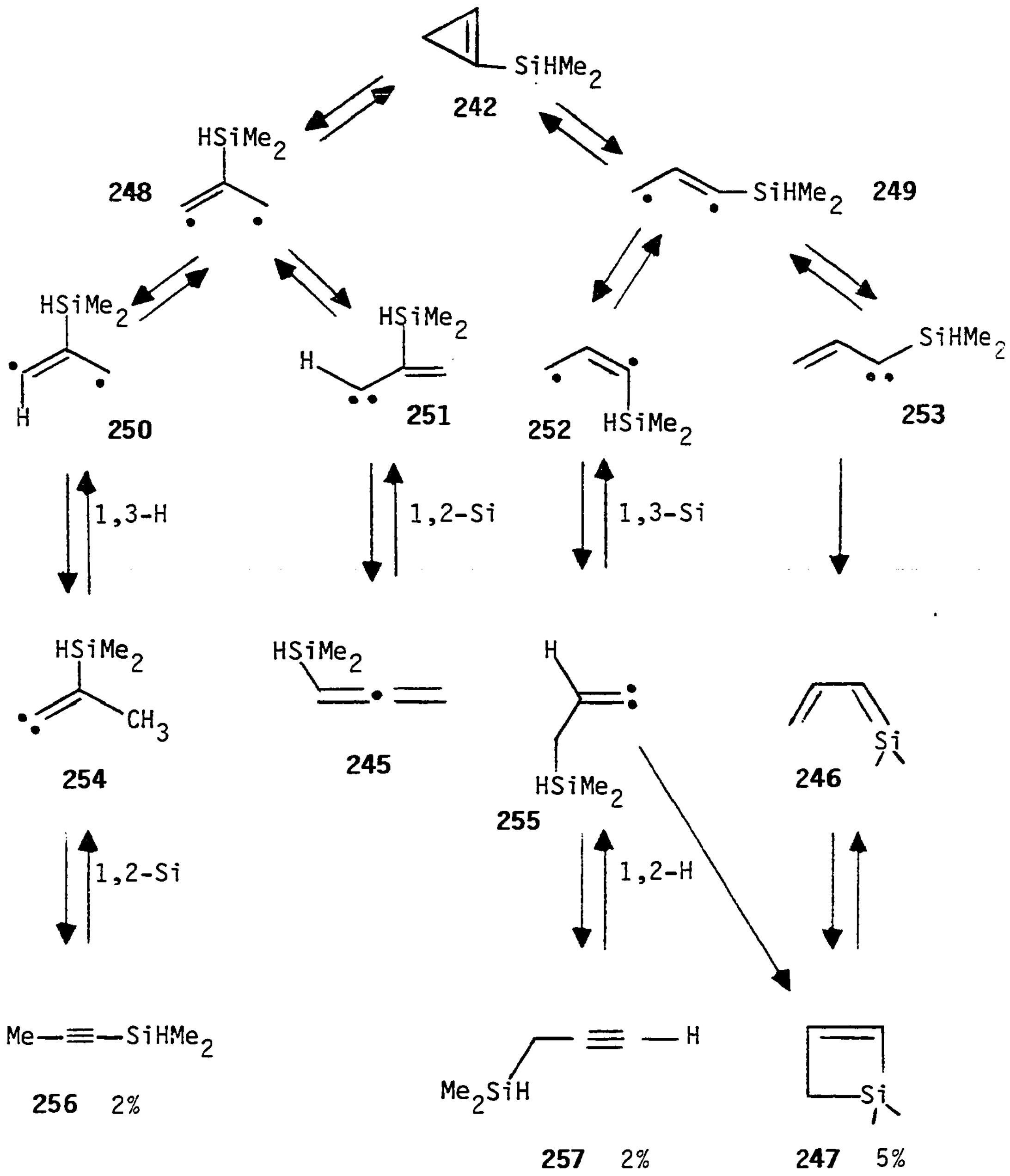


Scheme 56 (continued)



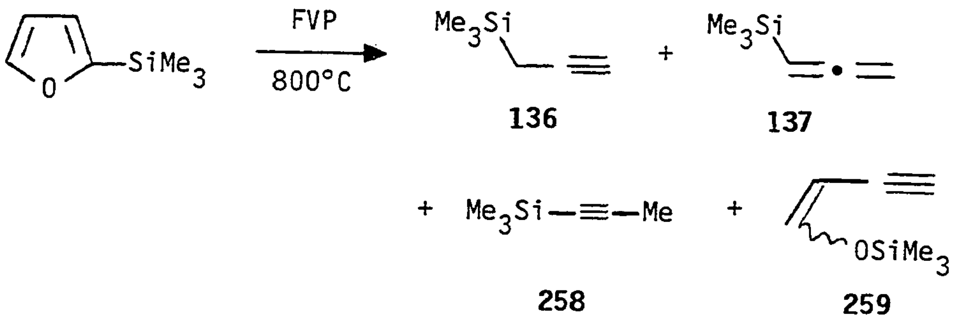
While the synthesis of silacycles from alkylidenecarbenes generated by the reductive elimination of a siloxane from an α-silyl vinyl ether gave poor yields, other interesting and competitive reactions were observed. Included are the the decomposition of hydridosilylketenes to acetylenes and dimethylsilanone and the formation of a silacyclobutene during the isomerization of dimethyl-

Scheme 57


SiHMe2
242
HSiMe2
248
SiHMe2
249
HSiMe2
250
H
HSiMe2
H
251
252
HSiMe2
SiHMe2
253
1,3-H
1,2-Si
1,3-Si
HSiMe2
CH3
254
HSiMe2
245
H
HSiMe2
255
Si
246
1,2-Si
1,2-H
Me—≡—SiHMe2
256 2%
Me2SiH
H
257 2%
Si
247 5%

(propargyl)silane to allenyldimethylsilane. Also revealed during the synthesis of 2-lithio-4,5-dihydrofuran was the competitive formation of dilithioketene and a possible new route to the synthesis of ketenes.

Scheme 58



The silylketene to acetylene decomposition is certainly deserving of further investigation as is the formation of alkylidenecarbenes from readily available (83) α-silyl vinyl ethers.

Attempted Intermolecular Trapping of Alkylidenecarbenes in the Gas Phase

Gas-phase intramolecular trapping of alkylidenecarbenes has been well documented, but no examples of intermolecular trapping have appeared in the literature. This potentially useful reaction was investigated in hope of providing such examples.

Since the intermolecular addition of alkylidenecarbenes to olefins in solution is well documented (1-3), the use of 2-methyl-2-

butene as an alkylidenecarbene trap in the gas phase was examined. The copyrolysis of phenylacetylene with a tenfold excess of 2-methyl-2-butene in a nitrogen flow at 490°C was carried out. Disappointingly, no products arising from trapping of an alkylidenecarbene intermediate were apparent. Since pyrolysis at higher temperatures leads to the decomposition of the trap, alternative traps were sought.

The use of an alcohol seemed warranted since intramolecular trapping of alkylidenecarbenes in the gas phase by insertion into an O-H bond occurs readily. Copyrolysis of phenylacetylene with a tenfold excess of methanol at a temperature of 600°C in a nitrogen flow gave recovered phenylacetylene and a small amount of styrene. The formation of styrene is probably the result of an undesirable radical process leading to reduction of phenylacetylene. The lack of trapping is probably not due to the inability of phenylacetylene to isomerize to phenylmethylidenecarbene since o-ethynyltoluene readily cyclized under these conditions (Scheme 19), and FVP of o-hydroxyphenylacetylene at 650°C affords benzofuran in 93% yield.

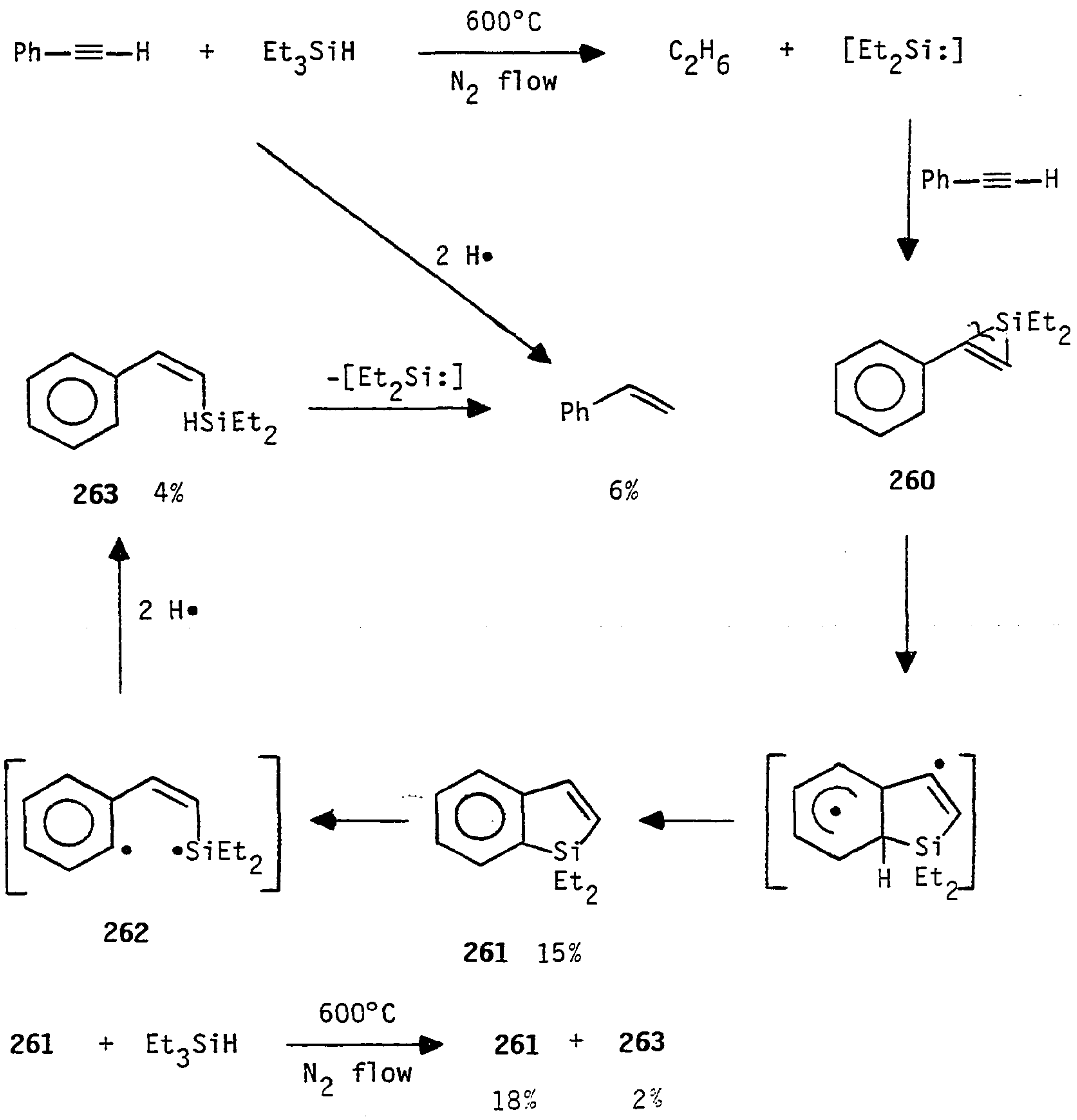
Similarly, the copyrolysis of (trimethylsilyl)phenylacetylene and a tenfold excess of methanol at 500°C and 600°C in a nitrogen flow failed to yield products derived from an alkylidenecarbene.

In a final attempt to trap phenylmethylidenecarbene, triethylsilane was copyrolyzed with phenylacetylene at 600°C in a nitrogen flow. The pyrolysate consisted of four components other than excess trap. Analysis of the products revealed the presence of phenylacetylene (5%), styrene (6%), 1,1-diethyl-1-silaindene (15%), **261**, and cis-2-diethylsilylstyrene (4%), **263**. The formation of **261** and **263** were completely unexpected. Mechanisms proposed for their formation are shown in Scheme 59. The α-elimination of ethane from triethylsilane produces diethylsilylene. The reaction of silylenes with acetylenes is a known reaction (84) and likely occurs here to initially give silacyclopropene **260** which opens by Si-C bond homolysis to form a diradical which subsequently adds to the neighboring phenyl ring. Hydrogen abstraction and rearomatization result in the formation of silaindene **261**. Styrene may result from a radical induced reduction or may be produced by α-elimination of diethylsilylene from silylstyrene **263**. The diethylsilylene thus formed may go on to yield **261**.

The presence of only cis-**263** suggests its origin may be **261** as a result of Si-phenyl bond homolysis and hydrogen abstraction (Scheme 59). As a test of this question, silaindene **261** was copyrolyzed with triethylsilane at 600°C in a nitrogen flow. Obtained in the pyrolysis was a 2% yield of the anticipated styrylsilane **263**, along with an 18% yield of silaindene **261**. The low yields reflect the poor mass recovery of this pyrolysis.

While attempted intermolecular trapping of alkylidenecarbenes has apparently failed in these preliminary investigations, a novel and simple route to silaindenes has been uncovered. Optimization of conditions and the utilization of other silanes and substituted arylacetylenes could reveal a simple route to the preparation of silaindenes whose chemistry has not been explored.

Scheme 59



With the completion of these last experiments, no additional examples of thermally induced 1,2-shifts were sought in this work. A discussion regarding the relative abilities of silyl-substituted and terminal acetylenes to undergo thermal 1,2-shifts is in order.

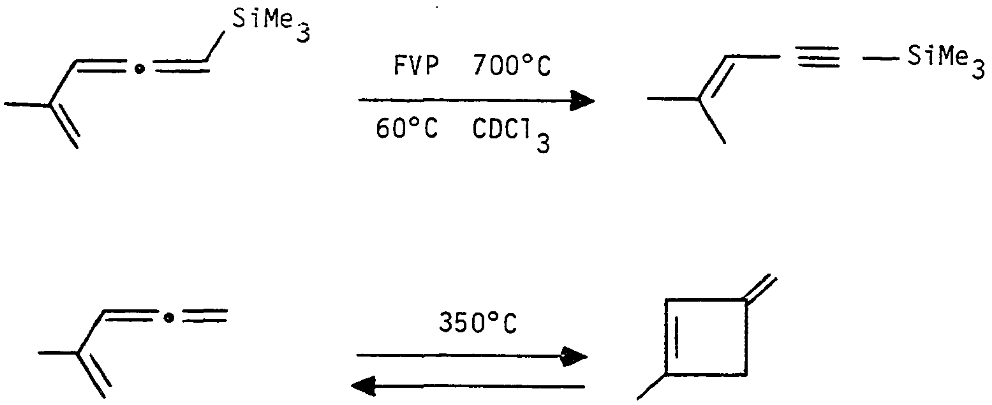
The products obtained from the FVP of acetylenes in this research were consistent with the intermediacy of alkylidenecarbenes produced by 1,2-shifts. It is also apparent from labeling studies and the products obtained that there were alternate pathways which were competitive with 1,2-shifts which led to many of these products.

Several comparisons were made regarding the abilities of silyl and hydrogen to undergo thermal rearrangements. In some examples, such as the FVP of o-(trimethylsilylethynyl)phenol or cis-1-trimethylsilyl-4-methoxy-3-buten-1-yne, the silyl-substituted acetylenes rearranged at lower temperatures than did the corresponding terminal acetylenes. In other cases, for example, the FVP of o-(dimethylsilyl)phenylacetylene, the terminal acetylenes rearranged at lower temperatures. The reasons for this large variability may be due to the importance of competitive processes responsible for the formation of the products. On the basis of this work, it seems evident that when alkylidenecarbene formation was involved in a pathway of major importance, the 1,2-silyl migrations required higher temperatures than did the analogous 1,2-hydrogen migrations. It must be kept in mind that these observations are based only on product formation which may not accurately reflect the ability of silyl groups to undergo 1,2-migrations. It is possible that silyl migrations leading to the formation of alkylidenecarbenes are indeed more facile than with hydrogen, but that the return to starting material is also faster which inhibits product formation. The return of a silyl-substituted alkylidenecarbene to starting material may be accelerated by the steric interaction between the bulky silyl group and the other substituent of the alkylidenecarbene.

If it is indeed true that 1,2-silyl migrations on acetylenes require higher temperatures than the analogous 1,2-hydrogen migrations, this difference may, at least in part, be attributable to the stability of a silyl-acetylene bond. Some experimental evidence supporting this stability comes from the FVP of the silyl-substituted methylenebenzocyclobutene **100** which produced **71** via an exclusive 1,5-hydrogen shift on allene **101** (Scheme 26). It is also of interest to note that the isomerization of **100** to **71** is complete at a lower temperature than is required for isomerization of the parent system (Scheme 27). Furthermore, Robinson (55) found that 1-trimethylsilyl-4-methyl-1,2,4-pentatriene isomerizes to 5-trimethylsilyl-2-methylbut-2-ene-4-yne at 60°C in $CDCl_3$ or at 700°C upon FVP (Scheme 60). In contrast, flow pyrolysis of 4-methyl-1,2,4-pentatriene at 350°C (85) leads to an equilibrium mixture (approximately 1:1) of starting material and 1-methyl-3-methylenecyclobutene (Scheme 60).

The surprising and exclusive 1,5-hydrogen migrations on 1-trimethylsilyl-4-methyl-1,2,4-pentatriene and silylallene **101** are more facile than the corresponding rearrangements on the parent systems. This may be an effect of the silyl substituent becoming bonded to an sp hybridized carbon center during the 1,5-hydrogen shift which causes a lowering of the activation energy of the 1,5-hydrogen shift while suppressing the 1,5-silyl shift. This stabilization may be similar to the 2 kcal/mole of stabilization energy gained when a silyl group undergoes a migration from an sp^3 center to an sp^2 center (50).

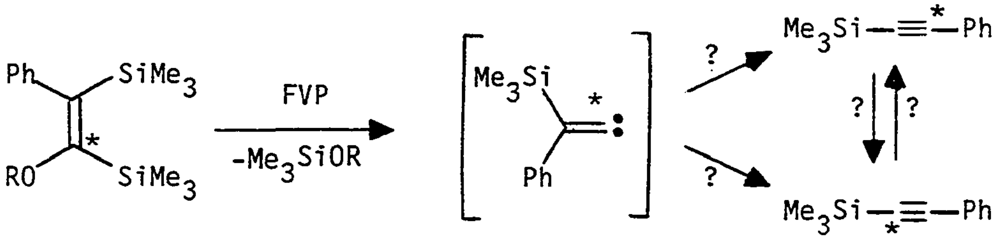
Scheme 60



Further evidence for the stability of silylacetylenes comes from the work of Barton and Burns (86). They found that the trimethyl(propargyl)silane-allenyl(trimethyl)silane equilibrium mixture can be bled to the thermodynamically most stable product, trimethyl(1-propynyl)silane, at high temperatures. Analogous results were obtained in this work where it was found that FVP of dimethyl(propargyl)silane at 800°C leads to the formation of dimethyl(1-propynyl)silane as a major project.

Since it is possible that either substituent may migrate on an acetylene, it may not be the silyl group but, rather, the other substituent on the acetylene that is actually undergoing the 1,2-shift. Though it seems likely, it has not been positively established in this work, nor any other, that silyl groups are even involved in 1,2-shifts on acetylenes. Though such studies were not undertaken in this work, the involvement of silicon in 1,2-shifts on acetylenes could be determined through labeling studies. The FVP of the labeled silyl vinyl ether shown in Scheme 61 would provide labeled trimethylsilyl(phenyl)methylidenecarbene. If the product was labeled in only one position, it would indicate which substituent undergoes a more facile 1,2-shift. Based upon the principle of microscopic reversibility, the same substituent must be responsible for the formation of the intermediate alkylidenecarbene produced by a 1,2-shift on the isomeric acetylene. The competitive migration of both substituents would be indicated by the label being found at both acetylenic positions. However, the outcome of these experiments depends upon the assumption that scrambling of the two labeled acetylenes would occur above the temperature required to decompose the labeled silyl vinyl ether. The temperature at which the onset of scrambling occurs in the singly labeled trimethysilyl(phenyl)acetylene could easily be established by preparation and pyrolysis of singly labeled trimethylsilyl(phenyl)acetylene. The answer to the question whether silyl groups undergo 1,2-migrations on acetylenes must remain unanswered until further studies are undertaken.

Scheme 61



Attempted Photochemical Generation of Alkylidenecarbenes from Acetylenes

While the thermal generation of alkylidenecarbenes has been examined by several researchers, as well as in this work, there have been no reports of the photochemical generation and trapping of alkylidenecarbenes. In view of this, preliminary studies were performed on some of the arylacetylenes previously examined in this work. Arylacetylenes **89**, **104**, and **134** were chosen since each showed a significant UV absorbance above 200 nm.

The first acetylene to be examined was **89**. A 1% solution of **89** in cyclohexane, degassed with argon, was irradiated with a high pressure mercury lamp. The photolysis was monitored by GC and ^{1}H NMR though the latter was found to be uninformative. The solution darkened readily during photolysis while only small amounts of products were apparent by GC analysis. Throughout the photolysis, the amounts of the products (relative to **89**) slowly increased concomitant with the formation of a resinous material adhering to the walls of the reaction vessel. After seven hours, the photolysis was terminated, and the products were analyzed by GC/MS. Only products of molecular weight 240-376 were present. No lower molecular weight products were present other than **89** which was clearly dominant in the GC trace. Changing the solvent to hexmethyldisiloxane and acetonitrile produced similar results though the rate of darkening of the solution and resin formation increased rapidly with increasing solvent polarity. In an attempt to reduce the formation of high molecular weight products, a pyrex filter was used, and the concentration of **89** was reduced to about 0.01%. The reaction appeared to be somewhat cleaner than the photolysis done at a higher substrate concentration, but the same high molecular weight products were formed. The only significant difference was the presence of a small amount of two products which apparently result from reduction of the acetylene bond. Photolysis of **89** (0.01% in cyclohexane) with a 350 nm light source for four hours failed to produce any products though discoloration of the solution had already started to occur after two hours. Because of the lack of formation of isomers of **89** as anticipated, the photolysis of **89** was not further investigated.

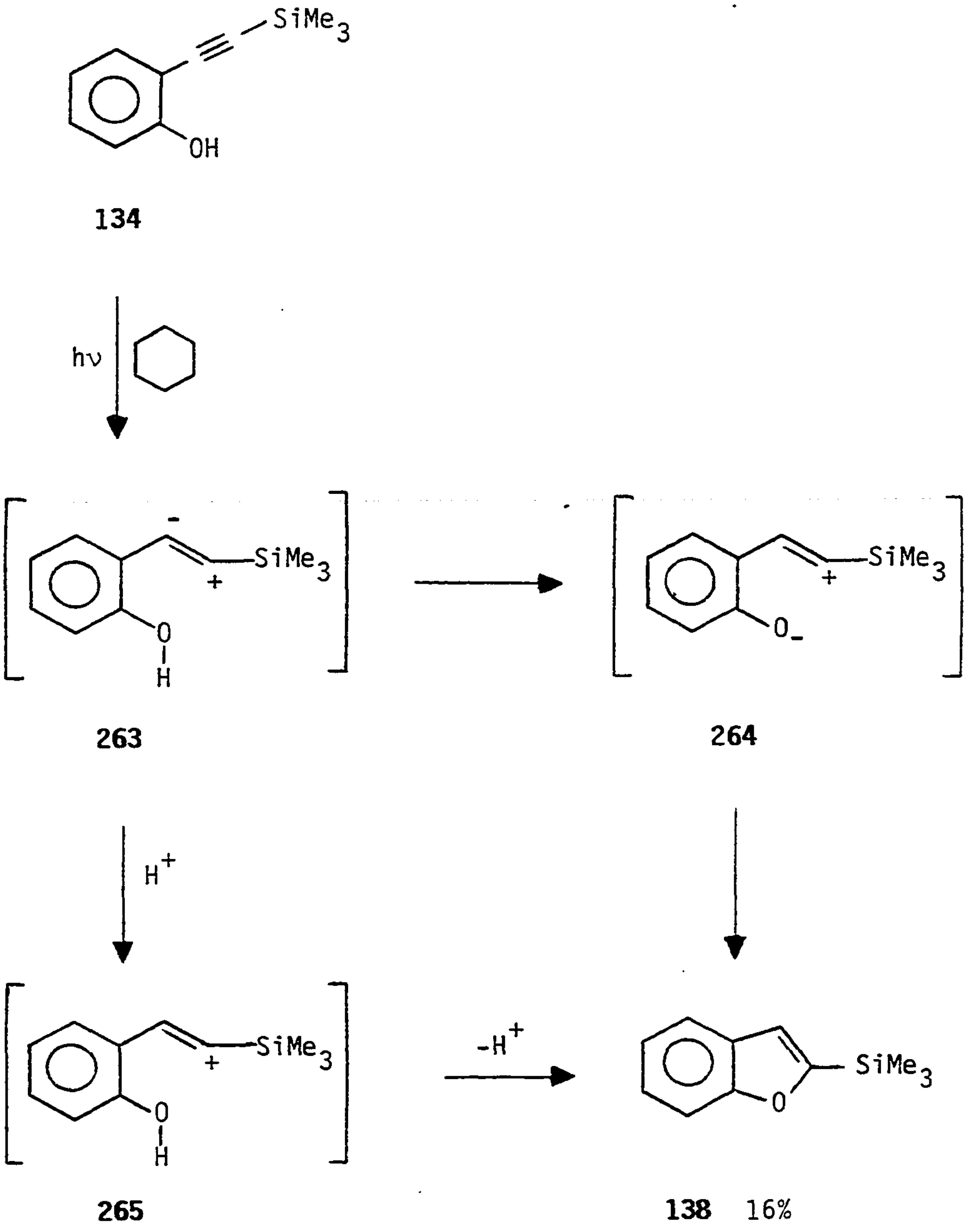
Next examined was acetylene **104**. Photolysis of **104** (1% solution in cyclohexane) with an unfiltered high pressure mercury lamp led to rapid discoloration within 30 minutes. Continued irradiation for a total of 3.5 hours resulted only in the formation of products with exceedingly long GC retention times. In order to favor intramolecular reactions, the concentration of **104** was reduced to approximately

0.01%. Photolysis again resulted in discoloration of the solution upon irradiation and produced a small amount of an isomer of **104** in addition to high molecular weight products. Again, reduction of **104** seemed to occur along with formation of products of high molecular weight. Isolation of the isomer of **104** was not attempted due to the complexity of the product mixture.

Finally, because of its significant UV absorption bands extending out to 304 nm, the photolysis of phenol **134** was investigated. Unfiltered irradiation of **134** (1% in cyclohexane) led to the formation of a single isomer and a high molecular weight product. The irradiation of **134** as a 0.01% solution in cyclohexane using a Pyrex filter nearly eliminated the formation of high molecular weight products while still permitting formation of the isomer. Though formation of small amounts of additional products and discoloration still occurred, the photolysis of **134** under these conditions was the most promising of those examined. Analysis of the isomer after isolation revealed it to be 2-trimethylsilylbenzofuran, **138**. This product was formed in 16% yield. Benzofuran **138** never seemed to be present in substantial yield probably because of its tendency to undergo photochemical polymerization (65).

The formation of **138** probably proceeds via zwitterion **263** (Scheme 62), analogous to that proposed for the photohydration of arylacetylenes (87). Intramolecular proton transfer would lead to zwitterion **264** which would cyclize to **138**. Intermolecular protonation is also possible and would lead to zwitterion **265** which can cyclize with the loss of a proton.

Scheme 62



The results obtained from these experiments are only preliminary. Further study is necessary before any conclusions can be drawn about the photochemistry of acetylenes. However, because of the lack of evidence for the formation of products derived from alkylidenecarbenes, the complex nature of products obtained from these photolyses, and the known tendency of acetylenes to undergo photopolymerization (88), further research in this area was precluded.

CONCLUSION

Many of the products obtained from the FVP of acetylenes in this research were consistent with the intermediacy of alkylidenecarbenes produced by 1,2-shifts. It is apparent from labeling studies and the products obtained that there were alternate pathways which were competitive with 1,2-shifts which led to many of these products.

Several comparisons were made regarding the abilities of silyl and hydrogen to undergo thermal rearrangements. In some examples, such as the FVP of o-(trimethylsilylethynyl)phenol or cis-1-trimethylsilyl-4-methoxy-3-buten-1-yne, the silyl-substituted acetylenes rearranged at lower temperatures than did the corresponding terminal acetylenes. In other cases, for example, the FVP of o-(dimethylsilyl)phenylacetylene, the terminal acetylenes rearranged at lower temperatures. The reasons for this large variability may be due to the importance of competitive processes responsible for the formation of the products. On the basis of this work, it seems evident that when alkylidenecarbene formation was involved in a pathway of major importance, the 1,2-silyl migrations required higher temperatures than did the analogous 1,2-hydrogen migrations. It must be kept in mind that these observations are based only on product formation which may not accurately reflect the ability of silyl groups to undergo 1,2-migrations. Though it seems likely, it has not been positively established in this work, nor any other, that silyl groups are even involved in 1,2-shifts on acetylenes. The involvement of silicon in

1,2-shifts on acetylenes could be determined through labeling studies, but such studies were not undertaken in this work. The answer to the question whether silyl groups undergo 1,2-migrations on acetylenes must remain unanswered until further studies are undertaken.

The employment of silylhydrides as alkylidenecarbene traps has provided a convenient synthetic route to unsaturated silacycles such as 1,1-dimethyl-1-silaindene. This method of silacycle formation should prove to be useful for the synthesis of five-membered rings difficult to prepare by other methods. Application of the alkylidenecarbene cyclization to the synthesis of six-membered silacycles was only partially successful, and the formation of other products became a major process.

Attempted synthesis of a substituted benzopyran derivative by the pyrolysis of o-(trimethylsilylethynyl)anisole resulted not in the formation of the desired silyl-substituted benzopyran but, instead, in elimination of dimethylsilylene to give 2-ethylbenzofuran as the only major product. Extension of this remarkable decomposition to cis-1-trimethysilyl-4-methoxy-3-buten-1-yne resulted not in the elimination of dimethylsilylene and formation of 2-ethylfuran but in decarbonylation of the starting material to yield 1-trimethylsilyl-1,2-butadiene. Various mechanisms for these decompositions were considered and discussed.

The FVP of 2-trimethylsilyl-4,5-dihydrofuran gave conclusive proof of the generation of an alkylidenecarbene by reductive elimination. This reaction certainly has potential as a method of gas-phase generation of alkylidenecarbenes.

The attempted synthesis of silacycles from alkylidene carbenes generated by the reductive elimination of a siloxane from an α-silyl vinyl ether gave poor yields but led to several other interesting observations. Included was the observation that hydridosilylketenes undergo decomposition during FVP to acetylenes and dimethylsilanone. An unprecedented mechanism involving a 1,2-silyl shift on a ketene was considered which may also be involved in the rearrangement of siloxyacetylenes to ketenes. Also realized during the thermal conversion of 2-dimethylsilylfuran to 1,1-dimethyl-1-silapyran was the formation of 1,1-dimethyl-1-silacyclobutene which appears to occur on the same energy surface as the interconversion of dimethyl(propargyl)silane and allenyldimethylsilane. Mechanisms accounting for these interconversions were postulated and discussed.

Also revealed during the synthesis of 2-silyl-4,5-dihydrofurans by the metalation of 2,3-dihydrofuran with n-butyllithium was the competitive formation of bis(silyl)ketenes. A mechanism was proposed to account for the formation of the ketene products. Optimization of the conditions of this reaction may yield a simple one step synthesis of ketenes.

The attempted intermolecular trapping of phenylmethylidene with triethylsilane has led to the surprising formation of 1,1-diethyl-1-silaindene. Optimization of the conditions may provide a synthetically useful, one step route to the preparation of silaindenes.

EXPERIMENTAL SECTION

Instrumentation

Routine ^1H NMR (60 MHz) spectra were recorded on a Varian EM-360A or L spectrometer. High resolution ^1H NMR (300 MHz) spectra were recorded on a Nicolet NT-300 spectrometer. ^{13}C NMR spectra were recorded on Nicolet NT-300 (75.5 MHz) or JEOL FX90Q (22.5 MHz) spectrometers. All chemical shifts are reported as parts per million (δ scale) from tetramethylsilane and were taken in $CDCl_3$ unless otherwise noted. Standard abbreviations are used to designate proton splitting except for the use of h which signifies a heptet. Mass spectra (MS) were recorded using a Finnigan 4000 (GC/MS), an AEI-MS-902, or a Kratos MS 50 operating at 70 eV and are reported as m/e (% relative intensity) unless otherwise indicated. IR spectra were recorded on a Beckman IR 4250 or an IBM 98 FT/IR spectrophotometer and were taken as neat samples except as indicated otherwise. UV spectra were recorded on a Perkin-Elmer 320 spectrophotometer.

Gas chromatographic (GC) analyses were performed on a Hewlett Packard 5790A fitted with a nonpolar 12.5 M capillary column. Preparative GC was performed on a GOW MAC 550P or a Varian 1700 using columns as specified within the experimental.

Yields of pyrolysates were determined by GC using internal standards after determination of the appropriate response factors or by ^1H NMR using internal standards.

Elemental analyses were performed by Galbraith Laboratories, Inc., or by Mic Anal Organic Microanalysis.

Procedures and Results

General Conditions for Flash Vacuum Pyrolyses (FVP)

All samples were distilled or sublimed from a bath maintained at a temperature allowing slow introduction of the sample into a horizontal, quartz tube packed with quartz chips and heated with an electric tube furnace. The heated zone of the quartz tube was ca. 1.8 cm X 30 cm. Pyrolysates were collected in a cold trap cooled with liquid N_2. Pressures were measured by an ionization gauge behind two liquid N_2 traps and, therefore, do not accurately reflect the actual pressure in the reaction zone.

General Conditions for Flow Pyrolyses

All samples were added slowly to a vertical quartz tube packed with quartz chips of the same dimensions used for flash vacuum pyrolyses. During addition, the pyrolysis tube was continually swept with a N_2 stream of 40 mL/min. The pyrolysate was collected in a cold trap cooled to -78°C.

Synthesis of β,β-dibromo-o-(methyl)styrene, 70

The procedure used to prepare 70 has been adapted from that described by Ramirez et al. who prepared β,β-dibromostyrene (89).

Triphenylphosphine (46.2 mmol) was added in one portion to a stirring solution of CBr_4 (23.1 mmol) in 215 mL of CH_2Cl_2 under N_2 at 0°C. After stirring for 15 min, o-tolualdehyde (10.6 mmol) was rapidly added. After stirring an additional 10 min at 0°C, the mixture was slowly added to 1 L of Skelly B with stirring. The mixture was filtered, and the solution was concentrated using a rotary evaporator. The residual oil, containing some Ph_3PO, was purified by column chromatography on a silica gel column eluted with hexane to give 70 in 86% isolated yield. Spectra of 70 include: ^1H NMR δ 2.20 (s, 3H), 7.0-7.5 (m, 5H); ^{13}C NMR δ 136.76, 135.98, 135.26, 130.06, 128.50 (two coincidental peaks), 125.70, 91.56, 19.83; IR 3060, 3020, 2980, 2950, 2920, 1610, 1485, 1460, 880, 855, 815, 745, 710 cm^{-1}; MS 278 (4) (M+4), 276 (8) (M+2), 274 (4) (M^+), 117 (10), 116 (100), 115 (93), 89 (12), 65 (9), 63 (17), 62 (8), 58 (45), 51 (10), 50 (9); calcd for $C_9H_8Br_2$ m/e 273.89927, measured m/e 273.89959.

Synthesis of o-(trimethylsilylethynyl)toluene, 71

A solution of n-butyllithium in hexane (36.0 mmol, 2.3 M) was added dropwise to a stirring solution of 71 (17.2 mmol) in dry THF (95 mL) under N_2 cooled to -78°C. The brownish-red solution was stirred at -78°C for 1 h and then warmed to room temperature and stirred for 20 min. Chlorotrimethylsilane (17.4 mmol), in an equal volume of THF, was added dropwise, and the reaction mixture was stirred for 40 min. Addition of the mixture to H_2O followed by extraction with pentane, washing with H_2O, and removal of solvent gave a yellow oil which was distilled at 82-83°C, 4 torr, to afford **71** in 93% yield. Spectra taken of **71** include: ^{1}H NMR δ 0.28 (s, 9H), 2.30 (s, 3H), 6.80-7.39 (m, 4H); ^{13}C NMR δ 140.60, 132.14, 129.34, 128.50, 125.44, 122.97, 104.18, 98.20, 20.61, 0.13; IR 3060, 3020, 2970, 2160, 1485, 1455, 1260, 1250, 870, 840, 755, 715 cm^{-1}; MS 188 (29), 174 (20), 173 (100), 145 (17), 143 (12), 115 (7), 105 (6), 86 (25), 53 (7); calcd for $C_{12}H_{16}Si$ m/e 188.10213, measured m/e 188.10285.

FVP of 71

A sample of **71** (305.7 mg), distilled (1 X 10^{-3} torr) from a bath slowly heated from 30-60°C, was pyrolyzed at 900°C. Excessive decomposition occurred throughout the hot zone of the pyrolysis tube. The yellow pyrolysate (155.6 mg, 59.0%) was analyzed by GC. The products were isolated by preparative GC on a 9 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 150-250°C at 5°C per min. The products were identified as indene (21%), **27**, and naphthalene (9%), **72**. The yields were determined by GC analysis and based on a 23% yield of recovered **71**. The products were identified by comparison of GC/MS and ^{1}H NMR data with those of authentic samples. Also formed was a small amount of at least four isomers of MW 130. Analysis of the isolated mixture by ^{1}H NMR revealed the presence of 1-, 2-, and 3-methylindenes by comparison with authentic GC/MS and ^{1}H NMR spectra (55). The total yield of these isomers was less than 8%. Pyrolysis of **71** at 560-800°C afforded only recovered **71**.

Synthesis of 1-trimethylsilylindene, 74

Compound **74** was prepared by metalation of indene followed by quenching of the anion with chlorotrimethylsilane according to the procedure described by Cedhem and Eberson (54).

FVP of 74

A sample of **74** (214.8 mg), distilled (1 X 10^{-3} torr) from a bath slowly heated from 30-60°C, was pyrolyzed at 900°C. Excessive decomposition occurred throughout the hot zone of the pyrolysis tube. The yellow pyrolysate (65.8 mg, 30.6%) was analyzed by GC and GC/MS. No starting material was recovered. Two products were identified as indene (24%) and napthalene (9%) by comparative GC/MS data, GC retention times, and ^{1}H NMR data. A mixture of MW 130 isomers, nearly identical in composition to that obtained in the FVP of **71**, was again present in small quantity.

Synthesis of (trimethylsilyl)phenylacetylene, 75

Compound **75** was prepared by the successive reaction of phenylacetylene with n-butyllithium and chlorotrimethylsilane following the procedure described by Eaborn and Walton (57).

FVP of 75

Acetylene **75** (361.3 mg), distilled (1 X 10^{-3} torr) from a bath warmed slowly from 25-60°C, was pyrolyzed at 900°C. Moderate decomposition occurred in the hot zone of the pyrolysis tube. The pyrolysate (253.4 mg, 70.1%) was analyzed by GC and GC/MS. The products were isolated by preparative GC on a 5 ft X 0.25 in. 20% SE-30 Chromosorb W column temperature programmed from 120-250°C at 6°C per min. Identified by ^{1}H NMR and comparative MS were phenylacetylene (17%), indene (4%), and 1-phenylpropyne (2%). Yields, determined by GC analysis, were based upon a 47% yield of recovered **75**.

Flow pyrolysis of 71

The N_2 flow pyrolysis of **71** (216 mg) at 630°C was carried out by the dropwise addition of **71** to the pyrolysis apparatus over a 40 min period. The pyrolysate (180 mg, 83.3%) was analyzed by GC and GC/MS. The products were isolated by preparative GC on a 9 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 150-250°C at 5°C per min. Identified were indene (36%), naphthalene (2%), and a mixture of 1-, 2-, and 3-trimethylsilylindene (30% combined yield). A product, believed to be a trimethylsilyl substituted naphthalene derivative, **78**, based upon GC/MS data, was obtained in approximately 6% yield but was not isolated. Confirmation of the identity of the isolated products was made by comparative ^{1}H NMR and GC/MS. For comparison, a mixture of 1-, 2-, and 3-trimethylsilylindene was prepared by heating a degassed sample of **71** in an evacuated sealed ampoule at 165°C for 5 h. Yields were determined by GC. The MS of **78** was recorded as: 200 (22), 186 (17), 185 (100), 183 (6), 169 (7), 167 (9), 155 (11), 141 (6), 129 (7), 115 (8), 93 (15), 73 (6), 53 (8).

Flow pyrolysis of **74**

The N_2 flow pyrolysis of **74** (216 mg), at 630°C, was carried out by the dropwise addition of **74** to the pyrolysis apparatus over a 35 min period. The pyrolysate (160 mg, 74.1%) was analyzed by GC and GC/MS and found to be very similar in composition to that obtained from the flow pyrolysis of **71**. Identified were indene (34%), naphthalene (1%), and silylnaphthalene **78** (3% approximate yield), and a mixture of 1-, 2-, and 3-trimethylsilylindene (45% combined yield). Identification was made by comparison of GC/MS and ^1H NMR data with that from the flow pyrolysis of **71**.

Synthesis of *o*-ethynyltoluene, **25**

The procedure used to prepare **25** was adapted from the preparation of **71** by using 0.5 M H_2SO_4 instead of chlorotrimethylsilane to quench the anion. An 86% yield of **25** was obtained after distillation (68°C, 27 torr) of the crude product.

Pyrolysis of **25**

(i) Acetylene **25** (106.4 mg), distilled (1×10^{-4} torr) from a bath at 15°C, was pyrolyzed at 800°C. The light yellow pyrolysate (96.9 mg, 91.1%) was analyzed by GC, GC/MS, and ^1H NMR. The only product present was indene, **27**, obtained in 86% yield based on a 30% yield of recovered **25**. Identification of **27** was confirmed by comparative GC/MS and ^1H NMR data. Yields were determined by GC.

(ii) Pyrolysis of **25** (174 mg) at 900°C, 1 X 10^{-4} torr, produced a pyrolysate (134 mg, 77%) consisting of **27** (75%, NMR yield, corrected for recovered **25**) and **25** (8%). Identification of **25** and **27** was accomplished by comparative ^{1}H NMR and GC/MS.

(iii) The N_2 flow pyrolysis of **25** (239 mg) at 630°C was carried out by the dropwise addition of **25** to the pyrolysis apparatus over a 40 min period. The yellow pyrolysate (143 mg, 59.8%) was analyzed by GC, GC/MS, and ^{1}H NMR. A 43% yield (GC) of indene was obtained. No **25** was recovered.

Synthesis of o-(β,β-dibromoethenyl)biphenyl, **266**

First, o-formylbiphenyl was prepared, according to a published procedure (90), by successive reaction of o-iodobiphenyl with Mg, methyl formanilide, and aqueous acid.

Then, o-formylbiphenyl (15.4 mmol) in an equal volume of CH_2Cl_2 was added rapidly to the reagent prepared from triphenylphosphine (30.8 mmol) and carbon tetrabromide in CH_2Cl_2 (40 mL) as described in the synthesis of **70**. After stirring for 10 min, the product was isolated and purified according to the scheme described for the isolation of **70**. The desired product was obtained as an oil in 77% yield. Spectra of **266** include: ^{1}H NMR δ 7.1-7.7 (m); ^{13}C NMR δ 141.18, 140.21, 137.60, 133.96, 129.93, 129.54, 129.28, 128.69, 128.30, 127.59, 127.20, 90.91; IR 3070, 3030, 1600, 1475, 1450, 1435, 1005, 885, 855, 795, 775, 745, 735, 700 cm^{-1}; MS 340 (0.1) (M+4), 338

(0.2) (M+2), 336, (0.1) (M^+), 179 (15), 178 (100), 177 (9), 176 (16), 152 (7), 151 (9), 150 (6), 89 (25), 88 (29), 76 (16), 75 (11), 74 (6).

Synthesis of o-(trimethylsilylethynyl)biphenyl, **79**

A solution of n-butyllithium in hexane (22.4 mmol, 2.7 M) was added dropwise to a stirring solution of **266** (10.6 mmol) in dry THF (66 mL) under N_2 cooled to -78°C. The solution was stirred at -78°C for 1 h, warmed to room temperature, and stirred for an additional hour. Chlorotrimethylsilane (5.7 mmol) was added dropwise, and the mixture was then stirred for 40 min. The reaction mixture was then added to cold H_2O, and the product was extracted with pentane. After removal of solvent using a rotary evaporator, the residual oil was purified by column chromatography on a silica gel column eluted with hexane to give pure **79** (86%): ^1H NMR δ 0.13 (s, 9H), 6.9-7.4 (m, 9H); ^{13}C NMR δ 144.30, 140.34, 133.25, 129.34 (2 peaks), 128.69, 127.72, 127.39, 126.87, 121.48, 114.84, 104.83, 97.54, -0.26; IR 3040, 2970, 2910, 2170, 1480, 1455, 1445, 1265, 1255, 870, 845, 760, 740, 700 cm^{-1}; MS 250 (31), 236 (21), 235 (100), 233 (10), 219 (30), 217 (19), 205 (15), 191 (15), 189 (15), 179 (11), 165 (22), 117 (34), 110 (12), 59 (10), 53 (20); calcd for $C_{17}H_{18}Si$ m/e 250.11778, measured m/e 250.11834.

FVP of **79**

A sample of **79** (234.2 mg), distilled (1 X 10^{-3} torr) from a bath heated from 25-140°C, was pyrolyzed at 900°C. Moderate decomposition occurred in the hot zone of the pyrolysis apparatus. The pyrolysate (136.0 mg, 58.1%), analyzed by GC and GC/MS, was found to contain phenanthrene (19%), **30**, 9-trimethylsilylphenanthrene (10%), **80**, and trimethylsilylbenzazulene (4%, uncorrected for its response factor), **81**. The products, except **81**, were identified by comparison of GC retention times and GC/MS data with those of authentic samples. Yields were determined by GC analysis. The identity of **81** was based solely upon MS data: MS 250 (2), 249 (14), 248 (70), 234 (17), 233 (100), 231 (5), 218 (7), 217 (11), 205 (14), 202 (11), 189 (7), 165 (7), 124 (5), 116 (16). For comparison, the mass spectrum of **80** is given: MS 251 (9) (M+1), 250 (39), 236 (20), 235 (100), 219 (13), 217 (10), 205 (10), 191 (7), 189 (6), 165 (6), 117 (16), 73 (5).

FVP of 80

A sample of **80** (166.6 mg), distilled (1 X 10^{-3} torr) from a bath heated from 100-200°C, was pyrolyzed at 900°C. Moderate decomposition occurred in the hot zone of the pyrolysis tube. A low mass recovery (86.3 mg, 51.8%) was due in part to the very low volatility of the pyrolysate and the difficulties involved in its collection. Analysis of the pyrolysate by GC/MS and GC revealed the presence of phenanthrene (10%). This yield was based on a 39% yield of recovered **80**. Phenanthrene was identified by comparison of GC/MS and GC retention times with an authentic sample.

Synthesis of o-ethynylbiphenyl, **82**

The procedure used to prepare **82** was adapted from the preparation of **79** by using 0.5 M H_2SO_4 instead of chlorotrimethylsilane to quench the anion. A 59% yield of **82** was obtained after distillation at 80-83°C, 0.3 torr. The ^1H NMR matched that described in the literature (31).

FVP of **82**

The pyrolysis of **82** has been described (31) and is repeated here for comparison. A sample of **82** (269.7 mg), distilled (1×10^{-4} torr) from a bath heated from 40-90°C, was pyrolyzed at 800°C. The deep blue pyrolysate (261.8 mg, 97.1%) was analyzed by GC and GC/MS. Based on a 17% yield of recovered **82**, phenanthrene and 1,2-benzazulene were formed in 51% and 41% yield, respectively, as determined by GC analysis.

Flow pyrolysis of **79**

The N_2 flow pyrolysis of **79** (240 mg) at 630°C was carried out by the dropwise addition of **79** to the pryolysis apparatus over a 25 min period. The pyrolysate (186 mg, 77.5%) was analyzed by GC/MS and GC. Identified were phenanthrene (32%) and 9-trimethylsilylphenanthrene (19%) by comparative GC/MS and GC retention times. The yields were made by GC analysis and are based upon a 63% yield of recovered **79**.

Flow pyrolysis of 80

The N_2 flow pyrolysis of **80** (207 mg) at 630°C was carried out by the dropwise addition of **80** to the pyrolysis apparatus. The pyrolysate (159 mg, 76.8%) was analyzed by GC and GC/MS. The only product obtained was phenanthrene (24%), the yield of which was based upon a 46% yield of recovered **80**. Identification was confirmed by comparison with an authentic sample of phenanthrene.

Flow pyrolysis of 82

The N_2 flow pyrolysis of **82** (242 mg) at 630°C was carried out by the dropwise addition of **82** to the pyrolysis apparatus. The pyrolysate (175 mg, 62%) was collected with the aid of 4 mL of hexane used to rinse all of the pyrolysate into the receiver. Identified by GC/MS were phenanthrene (38%) and 1,2-benzazulene (1%). No starting material was recovered.

Synthesis of dimethylsilyl(o-dimethylsilylphenyl)acetylene, 83

Phenylacetylene (197 mmol) was dimetalated using the procedure developed by Hommes et al. (60). The dark green suspension of the dianion was then cooled to -65°C and dimethylchlorosilane (669 mmol) was added as rapidly as possible while keeping the reaction mixture at or below -50°C at all times. After addition was complete, the yellow suspension was allowed to warm slowly to room temperature (approximately 4 h). The mixture was then poured into ice-cold, dilute H_2SO_4 and extracted with hexane. The organic portion was washed with cold

H_2O and then dried over $MgSO_4$. After removal of solvent, the residual yellow oil was fractionally distilled giving 30.1 g (70%) of **83**: bp 77-78°C, 0.5 torr; ^1H NMR δ 0.32 (d, 6H, J = 3.8 Hz), 0.41 (d, 6H, J = 3.8 Hz), 4.29 (h, 1H, J = 3.8 Hz), 4.52 (h, 1H, J = 3.8 Hz), 7.26-7.34 (m, 2H), 7.45-7.55 (m, 2H); ^{13}C NMR δ -3.27, -3.04, 94.24, 107.16, 128.02, 128.32, 129.09, 132.30, 134.73, 140.55; IR 3072, 3053, 2962, 2902, 2156, 2137, 1581, 1556, 1460, 1427, 1250, 1128, 1074, 887, 839, 771, 760, 734, 723, 702 cm^{-1}; MS 218 (7), 203 (32), 177 (10), 159 (13), 145 (46), 105 (11), 73 (100); calcd for $C_{12}H_{18}Si_2$ m/e 218.09471, measured m/e 218.09486. Anal. Calcd for $C_{12}H_{18}$: C, 65.98; H, 8:31. Found: C, 65.70; H, 8.03. Approximately a 20% yield of dimethylsilylphenylacetylene was also obtained: bp 55-61°C, 0.5 torr; ^1H NMR δ 0.3 (d, 6H, J = 4 Hz), 4.3 (h, 1H, J = 4 Hz), 7.4 (m, 4H); IR 3060, 2964, 2905, 2164, 2141, 1593, 1487, 1252, 883, 845, 771, 756, 741, 690 cm^{-1}; MS 160 (34), 159 (14), 145 (100) 129 (14), 105 (13).

Preparation of (o-hydroxydimethylsilylphenyl)acetylene, 84

Acetylene **83** (69 mmol) was added to a solution of MeOH (750 mL) and aqueous NaOH (250 mL, 0.5 M) with external cooling keeping the reaction temperature below 35°C. The reaction mixture (complete in 30 min) was acidified with dilute H_2SO_4, extracted several times with pentane, washed with H_2O, and dried over $MgSO_4$. After filtration of the $MgSO_4$ and removal of the solvent, the product was distilled to yield 10.2 g (84%) of **84**: bp 64-67°C, 0.15 torr; ^1H NMR δ 0.48 (s, 6H), 2.60 (broad s, 1H), 3.28 (s, 1H), 7.31-7.38 (m, 2H), 7.50-7.60

(m, 2H); ^{13}C NMR δ 0.13, 80.18, 85.22, 125.99, 128.23, 129.25, 133.09, 133.49, 142.26; IR 3300, 3080, 3060, 2965, 2100, 1585, 1465, 1430, 1260, 1125, 1070, 860, 830, 780, 760 cm^{-1}; MS 176 (15), 161 (100), 115 (11), 102 (4), 91 (9), 75 (6); calcd for $C_{10}H_{11}OSi$ (M^+-H) m/e 175.05792, measured 175.05755.

Synthesis of (o-chlorodimethylsilylphenyl)acetylene, 85

Acetylene **84** (53.4 mmol) was added in one portion to a stirring solution of PCl_5 (53.4 mmol) in 107 mL of CCl_4 at 0°C. The solution was then heated to reflux for 14 h. After distillation of the solvent and low boiling components, the residue was distilled at 56-57°C, 0.5 torr, to give 6.47 g (62%) of **85**: ^{1}H NMR δ 0.79 (s, 6H), 3.30 (s, 1H), 7.35-7.42 (m, 2H), 7.52-7.56 (m, 1H), 7.76-7.79 (m, 1H); ^{13}C NMR δ 2.80, 81.66, 84.28, 126.46, 128.36, 130.06, 133.36, 134.46, 138.56; IR 3310, 3090, 3070, 2980, 2100, 1590, 1460, 1430, 1255, 1120, 1060, 835, 810, 790, 755, 715 cm^{-1}; MS 181 (39), 179 (100), 143 (6), 115 (13), 103 (7), 91 (23), 73 (10), 60 (15), 58 (33); calcd for $C_{10}H_{11}ClSi$ m/e 194.03186, measured m/e 194.03162.

Synthesis of (o-dimethylsilylphenyl)acetylene, 86

Acetylene **85** (22.5 mmol) was added dropwise to a stirring suspension of lithium aluminum hydride (22.5 mmol) in Et_2O (30 mL) at 0°C. After complete addition, the reaction was warmed to room temperature and stirred for 15 h. The reaction mixture was hydrolyzed by adding it to ice-cold, dilute H_2SO_4 and then extracted with pentane, washed with H_2O, and dried with $MgSO_4$. After removal of the drying agent and solvents, the product was distilled to give 2.72 g (76%) of **86**: bp 83-87°C, 10 torr; ^1H NMR δ 0.42 (d, 6H, J = 3.80 Hz), 3.23 (s, 1H), 4.54 (h, 1H, J = 3.80 Hz), 7.29-7.38 (m, 2H), 7.48-7.57 (m, 2H); ^{13}C NMR δ -3.88, 80.18, 84.21, 127.60, 128.08, 129.13, 132.82, 134.68, 140.48; IR 3300, 3072, 3053, 2959, 2903, 2125, 1583, 1556, 1462, 1427, 1248, 1126, 1072, 889, 839, 762, 723, 702, 652 cm^{-1}; MS 160 (9), 159 (7), 145 (100), 129 (7), 119 (11), 105 (8), 77 (5), 53 (16); calcd for $C_{10}H_{12}Si$ m/e 160.07083, measured m/e 160.07055. Anal. Calcd for $C_{10}H_{12}$: C, 74.93; H, 7.55. Found: C, 74.89; H, 7.69.

Pyrolysis of (o-dimethylsilylphenyl)acetylene, **86**

(i) Acetylene **86** (73.6 mg) was pyrolyzed by distillation (40°C, 8 X 10^{-5} torr), over a 30 min period, through a horizontal quartz tube packed with quartz chips heated to 800°C. The pyrolysate (63.1 mg, 85.7%) was collected in a cold trap cooled with liquid nitrogen. The clear, colorless pyrolysate was analyzed by GC and ^1H NMR and found to contain only 1,1-dimethyl-1-silaindene **87** (84%, NMR yield) based on comparison of its spectra (GC/MS, ^1H NMR, ^{13}C NMR) with an authentic sample and published data (91).

(ii) Acetylene **86** (36.1 mg) was pyrolyzed by distillation (40°C, 2 X 10^{-5} torr), over a 15 min period, through a horizontal quartz tube packed with quartz chips heated to 700°C. The pyrolysate (34.0 mg, 94.2%) was collected in a cold trap cooled with liquid nitrogen. Analysis by GC/MS and ^1H NMR showed two isomers present.

The major isomer was determined to be 1,1-dimethyl-1-silaindene **87** (77%, NMR yield). It was not possible to separate the isomers on a packed GC column, and all attempts at preparative GC resulted in near complete destruction of the unidentified isomer. This isomer was determined to be 1,1-dimethyl-2-methylenebenzo-1-silacyclobutene, **88**, (17%, NMR yield) based on its spectra (subtracted of **87** for ^{1}H NMR and ^{13}C NMR and separately in GC/MS and GC/IR data): ^{1}H NMR δ 0.49 (s, 6H), 5.30 (d, 1H, J = 1.3 Hz), 5.92 (d, 1H, J = 1.3 Hz); ^{13}C NMR δ -0.84, 113.02, 118.42, 128.11, 130,58, 131.17, 148.79, 152.24, 155.16; GC/IR (gas phase) 3063, 2974, 2908, 1285, 1254, 1042, 899, 856, 795 cm^{-1}; GC/MS 160 (32), 145 (100), 119 (12), 105 (8), 93 (6), 77 (7), 53 (16).

<u>(iii)</u> Acetylene **86** (106.2 mg) was pyrolyzed by distillation (40°C, 2 X 10^{-5} torr), over a 40 min period, through a horizontal quartz tube packed with quartz chips heated to 650°C. The pyrolysate (94.5 mg, 89.0%) was collected in a cold trap cooled with liquid nitrogen. Analysis by ^{1}H NMR revealed starting material, **86**, 1,1-dimethyl-2-methylenebenzo-1-silacyclobutene, **88**, and 1,1-dimethyl-1-silaindene, **87**, in 2%, 34%, and 47% yield (NMR), respectively.

<u>(iv)</u> Acetylene **86** (94.7 mg) was pyrolyzed by distillation (40°C, 1 X 10^{-5} torr), over a 40 min period, through a horizontal quartz tube packed with quartz chips heated to 600°C. The pyrolysate (88.3 mg, 93.2%) was collected in a cold trap cooled with liquid nitrogen. Analysis by ^{1}H NMR revealed starting material, **86**, 1,1-

dimethyl-2-methylenebenzo-1-silacyclobutene, **88**, and 1,1-dimethyl-1-silaindene, **87**, in 22%, 28%, and 42% yield (NMR), respectively.

Copyrolysis of the mixture of (o-dimethylsilylphenyl)acetylene, 86, 1,1-dimethyl-2-methylenebenzo-1-silacyclobutene, 88, and 1,1-dimethyl-1-silaindene, 87

The mixture of isomers **86**, **88**, and **87** was obtained by the distillation (40°C, 2 X 10^{-5} torr) of **86** (222 mg), over a 70 min period, through a horizontal quartz tube packed with quartz chips heated to 640°C. The pyrolysate (215 mg, 97%) was collected in a cold trap cooled with liquid nitrogen. The pyrolysate was analyzed by ^{1}H NMR and determined to be comprised of a mixture of **86** (8%), **88** (58%), and **87** (34%). A sample (100.0 mg) of this mixture was then pyrolyzed by distillation (40°C, 1 X 10^{-4} torr), over a 40 min period, through a horizontal quartz tube packed with quartz chips heated to 800°C. The pyrolysate (93 mg, 93%) was collected in a cold trap cooled with liquid nitrogen. Analysis by GC and ^{1}H NMR showed only **87** (93%, NMR yield) to be present in the pyrolysate.

Synthesis of (o-deuterodimethylsilylphenyl)acetylene, 86-D

The procedure utilized was the same as used for the synthesis of **86**, but lithium aluminum deuteride was substituted for lithium aluminum hydride. From 10.7 mmol of **85**, 4.71 mmol (44%) of **86-D** was obtained, analytically pure, after preparative GC on a 5 ft X 0.25 in. 15% SE-30 Chromosorb W column at 170°C: ^{1}H NMR δ 0.41 (s, 6H), 3.23

(s, 1H), 7.24-7.34 (m, 2H), 7.5-7.53 (m, 2H); IR 3302, 3074, 3053, 2959, 2903, 2104, 1583, 1547 (Si-D), 1461, 1433, 1425, 1258, 1248, 1126, 1072, 839, 797, 762, 725, 683, 652 cm^{-1}; MS 161 (26), 160 (10), 147 (38), 146 (100), 144 (19), 130 (9), 129 (10), 120 (17), 119 (23), 106 (12), 105 (17), 103 (14); calcd for $C_{10}H_{11}DSi$ m/e 161.07711, measured m/e 161.07703. No Si-H was detected by NMR or IR, 1% would have been readily observed.

Pyrolysis of (*o*-deuterodimethylsilylphenyl)acetylene, **86-D**

(i) Acetylene **86-D** (112.3 mg) was pyrolyzed by distillation (40°C, 2 X 10^{-4} torr), over a 40 min period, through a horizontal quartz tube packed with quartz chips heated to 800°C. The pyrolysate (104.4 mg, 93.0%) was collected in a cold trap cooled with liquid nitrogen. Analysis by ^1H NMR revealed 2-deutero-1,1-dimethyl-1-silaindene **87-2D** and 3-deutero-1,1-dimethyl-1-silaindene **87-3D** in 73% and 19% yield (NMR), respectively: ^1H NMR δ 0.31 (s, 6H), 6.25 (s, 0.2H), 7.1-7.34 (m, 3.8H), 7.47-7.54 (d, 1H, J = 6.8 Hz); ^{13}C NMR δ -4.03, 124.08 126.87, 129.67, 131.62, 132.27, 138.45, 149.11, 149.35; MS 161 (100), 146 (13); calcd for $C_{10}H_{11}DSi$ m/e 161.07711, measured m/e 161.07709. The sp^2 resonance signals at δ 132.27 (C_1) and 149.11 (C_2) showed a strong correlation with the amount of deuterium incorporation (a 65% reduction and 29% reduction in the signal intensities, respectively, compared to the undeuterated material). Assignment of these signals was made possible with the additional

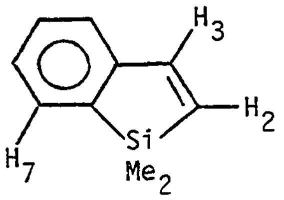
information gained below. (See ^{1}H and ^{13}C NMR elucidation of 1,1-dimethyl-1-silaindene **87**.)

(ii) Acetylene **86-D** (113.5 mg) was pyrolyzed by distillation (40°C, 2 X 10^{-5} torr), over a 40 min period, through a horizontal quartz tube packed with quartz chips heated to 600°C. The pyrolysate (109 mg, 96%) was collected in a cold trap cooled with liquid nitrogen. Analysis of ^{1}H NMR ($CDCl_3$) revealed **88-2D**, **87-3D**, 7-deutero-1,1-dimethyl-2-methylenebenzo-1-silacyclobutene, **88-D**, and starting material, **86-D**, in 17%, 2%, 27%, and 46% yield (NMR), respectively. The ^{1}H NMR of **88-D** shows singlet resonances at δ 5.29 (0.5H) and 5.90 (0.5H) revealing a 1:1 mixture of the E and Z isomers as expected. Additional supporting spectra of **88-D** include: GC/MS 161 (35), 146 (100), 119 (11), 105 (8), 93 (7), 67 (6), 53 (17); GC/IR (gas phase) 3063, 3009, 2974, 2908, 2233 (C-D), 1254, 1042, 852, 795 cm^{-1}.

^{1}H and ^{13}C NMR elucidation of 1,1-dimethyl-1-silaindene, 87

To determine the assignment of the proton and carbon resonance signals of the silaindenyl ring, the structure was probed with a Nicolet NT-300, 300 MHz ^{1}H, 75.5 MHz ^{13}C NMR spectrometer. First, the normal ^{1}H NMR ($CDCl_3$) spectrum was taken: δ 0.31, (s, 6H), 6.26 (d, $1H_2$, J = 10.3 Hz), 7.17-7.41 (m, 4H), 7.51 (d, $1H_7$, J = 6.9 Hz). Irradiation of the doublet at δ 6.26 resulted in the collapse of a doublet at δ 7.32. These two signals were tentatively ascribed to H_2

and H_3 of the indenyl ring. This assignment was then confirmed by performing a NOE experiment. A sample of 1,1-dimethyl-1-silaindene **87**



in $CDCl_3$ was degassed by ten freeze-thaw cycles and then sealed under vacuum. The ^1H spectrum was then acquired using a 20 second pulse delay while irradiating at the silicon methyl resonance, δ 0.31. A second ^1H spectrum was then acquired under the same conditions while irradiating at δ 11.6. The two Fourier transformed spectra were then subtracted from each other leaving only the silicon methyl signal and two residual NOE enhanced signals at δ 6.26 and δ 7.51. These two signals were assigned to H_2 and H_7. Quantitatively these signals showed 8% (H_2) and 16% (H_7) enhancements by integration of the spectrum irradiated at δ 0.31. No NOE was observed for the resonance at δ 7.32 (H_3).

The ^{13}C NMR spectrum of **87** was then taken in $CDCl_3$ (broad band decoupled): δ -4.05, 124.06, 126.91, 129.67, 131.61, 132.38, 138.50, 149.20, 149.34. A single off resonance decoupled (SORD) spectrum was acquired while irradiating at δ 6.26: δ -4.01, (q, J = 28.2 Hz), 124.05, 126.87, 129.65, 131.59 (d, J = 5.7 Hz), 132.38, 138.41, 149.18 (d, J = 5.7 Hz), 149.27. The signal at δ 132.38 was strongly enhanced relative to all other sp^2 resonance signals and was assigned to the carbon bearing H_2. A second ^{13}C NMR SORD spectrum was then acquired while irradiating at δ 7.32 within the aromatic multiplet: δ -4.00 (q, J = 30.1 Hz), 124.07, 126.87, 129.67, 131.61, 132.39 (d, J = 3.7 Hz), 138.40, 149.18, 149.27. Even though the resonance signals at 131.61 and 149.18 were both enhanced and collapsed into singlets, only the signals at δ 149.18 and δ 132.38 showed a reduction in intensities in the labeled compounds (see the Experimental Section, Pyrolysis of (o-deuterodimethylsilylphenyl)acetylene, **86-D**). Therefore, the carbon atom bearing H_3 was assigned to the signal at δ 149.18.

Pyrolysis of dimethylsilyl(o-dimethylsilylphenyl)acetylene, **83**

(i) Acetylene **83** (405.3 mg) was pyrolyzed by distillation (60°C, 1 X 10^{-3} torr), over a 60 min period, through a horizontal quartz tube packed with quartz chips heated to 800°C. The pyrolysate (351.5 mg, 86.7%) was collected in a cold trap cooled with liquid nitrogen. The clear, yellow pyrolysate was analyzed by GC and ^1H NMR and found to contain a mixture of 1,1-dimethyl-1-silaindene, **87**, 3-dimethylsilyl-1,1-dimethyl-1-silaindene, **93**, and 2-dimethylsilyl-1,1-dimethyl-1-silaindene, **97**, in 15%, 62%, and 4% yield (NMR), respectively. Components of the mixture were purified by preparative GC on a 5 ft X 0.25 in. 12% SE-30 Chromosorb W column temperature programmed from 200-250°C at 5°C per min. Compound **87** was isolated and identified by its ^1H NMR and mass spectrum. Isomers **93** and **97** were individually identified by GC/MS and GC/IR but were not separable by preparative GC. ^{1}H and ^{13}C NMR, high resolution mass spectra, and elemental analysis were performed on the isomer mixture. Supportive data for **93** includes: ^{1}H NMR δ 0.38 (s, 6H), 0.42 (d, 6H, J = 3.8 Hz), 4.56 (h, 1H, J = 3.8 Hz), 6.90 (s, 1H), 7.18-7.67 (m, 4H); ^{13}C NMR δ -4.02, -3.94, 124.54, 126.52, 129.68, 131.72, 139.17, 146.73, 151.60, 163.01; GC/IR (gas phase) 3055, 2960, 2120, 1585, 1440, 1250, 1150, 1130, 945, 870, 820, 780, 750 cm^{-1}; GC/MS 218 (69), 203 (100), 177 (12), 159 (11), 145 (40), 105, (6), 73 (41); high resolution mass spectrum (70 eV) calcd for $C_{12}H_{18}Si_2$ m/e 218.09471, measured m/e 218.09420. Anal. Calcd for $C_{12}H_{18}$: C, 65.98; H, 8.31. Found: C, 65.74; H, 8.47. Data for **97**: ^{1}H NMR δ 0.24 (d, 6H, J = 3.8 Hz), 4.32 (h, 1H, J = 3.8 Hz), the vinyl H is buried in the aromatic absorption, definitive analysis of the PMR spectra of **93** and **97** required the detailed analysis of the spectrum of **87** (vide infra); GC/IR (gas phase) 3055, 2960, 2120, 1520, 1440, 1250, 1130, 980, 880, 820, 780, 750 cm^{-1}; GC/MS 218 (17), 203 (27), 177 (3), 159 (5), 145 (31), 105 (8), 73 (100).

(ii) Acetylene **83** (409.4 mg) was pyrolyzed by distillation (60°C, 5 X 10^{-4} torr), over a 60 min period, through a horizontal quartz tube packed with quartz chips heated to 700°C. The pyrolysate (397.3 mg, 97.0%) was collected in a cold trap cooled with liquid nitrogen. The clear, yellow pyrolysate was analyzed by ^{1}H NMR and found to contain 1,1-dimethyl-2-methylenebenzo-1-silacyclobutene, **88**, 1,1-dimethyl-1-silaindene, **87**, 2-dimethylsilyl-1,1-dimethyl-1-silaindene, **97**, and 3-dimethylsilyl-1,1-dimethyl-1-silaindene, **93**, in

1%, 2%, 2%, and 64% yield (NMR) based on 53% recovered starting material **83**.

Copyrolysis of 2- and 3-dimethylsilyl-1,1-dimethyl-1-silaindenes, 97 and 93

A mixture of **93** and **97** (114.0 mg, 96:6) was pyrolyzed by distillation (60°C, 4 X 10^{-4} torr), over a 30 min period, through a horizontal quartz tube packed with quartz chips heated to 800°C. The pyrolysate (95.1 mg, 83.4%) was collected in a cold trap cooled with liquid nitrogen. The pyrolysate was analyzed by ^1H NMR and found to contain 1,1-dimethyl-1-silaindene, **87**, 2- and 3-dimethylsilyl-1,1-dimethyl-1-silaindenes, **97** and **93**, in 15%, 5%, and 63% yield (NMR), respectively.

Synthesis of benzocyclobutanone

A mixture of benzocyclobutanyl acetate (92) (39.8 mmol), Na_2CO_3 (39.8 mmol), MeOH (35 mL), and H_2O (70 mL) was sonicated in a Bransonic B-32 ultrasonic bath at 25-36°C for 3 h. The reaction mixture was extracted with Et_2O, washed with H_2O, and dried with $MgSO_4$. After removal of $MgSO_4$ and solvent, a crystalline solid, benzocyclobutanol (33.4 mmol, 84%), was obtained after recrystallization from pentane: mp 59-60°C (lit. (92) 58-60°C). Without the aid of ultrasound, the reaction requires 20 h at room temperature (92). Benzocyclobutanol (29.7 mmol) was added rapidly to $CrO_3(C_5H_5N)_2$ (178.2 mmol) prepared *in situ* in CH_2Cl_2 (445 mL). After 15 min at room temperature, the solution was decanted from the residue, which was subsequently washed with Et_2O (400 mL). The combined organic solutions were then washed successively, three times each, with 150 mL portions of 5% aqueous NaOH, 5% aqueous HCl, and 5% aqueous $NaHCO_3$. After drying of the organic layer with $MgSO_4$ and removal of solvents, the residue was distilled giving 26.7 mmol (90%) benzocyclobutanone: bp 69-71°C, 2 torr. The bp and IR spectrum matched that given by Newsoroff and Sternhell (92).

Synthesis of 7,7-dibromo-1-methylenebenzocyclobutene, 98

Triphenylphosphine (17.0 mmol) was added in one portion to a stirring solution of CBr_4 (8.5 mmol) in 50 mL of CH_2Cl_2 at 0°C. After stirring 15 min, benzocyclobutanone (8.5 mmol) in an an equal volume of CH_2Cl_2 was added dropwise. After stirring an additional 10 min, the mixture was slowly added to 500 mL of hexane. The solution was decanted and then concentrated, resulting in the precipitation of more Ph_3PO. Addition of recovered hexane followed by filtration to remove the precipitate and concentration gave the crude product. Crystallization from $EtOH/H_2O$, 4:1, gave 6.7 mmol of **98**: mp 49-51°C; ^1H NMR δ 3.5 (s, 2H), 7.1-7.5 (m, 4H); ^{13}C NMR δ 41.31, 78.96, 119.53, 122.46, 127.82, 130.37, 141.64, 142.45, 142.99; IR 3080, 3060, 2930, 2830, 1460, 1445, 1415, 1280, 1180, 1150, 1140, 1000, 830, 815, 790, 770, 750, 705 cm^{-1}; MS 276 (25), 274 (48), 272 (27), 195 (99), 193 (100), 113 (82), 97 (12), 95 (13), 86 (17), 72 (10), 61 (19), 57 (17); calcd for $C_9H_6Br_2$ m/e 271.88362, measured m/e 271.88339.

Synthesis of 7-bromo-1-methylenebenzocyclobutene, 99

Freshly distilled diethyl phosphite (8.97 mmol) was dissolved in 4.08 mmol of 7,7-dibromo-1-methylenebenzocyclobutene, **98**. Triethylamine (8.97 mmol) was then added and the reaction was followed by TLC. After 18 h, the reaction was complete, Et_2O was then added, and Et_3NHBr was removed by filtration. Column chromatography of the filtrate on a silica gel column eluted with hexane gave 3.85 mmol, 94%, of **99** as a 1:1 mixture of E and Z isomers: ^1H NMR δ 3.62 (apparent s, 4H), 5.95 (unresolved t, 1H), 6.35 (t, 1H, J = 2 Hz), 7.0-7.6 (m, 8H); ^{13}C NMR δ 39.09 (two coincidental peaks), 95.05, 96.13, 118.12, 120.56, 122.51, 122.95, 127.60 (two peaks), 129.39, 129.88 130.37, 140.50, 142.56, 142.99, 143.69, 144.40; IR 3090, 2930, 1670, 1465, 1445, 1415, 1330, 1230, 770, 740, 695, 690 cm^{-1}; MS 196 (17), 194 (17), 115 (100), 89 (13), 63 (12); calcd for C_9H_7Br m/e 193.97311, measured m/e 193.97294.

Synthesis of 7-trimethylsilyl-1-methylenebenzocyclobutene, 100

A solution of 7-bromo-1-methylenebenzocyclobutene (2.72 mmol) in Et_2O (30 mL) was cooled to -78°C. A solution of t-butyllithium in pentane (5.71 mmol, 1.9 M) was then added dropwise, and the reaction was allowed to stir for 45 min. Trimethylchlorosilane was then added dropwise, and the mixture was stirred for 20 min before warming to room temperature. After stirring at room temperature for 1 h, the reaction was then extracted with H_2O and additional Et_2O and dried over $MgSO_4$. After filtration of the $MgSO_4$ and removal of the solvent, the residue was chromatographed on silica gel and eluted with hexane giving 2.14 mmol of **100** as a 1:1 mixture of E and Z isomers: ^{1}H NMR δ 0.18 (s, 9H), 0.24 (s, 9H), 3.60 (unresolved d, 2H), 3.65 (d, 2H, J = 2 Hz), 5.48 (unresolved t, 1H), 5.94 (t, 1H, J = 2 Hz), 7.2-7.5 (m, 8H); ^{13}C NMR δ -0.57, -0.14, 40.33, 41.31, 101.66, 117.69, 117.85, 120.40, 120.56, 122.78, 123.00, 127.28, 128.80, 128.96, 129.34, 145.86, 146.02, 146.30, 147.00, 152.09; IR 3070, 2960, 2920, 1645, 1585, 1445, 1245, 855, 835, 750, 735 cm^{-1}; MS 188 (7), 173 (3), 145 (15), 73 (100), both isomers show identical breakdown patterns and vary only slightly in relative intensities. High resolution mass spectrum (of the mixture of the isomers) calcd for $C_{12}H_{16}Si$ m/e 188.10213, measured m/e 188.10176. Anal. (of the isomeric mixture) Calcd for $C_{12}H_{16}$: C, 76.53; H, 8.56. Found: C, 76.49; H, 8.87.

Pyrolysis of 7-trimethylsilyl-1-methylenebenzocyclobutene, **100**

(i) Compound **100** (46 mg) was pyrolyzed by distillation (30°C, 1 X 10^{-2} torr), over a 10 min period, through a horizontal quartz tube packed with quartz chips heated to 620°C. The pyrolysate (40 mg, 87%) was collected in a cold trap cooled with liquid nitrogen. The pyrolysate was analyzed by NMR and GC and found to contain only o-tolyltrimethylsilylacetylene (87%, NMR) based on comparison by ^{1}H NMR, IR, and GC/MS with an authentic sample.

(ii) Compound **100** (40 mg) was pyrolyzed by distillation (30°C, 1 X 10^{-2} torr), over a 10 min period, through a horizontal quartz tube packed with quartz chips heated to 520°C. The pyrolysate

(32 mg, 80%) was collected in a cold trap cooled with liquid nitrogen. The pyrolysate was analyzed by NMR and GC and found to contain o-tolyltrimethylsilylacetylene and starting material, **100**, in 35% and 45% yield (NMR), respectively.

Synthesis of o-(trimethylsilylmethyl)phenylacetylene, 102

A few drops of a solution of **71** (5.6 mmol) in an equal volume of CCl_4 was added to N-bromosuccinimide (7.0 mmol) in CCl_4 (11 mL) containing a small amount of AIBN. The reaction flask was then heated to reflux in an oil bath at 125°C at which time the dropwise addition of **71** was begun. After refluxing for 45 min, the reaction was nearly complete as determined by TLC. It was necessary to run this reaction in the presence of air and to partial completion in order to obtain a good yield of product. The hot suspension was cooled, and the succinimide was removed by filtration. The yellow solution was concentrated using a rotary evaporator. The residual yellow oil was purified by column chromatography on silica gel eluted with hexane. The product, (o-trimethylsilylethynyl)-α-bromotoluene, **267**, was obtained in 93% yield based on a 13% yield of recovered **71**. The identification of **267** was based upon its spectra: ^1H NMR δ 0.30 (s, 9H), 4.65 (s, 2H), 7.1-7.6 (m, 4H); ^{13}C NMR δ 139.69, 132.59, 129.61, 128.96, 128.31, 123.00, 101.98, 100.68, 31.72, -0.08; IR 3080, 2970, 2910, 2160, 1480, 1450, 1250, 1220, 880, 855, 840, 750 cm^{-1}; MS 268 (13) (M+2), 266 (13) (M^+), 253 (10), 251 (10), 188 (31), 187 (100), 173 (46), 172 (15), 171 (20), 159 (10), 157 (12), 155 (8), 145 (21), 131 (12), 129 (49), 128 (23), 125 (12), 123 (12), 86 (25), 72 (15), 59 (43); calcd for $C_{12}H_{15}BrSi$ m/e 266.01264, measured m/e 266.01244. This reaction is easily scaled up with no adverse effects on the yield of **267**.

Next, a small amount of **267** (6.7 mmol) in an equal volume of Et_2O was added to Mg (8.0 mmol, activated by treatment with ethylene dibromide and I_2) in 4 mL of Et_2O. A reaction begain immediately. Additional Et_2O (10 mL) was added, followed by the remainder of **267** at a rate which maintained a reflux. After addition was complete and the reaction had subsided, the mixture was stirred at room temperature for 2 h. (Heating caused the mixture to turn dark brown in another attempt.) Chlorotrimethylsilane (8.3 mmol) in an equal volume of Et_2O was added at a moderate rate. After 20 min at room temperature, the reaction mixture was refluxed for 2 h. The mixture was then cooled and acidified with 0.5 M H_2SO_4. Extraction of the organic layer with additional Et_2O, washing with H_2O, drying by $MgSO_4$, and removal of the solvent gave an orange oil. Purification by column chromatography on silica gel eluted with hexane gave trimethylsilyl(o-trimethylsilylmethylphenyl)acetylene, **268**, in 67% yield: ^1H NMR δ 0.00 (s, 9H), 0.24 (s, 9H), 2.34 (s, 2H), 6.96-7.01 (m, 2H), 7.15 (d of t, 1H, J = 1.3 and 7.5 Hz), 7.37 (d of d, 1H, J = 1.3 and 7.9 Hz); ^{13}C NMR δ 143.80, 132.43, 128.31, 128.09, 123.76, 121.48, 105.34, 97.59, 25.76, 0.14, -1.38; IR 3080, 3030, 2970, 2910, 2160, 1485, 1250, 1155, 870, 855, 840, 750 cm^{-1}; MS 260 (12), 245 (16), 229 (11), 172 (53), 157

(18), 128 (13), 73 (100), 59 (14); calcd for $C_{15}H_{24}Si_2$ m/e 260.14166, measured m/e 260.14099.

The acetylenic trimethylsilyl group of **268** was readily removed by the treatment of **268** (3.1 mmol) with a solution of NaOH (12.4 mmol), MeOH (39 mL), and H_2O (5 mL) at room temperature for 30 min. The mixture was acidified by the addition of 0.5 M H_2SO_4 and extracted with pentane. The solvent was removed after washing with H_2O and drying with $MgSO_4$. The product was purified by preparative GC on a 9 ft X 0.25 in. 10% SE-30 Chromosorb W column at 170°C to give analytically pure **102** (59%): ^1H NMR δ 0.0 (s, 9H), 2.32 (s, 2H), 3.16 (s, 1H), 6.8-7.4 (m, 4H); ^{13}C NMR δ 143.97, 132.91, 128.58, 128.25, 123.87, 120.45, 83.67, 80.58, 25.65, -1.38; IR 3320, 3080, 3030, 2970, 2910, 2110, 1600, 1485, 1450, 1250, 1160, 850, 775, 755 cm^{-1}; MS 188 (13), 145 (15), 131 (12), 115 (15), 73 (100); calcd for $C_{12}H_{16}Si$ m/e 188.10213, measured m/e 188.10226. Anal. Calcd for $C_{12}H_{16}$: C, 76.53; H, 8.56. Found: C, 76.57; H, 8.78.

FVP of 102

A sample of **102** (53 mg), distilled (1 X 10^{-2} torr) from a bath at 35°C, was pyrolyzed at 520°C. The pyrolysate (46 mg, 87%) was analyzed by GC and ^1H NMR and was found to consist only of **102**.

Synthesis of methylenebenzocyclobutane, 104

A solution of *t*-butyllithium in pentane (3.8 mmol, 1.9 M) was added dropwise to a solution of **99** (1.81 mmol) in 18 mL of Et_2O at -78°C. After stirring 45 min at -78°C, 1 mL of 95% EtOH was added, and the mixture was allowed to warm slowly to room temperature (approximately 2 h). The mixture was then extracted with H_2O and dried with $MgSO_4$. After filtration of the drying agent and removal of the solvent, the residue was purified by preparative GC on a 9 ft X 0.25 in. 10% SE-30 Chromosorb W column at 115°C yielding 1.21 mmol, 67%, of **104**. The product matched literature spectra (92), was stable, and could be stored at 0°C for one year without any detectable decomposition in contrast to the report of Brown and co-workers (31).

FVP of 104

Compound **104** (50 mg), distilled (1 X 10^{-2} torr) from a bath at 0°C over a 10 min period, was pyrolyzed at 620°C. The pyrolysate (49 mg, 98%) was analyzed by GC and ^{1}H NMR and was determined to consist of **104** and o-tolylacetylene, **25**, in a ratio of 82:18 (80% and 18% yield, respectively, by NMR).

Synthesis of (dimethylsilyl)dimethylphenylsilylacetylene, 105

A solution of n-butyllithium in hexane (32.5 mmol, 2.4 M) was added to dimethylphenylsilylacetylene (93) (29.6 mmol) in ether (60 mL) at -78°C. After stirring at -78°C, the mixture was warmed to room temperature and stirred an additional 30 min. After cooling to 0°C, chlorodimethylsilane (37.0 mmol) was added rapidly and stirred for 30 min at 0°C and then at room temperature for 30 min. Lithium chloride was then removed by filtration, and solvents were removed by distillation. Vacuum distillation of the residue gave 24.0 mmol (81%) of **105:** bp 66-74°C, 1.0 torr; ^{1}H NMR δ 0.26 (d, 6H, J = 3.7 Hz), 0.42

(s, 6H), 4.14 (h, 1H, J = 3.7 Hz), 7.35-7.43 (m, 2H), 7.60-7.68 (m, 2H); ^{13}C NMR δ -3.00, -0.84, 112.70, 113.41, 127.92, 129.50, 133.73, 136.56; IR 3071, 3051, 2962, 2902, 2141, 1429, 1252, 1113, 885, 839, 820, 781, 771, 737, 698 cm^{-1}; MS 218 (18), 203 (100), 159 (13), 145 (15), 135 (50), 105 (14), 73 (27); calcd for $C_{12}H_{18}Si_2$ m/e 218.09471, measured m/e 218.09499. Anal. Calcd for $C_{12}H_{18}$: C, 65.98; H, 8.31. Found: C, 66.16; H, 8.55.

Pyrolysis of (dimethylsilyl)dimethylphenylsilylacetylene, 105

Acetylene **105** (187.1 mg) was pyrolyzed by distillation (60°C, 4 X 10^{-4} torr), over a 40 min period, through a horizontal quartz tube packed with quartz chips heated to 800°C. The pyrolysate (141.3 mg, 75.5%) was collected in a cold trap cooled with liquid nitrogen. The products were isolated by preparative GC on a 5 ft X 0.25 in. 20% SE-30 Chromosorb W column temperature programmed from 100-250°C at 6°C per min. Identified from the mixture, by comparison of their ^{1}H NMR and GC/MS spectra with authentic samples, was dimethylphenylsilane, dimethylphenylsilylacetylene, and 1,1-dimethyl-1-silaindene **87** in 4%, 50%, and 3% yield (GC) based on 22% recovered starting material 105.

Pyrolysis of dimethylphenylsilylacetylene, 106

Acetylene **106** (202.1 mg) was pyrolyzed by distillation (20°C, 1 X 10^{-4} torr), over a 60 min period, through a horizontal quartz tube packed with quartz chips heated to 850°C. The pyrolysate (174.0 mg, 86.1%) was collected in a cold trap cooled with liquid nitrogen. The products were isolated by preparative GC on a 5 ft X 0.25 in. 20%

SE-30 Chromosorb W column temperature programmed from 100-250°C at 6°C per min. Identified from the mixture, by comparison of their ^1H NMR and GC/MS spectra with authentic samples, were phenylacetylene, dimethylphenylsilane, and 1,1-dimethyl-1-silaindene **87** in 7%, 3%, and 14% yield (GC) based on 71% recovered starting material, **105**.

Synthesis of dimethyl(propynyloxy)silane, 109

Compound **109** was prepared according to the procedure described by Mironov and co-workers (94).

FVP of dimethylpropynyloxysilane, 109

(i) Acetylene **109** (551.0 mg), distilled (1 X 10^{-4} torr) from a bath warmed slowly from -30°C to room temperature, was pyrolyzed at 700°C. The pyrolysate was collected (465.4 mg, 84.5%), and a very volatile component, a gas at room temperature, was transferred to a separate vial. Analysis of the gas by IR and ^1H NMR revealed allene to be present by comparison to literature spectra (95, 96). The remaining less volatile products were separated by preparative GC on a 9 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 100-250°C at 3°C per min. Isolated were 3,3-dimethyl-4-oxa-3-silacyclopentene, **110**, hexamethylcyclotrisiloxane (D_3), **111**, 3-hydrido-1-propynyloxy-1,1,3,3-tetramethyldisiloxane, **112**, 3,3,5,5-tetramethyl-4,6-dioxa-3,5-disilacycloheptene, **113**, 4,4,6,6-tetramethyl-3,5-dioxa-5,6-disilacycloheptene, **114**, and starting material, in 32%, 5%, 14%, 13%, 14%, and 3% yield, respectively. Identification of these compounds was based on their spectra. **109:** ^1H NMR δ 0.24

(s, 6H), 4.58 (overlapped d of d, appears as an unresolved t, 1H, J = 2 Hz), 6.04 (d of t, 1H, J = 10.5 Hz and 2.4 Hz), 6.91 (d of t, 1H, J = 10.5 Hz and 1.4 Hz); ^{13}C NMR δ 0.68, 72.99, 126.51, 149.68; IR 3070, 3050, 3010, 2970, 2890, 2860, 1655, 1605, 1565, 1255, 1185, 1115, 1095, 1025, 850, 785, 745 cm^{-1}; MS 114 (21), 101 (5), 100 (11), 99 (100), 58 (5), 55 (6); calcd for $C_5H_{10}OSi$ m/e 114.05010, measured m/e 114.04994. Anal. Calcd for C_5H_{10}: C, 52.58; H, 8.82. Found: C, 52.31; H, 8.88. **112:** ^{1}H NMR δ 0.14 (s, 6H), 0.20 (d, 6H, J = 2.9 Hz), 2.39 (t, 1H, J = 2.3 Hz), 4.33 (d, 2H, J = 2.3 Hz), 4.71 (h, 1H, J = 2.9 Hz); ^{13}C NMR δ -0.99, 0.70, 73.05, 73.88, 81.86; IR 3330, 2970, 2910, 2870, 2130, 1370, 1255, 1095, 1065, 910, 895, 820, 795, 765 cm^{-1}; MS 174 (15), 173 (95), 157 (17), 145 (9), 144 (15), 143 (100), 133 (32), 119 (15), 103 (9), 75 (13), 73 (18), 59 (12); calcd for $C_7H_{15}O_2Si_2$ m/e 187.06106, measured m/e 187.06108. Anal. Calcd for C_7H_{16}: C, 44.63; H, 8.56. Found: C, 44.57; H, 8.78. **113:** ^{1}H NMR δ 0.15 (s, 6H), 0.20 (s, 6H), 4.47 (overlapped d of d, appears as an unresolved t, 2H, J = 2.6 Hz), 5.56 (d of t, 1H, J = 15.3 Hz and 2.2 Hz), 6.42 (d of t, 1H, J = 15.3 Hz and 2.9 Hz); ^{13}C NMR δ -1.96, 1.42, 65.53, 127.52, 147.20; IR 2970, 2920, 2850, 1615, 1255, 1205, 1110, 990, 910, 845, 800 cm^{-1}; MS 188 (17), 174 (16), 173 (100), 145 (33), 134 (13), 133 (99), 120 (11), 119 (94), 103 (14), 79 (17), 75 (11), 73 (18), 66 (9), 59 (11), 55 (22); calcd for $C_7H_{16}O_2Si_2$ m/e 188.06889, measured m/e 188.06858. Anal. Calcd for C_7H_{16}: C, 44.63; H, 8.56. Found: C, 44.62; H, 8.73. **114:** ^{1}H NMR δ 0.17 (s, 6H), 0.22 (s, 6H), 1.52 (d of d, 2H, J = 7.7 Hz and 1.1 Hz), 4.96 (overlapped d of t, 1H, J = 7.7 Hz and 5.7 Hz), 6.22 (d of t, J = 5.7 Hz and 1.1 Hz); ^{13}C NMR δ -0.96, -0.13, 16.02, 109.65, 139.09; IR 3050, 2970, 2940, 2910, 2890, 1635, 1405, 1370, 1255, 1170, 1145, 1080, 1015, 950, 905, 870, 845, 800, 755, 715, 660, 630 cm^{-1}; MS 188 (32), 174 (10), 173 (65), 145 (29), 134 (13), 133 (100), 119 (77), 117 (10), 103 (10), 79 (14), 73 (27), 66 (13), 59 (12), 55 (17); calcd for $C_7H_{16}O_2Si_2$ m/e 188.06889, measured m/e 188.06883. Anal. Calcd for C_7H_{16}: C, 44.63; H, 8.56. Found: C, 44.62; H, 8.73.

(ii) Acetylene **109** (104.2 mg) was pyrolyzed at 650°C (3 X 10^{-5} torr). The pyrolysate was collected (91.7 mg, 88.0%), and the products, isolated by preparative GC, were identified by ^{1}H NMR. Compounds **112**, **113**, **114**, and D_3 were obtained in 20%, 7%, 9%, and 6% yield, respectively. Compound **109** was obtained as a mixture with its isomer, 4,4-dimethyl-2-oxa-4-silacyclopentene, **115**, in 27% combined yield in a ratio of 1.00:1.87. Yields, determined by GC, were based on a 31% yield of recovered starting material. Spectra obtained of **115** are as follows: ^{1}H NMR δ 0.30 (s, 6H), 1.31 (d of d, 2H, J = 3.5 Hz and 2.3 Hz), 5.08 (d of t, apparent quartet, 1H, J = 3.5 Hz), 6.44 (overlapped d of t, 1H, J = 3.5 Hz and 2.3 Hz); ^{13}C NMR δ -0.56, 13.10, 103.75, 146.79.

FVP of 3,3-dimethyl-4-oxa-3-silacyclopentene, 110

Compound **110** (57.4 mg), distilled (1 X 10^{-5} torr) from a bath warmed slowly from -30°C to room temperature, was pyrolyzed at

700°C. The pyrolysate (49.0 mg, 85%), analyzed by GC and ^{1}H NMR, was found to contain only starting material.

FVP of 3-hydrido-1-propynyloxy-1,1,3,3-tetramethyldisiloxane, **112**

Acetylene **112** (57.5 mg), distilled (1 X 10^{-5} torr) from a bath warmed from -30°C to ambient temperature, was pyrolyzed at 700°C. Analysis of the pyrolysate (42.9 mg, 74.6%) by GC and ^{1}H NMR revealed starting material in addition to compounds **110**, **113**, and **114** in 67%, 1%, 3%, and 3% yield (GC), respectively.

FVP of 3,3,5,5-tetramethyl-4,6-dioxa-3,5-disilacycloheptene, **113**

Compound **113** (54.2 mg), distilled (1 X 10^{-5} torr) from a bath warmed slowly from -30°C to room temperature, was pyrolyzed at 700°C. Analysis of the pyrolysate (53.0 mg, 97.8%) by GC and ^{1}H NMR revealed D_3, **110**, **114**, and starting material in 6%, 21%, 5%, and 63% yield (GC), respectively.

FVP of 4,4,6,6-tetramethyl-3,5-dioxa-4,6-disilacycloheptene, **114**

Compound **114** (53.9 mg), distilled (1 X 10^{-5} torr) from a bath warmed slowly from -30°C to room temperature, was pyrolyzed at 700°C. The pyrolysate (52.7 mg, 97.8%), analyzed by ^{1}H NMR and GC, contained **110**, D_3, and starting material in 2%, 1%, and 79% yield (GC), respectively.

FVP of isomers **110** and **115**

A mixture of isomers **110** and **115** (102.3 mg), obtained from the pyrolysis of **109** at 650°C in a 1.51:1.00 ratio, was pyrolyzed at 700°C

(3×10^{-5} torr). The pyrolysate was collected (90.5 mg, 88.4%), and products **110** and **115** were present in a ratio of 1.81:1.00 as determined by ^1H NMR. The yields of **110** and **115** were determined by ^1H NMR to be 56.6% and 39.9%, respectively.

Synthesis of dimethyl(3-deuteropropynyloxy)silane, **109-D**

A solution of n-butyllithium (209 mmol, 2.5 M in hexane) was added to propargyl alcohol (100 mmol) in 250 mL of Et_2O cooled to -70°C. After 20 min at -70°C, the suspension was warmed to room temperature and then stirred for 30 min. Excess D_2O was then added to quench the dianion. The excess D_2O was removed by successively drying with Na_2SO_4, $MgSO_4$, and finally with 4Å molecular sieves. The salts were removed by filtration. The crude reaction mixture was used in the next step. Subsequent to the addition of N,N-dimethylaniline (130 mmol), chlorodimethylsilane (130 mmol) was added to the reaction flask cooled to 0°C. After stirring for 12 h, the salts were removed by filtration, and the product, **109-D**, was isolated by fractional distillation (bp 93-95°C, 17.5 mmol). The product was found to be labeled to the extent of 79% at the acetylenic position by ^1H NMR integration. GC/MS data indicated the incorporation of only one deuterium. The carbon spectrum is reported as: δ 81.47 (s), 81.02 (t, J_{C-D} = 7.3 Hz), 73.55 (s), 73.32 (t, J_{C-D} = 38.2 Hz), 52.16 (s), -1.53 (t, J_{C-Si} = 29.5 Hz).

FVP of **109-D**

(i) Compound **109-D** (315.6 mg), distilled (1 X 10^{-4} torr) from a bath warmed slowly from -30°C to room temperature, was pyrolyzed at 650°C. The pyrolysate was collected (261.2 mg, 83%) and analyzed. The GC/MS data indicated single deuterium incorporation in the products, all of which were analogous to those obtained from the FVP of **109**. The products were isolated by preparative GC on a 10 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 80-250°C at 5°C per min. Recovered **109-D** showed no signs of scrambling by ^{1}H NMR nor did **112-D**. The other products all showed some degree of scrambling which was estimated by integration of the signals with respect to the silicon methyl resonances. The deuterium incorporation into products **110-D** and **113-D-115-D** caused severe broadening of the ^{1}H NMR signals resulting in a large uncertainty (± 0.1 D) in the estimate of deuterium incorporation. Based upon an average of several integrated values, and comparison with nondeuterated products, the relative values of deuterium incorporation were obtained and are shown in Scheme 31. The carbon spectra of **110-D** and **115-D** were uninformative showing no observable C-D coupling and only singlet signals (C-D) slightly upfield from the C-H resonances, except for the silicon methyl signals which showed only one signal each.

(ii) Acetylene **109-D** (323.7 mg) was pyrolyzed at 700°C. The pyrolysate (254.1 mg, 79%) was analyzed by GC/MS which indicated only single deuterium incorporation in the products. Analysis of **112-D** by ^{1}H NMR indicated that only the acetylenic position was labeled.

Analysis of **110-D** by ^1H NMR revealed the deuterium label was scrambled throughout the ring in the same ratios measured for **110-D** obtained from the FVP of **109-D** at 650°C. The ^{13}C spectrum of **110-D** was recorded as δ 149.67 (C-H), 149.62 (C-D), 126.51 (C-H), 126.35 (C-D), 73.00 (C-H), 72.92 (C-D), 0.68 (Si-Me). No **109-D** was recovered, and the remaining products (**113-D** and **115-D**) were not further analyzed.

Copyrolysis of dimethylpropynloxysilane, 109, and dimethoxydimethylsilane

Compound **109** (192.5 mg) in a 10.1 fold excess of dimethoxydimethylsilane was added dropwise, during a 40 min period, to a vertical, nitrogen flow pyrolysis apparatus. The pyrolysate (95.5% total mass recovery) was collected in a flask cooled to -78°C. Analysis of the pyrolysate by GC revealed **110**, **113**, and 1,3-dimethoxy-1,1,3,3-tetramethyldisiloxane, **120**, in 16%, 6%, and 40% yield, respectively. The yield of **120** is corrected for the amount formed by pyrolysis of the trap alone under identical conditions. In the control experiment, 634.5 mg of dimethoxydimethylsilane was pyrolyzed. The pyrolysate (606.0 mg, 95.5%) was found to contain a 1% yield of **120**, and the remainder was starting material. Product identification was based on GC/MS and ^1H NMR data by comparison with data from authentic samples after isolation by preparative GC on a 9 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 80-250°C at 3°C per min.

Synthesis of dimethyl(3-trimethylsilylpropynyloxy)silane, 121

The tetrahydropyranyl ether of propargyl alcohol (48.9 mmol), prepared using the general procedure of Robertson (97), was dissolved in 100 mL of Et_2O and cooled to -78°C. A solution of n-butyllithium in hexane (56.7 mmol, 2.5 M) was added slowly, and the reaction mixture was stirred for 20 min at -78°C. After warming to room temperature and stirring for 30 min, the suspension was cooled to 0°C. Subsequently, trimethylchlorosilane (68.5 mmol) was added dropwise. After stirring at 0°C for 30 min and at room temperature for 30 min, the suspension was added to a separatory funnel containing saturated aqueous $NaHCO_3$ and extracted. After drying with $MgSO_4$, the Et_2O was removed under reduced pressure. The crude product was then added to 60 mL of MeOH, and the mixture was cooled to 0°C prior to the addition of a small amount of p-toluenesulfonic acid. After 3 h at room temperature, K_2CO_3 was added, the mixture was stirred for 4 min, and then extracted with Et_2O and saturated aqueous $NaHCO_3$. Removal of Et_2O using a rotary evaporator followed by distillation (bp 72-75°C, 11 torr) gave 30.1 mmol (62%) of 3-trimethylsilylpropargyl alcohol.

The 3-trimethylsilylpropargyl alcohol (18.5 mmol) was dissolved in 75 mL of Et_2O containing Et_3N (41.8 mmol) and cooled to 0°C. Dimethylchlorosilane, in an equal volume of Et_2O, was slowly added to the mixture. After complete addition, the suspension was stirred overnight at room temperature. Triethylammonium hydrochloride was removed by filtration and volatile components were distilled (50°C, 0.1 torr) into a receiver cooled to -78°C. The clear distillate was then redistilled to give **121** (14.1 mmol) in 76%: bp 93-96°C at 70 torr; ^{1}H NMR δ 0.17 (s, 9H), 0.27 (d, 6H, J = 2.9 Hz), 4.32 (s, 2H), 4.68 (h, 1H, J = 2.9 Hz); ^{13}C NMR δ -1.43, -0.26, 52.94, 90.46, 103.40; IR 2963, 2901, 2858, 2178, 2120, 1364, 1252, 1094, 1007, 899, 845, 762, 729, 700, 650, 636 cm^{-1}; MS 171 (35), 155 (11), 143 (20), 142 (14), 141 (74), 131 (10), 117 (11), 85 (12), 83 (15), 78 (10), 75 (9), 74 (10), 73 (100), 63 (12), 59 (19), 55 (9); calcd for $C_8H_{17}OSi_2$ (M^+-1) m/e 185.08180, measured m/e 185.08161. Anal. Calcd for C_8H_{18}: C, 51.55; H, 9.73. Found: C, 51.47; H, 9.49.

FVP of dimethyl(3-trimethylsilylpropynloxy)silane, 121

Acetylene **121** (131.5 mg), distilled (1 X 10^{-4} torr) from a bath warmed from 0°C to room temperature over a 1 h period, was pyrolyzed at 700°C. The pyrolysate (115.9 mg, 88.1%) was analyzed by GC and ^{1}H NMR. The products were identified as trimethyl(2-propynyl)silane, **122**, allenyltrimethylsilane, **123**, D_3, 1,1,3,3,3-pentamethyl-1-(2-propynyl)disiloxane, **124**, 1-allenyl-1,1,3,3,3-pentamethyldisiloxane, **125**, 3,3-dimethyl-1-trimethylsilyl-4-oxa-3-silacyclopentene, **126**, 3-hydrido-1-(3-trimethylsilylpropynyloxy)-1,1,3,3-tetramethyldisiloxane, **127**, and 3,3,5,5-tetramethyl-1-trimethylsilyl-4,6-dioxa-3,5-disilacycloheptene, **128**, in 3%, 16%, 4%, 3%, 11%, 32%, 16%, and 14% yield (GC), respectively, based on 4% recovered starting material. The products were isolated by preparative GC on a 5 ft X 0.25 in. 20% SE-30 Chromosorb W column temperature programmed from 125-225°C at 5°C per min. To facilitate product characterization, an additional 518.0

mg of pyrolysate was obtained from the pyrolysis of 555.6 mg of **2** at 700°C. Both pyrolysates were combined, and the products were isolated from this mixture. Products **122**, **123**, and D_3 were identified by comparison of their spectra (^{1}H NMR, GC/MS, and IR) with authentic samples. Isomers **124** and **125** were not separable by preparative GC. Consequently, NMR, exact mass, and combustion analysis was performed on the mixture. Spectra of **124:** ^{1}H NMR δ 0.09 (s, 9H), 0.19 (s, 6H), 1.52 (d, 2H, J = 3.0 Hz), 1.89 (t, 1H, J = 3.0 Hz); GC/IR (gas phase) 3333, 2966, 2912, 1261, 1076, 849, 818 cm^{-1}; GC/MS 171 (19), 149 (8), 148 (16), 147 (100), 131 (15), 117 (11), 73 (23), 66 (9), 59 (9). **125:** ^{1}H NMR δ 0.82 (s, 9H), 0.17 (s, 6H), 4.35 (d, 2H, J = 7.2 Hz), 4.90 (t, 1H, J = 7.2 Hz); ^{13}C NMR δ 0.80, 1.97, 67.23, 81.39, 213.21; GC/IR (gas phase) 2966, 2912, 1936, 1261, 1219, 1072, 849, 810 cm^{-1}; GC/MS 171 (17), 149 (10), 148 (19), 147 (100), 131 (20), 117 (15), 78 (14), 73 (47), 66 (22), 59 (21). Additional data collected on the mixture of **124** and **125:** exact mass calcd for $C_8H_{18}OSi_2$ m/e 186.08963, measured m/e 186.08929. Anal. Calcd for C_8H_{18}: C, 51.55, H, 9.73. Found: C, 51.41; H, 9.76. The remaining compounds were isolated in pure form and identified by their spectra. **126:** ^{1}H NMR δ 0.13 (s, 9H), 0.22 (s, 6H), 4.71 (d, 2H, J = 2.4 Hz), 6.38 (t, 1H, J = 2.4 Hz); ^{13}C NMR δ -1.62, 0.52, 76.21, 136.95, 168.10; IR 3011, 2957, 2899, 2878, 2841, 1553, 1406, 1252, 1053, 995, 982, 841, 779, 752, 702, 652, 625 cm^{-1}; MS 186 (7), 171 (7), 143 (20), 117 (12), 98 (13), 75 (18), 73 (100), 59 (12), 58 (7); calcd for $C_8H_{18}OSi_2$ m/e 186.08963, measured m/e 186.08912. Anal. Calcd for C_8H_{18}: C, 51.55; H, 9.73. Found: C, 51.67; H, 9.84. **127:** ^1H NMR δ 0.15 (s, 6H), 0.17 (s, 9H), 0.22 (d, 6H, J = 2.8 Hz), 4.35 (s, 2H), 4.72 (h, 1H, J = 2.8 Hz); ^{13}C NMR -0.79, -0.13, 0.72, 51.18, 89.74, 103.92; IR 2964, 2905, 2866, 2181, 2129, 1456, 1410, 1367, 1254, 1063, 1007, 908, 843, 798, 762, 700, 654, 642 cm^{-1}; MS 245 (17), 215 (23), 205 (11), 172 (10), 147 (14), 133 (21), 117 (8), 115 (10), 111 (17), 100 (8), 97 (23), 83 (37), 81 (8), 75 (11), 74 (9), 73 (100), 59 (18); calcd for $C_9H_{21}O_2Si_3$ m/e 245.08494, measured m/e 245.08513. Anal. Calcd for $C_{10}H_{24}$: C, 46.10; H, 9.28. Found: C, 46.03; H, 9.50. **128:** ^1H NMR δ 0.10 (s, 9H), 0.16 (s, 6H), 0.22 (s, 6H), 4.59 (d, 2H, J = 2.1 Hz), 5.96 (t, 1H, J = 2.1 Hz); ^{13}C NMR -1.82, -1.62, 1.43, 67.37, 137.87, 164.46; IR 2959, 2901, 2839, 1570, 1406, 1256, 1115, 1051, 993, 972, 839, 812, 800, 775, 756, 690 cm^{-1}; MS 172 (23), 147 (18), 97 (8), 75 (6), 74 (8), 73 (100), 59 (6); calcd for $C_{10}H_{24}O_2Si_3$ m/e 260.10842, measured m/e 260.10808. Anal. Calcd for $C_{10}H_{24}$: C, 46.10; H, 9.28. Found: C, 46.26; H, 9.41.

Synthesis of β,β-dibromo-*o*-trimethylsiloxystyrene

Triphenylphosphine (48.0 mmol) was added to a stirring solution of carbon tetrabromide (24.0 mmol) in 120 mL of dry CH_2Cl_2 (under N_2) and cooled to 0°C (89). After 15 min, *o*-trimethylsiloxybenzaldehyde (98) (20.0 mmol) was added rapidly, and the mixture was stirred for 7 min. The orange solution was slowly poured into 1.8 L of stirring hexane, solids were allowed to coagulate, and the clear solution was decanted. Solvents down to ca. 50 mL were removed using a rotary evaporator, followed by removal of triphenylphosphine oxide by filtration. The filtrate was added to 500 mL of recovered hexane causing the precipitation of additional triphenylphosphine oxide which was again removed by filtration. After removal of the bulk of the hexane using a rotary evaporator, residual solvent was removed under high vacuum (0.1 torr) leaving nearly pure β,β-dibromo-o-trimethylsiloxystyrene as a greenish-yellow oil (6.34 g, 18.1 mmol): ^{1}H NMR δ 0.30 (s, 9H), 6.75-7.85 (m, 5H); ^{13}C NMR δ 0.35, 89.74, 115.90, 119.75, 121.27, 129.23, 129.77, 133.83, 134.21; IR 3070, 3030, 2960, 1600, 1570, 1480, 1450, 1280, 1265, 1250, 1100, 915, 870, 840, 770, 750, 690 cm^{-1}; MS 352 (17) (M+4), 350 (32) (M+2), 348 (16) (M$^+$), 139 (90), 137 (90), 73 (100); calcd for $C_{11}H_{14}Br_2OSi$ m/e 347.91806, measured m/e 347.91742. Attempts to further purify the product by distillation or chromatography resulted in its decomposition.

Synthesis of o-(trimethylsilylethynyl)phenol, 134

A solution of β,β-dibromo-o-trimethylsilylstyrene (2.86 mmol) in dry THF (20 mL) was cooled to -78°C. A solution of n-butyllithium in hexane (7.4 mmol, 2.3 M) was then added dropwise. After complete addition, the dark green solution was stirred for 1 h at -78°C, warmed to room temperature, and stirred 4 h longer. The solution was added to water saturated with NH_4Cl and extracted with three 25 mL portions of Et_2O. The organic portion was then washed with H_2O and dried over $MgSO_4$. After filtration and removal of solvent, the residual oil was purified by column chromatography on a silica gel column eluted with

1:9 hexane/ethyl acetate. A solid was isolated which after sublimation (0.1 torr, 50°C) gave pure **134**, 0.41 g (75%): mp 46-47°C; ^{1}H NMR δ 0.26 (s, 9H), 5.98 (s, 1H), 6.58-7.41 (m, 4H); ^{13}C NMR δ -0.026, 99.00, 109.51, 114.55, 120.18, 130.64, 131.61, 131.88, 157.13; IR (KBr pellet) 3250, 2960, 2870, 2150, 1600, 1480, 1450, 1290, 1245, 1060, 865, 840, 750 cm^{-1}; MS 190 (22), 175 (100), 159 (18), 135 (13), 115 (17); calcd for $C_{11}H_{14}OSi$ m/e 190.08140, measured m/e 190.08139. Anal. Calcd for $C_{11}H_{14}$: C, 69.42; H, 7.41. Found: C, 69.28; H, 7.50. This reaction gave poor yields (5-25%) in subsequent attempts.

FVP of o-(hydroxytrimethylsilyl)phenylacetylene, **134**

(i) Compound **134** (41 mg) was pyrolyzed at 480°C (1 X 10^{-2} torr). A sample of the pyrolysate (34 mg, 83%) was analyzed by ^{1}H NMR and found to contain starting material, **134**, o-trimethylsiloxyphenylacetylene, **137**, and 3-trimethylsilylbenzofuran, **136**, in ratios of 84.9:11.9:3.1. Identification of the products was made, after isolation by preparative GC (10 ft X 0.25 in. 15% SE-30 on Chromosorb W at 185°C), by comparison of ^{1}H NMR, ^{13}C NMR, IR, and GC/MS spectra with synthetic samples.

(ii) Compound **134** (53 mg) was pyrolyzed at 540°C (1 X 10^{-2} torr). A sample of the pyrolysate (50 mg, 94%) was analyzed by ^{1}H NMR and found to contain **134**, **137**, and **136** in ratios of 40.8:40.8:18.4.

(iii) Compound **134** (41 mg) was pyrolyzed at 650°C (1 X 10^{-2} torr). A sample of the pyrolysate (32 mg, 78%) was analyzed by ^{1}H NMR and found to contain **137**, 2-trimethylsilybenzofuran, **138**, and **136** in ratios of 50.1:18.8:31.1. Compound **138** was identified as a mixture with the 3-isomer, **136**, after preparative GC (10 ft X 0.25 in. 15% SE-30 on Chromosorb W at 185°C), by comparison of the ^{1}H NMR, ^{13}C NMR, IR, and GC/MS with a synthetic sample of **138**.

(iv) Compound **134** (41 mg) was pyrolyzed at 700°C (1 X 10^{-2} torr). A sample of the pyrolysate (30 mg, 73%) was analyzed by ^{1}H NMR and found to contain **137**, **138**, and **136** in ratios of 37.4:27.6:35.0.

(v) Compound **134** (56 mg) was pyrolyzed at 750°C (1 X 10^{-2} torr). A sample of the pyrolysate (51 mg, 91%) was analyzed by ^{1}H NMR and found to contain **137**, **138**, and **136** in ratios of 34.4:29.7:35.9.

(vi) Compound **134** (29 mg) was pyrolyzed at 800°C (1 X 10^{-2} torr). The pyrolysate was collected (22 mg, 76%), and a sample analyzed by ^{1}H NMR revealed **137**, **138**, and **136** in ratios of 36.7:28.4:34.9.

(vii) Compound **134** (80 mg) was pyrolyzed at 700°C at 1 X 10^{-5} torr instead of 1 X 10^{-2} torr. The pyrolysate was collected (74 mg, 92%), and a sample was analyzed by ^{1}H NMR. Compounds 137, 138, and **136** were found to be present in ratios of 43.4:20.3:36.3.

(viii) Compound **134** (43 mg) was pyrolyzed at 750°C (1 X 10^{-2} torr) through a pyrolysis tube which was washed with dilute acid and rinsed with distilled water. The pyrolysate was collected (41 mg, 95%), and a sample was analyzed by ^{1}H NMR. Compounds **137**, **138**, and **136** were found to be present in ratios of 37.0:27.6:35.3.

(ix) Compound **134** (43 mg) was pyrolyzed at 750°C (1 X 10^{-2} torr) through a pyrolysis tube which was washed with ethanolic KOH and rinsed with distilled water. The pyrolysate was collected (37 mg, 86%), and a sample was analyzed by ^1H NMR. Compounds **137**, **138**, and **136** were found to be present in ratios of 36.1:36.5:27.4.

Synthesis of 3-trimethylsilylbenzofuran, 136

3-Bromobenzofuran (7.42 mmol), prepared by the method of Stoermer and Kahlert (99), was dissolved in 35 mL of Et_2O and cooled to -115°C. A solution of n-butyllithium in hexane (7.43 mmol, 2.5 M) was slowly added dropwise followed by stirring at -115°C for 1 h. Trimethylchlorosilane (8.9 mmol) was then added dropwise, keeping the reaction temperature below -100°C at all times. The mixture was slowly warmed to room temperature over a 3 h period, and then extracted with additional Et_2O and aqueous NaCl. After drying with $MgSO_4$, followed by removal of the drying agent and solvent, the residue was chromatographed on silica gel eluted with hexane/ethyl acetate 9:1. A 31% yield (2.31 mmol) of **134** was obtained. In addition, 0.84 mmol (11%) of 3-trimethylsilylbenzofuran, **136**, was isolated from a second chromatographed sample after preparative GC on a 10 ft X 0.25 in. 15% SE-30 Chromosorb W column at 200°C: ^1H NMR δ 0.35 (s, 9H), 7.15-7.71 (m, 5H), included within the multiplet was a singlet at δ 7.47 which was assigned to the vinyl hydrogen adjacent to silicon on the furan ring; ^{13}C NMR δ -0.72, 111.36, 120.15, 121.99, 122.49, 124.03, 131.22, 149.56, 155.87; IR 3070, 2970, 1520, 1450, 1265, 1255, 1110, 1080, 1005, 835, 765, 745 cm^{-1}; MS 190 (23), 176 (19), 175 (100), 145 (5), 135 (5), 115 (6), 101 (4), 87 (9); calcd for

$C_{11}H_{14}OSi$ m/e 190.08140, measured m/e 190.08079. Anal. Calcd for $C_{11}H_{14}$: C, 69.42; H, 7.41. Found: C, 69.14; H, 7.24. A small amount (10%) of o-(trimethylsiloxy)trimethylsilylphenylacetylene was also obtained after preparative GC of the mixture obtained after column chromatography: ^1H NMR δ 0.24 (s, 9H), 0.28 (s, 9H), 6.75-7.50 (m, 4H); IR 3080, 3040, 2970, 2920, 2170, 1600, 1570, 1490, 1450, 1390, 1255, 1105, 920, 870, 840, 760 cm^{-1}; MS 262 (51), 248 (17), 247 (68), 231 (21), 207 (16), 193 (15), 73 (100); calcd for $C_{14}H_{22}OSi_2$ m/e 262.12093, measured m/e 262.12069. The procedure for lithium-bromine exchange used here was the same as that described by Cugnon de Sevricourt and Robba (100) who obtained 3-benzofuran carboxylic acid in 62%.

FVP of 3-trimethylsilylbenzofuran, **136**

(i) Compound **136** (38 mg), distilled (1 X 10^{-2} torr) from a bath at 40°C, was pyrolyzed at 700°C. The pyrolysate was collected (36 mg, 96%) and analyzed by ^1H NMR. Only starting material was present.

(ii) Compound **136** (40 mg) was pyrolyzed at 800°C (1 X 10^{-2} torr). Analysis of the pyrolysate (33 mg, 82%) by ^1H NMR revealed o-(trimethylsiloxy)phenylacetylene, **137**, 2-trimethylsilylbenzofuran, **138**, and starting material in ratios of 20.7:10.4:68.9. Products were further characterized, after separation of **137** from **136** and **138** by preparative GC (10 ft X 0.25 in. 15% SE-30 on Chromosorb W at 185°C), by comparison of ^1H NMR, IR, and GC/MS with authentic samples.

Synthesis of o-(trimethylsiloxy)phenylacetylene, **137**

The synthesis of **137** began with the synthesis of benzofuran (101) which was then converted to o-hydroxyphenylacetylene (102) followed by protection of the hydroxyl group as the trimethylsilyl ether (103).

FVP of o-(trimethylsiloxy)phenylacetylene, **137**

(i) Compound **137** (45 mg), distilled (1 X 10^{-2} torr) from a bath at 40°C, was pyrolyzed at 540°C. The pyrolysate (43 mg, 96%), analyzed by ^{1}H NMR, consisted only of starting material.

(ii) Compound **137** (57 mg) was pyrolyzed at 700°C (1 X 10^{-2} torr). Analysis of the pyrolysate (55 mg, 96%) by ^{1}H NMR revealed 2-trimethylsilylbenzofuran, **138**, and starting material in ratios of 39.4:60.6. Product identification was confirmed, after separation by preparative GC (10 ft X 0.25 in. 15% SE-30 on Chromosorb W at 185°C), by comparison of ^{1}H NMR, IR, and GC/MS with authentic samples.

(iii) Compound **137** (53 mg) was pyrolyzed at 750°C (1 X 10^{-2} torr). Analysis of the pyrolysate (50 mg, 94%) by ^{1}H NMR revealed 3-trimethylsilylbenzofuran, **136**, 2-trimethylsilylbenzofuran, **138**, and starting material in ratios of 11.8:38.4:49.8. The presence of **136** was confirmed, after separation from **137** by preparative GC (10 ft X 0.25 in. 15% SE-30 on Chromosorb W at 185°C), by comparison of ^{1}H and ^{13}C NMR spectra with those from an authentic sample.

(iv) Compound **137** (63 mg) was pyrolyzed at 800°C (1 X 10^{-2} torr). Analysis of the pyrolysate (57 mg, 88%) by ^{1}H NMR revealed

3-trimethylsilylbenzofuran, **136**, 2-trimethylsilylbenzofuran, **138**, and starting material in ratios of 31.2:20.2:48.6.

Synthesis of 2-trimethylsilylbenzofuran, 138

This compound was synthesized according to the procedure of Eaborn and Seconi (104).

FVP of 2-trimethylsilylbenzofuran, 138

(i) Compound **138** (216 mg), distilled (1 X 10^{-2} torr) from a bath at 40°C, was pyrolyzed at 700°C. Analysis of the pyrolysate (202 mg, 93.5%) by ^{1}H NMR revealed o-(trimethylsiloxy)phenylacetylene, **137**, and starting material in a ratio of 64.9:35.1. Identification of **137** and **138** was made, after separation by preparative GC (10 ft X 0.25 in. 15% SE-30 on Chromosorb W at 185°C), by comparison of ^{1}H NMR, IR, and GC/MS data with that obtained from authentic samples.

(ii) Compound **138** (43 mg) was pyrolyzed at 750°C (1 X 10^{-2} torr). Analysis of the pyrolysate (39 mg, 91%) by ^{1}H NMR revealed o-(trimethylsiloxy)phenylacetylene, **137**, 3-trimethylsilylbenzofuran, **136**, and starting material in ratios of 46.7:8.6:44.7.

(iii) Compound **138** (50 mg) was pyrolyzed at 800°C (1 X 10^{-2} torr). Analysis of the pyrolysate (42 mg, 84%) by ^{1}H NMR revealed compounds **136**, **137**, and **138** in ratios of 21.9:45.1:32.9. Product identification was confirmed, after separation of **137** from **136** and **138** by preparative GC (10 ft X 0.25 in. 15% SE-30 on Chromosorb W at 185°C), by comparison of ^{1}H and ^{13}C NMR, IR, and GC/MS data with spectra obtained from authentic samples.

Synthesis of o-hydroxyphenylacetylene, **131**

Compound **131** was prepared from benzofuran according to the procedure published by Prey (102).

FVP of o-hydroxyphenylacetylene, **131**

(i) Compound **131** (73 mg), distilled (1 X 10^{-2} torr) from a bath at 0°C, was pyrolyzed at 750°C. Analysis of the pyrolysate (52 mg, 71%) by ^{1}H NMR and GC revealed benzofuran (71%, GC yield), **133**, as the sole product. Identification was made by comparison of ^{1}H NMR, IR, and GC/MS data with that from an authentic sample.

(ii) Compound **131** (53 mg) was pyrolyzed at 650°C (1 X 10^{-2} torr). Analysis of the pyrolysate (39 mg, 74%) by ^{1}H NMR revealed benzofuran, **133**, and starting material in a ratio of 93:7.

(iii) Compound **131** (67 mg) was pyrolyzed at 540°C (1 X 10^{-2} torr.) Analysis of the pyrolysate (62 mg, 93%) by ^{1}H NMR and GC revealed **133** and **131** present in a ratio of 71:29 (determined by GC).

Synthesis of 4,5-dihydro-2-trimethylsilylfuran, **142**

Compound **142** was prepared from 2,3-dihydrofuran (Aldrich Chemical Co.) according to a procedure published by Erchák et al. (105).

FVP of 4,5-dihydro-2-trimethylsilylfuran, **142**

(i) Compound **142** (224.6 mg), distilled (1 X 10^{-4} torr) from a bath warmed slowly from -10 to 0°C, was pyrolyzed at 650°C. The pyrolysate was collected (198.1 mg, 88.2%), and the products were separated by preparative GC (9 ft X 0.25 in. 15% SE-30 on Chromosorb W temperature programmed from 80-250°C at 3°C per min). From the pyrolysate, 4-trimethylsiloxy-1-butyne, **144**, trimethylsilylketene, **147**, and 2-trimethylsiloxy-1,3-butadiene, **133**, were obtained in 49%, 33%, and 5% yield (by GC), respectively. Compound **144** was identified by comparison of its spectra with an authentic sample: ^{1}H NMR δ 0.12 (s, 9H), 1.96 (t, 1H, J = 2.6 Hz), 2.40 (d of t, 2H, J = 7.1 and 2.6 Hz), 3.70 (t, 2H, J = 7.1 Hz); IR 3320, 2965, 2930, 2890, 2130, 1390, 1255, 1100, 1060, 915, 870, 840, 750 cm^{-1}; GC/MS 127 (47), 109 (14), 103 (75), 97 (62), 75 (13), 73 (100). **147:** ^{1}H NMR δ 0.17 (s, 9H), 1.79 (s, 1H); ^{13}C NMR δ -0.06, 0.68, 179.51; IR 3370, 3050, 2970, 2910, 2115, 1270, 1250, 1050, 840 cm^{-1}; GC/MS 114 (21), 99 (100), 73 (7), 69 (7), 55 (7); spectra obtained for **147** matched published spectra (106-108). **133:** ^{1}H NMR δ 0.24 (s, 9H), 4.35 (s, 1H), 4.36 (s, 1H), 5.09 (d of t, 1H, J = 10.4 and 1.6 Hz), 5.47 (d of d, 1H, J = 17.0 and 1.8 Hz), 6.20 (d of d, 1H, J = 17.0 and 10.4 Hz); ^{13}C NMR δ 0.07, 96.45, 114.57, 134.67, 154.92; IR 3130, 3110, 3030, 2980, 2920, 1640, 1595, 1410, 1380, 1260, 1060, 1010, 985, 920, 880, 845, 750 cm^{-1}; GC/MS 142 (25), 127 (77), 111 (5), 99 (7), 85 (53), 75 (100), 73 (33), 61 (11), 59 (12). The ^{1}H NMR was consistent with that reported in the literature (109).

(ii) Compound **142** (174.6 mg) was also pyrolyzed at 600°C (4 X 10^{-5} torr). The pyrolysate was collected (164.6 mg, 94.3%) and analyzed by GC and NMR. Compounds **144**, **147**, and **133** were determined (by GC) to be present in 54%, 34%, and 5% yield, respectively, based on 13% recovered starting material.

FVP of 2,3-dihydrofuran

(i) A sample of 2,3-dihydrofuran (334.5 mg), distilled (2 X 10^{-5} torr) from a bath warmed slowly from -30 to 0°C, was pyrolyzed at 700°C. The pyrolysate was collected (272.8 mg, 81.6%) and products were isolated by preparative GC on a 9 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 80-250°C at 6°C per min. The products were identified by comparison of ^{1}H NMR and GC/MS with authentic samples as cyclopropanecarboxaldehyde, cis-, and trans-crotonaldehyde in a 1:1 ratio in 39% and 26% yield based on 44% recovered starting material. The flow pyrolysis of 2,3-dihydrofuran has already been reported and gave the same products (70).

(ii) A sample of 2,3-dihydrofuran (250.6 mg), distilled (2 X 10^{-5} torr) from a bath warmed slowly from -30°C to 0°C, was pyrolyzed at 600°C. The pyrolysate (223.2 mg, 89.1%) was analyzed by GC and ^{1}H NMR and was found to contain cyclopropanecarboxaldehyde (24%) and recovered starting material (83%).

Synthesis of 4-trimethylsilyl-3-butyn-1-ol, 137

The hydroxyl group of 3-butyne-1-ol was protected as the tetrahydropyranyl ether in 52% yield using the general procedure of Robertson (97). A solution of this butynyl ether (37.0 mmol in 75 mL Et_2O) was cooled to -78°C, and a solution of n-butyllithium (44.4 mmol, 2.5 M in hexane) was added rapidly. After 15 min at -78°C, the solution was warmed to room temperature and stirred for 30 min. The solution was then cooled to 0°C, and chlorotrimethylsilane (51.8 mmol) was added dropwise. The resulting suspension was stirred for 30 min at room temperature and then added to H_2O and extracted. The etheral layer was dried over anhydrous K_2CO_3, and the solvent was removed using a rotary evaporator. The crude product was added to 75 mL of MeOH followed by a small amount of p-toluenesulfonic acid. After 25 min, no starting material remained, as determined by TLC, and a small amount of K_2CO_3 was added. Extraction of the reaction mixture with pentane and H_2O, drying ($MgSO_4$), and removal of the solvent gave a clear liquid which was distilled (bp 72-76°C, 13 torr) to give **155** in 58% yield. This compound has previously been prepared by Shostakovskii et al. (110).

FVP of acetylene 137

A sample of **137** (102.3 mg), distilled (1 X 10^{-4} torr) from a bath at 10-30°C, was pyrolyzed at 700°C. The pyrolysate (91.1 mg, 89%) consisted of a white solid and a clear liquid. The solid was determined to be paraformaldehyde by comparison of its IR spectrum, mp, and mixed mp with an authentic sample. The liquid was analyzed by GC, GC/MS, and ^{1}H NMR and was found to consist of trimethylsilylallene and 3-trimethylsilylpropyne formed in 80% and 16% yield (NMR), respectively. Identification was confirmed by comparison with authentic samples. FVP at 650°C or lower gave starting material as the only other identifiable product present.

FVP of 3-butyn-1-ol

A sample of 3-butyn-1-ol (227.0 mg), distilled (1 X 10^{-4} torr) from a bath warmed from 0-25°C, was pyrolyzed at 700°C. The pyrolysate was analyzed by GC/MS, IR, and ^{1}H NMR and was found to contain only allene as has previously been demonstrated (72).

FVP of trimethylsilyl(o-trimethylsiloxyphenyl)acetylene, **140**

Acetylene **140** (52 mg), distilled (1 X 10^{-2} torr) from a bath heated slowly from 25-85°C, was pyrolyzed at 750°C. The pyrolysate (48 mg, 92%) was analyzed by GC, ^{1}H NMR, and IR and was determined to be starting material. Compound **140** was obtained as a side product in the synthesis of 3-trimethylsilylbenzofuran.

Synthesis of acetylene **141**

Compound **141** was prepared from 3-butyn-1-ol as has previously been accomplished (111).

FVP of **141**

A sample of **141** (84 mg), distilled (1 X 10^{-2} torr) from a bath warmed slowly from 0-20°C, was pyrolyzed at 800°C. Analysis of the pyrolysate by GC revealed at least eight products all more volatile than **141**. Some starting material was still present. Pyrolysis at 700°C gave the same product distribution but at a lower conversion.

Synthesis of **142**

Acetylene **142** was prepared in Et_2O from 3-butyn-1-ol and chlorotrimethylsilane using N,N-dimethylaniline to remove HCl. This compound has previously been prepared by Shostakovskii and co-workers (112).

FVP of **142**

Acetylene **142** (132.4 mg), distilled (1×10^{-3} torr) from a bath at 0°C, was pyrolyzed at 800°C. The pyrolysate was analyzed by GC and was found to contain some starting material and more than a dozen other compounds in significant quantities. ^1H NMR revealed numerous silicon methyl resonances. Pyrolysis of **142** at 700°C gave mostly recovered starting material in addition to numerous other products in small quantities.

Synthesis of β,β-dibromo-o-methoxystyrene

Triphenylphosphine (76.98 mmol) was added to a stirring solution of carbon tetrabromide (38.49 mmol) in 100 mL of dry CH_2Cl_2 under N_2 cooled to 0°C (89). After 15 min, o-anisaldehyde (38.49 mmol) was added rapidly. The reaction was complete in 15 min and was slowly poured into 1.5 L of stirring hexane. The supernatant liquid was decanated, and solvent was removed using a rotary evaporator. The triphenylphosphine oxide was removed by filtration and washed with additional hexane. Solvent was removed from the filtrate, and the oil was chromatographed on silica gel eluted with hexane/ethyl acetate

(9:1). After removal of solvent, the title compound (34.56 mmol, 90% yield) was obtained as a light yellow crystalline solid with mp 31-33°C: ^1H NMR δ 3.8 (s, 3H), 6.7-7.8 (m, 5H); ^{13}C NMR δ 55.5, 89.63, 101.55, 110.54, 120.18, 129.12, 129.93, 132.91, 156.59; IR 3040, 3020, 2980, 2950, 2850, 1600, 1580, 1485, 1465, 1440, 1290, 1250, 1110, 1050, 1025, 870, 810, 740 cm^{-1}; MS 294 (28) (M+4), 292 (55) (M+2), 290 (29) (M^+), 213 (35), 211 (36), 198 (55), 196 (57), 185 (16), 183 (16), 132 (85), 131 (100), 104 (32), 102 (22), 89 (96), 63 (44); calcd for $C_9H_8OBr_2$ m/e 289.89418, measured m/e 289.89452.

Synthesis of o-methoxyphenylacetylene, **143**

A solution of β,β-dibromo-o-methoxystyrene (14.94 mmol) in dry THF (90 mL) under N_2 was cooled to -78°C. A solution of n-butyllithium in hexane (31.4 mmol, 2.1 M) was then added dropwise resulting in a deep red solution which was stirred for 1 h at -78°C and 1 h at room temperature. Excess H_2O was then added, and the mixture was extracted with 75 mL of Et_2O, washed with more H_2O, and dried with $MgSO_4$. After removal of the drying agent and solvent, the residual oil was distilled (80-82°C, 1 torr) to give **143** (10.76 mmol, 72%): ^1H NMR δ 3.3 (s, 1H), 3.9 (s, 3H), 6.8-7.6 (M, 4H); MS 132 (100), 131 (91), 89 (37), 77 (12), 63 (27), 62 (12), 51 (11); GC/IR 3330, 3080, 3010, 2950, 2840, 2110, 1610, 1490, 1440, 1260, 1215, 1110, 1040 cm^{-1}.

FVP of o-methoxyphenylacetylene, **143**

Compound **143** (131.0 mg), distilled (2 X 10^{-5} torr) from a bath at 50°C, was pyrolyzed at 700°C. The pyrolysate was collected (90.0 mg, 68.7%), and the products were isolated by preparative GC on a 10 ft X 0.25 in. 15% SE-30 Chromosorb W Column temperature programmed from 100-250°C at 6°C per min. The isolated products, phenylacetylene (1%), styrene (5%), benzofuran (23%), **133**, and 2-methylbenzofuran (7%), **147**, were identified by comparison of GC/MS and ^{1}H NMR spectra with authentic material. Yields were determined by GC analysis and based on 14% recovered starting material.

Synthesis of 1,2-benzopyran, **145**

Compound **145** was prepared according to the procedure described by Iwai and Ide (113) by the sequence phenol → phenylpropargyl ether → 1,2-benzopyran.

FVP of 1,2-benzopyran, **145**

Compound **145** (201.2 mg), distilled (2 X 10^{-5} torr) from a bath heated slowly from 25-50°C over a 40 min period, was pyrolyzed at 700°C. Analysis of the pyrolysate (187.4 mg, 93.1%) by ^{1}H NMR and GC showed **145** unreacted (77%, by GC) and eight minor products present in low yield, but no 2-methylbenzofuran, **147**, or benzofuran, **133**.

Synthesis of 2-methylbenzofuran, **147**

The procedure of Baciocchi et al. (114) was used to prepare 2-methylbenzofuran from benzofuran.

FVP of 2-methylbenzofuran, **147**

Compound **147** (114.9 mg) was pyrolyzed under the same conditions as **143** at 700°C (2 X 10^{-5} torr). Only starting material was recovered (110.1 mg, 95.8%).

Synthesis of o-methoxyphenyl-1-propyne, **148**

A solution of β,β-dibromo-o-methoxystyrene (22.8 mmol) in dry THF (140 mL) under N_2 was cooled to -78°C. A solution of n-butyllithium in hexane (47.9 mmol, 2.4 M) was then added dropwise resulting in a deep red solution which was stirred for 1 h at -78°C and 1 h at room temperature. Dimethylsulfate (27.3 mmol) was added dropwise followed by stirring for 2 h. The reaction mixture was poured into 100 mL of H_2O and extracted with pentane. The organic layer was washed with several portions of H_2O and dried with $MgSO_4$. The drying agent was removed by gravity filtration, and solvent was removed using a rotary evaporator. The residual oil was distilled (115-117°C, 9 torr) to yield **148** (16.76 mmol, 74%): ^1H NMR δ 2.11 (s, 3H), 3.87 (s, 3H), 6.80-6.95 (m, 2H), 7.23 (d of t, 1H, J = 7.8 and 1.6 Hz), 7.37 (d of d, 1H, J = 7.5 and 1.6 Hz).

FVP of o-methoxyphenyl-1-propyne, **148**

(i) Acetylene **148** (117.7 mg), distilled (2 X 10^{-5} torr) at room temperature, was pyrolyzed at 700°C. The pyrolysate (85.3 mg, 72.5%) was analyzed by GC and found to contain five products which were isolated by preparative GC on a 9 ft X 0.25 in. 15% SE-30

Chromosorb W column temperature programmed from 100-250°C at a rate of 6°C per min. The products were identified as 2-methylbenzofuran (29%), **147**, 2-ethylbenzofuran (15%), **149**, and a mixture of o- and m- or p-methylstyrenes (9%) in approximately equal amounts. The yields were determined by GC analysis and based on 9% recovered starting material. Products were identified by comparison of the ^{1}H NMR and GC/MS spectra with authentic materials.

(ii) Pyrolysis of **148** (186.5 mg) at 650°C, 1 X 10^{-4} torr, produced a pyrolysate (151.6 mg, 81.3%) consisting of a mixture of o- and m- or p-methylstyrenes (11%), 2-methylbenzofuran (31%), and 2-ethylbenzofuran (11%). The yields were determined by GC analysis and were based on a 45% yield of recovered starting material.

(iii) Pyrolysis of **148** (198.6 mg) at 750°C, 1 X 10^{-4} torr, produced a pyrolysate (139.8 mg, 70.4%) consisting of a mixture of o- and m- or p-methylstyrenes (19%), 2-methylbenzofuran (29%), and 2-ethylbenzofuran (10%). No starting material was recovered. The yields were determined by GC analysis.

Synthesis of 2-ethylbenzofuran, **149**

The preparation of compound **149** was carried out by the sequence salicaldehyde → 2-acetylbenzofuran → 2-ethylbenzofuran according to published procedures (115).

FVP of 2-ethylbenzofuran, **149**

Pyrolysis of **149** (306.1 mg), distilled (2 X 10^{-5} torr) from a bath slowly heated from 25-60°C, was pyrolyzed at 700°C. The pyrolysate contained only 2-ethylbenzofuran (297.3 mg, 97.1%). However, pyrolysis of **149** (337.9 mg) at 800°C (2 X 10^{-5} torr) gave a pyrolysate (321.5 mg, 95.1%) containing **149** (80%), 2-methylbenzofuran (25%), **147**, and benzofuran (10%), **133**. Yields were determined by GC analysis and are corrected for recovered **149**. The products were identified by comparative GC/MS and ^{1}H NMR with authentic samples. Isolation of individual components was achieved by preparative GC on a 9 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 100-250°C at a rate of 6°C per min.

Synthesis of o-methoxy(trimethylsilyl)phenylacetylene, **178**

A solution of β,β-dibromo-o-methoxystyrene (18.68 mmol) in dry THF (110 mL) under N_2 was cooled to -78°C. A solution of n-butyllithium in hexane (39.22 mmol, 2.3 M) was then added dropwise which resulted in a deep red solution that was stirred for 1 h at -78°C and 1 h at room temperature. Trimethylchlorosilane (22.4 mmol) was then added rapidly, and the mixture was stirred for an additional 1 h. The product was extracted with 100 mL of Et_2O, washed with three 75 mL portions of H_2O, and dried with $MgSO_4$. After removal of the drying agent and solvent, the residual oil was distilled (72-74°C, 0.2 torr) yielding **178** (14.38 mmol, 77%): ^{1}H NMR δ 0.3 (s, 9H), 3.8 (s, 3H), 6.7-7.5 (m, 4H); ^{13}C NMR δ 0.08, 55.72, 98.30, 101.37, 110.76, 112.38, 120.29, 129.93, 134.11, 160.33; IR 3072, 3005, 2959, 2899, 2835, 2158, 1595, 1576, 1491, 1464, 1435, 1292, 1281, 1258, 1115, 1047, 1026, 866, 843, 752 cm^{-1}; MS 204 (52), 189 (100), 161 (38), 159 (35), 135 (8), 115 (45), 95 (17); calcd for $C_{12}H_{16}OSi$ m/e 204.09705, measured m/e 204.0952. Anal. Calcd for $C_{12}H_{16}$: C, 70.53; H, 7.89. Found: C, 70.46; H, 8.10.

FVP of o-methoxy(trimethylsilyl)phenylacetylene, **178**

(i) Compound **178** (131.2 mg), distilled (1 X 10^{-4} torr) from a bath heated from 80-120°C over a 1 h period, was pyrolyzed at 750°C. Only one major product was present and was isolated by preparative GC on a 9 ft X 0.25 in. 10% SE-30 Chromosorb W column temperature programmed from 180-250°C at 5°C per min. The product was determined to be 2-ethylbenzofuran (45%, by GC), **167**, by comparison of GC/MS, ^{1}H NMR, and ^{13}C NMR data with that from an authentic sample. Starting material (1%) was also recovered.

(ii) Pyrolysis of **178** (135.2 mg) at 700°C (1 X 10^{-4} torr) gave a pyrolysate (100.9 mg, 74.6%) primarily consisting of 2-ethylbenzofuran (42%, by GC), **167**, based on recovered starting material (12%).

(iii) Compound **178** (126.5 mg) was also pyrolyzed at 650°C (1 X 10^{-4} torr). The pyrolysate (101.2 mg, 80.0%) contained **167** (32%, by GC) based on 38% recovered **178**.

(iv) Pyrolysis of **178** (125.3 mg) at 600°C (1 X 10^{-5} torr) gave only recovered starting material (115.0 mg, 91.8%).

Synthesis of 2-methyl-3-trimethylsilylfuran, 181

Compound **181** was prepared using the procedure of Sato and Katsuno (116) from trimethylsilylpropargyl alcohol and acetonitrile. The product was purified by preparative GC on a 9 ft X 0.25 in. 20% SE-30 Chromosorb W column temperature programmed from 100-250°C at 5°C per min to give **181** in 28% yield: ^1H NMR δ 0.24 (s, 9H), 2.35 (s, 3H), 6.27 (d, 1H, J = 1.6 Hz), 7.32 (d, 1H, J = 1.6 Hz); ^{13}C NMR δ -0.42, 14.33, 112.04, 114.62, 140.19, 156.72; IR 2970, 1570, 1510, 1385, 1250, 1215, 1025, 890, 835, 755, 725 cm^{-1}; MS 154 (27), 139 (100), 111 (28), 109 (14), 99 (12), 83 (12), 73 (26), 69 (14), 65 (8), 61 (21), 59 (10), 53 (8); calcd for $C_8H_{14}OSi$ m/e 154.08140, measured m/e 154.08109. Anal. Calcd for C_8H_{14}: C, 62.28; H, 9.15. Found: C, 62.07; H, 9.20.

FVP of 2-methyl-3-trimethylsilylfuran, 181

Compound **181** (128.1 mg), distilled (1 X 10^{-5} torr) from a bath at 0°C, was pyrolyzed at 650°C. The pyrolysate (125.2 mg, 97.7%) contained only **181**. Pyrolysis of **181** (180.5 mg) at 800°C (1 X 10^{-3} torr) produced four products in addition to starting material. These products were isolated by preparative GC on a 9 ft X 0.25 in. 20% SE-30 Chromosorb W column temperature programmed from 100-250°C at 3°C per min. The products were identified as 1-trimethylsilyl-1,2-butadiene (9%), **182**, 1-trimethylsilyl-1-butyne (5%), **183**, cis-1-trimethylsiloxy-1-penten-3-yne (15%), **cis-184**, and trans-1-trimethylsiloxy-1-penten-3-yne (15%), **trans-184**. Yields were determined by GC analysis and based on 45% recovered starting material. Compounds cis-**184** and trans-**184** were identified by comparison of ^{1}H NMR and GC/MS data obtained from the FVP of **190**. 1-Trimethylsilyl-1-butyne: ^{1}H NMR δ 0.14 (s, 9H), 1.14 (t, 3H, J = 7.5 Hz), 2.23 (q, 2H, J = 7.5 Hz); GC/MS 126 (11), 111 (100), 109 (14), 83 (24), 78 (14), 59 (11), 55 (10), 53 (9). trans-**184**: ^{1}H NMR δ 0.19, (s, 9H), 1.90 (d, 3H, J = 2.3 Hz), 5.11 (d of q, 1H, J = 12.0 and 2.3 Hz), 6.72 (d, 1H, J = 12.0 Hz); ^{13}C NMR δ -0.47, 4.34, 75.42, 84.26, 92.91, 150.77; IR 3050, 2970, 2930, 2870, 2210, 1640, 1270, 1260, 1210, 1150, 885, 845, 750 cm^{-1}; MS 154 (42), 139 (45), 111 (23), 109 (11), 99 (9), 83 (9), 75 (8), 73 (100), 61 (19), 53 (9); calcd for $C_8H_{14}OSi$ m/e 154.08140, measured m/e 154.08137. Satisfactory elemental analysis could not be obtained for this compound.

Synthesis of cis-1-trimethylsilyl-4-methoxy-3-buten-1-yne, **190**

Compound **190** was prepared from cis-4-methoxy-3-buten-1-yne, **196**, (Aldrich Chemical Co.) after purification by extraction with H_2O and Et_2O, drying of the Et_2O layer with Na_2SO_4, and distillation (bp 122-125°C). A solution of n-butyllithium in hexane (45.0 mmol, 2.4 M) was added dropwise to **196** (44.4 mmol) in 110 mL of THF cooled to 0°C. After 20 min, trimethylchlorosilane (46.0 mmol) was rapidly added and stirred for 1 h. The mixture was poured into H_2O, extracted with pentane, and dried with $MgSO_4$. Solvent was removed by distillation at ambient pressure. The residual yellow liquid was distilled (25°C, 0.1 torr) into a flask cooled to -78°C. The product (32.4 mmol, 73%), which yellowed rapidly upon standing, could be further purified by preparative GC on a 9 ft X 0.25 in. 20% SE-30 Chromosorb W column at 125°C: ^{1}H NMR δ 0.17 (s, 9H), 3.76 (s, 3H), 4.54 (d, 1H, J = 6.5 Hz), 6.24 (d, 1H, J = 6.5 Hz); ^{13}C NMR δ 0.07, 60.63, 85.33, 97.62, 99.47, 157.09; IR 2970, 2140, 1635, 1455, 1385, 1270, 1250, 1110, 950, 840, 755, 725, 690 cm^{-1}; MS 154 (26), 139 (100), 109 (33), 83 (11), 69 (9), 59 (16); calcd for $C_8C_{14}OSi$ m/e 154.08140, measured m/e 154.08123. Anal. Calcd for C_8H_{14}: C, 62.28; H, 9.15. Found: C, 62.35; H, 9.39.

FVP of cis-1-trimethylsilyl-4-methoxy-3-buten-1-yne, **190**

Eneyne **190** (304.8 mg), distilled (8 X 10^{-4}torr) from a bath warmed slowly from 25-40°C, was pyrolyzed at 650°C. The pyrolysate was collected (175.5 mg, 57.6%), and the products were isolated by preparative GC using a 9 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 100-250°C at a rate of 5°C per min. Identified were 1-trimethylsilyl-1,2-butadiene (30%), **182**, and cis-1-trimethylsiloxy-1-penten-3-yne (7%), cis-**184**, based on 16% recovered starting material. Identification of **182** and cis-**184** was based on their spectra. **182**: ^{1}H NMR δ 0.08 (s, 9H), 1.16 (d of d, J = 7.0 and 4.0 Hz), 4.72 (overlapped d of q, apparent pentet, 1H, J = 7.0 and 7.0 Hz), 4.85 (m, 1H); ^{13}C NMR δ -0.85, 13.25, 77.80, 82.30, 210.96; IR 2970, 2930, 2900, 2870, 1945, 1365, 1250, 1195, 840, 755, 695 cm^{-1}; GC/MS 126 (16), 111 (10), 83 (26), 73 (100). cis-**184**: ^{1}H NMR δ 0.24 (s, 9H), 1.97 (poorly resolved d, 3H, J = 2 Hz), 4.60 (d of d, 1H, J = 2.3 and 6.0 Hz), 6.39 (d, 1H, J = 6.0 Hz); ^{13}C NMR δ -0.30, 4.65, 74.11, 88.87, 90.90, 147.92; IR 3040, 2970, 2930, 2870, 2220, 1630, 1440, 1410, 1270, 1255, 1165, 1085, 1070, 905, 840, 745 cm^{-1}; MS 154 (34), 139 (37), 111 (20), 99 (9), 83 (9), 75 (9), 73 (100), 61 (17); calcd for $C_8H_{14}OSi$ m/e 154.08140, measured m/e 154.08094. Anal. Calcd for C_8H_{14}: C, 62.28; H, 9.15. Found: C, 62.24; H, 9.24.

FVP of cis-4-methoxy-3-buten-1-yne, **196**

Compound **196** (410.0 mg), distilled (1 X 10^{-3} torr) from a bath at 0°C, was pyrolyzed at 650°C. The pyrolysate was collected at -196°C, and a portion of the most volatile components were transferred, using standard vacuum transfer techniques, to an NMR tube containing $CDCl_3$. An additional sample was utilized for GC/MS, and the remainder was transferred to a gas cell for IR analysis. Two major volatile components, 1-butyne and 1,2-butadiene, were identified spectroscopically. 1-Butyne: ^1H NMR δ 0.98 (t, 3H, J = 7.0 Hz), 1.85 (t, 1H, J = 2.7 Hz), 1.95 (d of q, 2H, J = 7.0 and 2.7 Hz); GC/MS 54 (96), 53 (44), 52 (11), 51 (24), 50 (30), 49 (10), 39 (100), 38 (21), 37 (13); IR (gas phase) 3360, 3340, 2140 cm^{-1}. 1,2-Butadiene: ^1H NMR δ 1.56 (overlapped d of t, 3H, J = 7.0 and 3.5 Hz), 4.65 (overlapped d of q, 2H, J = 7.0 and 3.5 Hz), 5.05 (m, 1H); GC/MS 54 (100), 53 (41), 52 (12), 51 (26), 50 (29), 49 (9), 39 (48), 38 (10), 37 (7); IR (gas phase) 1975 cm^{-1}. Although starting material was recovered (32%), none was present in the volatile samples examined by IR and NMR. The NMR spectra of both isomers were consistent with published data (117 as were the mass spectra (118).

Synthesis of o-(trimethylsiloxy)phenyl-1-propyne, **198**

The preparation of **198** was accomplished from 3-bromo-2-methylbenzofuran synthesized by the following sequence: benzofuran → 2-methylbenzofuran (114) → 2,3-dibromo-2-methylbenzofuran → 3-bromo-2-methylbenzofuran → 3-lithio-2-methylbenzofuran (119). The 3-lithio-2-methylbenzofuran was prepared from 3-bromo-2-methylbenzofuran (12.33 mmol) in Et_2O (60 mL) at -78°C by the slow addition of a solution of n-butyllithium in hexane (13.57 mmol, 2.4 M). After stirring 20 min at -78°C, the solution was slowly warmed to room temperature (2 h) and stirred an additional 2 h. Trimethylchlorosilane (14.79 mmol) was added rapidly and stirred for 12 h. Salts were removed by filtration and solvent was distilled off at ambient pressure. The residue was distilled (50°C, 0.1 torr) into a trap cooled to -78°C. This clear distillate was redistilled (93-97°C, 4 torr) to give **198** (2.12 mmol, 84%): ^1H NMR δ 0.28 (s, 9H), 2.07 (s, 3H), 6.80 (d, 1H, J = 8.1 Hz), 6.89 (t, 1H, J = 7.5 Hz), 7.14 (d of t, 1H, J = 8.2 and 1.3 Hz), 7.33 (unresolved d of d, 1H, J = 7.7 Hz); ^{13}C NMR δ 0.39 (t, J = 29 Hz), 4.42, 89.29, 114.91, 116.79, 120.24, 121.41, 128.63, 133.18, 156.33; IR 3071, 3032, 2959, 2916, 2233, 1597, 1568, 1489, 1445, 1283, 1264, 1254, 1107, 916, 845, 766, 741 cm^{-1}; MS 204 (39), 189 (61), 161 (33), 115 (100); calcd for $C_{12}H_{16}OSi$ m/e 204.09705, measured m/e 204.09728. Anal. Calcd for $C_{12}H_{16}$: C, 70.53; H, 7.89. Found: C, 70.74; H, 8.07.

FVP of o-(trimethylsiloxy)phenyl-1-propyne, **198**

(i) Compound **198** (150.4 mg), distilled (1 X 10^{-5} torr) from a bath heated from 60-80°C over a 20 min period, was pyrolyzed at 700°C. Only starting material was present in the pyrolysate (140.9 mg, 93.7%).

(ii) Pyrolysis of compound **198** (127.9 mg) at 800°C (2 X 10^{-4} torr) produced ten minor products in addition to recovered starting material which accounted for approximately two thirds of the total recovered pyrolysate (127.9 mg, 82.6%).

FVP of o-(trimethylsilyl)phenylacetylene, **199**

(i) Acetylene **199** was prepared according to the procedure of Hommes et al. (60). A sample (444.4 mg), distilled (1 X 10^{-4} torr) from a bath at 40°C, was pyrolyzed at 850°C. The pyrolysate was analyzed by GC and GC/MS and was found to contain several products which were separated by preparative GC on a 10 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 100-250°C at 5°C/min. Identified were indene (4%), 1,1-dimethyl-1-silaindene (6%), 3-methyl-1,1-dimethylsilaindene (5%), **203**, 2-methyl-1,1-dimethyl-1-silaindene (3%), **202**, 1,2-dihydro-1,1-dimethyl-3-methylene-1-silaindene (10%), **208**, 1,1-dimethyl-1-sila-1,4-dihydronaphthalene (4%), **211**, and 1,1-dimethyl-1-sila-1,2-dihydronapthalene (20%), **69**. The yields were determined by GC and are based on a 10% yield of recovered starting material. Indene and 1,1-dimethyl-1-silaindene were identified by comparison with authentic samples. The formation of 1,1-dimethyl-1-sila-1,2-dihydronapthalene was verified spectroscopically by comparison with the spectral data reported by Vuper (44). The other products were identified by their spectra. **202:** ^{1}H NMR δ 0.28 (s, 6H), 2.02 (d, 3H, J = 1.3 Hz), 6.88 (q, 1H, J = 1.3 Hz), 7.12-7.47 (m, 4H); ^{13}C NMR δ 149.59, 144.68, 142.80, 131.70, 129.76, 125.66, 123.35, 122.88, 17.39, -4.54; IR (gas phase) 3067, 2986, 1443, 1254, 1115, 887, 845, 798, 755, 748, 737 cm^{-1}; MS 174 (41), 160 (15), 159 (100), 143 (9), 131 (18), 105 (9), 53 (8); calcd for $C_{11}H_{14}Si$ m/e 174.08648, measured m/e 174.08638. **203:** ^{1}H NMR δ 0.38 (s, 6H), 2.23 (d, 3H, J = 1.3 Hz), 5.55 (q, 1H, J = 1.3 Hz), 7.10-7.50 (m, 4H); ^{13}C NMR δ 139.88, 131.30, 129.47 (two coincidental peaks), 127.88, 126.55, 121.26, 108.92, 19.65, -3.94; IR (gas phase) 3070, 1250, 1130, 855, 830, 815 cm^{-1}; MS 172 (34), 160 (16), 159 (100), 143 (6), 131 (8), 105 (6), 79 (4); calcd for $C_{11}H_{14}Si$ m/e 174.08648, measured m/e 174.08633. **208:** ^{1}H NMR δ 0.32 (s, 6H), 1.90 (d of d, apparent triplet, 2H, J = 1.9 Hz), 5.11 (m, 1H), 5.54 (m, 1H), 7.22-7.65 (m, 4H); ^{13}C NMR δ 149.63, 148.53, 141.57, 132.14, 129.61, 127.52, 121.93, 107.54, 21.85, -2.08; IR (gas phase) 3090, 3063, 3001, 2966, 1624, 1443, 1258, 1130, 879, 822, 791, 729 cm^{-1}; MS 174 (45), 160 (16), 159 (100), 143 (7), 133 (8), 131 (26), 105 (9), 53 (6); calcd for $C_{11}H_{14}Si$ m/e 174.08648, measured m/e 174.08661. **211:** ^{1}H NMR δ 0.26, (s, 6H), 3.66 (m, 2H), 6.03 (m, 1H), 6.90 (d of t, 1H, J = 3.9 and 14.5 Hz), 7.04-7.52 (m, 4H); ^{13}C NMR 145.76, 134.61, 133.34, 128.65, 128.40, 127.27, 126.07, 125.51, 36.48, -0.89; IR (gas phase) 3055, 3001, 2966, 1609, 1431, 1254, 1138, 849, 818, 779, 752, 737 cm^{-1}; GC/MS 174 (45), 160 (15), 159 (100), 143 (10), 131 (40), 115 (9), 105 (12), 59 (10), 53 (8).

(ii) Acetylene **199** (460.4 mg) was also pyrolyzed at 900°C (1 X 10^{-3} torr). The pyrolysate (242.3 mg, 55.6%) was analyzed and was found to contain indene (8%), 1,1-dimethyl-1-silaindene (9%), **203** (5%), **202** (3%), **208** (6%), **211** (2%), and **69** (8%) based on a 7% yield of recovered starting material. Yields were determined by GC analysis.

Synthesis of ^{13}C labeled (-O^{13}CH$_3$) o-ethynylanisole, 178

The hydroxyl group of o-hydroxyphenylacetylene (26.7 mmol) was selectively methylated using a mixture of CH_3I (6.9 mmol) and $^{13}CH_3I$ (2.3 mmol) in CH_3CN (35 mL) in the presence of KF on activity grade I alumina (10 mmol KF/1.0 g of alumina). After 8 h of stirring, the reaction was complete (monitored by TLC). The alumina was removed by filtration, and solvent was removed using a rotary evaporator. The product was then distilled (48-50°C, 0.5 torr) to give labeled **178** in 87% yield.

An excess of ethylmagnesium bromide, prepared from 27.7 mmol of ethylbromide and 39.9 mmol of Mg in 25 mL of Et_2O, was added slowly to labeled **178** (19.4 mmol) in 30 mL at Et_2O at 0°C. As the gray solution was allowed to warm to room temperature, it effervesced and turned milky white. After stirring for 2 h at room temperature, chlorotrimethylsilane (32.7 mmol) was added rapidly, and the reaction mixture was stirred an additional 3 h. The mixture was then hydrolyzed by addition to 100 mL of 0.2 M H_2SO_4, extracted with Et_2O, washed with

H_2O, and dried with $MgSO_4$. After removal of the $MgSO_4$ and solvent, the crude product was obtained in 86% yield contaminated with a small amount of starting material. Final purification was accomplished by preparative GC on an 8 ft X 0.25 in. 15% SE-30 Chromosorb W column at 230°C. The product was determined to be labeled at the $O^{13}CH_3$ group (δ 55.80) to the extent of 25% by comparison of its ^{13}C NMR with that of an unlabeled sample. The ^{1}H NMR showed a signal at δ 3.85 which showed strong doublet (J = 144.4 Hz) due to C-H coupling. Integration of the ^{13}C coupled satellites in the ^{1}H NMR indicated a 28% ^{13}C incorporation into the methoxy group.

FVP of ^{13}C labeled **178**

Pyrolysis of labeled **178** (287.0 mg), distilled (1 X 10^{-4} torr) from a bath at 90°C, at 700°C gave 2-ethylbenzofuran and recovered starting material. The label in the starting material was unscrambled and no change in the percent ^{13}C incorporation was seen. The 2-ethylbenzofuran, isolated by preparative GC on an 8 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 100-230°C at 6°C per min, was analyzed by GC/MS, ^{1}H NMR, and ^{13}C NMR. The MS appeared as expected for the ^{13}C enriched spectrum. The ^{1}H NMR revealed a strong C-H coupling for the triplet at δ 1.32 (J_{C-H} = 127.6 Hz, J_{CH-CH} = 7.6 Hz). A strong signal in the ^{13}C NMR at δ 11.90 was attributed to a label in the methyl group. This assignment was verified by taking the off resonance decoupled spectrum of an unlabeled sample of 2-ethylbenzofuran which showed a quartet at δ 11.73 (J = 60.6 Hz) confirming this assignment. Comparison of the ^{13}C labeled 2-ethylbenzofuran spectrum with that of unlabeled material revealed a 24% enhancement of the methyl resonance signal. Quantitation of the ^{1}H NMR ^{13}C-coupled satellites of the methyl group indicated a 27% ^{13}C incorporation into the 2-ethylbenzofuran. Both of these values are within the experimental error of their respective values measured for starting material and indicate no scrambling or loss of ^{13}C during the transformation of **178** to 2-ethylbenzofuran.

FVP of o-(hydroxydimethylsilyl)phenylacetylene, 102

A sample of **102** (125.2 mg), distilled (1×10^{-4} torr) from a bath heated slowly from 60-100°C, was pyrolyzed at 850°C. The pyrolysate (61.3 mg, 49%) was analyzed by GC and GC/MS and was found to contain a complex mixture of products which included **102** and two isomers. Because of the complex nature of the pyrolysate (>15 major products) further analysis was abandoned. Pyrolysis at 760°C and 650°C failed to improve the yield of any single product other than recovered starting material.

Synthesis of 4-dimethylsiloxy-1-butyne, 213

Compound **213** was prepared according to the general procedure of Mironov and co-workers (94).

FVP of 4-dimethylsiloxy-1-butyne, 213

Compound **213** (61.3 mg), distilled (3×10^{-4} torr) from a bath warmed slowly from -35-0°C, was pyrolyzed at 700°C. The pyrolysate

(49.4 mg, 80.6%) consisted of starting material (approximately 75%) and several other products which included a small amount (approximately 5%) of silapyran derivative **214** which was identified by comparison of its ^{1}H NMR spectrum with an authentic sample (120). Pyrolysis at temperatures up to 800°C failed to improve the yield of **214** and provided a complex mixture of products.

Synthesis of 2-dimethylsilyl-4,5-dihydrofuran, 215

The preparation of this compound has been reported by Lukevics and co-workers (121). Since the details of this preparation were not readily available, the procedure used to prepare 2-trimethylsilyl-4,5-dihydrofuran, **142**, was adapted to the preparation of **142** and is described here.

Metalation of 2,3-dihydrofuran (74.3 mmol) is accomplished by its addition to a solution of n-butyllithium (163 mmol, 2.3 M in hexane) in an equal volume of THF cooled to -23°C. After addition is complete, the reaction is warmed to 35°C at which temperature an exothermic reaction begins which maintains a temperature of 35-38°C (reaction pot temperature) without external heating. After the reaction subsides, the mixture is heated to 45°C for 1.5 h during which time gas evolution ceases. The orange solution is then cooled to -72°C and chlorodimethylsilane (196 mmol) is added at a rate which does not allow the reaction mixture to exceed -50°C. After addition is complete, the reaction is allowed to warm slowly to room temperature. The solvent and product are distilled (0.1 torr) into a receiver cooled to -78°C. The solvent is then removed by distillation at ambient pressure. The product (45%) is distilled at 74-75°C, 100 torr: ^{1}H NMR δ 0.21 (d, 6H, J = 3.6 Hz), 2.59 (d of t, 2H, J = 2.6 Hz and 9.6 Hz), 4.10 (h, 1H, J = 3.6 Hz), 4.28 (t, 2H, J = 9.6 Hz), 5.27 (t, 1H, J = 2.6 Hz); ^{13}C NMR δ 159.68, 112.36, 70.30. 30.63, -5.34 (J_{C-Si} = 26.8 Hz); IR 3088, 2963, 2916, 2885, 2856, 2133, 1595, 1250, 1099, 930, 891, 864, 837, 770, 729 cm^{-1}; MS 128 (32), 113 (33), 111 (35), 98 (14), 97 (13), 85 (24), 83 (38), 75 (9), 72 (13), 69 (16), 61 (14), 60 (100), 58 (14), 55 (11), 53 (11). Anal. Calcd for C_6H_{12}: C, 56.19; H, 9.43. Found: C, 56.05; H, 9.56.

If the reaction is not heated to 45°C after the initial reaction subsides, bis(dimethylsilyl)ketene, **226**, is formed which may constitute one half of the product mixture. Isolation of **226** is possible only after destroying **215** by FVP at 650°C. The identity of **226** was based upon its spectra: ^{1}H NMR δ 0.58 (d, 12H, J = 3.6 Hz), 4.61 (h, 2H, J = 3.6 Hz); ^{13}C NMR δ 165.97 (=C=O), -1.76 (Si-Me), -4.21 (C=•=O); MS 158 (20), 157 (14), 144 (10), 143 (63), 130 (32), 117 (11), 115 (47), 99 (21), 83 (38), 73 (100), 71 (11), 69 (22), 59 (48), 55 (10), 53 (10); calcd for $C_6H_{13}OSi_2$ m/e 157.0505, measured m/e 157.0504. Anal. Calcd for C_6H_{14}: C, 45.51; H, 8.91. Found: C, 45.10; H, 9.23.

<u>FVP of 215</u>

Compound **215** (294.8 mg), distilled (1 X 10^{-4} torr) at 0°C, was pyrolyzed at 650°C. The pyrolysate (246.9 mg), 83.8%) was analyzed by

GC and GC/MS. The products were isolated by preparative GC on a 14 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 70-230°C at 8°C per min. Identified were dimethylsilylketene (21%), **217**, 2-dimethylsiloxy-1,3-butadiene (4%), **218**, 4-dimethylsiloxy-1-butyne (41%), **219**, and 1-(3-butynyloxy)-1,1,3,3,3-pentamethyldisiloxane (8%), **225**. Spectra of the products, **217:** ^{1}H NMR δ 0.25 (d, 6H, J = 3.5 Hz), 1.84 (d, 1H, J = 2.7 Hz), 4.32 (broadened d of h, apparent octet, J = 3.4 Hz); ^{13}C NMR δ 178.96 (=C=O), -2.08 (SiMe), -2.27 (C=•=O); IR 3364, 3040, 2964, 2905, 2114, 1273, 1254, 1053, 883, 841 cm^{-1}; MS 100 (32), 99 (31), 86 (12), 85 (100), 72 (47), 69 (20), 59 (14), 55 (10), 53 (11); calcd for C_4H_8OSi m/e 100.0345, measured m/e 100.0341. Satisfactory elemental analysis could not be obtained for this unstable compound. **218:** ^{1}H NMR δ 0.32 (d, 6H, J = 3.2 Hz), 4.36 (broad s, 1H), 4.41 (broad s, 1H), 4.83 (h, 1H, J = 3.2 Hz), 5.08 (d, 1H, J = 10.5 Hz), 5.49 (d of d, 1H, J = 16.9 Hz), 6.19 (d of d, 1H, J = 10.5 Hz and 16.9 Hz); MS 128 (37), 127 (33), 114 (12), 113 (100), 87 (14), 85 (30), 75 (47), 71 (23), 69 (11), 61 (52), 59 (39), 53 (10), 50 (14). **219:** ^{1}H NMR δ 0.21 (d, 6H, J = 2.9 Hz), 1.97 (t, 1H, J = 2.6 Hz), 2.42 (d of t, 2H, J = 2.6 Hz and 7.0 Hz), 3.74 (t, 2H, J = 7.0 Hz), 4.62 (h, 1H, J = 2.9 Hz); MS 127 (2), 113 (25), 89 (78), 83 (20), 61 (11), 59 (100); calcd for $C_6H_{11}OSi$ m/e 127.0579, measured m/e 127.0581. **225:** ^{1}H NMR δ 0.09 (s, 6H), 0.19 (d, 6H, J = 2.7 Hz), 1.95 (t, 1H, J = 2.6 Hz), 2.41 (d of t, 2H, J = 2.6 Hz and 7.2 Hz), 3.76 (t, 2H, J = 7.2 Hz), 4.69 (h, 1H, J = 2.7 Hz); ^{13}C NMR δ 81.35, 69.45, 60.80, 22.70, 0.72, -1.17; IR 3314, 2962, 2920, 2880, 2125, 2080, 1259, 1109, 1065, 912, 862, 825, 798, 770, 650 cm^{-1}; MS 187 (25), 164 (10), 163 (60), 157 (25), 135 (19), 134 (15), 133 (100), 131 (12), 119 (13), 117 (10), 103 (10), 75 (10), 73 (23), 66 (11), 59 (23), 53 (11); calcd for $C_8H_{17}O_2Si_2$ m/e 201.07672, measured m/e 201.07677. Anal. Calcd for C_8H_{18}: C, 47.47; H, 8.96. Found: C, 47.50; H, 9.26.

Copyrolysis of bis(dimethylsilyl)ketene, **226**, and 2-(dimethylsilyl)-4,5-dihydrofuran, **215**

A mixture of **226** and **215** (1031.5 mg, 26.7:73.3), distilled (1 X 10^{-4} torr) at 0°C, was pyrolyzed at 650°C. The pyrolysate (891.5 mg, 86.4%) was analyzed by GC and GC/MS. The products were isolated by preparative GC on a 10 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 70-250°C at a rate of 8°C per minute. Identified were dimethylsilylacetylene (3%), dimethylsilylketene (17%), 4-dimethylsiloxy-1-butyne (27%), 2-dimethylsiloxy-1,3-butadiene (3%), bis(dimethylsilyl)ketene (15%), and 1-(4-butynyloxy)-1,1,3,3,3-pentamethyl-1,3-disiloxane (14%). The yields were determined by GC analysis. Dimethylsilylacetylene was identified by ^{1}H NMR and GC/MS: ^{1}H NMR δ 0.26 (d, 6H, J = 3.9 Hz), 2.41 (d, 1H, J = 1.0 Hz), 4.12 (d of h, 1H, J = 1.0 Hz and 3.9 Hz); GC/MS 84 (30), 83 (30), 70 (9), 69 (100), 68 (12), 67 (14), 66 (11), 59 (8), 58 (92), 55 (11), 53 (35).

Synthesis of dimethylsilyl(trimethylsilyl)ketene, 228

Preparation and dehydrohalogenation of 1-bromo-2-trimethylsiloxyethene was carried out according to the procedure of Pirrung and Hwu (122). The resultant anion was then quenched at -78°C with excess chlorodimethylsilane. The volatiles were distilled into a cooled receiver (-78°C) at 0.5 torr. The entire mixture was then distilled (50-125°C), and finally the solvent was removed by fractional distillation. The desired product was contaminated with diisopropylaminodimethylsilane and was not readily separable by preparative GC. However, this contaminant could be removed by treatment of the mixture with excess methyliodide in a sealed tube at 70°C for 14 h. The salts were removed by filtration, and the product was purified by preparative GC on a 10 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 100-250°C at 5°C per min. Ketene **228** was obtained in 11% yield. Spectra of **228**: ^1H NMR δ 0.20 (s, 9H), 0.26 (d, 6H, J = 3.5 Hz), 4.26 (h, 1H, J = 3.5 Hz); ^{13}C NMR 166.58, 0.97, -1.34, -1.53 (=C=O); IR 3361, 2959, 2901, 2077, 2031, 1408, 1292, 1254, 914, 843, 762, 692, 640, 629 cm^{-1}; MS 172 (12), 158 (16), 157 (100), 131 (16), 129 (10), 83 (37), 73 (84), 71 (14), 69 (11), 59 (36), 55 (9); calcd for $C_7H_{16}OSi_2$ m/e 172.07398, measured m/e 172.07366. Anal. Calcd for C_7H_{16}: C, 48.78; H, 9.36. Found: C, 48.95; H, 9.48.

FVP of **228**

Ketene **228** (26.7 mg), distilled (1×10^{-4} torr) from a bath at 0°C, was pyrolyzed at 700°C. The pyrolysate (21.6 mg) was analyzed by GC, GC/MS, GC/IR, and ^1H NMR. Identified from the pyrolysate were trimethylsilylacetylene (76%, NMR), hexamethylcylotrisiloxane (22%, GC), and octamethylcyclotetrasiloxane (16%, GC). The yields were based upon a 33% (NMR) yield of recovered starting material. The products were identified by comparison with authentic samples.

General procedure for the synthesis of bis(dimethylsilyl)- and bis(trimethylsilyl)ketene from 2,3-dihydrofuran

A solution of *n*-butyllithium (11.7 mmol, 2.5 M in hexane) was added slowly to THF (10 mL) at -23°C. The 2,3-dihydrofuran (10.6 mmol) was then added keeping the reaction temperature below -20°C. After 15 min, the mixture was warmed to 25°C and stirred for 24 h. The chlorosilane was then added to the reaction mixture, precooled to -70°C, while not allowing the temperature to exceed -60°C. After 15 min, the mixture was warmed to room temperature and stirred 45 min longer. The volatiles were then distilled (0.1 torr) into a receiver cooled to -70°C. Solvent was then removed by fractional distillation. When using chlorodimethylsilane, a 28% yield (by GC and NMR, 56% based on *n*-butyllithium as the limiting reagent) of bis(dimethylsilyl)ketene, **226**, was obtained along with a 19% yield of 2-dimethylsilyl-4,5-dihydrofuran. When using chlorotrimethylsilane, a 21% yield (42%, by GC based upon *n*-butyllithium) of bis(trimethylsilyl)ketene was obtained along with a 19% yield of 2-trimethylsilyl-4,5-dihydrofuran, **142**. When carrying out this reaction in Et_2O instead of THF, a 51% yield of 2-trimethylsilyl-4,5-dihydrofuran was obtained.

It was found the the yield of the ketene product could be improved by the addition of a second equivalent of n-butyllithium at -23°C, 24 h after the initial addition of n-butyllithium to 2,3-dihydrofuran, followed by stirring for 10 h at 25°C. Quenching the reaction mixture with chlorotrimethylsilane afforded a 33% yield of bis(trimethylsilyl)ketene and a 38% yield of **142**.

Metalation of 2,3-dihydrofuran was also attempted by its addition to a mixture of potassium t-butoxide and n-butyllithium (1 equivalent of each) in a mixture of THF and hexane (4:3) at -23°C. After 2 h at -23°C, the reaction was cooled to -70°C and quenched with chlorodimethylsilane to afford only **142**. If the reaction mixture was warmed to 20°C before cooling to -70°C followed by quenching, no ketene or dihydrofuran products were obtained. The reaction was also run using only hexane as the solvent. After stirring the reaction mixture for 2 h at -23°C and 1 h at 20°C, it was quenched at -70°C with chlorodimethylsilane to afford **142** and **226** in 17% and 13% yield, respectively.

Ketene **226** was identified previously in this work. Spectra of bis(trimethylsilyl)ketene matched those reported by Hoppe and Schöllkopf (77).

Synthesis of 2-silyl furans

Both 2-dimethylsilylfuran and 2-trimethylsilylfuran were prepared using the procedure described by Carman and Koser (123). Spectra matched those reported by Hussmann (65).

FVP of 2-dimethylsilylfuran, **230**

Compound **230** (159.3 mg), distilled (1 X 10^{-4} torr) from a bath warmed from -30°C to room temperature, was pyrolyzed at 800°C. Considerable decomposition occurred throughout the hot zone of the pyrolysis apparatus. The pyrolysate (103.8 mg, 65.2%) was analyzed by GC, GC/MS, and ^{1}H NMR. The products were isolated by preparative GC on a 10 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 60-250°C at a rate of 5°C per min. Identified by ^{1}H NMR, GC/IR, and GC/MS were 1,1-dimethyl-1-silacyclobut-2-ene (5%), dimethyl(2-propynyl)silane (2%), dimethyl(1,2-propadienyl)silane (5%), dimethyl(1-propynyl)silane (2%), 1,1-dimethyl-1-silapyran (15%), and starting material (15%). An unidentifiable isomer of **230** (7%), inseparable from 1,1-dimethyl-1-silapyran and starting material, was also obtained. Another isomer of **230** was present (8%) and was assigned the structure of 1,1-dimethyl-2-oxa-3-methylene-1-silacyclopent-3-ene (8%), **235**, based on its spectra: ^{1}H NMR δ 0.36 (s, 6H), 5.13 (m, 1H), 5.58 (apparent d, 1H, J = 2.4 Hz), 5.84 (apparent d, 1H, J = 3.4 Hz), 6.66 (m, 1H); ^{13}C NMR δ 151.22, 145.91, 116.32, 114.85, -0.80; IR (gas phase) 3063, 2963, 1558, 1258, 1184, 1030, 891, 864, 798 cm^{-1}; GC/MS 126 (54), 112 (10), 111 (100), 85 (28), 67 (5), 59

(7), 55 (6), 53 (6), 52 (6), 51 (6). This isomer, available only in minute quantities, was very unstable and readily decomposed during acquisition of the ^{13}C NMR spectrum. Further analysis was not possible.

While the identification of the silacyclobutene product and its isomers, all of which are known compounds (124-126), were based upon their spectra, silapyran **234** was identified by comparison with an authentic sample and published data (78). Yields were determined by ^{1}H NMR.

Synthesis of dimethyl(propargyl)silyl, **257**

Acetylene **257** was prepared from propargyl bromide using the procedure described by Slutsky and Kwart (50), but instead of quenching the reaction with chlorotrimethylsilane, chlorodimethylsilane was used. Carrying out this reaction in THF necessitates repeated extraction with water and pentane to remove the THF from the product. Final purification of the propargyl silane was accomplished by preparative GC on a 10 ft X 0.25 in. 15% SE-30 Chromosorb W column at 40°C.

FVP of **257**

A sample (149.2 mg), distilled (2 X 10^{-4} torr) from a bath warmed from -78°C to room temperature, was pyrolyzed at 800°C. The pyrolysate (99.1 mg, 66.4%) was analyzed by GC/MS and ^{1}H NMR and was found to contain dimethylsilylallene (9%), dimethyl(1-propynyl)silane (10%), and 1,1-dimethyl-1-silacyclobutene (20%) based on a 3% yield of recovered starting material. The products were identified by comparison of their spectra with those of the same products obtained from the pyrolysis of 2-dimethylsilylfuran.

FVP of 2-trimethylsilylfuran

A sample of 2-trimethylsilylfuran (158.7 mg), distilled (1×10^{-3} torr) at 25°C, was pyrolyzed at 800°C. Extensive decomposition occurred in the hot zone. The dark colored pyrolysate (119.3 mg, 75.2%) was analyzed by GC, GC/MS, and ^1H NMR. The major products were identified as trimethylsilylallene and 3-trimethylsilylpropyne by comparative MS and ^1H NMR. Also identified by comparative GC/MS and ^1H NMR was 1-trimethylsilylpropyne. Two isomers of starting material, inseparable from each other and starting material, were also present in low yield but were not identified.

Copyrolysis of phenylacetylene and 2-methyl-2-butene

Phenylacetylene (5.4 mmol) and 2-methyl-2-butene (53.7 mmol) were added dropwise, over a 40 min period, to a vertical N_2 flow (40 mL/min) pyrolysis apparatus heated to 490°C. The pyrolysate (nearly quantitative mass recovery) was analyzed by GC. Only 2-methyl-2-butene and phenylacetylene were present.

Copyrolysis of phenylacetylene and methanol

Phenylacetylene (5.4 mmol) and anhydrous methanol (53.6 mmol) were copyrolyzed by dropwise addition to a vertical N_2 flow (40 mL/min) pyrolysis apparatus at 600°C over a 40 min period. The pyrolysate (nearly quantitative mass recovery) was analyzed by GC. In addition to recovered phenylacetylene, a small amount of styrene (approximately 5%) was present. Identification was based upon the ^{1}H NMR spectrum of a mixture of styrene and phenylacetylene obtained by preparative GC on a 5 ft X 0.25 in. 20% SE-30 Chromosorb W column at 100°C. No other products were present.

Copyrolysis of trimethylsilylphenylacetylene, **75**, and methanol

Acetylene **75** (1.3-1.6 mmol) was copyrolyzed with methanol (15-17 mmol) at 500°C and 600°C by dropwise addition to a vertical N_2 flow (40 mL/min) apparatus. Analysis of the pyrolysate by GC revealed that only **75** and methanol were present.

Copyrolysis of phenylacetylene and triethylsilane

Phenylacetylene (5.0 mmol) and triethylsilane (30.6 mmol) were copyrolyzed at 600°C by dropwise addition to a vertical N_2 flow pyrolysis apparatus. Unlike previous attempts at intermolecular trapping, considerable decomposition occurred in the hot zone of this pyrolysis. Analysis of the pyrolysate by GC revealed the presence of three products. After isolation by preparative GC on a 9 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 100-250°C at a rate of 6°C per min, the products were identified as phenylacetylene (5%), styrene (6%), cis-β-diethylsilylstyrene (4%), **263**, and 1,1-diethyl-1-silaindene (14%), **261**. The yields were determined by GC analysis. Spectra of **263**: ^{1}H NMR δ 0.92 (m, 4H), 1.06 (t, 6H, J = 7.3 Hz), 4.56 (t, 1H, J = 3.2 Hz), 6.25 (d, 1H, J =

10.3 Hz), 7.20-7.37 (m, 4H), 7.43 (d, 1H, J = 10.3 Hz), 7.60 (d, 1H, J = 6.8 Hz); ^{13}C NMR δ 151.36, 132.81, 129.96, 128.07, 126.96, 124.32, 8.12, 2.75; IR 3053, 2997, 2955, 2874, 2124, 1591, 1524, 1439, 1124, 1084, 1011, 996, 837, 814, 781, 739, 708, 673 cm^{-1}; MS 160 (43), (M$^+$ - 30), 145 (11), 133 (12), 132 (75), 131 (100), 130 (16), 129 (13), 105 (71), 103 (10), 79 (8), 77 (8), 53 (26); calcd for $C_{10}H_{12}Si$ m/e 160.07083, measured m/e 160.07070. Satisfactory elemental analysis could not be obtained for this compound nor did the measured values match the formula $C_{10}H_{12}Si$. **261:** ^{1}H NMR δ 0.84 (m, 4H), 0.97 (complex t, 6H, J = 7.0 Hz), 6.22 (d, 1H, J = 10.4 Hz), 7.16-7.31 (m, 4H), 7.37 (d, 1H, J = 10.4 Hz), 7.51 (d, 1H, J = 6.8 Hz); ^{13}C NMR δ 150.23, 150.05, 136.62, 132.20, 130.32, 129.58, 126.63, 124.04, 7.80, 3.33; IR 3059, 2995, 2957, 2874, 1591, 1524, 1439, 1124, 1084, 1005, 787, 766, 731, 710 cm^{-1}; MS 188 (15), 160 (23), 159 (35), 132 (16), 131 (100), 130 (7), 129 (8), 105 (36), 53 (11); calcd for $C_{12}H_{16}Si$ m/e 188.10213, measured m/e 188.10225. Anal. Calcd for $C_{12}H_{16}$: C, 76.53; H, 8.56. Found: C, 76.58; H, 8.70.

Copyrolysis of 1,1-diethyl-1-silaindene, 261, and triethylsilane

Silaindene **261** (42.0 mg) was copyrolyzed with triethylsilane (173 mg) in a nitrogen flow. The pyrolysate (66.3 mg, 31%) was analyzed by GC/MS and was found to contain starting material (18%) and cis-β-diethylsilylstyrene (2%) by comparative MS. The yields were determined by GC analysis. The cause of the low mass recovery is unknown.

General procedure used for the photolysis of silyl substituted acetylenes

The photolyses were carried out using a 450 W Hanovia mercury arc lamp contained in a water cooled quartz well unless stated otherwise. The acetylenes were irradiated in quartz or Pyrex NMR tubes or in larger vessels placed adjacent to the UV light. The samples were degassed by purging with a stream of Ar prior to irradiation. The reactions were monitored either by GC or ^{1}H NMR and sometimes by both methods. The solvents were UV quality and were dried prior to use.

Photolysis of o-(trimethylsilylethynyl)toluene, 71

The photolysis of 71 was examined in cyclohexane, hexamethyldisiloxane, and acetonitrile at concentrations of 25 μL of 71 per 350 μL of solvent in quartz NMR tubes. The samples darkened during irradiation at rates directly proportional to the solvent polarity. Polymer formation occurred in each case and was accompanied by the formation of high molecular weight (m/e 240-376) products, possibly including some dimers, as determined by GC/MS analysis.

Irradiation of 71 in cyclohexane (2 μL of 71 in 2.0 mL of solvent) in a Pyrex NMR tube was also performed. The same results were obtained in this experiment.

The irradiation of 71 in cyclohexane (2 μL of 71 in 2.0 mL of solvent) using a Rayonet UV light source of 350 nm was also examined. Polymer formation again occurred and was accompanied by formation of the same high molecular weight products obtained in previous photolyses.

The UV spectrum of 71 in cyclohexane, λ_{max} (relative absorbance) 250 (1.58), 261 (1.46), 281 (0.09), 290 (0.08) nm.

Photolysis of o-(dimethylsilyl)phenylacetylene, **86**

The photolysis of **86** was examined in cyclohexane (at concentrations of 38 mg of **86** in 0.5 mL of solvent) in a quartz NMR tube. The photolysis was followed by GC and ^{1}H NMR. Only small amounts of products with exceedingly long retention times were present by GC. Only starting material was observed in the ^{1}H NMR. The sample rapidly discolored upon irradiation, and polymer formation was apparent.

The photolysis was also examined at low concentrations (1.8 mg of **86** per 2 mL of cyclohexane) in both quartz and Pyrex NMR tubes. Darkening of the sample, formation of high molecular weight products (up to 222 g/mole), and polymer formation again occurred. Irradiation of the sample in the pyrex tube led to the formation of an isomer and several products (all in low yield), probably derived from reduction of the triple bond. These compounds were not resolved by capillary GC, and their isolation or identification was not further examined.

The UV spectrum of **86** in cyclohexane, λ_{max} (relative absorbance) 240 (2.7), 250 (2.4), 270 (0.1), 280 (0.1), 290 (0.1) nm.

Photolysis of o-(trimethylsilylethynyl)phenyl, **134**

The photolysis of **134** was examined in cyclohexane at concentrations of 80-1.5 mg of **134** in 2 mL of solvent using both quartz and Pyrex NMR tubes. The most promising results were obtained at low concentration using the Pyrex tube. Using these conditions, the photolysis was scaled up to 50 mg of **134** in 80 mL of solvent. After 3 h of irradiation, the yields were determined and the solvent was removed under reduced pressure (29°C, 110 torr). The products were isolated by preparative GC using a 6 ft X 0.25 in. 15% SE-30 Chromosorb W column temperature programmed from 150-250°C at a rate of 6°C per min. Identified by comparative GC/MS and ^1H NMR were starting material (6% GC yield) and 2-trimethylsilylbenzofuran **138** (16% GC yield). Trace amounts of other products were present which appeared to be the result of reduction of the acetylene bond as determined by ^1H NMR and GC/MS data.

Irradiation of **134** (1 mg/1 mL cyclohexane) using a Rayonet UV source (350 nm) results in the formation of numerous products in trace quantities and was not further examined.

The UV spectrum of **134** in cyclohexane, λ_{max} (relative absorbance) 209 (0.56), 244 (0.30), 255 (0.31), 295 (0.12), 304 (0.12) nm.

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ACKNOWLEDGMENTS

I extend thanks to my colleagues of the Barton Group and to Dr. Philip M. Warner for stimulating discussions, helpful suggestions, and their friendship. I also thank Kathie Hawbaker whose skill and dedication greatly facilitated the final preparation of this dissertation.

This work has been accomplished under the supervision of Dr. Thomas J. Barton. His dedication to excellence in chemistry, his ability to direct a research group, and his sense of humor are truly inspirational. With discriminating guidance, he has provided me with the opportunity to pursue my doctoral degree. To him I am sincerely grateful.

I wish to thank my family for their support and confidence. Finally, I give special thanks to Cindy L. Johnson-Groh. With endless patience and understanding, she has provided constant support and friendship.