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A mechanistic study of the thermally-induced rearrangements of silylallenes in the gas phase

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Iowa State University, 1987

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A mechanistic study of the thermally-induced rearrangements of silylallenes in the gas phase

by

Larry Richard Robinson

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
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In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1987

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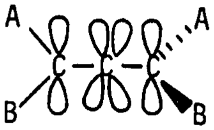
DEDICATION

To Kenneth and Loraine Robinson

HISTORICAL SECTION

Properties and Synthesis of Allenes and Silylallenes

Allenes, 1, comprise a class of compounds characterized by a 1,2-diene structure. The central carbon is sp-hybridized, with two sets of orthogonal p-orbitals available for bonding with the remaining p-orbitals of the two terminal sp^2-carbons. For maximum overlap to occur between the p- orbitals, the two π-bonds must be orthogonal to each other. As a result, substituents A and B lie in a plane at right angles to the plane of the adjacent π-bond.



1

van't Hoff in 1875 was the first to predict that unsymmetrically substituted allenes should exist in two enantiomeric forms (1). His prediction has been confirmed by various methods such as by resolution of an allenic acid with a variety of alkaloids and by synthesis with dissymmetric catalysts and reagents (2-6). Optically active allenes can be classified as either being asymmetric or dissymmetric. Asymmetric allenes have no element of symmetry and can be represented as an allene having three or four different types of achiral substituents, or as an allene containing one or two chiral groups. Allenes that possess a C_2 axis of rotation are defined as dissymmetric.

Dissymmetric allenes have either both ends of the allene bearing two different achiral groups or two configurationally and structurally identical groups, each containing one or more chiral centers.

Both asymmetric and dissymmetric allenes can exist in two enantiomeric forms. The configurational symbol for each enantiomer is assigned based on the Cahn, Ingold and Prelog nomenclature (7). The absolute configuration of allenic compounds can be assigned by chemically transforming the allene, via stereospecific reactions, to derivatives whose absolute configuration can be determined (8, 9).

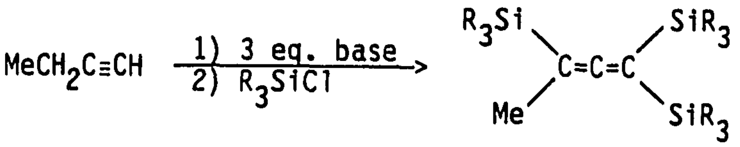
In 1887 Burton and Pechmann prepared the first allenic acid, but it was not until 1954 that its structure was confirmed (9, 10). The synthesis of a wide variety of allenes has been extensively reviewed and a detailed summary of methods is beyond the scope of this dissertation (11-13). Most allenes, however, are synthesized via one of five general methods: (1) rearrangements involving a carbene, (2) acetylene-allene rearrangement, (3) Wittig reaction, (4) 1,4-addition to 1,3-enynes, and (5) elimination methods.

Silylallenes are a relatively new class of compounds; however, they have recently found applicability as useful molecules in organic synthesis. Several reviews of the synthesis of silylallenes have been published (11-13).

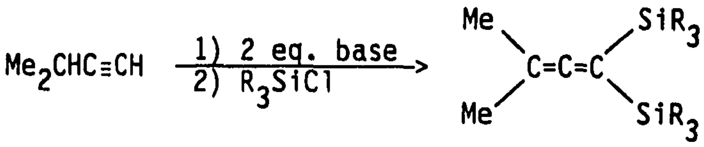
The synthesis of tetra-, tris-, and disilylated allenes 2-4 is commonly accomplished via the reaction of various propargyl acetylenes with either n-BuLi, LDA, t-BuLi, or n-BuLi/TMEDA (12, 14-17). Suzuki has prepared a number of monosilylallenes 5 from the reaction of trimethylsilylpropargyl phenyl ether and trialkylboranes in the presence of an excess of sodium methoxide (18). The excess sodium methoxide was used to desilylate trimethylsilylacetylene 6.

$$\mathrm{CH_3C{\equiv}CH} \xrightarrow[\text{2) } \mathrm{R_3SiCl}]{\text{1) 4 eq. base}} \mathrm{(R_3Si)_2C{=}C{=}C(SiR_3)_2}$$

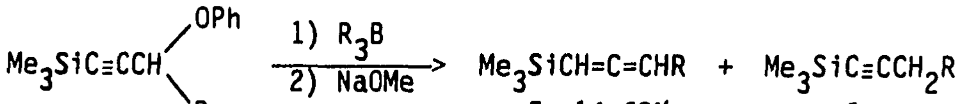
2 25-75%



3 8-70%



4 4-52%

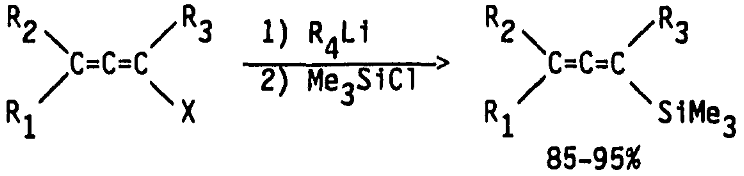


5 14-68%

6

R = Pr, Bu, i-Bu, S-Bu
Pentyl, Cyclopentyl

Silylallenes have been prepared via the coupling of allenyl lithium compounds and trimethylchlorosilane (19-21). Clinet has shown that allenyllithium compounds can be synthesized via metallation of allenylsilanes or by metal/halogen exchange of haloallenes (20-21).



R_1 = $\underline{n}$-C_3H_7, $\underline{n}$-C_8H_{17}, CH_3

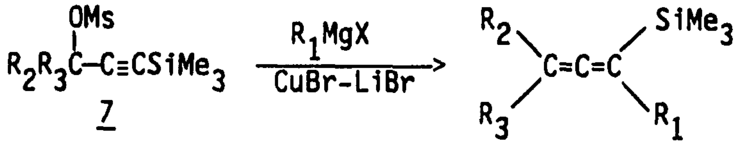
R_2 = H, CH_3

R_3 = H, $\underline{n}$-C_4H_9

R_4 = $\underline{n}$-C_4H_9, $\underline{t}$-C_4H_9

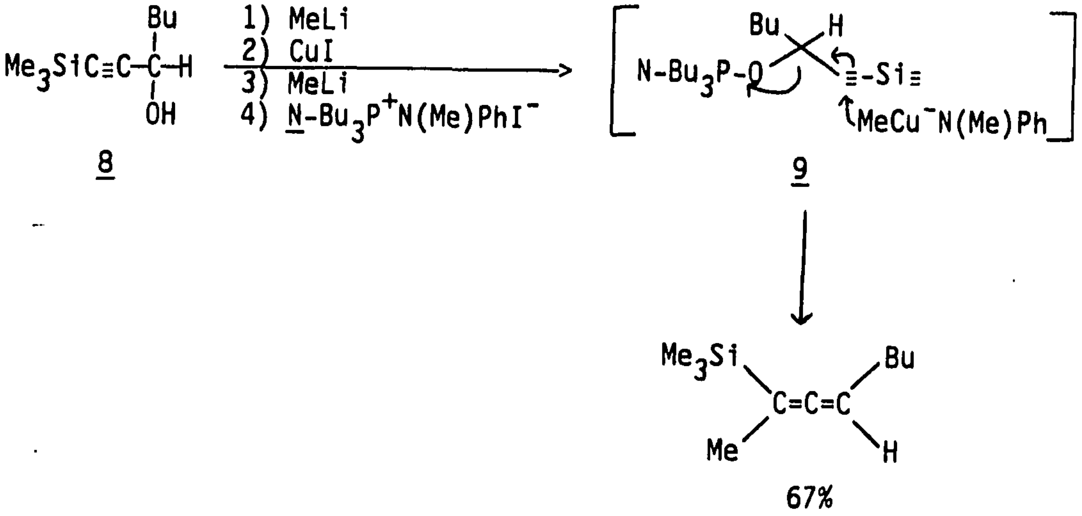
X = H, Br

A very good general route to silylallenes is the 1,3-addition of an organoheterocuprate to a trimethylsilylpropargylmesylate, 7. Westmijze has reported yields of greater than 85% and except where R^3 is $\underline{t}$-C_4H_9 or C_6H_5, little or none of the undesired acetylene was formed (22). The choice of leaving group appears to be important since Brinkmeyer has reported that the analogous acetates afford only substituted alkynes (23). Tanigawa has shown that one can start with a propargyl alcohol 8 instead of the propargyl mesylate (24). The alcohol is reacted with an organocuprate followed by treatment with (methylphenylamino)tributylphosphonium iodide to form 9. The alkyl(methylphenylamino)cuprate which is present couples in a 1,3 fashion to afford the silylallene.

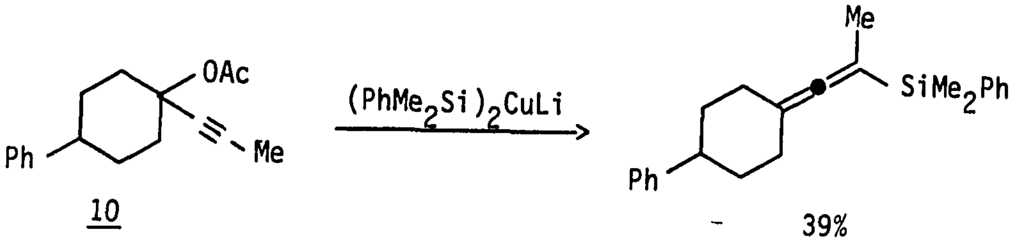


R_2, R_3 = alkyl

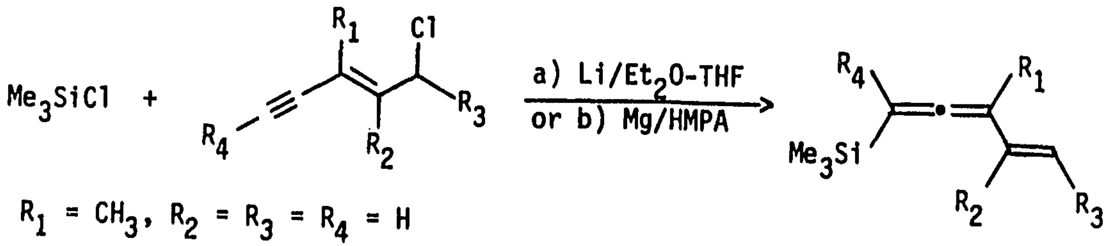
R_1 = Alkyl or C_6H_5



Fleming has reported that various silylcuprates add to propargyl acetates such as 10 to afford allenes (25-26).



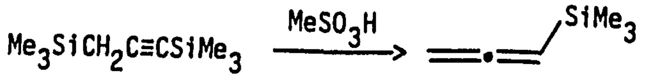
A number of examples of silylallenes have been synthesized making use of the rearrangement of organometallic compounds to allenic organometallics (27-30). The most useful example to date has been reported by Dulcere et al. (30). Dulcere has generated a number of silyl-substituted vinylallenes 11 from the coupling of 5-chloro-3-en-1-ynes and trimethylchlorosilane in the presence of either lithium or magnesium.



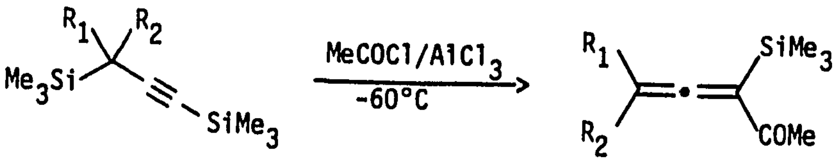
$R_1 = CH_3$, $R_2 = R_3 = R_4 = H$
$R_1 = R_2 = R_4 = H$, $R_3 = CH_3$
$R_1 = R_2 = CH_3$, $R_3 = R_4 = H$
$R_1 = R_2 = -(CH_2)_4-$, $R_3 = CH_3$, $R_4 = H$
$R_1 = CH_3$, $R_2 = R_3 = H$, $R_4 = -Si(CH_3)_3$

11 50-80%

The most convenient route to trimethylsilylallene, 12, is the reaction of 1,3-bis(trimethylsily)propyne with methanesulfonic acid (31). Methanesulfonic acid electrophilicly cleaves the silicon-propargylic carbon bond of the propyne, which rearranges to the allene. Other electrophilic reagents such as bromine and trimethylchlorosulfonate react in a similar fashion to afford the analogous allenes. Pillot has used similar chemistry to synthesize α-trimethylsilyl allenic ketones 13 (32).



12 84%

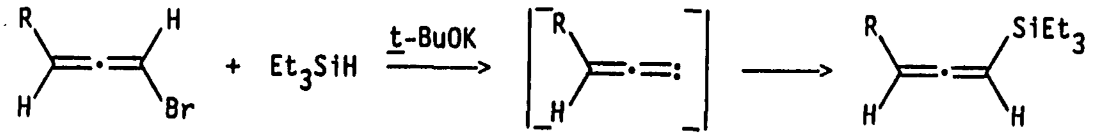


$R_1 = R_2 = H$

$R_1 = R_2 = Me$

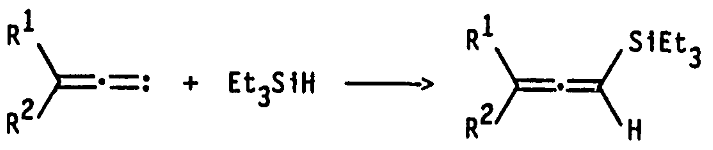
13 5=60%

There are two examples reported of vinylidenes inserting into a Si-H bond of triethylsilane to afford silylallenes 14 and 15 (33-34). Although the yields of the allenes were quite variable, there was no evidence for the presence of the isomeric acetylenes.



R = Me, Pr

14 29-33%

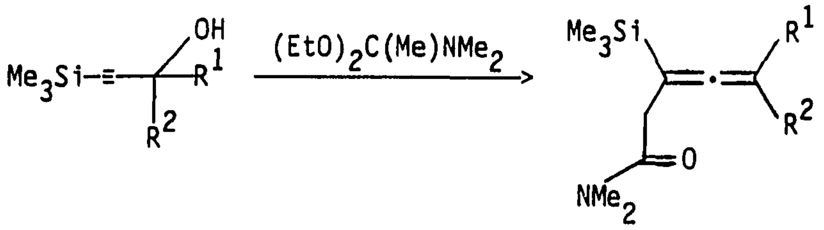


$R_1 = R_2 = Me$

$R_1 = H; R_2 = Me$

15

The Claisen rearrangement has been used to synthesize several highly functionalized silylallenes (35-37). Parker has reported that when trimethylsilylpropargyl alcohols are treated with dimethylacetamide diethyl acetal, allenic amides 16 are formed in good yield (35). Bertrand has also made use of the Claisen rearrangement to synthesize trimethylsilylallenic ester 17 (36).

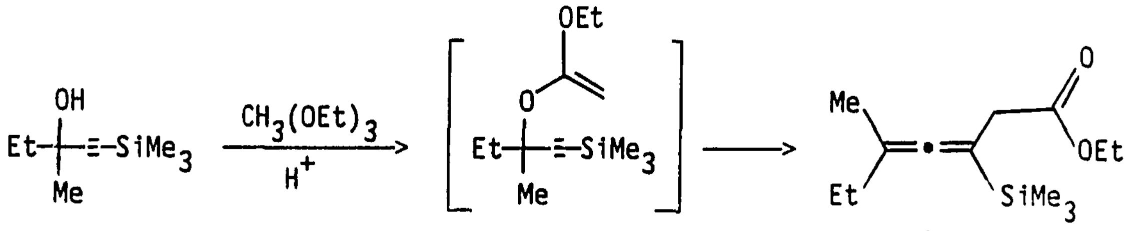


$R_1 = R_2 = CH_3$

$R_1 = CH_3$, $R_2 = H$

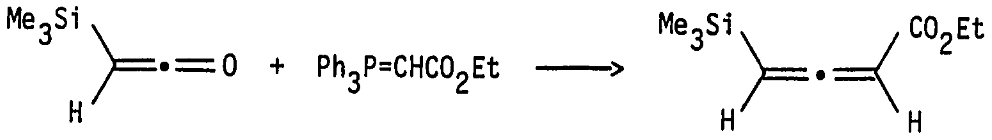
$R_1 = R_2 = H$

16 59-86%

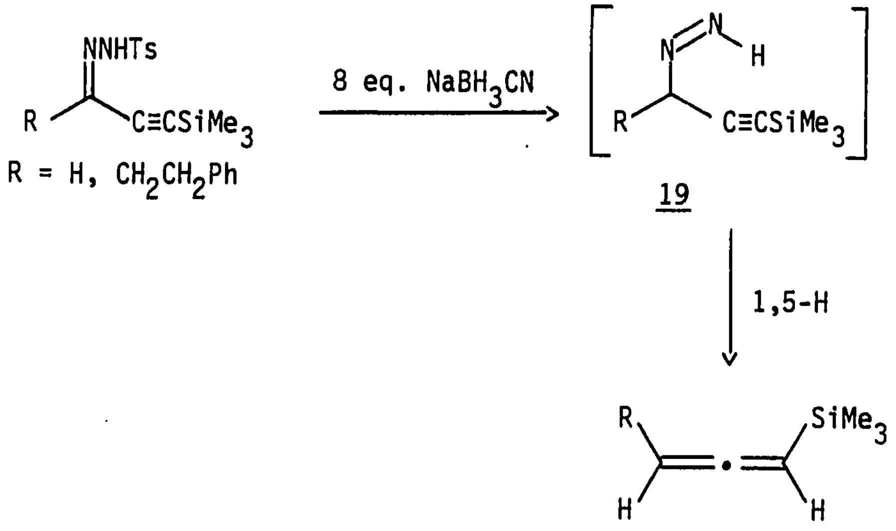


17

There are several examples of somewhat more elegant routes to silylallenes. Ruden has used the Wittig reaction to synthesize 1-trimethylsilylallene 18 in a 85% yield (38). Danheiser has shown that propargylic diazene 19 undergoes a sigmatropic (1,5)-H rearrangement to afford trimethylsilylallene 20 in good yield (39). Cherkasov has reported a quite simple route to 21 via addition of ethyl magnesium bromide to 22 (40).

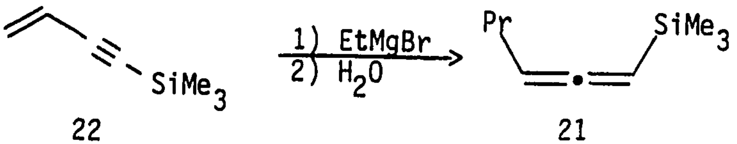


18 85%



19

20 51-69%



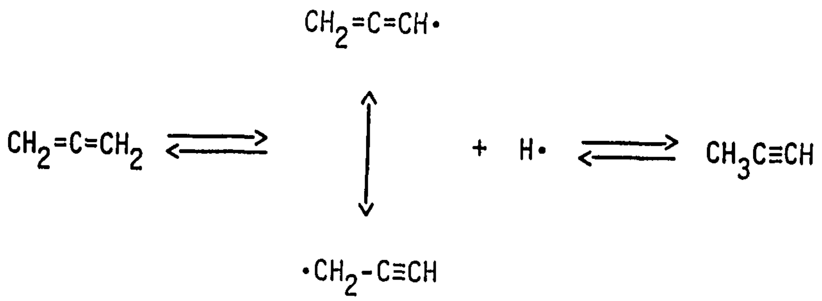
22

21

Thermally-induced Rearrangements of Allenes

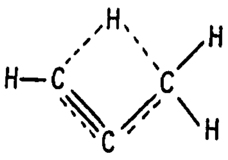
The thermally-induced equilbrium of allene and propyne has been known since 1948 (41). Sakakibara was the first to investigate the mechanism of the isomerization of allene to propyne under pyrolysis conditions (42). The mechanism that was proposed involved homolysis of either a C-H bond in allene or a methyl C-H bond of propyne to afford the C_3H_3 radicals (Scheme 1). Subsequent recombination of the radicals would form either of the two isomers.

Scheme 1



The first kinetic investigation of the allene to propyne isomerization was done by Levush in 1969 (43). Using a flow pyrolysis system, first-order rate constants were determined for two different mixtures of allene and propyne at 900-1150°C. An Arrhenius factor of 11.6 and a energy of activation of 55 kcal/mol was calculated. The fact that the two mixtures gave similar shaped plots of conversion versus time suggested that the reaction was first order with respect to the isomerized molecule.

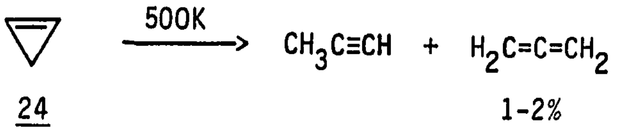
In 1975 Bradley using shock tube pyrolysis techniques tried to determine if the C_3H_3 radical was involved in the isomerization of allene to propyne (44). Pyrolysis of a mixture of allene and ($^2H_4$) allene, at temperatures of 1440-1700 K, afforded propyne where the (CD_3CCH)/(CD_3CCD) ratio was 0.14-0.20. The value of the ratio (CD_3CCH)/(CD_3CCD) is an indicator of what mechanism is involved. The ratio would be zero for a molecular mechanism and 2.0 for a radical chain. The ratio of 0.14-0.20 led Bradley to conclude that not more than 5% of the isomerization takes place via a radical chain. RRKM calculations were performed assuming the four-centered transition state 23 was involved. The calculations showed that the molecular mechanism is reasonable and that log k/s^{-1} = 14.48-92.7 $kcal/mol^{-1}$/ RTln10.



23

Lifshitz has studied the pyrolysis of allene, ($^2H_4$) allene and propyne at 1030-1220 K and pressures of 1.2-6.0 ATM. (45-46). It was concluded that the allene-propyne isomerization is unimolecular and does not involve free radicals. The unimolecular rate constant was calculated and the E_a was 61.2 $kcal/mol^{-1}$. A sigmatropic (1,3)-H shift mechanism was proposed.

Walsh was the first to suggest the possible involvement of cyclopropene as an intermediate in the isomerization of allene to propyne (47). Pyrolysis of cyclopropene 24 in a static system at 500 K yielded mostly propyne along with 1-2% of allene.



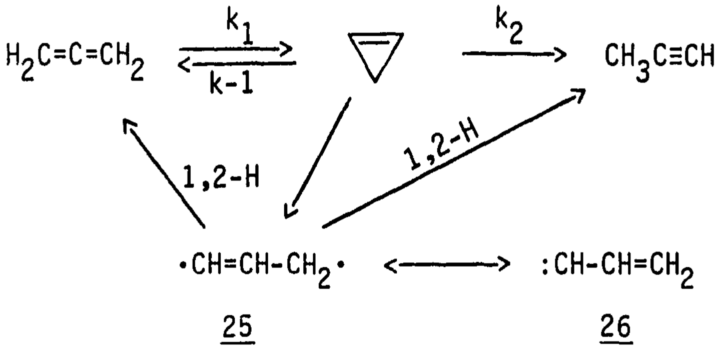
$$\xrightarrow{500K} CH_3C{\equiv}CH + H_2C{=}C{=}CH_2$$

24

1-2%

Although the yield of allene was small, its presence did suggest a new pathway for the isomerization of allene to propyne involving cyclopropene. Since the isomerization of cyclopropene was believed to involve 25/26, if cyclopropene is involved in the allene to propyne isomerization, the overall mechanism requires two 1,2-H shifts rather than the earlier proposed single (1,3)-H shift (Scheme 2) (44-46, 48). Walsh measured the Arrhenius parameters for the isomerization of cyclopropene to allene and propyne and obtained log (k_2/s^{-1}) = 13.25-37.5 kcal/mol^{-1}/RTln10. E_{-1} was estimated by assuming that $E_{-1}-E_2 \approx \Delta\Delta G^{+} \sim 6$ kcal/mol^{-1}, since the A factors will probably be similar. E_1 was then estimated from the equation $E_1 = \Delta H° + E_{-1}$. Therefore, from the value of E_{-1} of 43.5 kcal/mol^{-1}, E_1 was calculated to be 64.3 kcal/ mol^{-1}. This value of E_1 is quite close to that obtained by Lifshitz but much smaller than Bradley's (44-46).

Scheme 2

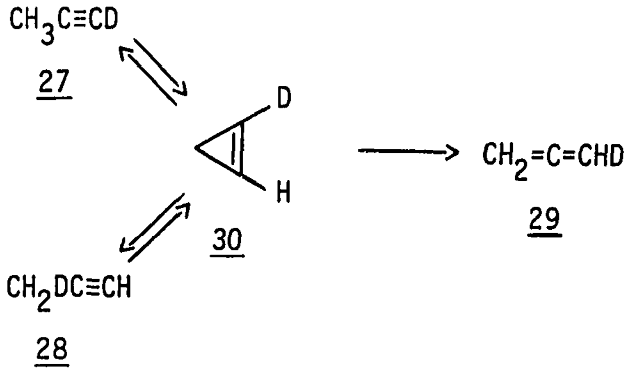


In 1977 Walsh determined that allene was being formed from cyclopropene via both an unimolecular route and a radical pathway (49). The radical pathway was suggested by the lower (allene)/(propyne) ratio when a radical trap is added. The estimated value of k_1 was $\log(k_1/s^{-1}) = 13.05-63.7$ kcal/mol^{-1}/RTln10. The estimated k_1 and the observed k, as measured by Lifshitz, are not substantially different, thereby lending support to the intermediacy of cyclopropene.

The mechanism of the allene-propyne isomerization has also been investigated through the construction of potential energy surfaces (50). It was concluded that the energetically preferred paths for passage from allene to propyne lead through cyclic intermediates with a bridging hydrogen atom rather than a direct hydrogen atom transfer.

Hopf realized that the question of whether the allene-propyne equilibrium involves a sigmatropic (1,3)-H shift or a mechanism involving the intermediacy of cyclopropene could be in principle distinguished by starting with deuteriopropyne 27 (Scheme 3) (51). A mechanism involving cyclopropene would likely produce both propyne-3-d$_1$, 28, and d$_1$-allene, 29, in addition to 27. The presence of 28 would provide evidence for a mechanism involving cyclopropene.

Scheme 3



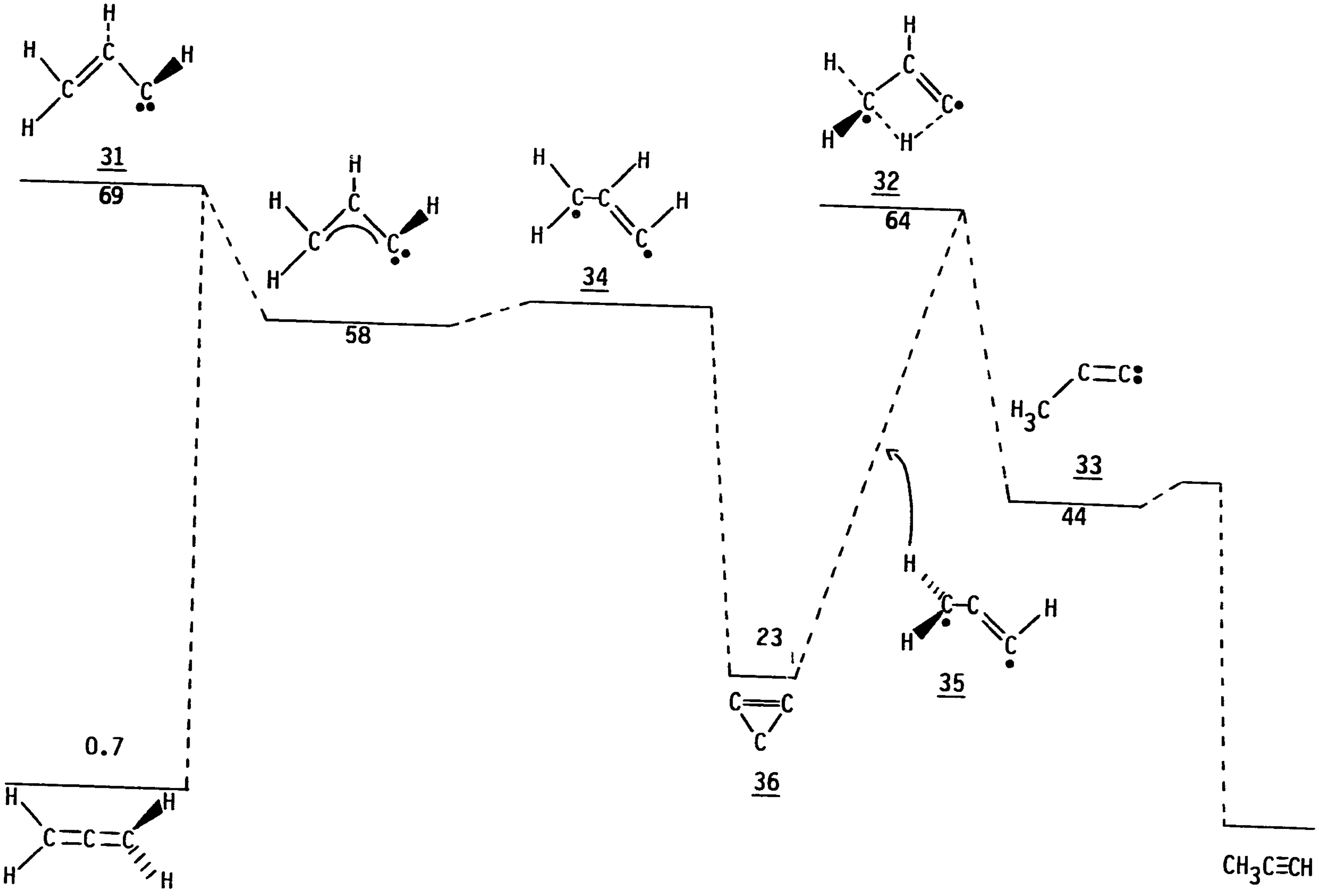
Flow pyrolysis of 27 was carried out in the range of 500-760°C (Table 1). At temperatures below 700°C only 27-29 were observed as products. The yield of 29, the product that one would expect if a sigmatropic (1,3)-H shift initially occurs, was always much less than the yield of 28. The results demonstrate that 28 is formed more readily than 29 from 27 and supports the contention that cyclopropene-1-d$_1$, 30, is involved. If 29 does come solely from cyclopropene, than the ratio of 28/29 can be explained by the higher E_a required for cyclopropene to isomerize to allene versus isomerization to propyne (49).

Table 1. Yields of products from the flow pyrolysis of 27

T, °C	27	28	29	Other
580	98	1.7	0	0
680	60	30	9	0
720	30	49	19	1.3
760	18	54	23	5.3

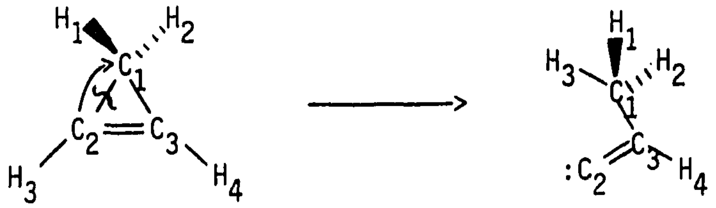
Yoshimine has done some extensive ab initio calculations on the C_3H_4 singlet energy surface (Scheme 4) (52). These calculations suggest that the lowest energy reaction path for the interconversion of allene and propyne does indeed involve cyclopropene as suggested by Walsh. It is interesting to note that, in fact, cyclopropene is the lowest energy minima on the surface. The calculated reaction path indicates that the first transition state is vinyl carbene 31, which rearranges to cyclopropene. The cyclopropene ring opens to the four center transition state 32 which then rearranges to propenylidene 33. It is surprising that the expected initial biradical 35, is neither a transition state nor an energy minimum. A pathway between allene and propyne via direct (1,2)- and (1,3)-H shifts was also calculated. The transition states for the direct (1,3)- and (1,2)-H shifts are respectively 95.6 and 79.9 kcal/mol above propyne.

Scheme 4

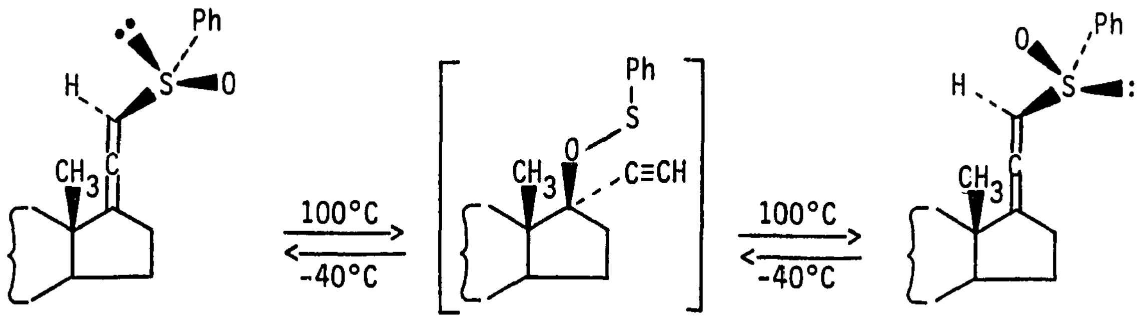


Recently, Yoshimine has done SCF and CI calculations for a number of reasonable isomers on the C_3H_4 singlet and triplet surface (53). The results suggest that since singlet propenylidene 33 is lower in energy (44 kcal/mol) than the bisected diradicals 34 and 35 (63-68 kcal/mol), a pathway to propyne from allene via propenylidene is possible. A direct pathway from cyclopropene to propyne via propenylidene is possible if a synchronous 1,2-hydrogen shift of H_3 to C_1 occurs with the cleavage of the C_1C_2 bond (Scheme 5).

Scheme 5



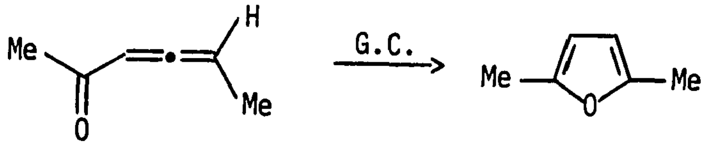
Thermally-induced rearrangements of substituted allenes have also been reported. The most common is the (3,3) sigmatropic rearrangement and an excellent review is available (54). The (3,3) sigmatropic rearrangements reported, however, do not involve the actual migration of a substituent from one of the allenic sp^2 carbons. A (2,3) sigmatropic shift involving actual migration of a substituent from an allenic sulfoxide 37 has been observed by VanRheenen and Shephard (55). The chiral center at sulfur is being racemized thermally by the (2,3) sigmatropic rearrangement to yield a mixture of 37 and 38.



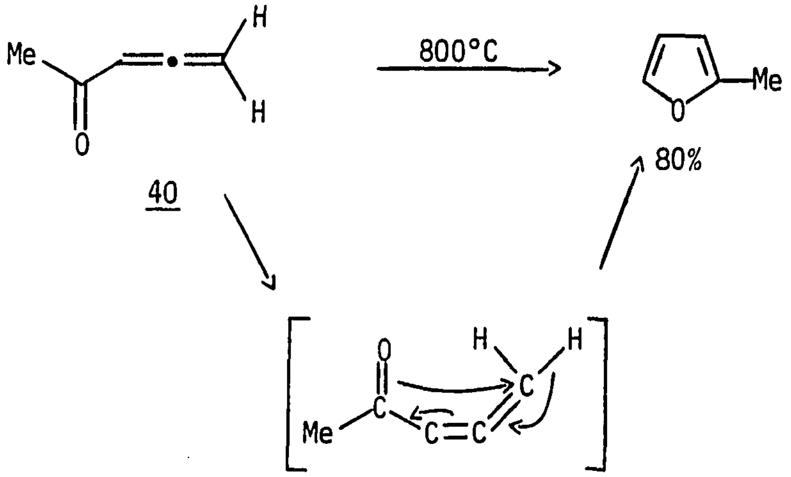
37

38

Allenyl ketones have been observed to rearrange to the corresponding furans under various thermal conditions. Srinivasan observed that hexa-3,4-dien-2-one, 39, isomerizes in the injection port of a gas chromatograph to give 2,5-dimethylfuran as the major product (56). No mechanism was proposed by Srinivasan. Jullien has shown that when 1,2-pentadiene-4-one, 40, is pyrolyzed at 800°C in a quartz wool packed reactor, 2-methylfuran is obtained in 80% yield (57). A mechanism involving a 1,2-H migration was proposed.

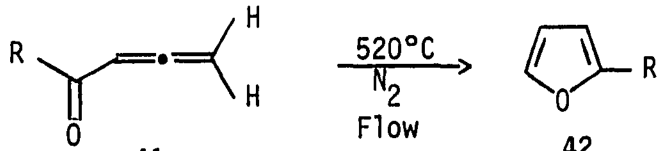


39



Huntsman has found that flow pyrolysis of allenyl ketones 41 at 520°C afforded 2-substituted furans 42 in high yields (Scheme 6) (58). Two mechanisms were proposed to account for the products (Scheme 7). One route starts with a 1,2-H shift to generate carbene 43, which then cyclizes to yield 42. The formation of 43 is analogous to the first step of the mechanism proposed for the isomerization of allene to propyne (47). An alternative mechanism to explain 42 starts with ring formation to yield carbene 44 and followed by a 1,2-H migration.

Scheme 6



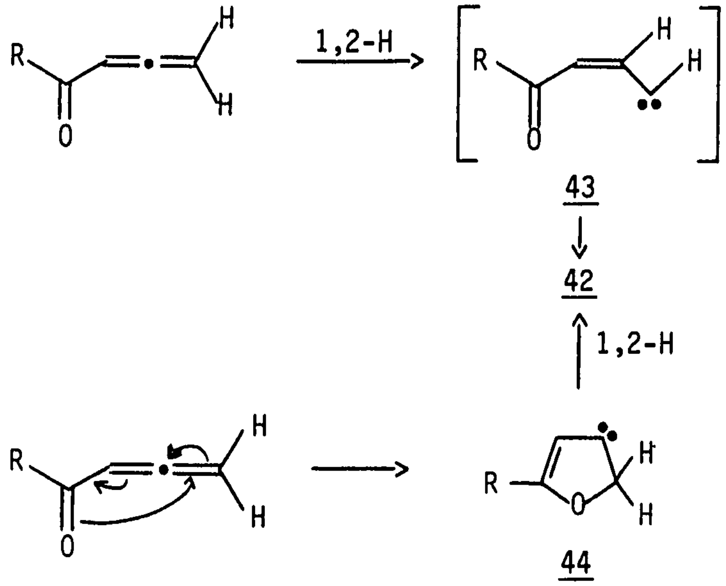
41

R = Me, Et, Ph, *t*-Bu

42

67-78%

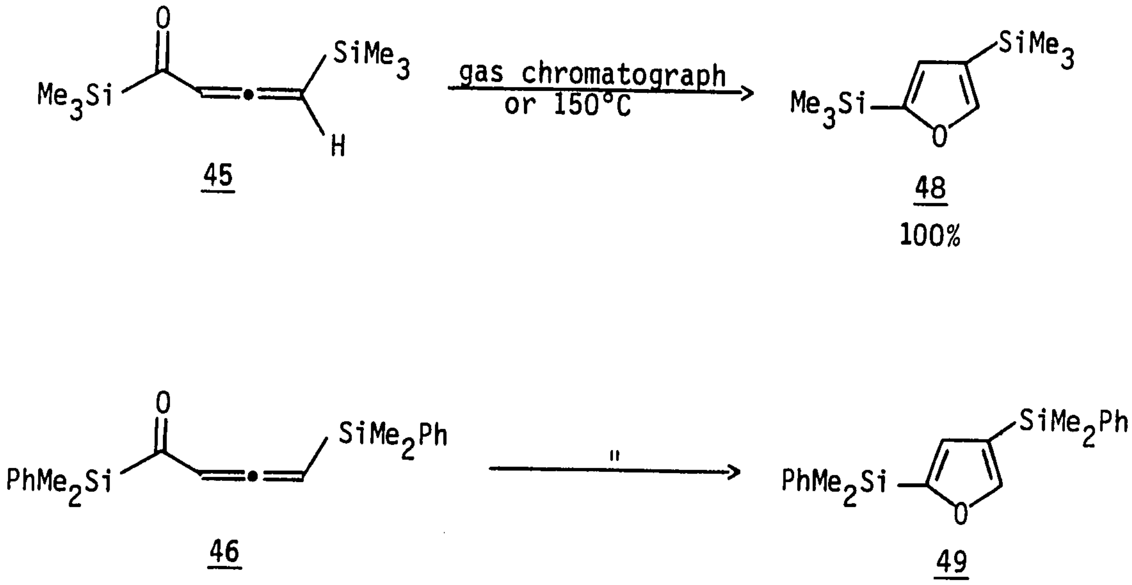
Scheme 7



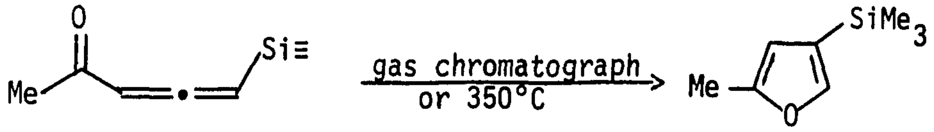
RESULTS AND DISCUSSION

Interest in investigating the thermally-induced rearrangements of silylallenes was sparked by Hussmann's observation that allenyl ketones 45-47 undergo a very facile thermal isomerization to the corresponding furans 48-50 (Scheme 8) (59). In the previous section, three other examples of thermally-induced rearrangements of allenyl ketones were mentioned (56-58). Comparison of these results with Hussmann's reveals two significant differences. Except for hexa-3,4-dien-2-one, isomerization of silyl-substituted allenyl ketones occur at lower temperatures, and 2,4-disubstituted furans, not 2,5-disubstituted furans, are the products of isomerization.

Scheme 8

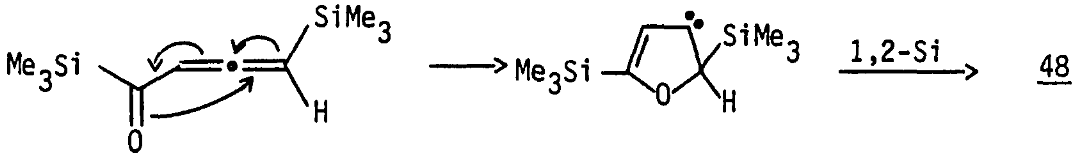


Scheme 8 (continued)



47 50 16%

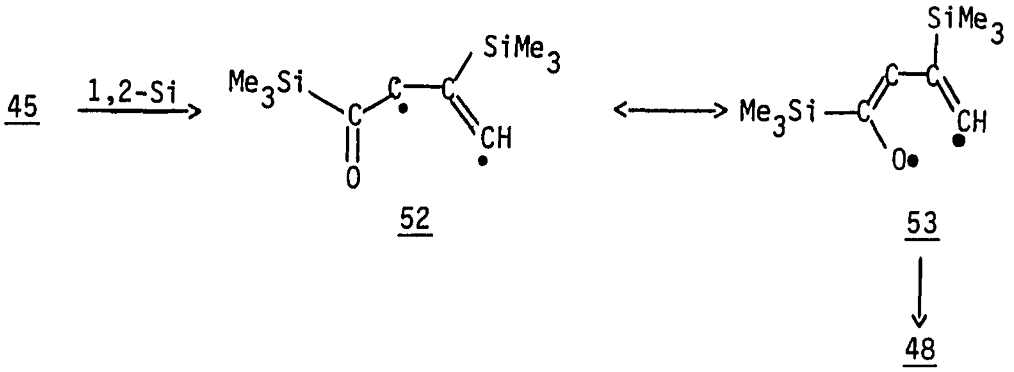
Two distinctly different mechanisms were suggested by Hussmann to explain the furan products. The thermal isomerization of 45 to 48 can be imagined to occur through cyclization of 45 to carbene 51, followed by an exclusive 1,2-silyl migration. This route is analogous to one of the mechanisms proposed later by Huntsman to explain the thermal rearrangement of allenyl ketones (58). The need for exclusive 1,2-silyl migration should not detract from the likelihood of this mechanism. It has been generally observed that for a given system, a silyl group migrates with considerably greater facility than does a corresponding hydrogen (60). The major problem with this cyclization mechanism is that the geometry of 45 is such that a significant distortion of the allenic framework would be required in order to have involvement of oxygen with the terminal carbon.



45 51

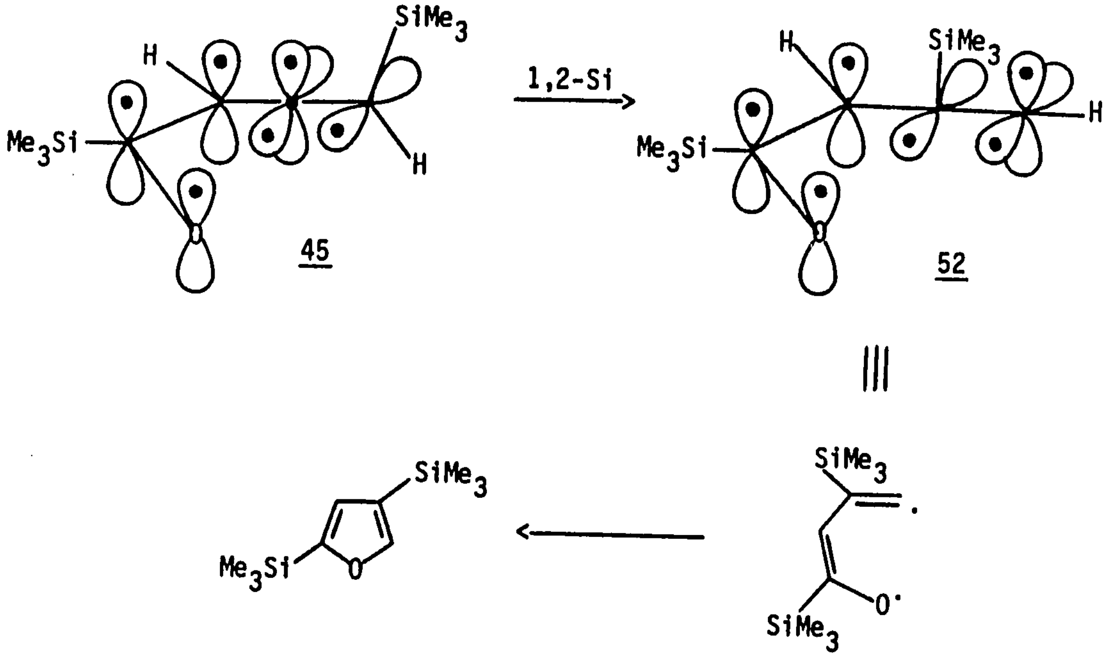
An alternative mechanism to explain formation of 48 is illustrated in Scheme 9. An initial 1,2-silyl shift would afford diradical 52, which can also be represented as the resonance structure 53. Simple closure of 53 would yield the observed furan. Although a 1,2-silyl migration from a sp^2 carbon is unprecedented, the isomerization of 45 to 48 suggests that silyl migration from the terminal allenic carbon somehow takes place.

Scheme 9



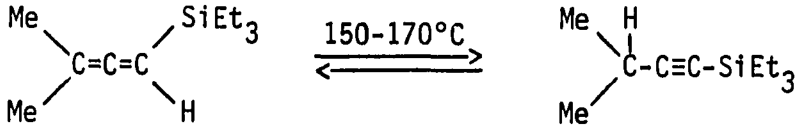
Even though allenes are alkenes, a simple alkene cannot serve as a good model to determine whether the mechanism in Scheme 9 is reasonable. It is known that the isomerization of an alkene to a carbene via a 1,2-hydrogen migration is a very high energy process. For example, the isomerization of ethylene to methyl carbene has been calculated to require 77 kcal/mol^{-1} (61). Therefore, it might seem highly unlikely that allenes 45-47 would rearrange via a 1,2 shift at only 150°C. A closer examination of the p-orbitals of 45 shows that, unlike a simple olefin, one of the p-orbitals of the central sp hybridized carbon is perfectly lined up to allow a suprafacial, 1,2-silyl shift to occur (Scheme 10). In addition, in the case of 45, the silyl migration immediately results in the formation of the resonance stabilized diradical 52. It was concluded that the geometry of the p-orbital, the migratory aptitude of silicon, and the direct stabilization of the intermediate diradical could account for the facility of isomerization of silyl-substituted allenyl ketones to furans.

Scheme 10



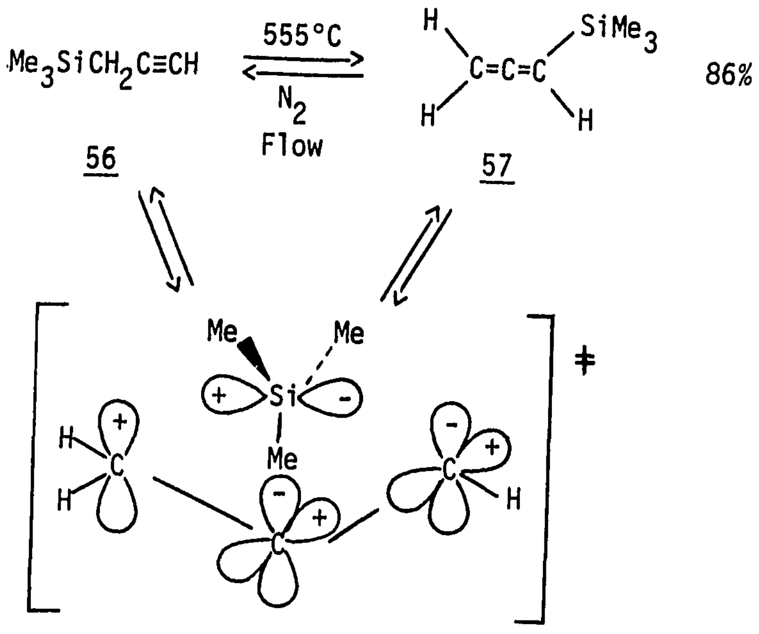
Synthesis and FVP of 1-Trimethylsilyl-3-vinylallenes

There were two original goals in this work: (1) determine if the facile thermally-induced rearrangement that Hussmann observed was indeed a general reaction of silylallenes and (2) obtain more experimental evidence to support or rule out a mechanism involving an initial 1,2-silyl migration. A review of the known thermal rearrangements of silylallenes is warranted. Besides the work of Hussmann, only two additional examples have been reported. Patrick has observed that 1-(triethylsilyl)-3-methyl-1,2-butadiene, 54, undergoes a thermal, prototropic rearrangement at 150-170°C in a sealed tube to give a 2:1 equilibrium mixture of 54 and 55 (62). No mechanism was proposed nor was unimolecularity established.



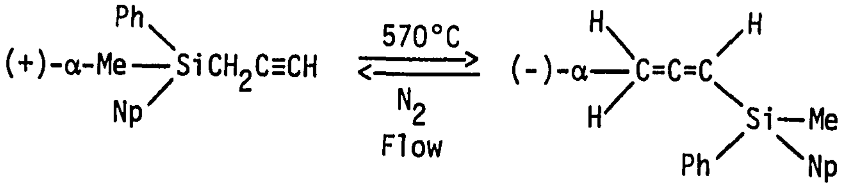
54 2 : 55 1

Kwart has found that when propargyltrimethylsilane, 56, is heated to 555°C, a reversible unimolecular rearrangement occurs to afford a mixture of 56 and 57 (63). The kinetic characteristics of this rearrangement (E_a = 49.9, $\Delta S^{\ddagger}$ = -4.0) led Kwart to propose a symmetrical, concerted transition state, 58, which is similar to the transition state proposed for a silylallylic rearrangement (63).



56 57 58

Kwart recognized that if transition state 58 was correct, migration would take place with complete inversion of the silicon configuration. In order to determine if inversion was taking place, 59 was synthesized and subjected to the same gas-phase thermolysis conditions as was 56. The pyrolysate contained only 59 and 60. Catalytic reduction of 59 and 60 to propyl-α-naphthylphenylmethylsilane afforded the two optically active silanes with opposite signs of rotation and, therefore, configurations.

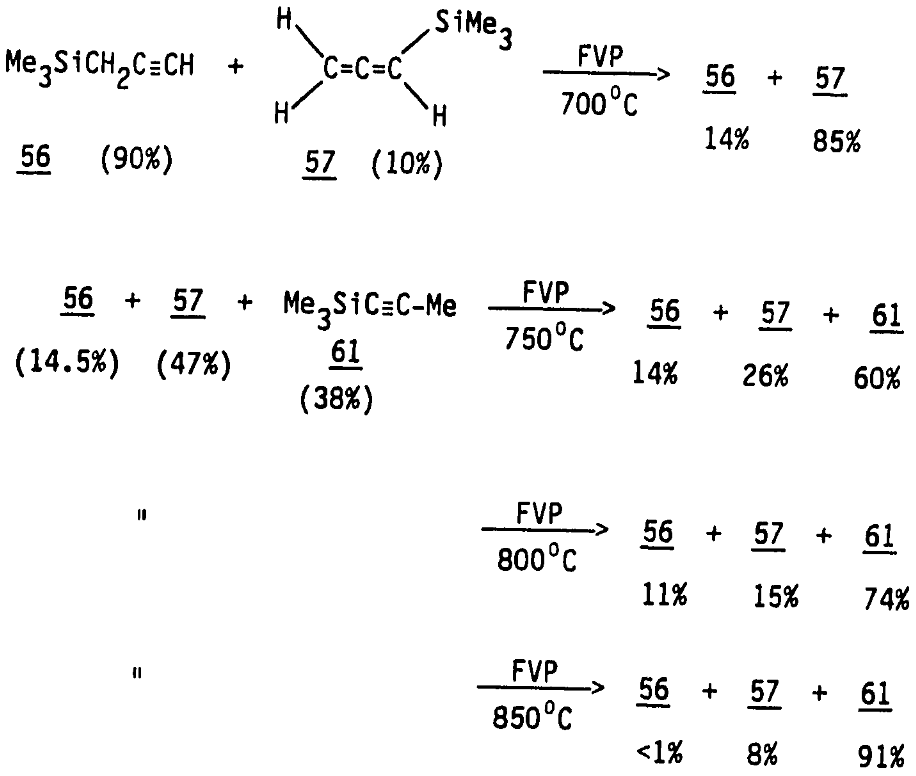


59

60 80%

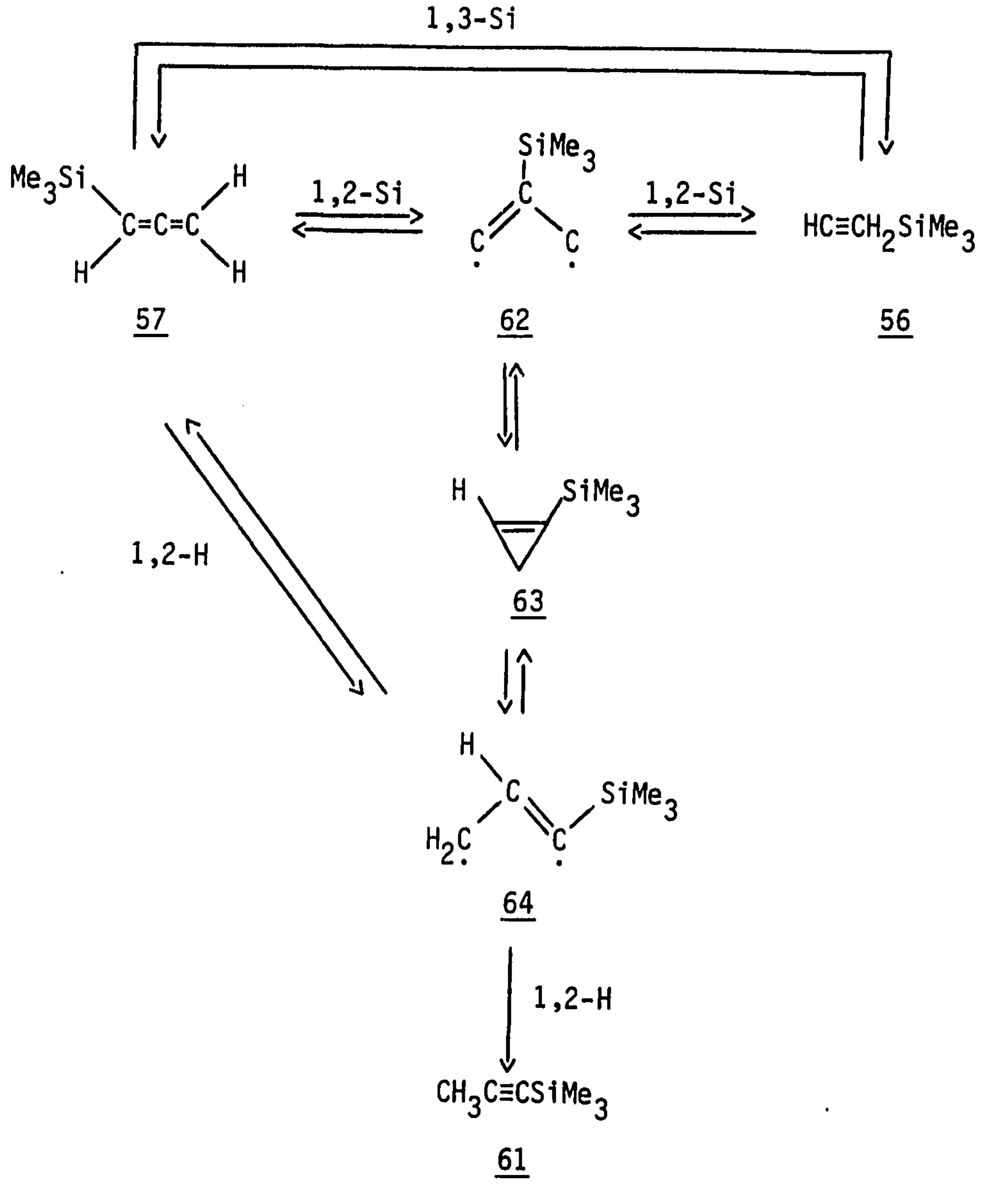
The thermolysis of propargyltrimethylsilane, 56, was reinvestigated by this author under flash vacuum pyrolysis (FVP) conditions (Scheme 11). FVP of a mixture of 56 and 57 at 700°C/10^{-5} torr afforded an equilibrium mixture of 56 and 57 in a ratio similar to that reported by Kwart (63). Pyrolysis of a mixture of 56, 57, and 61 at 850°C unexpectedly afforded as the major product trimethylsilylpropyne, 61, along with a minor amount of 57. Decreasing the temperature of the pyrolysis to 750 and 800°C afforded product mixtures containing 56, 57, and 61 in yields which fit the trend that as the temperature increases, the amount of 61 increases, while the yield of 56 and 57 decreases.

Scheme 11



Scheme 12 illustrates several possible mechanisms to account for the products isolated from the pyrolysis of 56 and the mixture of 56, 57, and 61. The equilibrium between 56 and 57 could be explained via the 1,3-silyl migration suggested earlier by Kwart (63). An alternative route could involve an initial 1,2-silyl migration to afford diradical 62. From the work of Walsh, 62 is expected to be in equilibrium with 63. A second 1,2-silyl migration would generate 57. There are two potential problems with this mechanism. Since 61 was not observed at 700°C, one would have to argue that 63 ring opens to only 62 not 64 . This is not a unreasonable assumption since 62, having both radical centers beta to silicon, is expected to be a more stable diradical than 64. Carbon-centered radicals that are beta to silicon are well known to be more stable than a radical alpha or gamma to silicon (64). The second problem stems from Kwart's observation of overall inversion of the silicon configuration as 56 rearranges to 57. To get overall inversion via a mechanism involving two 1,2-silyl migrations, one migration would have to occur with inversion and the second with retention. Based on the earlier description of a 1,2-silyl shift on allene 45, one would conclude that both 1,2-silyl migrations ought to occur with retention (Scheme 10). Therefore, it seems that either Kwart's results indicating inversion of configuration at silicon are incorrect, or the best mechanism to explain the results involves a 1,3-silyl migration, not two 1,2-silyl shifts. No attempt was made to repeat the pyrolysis of the optically active allene studied by Kwart.

Scheme 12

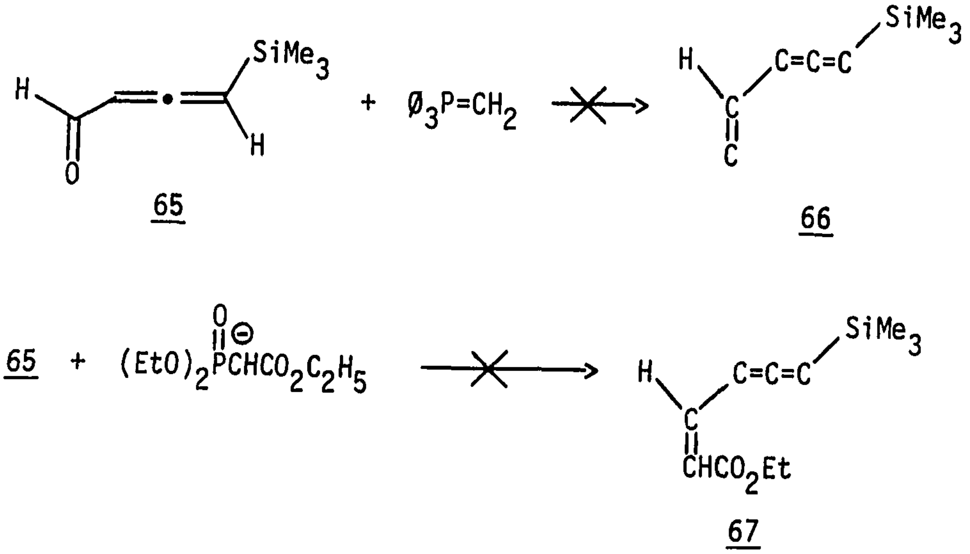


Two possible routes to trimethylsilylpropyne from either 56 or 57, are suggested in Scheme 12. One route consists of either 56 or 57 undergoing an initial 1,2-silyl migration to afford 62, followed by cyclization to 63. At the higher temperature necessary to observe 61, 63 could be expected to give the less stable diradical 64, followed by hydrogen abstraction to yield 61. An alternative mechanism involves generation of 64 directly from 57 via a 1,2-H shift. Since, in general, the migratory aptitude of silicon is greater than hydrogen, the route to 61 involving a 1,2-silyl shift, rather than 1,2-hydrogen shift, looks more reasonable. The overall conclusion from this work is that the observation of 57 isomerizing to 61 provides support for the earlier suggestion that silylallenes may rearrange via an initial 1,2-silyl shift.

Comparison of the reaction conditions needed to isomerize 57, with those reported for the isomerization of 45, suggests that a carbonyl group at C_3 drastically lowers the amount of energy required for isomerization. As stated earlier, a possible explanation of this observation is that the carbonyl group is providing immediate resonance stabilization of the initially formed diradical. To verify if indeed the presence of a substituent at C_3 capable of resonance stabilization is important, an attempt was made to synthesize and study the thermally-induced rearrangements of various vinyl allenes. Vinyl allenes were chosen because the vinyl group should be able to provide resonance stabilization as well or better than a carbonyl group.

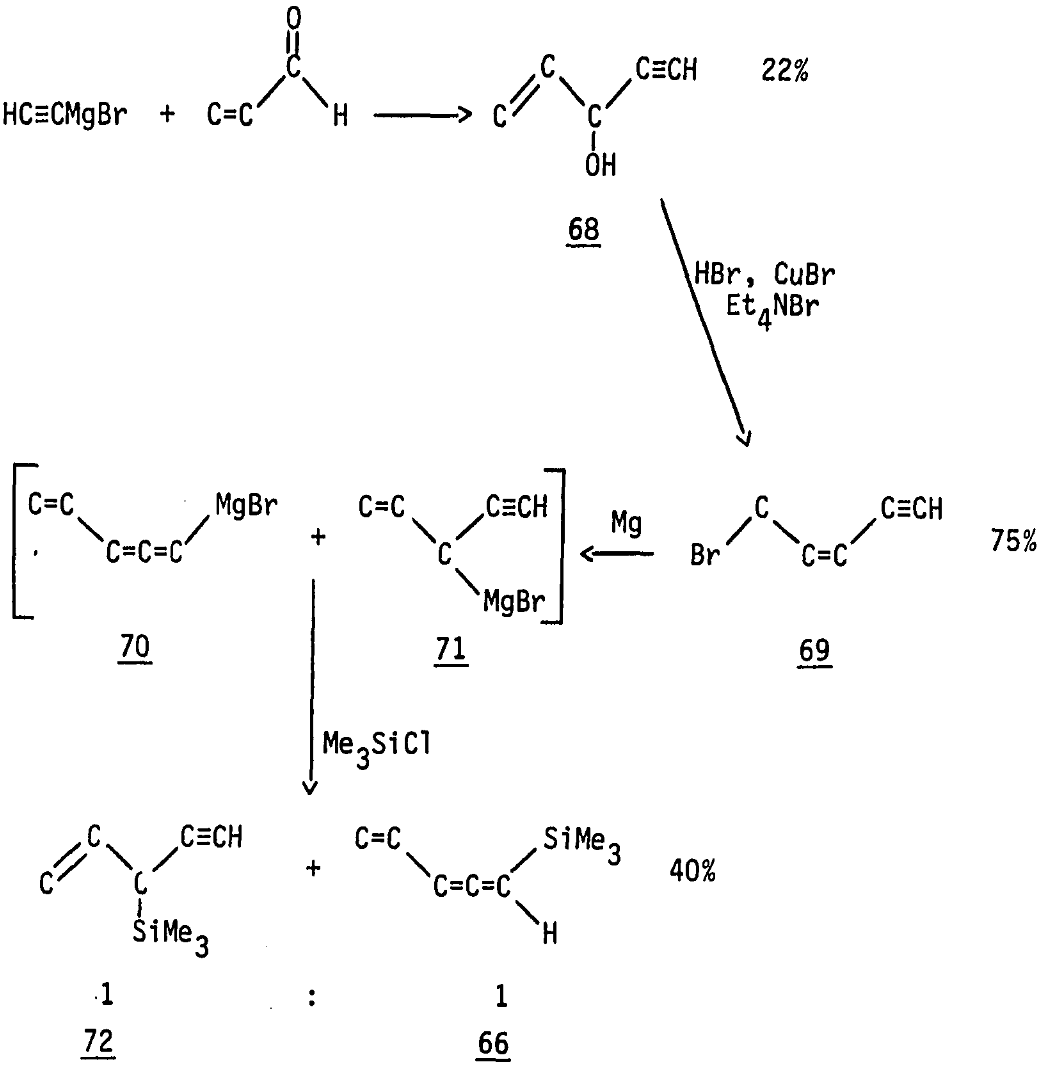
It was thought that a variety of vinyl allenes could be synthesized from silylallenes such as 65 via a Wittig reaction. This route seemed particularly attractive since Hussmann had shown that various allenic ketones and aldehydes could be synthesized in high yields from the photolysis of the corresponding furan (59). Unfortunately, when the Wittig reaction of 65 was carried out under a variety of conditions and using several different Wittig reagents, none of the desired allene 66 or isomer thereof was ever isolated (Scheme 13).

Scheme 13

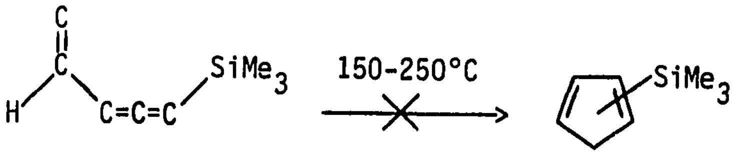


An alternate route similar to a procedure reported by Dulcere, has been successfully used to generate 66 (Scheme 14) (30). The reaction of acrolein with the Grignard of acetylene afforded 68 in a 22% yield. The low yield was probably due to the reactions of the di-Grignard of acetylene with acrolein and 68. Bromination of 68 with HBr using phase transfer conditions resulted in the formation of 69 in good yield. Treatment of 69 with magnesium apparently generates 70 and 71, which are subsequently reacted with trimethylchlorosilane to yield 66 and 72. Compound 66 was isolated by preparative GC.

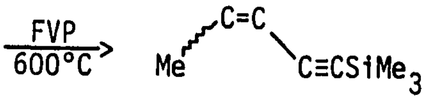
Scheme 14



It was expected that 66 would rearrange at temperatures similar to those needed to isomerize 45 (150-250°C) and would afford trimethylsilyl-substituted cyclopentadienes. Surprisingly, when crude 66 was subjected to preparative gas chromatographic conditions (150-250°C), 66 was recovered and no trimethylsilylcyclopentadiene was observed. Pyrolysis of 66 at 600°C did result in an isomerization; however, the products were E- and Z-1-trimethylsilyl-pent-3-en-1-yne, 73. At 700°C, 66 rearranged completely to afford 73 in a 41% yield. The much higher temperatures required for 66 to rearrange as compared to 45 suggested that the carbonyl substituent is playing a more critical role than just providing resonance stabilization.



66



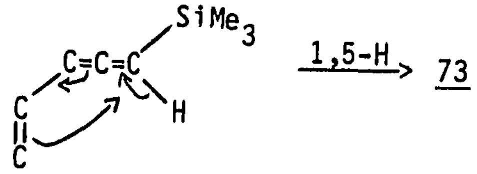
12%

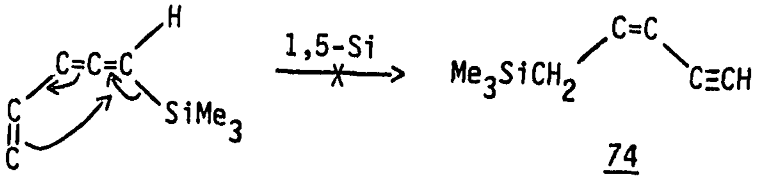
73 59% (E:Z = 1:14)

66 $\xrightarrow[700°C]{FVP}$ 73

41% (E:Z = 1:2)

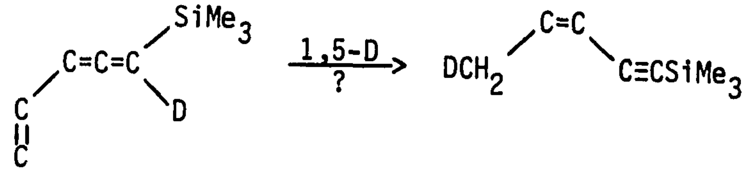
The first mechanism that was considered to explain the formation of 73 consisted of a sigmatropic (1,5)-hydrogen migration of the terminal allenic hydrogen. Although this mechanism is consistent with the product, a (1,5)-hydrogen shift of an allenic hydrogen has never been observed. Also, since it has been established that silyl groups migrate in preference to hydrogen, one would have expected that 74, the product generated if a (1,5)-silyl shift occurs, would have been formed.





74

One way to determine if a sigmatropic (1,5)-H migration is occurring is to replace the hydrogen with deuterium and identify where the deuterium ends up in the final product. If the deuterium ends up exclusively in the methyl group, then such a result would be consistent with a sigmatropic (1,5) migration.

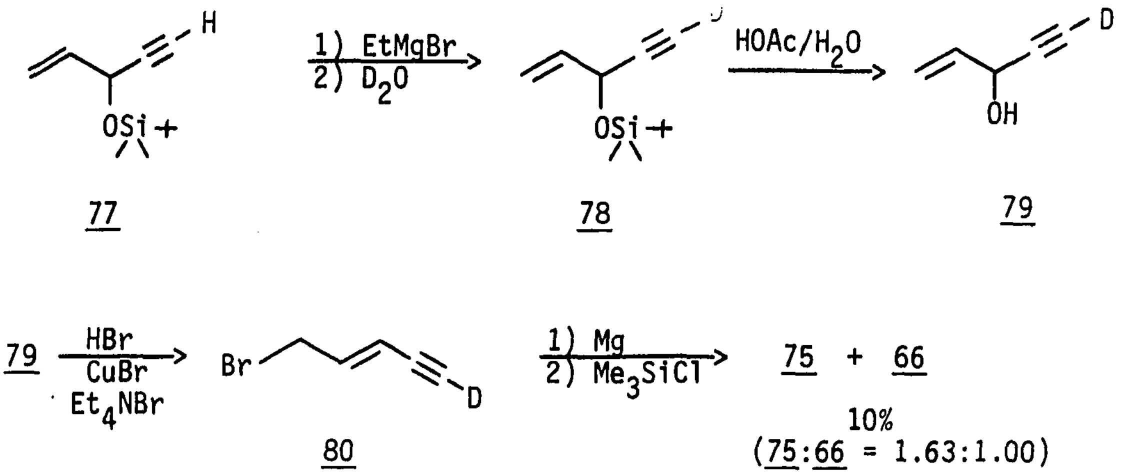


75

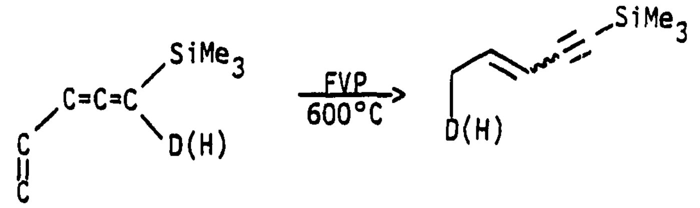
76

The synthetic steps that were used to form 75 are illustrated in Scheme 15. The first step was to protect alcohol 68 by converting it to the silyl ether 77. Reaction of 77 with ethyl magnesium bromide, followed by quenching with D_2O, afforded 78 in 80% yield. Compound 78 was deprotected via reaction with aqueous acetic acid to generate 79. The ^1H NMR spectrum of 79 indicated that the ratio of deuterated 79 to undeuterated 79 was 9:1. Allylic bromide 80 and allene 75 were synthesized using the same procedures as earlier described for the synthesis of 66. A 1.63:1.00 mixture of 75 and 66 was isolated by preparative GC.

Scheme 15



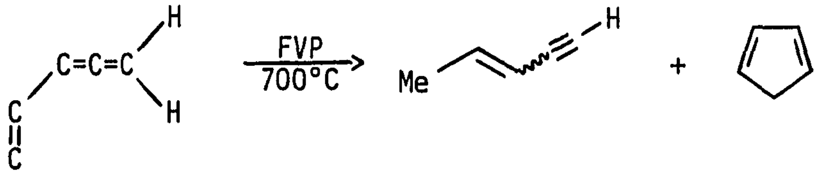
If the mechanism for the isomerization of 66 to 73 was a sigmatropic (1,5)-hydrogen shift, then 75 should rearrange to 76 under the same conditions. When the mixture of 75 and 66 was pyrolyzed at 600°C, the only products observed were the expected acetylenes 76 and 73 in 28% yield. The ^{1}H NMR spectrum proved that deuterium was only incorporated in the methyl group. This experiment, although not proving that the rearrangement of 66 to 73 occurs via a sigmatropic (1,5)-H migration, is certainly consistent with such a mechanism.



75 + 66

76 + 73
23% (E:Z = 1:2)

As a control experiment 1,2,4-pentatriene, 81 was synthesized and pyrolyzed. If 66 and 75 are isomerizing via a concerted (1,5)-H shift, one would not expect the trimethysilyl substituent in either 66 or 75 to play any major role in the rearrangement. Therefore, the pyrolysis of 81 was expected to behave much the same as 66. Surprisingly, even when the pyrolysis temperature was increased to 700°C, 31% of 81 remained. Acetylene 82 was the major product; however, cyclopentadiene, 83, was also formed. The low conversion of 81 to 82 at 700°C, as compared to the isomerization of 66 at 600°C, suggested that the silyl group on 66 is playing an important role in the mechanism. Therefore, the results appear to be inconsistent with a simple (1,5)-hydrogen shift.



81
31%

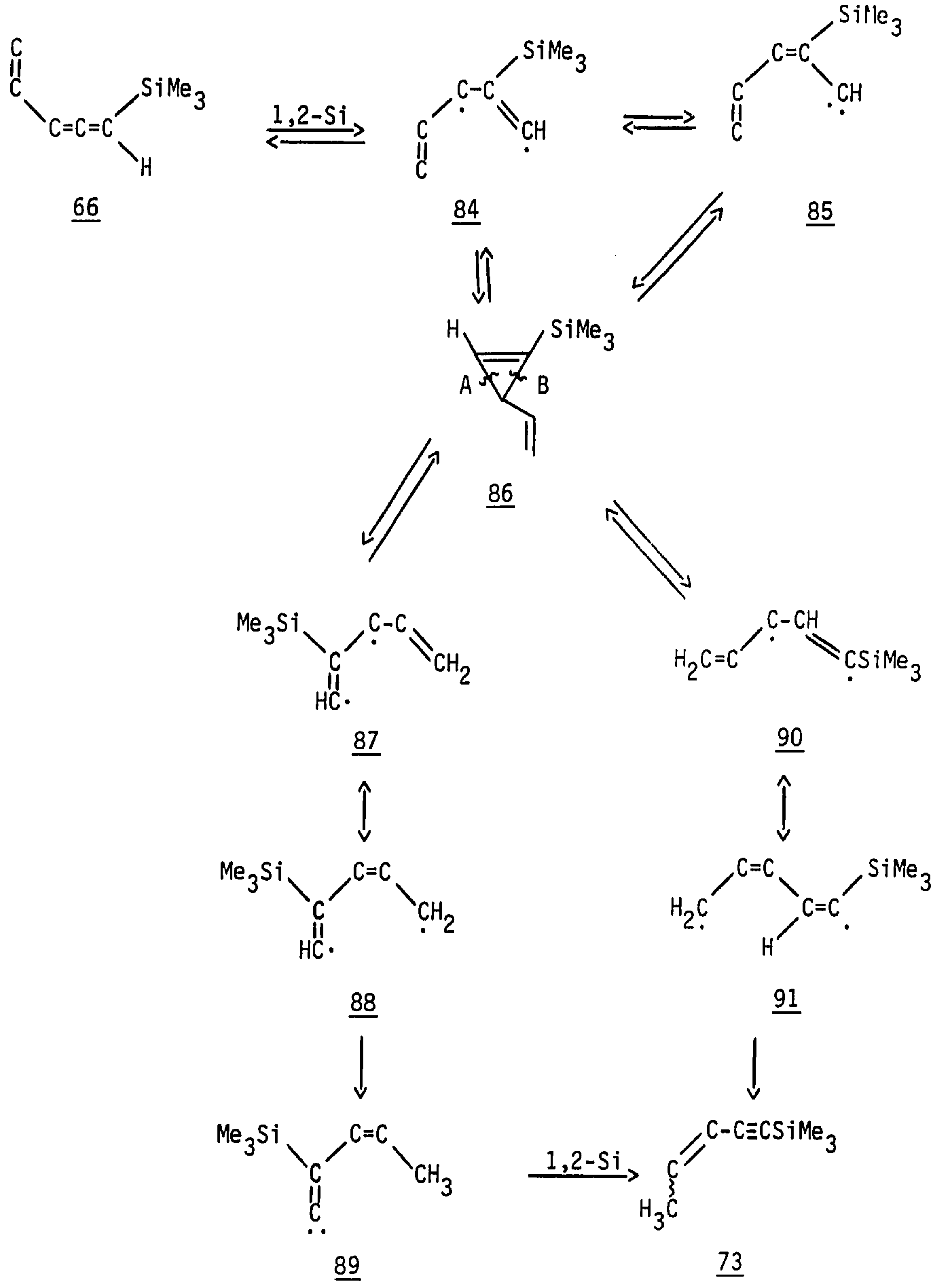
82
53% (E:Z = 3.4:1.0)

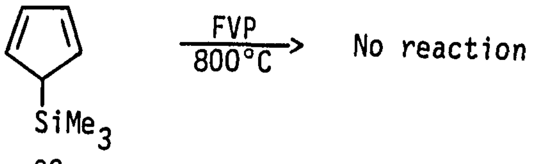
83
13%

Another pathway to explain the observed products of the pyrolysis of 66 is shown in Scheme 16. The initial step is a 1,2-silyl migration to afford 84. Based on the earlier work of Walsh and Yoshimine, isomers 84 and 85 would be expected to be in equilibrium with cyclopropene 86 (49, 52). Homolysis of the "A" bond would afford 87 and 88. A 1,5-hydrogen abstraction to generate vinylidene 89, followed by a 1,2-silyl migration, would lead to the observed product 73. Cyclopropene 86 could also ring open via cleavage of the "B" bond to afford 90 and 91. A subsequent 1,4-hydrogen abstraction would yield 73 directly. Since diradical 87 should be more stable than 90, the route to 73 via initial cleavage of 86 to afford 87 would likely be favored.

There are several potential problems with this proposed mechanism. If 88 is indeed present as a reactive intermediate, why doesn't it close to the unobserved trimethylsilylcyclopentadiene? The possibility that trimethylsilylcyclopentadiene was being formed, but that was ring opening to afford 88 and eventually 73, was checked. Pyrolysis of 92 at temperatures up to 800°C failed to yield any 73, therefore, suggesting that 92 was not formed in the pyrolysis of 66, and then rearranging to 73.

Scheme 16



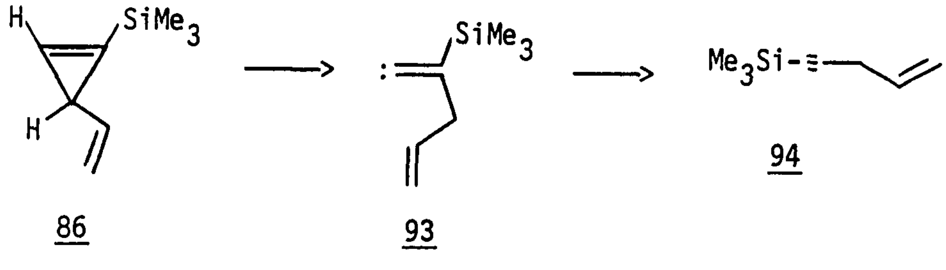


92

The formation of a vinylidene like 89 via a 1,5-hydrogen abstraction is an unprecedented reaction. Yoshimine's calculations of the allene to propyne energy surface, however, have indicated that a 1,3-hydrogen abstraction occurs to form propenylidene (52). Therefore, it perhaps is not unreasonable to propose 88 rearranging to 89.

Another possible pathway from 86 to 73 could involve a synchronous 1,2-hydrogen shift of H_2 to C_3 with the cleavage of the C_2C_3 bond to afford 93 (Scheme 17). A similar route was earlier described for the isomerization of allene to propyne (53). Vinylidene 93 would likely undergo a 1,2-silyl migration to yield 94. Although 94 was not observed as a pyrolysis product, it is conceivable that it was formed and isomerized to 73.

Scheme 17



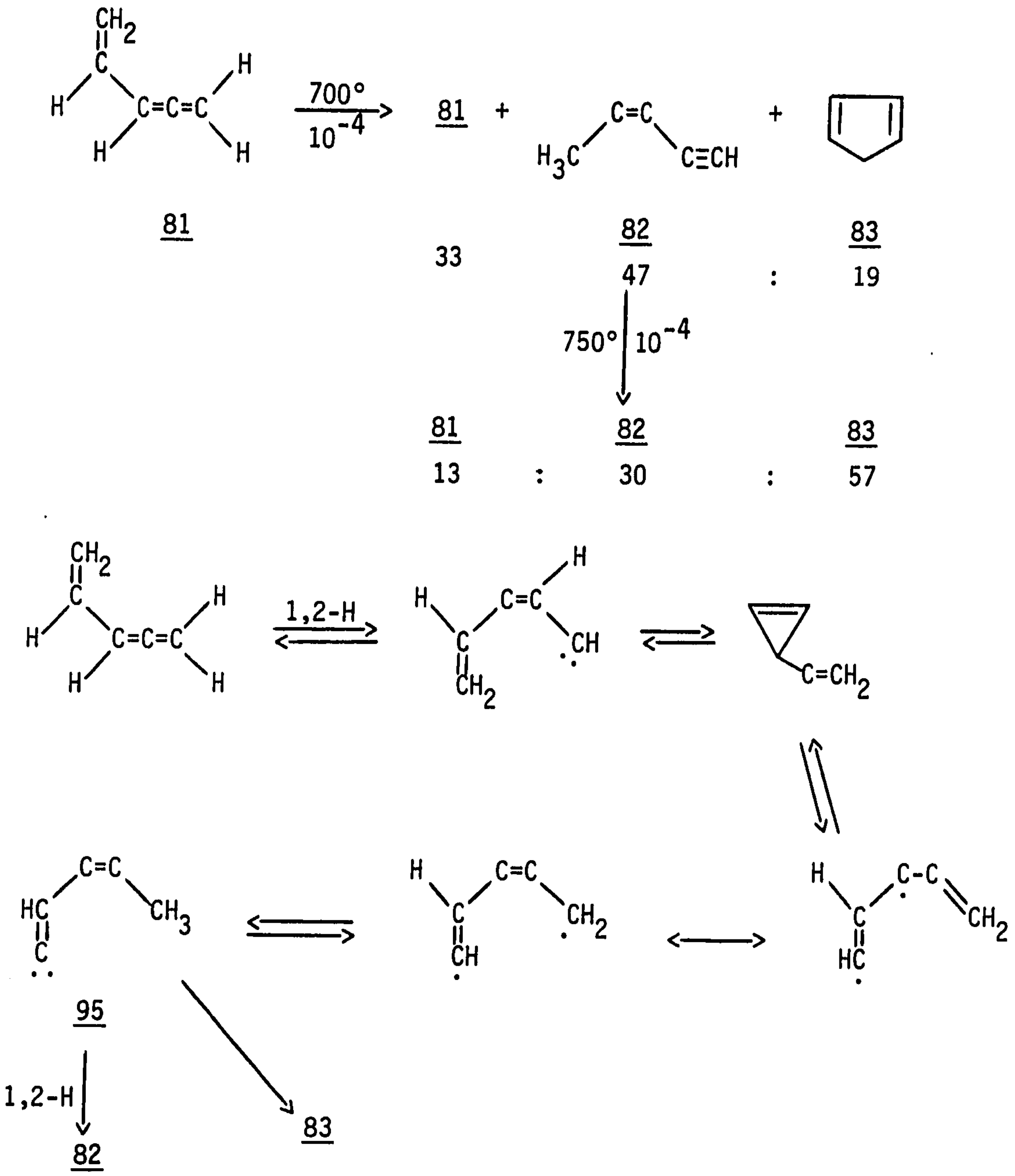
The possible isomerization of 94 to 73 was checked by independently synthesizing 94 and pyrolyzing it under conditions similar to those employed for the pyroloysis of 66 (Scheme 18). At 800°C, which is 200°C higher than required for the isomerization of 66, a significant amount of 94 was recovered along with 73. The presence of 94 at 800°C, along with the absence of 94 as a product of the pyrolysis of 66, indicates that 94 is not involved in the isomerization of 66. It is, however, possible that 93 could isomerize to 89. Therefore, at this point a mechanism to explain the formation of 73 via 93 cannot be ruled out.

Scheme 18

$$94 \xrightarrow[800°C]{FVP} \underset{13\%}{\underline{94}} + \underset{25\%}{\underline{73}} + \underset{16\%}{Me_3Si-\equiv-H} + \underset{5\%}{TMS}$$

As mentioned earlier, when 81 was pyrolyzed at 700°C, a considerable amount of 81 was recovered along with 82 and 83. When the pyrolysate was pyrolyzed at 750°C, the major product isolated was 83. Scheme 19 illustrates a mechanism to account for the observed products that is analogous to that proposed for the isomerization of 66. The fact that 81 was recovered, even at 750°C, can be viewed as support for the idea that an initial 1,2-hydrogen shift is less facile than the 1,2-silyl migration proposed for the analogous silylallene 66.

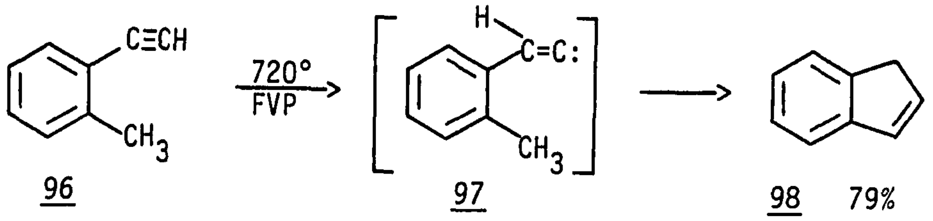
Scheme 19



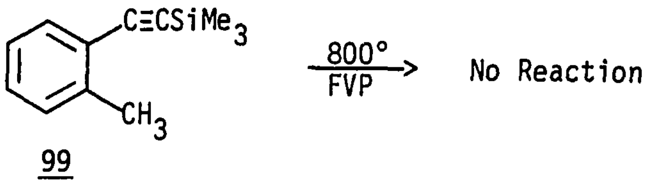
An explanation is required to account for the formation of 83 from 81 and the absence of trimethylsilylcyclopentadiene when 66 is pyrolyzed. It was thought that perhaps 95 and 82 were in equilibrium under these conditions, and 95 was being bled off to 83 via an intramolecular C-H insertion (Scheme 20). The higher yield of 83 at higher temperatures is consistent with the C-H insertion being a higher energy process than a 1,2-hydrogen shift. The absence of trimethylsilylcyclopentadiene could be due to the lack of an equilibrium between 89 and 73, or that C-H insertion is not competitive with a 1,2-silyl migration from 89 to 73.

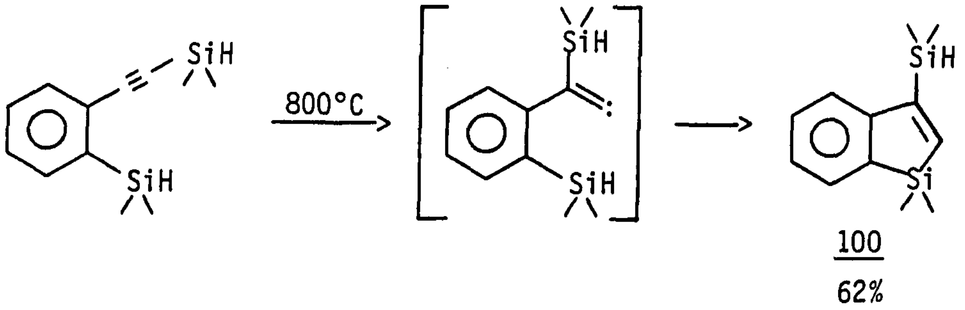
There have been a number of studies reported in the literature dealing with the generation and intramolecular trapping of vinylidenes. Brown has found that when acetylene 96 was pyrolyzed at 720°C, apparently vinylidene 97 is generated, and trapped in an intramolecular fashion, via C-H insertion into the *o*-methyl group to yield 98 (65). Groh has reported that the analogous trimethylsilylacetylene 99 undergoes no rearrangement even at 800°C (66). Further work by Groh suggested that 99 was rearranging to the vinylidene; however, the 1,2-silyl shift back to 99 was much faster than C-H insertion into the *o*-methyl group. If, for example, the methyl group is replaced by a better carbene trap like a dimethylsilyl moiety, the expected trapping product 100 is observed in good yield.

Brown



Groh

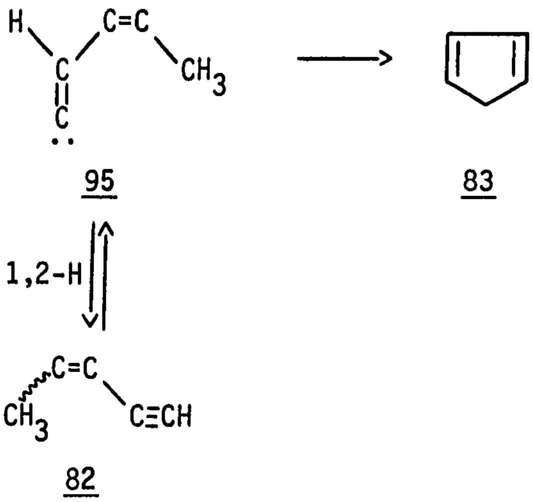




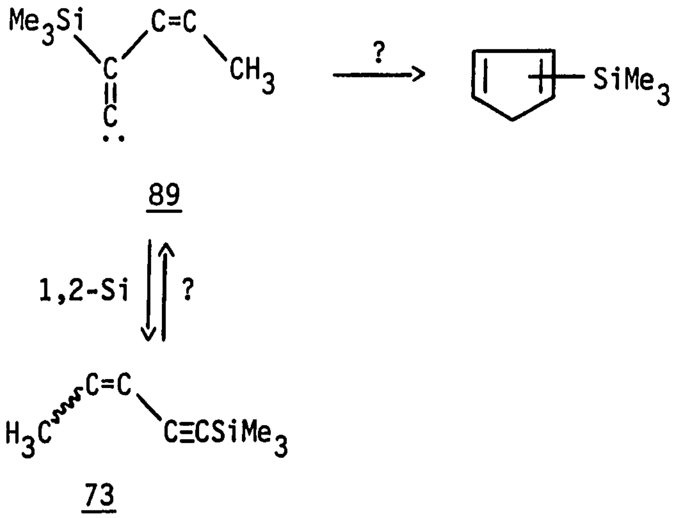
Brown and Groh's results are consistent with the mechanisms proposed in Scheme 20 to explain the formation of 83 and lack of formation of trimethylsilylcyclopentadiene. Apparently, at temperatures greater than 600°C, 95 readily undergoes C-H insertion to afford 83. However, even at 700°C, 89 would rather migrate a trimethylsilyl group in a 1,2 fashion rather than C-H insert. These

Scheme 20

Perhaps



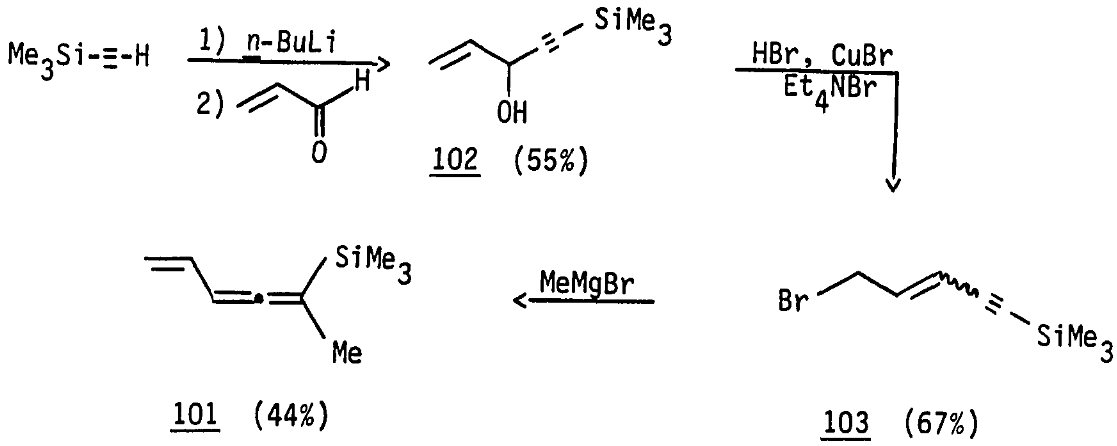
While



results can also be viewed as an additional example of the better migrating ability of a trimethylsilyl group as compared to hydrogen.

Allene 101 was synthesized and pyrolyzed because it eliminates the possibility of the earlier considered sigmatropic (1,5)-hydrogen shift mechanism. The synthesis of 101 is described in Scheme 21. Trimethylsilylacetylene was metallated with *n*-BuLi and then reacted with acrolein to afford 102 in 55% yield. Treatment of 102 with HBr and CuBr generated bromide 103 in a 67% yield. The intramolecular Grignard rearrangement that was used in the synthesis of 66 did not work for the preparation of 101. An intermolecular 1,5 addition of MeMgI to the disubstituted acetylene 103, however, afforded 101 in a 44% yield.

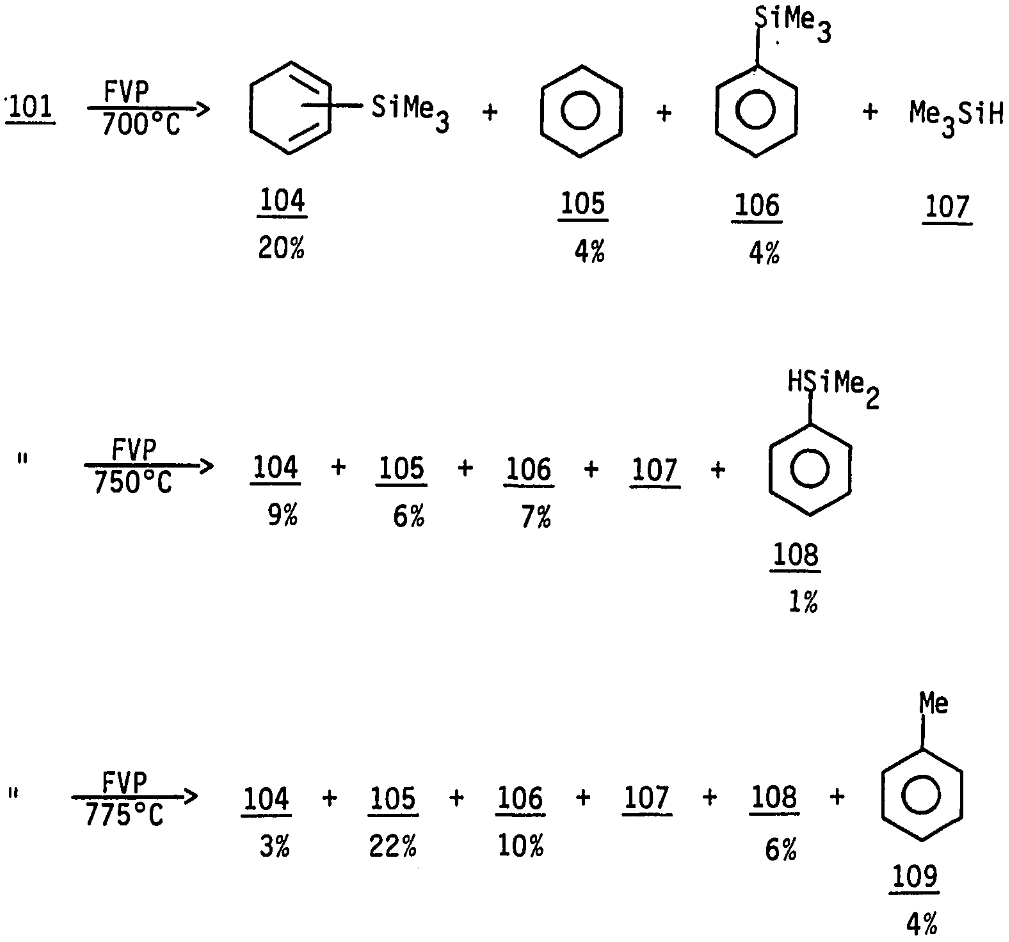
Scheme 21



Allene 101 was pyrolyzed at 700, 750, and 775°C (Scheme 22). At 700°C one major product, 104, was formed along with small amounts of

105-107. The pyrolysis apparatus used was not set up for isolation of volatile compounds like 107; therefore, no accurate yield was obtained for 107. Pyrolysis at 750°C increased the yields of 105-107 and decreased the amount of 104 formed. A small amount of 108 was also formed. At 775°C the major products were 105 and 106. An additional compound that was not present at lower temperatures, toluene, 109, was also isolated.

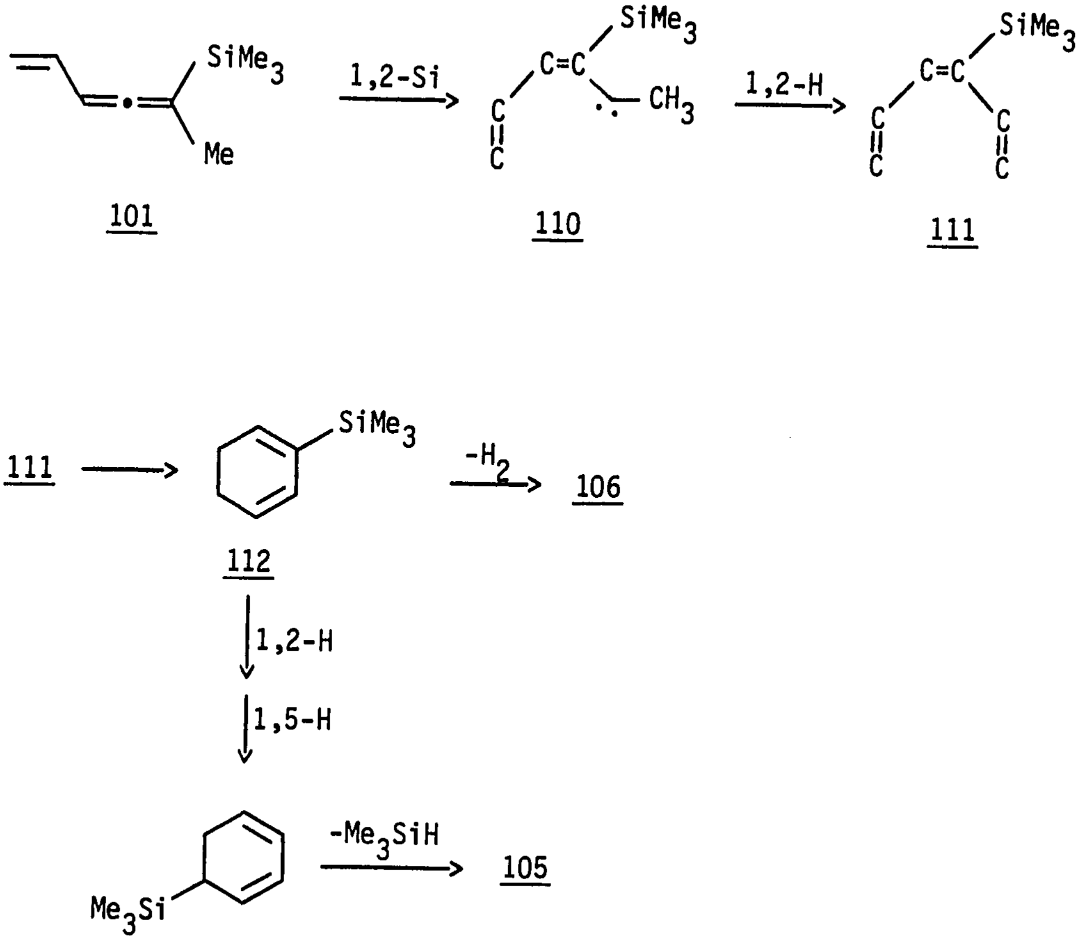
Scheme 22



A possible mechanism to explain the formation of 104-107 is shown in Scheme 23. An initial 1,2-silyl shift to afford carbene 110, is followed by an intramolecular 1,2-hydrogen migration to yield 111. This is the first example of the initially formed carbene not rearranging to the corresponding cyclopropene. Triene 111 would be expected to cyclize to diene 112, which then can either extrude hydrogen or trimethylsilane to afford 106 and 105, respectively. The products derived from the intramolecular trapping of 110 provide more evidence to support a mechanism involving an initial 1,2-silyl migration.

A mechanism consistent with the formation of toluene at 775°C is illustrated in Scheme 24. The key assumption in this mechanism is that at this higher temperature an initial 1,2-methyl migration becomes competitive with the earlier proposed 1,2-silyl shift. Isomerization of 101 via a 1,2-methyl migration would generate carbene 113, which could insert into a silicon methyl group to afford 114. Silacyclopropanes are thermally unstable compounds and are known to extrude silylene. In this case, extrusion of dimethylsilylene to form 115 followed by cyclization and aromatization would lead to toluene, 109.

Scheme 23

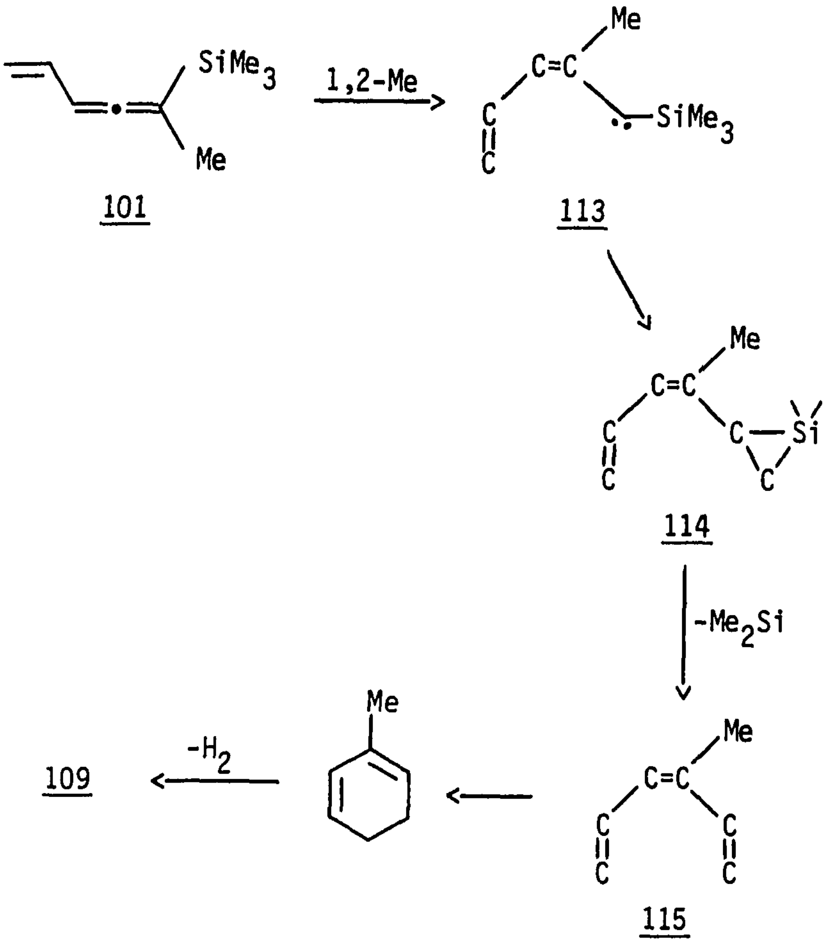


101 110 111

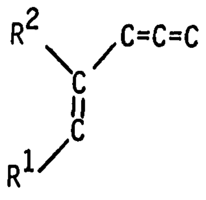
111 112 106

105

Scheme 24



In deciding what other silylallenes to study, it was recalled that Hussmann observed that only allenic ketones, not allenic aldehydes, rearranged under mild conditions to the 2,4-disubstituted furans. Through analogy, it was thought that perhaps allenes like 116 that have vinyl substituents would also rearrange at lower temperatures.

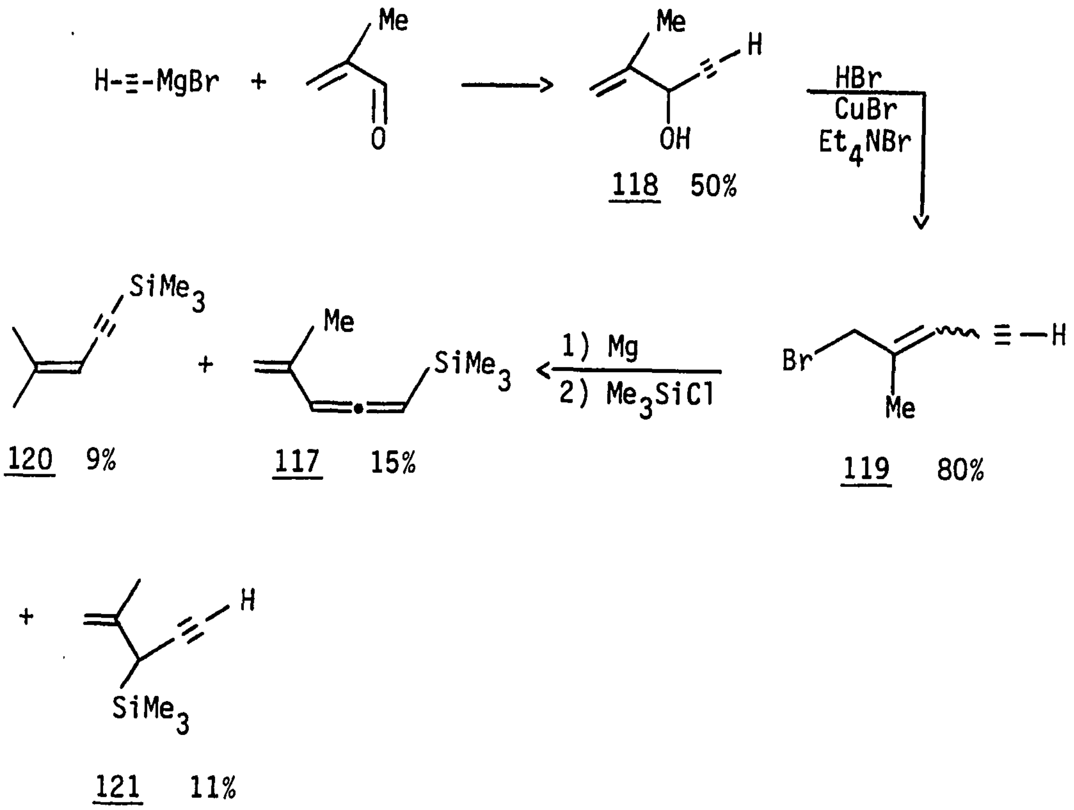


116

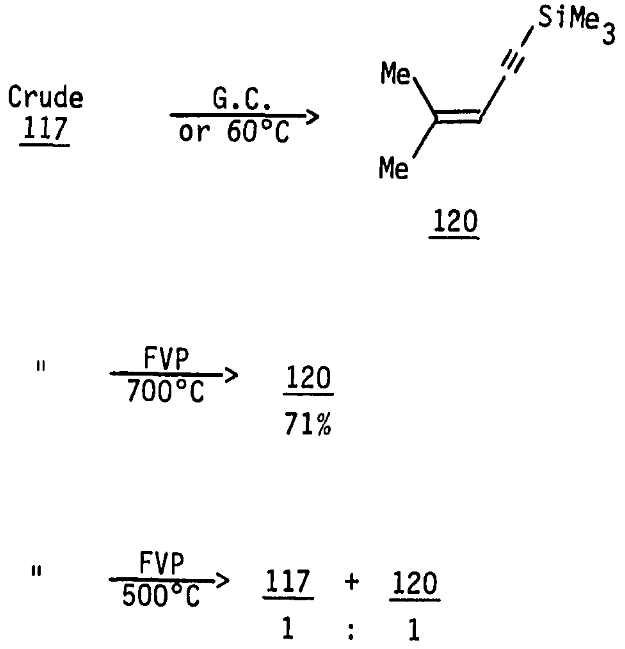
R_1 and/or R_2 = Alkyl

Allene 117 was synthesized in the same fashion as 66; however, 117 could not be cleanly isolated by distillation or preparative gas chromatography (Scheme 25).

Scheme 25



When crude 117 was injected onto a gas chromatograph, the major product isolated was 120 and little 117 was recovered. Such a facile rearrangement is reminiscent of how 4-trimethylsilyl-2,3-butadienal, 45, behaved under these conditions. Heating a dilute solution of crude 117 for one hour at 60°C resulted in 89% of 117 rearranging to 120. FVP of crude 117 at 700°C led to the quantitative conversion of 117 to 120. Pyrolysis at 500°C, which is 100°C lower than needed to isomerize 66, resulted in 56% of 117 rearranging to 120.

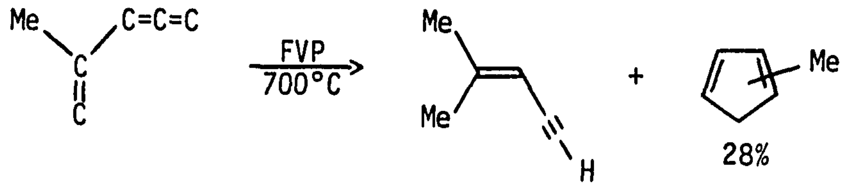


It is difficult to imagine how a methyl group could have such a drastic affect of the rate of isomerization. A possible explanation of this rate enhancement is that since only impure 117 was used, perhaps an impurity such as a salt is catalyzing the rearrangement. In an attempt to verify this hypothesis, crude 117 was pyrolyzed at

500°C in order to recover 117 devoid of any salts. When the recovered 117 was diluted with $CDCl_3$ and heated to 60°C for one hour, nearly all of 117 isomerized to 120. Therefore, it was concluded that the facile rearrangement of 117 to 120 was not due to a salt catalyzing the isomerization.

The corresponding allene with no silyl substituent 122 was synthesized and was isolated via preparative gas chromatography. The route to 122 was identical to that described earlier for the synthesis of 117, except that the allenic Grignard was quenched with water not trimethylchlorosilane. Heating of a dilute solution of 122 at 60°C for 44 hours did not result in any isomerization. Pyrolysis of 122 at 700°C did generate the two expected products, 123 and methylcyclopentadiene; however, a considerable amount of 122 still remained (Scheme 26). Therefore, 122 isomerizes at a rate similar to that observed for 1,2,4-pentatriene, 81, instead of like 1-trimethylsilyl-4-methyl-1,2,4-pentatriene, 117.

Scheme 26



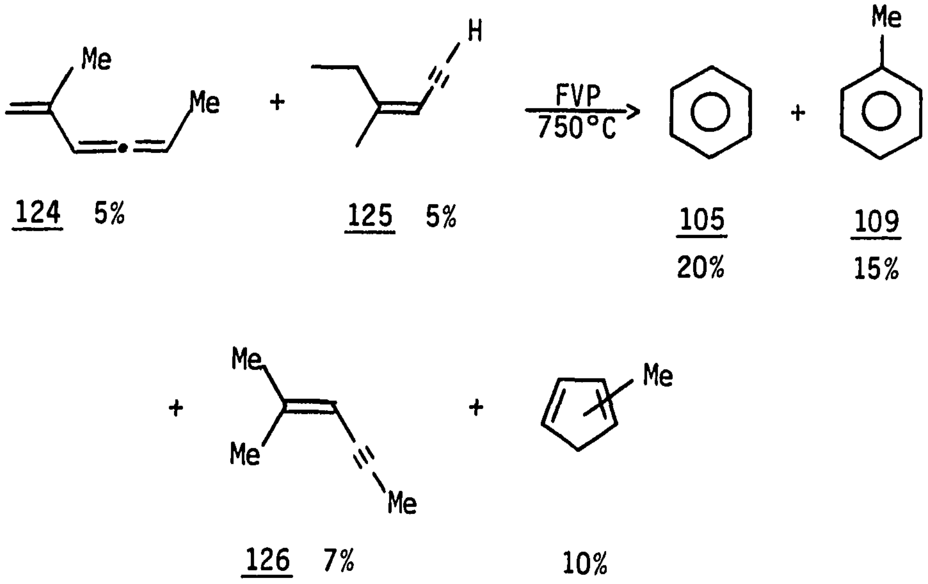
122 27%

123 46%

The difference in the rates of isomerization of 117 and 122 appears to be due to the greater migratory aptitude of a trimethylsilyl group compared to hydrogen. In summary, the results of the thermolyses of 117 and 122 suggest that although a methyl group on C_4 may enhance the rate of rearrangement, the overriding factor is the ability of the C_1 substituent to migrate in a 1,2 fashion.

The last example in this family of allenes that was studied was 124. The synthetic steps to 124 were similar to those used to generate 101. FVP of a mixture of 124 and 125 (2:1) at 750°C generated four products (Scheme 27). The major products, benzene and toluene, were consistent with a mechanism involving an initial 1,2-hydrogen migration and intramolecular trapping of the carbene via another 1,2-hydrogen migration (Scheme 28). The presence of acetylene 126 indicates that 128 also cyclizes to 129. Subsequent ring opening of 129, hydrogen abstraction and methyl migration would yield 126. An alternative route to 126 could involve a 1,5-H shift from 124 to form 126 directly.

Scheme 27



124 5%

125 5%

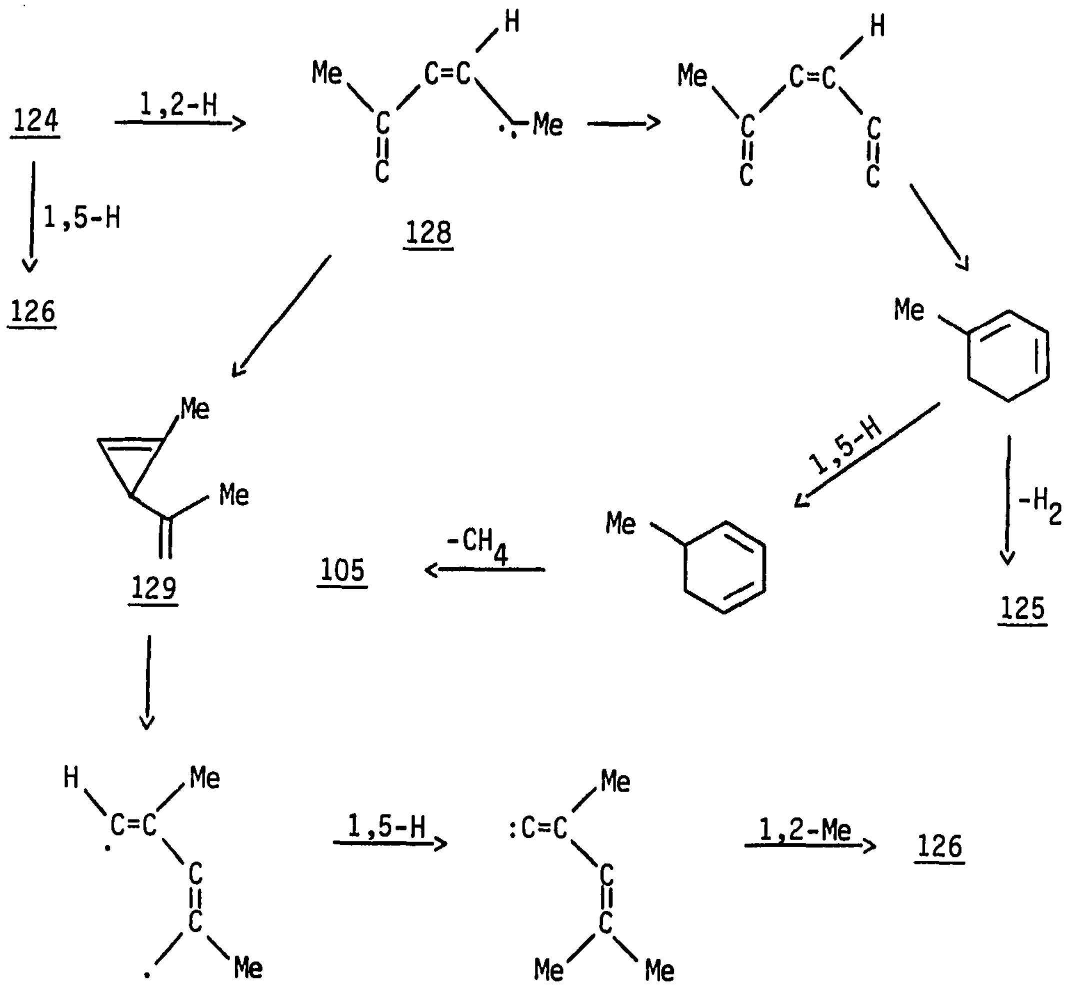
105 20%

109 15%

126 7%

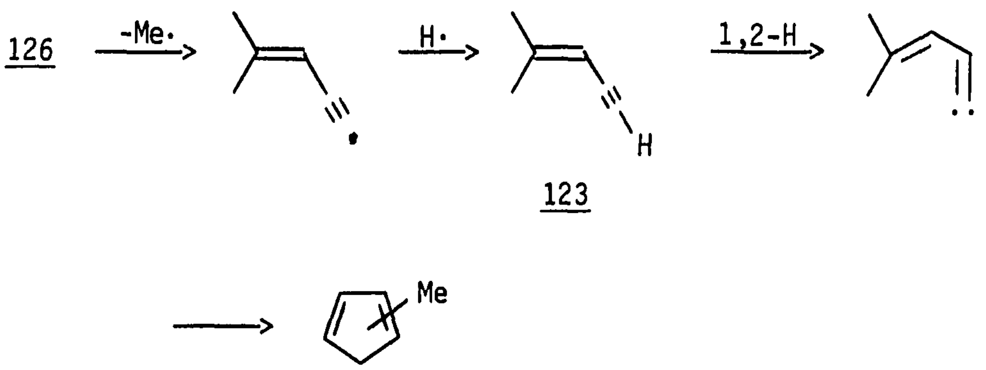
10%

Scheme 28



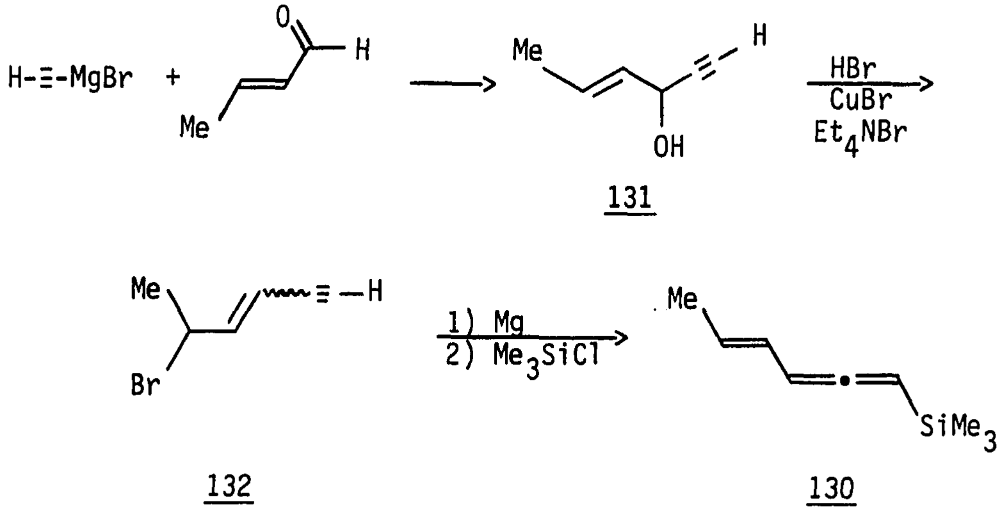
The formation of methylcyclopentadiene, 123, corresponds to the loss of methylene from 124. The direct loss of methylene from 124 is unlikely, and a more reasonable mechanism is shown in Scheme 29. Cyclopentadiene and methylcyclopentadiene were earlier formed from the FVP of the corresponding terminal acetylenes 82 and 122. Although 126 is not a terminal acetylene, at 750°C the loss of methyl group would not be unexpected.

Scheme 29



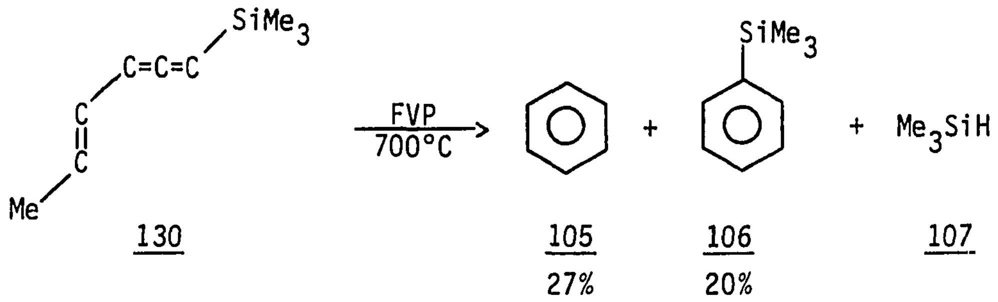
Because the reaction conditions needed to observe isomerization of 117 were so different than required for 66, a logical extension of the series was to determine how 130 behaved thermally. Allene 130 was synthesized starting with crotonaldehyde via the same route used to prepare 1-trimethylsilyl-1,2,4-pentatriene, 66 (Scheme 30).

Scheme 30

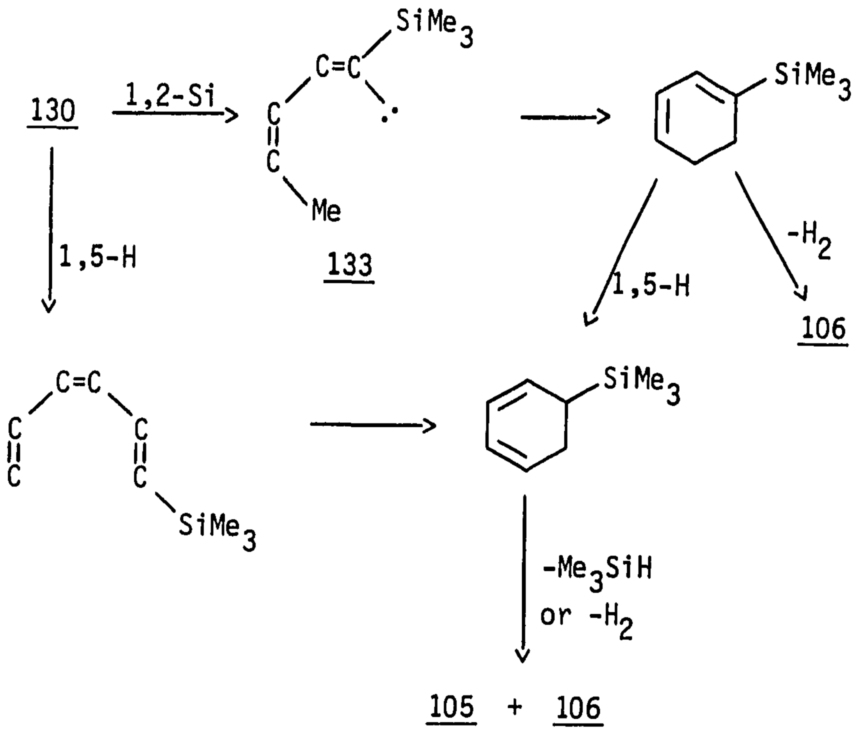


The conditions needed to observe isomerization of 130 were similar to those required for 1-trimethylsilyl-1,2,4-pentatriene rather than 1-trimethylsilyl-4-methyl-1,2,4-pentatriene. FVP at 700°C generated three products, benzene, 105 (27%), trimethylsilylbenzene, 106 (20%), and trimethylsilane, 107 (Scheme 31). No accurate yield of 107 was determined. Two different mechanisms can be drawn to account for 105-107 (Scheme 32). One pathway involves an initial 1,2-silyl shift to carbene 133 followed by cyclization and rearomatization to 105 and 106. An alternative mechanism to 105 and 106 consists of an initial 1,5-hydrogen migration to form 1-trimethylsilyl-1,3,5-hexatriene, followed by cyclization and aromatization. It is suggested here that a mechanism involving a 1,6-hydrogen insertion is unlikely. There is literature precedent that indicates that cyclization to form six membered rings via a 1,6 C-H insertion is not a facile process (66).

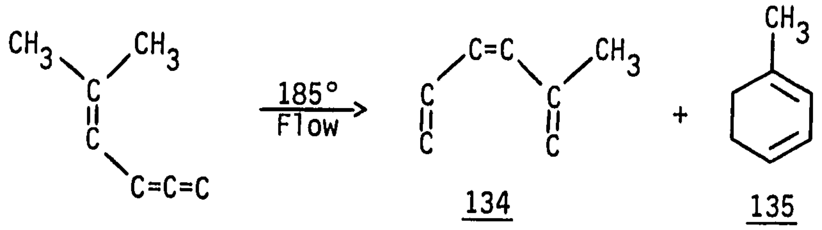
Scheme 31



Scheme 32

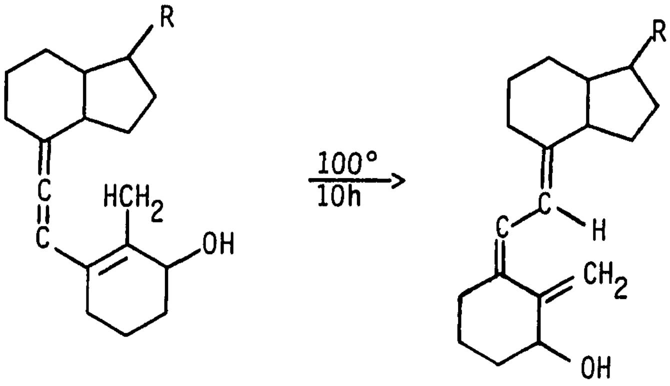


The route to 105-107 via the sigmatropic 1,5-hydrogen migration is very well precedented (67). Skattebol reported in 1969 that when 5-methyl-1,2,4-hexatriene is pyrolyzed at 185°C, in a N$_2$ flow system, triene 134 and cyclic diene 135 were formed (68). An initial (1,5)-hydrogen shift was proposed to account for 134. Okamura has made synthetic use of the (1,5)-hydrogen shift of appropriately substituted allenes to synthesize several Vitamin D analogs 136 (69).



134

135

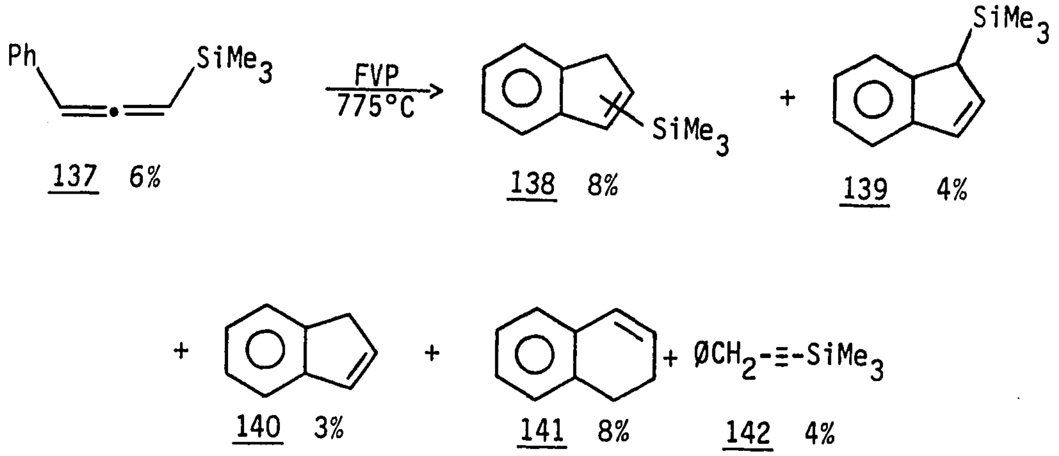


136

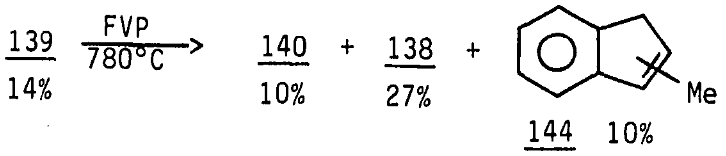
Continuing the search for silylallenes which would rearrange under milder thermal conditions, 3-phenyl-1-trimethylsilylallene, 137, was synthesized to determine if a phenyl substituent on C_3 would increase the reactivity of the allene. It was thought that the phenyl group could provide resonance stabilization of a radical center at C_3 and, therefore, perhaps reduce the temperature required for the initial 1,2 shift. The synthesis of 137 was carried out according to the procedure reported by West (70). Surprisingly, 137 turned out to be one of the least reactive silylallenes studied. At 700°C, under

FVP conditions, no new products were observed. At 775°C five compounds, 138-142, were isolated in quite poor overall yield (27%) (Scheme 33).

Scheme 33



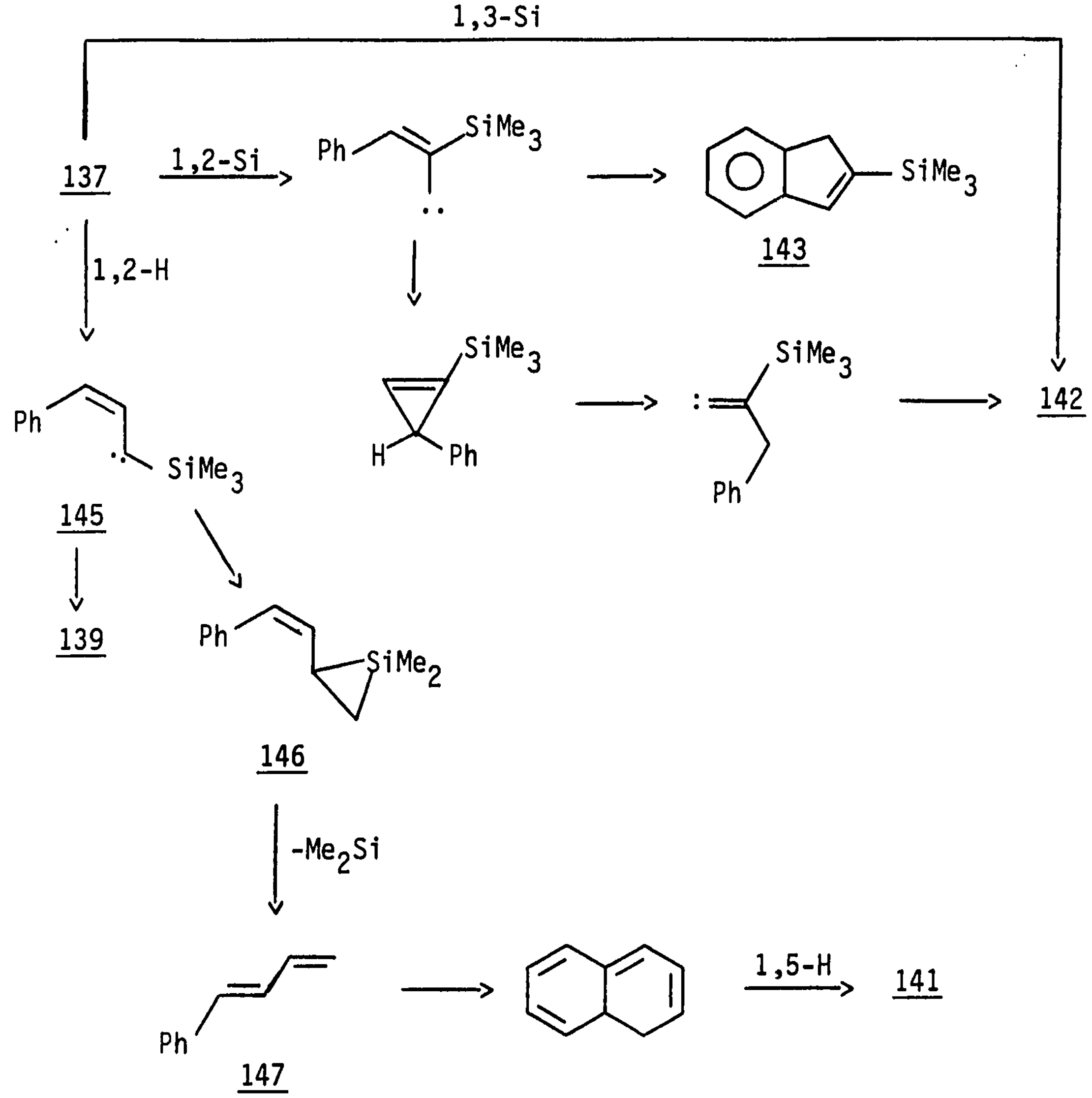
It appears at this higher temperature (775°C) that three distinctly different initial migrations take place which lead to the various products isolated (Scheme 34). Propargyl silane 142 can be formed directly from 137 via a (1,3)-silyl shift. Another route to 142 that is possible is the now well-precedented allene to cyclopropene to vinylidene pathway. Silylindene 139 is thought to be derived from 137 via an initial 1,2-hydrogen migration, followed by a C-H insertion into a phenyl C-H bond. Independent synthesis and pyrolysis of 139 showed that 140, 138 and 144 were formed in 10%, 27%, and 10% yields, respectively, along with recovered 139. Therefore the presence of 140 and 138 in the FVP of 137 is consistent with the secondary rearrangement of 139. Besides generating 139, carbene 145 could also insert into a C-H bond of a silicon methyl to generate 146. Subsequent elimination of dimethylsilylene from 146 would afford 147. An intramolecular Diels-Alder reaction followed by a (1,5)-H migration would complete the pathway to 141.



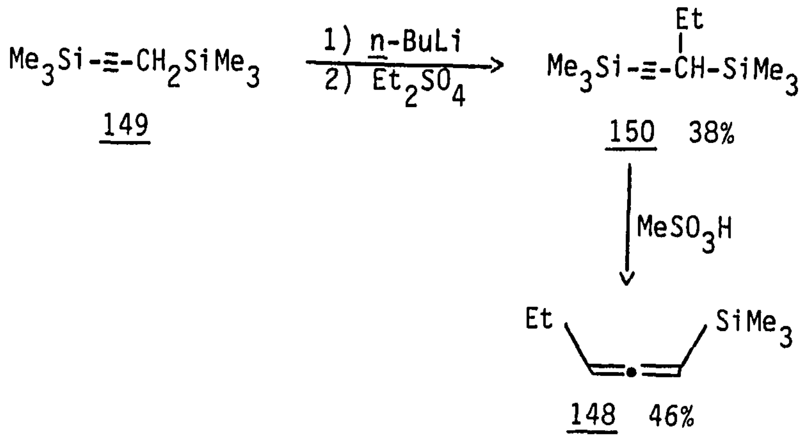
In summary, the vinyl substituted silylallenes studied so far all require temperatures of at least 600°C in a FVP system to appreciably isomerize. The conditions necessary to isomerize the allenes in this investigation are much greater than what was needed to isomerize silylallenyl ketones. This suggests that the ability of substituents to provide resonance stabilization is not the major factor controlling the facility of isomerization. The results so far suggest that if the allene has the choice of rearranging via an initial 1,2-silyl or by a 1,2-hydrogen migration, the silyl migration is preferred. Products derived from a 1,2-hydrogen migration are only observed at temperatures above that required for the 1,2-silyl shift to occur.

To further probe how substituents may or may not have an effect on the ability of silylallenes to isomerize, a number of simple alkyl silylallenes were synthesized. The thermally-induced rearrangements of allene 148 were investigated because it is the saturated analog of the earlier studied 1-trimethylsilyl-1,2,4-pentatriene, 66. The synthetic route to 148 is shown in Scheme 35. Starting with silylacetylene 149, treatment with n-BuLi and quenching the subsequent anion with Et_2SO_4 afforded 150 in 38% yield. Acetylene 150 was then treated with methanesulfonic acid which electrophilicly cleaved the propargyl carbon-silicon bond to generate 148 in a 46% yield.

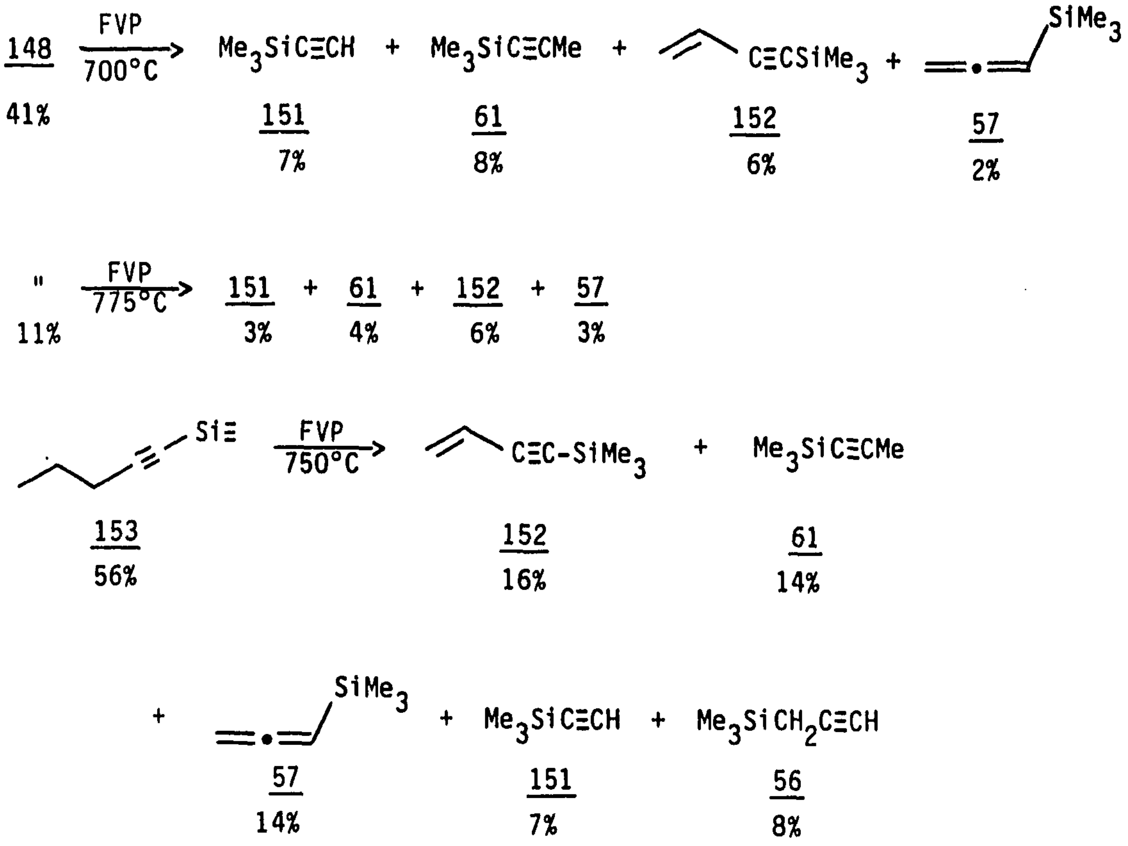
Scheme 34



Scheme 35

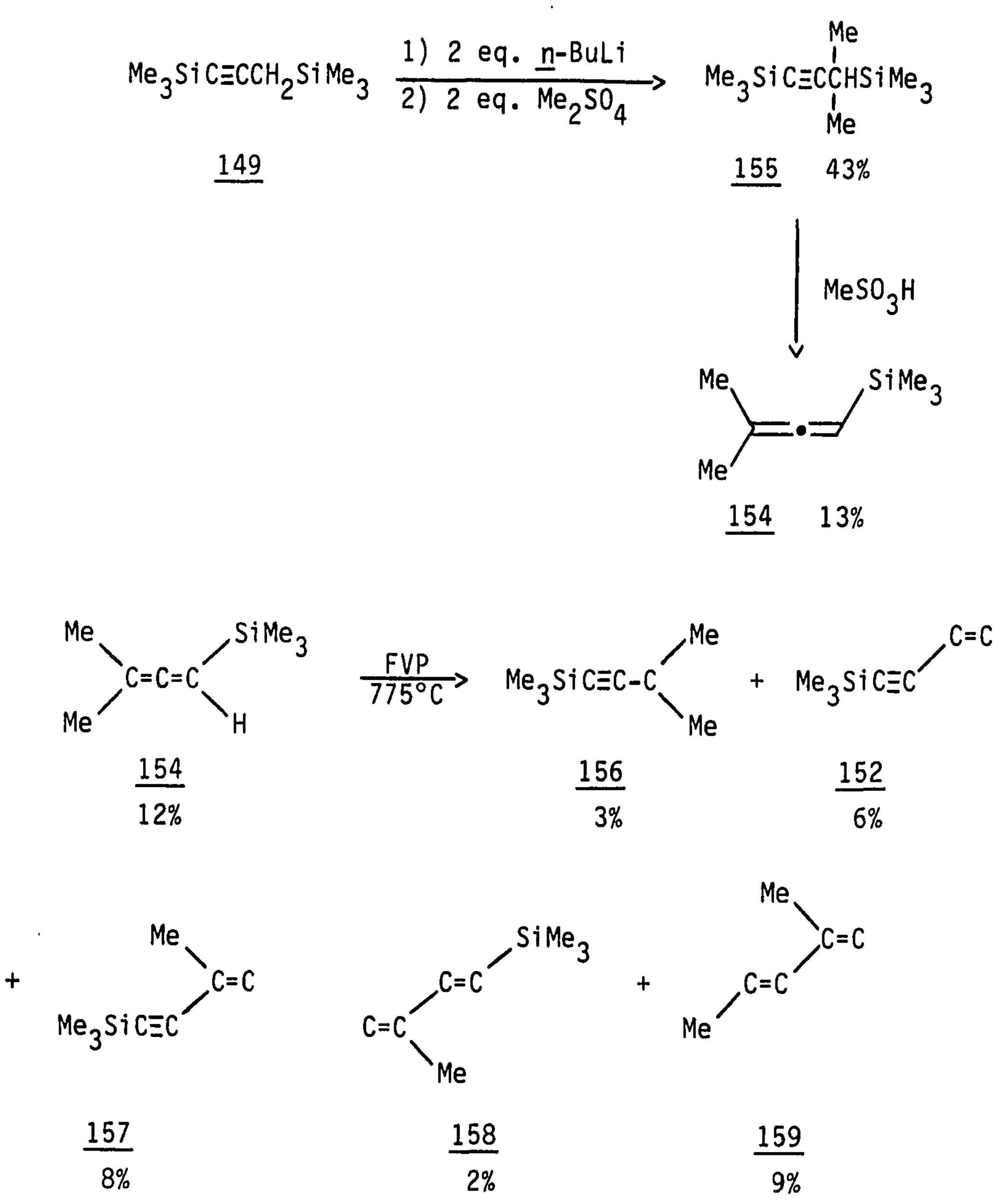


Pyrolysis of 148 at 700°C afforded mostly 148 (41%) along with trimethylsilylacetylene, 151 (7%), trimethylsilylpropyne, 61 (8%), trimethylsilylallene, 57 (2%), and vinyltrimethylsilylacetylene, 152 (6%). Increasing the pyrolysis temperature to 775°C decreased the amount of recovered 148; however, the yields of 61, 57, 151, and 152 did not increase. The product that was expected from the rearrangement of 148, 1-trimethysilyl-1-pentyne, 153, was not observed. In an effort to determine if it was possible that 153 was being formed and then reacting further to afford the observed products, 153 was independently synthesized and pyrolyzed at 750°C. Compound 153 was synthesized in a 53% yield by reacting 1-pentyne with *n*-BuLi and quenching the resulting anion with trimethylchlorosilane. FVP of 153 at 750°C resulted in the formation of 152 (16%), 61 (14%), 57 (14%), 56 (8%), and 151 (7%) along with recovered 153 (56%). Therefore, this result is consistent with the proposal that 148 initially isomerizes to 153, and 153 further rearranges and fragments to the observed products.



Allene 154 was the only 3,3-disubstituted silylallene studied. The synthetic route to 154 was similar to that used for the preparation of 148, except that the dianion was formed and quenched with two equivalents of dimethyl sulfate (Scheme 36). When 154 was pyrolyzed at 775°C, five products along with 12% of 154 were isolated. The low yields are a consequence of the poor mass recovery (38%).

Scheme 36

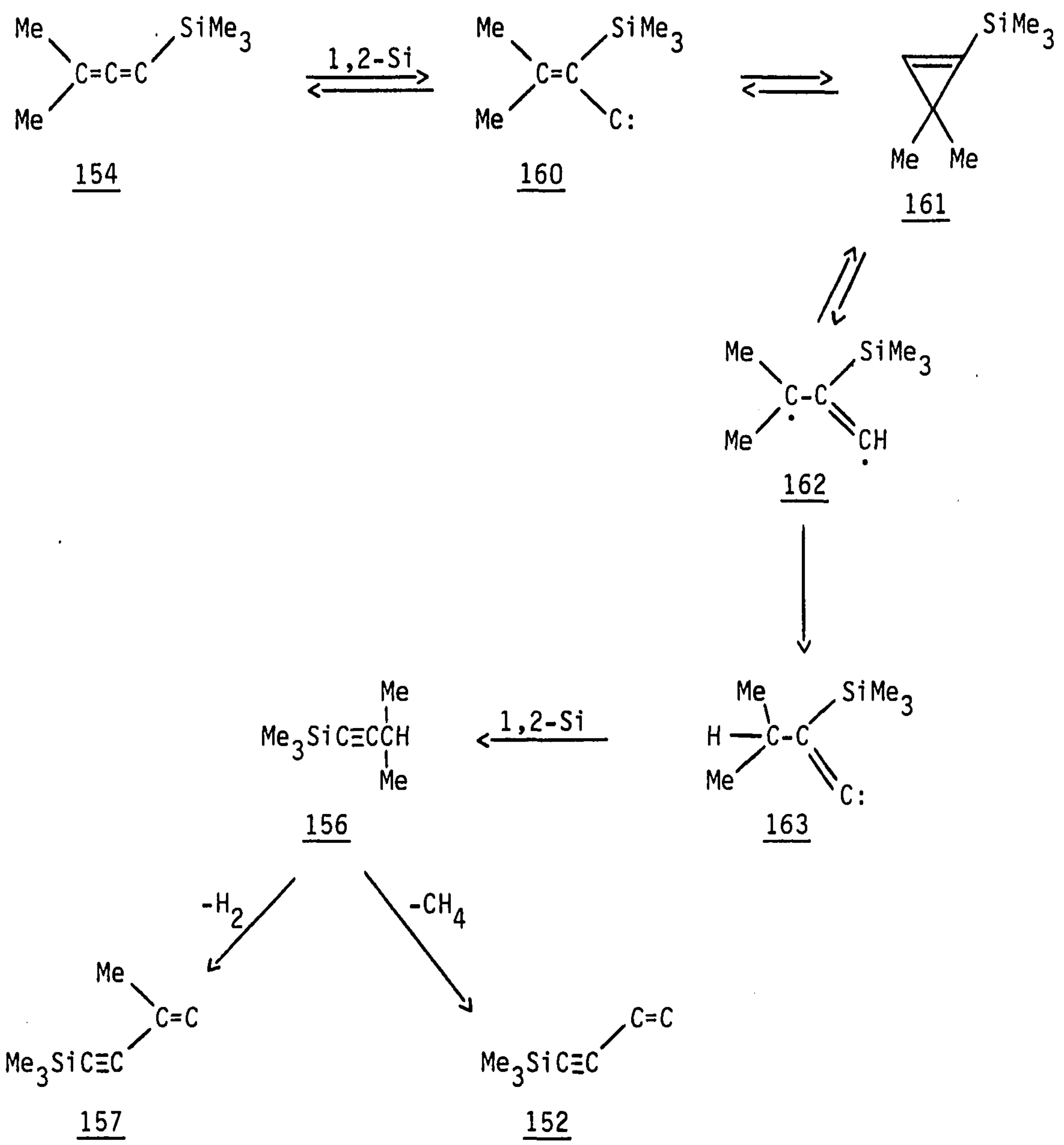


A reasonable mechanism to explain the formation of 152, 155, and 157 is described in Scheme 37. The initial step is a 1,2-silyl migration to afford carbene 160, which then cyclizes to cyclopropene 161. Homolysis of a cyclopropene bond would generate the 1,3-diradical 162, which if followed by a 1,3-H abstraction would yield 163. A similar 1,3-H abstraction was earlier suggested by Yoshimine (52). Vinylidene 163 would likely rearrange via another 1,2-silyl shift to afford 156. Acetylenes 152 and 157 were thought to be secondary products from the decomposition of 156. Independent synthesis of 156 and pyrolysis at 800°C did afford 152 (36%) and 157 (3%) along with tetramethylsilane (15%) and trimethylsilylacetylene (19%).

$$\underline{156}\ \xrightarrow[800^\circ C]{FVP}\ \underset{36\%}{\underline{152}} + \underset{3\%}{\underline{157}} + \underset{19\%}{\underline{151}} + \underset{15\%}{Me_4Si}$$

The presence of 2-methyl-1,3-pentadiene, 159, as a product of the FVP of 154 requires the overall loss of dimethylsilylene from 154. As the FVP of 81 and 124 have shown, it appears that allenes are capable of undergoing 1,2-hydrogen shifts when pyrolysis temperatures are higher than needed for a 1,2-silyl migration to occur. In this case, the pyrolysis of 154 was done at 775°C which is a higher temperature than required for many of the earlier pyrolyses of silylallenes. Therefore, the mechanism described in Scheme 38, which is characterized by an initial 1,2-hydrogen migration, seems reasonable. Vinyl carbene 164 has the opportunity to undergo two distinctly different

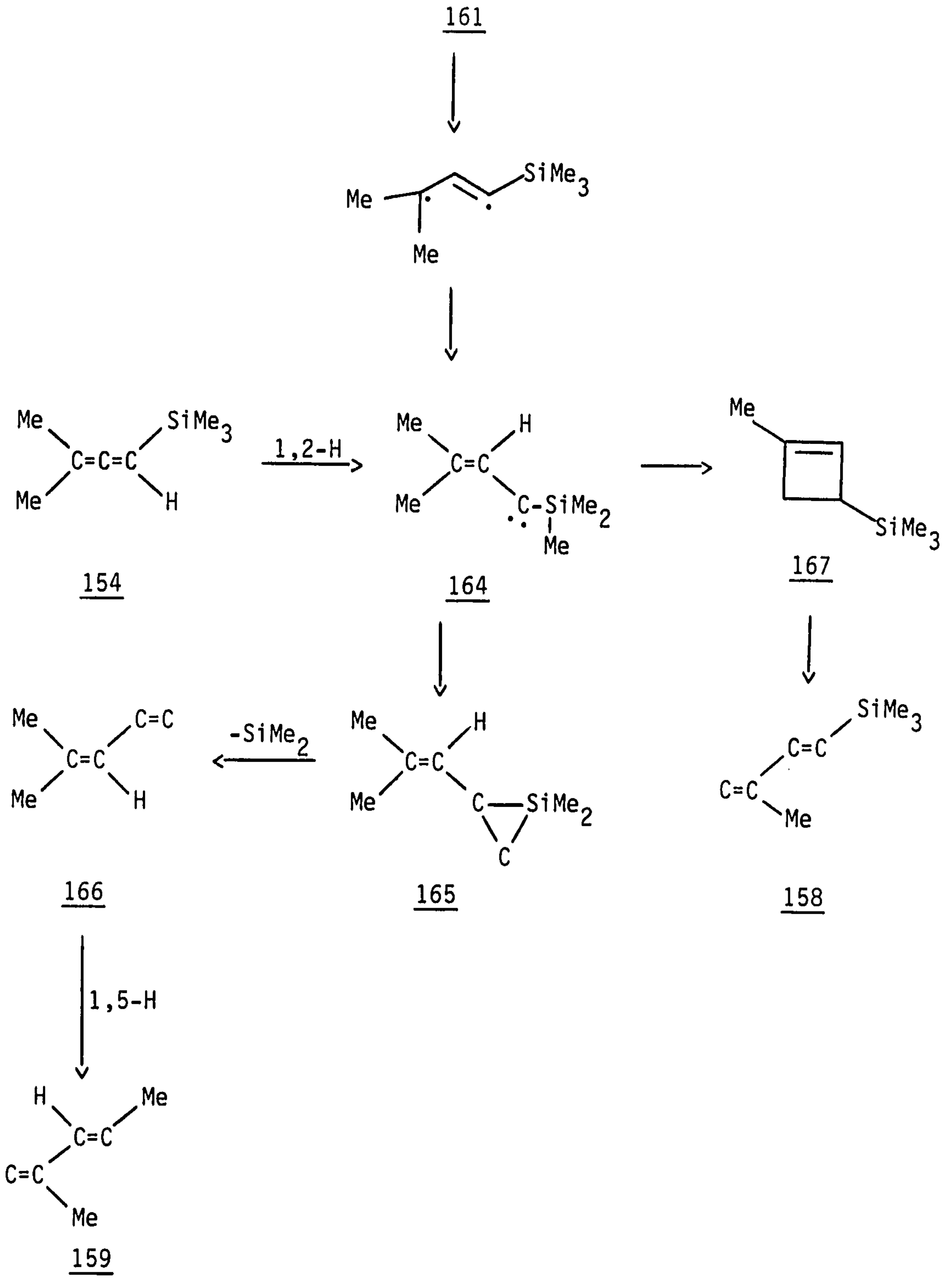
Scheme 37



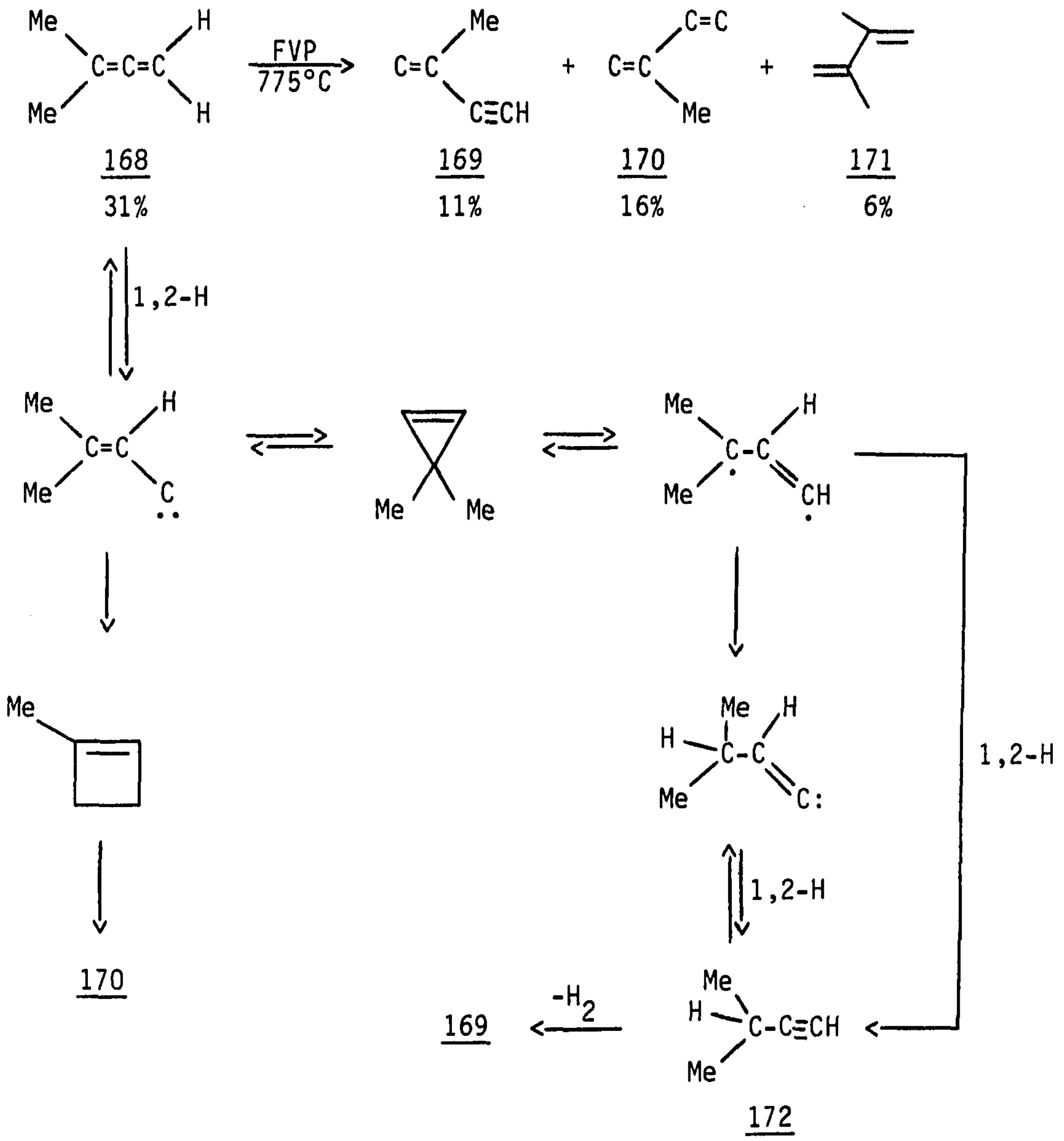
C-H insertions. Insertion into a silicon methyl group would lead to silacyclopropene 165. As mentioned earlier, silacyclopropenes are thermally unstable compounds and are known to extrude dimethylsilylene. If 165 loses dimethylsilylene, 166 would be generated. Diene 166 would likely rearrange via a sigmatropic (1,5)-hydrogen shift to afford 159. Carbene 164 could also C-H insert into one of the vinyl methyl groups to afford 167. Under these conditions, 167 would be expected to undergo an electrocyclic ring opening to yield 158. An alternative route to 158 and 159 from an initial homolysis of 161 is also possible.

The thermolysis of 2-methyl-1,2-butadiene, 168, an analogue of 154, was carried out to see if 168 isomerized in a similar fashion as 154. The FVP of 168 at 775°C generated three major products, 169-171, along with a large amount of 168. Acetylene 172 was not observed nor was vinylacetylene. The absence of 172 is not too surprising since it was shown earlier that 156 was not thermally stable at 775°C. The fact that no vinyl acetylene was observed may be due to the volatility of the compound. No special effort was taken to avoid loss of vinylacetylene or of compounds of similar volatility during collection and analysis of the pyrolysate. Compounds 169 and 170 were two of the expected products if 168 rearranged in an analogous fashion a 154. A mechanistic pathway similar to that proposed for the rearrangement of 154 is shown in Scheme 39. The large amount of recovered 168 indicates that even though a 1,2-H migration is possible, it is not a very facile process at 775°C.

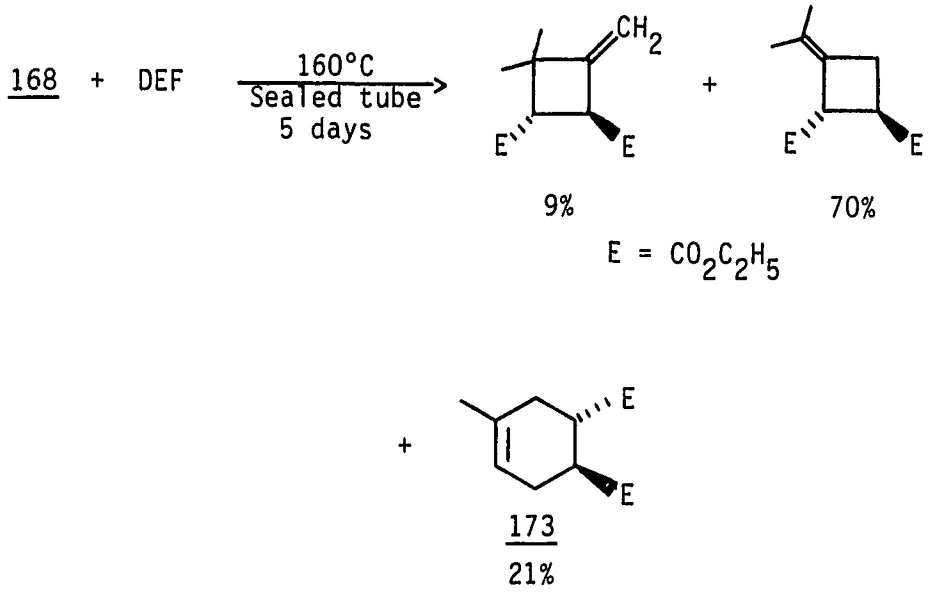
Scheme 38


161
Me
Me
SiMe3
Me
Me
SiMe3
H
C=C=C
154
1,2-H
Me
Me
H
C=C
C-SiMe2
Me
164
Me
SiMe3
167
Me
Me
H
C=C
C—SiMe2
C
165
-SiMe2
Me
Me
C=C
C=C
H
166
SiMe3
C=C
C=C
Me
158
1,5-H
H
Me
C=C
C=C
Me
159

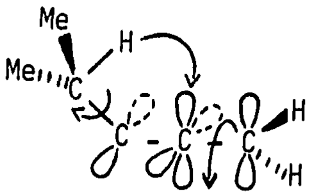
Scheme 39



The mechanism that is shown in Scheme 39, which consists of an initial 1,2-hydrogen migration to account for the isomerization of 168 to 170, is not the only possible mechanism to explain this rearrangement. Pasto has reported that when 168 was heated in a sealed tube in the presence of diethyl fumarate (DEF), a significant amount of 173 (21%) was isolated along with the expected "2+2" adducts (71). By using toluene as the solvent rather than excess DEF, it was found that 173 was generated in 60% yield. Pasto has proposed that 168 isomerizes initially to isoprene and then is trapped by DEF to afford 173.

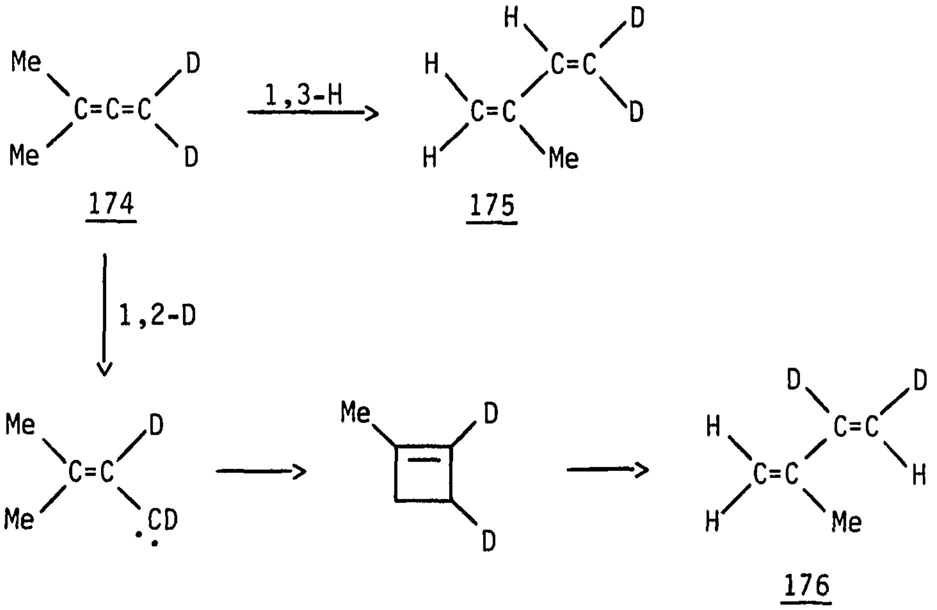


Pasto reported that 168 isomerizes to 170 via a sigmatropic (1,3)-hydrogen migration. Although, in general, 1,3-H migrations are symmetry "forbidden", a suprafacial hydrogen migration to the 2p orbital of C_2 of the $\pi_{2,3}$ bond is "allowed" (72).



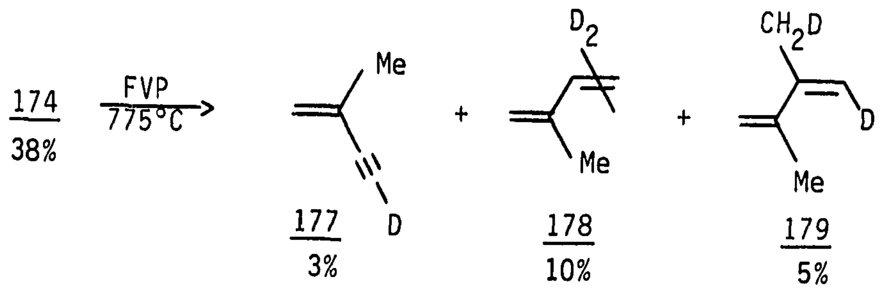
A logical way to distinguish between the two mechanisms is to select an appropriately labeled allene which, depending on the mechanism, affords different products. The allene that was chosen was 174. If 174 rearranges via a 1,3-hydrogen migration, isoprene 175 would be formed (Scheme 40). If the isomerization takes place by an initial 1,2-hydrogen migration, then isoprene 176 would be generated.

Scheme 40



For the preliminary experiment, the FVP of 174 at 775°C was chosen. Pyrolysis of 174 afforded 177-179 (Scheme 41). The isoprene isomers were isolated via preparative gas chromatography. The complexity of the ^1H NMR and the ^2H NMR spectra suggested that more than one isomer was present. The characteristic resonance in the ^1H NMR spectrum of the proton bonded to C_3, would allow for the distinction of 175 and 176. The chemical shift of this proton in isoprene is 6.44 ppm. The ^1H NMR of the isolated isoprene did possess a multiplet at 6.44 ppm; however, it did not integrate out as one proton. Furthermore, ^1H decoupling at 6.44 revealed that it was coupled to protons at 5.16 and 5.05 ppm. The coupling constant between the proton at 6.44 and 5.16 ppm was 17 Hz, which is consistent with trans vinyl coupling. The lack of trans hydrogens in either 175 or 176 was proof that an isomer besides 175 or 176 was also present. The presence of a peak at 6.5 ppm in the ^2H NMR spectrum is consistent with isoprene 176. Although the results from this one pyrolysis do not provide any conclusive evidence to support the presence of 175, the inability to completely interpret the spectral data prevents ruling it out also.

Scheme 41



The FVP of 174, besides affording isoprene, also generated, as expected, the deuterium isomer of 169, 177. The deuterium was located exclusively on the terminal acetylene carbon which is consistent with the mechanism that was proposed in Scheme 39.

Another way to distinguish whether isoprene was formed via a route involving a 1,2 or 1,3-hydrogen migration was to determine if there was a primary deuterium isotope effect. If the rearrangement takes place via a 1,2-hydrogen shift, the k_H/k_D ratio should be greater than one. If the rearrangement occurs via a 1,3-hydrogen migration, no primary deuterium isotope would be observed. The kinetic measurements were done using a stirred-flow reactor (SFR). The thermolysis of allenes 168 and 174 were done at three different temperatures, and the results are shown in Table 2.

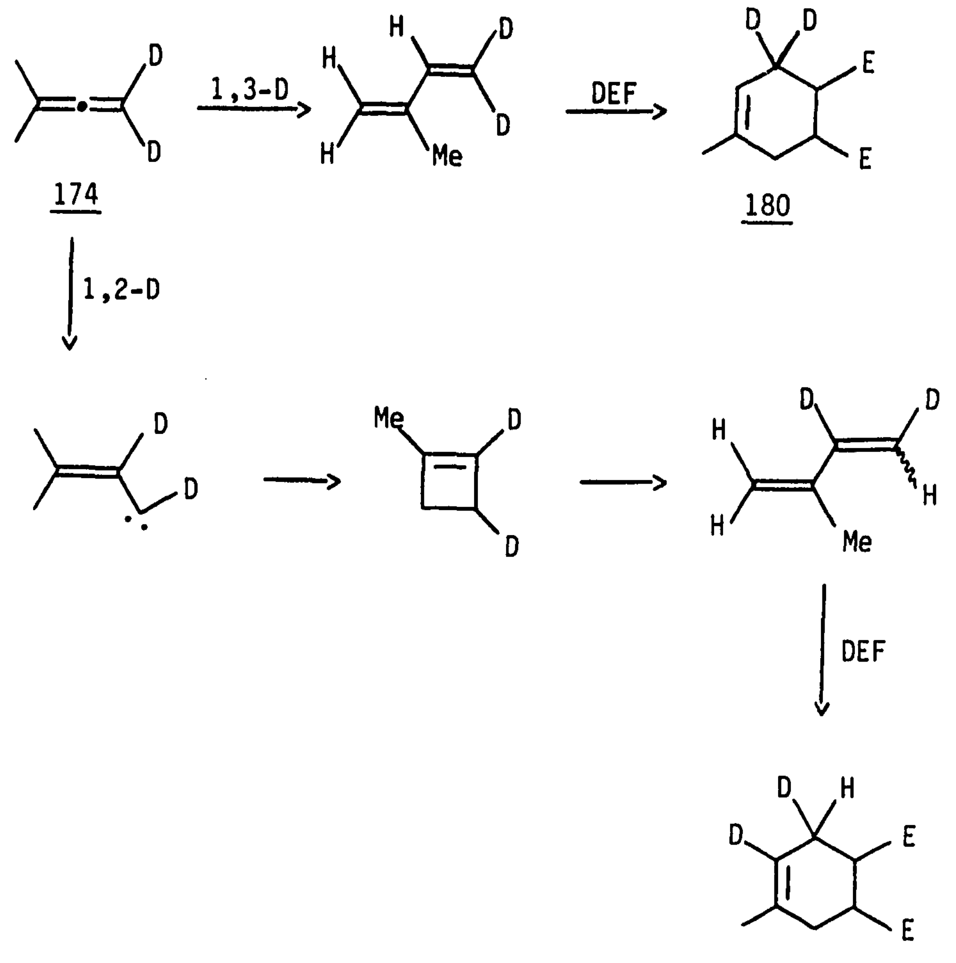
Table 2. SFR rate constants from the thermolysis of 168 and 174 at 658°C to 696°C

t (°C)	168	174	k_H/k_D
696	0.153	0.139	1.10
678	0.078	0.066	1.18
658	0.041	0.033	1.24

From the apparent rate constants, a deuterium isotope effect of 1.17 (± 0.07) was calculated. Unfortunately, there are no values reported in the literature for a deuterium isotope effect derived from a 1,2-hydrogen shift. Therefore, it is not known whether a value of 1.17 is a reasonable number. Another problem is that since the FVP of 174 resulted in the formation of more than one isomer of isoprene, the deuterium isotope effect measured may be due to one or more processes.

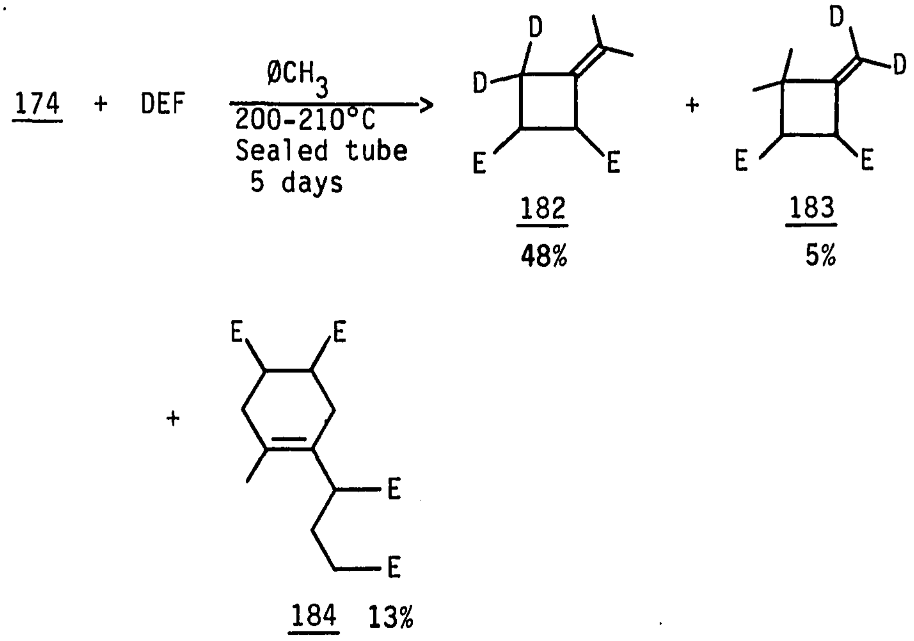
The conclusions that can be made from the pyrolysis of 174 and the kinetic work done so far are certainly very tentative; however, the results seem to support a mechanism involving an initial 1,2-hydrogen migration rather then a 1,3-hydrogen migration. Since the results of the FVP of 174 are so inconclusive, it was thought that the sealed tube thermolysis of 174 in the presence of DEF might provide better evidence for how the isomerization of 174 takes place. Two different cyclohexenes, 180 or 181, would be formed depending on which mechanism is involved (Scheme 42).

Scheme 42



A solution of 174, DEF, and toluene was prepared and placed into a dry, glass tube that had been treated with 1N HCL, 1N NaOH, water, and methanol as described by Pasto (71). The contents of the tube were triply freeze-degassed, and the tube was sealed under reduced pressure. The sealed tube was then completely immersed for 5 days in an oil bath which was maintained at 200-210°C. After 5 days of heating, the reaction mixture was analyzed by GC/MS and three major products were detected (Scheme 43). Two compounds having a molecular weight of 242 were isolated by preparative GC and identified by ^{1}H NMR as the expected "2+2" products <u>182</u> (48%) and <u>183</u> (5%). A product that had a molecular weight of 414 was isolated by distilling off all other compounds and identified as <u>184</u> (13%). The 1:2 adduct <u>184</u> was also observed by Pasto but in less than 5% yield. Unfortunately, neither of the expected products, <u>180</u> or <u>181</u> were isolated.

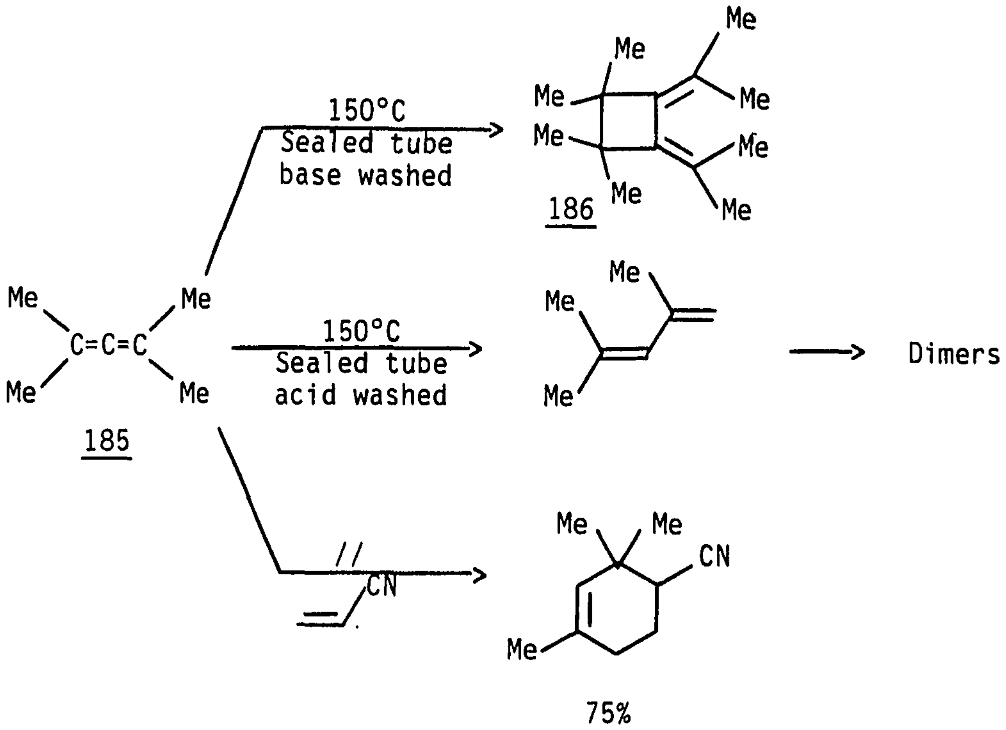
<u>Scheme 43</u>



Since the above reaction conditions were identical to those reported by Pasto, in which he obtained a 60% yield of substituted cyclohexene, suggested that perhaps an impurity was promoting the isomerization of 168 to isoprene. Previous work by Pasto involving the reaction of 168 with either 1,1-dichloro-2,2-difluoroethene or N-phenylmaleimide did not afford products derived from isoprene (73). Kiefer has also reacted 168 with DEF or DEM and did not observe any product derived from isoprene (74).

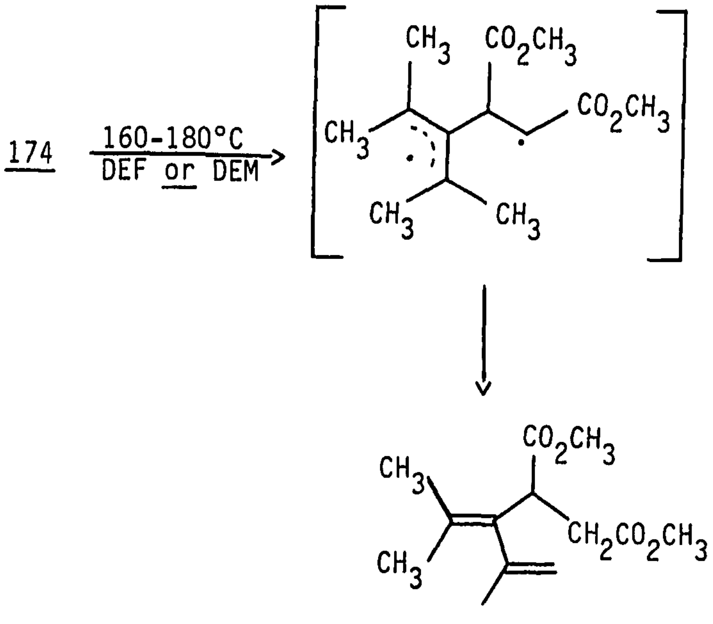
The only example of a sigmatropic 1,3-H migration similar to that proposed by Pasto is the acid catalyzed isomerization of tetramethylallene, 185 (75). Taylor has reported that when 185 is heated in either an unwashed or acid washed glass tube at 150°C, 2,4-dimethylpenta-1,3-diene was formed (Scheme 44). If 185 is heated in the presence of acrylonitrile, the intermediate 2,4-dimethylpenta-1,3-diene is trapped to afford the expected "4+2" cycloaddition product. If the thermolysis is carried out in a base washed tube only, the allene dimer 186 is formed. Kiefer has shown that 185 reacts with DEF or DEM to afford 187 and not the "4+2" adduct from the trapping of 2,4-dimethylpenta-1,3-diene (Scheme 45).

Scheme 44



In summary, since the reaction of 174 with DEF did not generate any isoprene or derivative of isoprene, it was not possible to determine the mechanism of its formation from 168 or 174. The results of the thermolysis of 174, however, do fit well with a majority of "2+2" reactions of allenes. The work reported in this dissertation along with the results of Kiefer and Taylor suggest that the products derived from isoprene that Pasto isolated were due to an acid catalyzed process rather than a 1,3-H migration.

Scheme 45



187

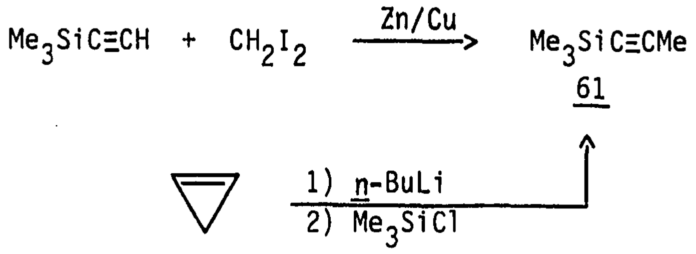
Synthesis and FVP of 1-Trimethylsilylcyclopropenes

Throughout this investigation of the thermally-induced rearrangements of silylallenes, the mechanisms that have been proposed have been based on the products observed. A logical way to provide supporting evidence for the suggested pathways was to generate independently the intermediates and determine if under the same conditions they indeed do yield the observed products. Unfortunately, most of the intermediates that have been proposed are carbenes or diradicals which are not easily independently synthesized. The family of intermediates that appeared to be most adaptable to independent synthesis are the various 1-trimethylsilylcyclopropenes proposed.

There are many synthetic routes to cyclopropenes described in the literature. Therefore, it was thought that adaptation of one or more of these methods to the synthesis of the appropriately substituted trimethylsilylcyclopropenes would be possible.

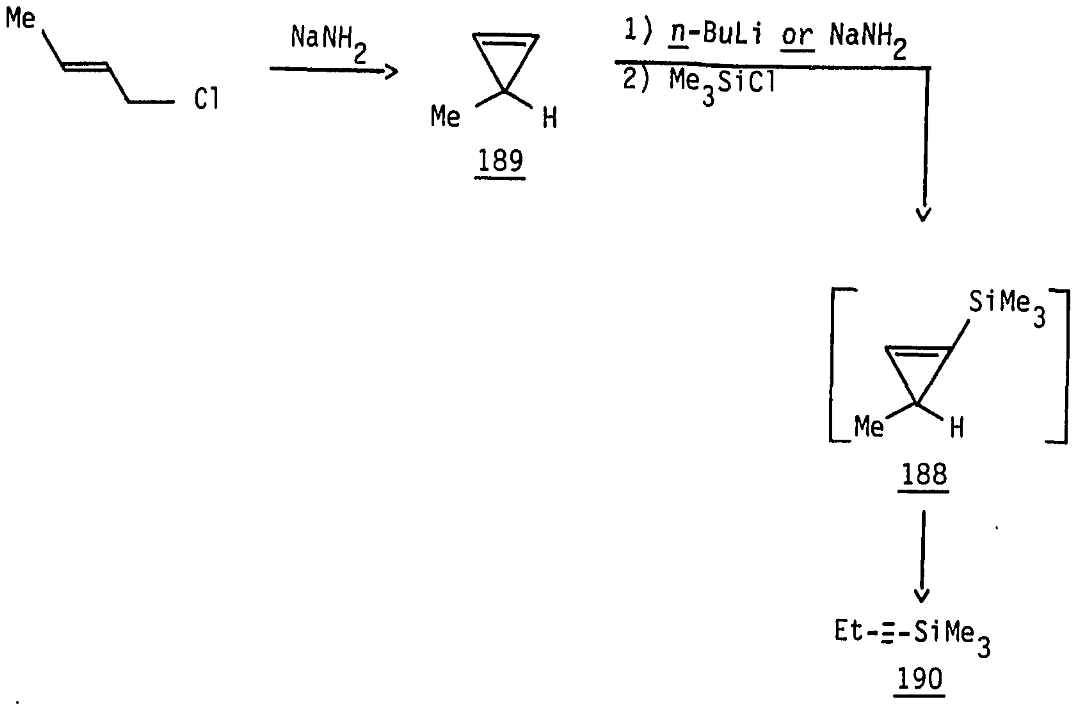
One major problem with working with cyclopropenes is their instability, especially if a hydrogen atom is present at the C_3 atom of the cyclopropene ring (76-79). Dimerization and polymerization of such cyclopropenes is very common and may be due to intermolecular ene reactions (79-81). Unfortunately, most of the cyclopropenes that have been invoked in this investigation possess a hydrogen atom at C_3.

The first cyclopropene that was chosen for synthesis was 1-trimethylsilylcyclopropene 63. Cyclopropene 63 was selected because it was the simplest example of a 1-silyl substituted cyclopropene and because it was believed to be an intermediate in the isomerization of 57 to 61 (Scheme 12). The first route to 63 that was tried was to carry out a Simmons-Smith reaction on trimethylsilylacetylene. The only isolated product that had the correct molecular weight was not 63, but rather trimethylsilylpropyne, 61. Another attempted route to 63 was to metallate cyclopropene and quench the resulting anion at -78°C with trimethylchlorosilane. Unfortunately, again only 61 was isolated. One concern was that perhaps 63 was being made, but upon workup of the reaction mixture or identification of the reaction products by GC/MS, 63 was being isomerized to 61. Such a process was earlier invoked to explain the formation of 61; however, the conditions (700°C) were quite different. There are no reports in the literature that suggest that cyclopropenes rearrange in this fashion under such mild conditions. To determine if this indeed was happening, aliquiots were removed from the Simmons-Smith reaction and analyzed by ^1H NMR. The spectra contained no evidence to suggest that 63 was present.



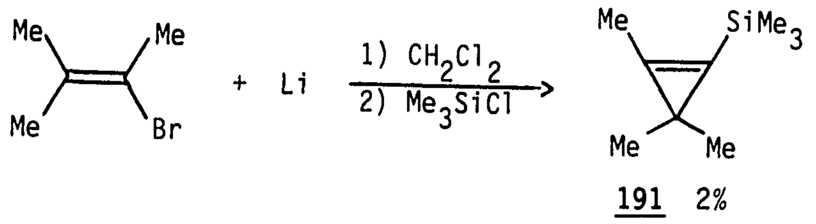
A literature search revealed that no 1-trimethylsilylcyclopropenes have been isolated having two hydrogens at C_3. Bolesov has suggested that products derived from such cyclopropenes are consistent with an intermolecular ene reaction having taken place. It appears that having a silicon substituent on C_1 and two hydrogens at C_3 significantly increases the reactivity of the cyclopropene.

Since the presence of hydrogen atoms at C_3 seems to increase the instability of cyclopropenes, it was hoped that exchange of one of the C_3 hydrogens in 63 for a methyl group would allow isolation of 188. Unfortunately, no 188 was isolated when 189 was reacted with either n-BuLi or $NaNH_2$, followed by quenching of the anion with trimethylchlorosilane. The only isomer of 188 that was isolated was a small amount of 190.



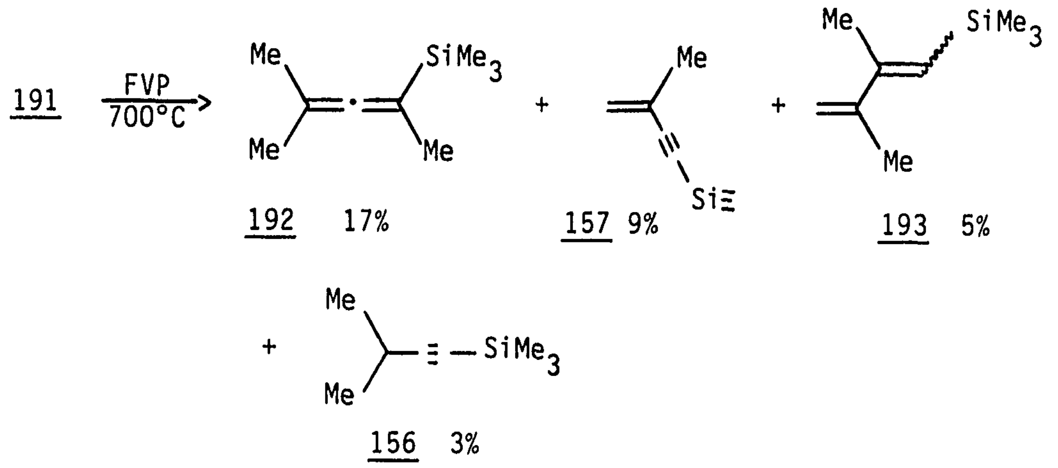
Levina has reported that 2,3,3-trimethyl-1-(trimethylsilyl)cyclopropene, 191, can be synthesized and isolated (82). Although 191 has not been proposed as an intermediate in any of the mechanisms so far, the thermally-induced rearrangements of 191 could provide some insight of how in general 1-trimethylsilylcyclopropenes isomerize. The synthetic route to 191 that was used in this work is shown in Scheme 46.

Scheme 46

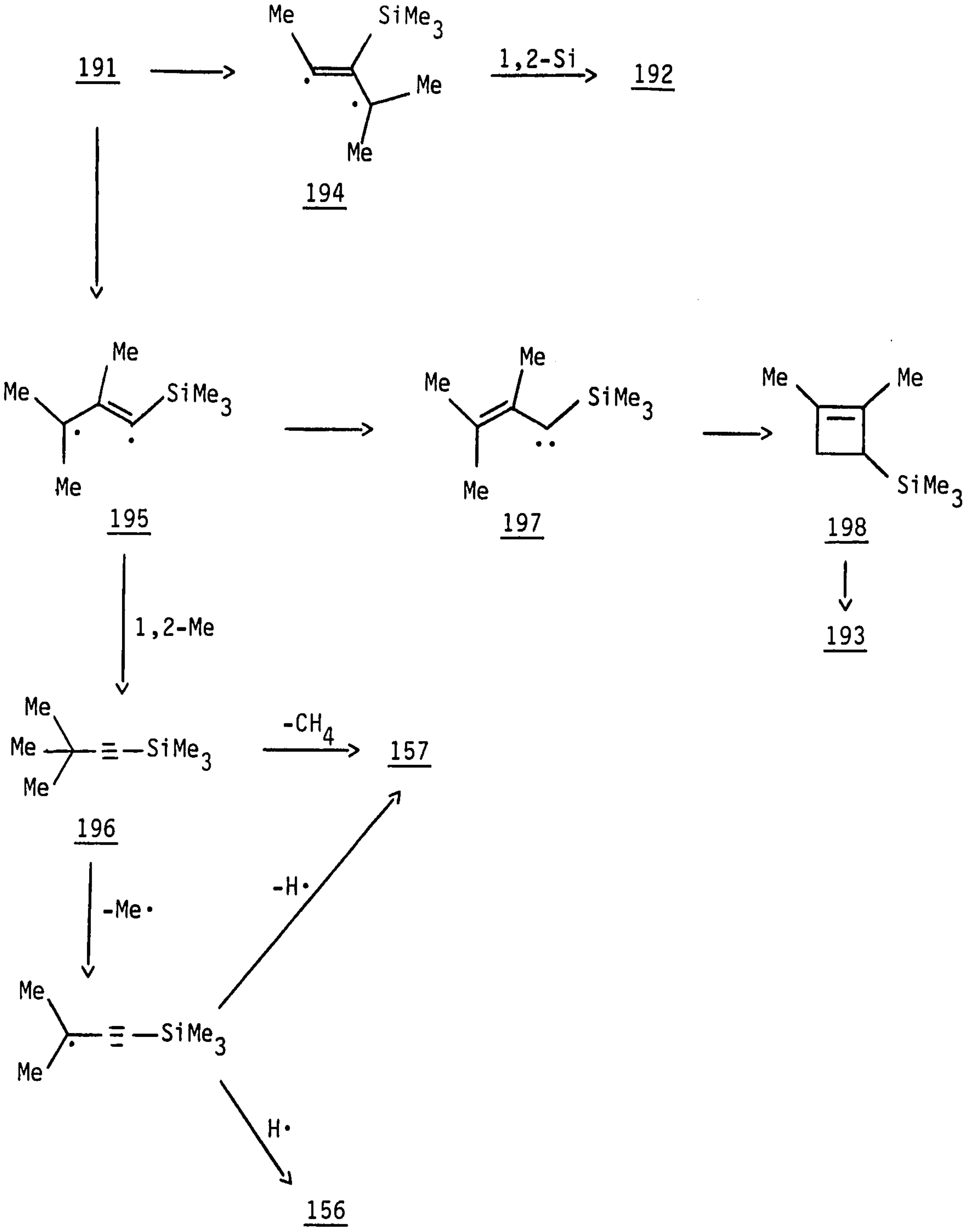


The pyrolysis of 191 at 700°C afforded four major products (Scheme 47). The formation of 192 is consistent with an initial homolysis of the C_2-C_3 bond to form 194, the biradical having both radical centers β to silicon (Scheme 48). A subsequent 1,2-silyl migration to the dimethyl radical center would afford 192 directly. An alternative fragmentation of 191 would generate biradical 195. Biradical 195 could be the reactive intermediate that leads to 156, 157, and 193. If 195 undergoes a 1,2-methyl shift, 196 would be formed. Although 196 was not observed as a product, the earlier example of the elimination of methane from 156 suggests that a similar process would in this case lead to 157. Besides eliminating methane, 196 could conceivably lose a methyl radical, followed by an abstraction of a hydrogen radical to yield 156. Diene 193 is proposed to arise also from 188. A different resonance form of 195, 197 could C-H insert into a methyl group to afford 198. Electrocyclic ring opening of 198 would lead to 193.

Scheme 47



Scheme 48

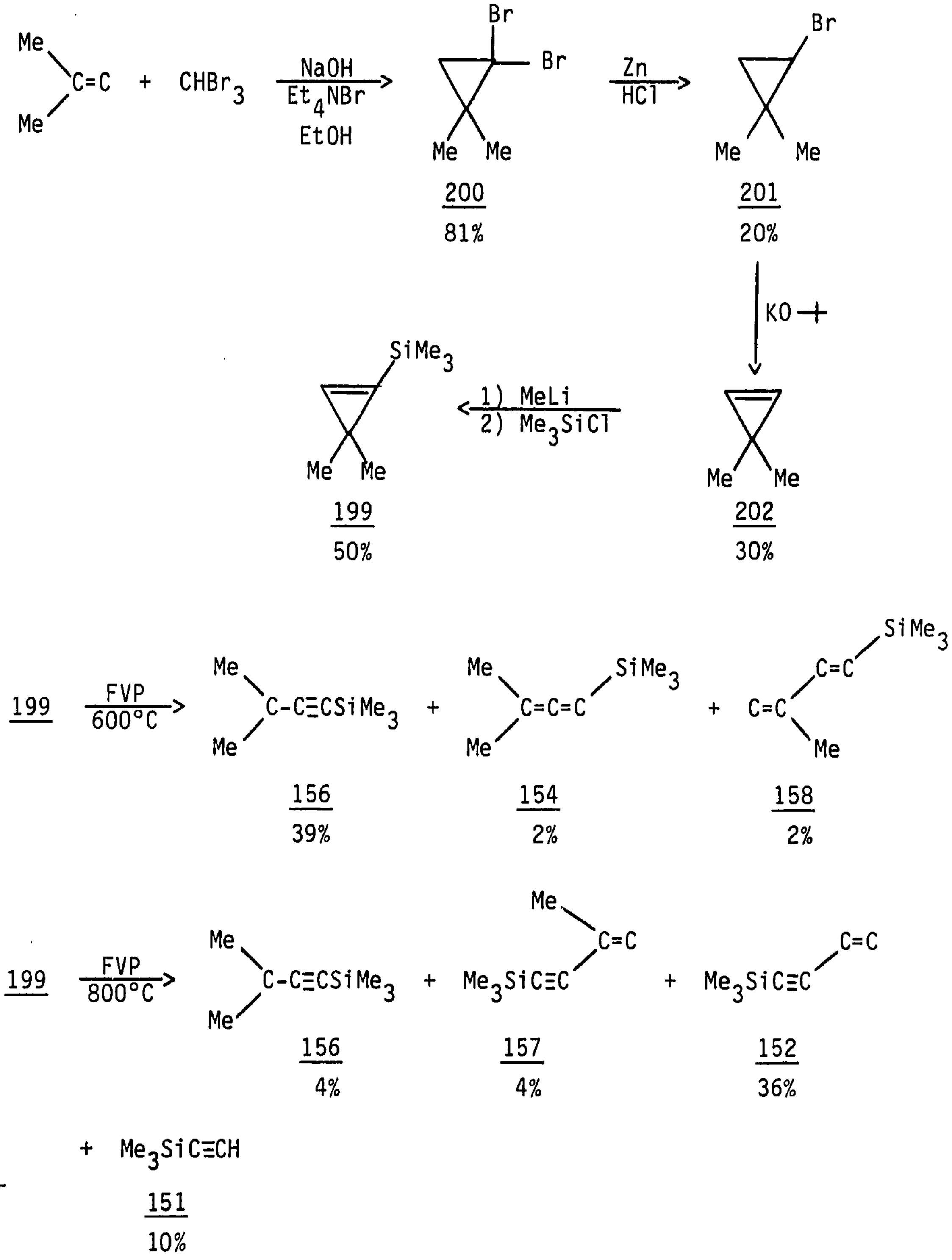

191
Me
SiMe3
Me
Me
194
1,2-Si
192
Me
Me
SiMe3
Me
195
Me
Me
SiMe3
Me
197
Me
Me
SiMe3
198
193
1,2-Me
Me
Me
Me
SiMe3
196
-CH4
157
-Me·
-H·
Me
Me
SiMe3
H·
156

Several conclusions can be made from the results of the FVP of 191. It appears that 191 opens to afford two different biradicals. In this case, the yields of products suggested that the β-silyl biradical was not favored over the α,γ-silyl biradical. The products formed from the FVP of 191 are analogous to those from the FVP of 154 and 168. Since analogous products were isolated, it is consistent with the proposal that cyclopropenes were formed during the isomerization of allenes 154 and 168.

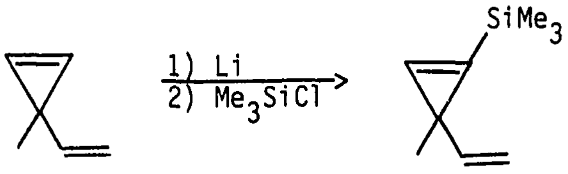
The only 1-trimethylsilylcyclopropene that has been synthesized, isolated, and proposed as an intermediate in the isomerization of the corresponding allene is 199. Therefore, 199 provided the first opportunity to find out if the products derived from the FVP of a silylallene are consistent with intermediacy of a cyclopropene. Cyclopropene 199 was formed via treatment of 202 with methyl lithium and quenching of the anion with trimethylchlorosilane (Scheme 49).

The FVP of 199 at 600°C generated three products, 156, 154, and 158 with 156 by far the major product. As expected, at 800°C 156 became a minor product and the two acetylenes, 157 and 152, derived from the elimination of hydrogen and methane, respectively, were present. Trimethylsilylacetylene was also formed at 800°C. The products isolated were exactly those found earlier from the pyrolysis of 154 except for the lack of 159. Since 159 was not thought to be formed from 199, it was, in fact, reassuring that it was not detected. At least in this case, the results fully support the intermediacy of 199 during the FVP of 154.

Scheme 49


Me
Me
C=C
+ CHBr3
NaOH
Et4NBr
EtOH
Br
Br
Me
Me
200
81%
Zn
HCl
Br
Me
Me
201
20%
KO+
SiMe3
Me
Me
199
50%
1) MeLi
2) Me3SiCl
Me
Me
202
30%
199
FVP
600°C
Me
Me
C-C≡CSiMe3
156
39%
+
Me
Me
C=C=C
SiMe3
154
2%
+
C=C
C=C
SiMe3
Me
158
2%
199
FVP
800°C
Me
Me
C-C≡CSiMe3
156
4%
+
Me
C=C
Me3SiC≡C
157
4%
+
C=C
Me3SiC≡C
152
36%
+ Me3SiC≡CH
151
10%

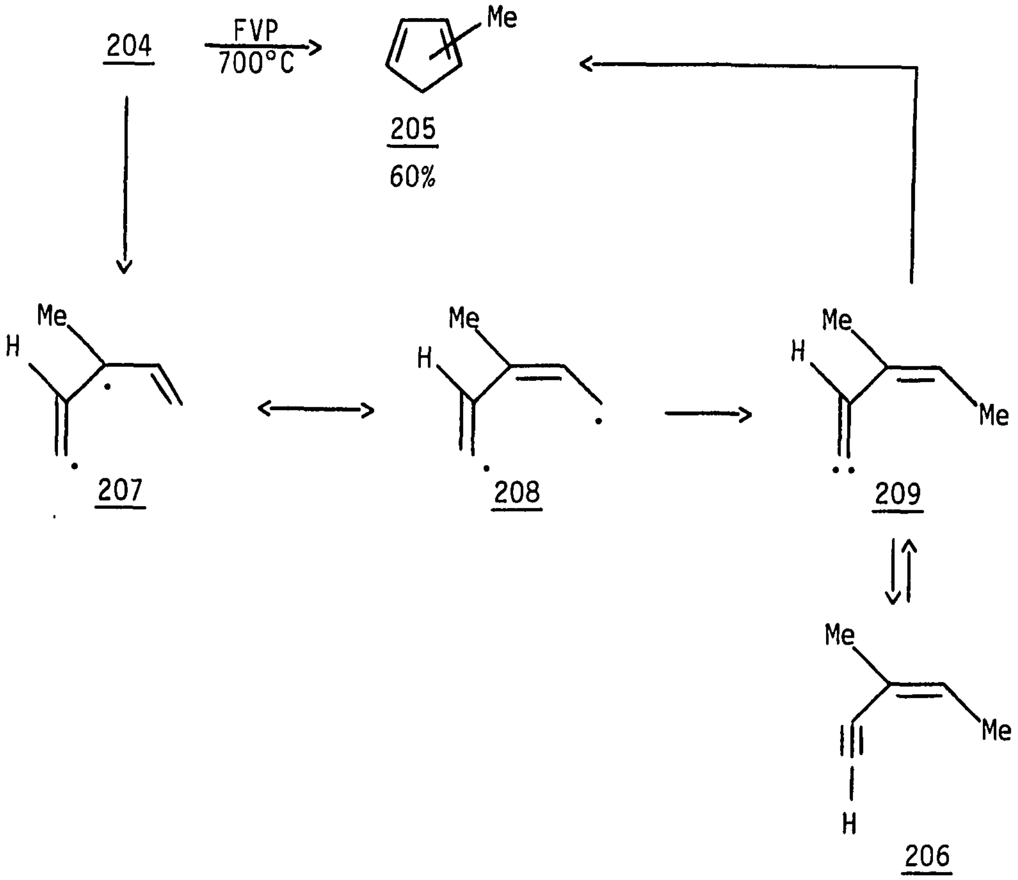
In the earlier investigation of 1-trimethylsilyl-1,2,4-pentatrienes, the cyclopropenes that were proposed all had a vinyl substituent on C_3. In order to verify if this type of cyclopropene could be playing a role in the isomerization of vinyl substituted silylallenes, it was necessary to pyrolyze such a cyclopropene under the same conditions. Bolesov has reported the synthesis of 203 in 67% yield from 204 (83). Unfortunately, this reaction has not been reproducible in our hands. The problem with this reaction may be due to the inability on a small scale to isolate pure 204. The 204 that was isolated always contained some t-butanol. The FVP of crude 204 was investigated because it is very similar to the cyclopropene proposed to be involved in the isomerization of 1,2,4-pentatriene, 81 (Scheme 19). Pyrolysis of 204 at 700°C afforded a 1:1 mixture of the 2- and 3-methyl-cyclopentadienes, 205, in 60% yield. Based on the results of the pyrolysis of 81, it was expected that the pyrolysis of 204 ought to form 205 and acetylene 206. A mechanism for the isomerization of 204 to 205 is shown in Scheme 50. The pathway proposed consists of an initial C-C bond homolysis to afford 207 and 208, followed by a 1,5-hydrogen migration to generate vinylidene 209. It was disappointing that the expected product of a 1,2-hydrogen migration, 206, was not observed. The pyrolysis of 204 at 700°C may indeed form 206 initially; however, as suggested earlier, it is believed that 206 is in equilibrium with 209, and the equilibrium can be bled off to 205 at a somewhat higher temperature. Since the pyrolyses of 81 and 204 were both done at 700°C, it was expected that similar product yields would be observed. The fact that the yields of cyclopentadiene and 205 were not the same leads to the conclusion that 204 requires a lower temperature to rearrange then does 81.



204 203

In summary, although only a few representative cyclopropenes have been successfully isolated, the pyrolysis of these examples have yielded products which are totally consistent with those obtained from the pyrolysis of the corresponding allene. Therefore, although the mechanisms for the thermally-induced rearrangements of allenes do not require the involvement of cyclopropenes as intermediates, the results are certainly consistent with such a role.

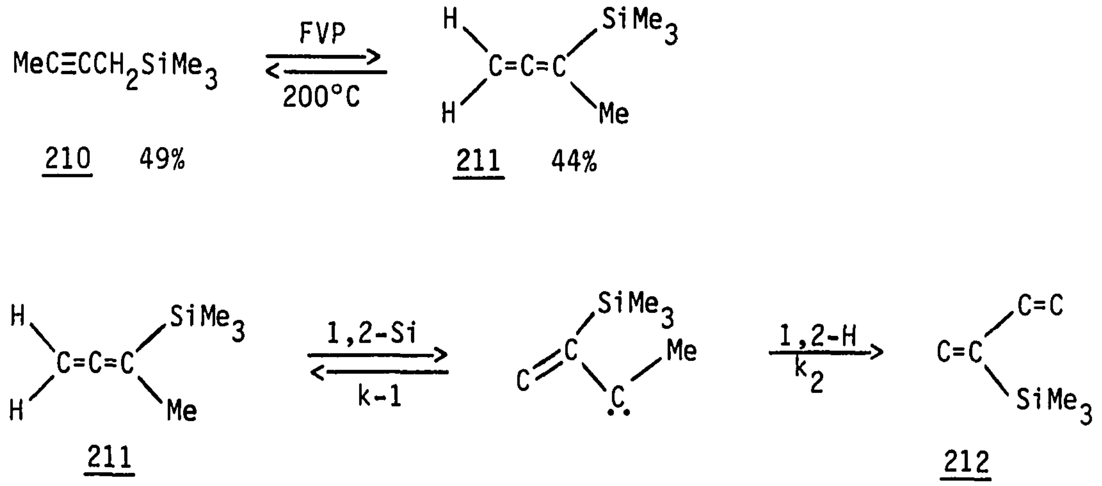
Scheme 50



Synthesis and FVP of α,β-Unsaturated Aldehydes and Ketones

During the study of the thermal isomerizations of simple alkyl substituted silylallenes, it was found that 210 and 211 are in equilibrium at 700°C (Scheme 51). Based on earlier work, it was predicted that 211 would undergo a 1,2-silyl migration, followed by a 1,2-H shift to afford 212. Surprisingly, no 212 was isolated. One possible explanation for the lack of 212 was that it was not stable under the reaction conditions. To test this hypothesis, 212 was synthesized from 213 via a Wittig reaction (Scheme 52). Pyrolysis of 212 at 750°C afforded only recovered 212. This indicates that if 212 was formed as a product of the rearrangement of 211, it would have been observed. Two possible explanations for the lack of 212 are either that a temperature of 700°C is not sufficient to promote the isomerization of 211 to 212 or that k_{-1} is much greater than k_2. It was shown earlier that the pyrolysis temperature required to observe significant amount of rearrangement of alkyl substituted silylallenes like 148 and 154 was greater than 700°C.

Scheme 51



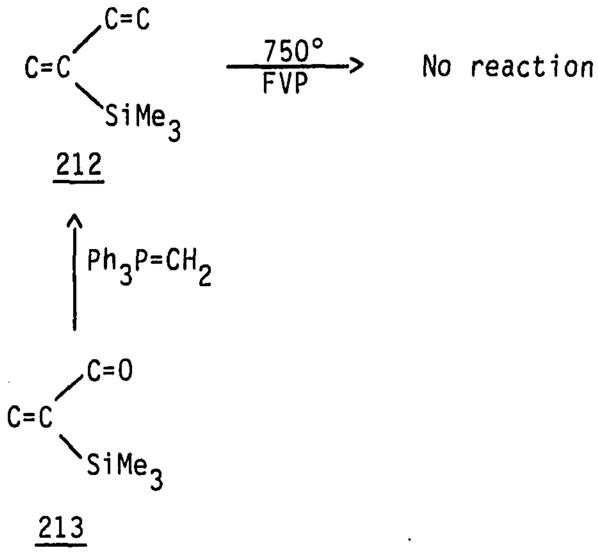
210 49%

211 44%

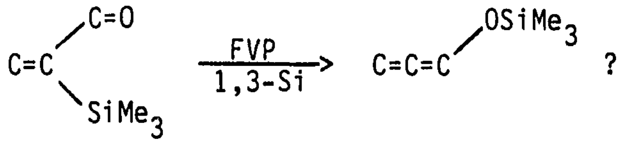
211

212

Scheme 52



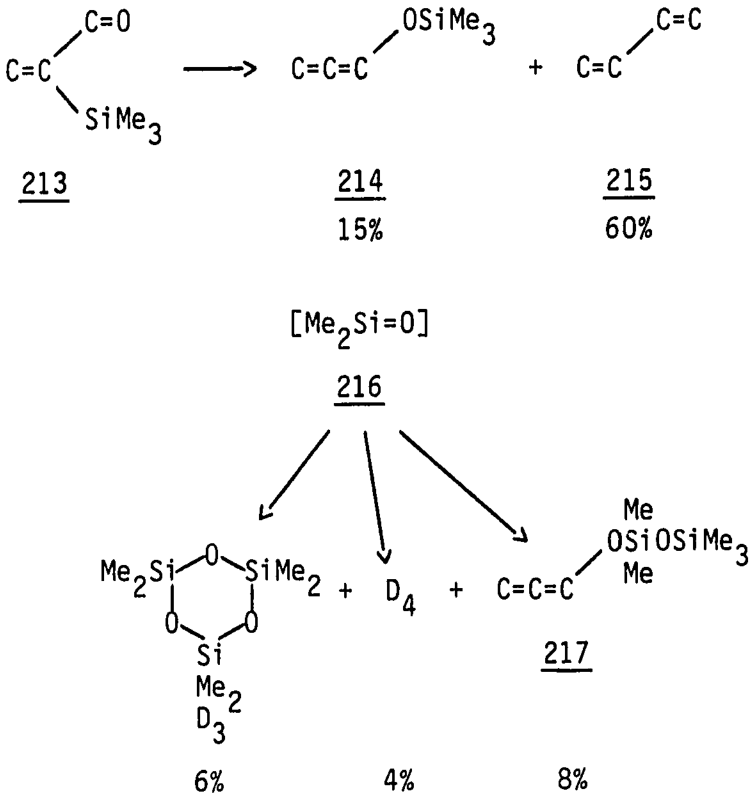
At first it seemed that the effort to independently synthesize 212 was wasted. A closer examination of the precursor to 212, 213 suggested that 213 itself could undergo an interesting thermally-induced rearrangement. It was thought that 213 might rearrange via a 1,3-silyl migration to oxygen to afford 1-((trimethylsilyl)oxy)-1,2-propadiene, 214. Allenol silyl ethers such as 214 belong to a class of silyl ethers which have been synthesized only a few times (84-91). Since enol silyl ethers are widely used as enol and enolate equivalents in synthetic organic chemistry, better synthetic routes to allenol silyl ethers would be of value (92, 93). It was thought that if 213 indeed did isomerize to 214, that this would provide a short and simple route to a variety of allenol silyl ethers.



213 214

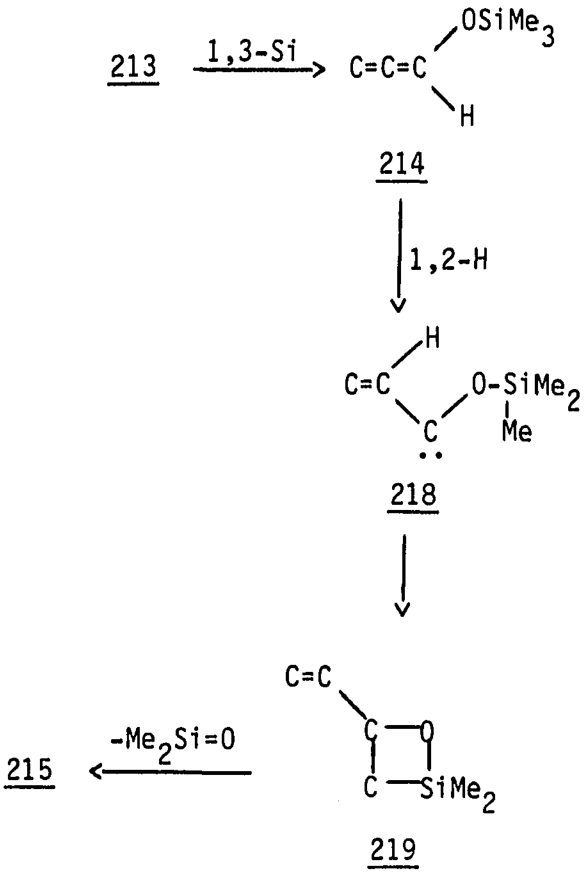
The pyrolysis of 213 at 650°C did generate 214; however, in a relatively poor isolated yield (15%) (Scheme 53). The major product unexpectedly was 1,3-butadiene, 215. The formation of 215 from 213, requires the loss of C_2H_6SiO from 213 and is probably lost as dimethylsilanone 216. Dimethylsilanone is a very kinetically unstable compound that readily trimerizes to yield hexamethylcyclotrisiloxane, D_3, and the corresponding tetramer, octamethylcyclotetrasiloxane, D_4. The formation of dimethylsilanone from the pyrolysis of 213 was confirmed when D_3 and D_4 were isolated as products. Another common reaction of dimethylsilanone is the insertion into silicon-oxygen bonds of existing compounds. In this case, the only compound available to react with dimethylsilanone in this fashion was 214. As expected, the product of such an insertion reaction, 217, was isolated in 8% yield.

Scheme 53



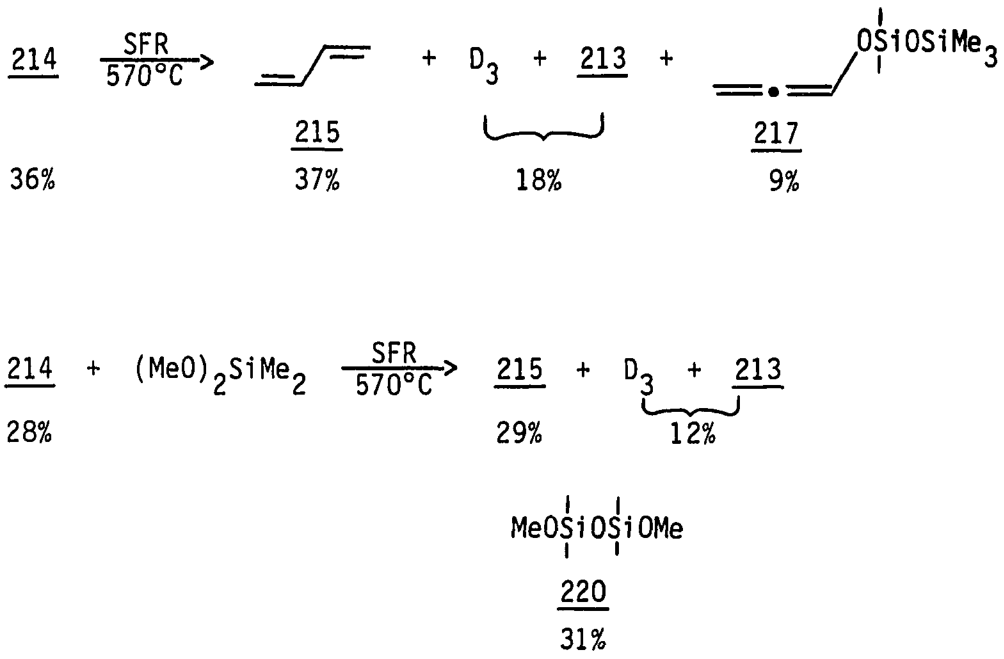
The isolation of 214 is consistent with a mechanism involving a 1,3-silyl migration (Scheme 54). The 1,3-butadiene may be derived from 214 starting with a 1,2-hydrogen migration to afford vinyl carbene 218. An intramolecular C-H insertion of carbene 218 into a methyl group on silicon would subsequently lead to siloxatane 219. Siloxatanes are known to extrude silanones, and in this case extrusion of dimethylsilanone would afford 1,3-butadiene, 215 (59).

Scheme 54



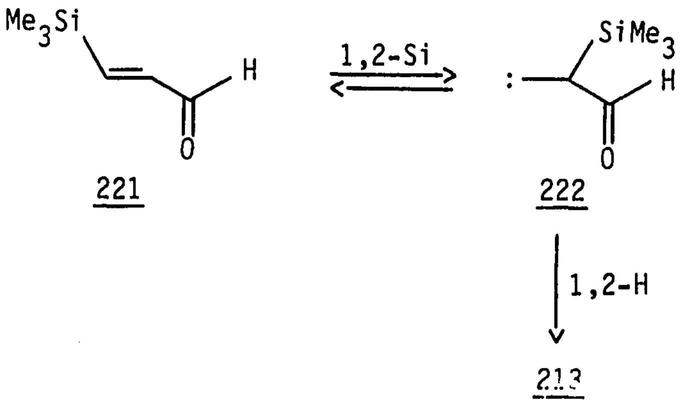
Allene 214 was isolated from the pyrolysate of 213 by preparative GC and pyrolyzed to determine if it does yield 215 and products derived from dimethylsilanone. The pyrolysis was done in a stirred-flow reactor (SFR) at 570°C. The products were identified by GC retention times and MS as 1,3-butadiene, 217, D_3, 213, and unreacted 214 (Scheme 55). Unfortunately, D_3 and 213 had identical GC retention times and, therefore, preventing determination of yields of each. Compound 213 is probably formed from 214 via 1,3-silyl shift. To further prove that dimethylsilanone was being generated, a copyrolysis of 214 and a 12-fold excess of dimethyldimethoxysilane was done. The expected siloxane from trapping of dimethylsilanone, 220, along with 215, 213, D_3, and 214 were present. Only a trace of 217 was detected. The results of these two experiments fully support the earlier proposal that 214 rearranges and fragments to yield 215 and dimethylsilanone.

Scheme 55



The interesting results obtained from the pyrolysis of 213 lead to the investigation of the beta isomer 221. It was thought that 221 could possibly undergo a 1,2-silyl migration to 222, followed by either a 1,2-silyl migration back to 221 or a 1,2-hydrogen shift to 213 (Scheme 56).

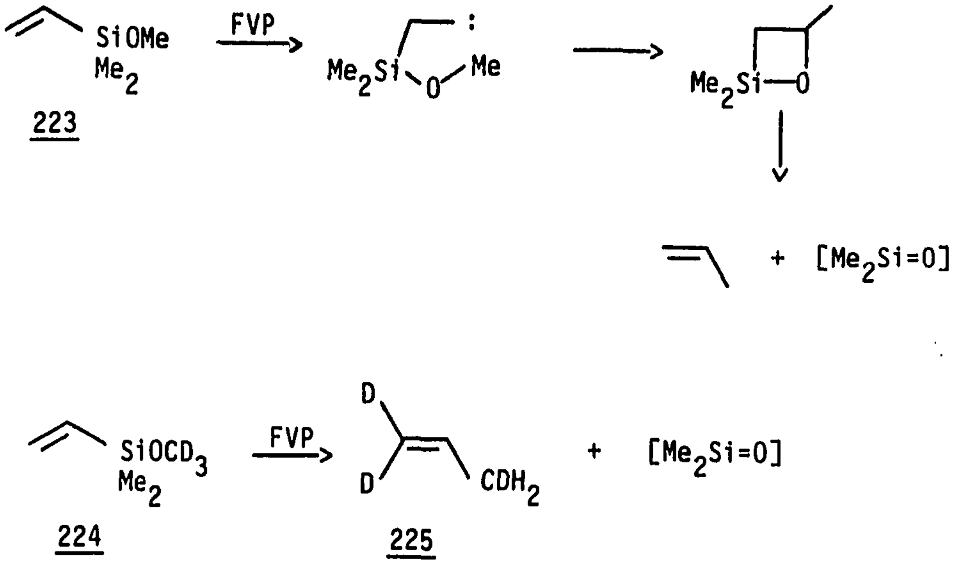
Scheme 56



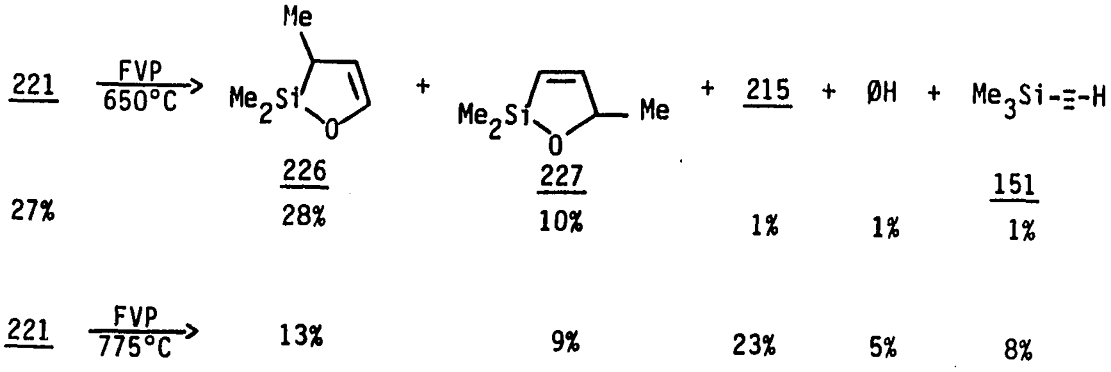
The possibility of a 1,2-silyl shift was suggested from a preliminary result obtained by Bain of the pyrolysis of 223 (94). Bain proposed that propene and products derived from dimethylsilanone could be conveniently explained via a mechanism that starts with a 1,2-silyl migration (Scheme 57). Recently, Bain has disproved this mechanism by pyrolyzing 224 and observing only propene 225 along with dimethylsilanone products. The presence of only 225 rules out the 1,2-silyl migration mechanism proposed for 223.

The pyrolysis of 221 at 650°C yielded five products along with recovered 221 (Scheme 58). The two major products, 226 and 227, were totally unexpected. FVP at 775°C afforded the same products; however, the major product was 1,3-butadiene, 215, and the yields of benzene and trimethylsilylacetylene, 151 were much higher.

Scheme 57

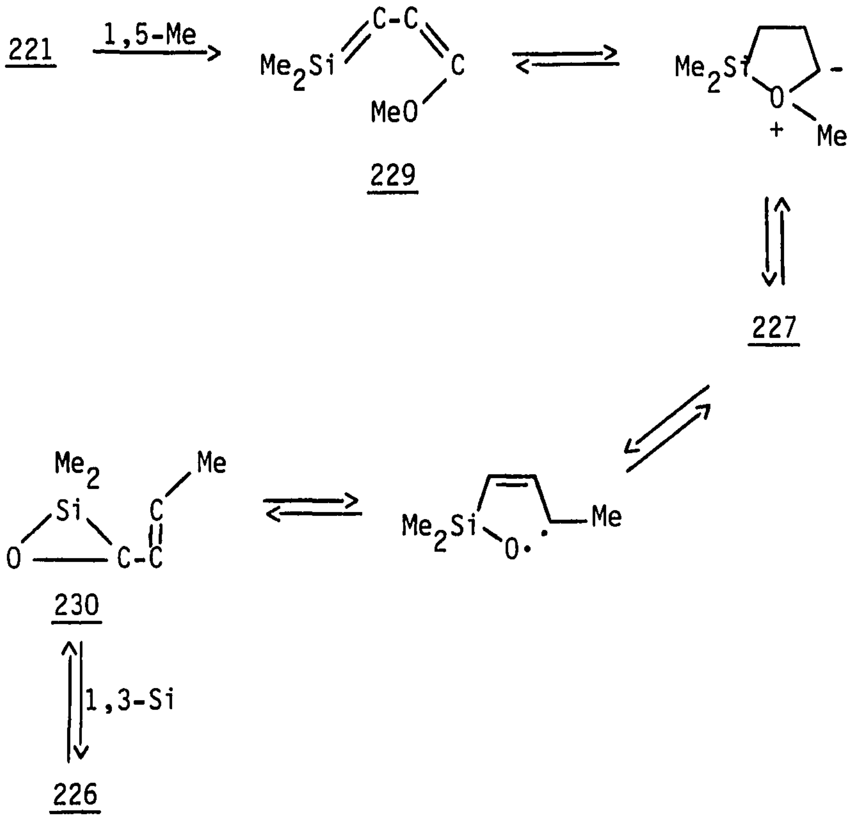


Scheme 58



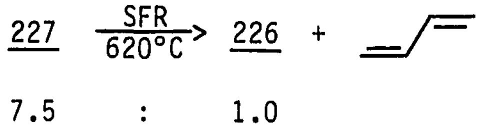
A pathway to 227 is shown in Scheme 59. The initial 1,5-methyl migration from silicon to form silene 229 is unprecedented; however, sigmatropic 1,5-methyl migrations are well established in organic chemistry (95). It is possible to envision 226 coming from 227 via an initial homolysis of the C-O bond, cyclization to siloxarane 230, followed by a 1,3-silyl migration.

Scheme 59

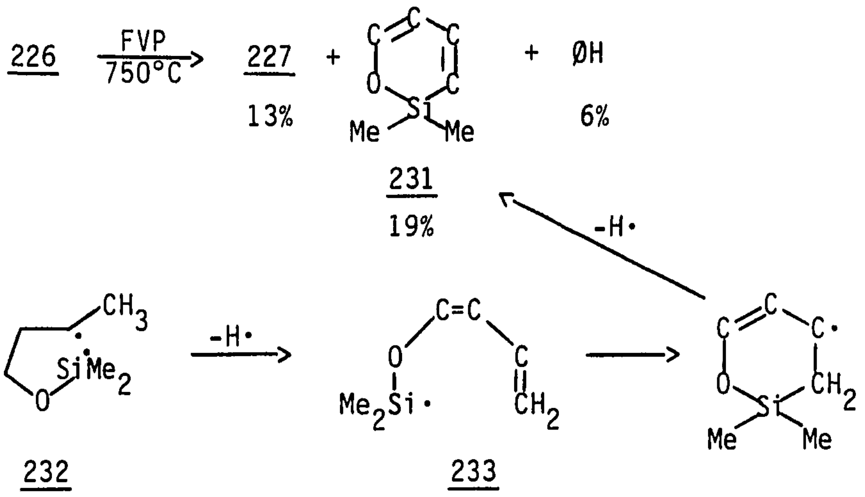


Compound 227 was pyrolyzed in a SFR to determine if 227 was the precursor to 226 and 1,3-butadiene. Pyrolysis of 227 at 620°C did afford 226, along with a small amount of 1,3-butadiene and unreacted 227 (Scheme 60). The GC area ratio of 227:226 was 7.5:1.0. The FVP of 226 at 750°C also generated a trace of 1,3-butadiene; however, the major two products were 227 (13%) and 231 (19%) (Scheme 61). Silyl ether 231 can be derived from 226 starting with the homolysis of the Si-C bond to form 232, which then loses a hydrogen radical to generate 233. Addition of the silyl radical to the terminal double and loss of a hydrogen radical would yield 231.

Scheme 60



Scheme 61



In summary, the results from the pyrolysis of 226 and 227 suggest that under FVP conditions 226 and 227 are interconvertible and, therefore, support the mechanism in Scheme 59. The generation of 1,3-

butadiene from the FVP of 226 and 227 suggests that these two ethers are the precursors to the 1,3-butadiene that is formed by the pyrolysis of 221.

CONCLUSION

Unlike trimethylsilylallenyl aldehydes and ketones, which are known to rearrange to trimethylsilylfurans under mild thermal conditions (150°C), 1-trimethylsilyl-3-vinylallenes, in general, are stable at 150°C. Isomerization does occur upon FVP (600-700°C); however, trimethylsilylacetylenes are isolated rather than trimethylsilylcyclopentadienes.

Based on the products isolated from the FVP of a number of 1-trimethylsilyl-3-vinylallenes, a possible mechanism was deduced. The proposed mechanism consists of an initial 1,2-silyl migration and cyclization to a 1-trimethylsilylcyclopropene. Subsequent ring opening, 1,5-hydrogen abstraction to generate a vinylidene and another 1,2-silyl migration would account for the trimethylsilylacetylenes isolated.

The pyrolysis of 5-trimethylsilyl-1,3,4-hexatriene afforded products consistent with trapping of the initially formed vinyl carbene via C-H insertion into an α-methyl group. The only trimethylsilylallene that was found to not afford products consistent with an initial 1,2-silyl migration was 1-trimethylsilyl-1,2,4-hexatriene which isomerized via a 1,5-hydrogen migration.

The FVP of analogous vinylallenes not having a trimethylsilyl substituent required a higher temperature and afforded the corresponding acetylene and cyclopentadiene. It was proposed that the C-H insertion of the intermediate vinylidene into a terminal methyl group to form a cyclopentadiene was competitive with the 1,2-hydrogen migration to an acetylene.

Alkyl and aryl substituted trimethylsilylallenes also were found to require higher temperatures to isomerize than did 1-trimethylsilyl-3-vinylallenes. At the higher temperatures, products derived from initial 1,2-silyl and 1,2-hydrogen shifts were isolated.

The only proposed intermediate cyclopropene that was successfully independently synthesized and isolated was 3,3-dimethyl-1-trimethylsilylcyclopropene. The FVP of 3,3-dimethyl-1-trimethylsilylcyclopropene afforded the same products as were obtained from the FVP of the analogous allene. It was, therefore, concluded that at least in this case the results were consistent with the intermediacy of a cyclopropene in the FVP of the corresponding allene. Attempts to generate other 1-trimethylsilylcyclopropenes resulted in the isolation of only the isomeric trimethylsilylacetylenes.

The pyrolysis of 3-methyl-1,2-butadiene afforded among other products isoprene, and a mechanism involving a 1,2-hydrogen migration was postulated. Pasto has claimed that isoprene is formed from the thermolysis of 3-methyl-1,2-butadiene via a sigmatropic 1,3-hydrogen migration and trapped by DEF. The sealed tube thermolysis of 1,1-dideuterio-3-methyl-1,2-butadiene and DEF was carried out to determine which hydrogen migration was actually involved; however, no products derived from d_2-isoprene were isolated.

The FVP of 2-trimethylsilylpropenal afforded ((trimethylsilyl)-oxy)-1,2-propadiene, 1,3-butadiene, and siloxanes derived from dimethylsilanone. An initial 1,3-silyl migration was proposed to account for the ((trimethylsilyl)oxy)-1,2-propadiene. It was shown that the 1,3-butadiene and derivatives of dimethylsilanone were products of the decomposition of ((trimethylsilyl)oxy)-1,2-propadiene and a mechanism was discussed.

The FVP of 3-trimethylsilylpropenal generated 2,2,3-trimethylsila-α-2,3-dihydrofuran and 2,5,5-trimethylsila-α-2,5-dihydrofuran. The two furans were found to be interconvertible under FVP conditions. A possible mechanism was proposed.

EXPERIMENTAL SECTION

Instrumentation

Routine ^{1}H NMR (60 MHz) spectra were recorded on a Varian EM-360A or L spectrometer. High resolution ^{1}H NMR (300 MHz) spectra were recorded on a Nicolet NT-300 or a Bruker WM-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. Gas chromatograph-mass spectra (GC/MS) were recorded on a Finnigan 4023 or a Hewlett Packard 5970. Exact mass measurements were obtained on an AEI-MS-902 or a Kratos MS 50 spectrometer. All mass spectra were recorded at 70 eV and are reported as m/e (% relative intensity). IR spectra were recorded on a Beckman IR 4250 or an IBM 98 FT/GC/IR spectrophotometer and were taken as neat samples except as indicated otherwise.

Gas chromatographic (GC) analyses were performed on a Hewlett Packard 5790A or 5890 fitted with a nonpolar 12.5 M or 30 M capillary column. Preparative GC was performed on a GOW MAC 550P, a Varian 920, 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 ^{1}H NMR using internal standards.

The pulse stirred-flow reactor (SFR) used was designed after Davidson's et al. (96). The quartz sample chamber had a volume of 3

cm^3 and $\tau = 2.39$ s. The sample chamber was heated by an oven that was controlled by a Digi-Sense temperature controller. A Varian 6000 GC, equipped with a 25 foot X 1/4 inch, 25% SE-30 column was used to separate the products. A splitter directed half of the gas stream to a quadrupole mass spectrometer (VG-SX300).

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 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. If a Baratron gauge was located before the furnace, pressures of approximately an order of magnitude greater were measured.

Synthesis of trimethylpropargylsilane, 56

Compound 56 was prepared via the procedure reported by Kwart et al. (63). This route always yielded a mixture of 56 and trimethylallenylsilane, 57, which could not be separated by distillation or preparative GC. Silane 56 was always by far the major product.

FVP of crude 56

A sample of crude 56 (90% 56, 10% 57, 109 mg), distilled (2 X 10^{-4} torr) from a bath warmed slowly from -78°C to room temperature, was pyrolyzed at 700°C. The yellow pyrolysate (86 mg, 79%) was analyzed by GC. No new products were formed based on GC retention times. The pyrolysate contained 56 and 57 in a ratio of 1.0:5.9, respectively, based on GC area percentages.

Synthesis of trimethylallenylsilane, 57

Silane 57 was prepared from 1,3-bis(trimethylsilyl)propyne and methanesulfonic acid according to the procedure described by Bourgeois and Merault (31). A mixture of 57, 56, and trimethylsilylpropyne, 61, was isolated in a ratio of 3.4:1.0:2.7. The product ratio was determined by ^{1}H NMR.

FVP of crude 57

A sample of crude 57 (47% 57, 38% 61, 14% 56, 116 mg), distilled (6 X 10^{-4} torr) from a bath warmed slowly from -78°C to room temperature, was pyrolyzed at 850°C. The pyrolysate (72 mg, 62%) was analyzed by ^{1}H NMR. No new products were identified, and only a trace of 56 was present. The pyrolysate consisted of 57 and 61 in a ratio of 1.0:11.3. Pyrolysis of crude 57 at 800°C afforded 57, 61, and 56 in a 1.4:6.7:1.0 ratio. Pyrolysis at 750°C yielded 57, 61, and 56 in the ratio of 1.9:4.3:1.0.

Synthesis of 4-trimethylsilyl-2,3-butadienal, 65

Compound 65 was synthesized via photolysis of 2-trimethylsilylfuran as described by Hussmann (59).

Attempted synthesis of 1-trimethylsilyl-1,2,4-pentatriene, 66

A mixture of triphenylphosphine (9.2 mmol), methyl iodide (9.2 mmol), and dry Et_2O (30 mL) was stirred at room temperature for 1 h. The mixture was cooled to 0°C and n-butyllithium in hexane (9.1 mmol, 2.4 M) was added dropwise. After the addition of n-butyllithium was complete, the solution was yellow in color. The solution was allowed to warm to room temperature, which resulted in the solution turning red in color. The solution was transferred via a double ended needle to a stirring mixture of 65 (11 mmol) and Et_2O at -78°C. After stirring at -78°C for 0.75 h, 25 mL of pentane was added and stirred overnight at 0°C. The pentane and Et_2O were removed by trap-to-trap distillation. The remaining residue was analyzed by GC and GC/MS. No 65 remained; however, also 66 was not detected. No isomers of 66 were detected by GC/MS.

Attempted synthesis of ethyl 5-trimethylsilyl-1,3,4-pentatrienoate, 67

To a stirring mixture of NaH (50% oil dispersion, 8.3 mmol) and dry benzene (5 mL) was added dropwise triethyl phosphonoacetate (7.8

mmol). Allene 65 (7.8 mmol) was added rapidly, and the mixture was heated to 65°C for 0.5 h. All volatile material was removed via trap-to-trap distillation (0.1 torr). ^1H NMR of the volatiles or of the remaining liquid did not indicate the presence of 65 or the desired vinyl allene 67.

Synthesis of 3-hydroxypent-4-en-1-yne, 68

The procedure used to prepare 68 was adapted from that described by Skattebol et al. who prepared 1-phenyl-1-penten-4-yn-3-ol (97). To a stirring mixture of ethynyl magnesium bromide (550 mmol) and dry THF (300 mL) at 0°C was added dropwise acrolein (500 mmol). Stirring was continued overnight and allowed to warm to room temperature. The reaction mixture was poured into 1.5 L of cooled, saturated NH_4Cl and the aqueous phase was extracted with three 250 mL portions of Et_2O. The organic solution was dried over anhydrous $MgSO_4$ and solvents removed via rotary evaporation. Pure 68 was isolated by distillation (60°C/20 torr) in a 22% yield: ^1H NMR δ 6.25-5.10 (m, 3H), 4.85 (m, 1H), 2.55 (d, 1H, J = 4 Hz), 2.37 (d, 1H, J = 6 Hz).

Synthesis of 1-bromopent-2-en-4-yne, 69

A mixture of 68 (61 mmol), HBr (48% in water, 134 mmol), tetraethylammonium bromide (61 mmol), CuBr (61 mmol), and copper metal (6 mmol) was stirred at room temperature for 3 h. The suspension was extracted with Skelly A, and the extracts were neutralized with $NaHCO_3$. The solution was dried over $MgSO_4$, and the Skelly A was distilled off on a rotary evaporator. Compound 69 was isolated in 75% yield with a cis:trans ratio of 39:48. Spectra of cis-69 include: ^1H NMR δ 6.7-5.3 (m, 2H), 4.2 (d, 2H, J = 8 Hz), 3.3 (d, 1H, J = 2 Hz); MS 146 (11.4), 144 (M^+, 11.5), 65 (100). Spectra of trans-69 include: ^1H NMR δ 6.7-5.3 (m, 2H), 4.0 (d, 2H, J = 8 Hz), 3.0 (d, 1H, J = 2 Hz); MS 146 (34.8), 144 (M^+, 35.6), 65 (100).

Synthesis of 66

The procedure used for the preparation of 66 was adapted from a method reported by Dulcere et al. who prepared a number of vinyl allenes from various 1-chloro-pent-2-en-4-ynes (98). To a stirring mixture of magnesium (30 mmol) and Et_2O (10 mL) was added a small amount of dibromoethane to initiate Grignard formation. Once initiated, the flask was cooled to 0°C and a solution of 69 (20 mmol) and Et_2O (90 mL) was added slowly over 1 h. The mixture was stirred for an additional 1 h at 0°C. Trimethylchlorosilane (30 mmol) was added rapidly, and the mixture allowed to warm to room temperature. After stirring at room temperature for 3.5 h, the reaction mixture was poured into ice/water and extracted several times with Et_2O. The Et_2O extracts were combined and dried over $MgSO_4$. The ether solution was decanted from the $MgSO_4$ and the Et_2O was removed via distillation. A 40% yield of 66 was obtained. Pure 66 was isolated by preparative GC (9 ft X 1/4 in. 20% OV-101). ^1H NMR δ 6.15 (d of t, 1H, J = 17 Hz and 10 Hz), 5.55 (d of d, 1H, J = 10 Hz and 7 Hz), 5.15 (m, 1H), 5.07 (d, 1H, J = 17 Hz), 4.82 (d, 1H, J = 10 Hz), 0.11 (s, 9H); ^{13}C NMR δ

212.45, 132.99, 112.76, 88.05, 84.34, -0.91; IR 2960, 1915, 1600, 1400, 1240, 1140, 980 cm^{-1}; MS 140 (0.46), 139 (1.7), 138 (M$^+$, 14), 123 (4.4), 95 (9.0), 73 (100); calcd for $C_8H_{14}Si$ m/e 138.08648, measured m/e 138.08648. Anal. Calcd for $C_8H_{14}Si$: C, 69.48; H, 10.20. Found: C, 69.28; H, 10.36.

FVP of 66

(i) A sample of 66 (56 mg), distilled (3 X 10^{-4} torr) from a bath that was allowed to warm from 0°C to room temperature was pyrolyzed at 600°C. The pyrolysate (49 mg, 88%) was analyzed by GC and GC/MS. The products were identified as cis- and trans-1-trimethylsilylpent-3-en-1-yne, 73 (41%, cis:trans = 28:13), from the ^{1}H NMR, IR, ^{13}C NMR, and MS (99). The yield was obtained by ^{1}H NMR.

(ii) FVP of 66 (32 mg) at 600°C, 1 X 10^{-5} torr, afforded a pyrolysate (29 mg, 91%) consisting of 73 (59%, cis:trans = 55:4, ^{1}H NMR yield) and recovered 66 (12%). Spectra of cis-73 include: ^{1}H NMR δ 6.00 (m, 1H), 5.50 (d of d, 1H, J = 11 Hz and 1.5 Hz), 1.88 (d of d, 3H, J = 6.8 Hz and 1.5 Hz), 0.19 (s, 9H); ^{13}C NMR δ 139.9, 110.2, 101.9, 99.0, 16.1, 0.07; IR 3035, 2965, 2155, 1360, 1250, 1015, 840 cm^{-1}; MS 140 (3.0), 139 (3.0), 138 (M$^+$, 24), 123 (100), 95 (17), 83 (13), 73 (19), 69 (16), 53 (18). Spectra of trans-73 include: ^{1}H NMR δ 6.21 (m, 1H), 5.51 (d of q, 1H, J = 15.8 Hz and 1.8 Hz), 1.77 (d of d, 3H, J = 6.8 Hz and 1.8 Hz), 0.17 (s, 9H); ^{13}C NMR δ 141.0, 111.0, 104.2, 93.0, 18.7, 0.07; IR 2955, 2120, 1245, 1075, 945 cm^{-1};

MS 140 (0.63), 139 (2.4), 138 (M^+, 19), 123 (100), 95 (7.9), 83 (9.1), 69 (11), 53 (12).

Synthesis of 3-(*t*-butyldimethylsiloxy)pent-4-en-1-yne, 77

A solution of 68 (24 mmol), *t*-butyldimethylchlorosilane (29 mmol), imidazole (60 mmol), and DMF (4 mL) was stirred and heated to 35°C for 20 h. The solution was extracted with saturated $NaHCO_3$ and with Skelly A. The organic layer was dried over $MgSO_4$. The Skelly A was distilled off to afford 77 in a 93% isolated yield. The identity of 77 was based solely upon MS data: 196 (M^+, 0.5), 139 (70), 111 (80), 83 (100), 75 (40).

Synthesis of 3-(*t*-butyldimethylsiloxy)-1-deuteropent-4-en-1-yne, 78

To a stirring solution of 77 (16 mmol) and THF (50 mL) was added EtMgBr in THF (20 mmol). Stirring was continued for 4 h at room temperature. Deuterium Oxide (100 mmol) was added slowly to the mixture and stirred overnight. The liquid layer was decanted from the solid residue and extracted with saturated NH_4Cl. The organic layer was dried over $MgSO_4$ and volatiles removed via rotary evaporation. GC/MS indicated that the remaining liquid (2.5 g) was >90% 78 (80%): MS 197 (M^+, 0.42), 140 (71), 112 (51), 111 (42), 84, (100), 69 (40).

Synthesis of 1-deutero-3-hydroxypent-4-en-1-yne, 79

A solution of 78 (13 mmol), acetic acid (2.3 mL), THF (1 mL), and water (1 mL) was stirred and heated to 60°C for 24 h. The mixture was extracted with saturated $NaHCO_3$ and with Et_2O. The Et_2O layer was dried over $MgSO_4$. The Et_2O was removed via rotary evaporation and 0.93 g of crude 79 remained. The crude 79 was analyzed by GC and GC/MS. An analytically pure sample of 79 was isolated by preparative GC (10 ft X 1/4 in., 15% SE-30). The ^1H NMR spectrum indicated that the ratio of 79:68 was 85:15. Spectra of 79 include: ^1H NMR δ 5.99 (d of q, 1H, J = 17 Hz and 5.3 Hz), 5.50 (d of t, 1H, J = 17 Hz and 1.1 Hz), 4.88 (m, 1H), 1.95 (d, 1H, J = 6.6 Hz); MS 83 (M^+, 2.2), 82 (42), 81 (12), 65 (19), 64 (19), 56 (36), 55 (70), 54 (100).

Synthesis of cis- and trans-1-bromo-5-deuteriopent-2-en-4-yne, 80

Compound 80 was synthesized using the procedure earlier described for the synthesis of 69. Starting with 37 mmol of 79, cis-80 and trans-80 were generated in 25% and 16% yields (^1H NMR yields), respectively: cis-80; ^1H NMR δ 6.5-5.4 (m, 2H), 4.1 (d, 2H, J = 8 Hz); MS 147 (8.5), 145 (M^+, 9.0), 81 (7.1), 79 (6.8), 66 (100), 65 (52); trans-80; ^1H NMR δ 6.5-5.4 (m, 2H), 3.9 (d, 2H, J = 8 Hz); MS 147 (9.7), 145 (M^+, 10), 81 (6.0), 79 (5.9), 66 (100), 65 (44).

Synthesis of 1-deuterio-1-trimethylsilyl-1,2,4-pentatriene, 75

Compound 75 was prepared via the procedure earlier described for the synthesis of 66. Starting with 5 mmol of 80, 1.14 g of crude product was isolated. The crude product was analyzed by GC and GC/MS. A mixture of 75 and 66 (10% GC yield, based on 5 mmol of 80) was isolated by preparative GC (10 ft X 1/4 in., 15% SE-30). Analysis by ^{1}H NMR indicated a 1.63:1.00 mixture of 75 and 66. The spectra of 75 include: ^{1}H NMR δ 6.15 (d of t, 1H, J = 17 Hz and 10 Hz), 5.55 (m, 1H), 5.07 (d, 1H, J = 17 Hz), 4.82 (d, 1H, J = 10 Hz); MS 140 (1.0), 139 (M^+, 6.7), 138 (5.2), 73 (100), 45 (17), 43 (13).

FVP of a mixture of 75 and 66

A mixture of 75 and 66 (17 mg, 62% 75), distilled (6 X 10^{-4} torr) slowly from a bath warmed from 0°C to room temperature, was pyrolyzed at 700°C. The pyrolysate was analyzed by GC, GC/MS, and ^{1}H NMR and four products, cis- and trans-1-trimethylsilyl-5-deuteriopent-3-en-1-yne, 76, and cis- and trans-66 were identified. The yields of trans-76/trans-66 (8%) and cis-76/cis-66 (15%) were determined by ^{1}H NMR. The ^{1}H NMR of trans-76 was recorded as: δ 6.20 (m, 1H), 5.50 (m, 1H), 1.76 (m, 2H), 0.17 (s, 9H). The ^{1}H NMR of cis-76 was recorded as: δ 6.02 (m, 1H), 5.50 (m, 1H), 1.87 (m, 2H), 0.21 (s, 9H).

Synthesis of 1,2,4-pentatriene, 81

Triene 81 was prepared from 1-chloropent-2-en-4-yne according to the procedure of Dulcere et al. (98).

FVP of 81

Allene 81 (68 mg), distilled (1 x 10^{-4} torr) slowly at -°78, was pyrolyzed at 700°C. The yellow pyrolysate (68 mg, 100%) was analyzed by GC and ^{1}H NMR. By comparing ^{1}H NMR spectra of authentic samples and known literature values, cyclopentadiene, 83 (13%), E-pent-3-en-1-

yne (12%), and Z-pent-3-en-1-yne, 82 (41%), were identified as products along with recovered 81 (31%). The yields were determined by ^{1}H NMR and based on recovered 81.

FVP of crude 82

A mixture of 83, 82, and 81 in a ratio of 1.00:2.50:1.76 (343 mg) was slowly distilled at -78°C and pyrolyzed at 750°C/4 X 10^{-4} torr. The yellow pyrolysate (255 mg) was analyzed and yields determined by ^{1}H NMR. The pyrolysate consisted of 83, 82, and 81 in a ratio of approximately 4:2:1.

FVP of 1-trimethylsilylcyclopentadiene, 92

(i) Compound 92 (137 mg), distilled (1 X 10^{-4} torr) slowly from a bath warmed from -23°C to room temperature, was pyrolyzed at 700°C. The yellow pyrolysate (90 mg, 65%) was analyzed by GC/MS. The pyrolysate consisted of only 92.

(ii) Pyrolysis of 92 (90 mg), 4 X 10^{-4} torr, afforded a yellow pyrolysate (11 mg, 12%) which was analyzed by GC and GC/MS. Only unreacted 92 was present by GC/MS.

Synthesis of 1-trimethylsilylpent-4-en-1-yne, 94

To a stirring solution of trimethylsilylacetylene (10 mmol) and THF (15 mL) was added slowly EtMgBr (11 mmol, in THF). After stirring for 1 h, CuCl (1 g) was added and an immediate exotherm was noted. Allyl bromide (11 mmol) was added dropwise to the stirring mixture, and stirring was continued overnight. The reaction mixture was extracted with saturated NaCl and with Et_2O. The Et_2O layer was dried over $MgSO_4$ followed by the removal of Et_2O and THF by distillation. The remaining crude product (1.8 g) was analyzed by GC and GC/MS. The only product, 94 (96%), was identified from the following spectra: ^1H NMR δ 5.80 (m, 1H), 5.32 (d of q, 1H, J = 18 Hz and 1 Hz), 5.12 (d of q, 1H, J = 9 Hz and 1 Hz), 3.00 (d of t, 2H, J = 6 Hz and 2 Hz), 0.16 (s, 9H); IR 2963, 2899, 2178, 1643, 1418, 1252, 999, 914, 843 cm^{-1}; MS 138 (M^+, 1.9), 123 (100), 95 (23), 73 (16), 43, (32).

FVP of 94

Acetylene 94 (95 mg), distilled (4 X 10^{-4} torr) slowly from a bath warmed from -23°C to room temperature, was pyrolyzed at 800°C. The yellow pyrolysate (70 mg, 74%) was analyzed by GC and GC/MS. The products, Z-73 (18%), E-73 (7%), trimethylsilylacetylene (16%), and tetramethylsilane (5%) along with recovered 94 (13%) were identified by comparative GC retention times and mass spectra. The yields were determined by GC.

Synthesis of 3-hydroxy-1-trimethylsilylpent-4-en-1-yne, 102

To a stirring solution of trimethylsilylacetylene (180 mmol) and hexane (3 mL) at -78°C was added n-BuLi (180 mmol, 2.3 M in hexane) dropwise. After the addition was complete, the mixture was allowed to warm to room temperature. The flask was cooled to 0°C, and a solution of acrolein (180 mmol) and hexane (10 mL) was added slowly. The mixture was warmed to room temperature and stirred for 3 h. The flask contents were poured into saturated NH_4Cl and extracted several times with Et_2O. The combined organic layers were dried over $MgSO_4$, and volatiles were removed via rotary evaporation. Distillation (55-65°C/5 torr) of the remaining liquid afforded 102 in a 55% isolated yield. Acetylene 102 was identified by ^1H NMR and MS: ^1H NMR δ 5.95 (overlapping d of q, 1H, J = 18 Hz and 9 Hz), 5.45 (d, 1H, J = 18 Hz), 5.20 (d, 1H, J = 9 Hz), 4.84 (m, 1H), 2.01 (d, 1H, J = 7.5 Hz), 0.17 (s, 9H); MS 155 (0.35), 154 (M^+, 2.4), 139 (37), 111 (18), 99 (51), 85 (22), 73 (90), 61 (100).

Synthesis of *E*- and *Z*-1-bromo-5-trimethylsilylpent-2-en-4-yne, 103

Compound 103 was prepared from 102 (55 mmol) via the procedure used for the synthesis of 69. A 67% isolated yield of 103 having a 2:1 *Z*:*E* ratio was obtained. The spectra of *E*- and *Z*-103 include: *E*-103; ^1H NMR δ 6.29 (m, 1H), 5.74 (m, 1H), 3.96 (d, 2H, J = 9 Hz), 0.18 (s, 9H); ^{13}C NMR δ 138.9, 114.5, 102.0, 97.7, 31.4, -0.13; MS 218 (6.2), 216 (M^+, 6.4), 137 (88), 123 (56), 122 (27), 121 (35), 109 (33), 107 (27), 79 (39), 59 (100), 53 (60), 43 (97). *Z*-103: ^1H NMR δ 6.14 (overlapping d of t, 1H, J = 12 Hz and 9 Hz), 5.60 (d, 1H, J = 12 Hz), 4.17 (d, 2H, 9 Hz), 0.18 (s, 9H); ^{13}C NMR δ 138.1, 113.2, 103.3, 99.4, 28.2, -0.10; MS 218 (4.1), 216 (M^+, 3.9), 137 (86), 122 (42), 59 (100), 53 (46), 43 (85).

Synthesis of 1-methyl-1-trimethylsilyl-1,2,4-pentatriene, 101

To a stirring solution of 103 (20 mmol) and Et_2O (10 mL) at 0°C was added MeMgBr (21 mmol, 3.0 M in Et_2O) dropwise over 1 h. The mixture was allowed to warm to room temperature and stirring was continued for 17 h. The reaction mixture was poured into dilute acid and extracted with Et_2O. The Et_2O layer was dried over $MgSO_4$ and volatiles removed via rotary evaporation. The remaining yellow liquid (3.07 g) was analyzed by GC and GC/MS. Pure 101 (44%) was isolated via preparative GC (8 ft x 1/4 in., 10% SE-30). The spectra of 101 include: ^1H NMR δ 6.14 (d of t, 1H, J = 17 Hz and 10 Hz), 5.51 (m, 1H), 5.06 (d of d, 1H, J = 17 Hz and 1.2 Hz), 4.79 (m, 1H), 1.71 (d, 3H, J = 3 Hz), 0.09 (s, 9H); ^{13}C NMR δ 208.0, 134.2, 112.4, 92.7, 88.7, 15.2, -1.8; IR 2959, 1923, 1612, 1250, 891, 839 cm^{-1}; MS 154 (0.31), 153 (1.2), 152 (M^+, 7.8), 137 (4.9), 73 (100), 59 (7.6); calcd for $C_9H_{16}Si$ m/e 152.10213, measured m/e 152.1020. Anal. Calcd for $C_9H_{16}Si$: C, 70.97; H, 10.59. Found: C, 71.24; H, 10.68.

FVP of 101

(i) Compound 101 (100 mg), distilled (6 X 10^{-4} torr) slowly from a bath warmed from 0°C to room temperature, was pyrolyzed at 700°C. The yellow pyrolysate (72 mg, 72%) was analyzed by GC, GC/MS, and ^1H NMR. Interpretation of the spectral data allowed for assignment of benzene (4%), trimethylsilylbenzene (4%), 106, and trimethylsilane as products. The major product, 104 (20%), could not be cleanly isolated by preparative GC; therefore, the assignment as a mixture of trimethylsilylcyclohexadienes was based on only MS and crude ^{1}H NMR. The spectra of 104 is as follows: ^{1}H NMR δ 6.7-6.0 (m, 3H), 2.06 (m, 4H), -0.05 (s, 9H); MS 152 (M$^+$, 11), 137 (10), 73 (100), 59 (24), 45 (18), 43 (16); GC/IR (gas phase) 2963, 2928, 1261, 1065, 845 cm^{-1}.

(ii) Allene 101 (92 mg) was pyrolyzed at 750°C, 5 X 10^{-4} torr, to afford a pyrolysate (41 mg, 45%) which consisted of 104 (9%), 105 (6%), 106 (7%), dimethylsilylbenzene (1%), 108, and trimethylsilane, 107. Identification of 104, 105, 106, and 107 was accomplished by comparative GC retention times and GC/MS. Compound 108 was identified by ^{1}H NMR, MS, and IR: ^{1}H NMR δ 7.53 (m, 2H), 7.36 (m, 3H), 4.42 (hept, 1H, J = 4.5 Hz), 0.30 (d, 6H, J = 4.5 Hz); MS 138 (1.8), 137 (6.4), 136 (M$^+$, 39), 135 (26), 121 (100), 105 (22), 58 (71), 43 (63); GC/IR (gas phase) 3067, 3017, 2129, 1427, 1261, 1115, 887 cm^{-1}.

(iii) Compound 101 (92 mg) was pyrolyzed at 775° C, 4 X 10^{-4} torr, and afforded 41 mg (36%) of pyrolysate. The products were identified by comparative GC retention times and GC/MS as 104 (3%), 105 (22%), 106 (10%), 108 (6%), toluene (4%), and 107.

Synthesis of 3-hydroxy-4-methylpent-4-en-1-yne, 118

Acetylene 118 was prepared from methacrolein (500 mmol) via the procedure described for the synthesis of 68. A 50% isolated yield of 118 was obtained by distillation (61-68°C/15 torr). Compound 118 was characterized by GC and ^{1}H NMR: ^{1}H NMR δ 5.10 (m, 1H), 4.90 (m, 1H), 4.77 (m, 1H), 2.50 (d, 1H, J = 2 Hz), 2.30 (d, 1H, J = 6 Hz), 1.87 (m, 3H).

Synthesis of E- and Z-1-bromo-2-methylpent-2-en-4-yne, 119

Compound 119 was synthesized from 118 (121 mmol) using the route described for the synthesis of 69. This procedure yielded E-119 (48%) and Z-119 (19%). E-119: ^{1}H NMR δ 5.57 (m, 1H), 3.90 (s, 2H), 3.20 (m, 1H), 2.10 (s, 3H). Z-119: ^{1}H NMR δ 5.40 (m, 1H), 4.20 (s, 2H), 3.20 (m, 1H), 1.97 (m, 3H); E- and Z-119: IR 3310, 2970, 2110, 1445, 1390, 1350, 1220, 1045, 840 cm^{-1}.

Synthesis of 1-trimethylsilyl-4-methyl-1,2,4-pentatriene, 117

Allene 117 was prepared from 119 (16 mmol) via the procedure described for the synthesis of 66. The crude product (1.67 g) was analyzed by GC/MS and ^{1}H NMR, and 117, 120, and 121 were identified as products. Compound 117 (15%, NMR yield) could not be isolated from 120 (9%, NMR yield) by preparative GC, distillation, or column chromatography. Acetylene 120 was isolated and characterized allowing the spectral identification of 117 by subtraction: ^{1}H NMR δ 5.65 (d, 1H, J = 7.5 Hz), 5.23 (m, 1H), 4.80 (m, 1H), 4.67 (m, 1H), 1.77 (s, 3H), 0.12 (s, 9H); ^{13}C NMR δ 211.2, 150.4, 105.5, 91.2, 85.9, 24.8, 0.19; IR 2959, 1923, 1450, 1250, 843 cm^{-1}; MS 154 (0.34), 153 (1.4), 152 (M$^+$, 10), 137 (3.1), 73 (100), 59 (12). The spectra of 120 include: ^{1}H NMR δ 5.28 (m, 1H), 1.90 (s, 3H), 1.79 (m, 3H), 0.19 (s, 9H); ^{13}C NMR δ 139.0, 110.9, 103.6, 96.1, 21.1, 19.9, -0.85; IR 2961, 2935, 2154, 2129, 1250, 1109, 843, 760 cm^{-1}; MS 154 (0.92), 153 (3.3), 152 (M^+, 23), 137 (100), 83 (24), 69 (28), 59 (58), 53 (23). Spectra of 121 include: ^1H NMR δ 4.77 (s, 2H), 2.56 (d, 1H, J = 3 Hz), 2.19 (d, 1H, J = 3 Hz), 1.77 (m, 3H), 0.12 (s, 9H); IR 3315, 2959, 2106, 1639, 1250, 843 cm^{-1}; MS 153 (0.67), 152 (M^+, 4.8), 137 (4.2), 109 (2.9), 83 (3.9), 73 (100), 59 (16).

Thermolysis of crude 117

(i) Crude 117 (89 mg, 0.295 mmol of 117, 120, and 121), distilled (2 X 10^{-4} torr) slowly from a bath at 0°C, was pyrolyzed at 700°C. The yellow pyrolysate (67 mg, 75%) was analyzed by GC and ^1H NMR. The sole product was 120 (71%, NMR yield), and the yield was based on the assumption that both 117 and 121 isomerized to 120.

(ii) Crude 117 (80 mg, 0.265 mmol of 117, 120, and 121) was pyrolyzed at 500°C, 4 X 10^{-5} torr, and afforded 47 mg (59%) of pyrolysate. Analysis of the pyrolysate by ^1H NMR indicated that 56% of 117 had isomerized to 120.

Synthesis of 4-methyl-1,2,4-pentatriene, 122

To a stirring mixture of magnesium (21 mmol) and Et_2O (2 mL) was added dibromoethane (0.1 mL) to initiate Grignard formation. The mixture was cooled to 0°C, and a solution of 119 (19 mmol) and Et_2O (20 mL) was added dropwise. The mixture was allowed to warm to room temperature and stirring was continued for 3 h. The reaction mixture was poured into cold, saturated NH_4Cl and extracted with Et_2O. The

Et_2O layer was dried over $MgSO_4$, and a majority of the Et_2O was distilled off. The remaining liquid consisted of Et_2O and 122 (7%). Allene 122 was isolated via preparative GC (9 ft X 1/4 in., 15% SE-30): ^1H NMR δ 5.91 (t, 1H, J = 3 Hz), 4.97 (d, 2H, J = 3 Hz), 4.90 (s, 1H), 4.80 (s, 1H), 1.80 (s, 3H); IR 2874, 2656, 1940, 1280, 885, 849 cm^{-1}; MS 81 (3.4), 80 (M^+, 57), 79 (100), 78 (10), 77 (56), 65 (20), 63 (11), 53 (15), 52 (23), 51 (24), 50 (18).

FVP of 122

Allene 122 (56 mg), distilled (2×10^{-4} torr) slowly from a bath warmed from -78°C to room temperature, was pyrolyzed at 700°C. The yellow pyrolysate (48 mg, 86%) was analyzed by ^1H NMR and GC/MS. Based on a 27% NMR yield of unreacted 122, 4-methylpent-3-en-1-yne, 123, and methylcyclopentadiene were formed in 46% and 28% yield, respectively. Methylcyclopentadiene was identified from comparative spectra of an authentic sample. The spectra of 123 include: ^1H NMR δ 5.11 (m, 1H), 2.85 (m, 1H), 1.77 (s, 3H), 1.66 (s, 3H); IR 3310, 2253, 1379, 916, 903, 746, 725 cm^{-1}; MS 81 (5.8), 80 (M^+, 99), 79 (100), 77 (60), 65 (28), 63 (23), 52 (31), 51 (31), 50 (24).

Synthesis of 2-methyl-1,3,4-hexatriene, 124

To a stirring solution of 119 (21 mmol) and Et_2O (10 mL) at 0°C was added dropwise MeMgI (27 mmol, 3 M in Et_2O). The solution was allowed to warm to room temperature and stirred for 7 h. The mixture was extracted with water followed by Et_2O, and the organic layer was dried over $MgSO_4$. The Et_2O was distilled off, and 3.6 g of crude product remained. Allene 124 (40%) could not be separated from 4-methylpent-3-en-1-yne (19%), 125, by distillation or preparative GC. The spectra of 124 include: ^1H NMR δ 5.85 (m, 1H), 5.33 (m, 1H), 4.88 (m, 1H), 4.79 (m, 1H), 1.77 (m, 3H), 1.70 (d of d, 3H, J = 7 Hz and 3 Hz); IR 2970, 1944, 1629, 1460, 887 cm^{-1}; MS 96 (1.6), 95 (7.9), 94 (M^+, 85), 93 (17), 91 (23), 79 (95), 78 (16), 77 (100), 65 (16), 63 (15), 53 (25).

FVP of crude 124

Crude 124 (139 mg, 0.97 mmol of 124), distilled (6 X 10^{-4} torr) slowly from a bath warmed from -78°C to room temperature, was pyrolyzed at 750°C. The yellow pyrolysate (123 mg, 88%) was analyzed by GC and GC/MS. Benzene (20%), toluene (15%), methylcyclopentadiene (10%), and unreacted 124 (5%) and 125 (5%) were identified as products by comparison of GC retention times and GC/MS. Compound 126 (7%) was isolated via preparative GC (10 ft X 1/4 in., 15% SE-30). Spectra of 126 include: ^1H NMR δ 5.20 (s, 1H), 1.96 (s, 3H), 1.86 (s, 3H), 1.77 (s, 3H); MS 95 (6.2), 94 (M^+, 84), 93 (11), 91 (28), 79 (62), 77 (100).

Synthesis of 3-hydroxyhexa-4-en-1-yne, 131

Compound 131 was prepared from crotonaldehyde (500 mmol) according to the method described earlier for the synthesis of 68. Distillation (75-78°C/10 torr) afforded 29 g of 131 (60%): ^1H NMR δ

6.3-5.4 (m, 2H), 4.8 (m, 1H), 2.63 (d, 1H, J = 2 Hz), 2.50 (m, 1H), 1.77 (d, 3H, J = 4 Hz); ^{13}C NMR δ 129.8, 129.0, 83.4, 73.8, 62.5, 17.4; IR 3280, 2910, 2100, 1670, 1440, 1000, 950, 915 cm^{-1}; MS 96 (M$^+$, 8.2), 95 (14), 81 (100), 77 (18), 67 (13), 55 (23), 53 (43), 51 (19).

Synthesis of E- and Z-5-bromohexa-3-en-1-yne, 132

Acetylene 132 was synthesized from the reaction of 131 (300 mmol) and HBr (75 mL, 48% in water) according to the procedure of Dulcere et al. (98). A mixture of E- and Z-132 (58%) was isolated with a E to Z ratio of 2.3:1.0. The ^{1}H NMR matched that reported by Dulcere et al.

Synthesis of E- and Z-1-trimethylsilyl-1,2,4-hexatriene, 130

To a stirring mixture of magnesium (82 mmol) and Et$_2$O (5 mL) was added a small amount of dibromoethane to initiate Grignard formation. The mixture was cooled to 0°C, and a solution of 132 (28 mmol) in Et$_2$O (15 mL) was added dropwise. Stirring was continued for 1 h at 0°C after the addition of 132 was complete. A solution of trimethylchlorosilane (39 mmol) and Et$_2$O (10 mL) was added, and the solution was allowed to warm to room temperature. The flask was irradiated in an ultrasonic bath (150 watts) for 45 min. The mixture was extracted with water and pentane, and the organic phase was dried over MgSO$_4$. The Et$_2$O and pentane were removed by rotary evaporation. The remaining liquid consisted of 130 (E:Z, 1.00:1.58) in a 37% yield by GC. Analytically pure E-130 and Z-130 could not be isolated by preparative GC (12 ft X 1/4 in., 15% SE-30). The assignment of isomers was based only on GC retention times. The spectra of E-130 include: ^{1}H NMR δ 5.77 (m, 1H), 5.31 (m, 2H), 5.14 (m, 1H), 1.67 (m, 3H), 0.10 (s, 9H); MS 154 (0.51), 153 (1.9), 152 (M^+, 14), 137 (4.3), 73 (100), 59 (14). The spectra of Z-130 include: ^{1}H NMR δ 5.80 (m, 1H), 5.51 (m, 2H), 5.13 (m, 1H), 1.72 (m, 3H), 0.09 (s, 9H); MS 154 (0.65), 153 (2.4), 152 (M^+, 15), 137 (4.3), 73 (100), 59 (9.2). Spectra of a mixture of E- and Z-130 include: IR 2945, 1915, 1240, 950, 830 cm^{-1}; calcd for $C_9H_{16}Si$ m/e 152.1021, measured m/e 152.1022. Anal. Calcd for $C_9H_{16}Si$: C, 70.97; H, 10.59. Found: C, 70.27; H, 10.57.

FVP of E- and Z- 130

A mixture of E- and Z-130 (54 mg), distilled (3×10^{-4} torr) slowly from a 0°C bath, was pyrolyzed at 700°C. The yellow pyrolysate (39 mg, 72%) was analyzed by GC and GC/MS. Benzene (27%), trimethylsilylbenzene (20%), 106, and trimethylsilane were identified as products by comparison of spectral data of authentic samples.

Synthesis of 3-phenyl-1-trimethylsilylallene, 137

Allene 137 was synthesized by reacting 3-phenyl-1-trimethylsilylpropyne with n-BuLi according to the procedure described by West and Gornowicz (70).

FVP of 137

Compound 137 (139 mg), distilled (3 X 10^{-4} torr) from a bath slowly heated from 25-80°C, was pyrolyzed at 775°C. The pyrolysate (91 mg, 65%) was analyzed by GC and GC/MS. The products were identified as trimethylsilylindenes, 138 (8%) and 139 (4%), indene (3%), 140, dihydronaphthalene (8%), 141, 3-phenyl-1-trimethylsilylpropyne (4%), 142, and unreacted 137 (6%). The yields were determined by GC analysis. The products were identified by comparison of GC/MS and ^{1}H NMR data with those of authentic samples.

FVP of 3-trimethylsilylindene, 139

Compound 139 (131 mg), distilled (4 X 10^{-7} torr) from a bath slowly heated from 25-45°C, was pyrolyzed at 780°C. The pyrolysate (93 mg, 71%) was analyzed by GC and GC/MS. The products were identified as 140 (10%), 138 (27%), methylindene (10%), 144, and unreacted 139 (14%).

Synthesis of 1,3-bis(trimethylsilyl)propyne, 149

Propyne 149 was prepared from the reaction of trimethylsilylpropyne and *n*-BuLi/TMEDA followed by quenching with trimethylchlorosilane as reported by Yamakado et al. (100).

Synthesis of 3-ethyl-1,3-bis(trimethylsilyl)propyne, 150

To a stirring solution of 149 (26 mmol) and Et_2O (150 mL) at -78°C was added *n*-BuLi (32 mmol, 2.72 M in hexane) dropwise. After all the n-BuLi was added, the solution was allowed to warm to room temperature. The reaction mixture was cooled to 0°C and diethylsulfate (32 mmol) was added. Stirring was continued overnight and allowed to warm to room temperature. The reaction mixture was extracted several times with Et_2O and water. The organic phase was dried over $MgSO_4$, and the Et_2O and hexane were removed by rotary evaporation. The crude product was distilled (70°C/5 torr) to afford 150 (38%) and 1,1-bis(trimethylsilyl)-1,2-pentadiene (25%). Compound 150 was isolated by preparative GC (10 ft X 1/4 in., 15% SE-30): ^1H NMR δ 1.63-1.26 (m, 3H), 1.05 (t, 3H, J = 7 Hz), 0.12 (s, 9H), 0.06 (s, 9H); ^{13}C NMR δ 109.98, 84.91, 23.71, 22.63, 14.30, 0.51, -3.09; MS 212 (M^+, 1.4), 155 (4.4), 124 (22), 109 (15), 73 (100). Anal. Calcd for $C_{11}H_{24}Si_2$: C, 62.18; H, 11.39. Found: C, 62.10; H, 11.39.

Synthesis of 1-trimethylsilyl-1,2-pentadiene, 148

To a stirring solution of crude 150 (16.5 mmol, 56% 150) and Et_2O (15 mL) was added methanesulfonic acid (16.5 mmol), and the solution was stirred for 18 h. The reaction mixture was treated with $NaHCO_3$, and the Et_2O was removed by distillation. The crude product mixture was analyzed by GC and GC/MS. Compounds 148 (46%) and 3-ethyl-1-trimethylsilylpropyne (24%) were identified as the products. Pure 148 was isolated via preparative GC (12 ft X 1/4 in., 15% SE-30). Spectra of 148 include: ^1H NMR δ 4.91 (m, 1H), 4.83 (m, 1H), 1.96 (m, 2H), 0.99 (t, 3H, J = 7.5 Hz), 0.08 (s, 9H); ^{13}C NMR δ 210.02, 85.24, 83.26, 20.98, 13.92, -0.86; MS 142 (0.2), 141 (0.5), 140 (M^+, 3.5), 125 (3.5), 83 (16), 73 (100). Anal. Calcd for $C_8H_{16}Si$: C, 68.48; H, 11.50. Found: C, 67.15; H, 11.61.

FVP of 148

(i) Allene 148 (85 mg), distilled (4 X 10^{-4} torr) slowly from a bath warmed from -23°C to room temperature, was pyrolyzed at 700°C. The yellow pyrolysate (59 mg, 69%) was analyzed by GC and GC/MS. Trimethylsilylacetylene (7%), 151, trimethylsilylpropyne (8%), 61, and trimethylsilylallene (2%), 57, were identified as products along with recovered 148 (41%) by comparison of spectral data of authentic samples. Another product that was present, 1-trimethylsilylbuta-3-en-1-yne (6%), 152, was isolated by preparative GC (12 ft X 1/4 in., 15% SE-30): ^1H NMR δ 5.87 (d of d, 1H, J = 8.1 Hz and 2.7 Hz), 5.75 (m, 2H), 0.19 (s, 9H); MS 125 (1.9), 124 (M^+, 12), 109 (100), 83 (15), 67 (19).

(ii) Pyrolysis of 148 (62 mg) at 775°C, 3 X 10^{-4} torr, produced a pyrolysate (23 mg, 37%) consisting of 151 (3%), 61 (4%), 152 (6%), 57 (3%), and unreacted 148 (11%). Identification of all products was accomplished by ^1H NMR and/or GC/MS.

Synthesis of 1-trimethylsilyl-1-pentyne, 153

To a stirring solution of 1-pentyne (37 mmol) and Et_2O (100 mL) at -78°C was added dropwise n-BuLi (37 mmol, 1.66 M in hexane). The solution was stirred for an additional 1 h after the addition of n-BuLi was complete. Trimethylchlorosilane (42 mmol) was added rapidly, and the mixture was allowed to warm to room temperature overnight. The reaction mixture was extracted with saturated NaCl and Et_2O. The organic layer was dried over $MgSO_4$, and the Et_2O and hexane was stripped off on a rotary evaporator. The remaining liquid (5.2 g) consisted of 153 in a 53% yield. Analytically pure 153 was isolated via preparative GC (10 ft X 1/4 in., 15% SE-30): ^1H NMR δ 2.19 (t, 2H, J = 7 Hz), 1.53 (sept, 2H, J = 7 Hz), 0.97 (t, 3H, J = 7 Hz), 0.14 (s, 9H); IR 2964, 2937, 2178, 1250, 980, 843, 760 cm^{-1}; MS 140 (M^+, 6.5), 126 (19), 125 (100), 83 (31), 43 (38).

FVP of 153

Acetylene 153 (197 mg), distilled (6 X 10^{-4} torr) from a bath warmed slowly from -78°C to room temperature, was pyrolyzed at 750°C. The yellow pyrolysate (148 mg, 75%) was analyzed by GC and GC/MS. Compounds 152 (16%), 61 (14%), 57 (14%), 56 (8%), 151 (7%), and unreacted 153 (56%) were identified by comparison of GC retention times and GC/MS data.

Synthesis of 3,3-dimethyl-1,3-bis(trimethylsilyl)propyne, 155

To a stirring solution of 149 (42 mmol) and Et_2O (200 mL) at -78°C was added *n*-BuLi (84 mmol, 2.72 M in hexane) dropwise. After the *n*-BuLi was added, the solution was allowed to warm to room temperature. The reaction mixture was cooled to 0°C and dimethylsulfate (84 mmol) was added. Stirring was continued overnight and allowed to warm to room temperature. The reaction mixture was extracted several times with Et_2O followed by removal of the Et_2O and hexane via rotary evaporation. The remaining liquid consisted of 155 in a 43% yield. Pure 155 was isolated by preparative GC (12 ft X 1/4 in., 15% SE-30): ^1H NMR δ 1.13 (s, 6H), 0.11 (s, 9H), 0.05 (s, 9H); IR 2959, 2899, 2141, 1250, 841, 758 cm^{-1}; MS 212 (M^+, 11), 197 (5.1), 155 (18), 124 (82), 109 (19), 97 (13), 73 (100).

Synthesis of 1-trimethylsilyl-3-methyl-1,2-butadiene, 154

Allene 154 was prepared from crude 155 (22 mmol of 155) by the procedure described for the synthesis of 148. Distillation (50-60°C/10 torr) afforded 1.72 g of crude 154 (13%). Analytically pure 154 was isolated by preparative GC (12 ft X 1/4 in., 15% SE-30): ^1H NMR δ 4.76 (pent, 1H, J = 3.6 Hz), 1.64 (d, 6H, J = 3.6 Hz), 0.06 (s, 9H); ^{13}C NMR δ 209.45, 89.03, 87.34, 19.62, -0.73; IR 2957, 2932, 1948, 1346, 1248, 841 cm^{-1}; MS 141 (2.7), 140 (M^+, 22), 125 (14), 83 (33), 73 (100). Anal. Calcd for $C_8H_{16}Si$: C, 68.48; H, 11.50. Found: C, 68.31; H, 11.44.

FVP of 154

Compound 154 (140 mg), distilled (8×10^{-4} torr) from a bath warmed slowly from -23°C to room temperature, was pyrolyzed at 775°C. The yellow pyrolysate (54 mg, 39%) was analyzed by GC and GC/MS. 3,3-Dimethyl-1-trimethylsilylpropyne (3%), 156, 1-trimethylsilylbuta-3-en-1-yne (6%), 152, 1-trimethylsilyl-3-methylbuta-3-en-1-yne (8%), 157, 1-trimethylsilyl-3-methyl-1,3-butadiene (2%), 158, 2-methyl-1,3-pentadiene (9%), 159, and unreacted 154 (12%) were isolated by preparative GC (12 ft X 1/4 in., 15% SE-30). Compounds 154, 152, and 159 were identified by comparison of spectra data of authentic samples. Compounds 156, 157, and 158 were analyzed by GC, ^1H NMR, MS, and IR. 156: ^1H NMR δ 2.56 (pent, 1H, J = 7 Hz), 1.15 (d, 6H, J = 7 Hz), 0.13 (s, 9H); IR 2974, 2168, 1315, 1258, 968, 856 cm^{-1}; MS 141 (1.4), 140 (M^+, 11), 125 (100), 97 (12), 83 (57). 157: ^1H δ NMR 5.34 (m, 1H), 5.24 (m, 1H), 1.88 (s, 3H), 0.18 (s, 9H); ^{13}C NMR δ 127.04, 122.64, 106.58, 93.03, 23.31, 0.046; IR 2966, 2148, 1265, 980, 872 cm^{-1}; MS 140 (1.2), 139 (2.1), 138 (M^+, 16), 123 (100), 97 (13), 73 (11); calcd for $C_8H_{14}Si$ m/e 138.08648, measured m/e 138.08633. Anal. Calcd for $C_8H_{14}Si$: C, 69.48; H, 10.21. Found: C, 69.04; H, 10.49. 158: ^1H NMR δ 6.60 (d, 1H, J = 19 Hz), 5.82 (d, 1H, J = 19 Hz), 5.03 (m, 2H), 1.59 (s, 3H), 0.09 (s, 9H); IR 2963, 2901, 1585, 1258, 868, 849 cm^{-1}; MS 141 (2.5), 140 (M^+, 18), 125 (91), 109 (18), 97 (33), 85 (25), 83 (24), 73 (23), 59 (100).

Synthesis of 3,3-dimethyl-1-trimethylsilylpropyne, 156

Propyne 156 was prepared from the reaction of 3-bromo-3-methyl-1-trimethylsilylpropyne (7 mmol) and methylmagnesium bromide (9 mmol, 3 M in Et_2O). The procedure was adapted from the synthesis of 1,3,3-trimethylpropyne reported by Jacobs and Prempree (101). Compound 156 was synthesized in 21% yield.

FVP of 156

Compound 156 (104 mg), distilled (4 X 10^{-4} torr) from a bath warmed slowly from -78°C to room temperature, was pyrolyzed at 800°C. The pyrolysate (33 mg) was analyzed by GC and GC/MS, and 152 (36%), 157 (3%), 151 (19%), and tetramethylsilane (15%) were identified as products.

FVP of 3-methyl-1,2-butadiene, 168

Allene 168 (208 mg, Aldrich Chem. Co.), distilled (4 X 10^{-4} torr) slowly from a bath warmed from -78°C to room temperature, was pyrolyzed at 775° C. The pyrolysate (148 mg, 71%) was analyzed by GC and GC/MS. Preparative GC (12 ft X 1/4 in., 15% SE-30) allowed for the isolation of 3-methylbut-3-en-1-yne (11%), 169, isoprene (16%), 170, 2,3-dimethyl-1,3-butadiene (6%), 171, and unreacted 168 (31%). Isoprene and recovered 168 were identified by comparison of spectra data with that of authentic samples. Compound 171 was identified by the following data: ^{1}H NMR δ 5.05 (s, 2H), 4.97 (s, 2H), 1.93 (s, 6H); IR 3113, 2978, 1597, 1447, 895, 879 cm^{-1}; MS 83 (2.5), 82 (M$^+$, 41), 67 (86), 54 (24), 41 (63), 39 (100). Acetylene 169 was characterized only by GC/MS: MS 67 (4.4), 66 (M$^+$, 83), 65 (49), 54 (55), 51 (48), 50 (42), 40 (50), 39 (100).

Synthesis of 1,1-dideuterio-3-methyl-1,2-butadiene, 174

Allene 174 was prepared by the reaction of 3-chloro-3-methyl-1-deuterio-1-butyne and LAD according to the procedure of Pasto et al. (102).

FVP of 174

Compound 174 (96 mg), distilled (4 X 10^{-4} torr) from a bath warmed slowly from -78°C to room temperature, was pyrolyzed at 775°C. The pyrolysate (68 mg, 71%) was analyzed by GC and GC/MS. Preparative GC (12 ft X 1/4 in., 15% SE-30) allowed for the isolation of 1-deuterio-3-methyl-1-butyne (3%), 177, dideuterio-2,3-dimethyl-1,3-butadiene (5%), 179, and unreacted 174 (38%). A dideuterio isomer of isoprene, 178 (10%) was also isolated; however, the complexity of the ^{1}H NMR and the ^{2}H NMR suggested that more than one regioisomer was present. The ^{1}H NMR resonance of 6.44 ppm suggested that 1,2-dideuterioisoprene was present; however, decoupling at 6.44 ppm indicated that it was coupled to protons at 5.16 and 5.05 ppm. The coupling constant of 17 Hz between protons at 6.44 ppm and 5.16 ppm is not consistent with 1,2-dideuterioisoprene. Spectra of 177 include: ^{1}H NMR δ 5.38 (m, 1H), 5.29 (t, 1H, J = 1.2 Hz), 1.90 (s, 3H); IR 2960, 2947, 2588, 1609, 1450, 1265, 903 cm^{-1}; MS 68 (1.4), 67 (M$^+$, 13), 66 (7.8), 58 (18), 43 (100). Spectra of 179 include: ^{1}H NMR δ 5.09-4.92 (m, 3H), 1.91 (s, 5H); MS 86 (3.1), 85 (12), 84 (M$^+$, 69), 83 (25), 69 (99), 68 (86), 67 (52), 55 (31), 43 (64), 42 (85), 41 (100). Spectra of 178 include: ^{1}H NMR δ 6.44 (m), 5.36 (m), 5.22-5.12 (m), 5.10-5.02 (m), 5.02-4.94 (m), 1.84 (s); IR 3082, 2986, 1562, 1443, 1389, 891 cm^{-1}; MS 71 (16), 70 (M$^+$, 80), 69 (100), 68 (41), 55 (49), 54 (59), 53 (39), 41 (52), 39 (64). ^{2}H NMR of pyrolysate: δ 6.48 (m), 5.08 (m), 4.54 (s, from 174), 2.88 (s, from 177), 2.10-1.71 (m).

Thermolysis of 168 and 174 in a stirred-flow reactor (SFR)

Compounds 168 and 174 (0.095-0.099 torr) were pyrolyzed in a stirred-flow reactor at temperatures of 658, 678 and 696°C. By measuring the amount of isoprene formed, the apparent rate constants were calculated and are listed in Table 1. From the apparent rate constants a k_H/k_D of 1.17 (± 0.07) was calculated.

Thermolysis of 174 in the presence of DEF

A clean glass tube was washed with 1 N HCl, then 1 N NaOH, then extensively with distilled water, and finally with methanol. To the dry tube was added 174 (99 mg, 1.41 mmol), DEF (1.56 mmol), and 0.75 mL of toluene. The solution was triply freeze-degassed, and the tube was sealed under reduced pressure. The tube was completely immersed for five days in an oil bath that was maintained at 200-210°C. The contents of the tube were removed and analyzed by GC and GC/MS. Products 182 (48%) and 183 (5%) were isolated by preparative GC (10 ft X 1/4 in., 15% SE-30). The ^{1}H NMR spectra of 182 and 183 matched those reported by Pasto (71). Compound 184 (13%, NMR yield) was isolated pure by distilling off all of the other products at 100°C/0.5 torr. From the ^{1}H NMR and ^{13}C NMR spectra, 184 exists as both diastereoisomers. Spectra of 184 include: ^{1}H NMR δ 4.18-3.92 (m), 2.97-2.64 (m), 2.39-2.08 (m), 1.72 (s), 1.69 (s), 1.26-1.12 (m); ^{13}C NMR δ 174.27, 174.18, 172.48, 171.61, 129.56, 129.33, 124.40, 60.81, 60.57, 43.53, 43.41, 41.64, 41.56, 41.47, 34.54, 34.38, 34.07, 14.12; MS 414 (M^+, 4.7), 369 (18), 294 (24), 267 (35), 220 (100), 192 (52), 175 (28), 150 (34), 121 (41), 107 (31).

Attempted synthesis of 1-trimethylsilylcyclopropene, 63

(i) Zinc/Copper couple that was prepared according to the procedure of LeGoff was added to a stirring solution of Et_2O (10 mL) and a small amount of methylene iodide (103). The mixture was heated to reflux, and the remaining methylene iodide (43 mmol) and trimethylsilylacetylene (29 mmol) was added dropwise. The mixture was stirred rapidly and heated at reflux for 24 h. The liquid layer was decanted from the residual couple and extracted with cold 3 M HCl and Et_2O. The Et_2O layer was separated and dried over $MgSO_4$. The crude Et_2O solution was analyzed by GC/MS and found to contain trimethylsilylpropyne, 61, rather than 63.

(ii) Cyclopropene generated via the route described by Schipperijn was added to a mixture of LDA and THF at -78°C (104). After stirring for 5 min, an excess of trimethylchlorosilane was added, and the solution was stirred for 1 h at -78°C. The reaction mixture was stored overnight at 5°C. The mixture was extracted with water and Skelly B, and the Skelly B layer was separated. After drying the Skelly B layer over $MgSO_4$, the Skelly B was distilled off. The remaining liquid residue was analyzed by GC and GC/MS. By MS only one product had a molecular weight corresponding to 63; however, the MS and the IR spectrum matched that of 61 not 63.

Synthesis of 3-methylcyclopropene, 189

Cyclopropene 189 was prepared from 1-chloro-2-butene and sodium amide according to the procedure of Koster, Arora, and Binger (105).

Attempted synthesis of 1-trimethylsilyl-3-methylcyclopropene, 188

To a stirring mixture of 189 (~10 mL) and Et_2O (60 mL) at -78°C was added *n*-BuLi (80 mL, 2.33 M in hexane). The solution was stirred and allowed to warm to room temperature overnight. After cooling to 0°C, trimethylchlorosilane (197 mmol) was added rapidly. The reaction mixture was distilled and two fractions were isolated. The fraction which was collected at 50-60°C/40 torr was analyzed by GC and GC/MS. The only product which had a molecular weight of 126 was isolated by preparative GC (30 ft X 1/4 in., 15% SE-30). From the ^1H NMR, IR, and GC/MS spectra, the product was identified as 1-trimethylsilyl-1-butyne, 190. A similar procedure using sodium amide as the base rather than *n*-BuLi also afforded 190 rather than 188. 190: ^1H NMR δ 2.22 (q, 2H, J = 7.5 Hz), 1.14 (t, 3H, J = 7.5 Hz), 0.14 (s, 9H); IR 3063, 2997, 2961, 2928, 2874, 2179, 1454, 1379, 1020, 842, 760 cm^{-1}; MS 126 (M^+, 11), 112 (13), 111 (100), 83 (20).

Synthesis of 1-trimethylsilyl-2,3,3-trimethylcyclopropene, 191

To a stirring mixture of lithium wire (1.57 mol) and THF (80 mL) was added a solution of 2-bromo-3-methyl-2-butene (0.5 mol) and THF (240 mL). The mixture was allowed to warm to -10°C, and the liquid layer was transferred from the excess lithium to a separate flask by means of a double ended catheter tube. After cooling this solution to -50°C, methylene chloride (176 mmol) was added dropwise. The resulting mixture was allowed to warm to -30°C, and trimethylchlorosilane (77 mmol) was added rapidly. Stirring was continued overnight, and the solution was allowed to warm to room temperature. The reaction mixture was extracted repeatedly with water and Skelly A to remove the THF. The Skelly A layer was dried over $MgSO_4$, and the Skelly A was removed via rotary evaporation. The remaining liquid was distilled and two fractions, 25-50°C/100 torr (3.6 g) and 50-60°C/40 torr (1.5 g) were isolated. A mixture of cyclopropene 191 (2%) and 2-bromo-3-methyl-2-butene was isolated by preparative GC (15 ft X 1/4 in., 15% SE-30). 191: ^{1}H NMR δ 2.08 (s, 3H), 1.07 (s, 6H), 0.13 (s, 9H); ^{13}C NMR δ 144.80, 121.54, 27.22, 20.25, 11.69, -0.47; IR 2957, 1794, 1778, 1437, 1247, 1124, 1066, 840 cm^{-1}; MS 155 (1.9), 154 (M^+, 11), 139 (6.0), 125 (4.9), 97 (19), 73 (100).

FVP of 191

A mixture of 191 and 2-bromo-3-methyl-2-butene (175 mg), distilled (8 X 10^{-4} torr) from a bath warmed slowly from -23°C to room temperature, was pyrolyzed at 700°C. The pyrolysate (134 mg) was analyzed by GC and GC/MS. The major products were isolated by preparative GC (15 ft X 1/4 in., 15% SE-30) and identified as 2-trimethylsilyl-4-methyl-2,3-pentadiene (17%), 192, 157 (9%), 1-trimethylsilyl-2,3-dimethyl-1,3-butadiene (5%), 193, and 156 (3%). No 191 remained; however, a trace of 2-bromo-3-methyl-2-butene was identified by GC/MS. Compounds 156 and 157 were identified based on comparison of spectral data of authentic samples. The spectra of 192 include: ^{1}H NMR δ 1.62 (m, 9H), 0.036 (s, 9H); ^{13}C NMR δ 205.0, 89.5, 88.1, 20.1, 15.7, -1.8; MS 156 (0.6), 155 (2.1), 154 (M$^+$, 15), 139 (4.1), 97 (21), 73 (100); calcd for $C_9H_{18}Si$ m/e 154.11778, measured m/e 154.11768. Anal. Calcd for $C_9H_{18}Si$: C, 70.04; H, 11.76. Found: C, 70.14; H, 11.99. The spectra of 193 include: ^{1}H NMR δ 5.63 (s, 1H), 5.09 (s, 1H), 4.98 (s, 1H), 1.97 (s, 3H), 1.91 (s, 3H), 0.14 (s, 9H); ^{13}C NMR δ 151.6, 145.9, 126.6, 112.5, 21.1, 19.6, 0.16; IR 2963, 1578, 1258, 860 cm^{-1}; MS 155 (1.9), 154 (M$^+$, 13), 139 (79), 99 (23), 73 (100), 59 (67).

Synthesis of 1,1-dibromo-2,2-dimethylcyclopropane, 200

Cyclopropane 200 was prepared in 81% yield according to the procedure described by Nesmeyanova and co-workers (106).

Synthesis of 1-bromo-2,2-dimethylcyclopropane, 201

Cyclopropane 201 was prepared in 20% yield according to the procedure described by Nesmeyanova and co-workers (106).

Synthesis of 3,3-dimethylcyclopropene, 202

Cyclopropene 202 was synthesized via the procedure reported by Binger in 30% yield (107).

Synthesis of 1-trimethylsilyl-3,3-dimethylcyclopropene, 199

To a flask equipped with a dry ice condenser and cooled to -78°C was added cyclopropene 202 (13.8 mmol). The dry ice condenser was maintained at -78°C, and methyl lithium (13.8 mmol, 1.7 M in Et_2O) was added dropwise. The stirring mixture was allowed to warm to room temperature while maintaining the condenser at -78°C. Overnight the flask was cooled to -78°C. After stirring for an additional 9 h at 25°C, the flask was cooled to -78°C and an excess of trimethylchlorosilane was added rapidly. The solution was allowed to warm to room temperature and stirring was continued. The reaction mixture was poured into saturated NH_4Cl and extracted with Et_2O. The Et_2O layer was separated and dried over $MgSO_4$. The Et_2O was removed via distillation, and 199 (50%) was isolated by preparative GC. The spectra of 199 include: ^1H NMR δ 7.87 (s, 1H), 1.13 (s, 6H), 0.16 (s, 9H); ^{13}C NMR δ 136.60, 134.22, 28.88, 17.00, -0.86; MS 141 (0.2), 140 (M^+, 1.8), 125 (11), 83 (26), 73 (100), 45 (22), 43 (26). Anal. Calcd for $C_8H_{16}Si$: C, 68.48; H, 11.49. Found: C, 68.43; H, 11.41.

FVP of 199

(i) Cyclopropene 199 (43 mg), distilled (6 X 10^{-5} torr) from a bath warmed slowly from -23° C to room temperature, was pyrolyzed at

600°C. The pyrolysate (30 mg, 70%) was analyzed by GC and GC/MS. Compounds 156 (39%), 154 (2%), 158 (2%), and 157 (1%) were identified by comparison of spectral data of authentic samples.

(ii) Cyclopropene 199 (39 mg) was pyrolyzed at 775°C, 1 X 10^{-4} torr to afford a pyrolysate (31 mg, 79%) which consisted of 156 (4%), 157 (4%), 152 (36%), and 151 (10%). The products were identified by comparative GC retention times and GC/MS.

Synthesis of 3-methyl-3-vinylcyclopropene, 204

Cyclopropene 204 was synthesized according to the procedure of Yakushkina and Bolesov from 1-bromo-3-methyl-3-vinylcyclopropane (108). The only modification of the above procedure was that the reaction was carried out at 90°C rather than 40°C. A 1:1 mixture of 204 (19%) and t-butanol was isolated.

FVP of crude 204

A mixture of 204 (62 mg) and t-butanol, distilled (4 X 10^{-4} torr) from a bath at -50 to -78°C, was pyrolyzed at 700°C. The bath temperature was kept below -50°C to prevent the t-butanol from pyrolyzing. The pyrolysate (40 mg, 65%) was analyzed by GC and GC/MS, and the products identified as 2- and 3-methylcyclopentadiene (60%), 205. The two isomers (1:1 by NMR) could not be separated by preparative GC. The spectra of mixture 205 include: ^{1}H NMR δ 6.37 (d, 3H, J = 1.8 Hz), 6.20 (d of d, 1H, J = 5.0 Hz and 1.0 Hz), 6.11 5.98 (sext, 1H, J = 1.5 Hz), 2.92 (t, 2H, J = 1.8 Hz), 2.84 (d, 2H, J

= 1.2 Hz), 2.05 (d, 3H, J = 1.2 Hz), 2.00 (q, 3H, J = 1.8 Hz); ^{13}C NMR δ 135.87, 133.67, 132.70, 130.43, 128.35, 127.35, 126.78, 44.97, 41.50, 15.95, 15.14; MS 81 (3.7), 80 (M$^+$, 54), 79 (100), 77 (42), 65 (9.5), 52 (15), 51 (24), 50 (21), 39 (44).

Synthesis of 1-trimethylsilyl-2-butyne, 210

To a stirring solution of crude propargyltrimethylsilane (7.3 mmol) and Et_2O (40 mL) at -78°C was added dropwise *n*-BuLi (15 mmol, 2.87 M in hexane). After stirring for 0.5 h, dimethylsulfate (15 mmol) was added, and the mixture was allowed to warm to room temperature overnight. The mixture was extracted with water and Skelly B. The Skelly B layer was separated, neutralized with $NaHCO_3$, and dried over $MgSO_4$. The Et_2O and Skelly B were removed via rotary evaporation, and 210 (63%) was isolated by preparative GC (10 ft X 1/4 in., 10% SE-30). 210: ^{1}H NMR δ 1.76 (t, 3H, J = 2.7 Hz), 1.38 (q, 2H, J = 2.7 Hz), 0.073 (s, 9H); MS 127 (1.3), 126 (M$^+$, 10), 111 (14), 83 (27), 73 (100).

FVP of 210

Acetylene 210 (113 mg), slowly distilled (2 X 10^{-4} torr) from a bath warmed from -23°C to room temperature, was pyrolyzed at 700°C. The yellow pyrolysate (95 mg, 84%) was analyzed by GC and GC/MS. The two major compounds were identified as 3-trimethylsilyl-1,2-butadiene (44%), 211, and 210 (49%) by GC/MS and ^{1}H NMR. 211: ^{1}H NMR δ 4.25 m, 8.9), 83 (18), 73 (100).

Synthesis of 2-trimethylsilylpropenal, 213

Aldehyde 213 was prepared from 2-bromo-3,3-diethoxypropene according to the procedure of Okumoto and Tsuji (109).

Synthesis of 2-trimethylsilyl-1,3-butadiene, 212

To a stirring solution of triphenylphosphonium iodide (8.6 mmol) and Et_2O (20 mL) was added 3.4 mL of *n*-BuLi (8.7 mmol, 2.55 M in hexane). Upon addition of the *n*-BuLi, the mixture changed from a white color to yellow. After stirring for 3 h, 1.1 g of 213 were added dropwise and an exotherm was observed. The mixture was stirred overnight and then extracted with saturated NH_4Cl and Et_2O. The Et_2O layer was separated and dried over $MgSO_4$. The Et_2O was removed via distillation, and 212 (5%) was isolated by preparative GC (15 ft X 1/4 in., 15% SE-30). 212: ^1H NMR δ 6.44 (d of d, 1H, J = 10 Hz and 11 Hz), 5.72 (d, 1H, J = 4 Hz), 5.42 (d, 1H, J = 4 Hz), 5.22 (d, 1H, J = 18 Hz), 5.05 (d, 1H, J = 9 Hz) 0.16 (s, 9H); MS 127 (1.3), 126 (M^+, 11), 111 (28), 85 (29), 73 (100), 59 (20).

FVP of 212

Diene 212 (10 mg), slowly distilled (1×10^{-5} torr) from a bath warmed from -23°C to room temperature, was pyrolyzed at 750°C. A GC/MS of the pyrolysate indicated the presence of only 212.

FVP of 213

Aldehyde 213 (318 mg), slowly distilled (4 X 10^{-4} torr) from a bath warmed from -23°C to room temperature, was pyrolyzed at 650°C. The pyrolysate (209 mg, 66%) was analyzed by GC and GC/MS. The major product, 1,3-butadiene (60%), 215, along with D_3 (6%), D_4 (4%), and unreacted 213 (6%) were identified by comparison of GC retention times and GC/MS of authentic samples. Two other products, ((trimethylsilyl)oxy)-1,2-propadiene (15%), 214, and ((pentamethylsiloxy)oxy)-1,2-propadiene (8%), 217, were isolated by preparative GC (10 ft X 1/4 in., 15% SE-30). 214: ^{1}H NMR δ 6.56 (t, 1H, J = 5.7 Hz), 5.26 (d, 2H, J = 5.7 Hz), 0.21 (s, 9H); IR 2970, 1952, 1261, 1211, 1026, 856 cm^{-1}; MS 128 (M^+, 4.3), 113 (100), 73 (53), 59 (76), 45 (43). The spectra of 217 include: ^{1}H NMR δ 6.59 (t, 1H, J = 6.0 Hz), 5.25 (d, 2H, J = 6.0 Hz), 0.16 (s, 6H), 0.11 (s, 9 H); IR 2966, 1949, 1265, 1215, 1072, 1030, 852 cm^{-1}; MS 202 (M^+, 1.4), 187 (30), 159 (13), 147 (34), 133 (100), 73 (28), 54 (35).

Thermolysis of 214

(i) Allene 214 (~0.4 torr) was pyrolyzed in a SFR at 570°C. The pyrolysis products were identified by GC retention times and GC/MS to be 1,3-butadiene (37%), 214, 217 (9%), D_3, and 213 (18%) along with unreacted 214 (36%). The yields are uncorrected GC area ratios. D_3 and 213 could not be separated by GC/MS, therefore, preventing determination of individual yields.

(ii) A mixture of 214 (~0.1 torr) and dimethyldimethoxysilane (~1.2 torr) was pyrolyzed in a SFR at 570°C. The major products, 215 (29%), D_3 and 213 (12%), dimethoxytetramethyldisiloxane (31%), 220, and unreacted 214 (28%) were identified by GC retention times and GC/MS. The yields are uncorrected GC area ratios.

Synthesis of E-3-trimethylsilylpropenal, 221

Aldehyde 221 was prepared from 3-trimethylsilylprop-2-en-1-ol according to the procedure of Jung and Gaede (110).

FVP of 221

(i) Aldehyde 221 (150 mg), slowly distilled (2 X 10^{-4} torr) from a bath warmed from -23°C to room temperature, was pyrolyzed at 650°C. The yellow pyrolysate (113 mg, 75%) was analyzed by GC and GC/MS. Benzene (1%), 215 (1%), and unreacted 221 (27%) were identified by GC/MS. The two major products, 2,2,3-trimethylsila-α-2,3-dihydrofuran (28%), 226, and 2,5,5-trimethylsila-α-2,5-dihydrofuran (10%), 227, were isolated by preparative GC (15 ft X 1/4 in., 15% SE-30). 226: ^{1}H NMR δ 6.39 (m, 1H), 5.02 (t, 1H, J = 3 Hz), 1.65 (m, 1H), 1.04 (d, 3H, J = 7.5 Hz), 0.26 (s, 6H); ^{13}C NMR δ 145.34, 111.89, 19.54, 15.19, -0.92, -4.30; IR 3607, 2963, 2874, 1597, 1261, 1184, 1026, 845 cm^{-1}; MS 130 (0.9), 129 (3.0), 128 (M^+, 25), 113 (100), 111 (32), 85 (20), 59 (25), 45 (28), 43 (30). 227: ^{1}H NMR δ 6.81 (d of d, 1H, J = 2.1 Hz and 10 Hz), 5.99 (d of d, 1H, J = 2.1 Hz and 10 Hz), 4.78 (m, 1H), 1.26 (d, 3H, J = 6.6 Hz), 0.25 (s, 3H), 0.22

(s, 3H); ^{13}C NMR δ 154.7, 126.2, 79.0, 23.4, 1.77, 0.51; IR 2974, 2874, 1258, 1138, 1034, 945, 856 cm^{-1}; MS 130 (0.9), 129 (3.2), 128 (M^{+}, 25), 113 (100), 45 (40); calcd for $C_6H_{12}OSi$ m/e 128.06575, measured m/e 128.06597. Anal. Calcd for $C_6H_{12}OSi$: C, 56.19; H, 9.43. Found: C, 56.14; H, 9.71.

(ii) Pyrolysis of 221 (270 mg) at 775°C, 4 X 10^{-4} torr, afforded a pyrolysate (130 mg, 48%) consisting of 215 (23%), 151 (8%), benzene (5%), 227 (9%), and 226 (13%).

Thermolysis of 227

Silyl ether 227 (~4 torr) was pyrolyzed in a SFR at 650°C. The pyrolysis products were identified by GC retention times and GC/MS as 226, 215, and unreacted 227. The ratio of 227 to 226 was 7.5:1.0 based on uncorrected GC areas. Only a trace of 215 was detected.

FVP of 226

Silyl ether 226 (92 mg), slowly distilled (2 X 10^{-4} torr) from a bath warmed from -23°C to room temperature, was pyrolyzed at 750°C. The pyrolysate (29 mg, 32%) was analyzed by GC and GC/MS. Compound 227 (13%) was isolated via preparative GC (15 ft X 1/4 in., 15% SE-30); however, dimethylsila-α-pyran (19%), 231, could not be separated from what appears to be 226 by GC/MS. The ratio of 231 to 226 was 1.23:1.00 by ^{1}H NMR. Benzene (6%) and a trace of 1,3-butadiene was also present.

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