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Mechanistic study of the thermal rearrangement of silylheterocumulenes and their propargyl isomers

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Magrum, Glenn Robert, Ph.D.

Iowa State University, 1989

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Mechanistic study of the thermal rearrangement of silylheterocumulenes and their propargyl isomers

by

Glenn Robert Magrum

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

Department: Chemistry
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1989

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DEDICATION

To my parents,
who have supported me in all my endeavors

INTRODUCTION

The chemistries of ketenes, thioketenes and other heterocumulenes have recently been reviewed.[1] Most of the work appearing in the literature deals exclusively with alkyl- and arylheterocumulenes.

Most heterocumulenes are very reactive, thus requiring complicated experimental equipment for their study. They are generally generated in-situ, in solution, which limits the full understanding of the chemistry of these compounds. Silyl-substituted ketenes and -thioketenes, on the other hand, are relatively stable and of recent interest.[2]

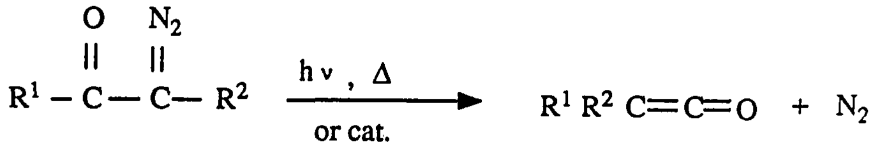
Hydroxyacetylene has not been prepared and the chemistry of siloxyacetylenes, only recently prepared, remains to be explored. The chemistry of the analogous sulfur compounds, though these compounds are both known,[3,4] remains virtually unexplored.[5,6]

This dissertation will therefore examine the kinetic and mechanistic aspects of the thermal rearrangement of silylheterocumulenes and their propargyl isomers and routes to preparing such compounds.

HISTORICAL

Ketenes, thioketenes and their propargyl isomers are an important class of organic molecules due to their high degree of reactivity. A great deal of the literature on ketenes and thioketenes was recently reviewed.[1] Of the two, ketenes are viewed as the most important due to their extensive use in organic syntheses. They are generally generated in situ and reacted with alkenes, alkynes and other unsaturated compounds, both intermolecularly and intramolecularly. There are a number of methods for preparing ketenes, with many of the most widely used methods developed at the beginning of this century. Some important general methods are shown in Scheme 1.[5]

Scheme 1

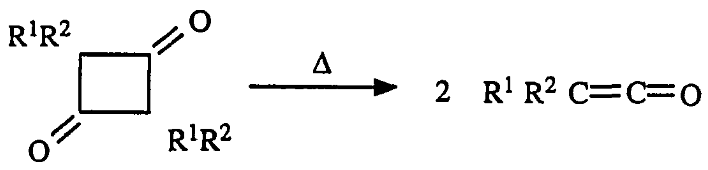
1. 

$$R^1-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle N_2}{\|}}{C}-R^2 \xrightarrow[\text{or cat.}]{h\nu\text{ , }\Delta} R^1R^2C{=}C{=}O + N_2$$

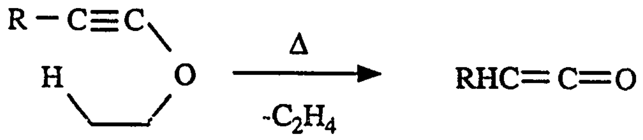
2. $R^1R^2CHCOCl \xrightarrow{Et_3N} R^1R^2C{=}C{=}O + Et_3N^+HCl^-$

3. $R^1R^2CBrCOBr \xrightarrow{Zn} R^1R^2C{=}C{=}O + ZnBr_2$

4.

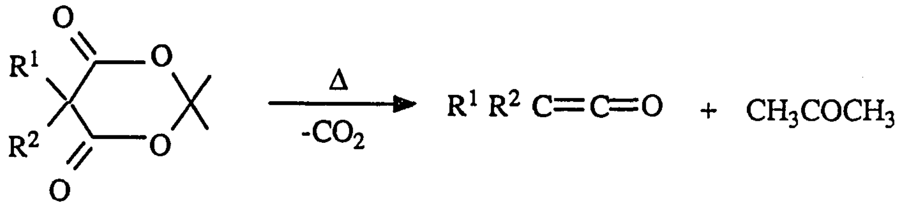


5.



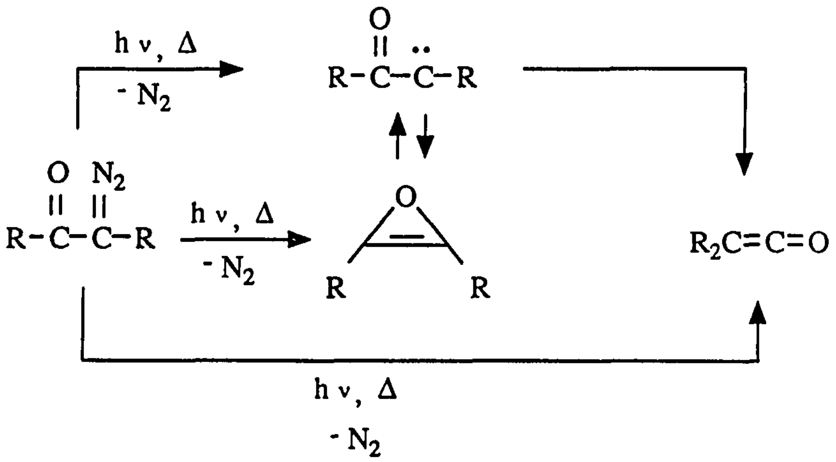
6. $(R^1R^2CHCO)_2O \xrightarrow{550°C} R^1R^2C{=}C{=}O + R^1R^2CHCO_2H$

7.



The Wolff rearrangement (WR) of alpha-diazocarbonyl compounds to form ketenes will be discussed in more detail due to its relevance to this work. The WR can be initiated by thermolysis, photolysis or catalysis.[3,7,8] The photochemically-induced WR is superior to other methods when C-H insertion is a problem as the intermediate carbene is avoided. Several mechanisms have been proposed for the WR[7] and are summarized in Scheme 2.

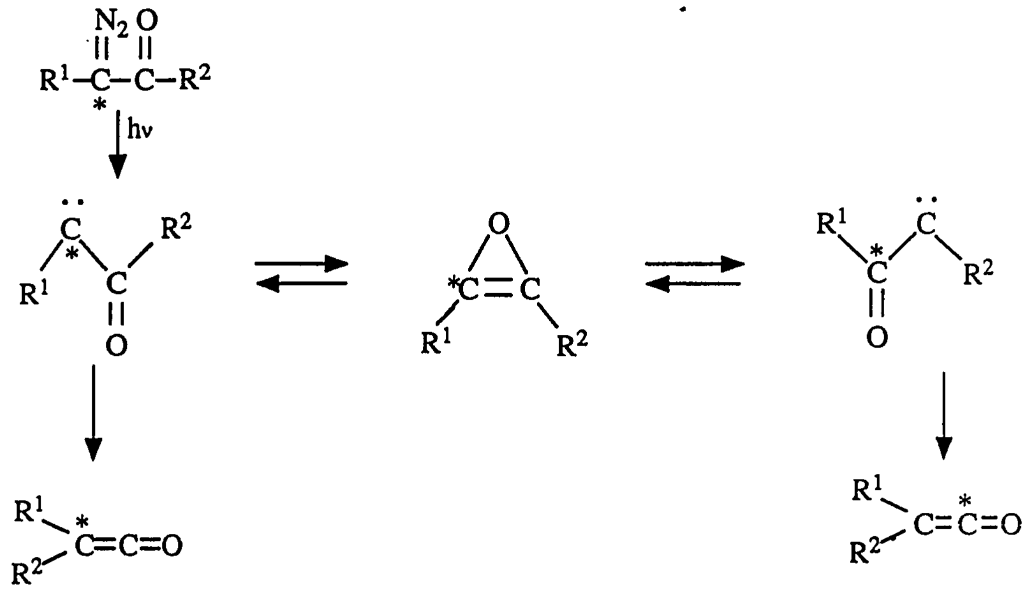
Scheme 2



The commonly accepted mechanism for many years involved the intermediacy of a ketocarbene, despite a lack of direct evidence.[7] The intermediacy of a ketocarbene (as a precursor of ketene) was later confirmed by E.S.R. spectra and by trapping experiments.[3,8] Recently, spectroscopic characterization (by UV-vis, IR and E.S.R.) of alpha-ketocarbenes (from conformationally rigid alpha-diazoketones) and their trapping adducts with carbon monoxide and dioxygen was reported.[9] They claim this to be the first direct observation of nonconcerted Wolff rearrangements which proceed through alpha-ketocarbene intermediates.

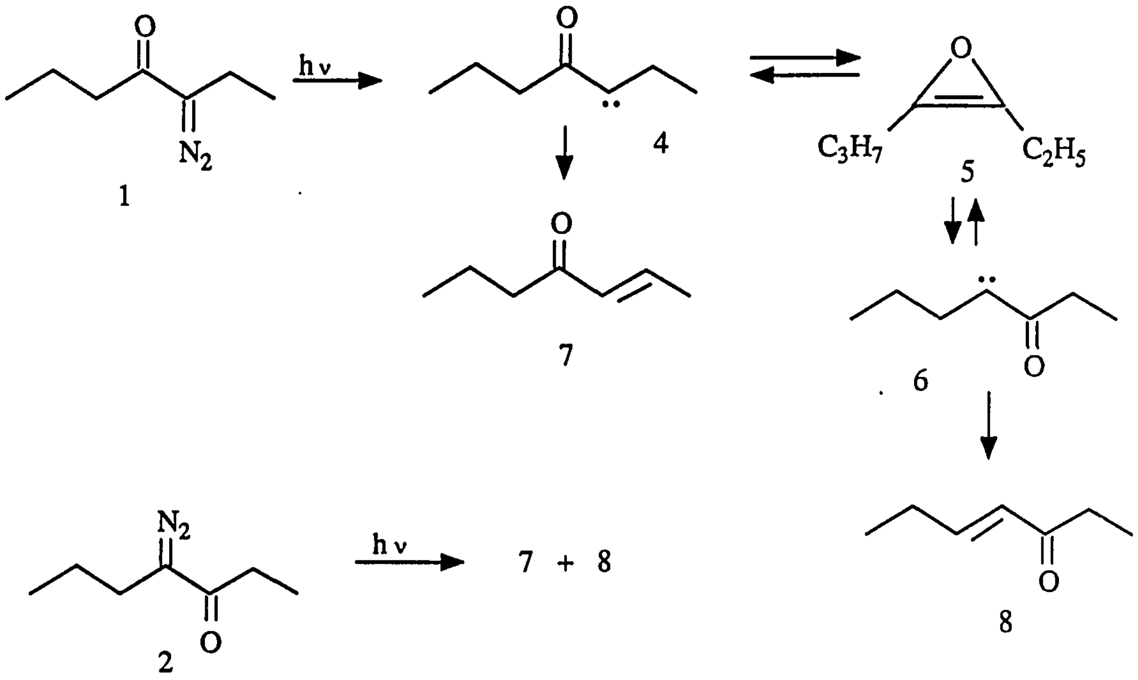
Carbon-13 labelling experiments have established the involvement of a species in the Wolff rearrangement that possesses the symmetry of oxirene.[3,8,10] The gas phase photochemical WR of carbon-13 labelled 3-diazo-2-butanone and diazoacetone led to scrambling of the label in the ketene products,[10] from which calculations indicate oxirene participation to be 100 and 16%, respectively (Scheme 3).

Scheme 3



Ketocarbene-ketocarbene interconversion through an oxirene or oxirene-like intermediate has also been established from both thermal and photochemical studies of unsymmetrically substituted diazoketones (Scheme 4).[3,8] The thermal

Scheme 4



decomposition of alpha-diazoketones has also been shown to involve oxirene intermediates and oxirene participation found to be strongly temperature dependent, higher temperatures favoring oxirene formation.[3,8]

Thus, oxirene participation has been demonstrated in both thermal and photochemically induced WR of alpha-diazoketones. Evidence suggests that ketocarbene-oxirene interconversion takes place on a singlet energy surface and only when the ketocarbene is vibrationally excited,[3,8] which is more common in photochemical reactions where excess vibrational energy is abundant. However, it is possible to acheive this excited state by thermal means, as has been demonstrated, and as one would expect, oxirene participation increases with increasing temperature.

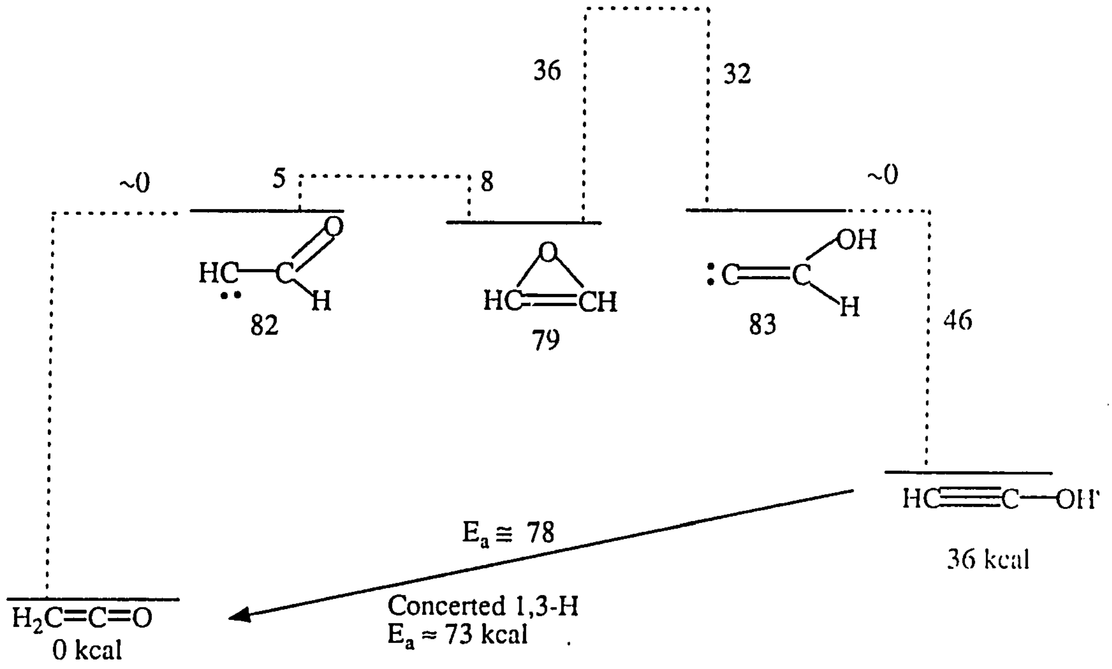
The extent of oxirene involvement in the WR of alpha-diazoketones also depends on a number of other factors, the major ones being relative rates of substituent migration and ring closure, the nature of the substituent, the phase, the solvent, if any, and the rate of S_1-T_0 intersystem crossing in the ketocarbenes.[1] Ring strain has also been shown to be a factor, with oxirene participation ruled out in cyclic and annelated systems because of high ring strain.[3,8]

Despite great effort, direct experimental evidence for oxirene formation is rather weak. Torres et al.[11] reported infrared characterization of both bis(trifluoromethyl)oxirene and trifluoroacetyl(trifluoromethyl)carbene using matrix isolation techniques. It has been demonstrated, however, that the species assigned as the ketocarbene is actually the alpha-keto-diazirine isomer of the starting diazoketone.[12] Attempts at generation of the oxirene under conditions similar to those reported by Torres et al. were unsuccessful.

Another isomeric form of ketene, hydroxyacetylene, has only been observed by tandem mass spectroscopy in the gas phase.[13] Other hydroxyalkynes are not known and outside of some theoretical calculations little is known about the ketene-alkynol isomerization.[14a,14b] A diagram for the potential energy profile of this isomerization is shown on the following page.[14a] This has been calculated as the lowest energy pathway, 78 kcal/mol, for this isomerization via 1,2-hydrogen shifts. A 1,3-hydrogen shift pathway has also been calculated and preliminary results indicate it requires 5 kcal/mol less energy than the 1,2-shift, though no further results have since been reported.[14a] The difficulty in isolating an oxirene is readily understandable from this profile, which shows the isomerization of oxirene to ketene requires only 8 kcal/mol.

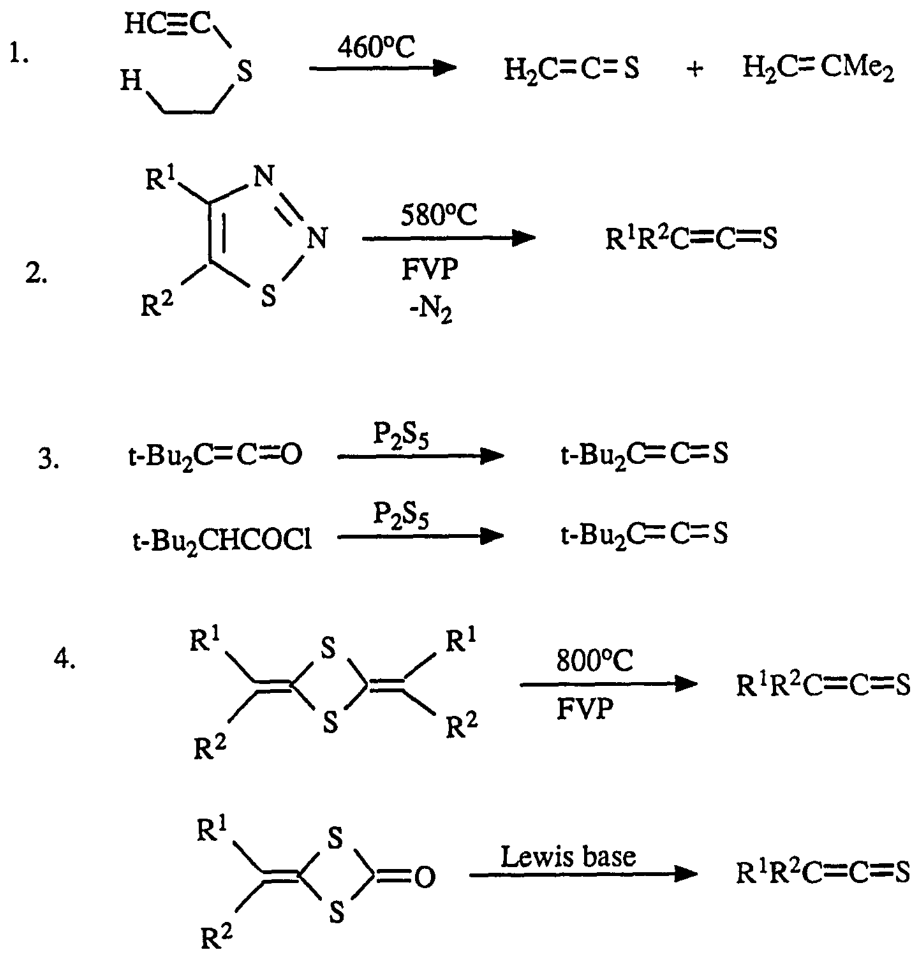
Thioketenes are less stable than the analogous ketenes, with only sterically hindered thioketenes being stable at room temperature. Some typical preparation methods are shown in Scheme 5,[5] with equations 2 and 4 representing general preparations.[15] The intermediacy of thiirene has been proposed in the general preparation of thioketenes from 1,2,3-thiadiazoles (equation 2).[15] But, unlike oxirene, transient thiirene and its derivatives are now well characterized spectroscopically at low temperatures.[3,16] Analysis of the photolysis products of argon matrix isolated 1,2,3-thiadiazole by infrared spectroscopy indicated that only ethynyl mercaptan and thioketene had formed.[3,16] Photolysis of this thiadiazole that has been deuterated at either the 4 or 5 position produced monodeuterated thioketene

Diagram 1



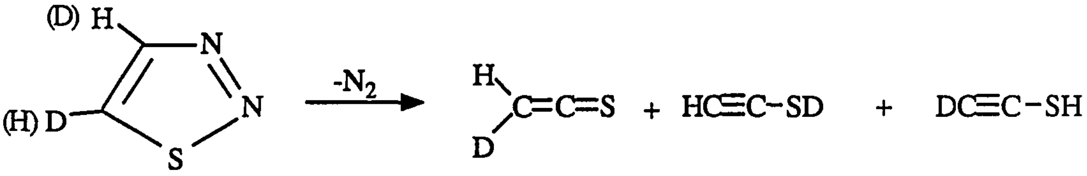
L. Radom, J. Org. Chem., **47**, 1869 (1982) MP3 w/ 6-31G**

Scheme 5


1.
460°C
H₂C=C=S + H₂C=CMe₂
2.
580°C
FVP
-N₂
R¹R²C=C=S
3.
t-Bu₂C=C=O
P₂S₅
t-Bu₂C=C=S
t-Bu₂CHCOCl
P₂S₅
t-Bu₂C=C=S
4.
800°C
FVP
R¹R²C=C=S
Lewis base
R¹R²C=C=S

and two isomeric mercaptans (Scheme 6). This implies a symmetrical precursor, presumably thiirene. Further studies on both the deuterated and non-deuterated thiadiazoles

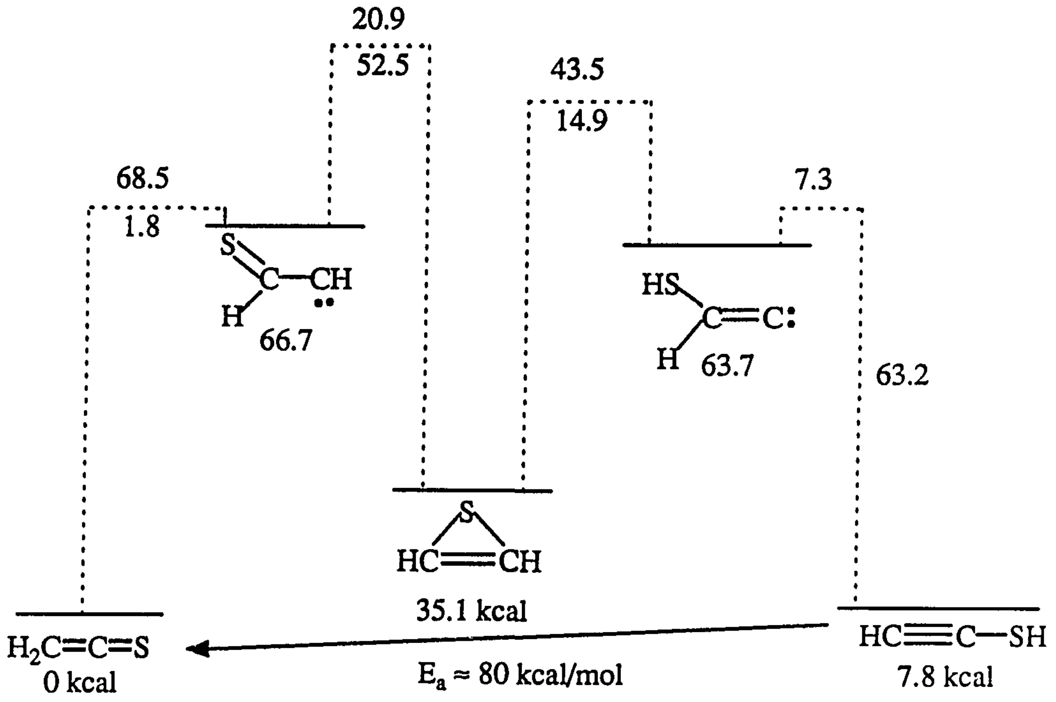
Scheme 6



yielded transient spectra attributed to thiirene.[16] Further photolytic studies of substituted and/or carbon-labelled 1,2,3-thiadiazoles further support the intermediacy of thiirene.[3,16]

Theoretical calculations of the thioketene-ethynylmercaptan isomerization has yielded an energy profile very similar to that calculated for the ketene-hydroxyacetylene isomerization (Diagram 2).[17] The lowest energy pathway is calculated to be via a series of 1,2-hydrogen shifts and found to have a similar energy of activation, 80 kcal/mol, to that for ketene isomerization (78 kcal/mol). The 1,3-hydrogen shift has been ruled out, requiring greater than 90 kcal/mol.

Diagram 2



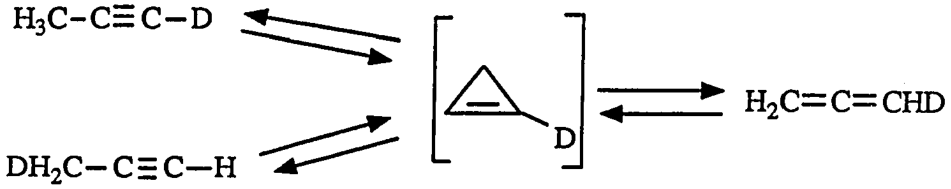
CIDSQ w/ 6-31* basis set

Strausz, Can. J. Chem., **61**, 2596 (1983)

cf. J.Chem. Phys., 78, 1384 (1983)

The allene-propyne isomerization, the parent hydrocarbons for the ketene and thioketene systems, was long thought to occur via a concerted 1,3-hydrogen shift.[18] Recent studies suggest, however, a two-step process involving a cyclopropene intermediate.[19] When 1-deuteriopropyne was pyrolyzed in a nitrogen flow at 500-700°C it isomerized more rapidly to 3-deuteriopropyne than to deuterioallene (Scheme 7). This was rationalized by postulating the intermediacy of

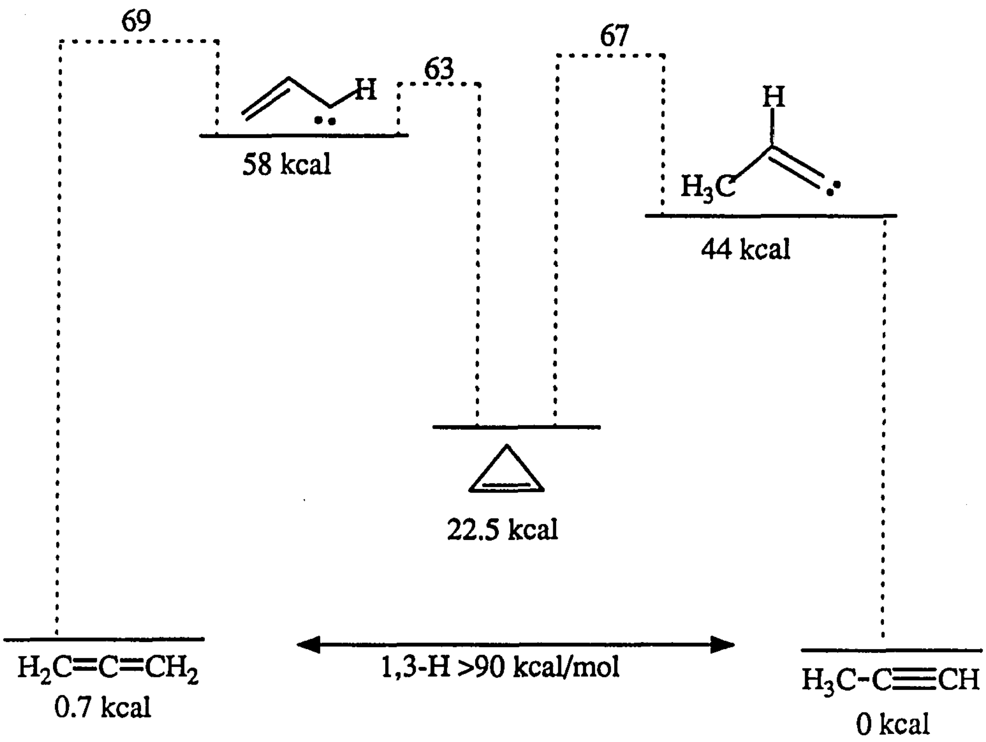
Scheme 7



cyclopropene. This postulate has been confirmed by recent ab initio calculations which show the most favorable energy pathway involves 1,2-hydrogen migrations and the intermediate cyclopropene.[20] The potential energy profile for this isomerization is shown in Diagram 3. This diagram is very similar to the two previous energy diagrams for the ketene and thioketene isomerizations, though the activation energy here is lower, 68 kcal/mol.

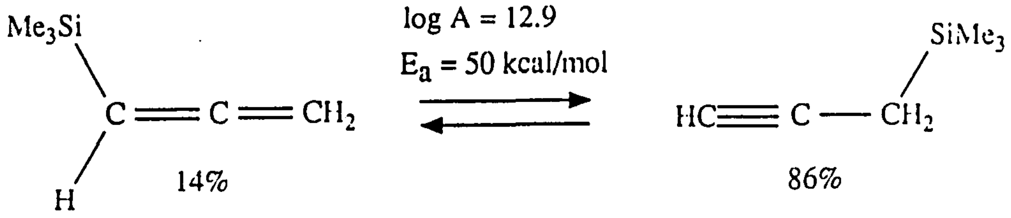
The (trimethylsilyl)allene-propargylsilane isomerization was studied a number of years ago by Kwart and Slutsky[21] in a flow pyrolysis at 500°C (Scheme 8). They concluded the isomerization occurred via a concerted 1,3-silyl shift, requiring 50 kcal/mol activation energy. This isomerization has been studied at higher temperatures by Barton and Groh[22] using flash vacuum pyrolysis (FVP) of 3-(dimethylsilyl)-propyne and reported to give three isomeric products. Silanes 43 and 44 are in equilibrium and at these higher temperatures bled off to form 45. One possibility for the

Diagram 3



Yoshimine, JACS, 107, 5332 (1985)

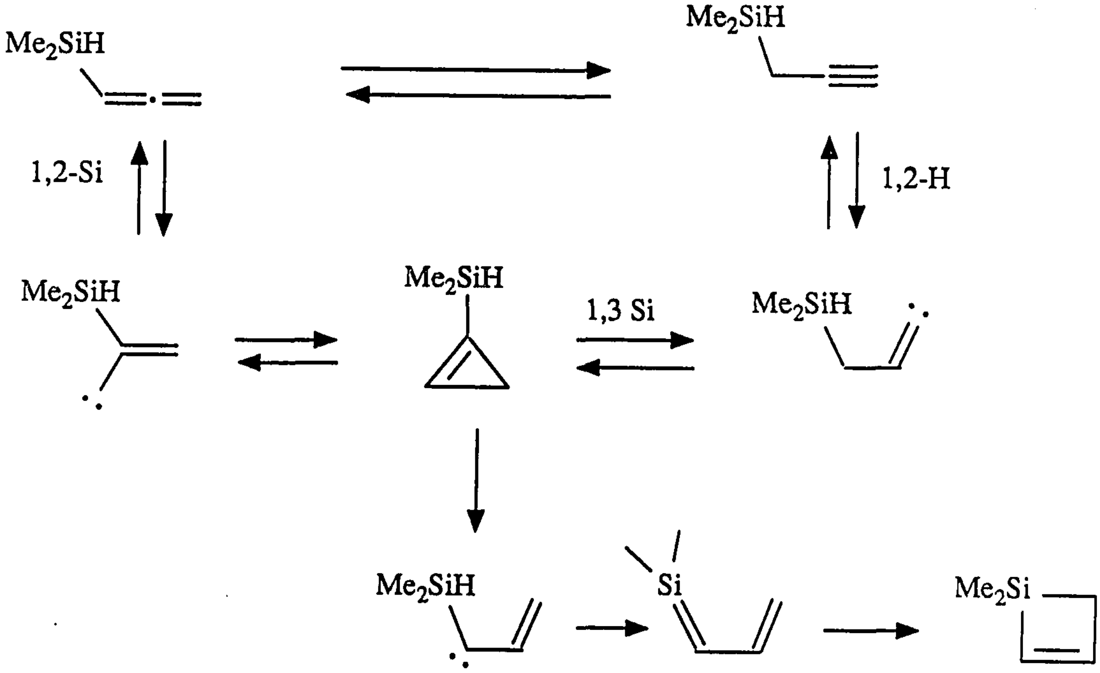
Scheme 8



Kwart, JACS, *95*, 8678 (1973)

formation of 46 is via an initial 1,2-silyl shift, as shown in Scheme 9. This pathway involving 1,2-silyl shifts is in agreement with the calculations for the allene-propyne isomerization.

Scheme 9



RESULTS AND DISCUSSION

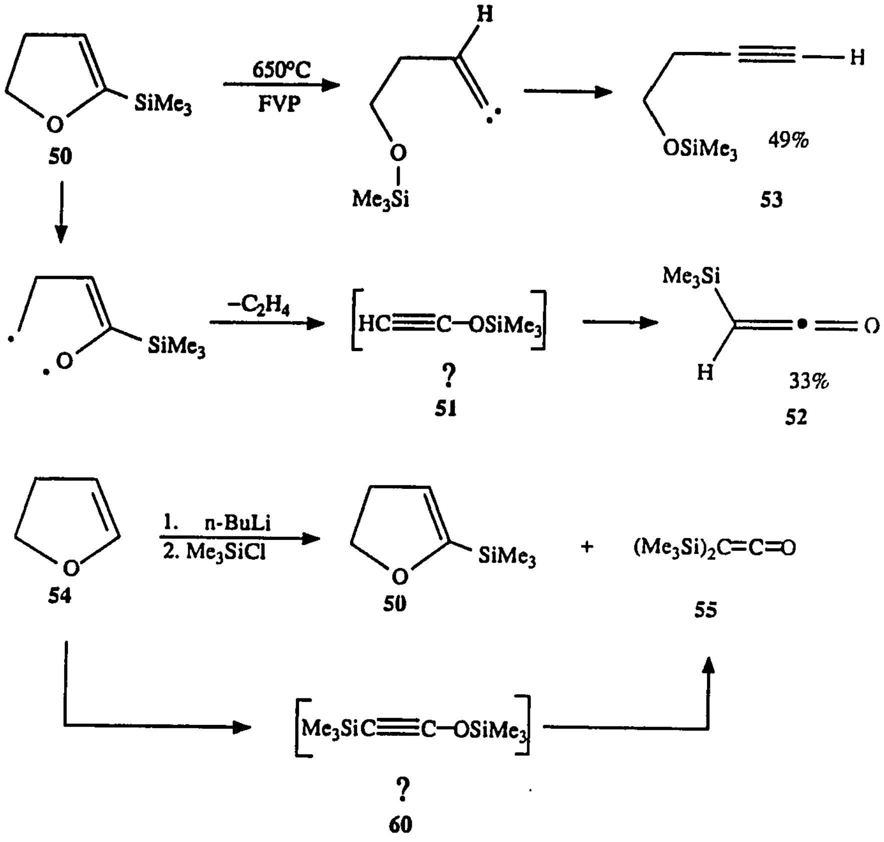
The investigation of the thermal rearrangement of siloxyacetylenes and their sulfur analogs to the corresponding heterocumulenes was prompted by two unexpected preparations of silylketenes.[23,24] The first occurred when 2,3-dihydro-5-(trimethylsilyl)dihydrofuran, **50**, was subjected to FVP at 650°C. The second occurred when 2,3-dihydrofuran, **54**, was metallated in THF by n-BuLi, warmed to room temperature, and then quenched with a chlorosilane. The only compound expected to be formed was **50**. The intermediates proposed as precursors to these silylketenes were both siloxyacetylenes (Scheme 10). As there was no conclusive evidence supporting this unique isomerization, we thought it prudent to study it.

Cyclic Vinyl Ethers

Metallation of 2,3-dihydrofurans and 2,3-dihydrothiophene

There are few methods for preparing bis(silyl)ketenes and these routes are both lengthy and tedious, and quite often expensive.[1,25] Upon finding that bis(silyl)ketenes are formed when **54** is metallated by n-BuLi at -23°C in THF, warmed to room temperature and quenched with a chlorosilane,[24] we set out to try and improve upon the

Scheme 10



initially low yields, approximately 20% depending upon the chlorosilane quenching reagent. This route allows one to prepare said ketenes in one step from inexpensive, commercially-available starting materials.

In an attempt to drive the reaction toward formation of the ketene product, the reaction mixture was heated to between 35° and 45°C for two hours. This completely eliminated ketene formation. However, after initial metallation of the dihydrofuran by one equivalent of n-BuLi in THF solvent, prolonged stirring at room temperature favored formation of the ketene product. After 24 hours at 25°C and quenching with chlorodimethylsilane, the corresponding bis(silyl)ketene and silylated dihydrofuran were formed in 28% and 19% yield, respectively. An additional 24 hours at room temperature decreased the yield of ketene to 21% and the dihydrofuran to 7%.[26]

One should also note that optimal yields would require two equivalents of base, but because n-BuLi will react with THF under these conditions, each equivalent must be added separately. Therefore, after stirring 2,3-dihydrofuran with one equivalent of n-BuLi for 24 hours at room temperature, a second equivalent was then added after cooling to -23°C. This is then allowed to come to room temperature slowly and stir for an additional 10 hours. The reaction mixture was then quenched with chlorotrimethylsilane to form ketene **59** in 33% yield, the highest yield obtained from the decomposition of 2,3-dihydrofuran, along with a 38% yield of **50**.

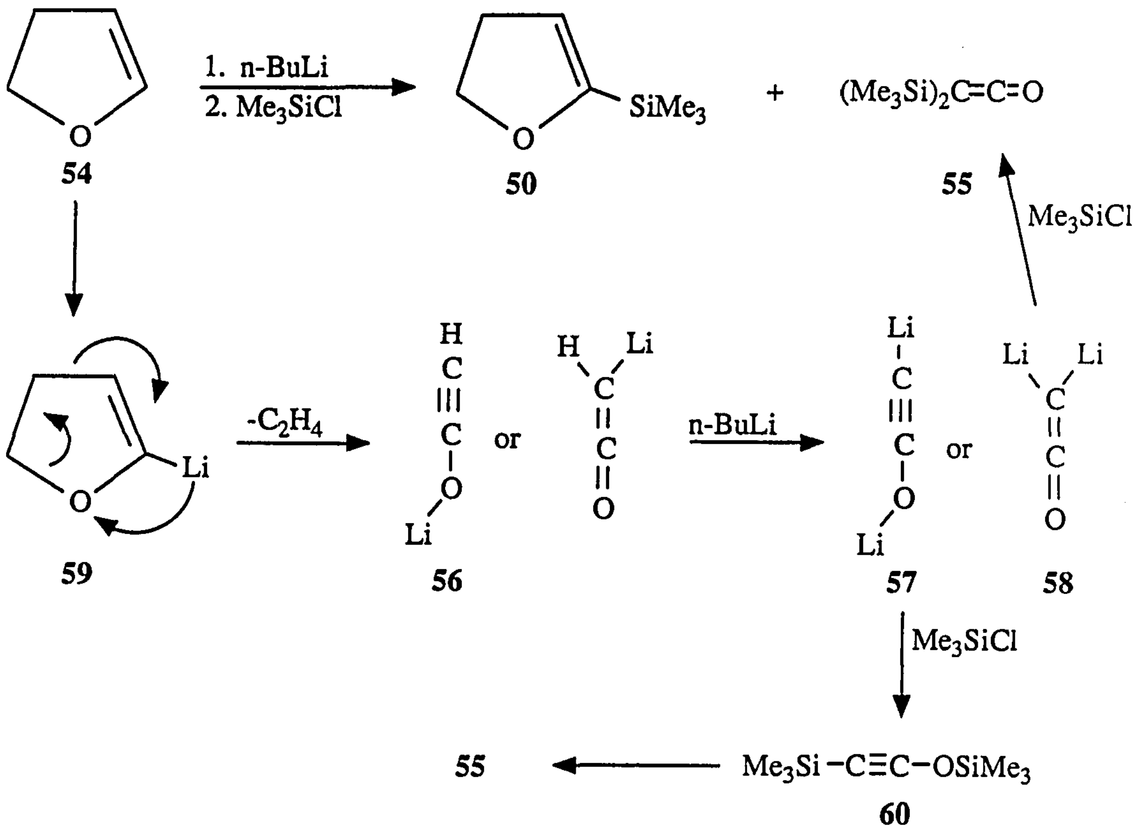
Addition of various amounts of HMPA to the reaction mixture caused complete decompostion of the dihydrofuran. Adding an equivalent of TMEDA had no effect. Changing the solvent to ethyl ether prevented decomposition, and only silylated dihydrofurans were produced in yields up to 78%. Hoping that a different counter ion might shift the product ratio towards ketene, an equivalent of potassium t-butoxide was added to the reaction mixture containing a 4:3 ratio of THF to hexane. At -23°C only furan product was formed on quenching with chlorosilanes. Higher temperatures afforded neither product on quenching. When the solvent was hexane alone and the reaction run for two hours at -23°C before quenching with chlorotrimethylsilane, **50** and **55** were produced in yields of 17% and 13% respectively.

It should also be noted that only chlorosilanes afforded discernible products. This has been reported by others working with similar compounds.[25,27] Attempts with adipyl chloride, dimethyl sulfate, benzyl chloride, allyl chloride, 4-bromo-1-butene and methyl iodide failed to form the expected products.

The formation of the bis(silyl)ketenes from 2,3-dihydrofuran (**54**) obviously involves the loss of ethylene. But what is the intermediate responsible for its formation? This is one of the questions we tried to address.

Metallation of **54** to produce an alpha-lithiodihydrofuran (**59**) is a well-established reaction, being conveniently prepared at ambient temperatures with n-BuLi in hexane and a catalytic amount of TMEDA, and the carbanion structure has been studied by ^{13}C NMR.[28] Boeckman and Bruza[29] have used

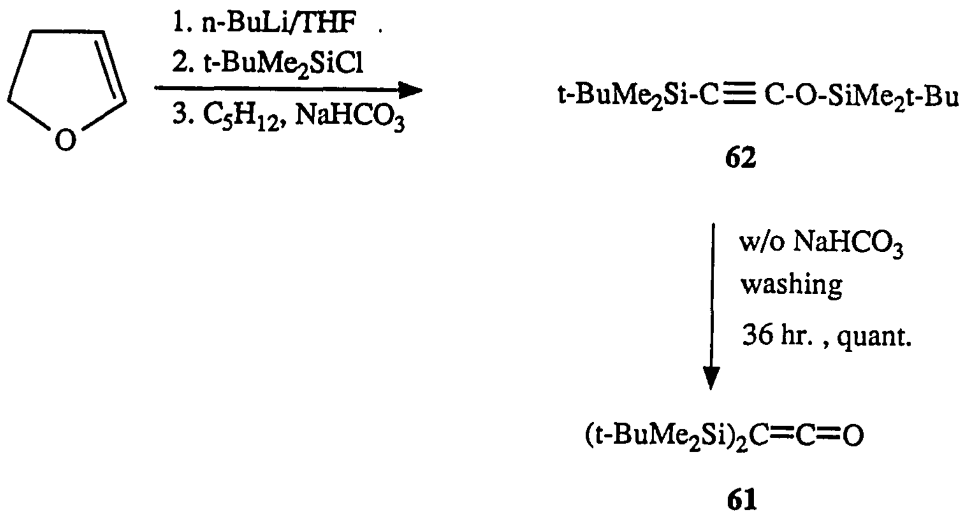
Scheme 11



this carbanion to react with a variety of electrophiles. Carbanion **59** may then decompose to lithium alkynolate **56** or its ketenic isomer (Scheme 11). There is ample precedent for this type of decomposition in heterocyclopentadienes.[30] A second molecule of n-BuLi would then abstract another proton to form either dilithioalkynolate **57** or dilithioketene **58**. Quenching of **58** by chlorotrimethylsilane would lead directly to silylketene **55**. However, it also could be that siloxyacetylene **60** is formed but then rearranges to form silylketene **55**. Initial elimination of ethylene may also occur from a dimetalated dihydrofuran. Attempts have been made to study these anions via ^{13}C NMR by preparation of the anion in D_8 THF, but the numerous signals have prevented any dependable conclusions from being drawn.

Attempts were made with a variety of chlorosilanes of differing steric bulk to try and isolate the possible siloxyacetylene intermediates but always produced only bis(silyl)ketenes on workup. Even the sterically hindered chlorotriphenylsilane failed to allow isolation of a siloxyacetylene. After reports by Kowalski et al.[31] and Stang and Roberts[32] on the first silylations of ynolate anions on oxygen using t-butyldimethylchlorosilane or triisopropylchlorosilane, trapping our dianion with t-butyldimethylchlorosilane was attempted. It was then possible to isolate siloxyacetylene **62** when the reaction mixture was worked up within one hour after quenching by first diluting with pentane, followed by washing with aqueous sodium bicarbonate (Scheme 12). Analysis by infrared spectroscopy (IR) indicated only the presence of a siloxyacetylene by a band at 2185 cm^{-1} and no ketene (2075 cm^{-1}).[33] It should be noted that this reaction was only sporadically successful, forming only the silylketene instead

Scheme 12

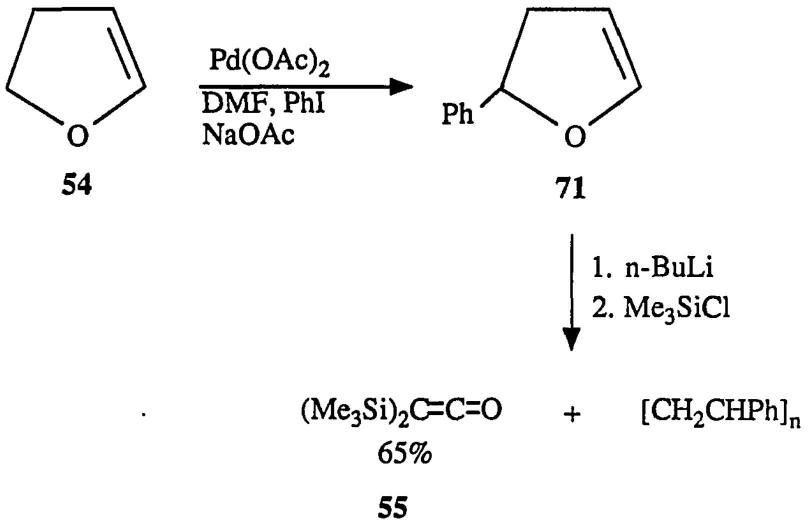


of the desired siloxyacetylene, indicating that whatever was inducing the isomerization had not been completely removed. Kowalski has also had problems with the formation of siloxyacetylenes that he suspects is due to the presence of n-butoxide.[34]

Interestingly, if the reaction mixture was allowed to stir for 8 hours before pentane/aqueous sodium bicarbonate workup, the IR showed both acetylenic and ketene stretches in approximately a 1:1 ratio. If allowed to stir for 20 hours without workup the ratio changes to 1:3 and after 36 hours the only IR band present is that of the bis(silyl)ketene. A dried pentane solution (anyhydrous magnesium sulfate) of the aqueous sodium bicarbonate washed products showed no evidence of isomerization of siloxyacetylene to silylketene. Thus the actual dianion formed by decomposition of 2,3-dihydrofuran was dilithioalkynolate **57** and not dilithioketene **58**. Isomerization of a siloxyacetylene was therefore shown to be responsible for the formation of bis(silyl)ketenes in these decompositions.

Since a mixture of silylated ketene (and/or siloxyacetylene) and silylated dihydrofuran was always obtained on metalation of **54**, the furan was modified so as to make olefin extrusion more favorable. It was hoped this would serve to both aid in purification by eliminating the formation of the silylated furan and increase yields of siloxyacetylenes or silylketenes, which, as mentioned earlier, are quite often tedious and expensive to prepare. Use of 2,3-dihydro-2-phenylfuran[35,36,37] (**71**), which can be prepared cheaply in one step, has the potential for styrene extrusion, rather than ethylene, making it an ideal choice. Indeed, sequential metalation of **71** with two successive equivalents of n-BuLi, with shorter reaction times, followed by quenching with chlorotrimethylsilane (TMSCl) affords **55** in 65% yield, as is shown in Scheme 13. This was significantly higher than the 38% yields obtained by utilizing 2,3-dihydrofuran, and better still, was uncontaminated by silylated dihydrofuran or

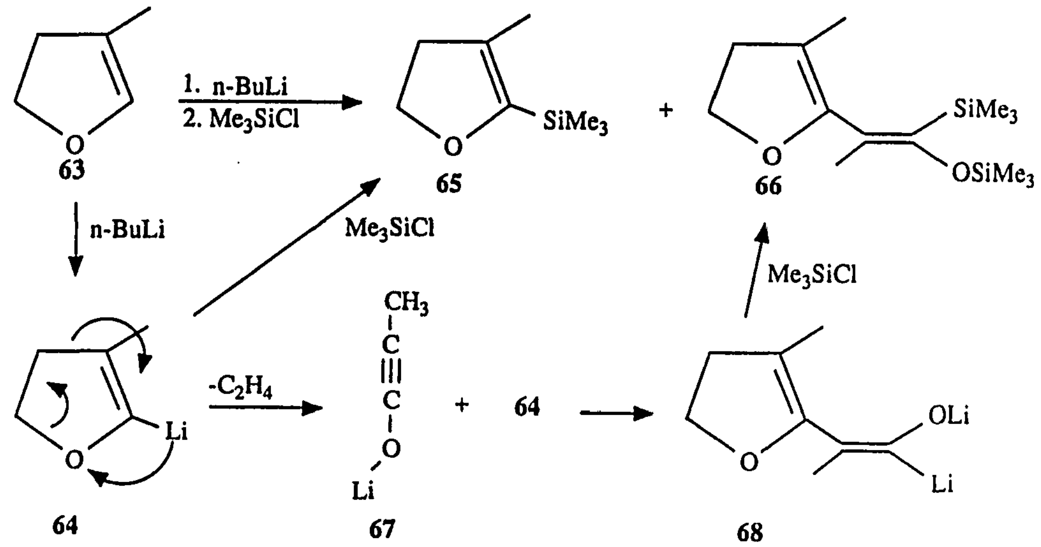
Scheme 13



styrene, which was demonstrated to polymerize under these conditions.

To investigate further into the effect of ring substitution 2,3-dihydro-4-methylfuran, **63**, was also prepared by the route of Stefani et al.[38] It was hoped that metalation of **63** would allow direct preparation of a trimethylsiloxy-acetylene due to the low temperatures and the one end of the expected acetylene product, **67**, blocked by a methyl group as shown in Scheme 14. Dihydrofuran **63** was reacted with one equivalent of n-BuLi in THF at -23°C and subsequently quenched with TMSCl after allowing 24 hours stirring at ambient temperature, addition of a second equivalent of n-BuLi, and stirring for an additional 11 hours

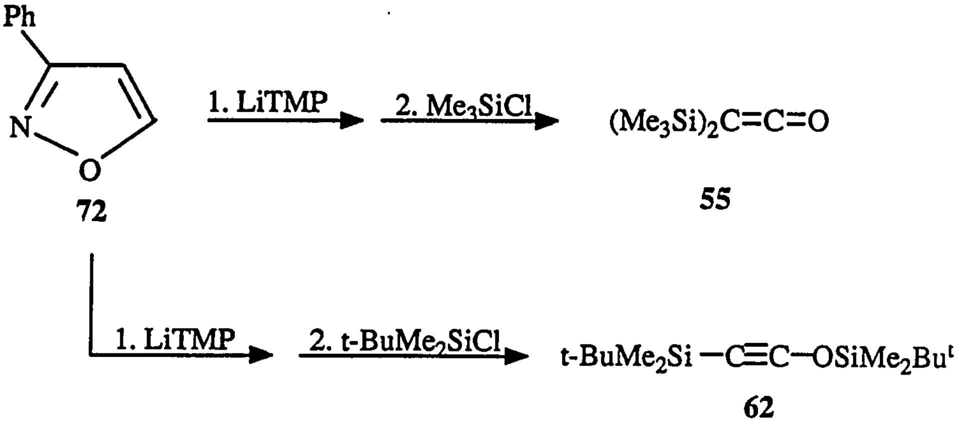
Scheme 14



at ambient temperature. Quenching with TMSCl formed a 21% yield of silylated dihydrofuran **65** and a 28% yield of the unexpected alkene-substituted dihydrofuran assigned structure **66** by proton, carbon-13, IR and mass spectral data. Dihydrofuran **66** is envisioned as being formed by the reaction of dihydro-furan anion **64** with the extruded acetylene **67**, which would then be quenched by TMSCl. It was decided further investigation into the possible mechanism to be outside the scope of our topic and too costly to pursue.

The results of the preceding experiments call into question the single report of dilithioketene by Hoppe and

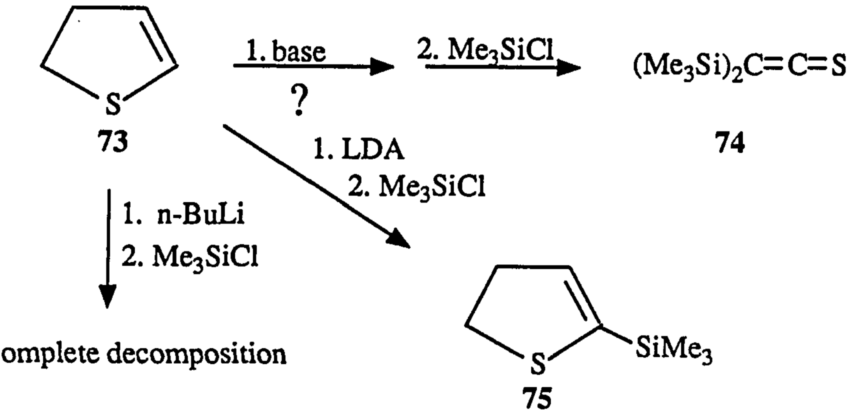
Scheme 15



Schollkopf.[25] They reported metalation of 3-phenylisoxazole (72) by lithium tetramethylpiperidide eliminates benzonitrile to form dilithioketene, which can then be quenched by either TMSCl or chlorotrimethylstannane to afford the corresponding dimetalated ketene products. This work has been repeated under the reported conditions and found that indeed bis(trimethylsilyl)ketene was produced when the reaction was quenched with chlorotrimethylsilane. But when using t-butyldimethylchlorosilane as the electrophile a small quantity of siloxyacetylene **62** has been identified by both gas chromatography with mass selective detector (GC\MS) and IR spectral comparison with our own sample. However, the major product is the corresponding bis(silyl)ketene, formed in an 8:1 ratio with the siloxyacetylene. The fact that any siloxyacetylene was formed would seem to indicate that at least some of the dilithioalkynolate was present, but the results are ambiguous as to whether it is the only dianion in solution. What most likely occuring was a salt- or solvent-promoted isomerization of the siloxyacetylene, as suspected in the decomposition of 2,3-dihydrofuran.

To determine if this chemistry could be extended to another heteroatomic system the metalation of 2,3-dihydrothiophene[39] (**73**) was attempted, which would be expected to produce the bis(silyl)thioketene **74** by analogy to dihydrofuran decomposition (Scheme 16). When **73** is reacted with two successive equivalents of n-BuLi using varied reaction times, including those which provided the highest

Scheme 16



yields of bis(silyl)ketenes, complete degradation occurred, as was evidenced by a multitude of peaks in the gas chromatograph(GC) and GC/MS with none found that corresponded to **74** or silylated thiophene **75**. Thioketene formation was not indicated by IR. Similar results were produced when only one equivalent of n-BuLi was added to **73** at -70°C, followed by warming to room temperature and stirring for 12 hours before cooling to -70°C and quenching with TMSCl. Similar results have been noted for the reaction of n-BuLi with other vinylthioethers.[40] If one equivalent each of TMEDA and n-BuLi are used[41] and the reaction mixture maintained at -70°C, quenching with TMSCl forms only dihydrothiophene **75**. Warming to room temperature for 24 hours destroyed even this product however.

The deprotonation of **73** was also attempted with lithium diisopropylamine, which has proven successful in metalating other vinylthioethers.[42] When the reaction was carried out at -70°C in hexane and stirred for one hour before TMSCl quench, followed by dilution with pentane, filtering through anyhydrous magnesium sulfate, and eventually vacuum distillation to ensure the absence of any moisture which would destroy any thioketene formed, all spectral and chromatographic data (IR, GC/MS, ^{1}H NMR) indicated only the presence of dihydrothiophene **75**, which was formed in 66% yield (GC analysis). If after stirring for one hour at -70°C the reaction mixture was then warmed to room temperature for four hours, then recooled and quenched as before, only **75** was produced and the yield increased to 74%. If the reaction time at room temperature was extended to 12 hours or more there was still no thioketene formation and yields of dihydrothiophene **75** begin to drop. It should be noted that this is the first reported instance of metalation of 2,3-dihydrothiophene.

Another base tried was t-BuLi. When t-BuLi was reacted with **73** at -70°C for 20 minutes in THF, then quenched with TMSCl and worked up as previously described, an 81% yield of **75** is formed but again no thioketene. If after the 20 minutes the reaction mixture was warmed to room temperature for four hours then recooled to -70°C and quenched the yield of **75** is diminished to 62% and there was still no thioketene observed by any spectral means. When the time at room temperature was extended to 24 hours the yield of **75** drops to 46% and still no thioketene was observed. Addition of a second equivalent of t-BuLi causes extensive degradation of **73**, though trace amounts of **75** were noted.

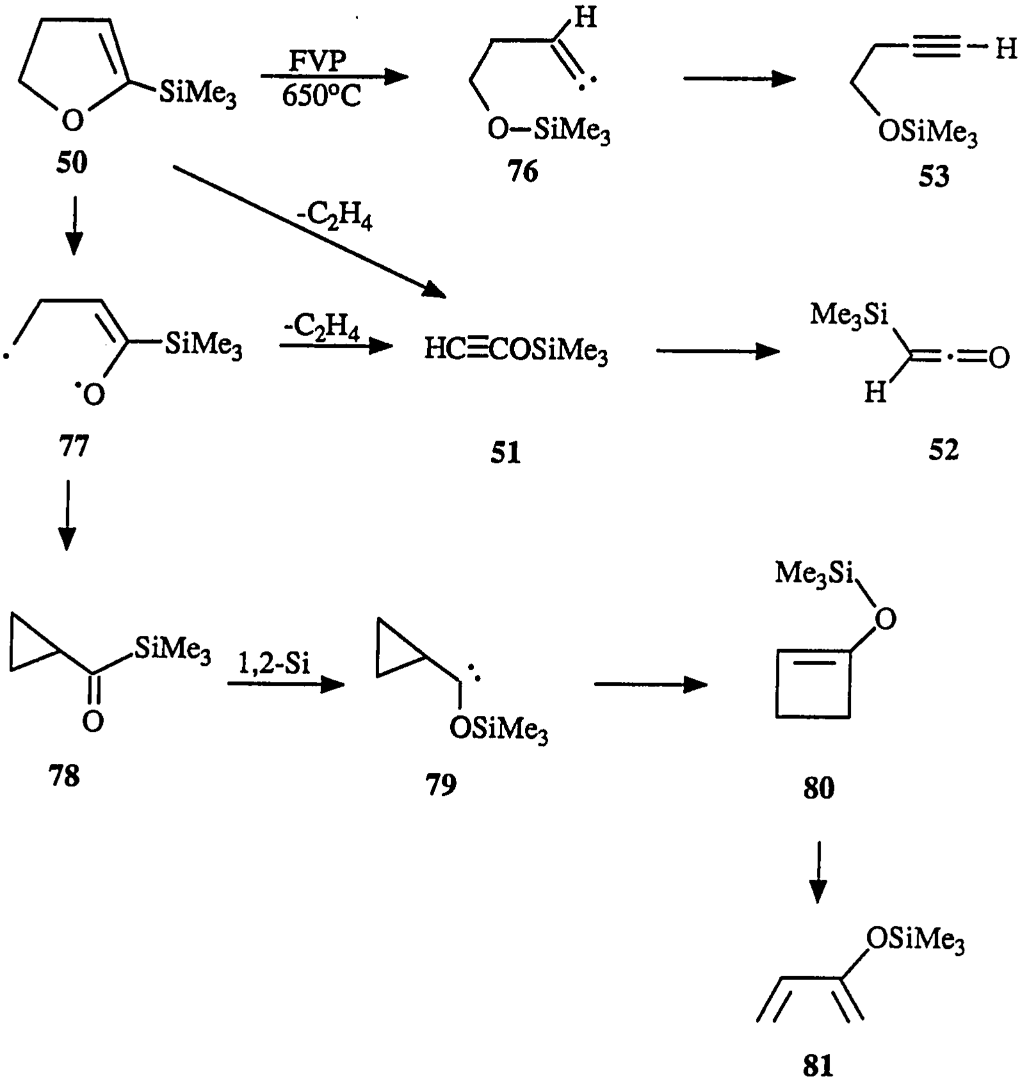
There can be no doubt that the alpha vinyl hydrogen has been abstracted, as evidenced by the formation of **75**, yet elimination of ethylene to form a thioketene does not occur. One explanation for this difference could be that the presence of sulfur atom stabilizes the vinyl anion enough that rearrangement and elimination are unfavorable. However, it is hard to believe that this could overcome the difference in bond energies between the C-S and C-O bonds (the C-S bond is weaker by >6 kcal/mol in the saturated case[43]) which would favor the elimination reaction. A suitable explanation remains to be found.

Flash vacuum pyrolysis of cyclic alpha-silyl vinyl ethers

Barton and Groh[23] have reported the first example of a gas-phase reductive elimination to form a vinylidene. They found that 2,3-dihydro-5-(trimethylsilyl)furan (**50**) rearranges to vinylidene **76**, which collapses to form acetylene **53** in 49% yield upon FVP at 650°C. Interestingly, they found a second major product, (trimethylsilyl)ketene (**52**), which was formed in 33% yield along with a small amount (5%) of butadiene **81**. They suggested that both the latter products could be formed from bond homolysis to **77** as shown in Scheme 17. The suggestion of siloxyacetylene **51** being the precursor to silylketene **52** prompted us to look into the thermal decomposition of other heterocyclic compounds, as well as investigate further into the isomerization of silylheterocumulenes and their propargyl isomers.

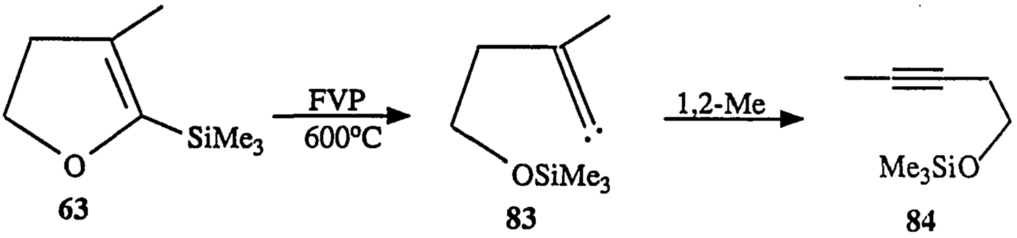
The FVP of 2-(trimethylsilyl)-3-methyl-4,5-dihydrofuran (**65**) at 600°C was found to form a sole product, 5-(trimethylsiloxy)-2-pentyne (**84**), in an amazing 68%

Scheme 17


SiMe$_3$
O
50
FVP
650°C
H
O–SiMe$_3$
76
H
OSiMe$_3$
53
-C$_2$H$_4$
SiMe$_3$
O
77
-C$_2$H$_4$
HC≡COSiMe$_3$
51
Me$_3$Si
H
O
52
SiMe$_3$
O
78
1,2-Si
OSiMe$_3$
79
Me$_3$Si
O
80
OSiMe$_3$
81

isolated yield (by preparative GC). This presumably occurs via vinylidene **83**, in analogy to the preceding work, which would undergo a methyl shift to form **84** (Scheme 18). This

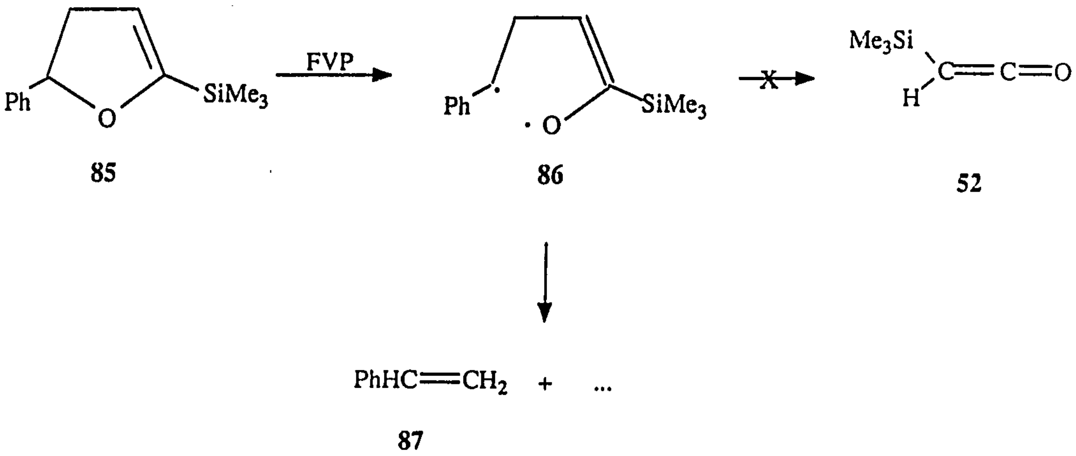
Scheme 18



was remarkable in that the molecule chose to undergo only the reductive elimination to form a vinylidene in preference to bond homolysis to give ethylene and the corresponding silylketene from virtually the same substrate. This result would seem to argue against the homolysis mechanism as responsible for the formation of silylketene **52** from **50**.

Should the formation of silylketene **52** be formed by the bond homolysis mechanism, 2,3-dihydro-2-phenyl-5-(trimethylsilyl)furan (**85**) would prove a better precursor to (trimethylsilyl)ketene as it would have the advantage of styrene extrusion as opposed to ethylene extrusion and the initial formation of a benzyl radical (**86**) (Scheme 19). The FVP of **85** at 660°C forms styrene in 25% yield, but there

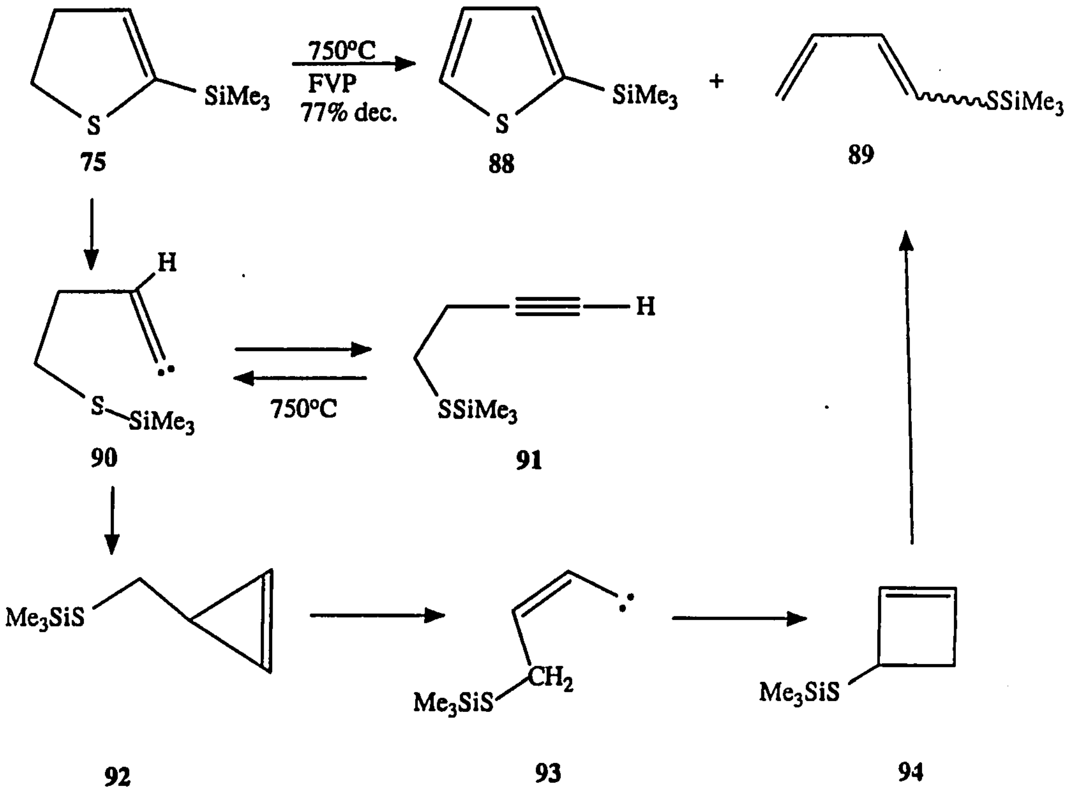
Scheme 19



was no indication of the formation of silylketene **52** by either IR or GC/MS. Instead, a multitude of products are formed. When the pyrolysis was conducted at 500°C styrene was still produced (14%), but there was still no indication by either GC/MS or IR of the formation of a silylketene. Temperatures between the two aforementioned have also been fruitless. There were, however a myriad of products besides styrene which were produced in increasing abundance and yield with the elevation of pyrolysis temperatures. Little effort has been expended in trying to identify these products due to their great number and low yields. It would seem then that the phenyl substituent does indeed favor the formation of the benzyl radical on thermal decomposition of **85**, but that this was not the route by which the silylketenes were formed on thermal decomposition of **50**. This leaves the formation of the siloxybutadiene **81** unexplained if there were no homolysis of **50**, unless **81** was the sole product of this route of decomposition.

The effects of further perturbation of the system by substitution of a sulfur atom for the oxygen atom in the dihydrofuran system was examined. Therefore 2,3-dihydro-5-(trimethylsilyl)thiophene (**75**) was pyrolyzed at 550°C, from which only starting material was recovered. The same was true when the temperature was increased to 650°C. When the temperature was increased to 750°C three major products were formed and 37% of the starting material remained (Scheme 20). The first product, 2-(trimethylsilyl)thiophene (**88**), was formed in 31% yield by hydrogen elimination, driven by the energy gain of aromaticity. The other two products were the cis and trans isomers of 1-(trimethylsilylthio)-1,3-butadiene (**89**), identified by GC/MS, IR and ^{1}H and ^{13}C NMR, which were formed in a 62% combined yield. Notably absent was 4-(trimethylsilylthio)-1-butyne (**91**), the product expected to be formed via a reductive elimination similar to that of the dihydrofuran case which produces vinylidene **90** that rearranges to form **91**. It may be that the reductive elimination does occur, but that the acetylene **91** is not stable at these temperatures and that an equilibrium exists

Scheme 20



that bleeds off to form the butadienes **89**. This could occur by having vinylidene **90** insert into the allylic carbon-hydrogen bond to form cyclopropene **92**, which would then open to vinyl carbene **93**, which then cyclizes to cyclobutene **94** that then opens to form the butadienes. To test this hypothesis the pure (water-sensitive) acetylene **91** was prepared from the corresponding thiol,[44] sodium hydride and TMSCl, followed by trap to trap distillation and preparative

GC. Acetylene **91** was then subjected to FVP at 750°C and $2x10^{-4}$mm, conditions identical to the dihydrothiophene decomposition. The resulting product mixture was nearly identical to that obtained from the decomposition of thiophene **75** by IR, GC, GC/MS, and ^{1}H NMR, including the formation of thiophene **75** in 36% yield, and contained no remaining **91**. These results would seem to confirm the proposed pathway and explain the absence of **91** in the pyrolysate.

The lack of formation of a thioketene would again seem to point toward the formation of silylketene **52** arising by a concerted mechanism to form siloxyacetylene **51**, not by homolysis, which should occur more readily in the sulfur system where the C-S bond is weaker.[43] The concerted mechanism is most likely not operative here due to lack of driving force, the formation of a Si-S bond providing only 99 kcal/mol of energy versus the 127 kcal/mol for the formation of a Si-O bond,[2] a huge difference.

Siloxyacetylenes and Silylketenes

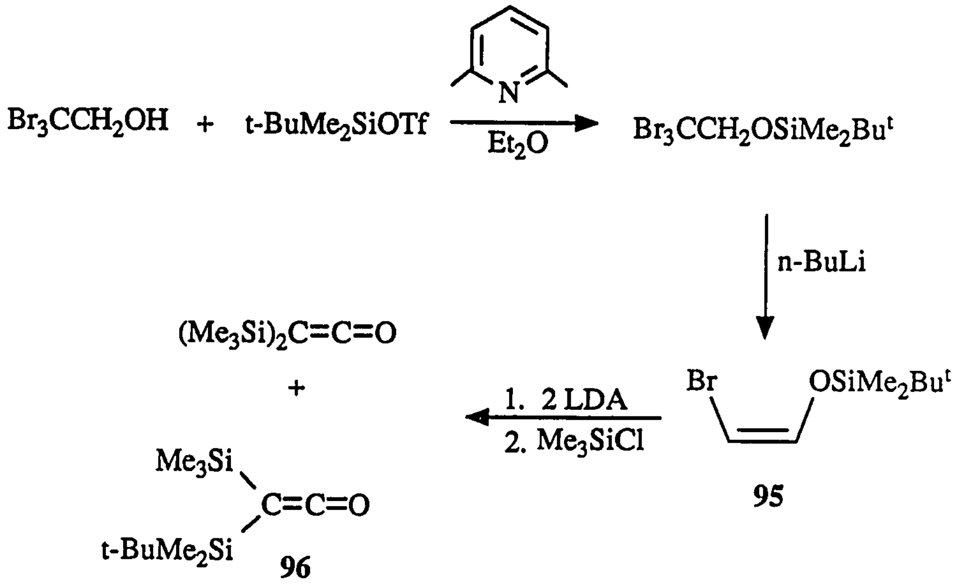
Preparation of siloxyacetylenes and their sulfur analogs

At the time it was decided to study the isomerization of siloxyacetylenes to silylketenes there were only two reports of the preparation of isolable siloxyacetylenes. The first reported producing siloxyacetylenes from alpha-silyl alpha-diazoketones and required an aryl group attached to one acetylenic carbon, and it was reported that there was no observed isomerization of siloxyacetylenes to the corresponding silylketenes, a discrepancy between our work and theirs that has been addressed, at temperatures up to 120°C.[45] The second report was a general preparation that involved metalation of a 1-bromo-2-siloxyethylene which we have proven to be in error and has now been retracted by the authors, which will be explained in the following discussion.[46] It soon became obvious that a general preparation of siloxyacetylenes was lacking in the literature, which we have attempted to address. After spending over a year attempting to either reproduce the above work or find our own route to these acetylenes, other than from silylated dihydrofurans and metalated dihydrofurans, the works of Kowalski et al.[31] and Stang and Roberts[32] appeared in which they reported the preparation of siloxyacetylenes, thus diminishing the need and time spent at this endeavor.

Our first attempts at an independent preparation of a siloxyacetylene were by the method of Pirrung and Hwu.[46] They reported that 1-bromo-2-siloxyethenes could be deprotonated by two equivalents of lithium diisopropylamine (LDA) in THF, then quenched by TMSCl to produce siloxyalkynes. 1-Bromo-2-(t-butyldimethylsiloxy)ethene

(**95**)[46] was prepared and reacted with two equivalents of

Scheme 21



LDA at 0°C in THF. After one hour 1.1 equivalents of TMSCl was added. After 30 minutes the reaction mixture was warmed to room temperature and eventually vacuum distilled to remove all salts. Instead of the expected siloxyalkyne, it was found <u>two</u> silylketenes had been formed, identified as bis(trimethylsilyl)ketene (**55**) and (trimethylsilyl)(t-butyldimethylsilyl)ketene (**96**) (Scheme 21). That the products were not siloxyalkynes was readily apparent by their IR spectra, **55** and **96** exhibiting bands at 2081 and 2079 cm^{-1}, respectively, whereas the corresponding siloxyalkynes would be expected to exhibit stretches at greater than 2200 cm^{-1}.

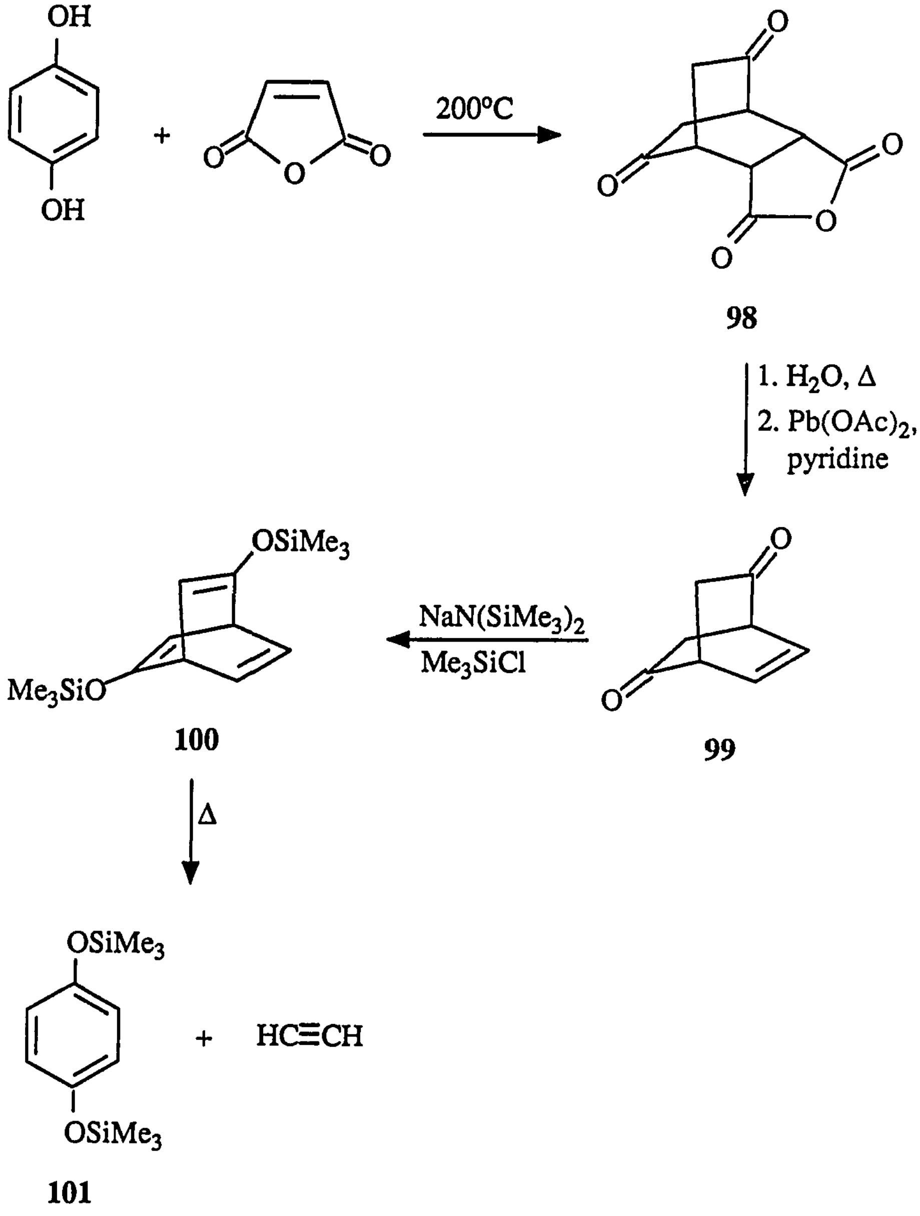
These uncommon spectral characteristics have caused problems with misassignment of the siloxyacetylene structure to silylketenes in previous literature as well.[33] Further confirmation of structure is obtained by carbon-13 spectra. The sp hybridized carbon of silylketenes is typically near 170 ppm and the sp^2 hybridized carbon is shifted upfield to near zero ppm,[47] very unusual for a sp hybridized carbon, values which correspond very well with these products. Siloxyalkynes generally exhibit peaks in their carbon-13 spectra near 90 ppm for the alkyl substituted acetylenic carbon and near 40 ppm for the heteroatom substituted acetylenic carbon.[31,45] In the case where a silyl group was substituted for the alkyl group both acetylenic carbon peaks occur near 100 ppm.

The formation of two ketenes can be explained by the desilylation of the intermediate t-butyldimethylsiloxyacetylene by base, which has been reported for isolated siloxyacetylenes by Kowalski,[31] quenching of this anion with TMSCl, followed by isomerization to ketene **55**.

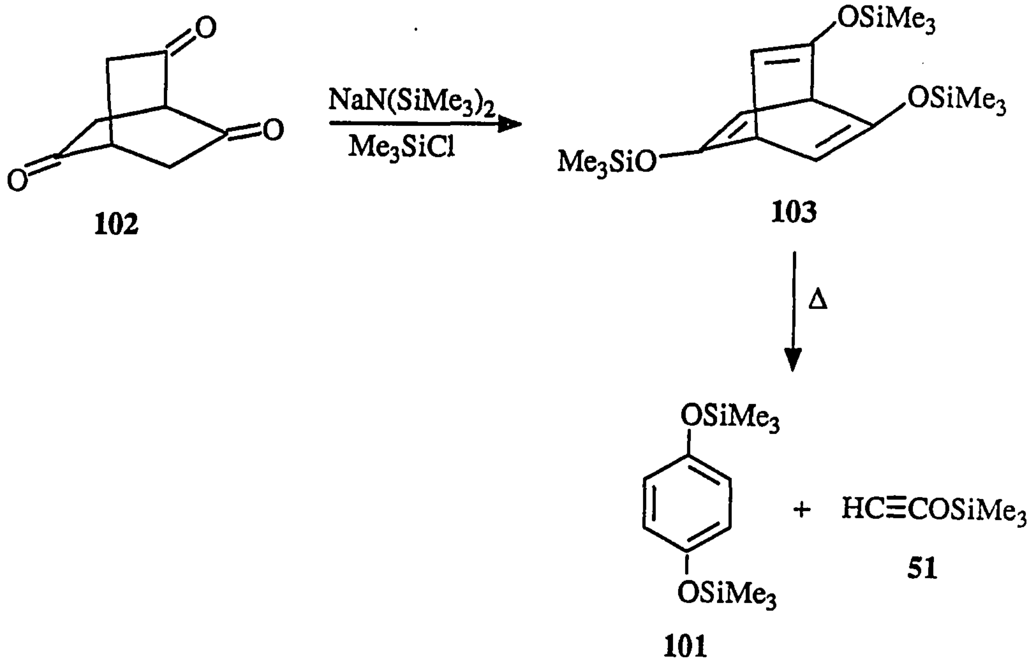
When 1-bromo-2-(trimethylsiloxy)ethene (**97**) was reacted in a manner similar to **95** and quenched with TMSCl the only product was ketene **55**, identified by comparison of IR, GC/MS and ^1H and ^{13}C NMR spectra to that of an authentic sample. This method was therefore abandoned as a route to siloxyacetylenes.

A good method for preparing reactive intermediates is by pyrolysis of a substrate that will extrude the desired molecule in order to form an aromatic molecule via a retro-Diels-Alder reaction, though few works have been published using this method for the preparation of functionalized alkynes.[48] As 2,5-bis(trimethylsiloxy)bicyclo[2.2.2]triene (**100**) was a possible precursor to trimethylsiloxyacetylene (**51**) and presumably be prepared easily by a literature procedure,[49] it was decided to prepare and pyrolyze it. The Diels-Alder adduct (**98**) of hydroquinone and malonic anyhydride was hydrolyzed and the resulting diacid decarboxylated to yield diketone **99**, as shown in Scheme 22. Compound **99** was then reacted with sodium bis(trimethylsilyl)-amide, followed by quenching with TMSCl to afford **100**. Triene **100** was subsequently pyrolyzed at 450°C and found to cleanly form only bis(trimethylsiloxy)benzene (**101**) and presumably acetylene. The absence of any (trimethylsiloxy)-benzene and either (trimethyl-silyl)ketene or (trimethylsiloxy)acetylene indicated that it would be necessary to form 2,5,7-tris(trimethylsiloxy)-bicyclo[2.2.2]triene (**103**) to necessitate the extrusion of acetylene **51**. This would require the preparation of bicyclic trione **102** which, though known,[50] proved to be very difficult. Trione **102** would then be converted to the trisiloxy derivative in the same manner as had the dione.

Scheme 22

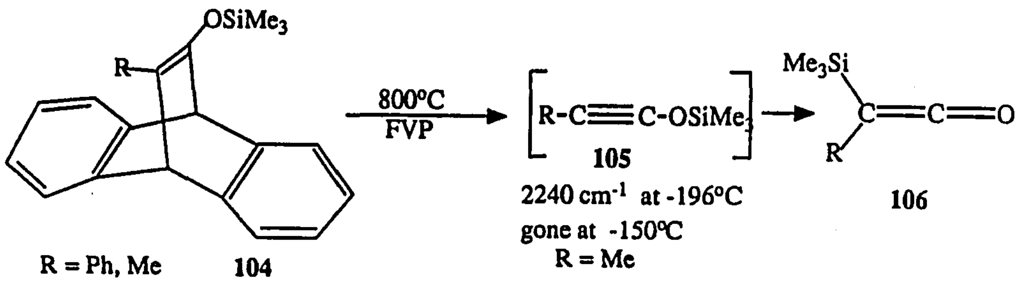

OH
OH
+
200°C
98
1. H_2O, Δ
2. $Pb(OAc)_2$, pyridine
99
$NaN(SiMe_3)_2$
Me_3SiCl
$OSiMe_3$
Me_3SiO
100
Δ
$OSiMe_3$
+
HC≡CH
$OSiMe_3$
101

Scheme 23



Subsequent pyrolysis would then be expected to form the desired siloxyacetylene **51** (Scheme 23). But before the preparation of **102** could be completed a literature report was published in which other investigators had succeeded in preparing a different pyrolytic precursor to siloxyacetylenes, as shown in Scheme 24.[51] They were able to observe, using low temperature IR, bands indicative of a siloxyalkyne (2240 cm^{-1}) at $-196^{o}C$. When the temperature was raised to a mere $-150^{o}C$ these bands would disappear, being replaced by bands indicative of silylketenes (2080 cm^{-1}),

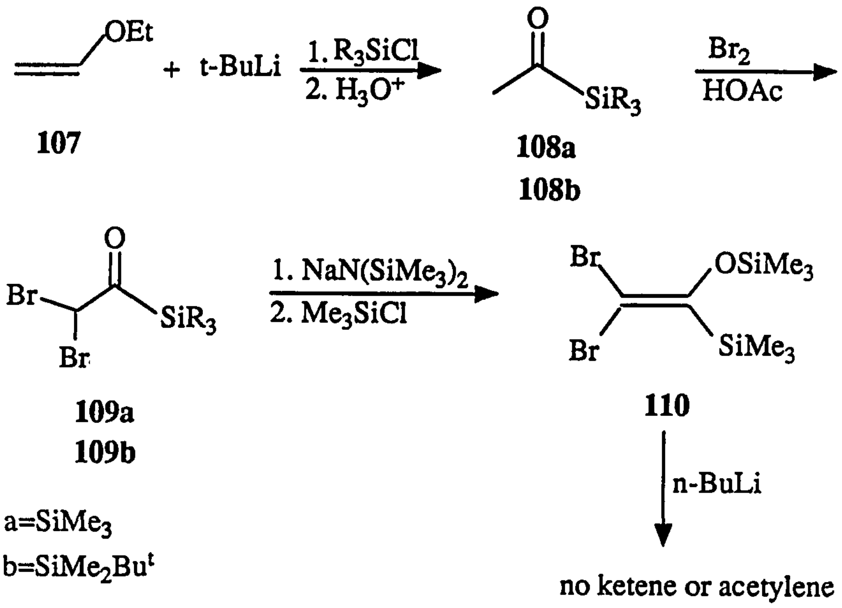
Scheme 24



which were the only silylated compounds found in the pyrolysate. These results were in accord with our proposed mechanism for the thermal decomposition of silylated dihydrofurans and supported our own findings on the pyrolyses of siloxyalkynes, to be discussed later in this section. However, it does seem incredulous that the siloxyacetylene formed refused to isomerize at 800°C, the pyrolysis conditions, but then surrended to it at a mere -150°C later.

Another possible route for the general preparation of siloxyalkynes required the gem-dibromoethene **110**, as shown in Scheme 25. When SiR_3 was trimethylsilyl it was possible to prepare **110** from trimethylsilylketone **108a**, a known compound.[52] Treatment of ethylvinylether with t-BuLi and quenching with TMSCl formed **108a** in 66% yield on acidic workup. After purification of **108a** by distillation, reaction

Scheme 25

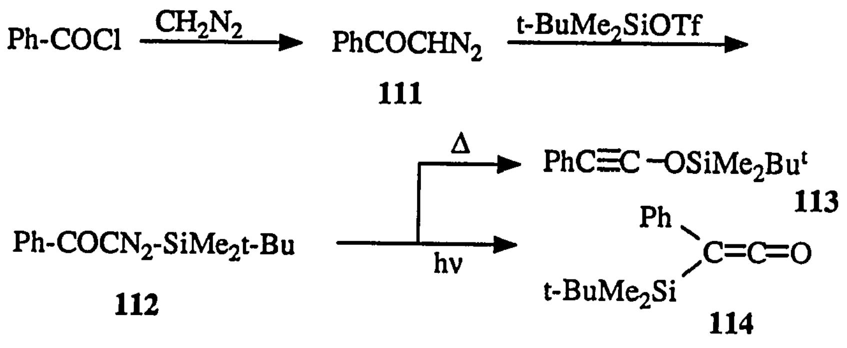


with bromine in glacial acetic acid formed dibromoketone **109a** in quantitative yield. Ketone **109a** was then reacted with sodium bis(trimethylsilyl)amide followed by TMSCl to afford an 85% yield of **110**. Reaction of **110** with n-BuLi unfortunately failed to form either a silylketene or siloxyacetylene based upon analysis by GC/MS and IR. Due to the complexity of the gas chromatographic trace, the lack of a major product (four peaks between 10-15%, remainder less than 10%), and the lack of any silylketenes or siloxyacetylenes no further effort was made to isolate or identify any of the products formed.

When the silyl group was t-butyldimethylsilyl the same procedure was used to form dibromoketone **109b**. However, upon attempted vacuum distillation of **109b**, elimination of t-butyldimethylsilylbromide occurred. Numerous attempts to get around this problem met with failure and further work on this method was discontinued.

To try and correct the discrepancy between our work and that of Maas and Bruckmann,[45] who report no isomerization between siloxyacetylenes and silylketenes, arylsiloxyalkynes were prepared from alpha-silylated alpha-diazoketones. This required the preparation of alpha-diazophenylketone (**111**) which was quantitatively accomplished by reacting benzoyl chloride with more than two equivalents of diazomethane at 0°C (Scheme 26). After recrystallization, **111** was reacted with t-butyldimethylsilyltriflate with diisopropylethylamine present as a proton scavenger, as the product was very proton

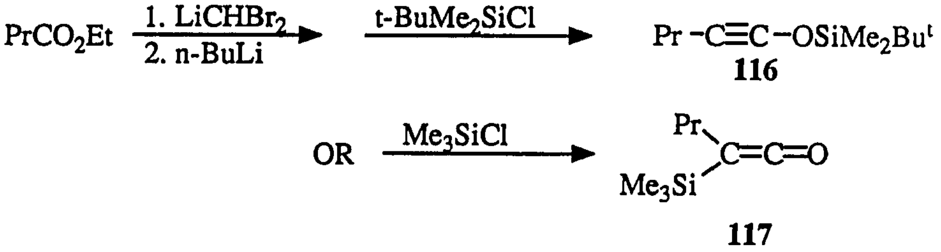
Scheme 26



sensitive. The reaction was carried out at 0°C for approximately two hours, a modification of the published procedure, following the reaction by IR to ascertain when the starting material was completely consumed. At this time the reaction mixture was transferred to a nitrogen flushed, enclosed filter that was padded with dried celite via a cannula and nitrogen pressure. The reaction mixture was then attached to a vacuum line and the solvents removed. This crude mixture of **112** was then diluted with benzene and warmed to 70°C until the lack of a diazo stretch for the starting material in the IR indicates the reaction was complete. This was then placed on the vacuum line and the solvent removed, leaving nearly pure phenyl(t-butyldimethylsiloxy)ethyne (**113**), which has been fully characterized. This compound was then used in subsequent pyrolysis studies which are discussed later. Irradiation of diazo compound **112** in benzene contained in a pyrex tube forms phenyl(t-butyldimethylsilyl)ketene (**114**) quantitatively.[45]

Another route to the siloxyacetylenes was reported by Kowalski et al.[31] after the start of our work, which we have used to prepare alkylsiloxyacetylenes. One starts with the appropriate ester, which is reacted first with the lithium salt of methylene bromide, then with n-BuLi to form an alkynolate which is then quenched with the desired chlorosilane. An example is shown in Scheme 27. They too

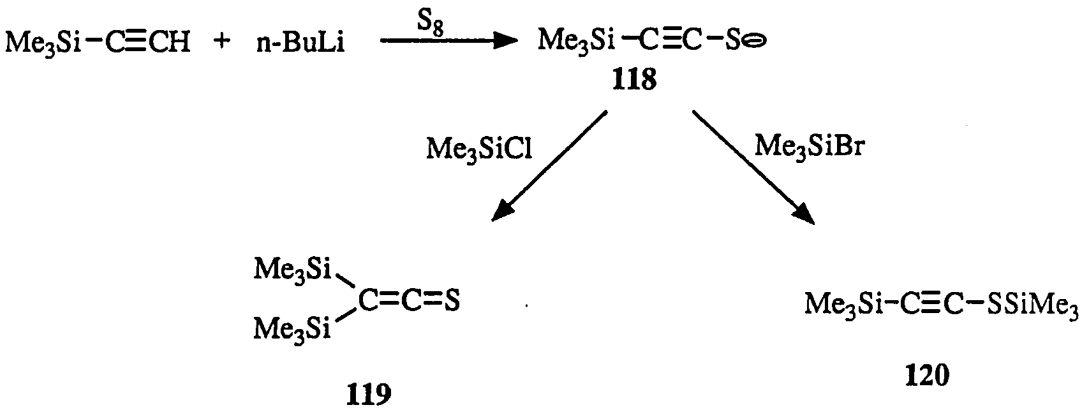
Scheme 27



have reported that use of chlorosilanes that are not sterically hindered do not yield the desired siloxyalkynes, but instead find only silylketenes produced. It should be noted that this reaction has proven very difficult to reproduce consistently and great care is necessary in the purification of starting materials and it is best to use fresh n-BuLi as the authors report salts in the solution were also a problem.[34]

Preparations of both bis(trimethylsilyl)thioketene (**119**) and its propargyl isomer (**120**) by a very convenient and high yield route have already been published and no attempt has been made to improve it (Scheme 28).[4] The authors report that to prepare the silylthioketene (**119**) one quenches alkynthiolate **118** with trimethylchlorosilane at -45°C to form only the thioketene **119** but that if one uses the bromosilane instead that only silylated thioacetylene **120** is produced. This has been found to be untrue and the desired product (**119**) can actually be formed by careful attention to the

Scheme 28



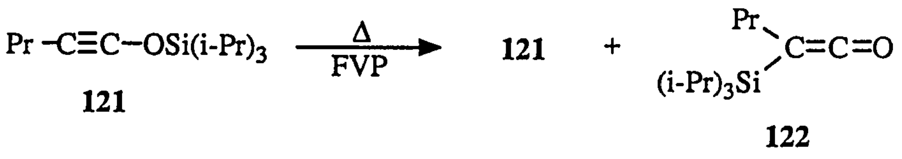
temperature of the reaction mixture on quenching. At -45°C only the thioketene **119** was formed with either chloro- or bromotrimethylsilane serving as the electrophile. However, if one reduces the temperature of the reaction mixture to -70°C for quenching then acetylene **120** was the only product formed with either electrophile. It is suspected that the prior work failed to note this difference in reaction temperature as the cause of different product formation, possibly failing to take note of the actual bath temperature when said reactions were run. These results would also seem to be much more in line with what has been oberved in the preparation of siloxyalkynes. This chemistry has been extended to acetylenes other than trimethylsilylacetylene, including propyne, butyne, phenylacetylene and t-butylacetylene. In the course of this work it was found that using t-butyldimethylchlorosilane forms only silylated thioacetylenes even when the quenching temperature is -45°C (instead of having to lower it to -70°C), showing that steric hinderance is a factor in the sulfur system as well.

Gas-phase thermal isomerization of siloxyalkynes, silylketenes and their sulfur analogs

Once able to prepare and isolate stable siloxyalkynes it was then possible to study their thermal stability, which would set precedent for our proposed mechanistic pathway for the thermal decomposition of alpha-silylated dihydrofurans to silylketenes.

In the first attempt at thermally isomerizing a siloxyalkyne to a silylketene propyl(triisopropylsiloxy)-ethyne (**121**) was pyrolyzed at 400°C and 2×10^{-5}mm (Scheme 29).

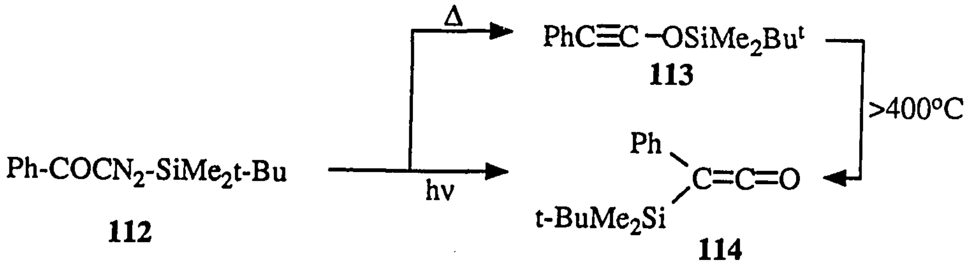
Scheme 29



An IR spectrum of the crude pyrolysate exhibited only a weak band indicative of a silylketene at 2079 cm^{-1}, while the band at 2280 cm^{-1} of **121** was still very strong. When the temperature was increased to 500°C both bands became very strong in the IR. However, a GC trace of the pyrolysate shows no separation of the two isomeric compounds. Further increase of the temperature to 600°C effects nearly complete isomerization of **121** to silylketene **122**, as indicated by nearly complete disappearance of the band at 2280 cm^{-1}. The isomerization would also appear to be quantitative as there is nearly always a quantitative mass recovery and no other products were detected by IR, GC or GC/MS.

This still left the discrepancy between our work and that of Maas and Bruckmann[45] who reported no isomerization between arylsiloxyacetylenes and arylsilylketenes. Phenyl-(t-butyldimethylsiloxy)acetylene (**113**) was therefore prepared by their diazo route described previously. At temperatures below 200°C there was indeed no isomerization of **113** to silylketene **114**, as reported (Scheme 30). But when acetylene

Scheme 30

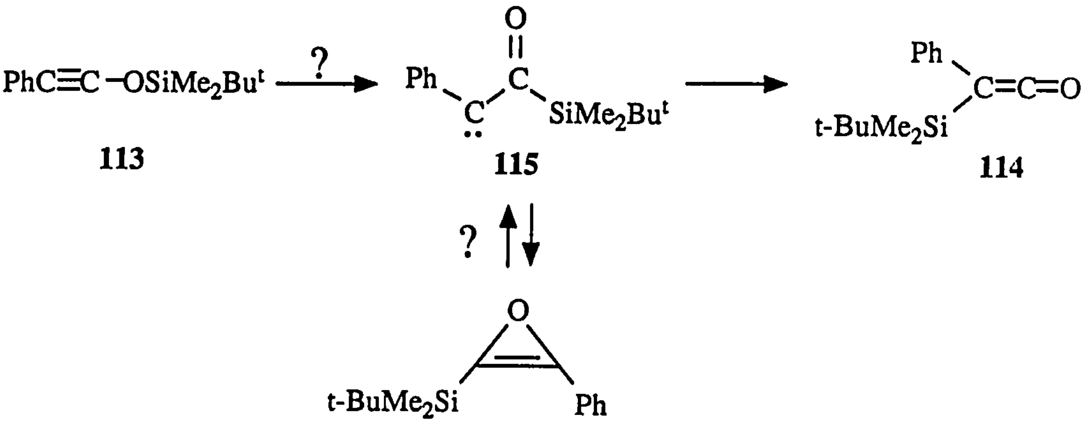


113 was pyrolyzed at 400°C and $1x10^{-5}$mm the IR spectrum indicates a small amount of isomerization to silylketene **114** (2083 cm^{-1}), which was also detected by GC/MS. Increasing the temperature increases the amount of silylketene produced until at 600°C there was a quantitative conversion to **114**. Thus siloxyacetylenes do isomerize to silylketenes, provided enough energy is supplied to the system.

With the isomerization of siloxyalkynes to silylketenes established, a study the mechanism and kinetics of this isomerization was undertaken. Two unimolecular mechanisms would seem to be the most likely, one a series of 1,2-silyl shifts and the other a direct 1,3-silyl shift. From a search of the literature for information on rearrangement of the parent ketenes, thioketenes and allenes it appeared that the unanimous choice would be for a series of 1,2-silyl shifts, based upon theoretical calculations discussed earlier.[14,17,20] In summary, taking siloxyacetylene **113** as an example, the first 1,2-silyl shift would form ketocarbene **115**, which then undergoes the Wolff rearrangement to form silylketene **114**, presumably with some oxirene participation (Scheme 31). The same is expected to hold true for the sulfur system. Regressing to Schemes 4 and 6, one notes that in both cases the activation energy for the isomerizations was greater than 70 kcal/mol.[14]

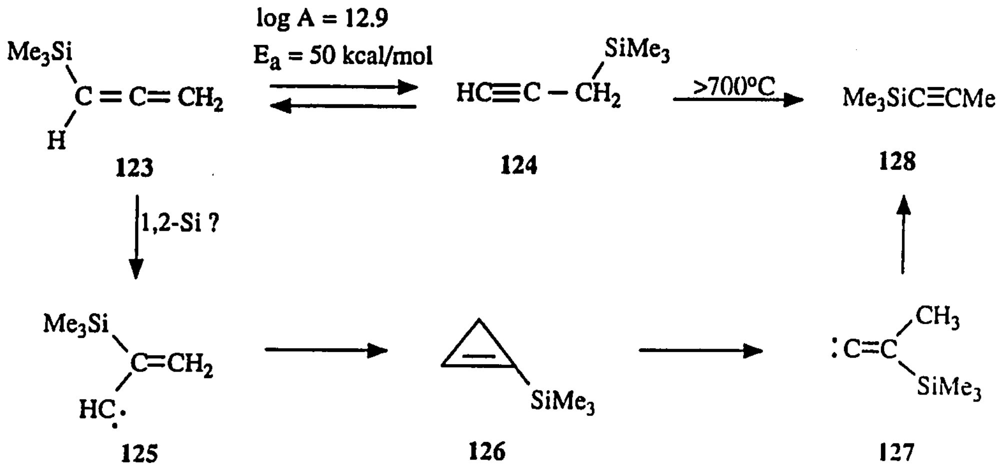
However, a case could still be made for a 1,3-silyl

Scheme 31



shift, which was proposed a number of years ago by Kwart and Slutsky[21] for the isomerization of trimethylsilylallene (**123**) to 3-(trimethylsilyl)propyne (**124**) at 500°C. They reported an energy of activation for this isomerization of 50 kcal/mol, with a log A of 12.9. At higher temperatures (>700°C) Barton and Groh[22] found a third isomer was produced, 1-(trimethyl-silyl)propyne (**128**), and propose that the formation of the third product can be explained by invoking the 1,2-silyl shift mechanism, thus forming a cyclopropene and carbene intermediates (Scheme 32). It would seem then that there are two energy surfaces by which these isomerizations can proceed, the lower energy pathway proceeding through a 1,3-silyl shift, the higher energy pathway through a 1,2-silyl shift mechanism.

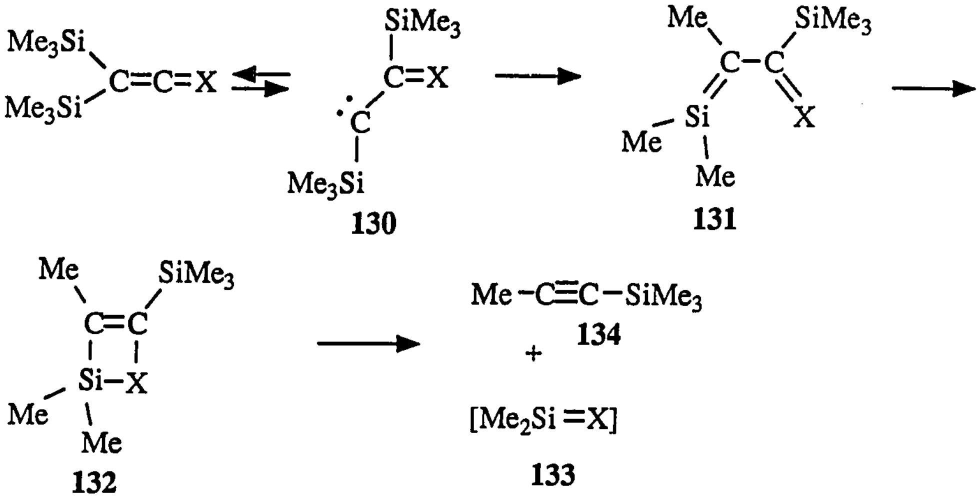
Scheme 32



The direct relevancy to this work is obvious when it is also known that the thermal rearrangement of silylketenes and silylthioketenes have been studied earlier by Barton[22,53] and found to proceed through what appears to be a retro-Wolff rearrangement, initiated by a 1,2-silyl shift, to extrude silanones or silathiones at higher temperatures (>650°C), as shown in Scheme 33. By analogy, this could represent the higher energy surface, with our investigation of the siloxyacetylene to silylketene rearrangement the lower energy surface.

It was decided that reliable kinetics would be very helpful in differentiating between the two mechanisms, as the

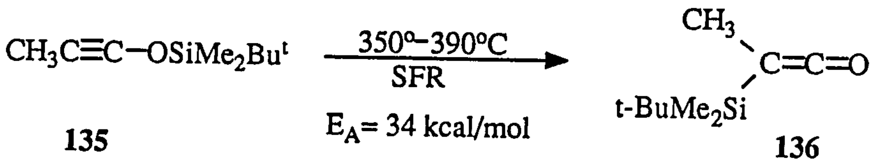
Scheme 33



X=O,S

1,3-silyl shift would avoid the high energy carbenes and might be expected to avoid high activation energies (>70 kcal/mol by theoretical calculations) of the 1,2-silyl shift as well, based on the report by Kwart and Slutsky.[21] As products that could be separated by GC were desired for kinetic studies utilizing a stirred-flow reactor (SFR),[54] methyl-(t-butyldimethylsiloxy)ethyne (135) was prepared. From previous work with the trapping of dilithioalkynolate with various chlorosilanes it was known that other t-butyldimethylsiloxyacetylenes and the isomeric silylketenes were separable by GC. Siloxyalkyne 135 was first pyrolyzed at 450^{o}C and $1x10^{-5}$mm and found to undergo partial isomerization to the corresponding silylketene **136** based upon the presence of bands indicative of **135** in the IR (2291 cm^{-1}) and the appearance of a very strong band in the IR at 2074 cm^{-1} indicative of a silylketene. This product was purified by preparative GC and identified as methyl(t-butyldimethylsilyl)ketene (**136**), which has been fully characterized (Scheme 34). The GC/MS trace indicated it was possible to separate the two by GC, making it suitable for the SFR studies.

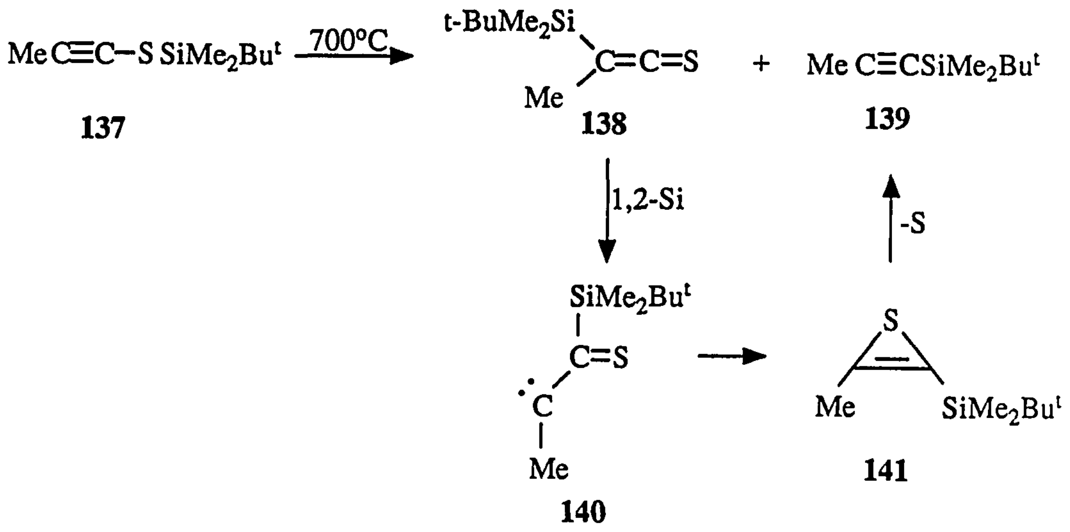
Scheme 34



It was disappointing to find that the volatility of **135** was not sufficient to allow for gaseous injection when conducting our kinetic studies using the SFR. Therefore **135** was injected directly into the pyrolysis oven. Kinetic data was gathered for the isomerization in the temperature range between 351.5 and 389.3°C and an energy of activation of 34.1+0.9 kcal/mol and log A of 10.4+0.3 with a correlation coefficient of 0.997 was calculated. To demonstrate that the isomerization was indeed unimolecular the sample size was varied up to ten times the typical injection size of 0.01 microliters. There was no measurable effect when this was done, thus showing that the isomerization was indeed unimolecular. However, this data was tainted in that there is an inseparable impurity present that, although found to be stable under these conditions, it was necessary to correct for it. Also, it has been demonstrated that kinetic data obtained by liquid phase injection does not agree with the values obtained using gaseous injection, which will be discussed shortly, though the activation energies are still quite close. It is also evident from the low temperatures required that the activation energy value does not contain enough error to bring it up to the values that theoretical calculations indicate are necessary for the isomerization to occur by a series of 1,2-silyl shifts (>70 kcal/mol).

To investigate the generality of this isomerization, silylated alkynethiol **137** was subjected to FVP over the temperature range of 500 to 800^{o}C. At 500^{o}C and $1x10^{-5}$mm the pyrolysate was found to consist of only acetylene **137** and the isomeric thioketene **138** in a ratio of 3.2 to 1, respectively, with no other products produced (Scheme 35). Incredibly, increasing the temperature to 600^{o}C produced the same results. At 700^{o}C the ratio of **137** to **138** remained at 3.2:1, though some decomposition was noted. The only other major

Scheme 35



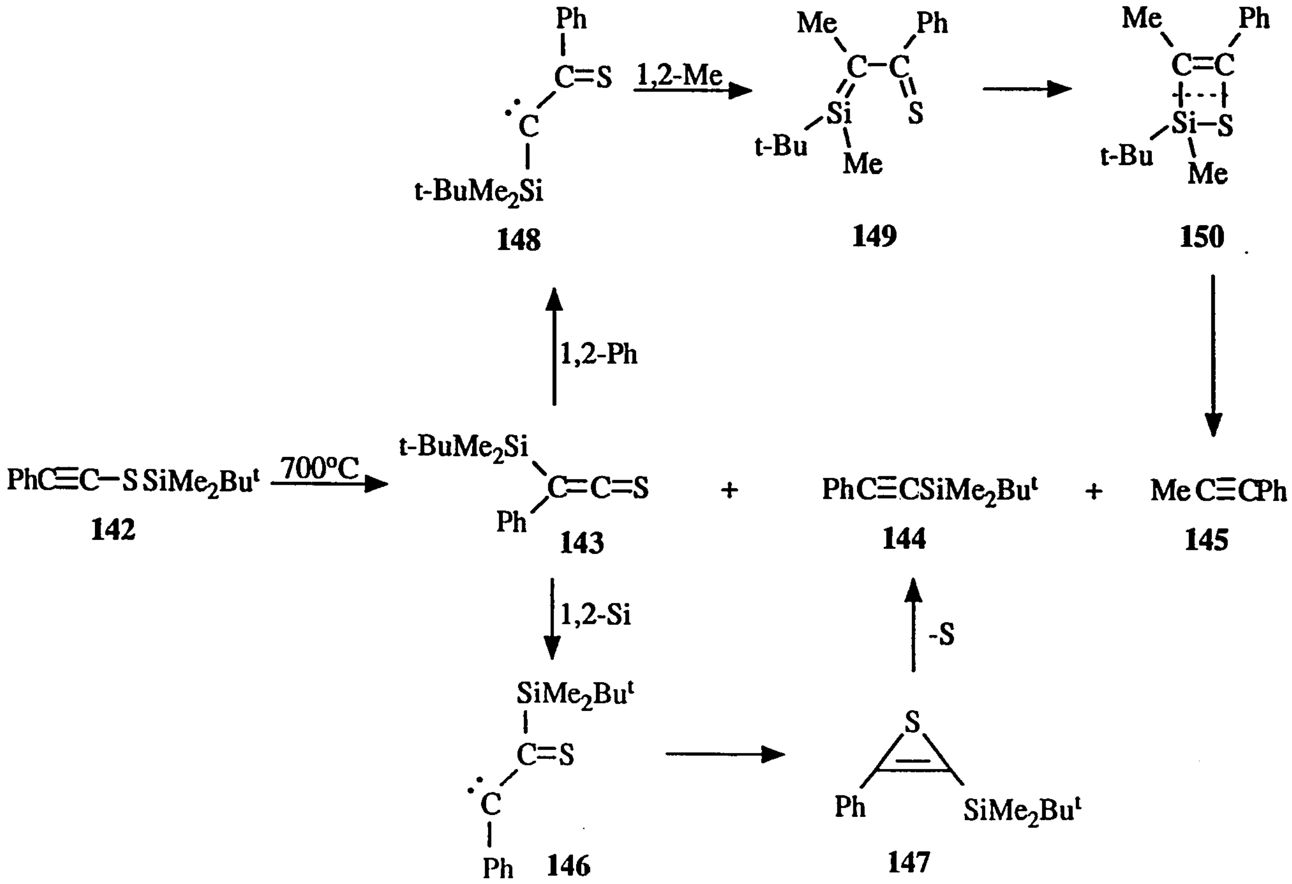
product was produced in 8% yield and identified by comparison of spectra to that of an authentic sample as methyl-(t-butyldimethylsilyl)ethyne (**139**). It is believed to arise from the decomposition of thioketene **138** via an initial 1,2-silyl shift to thioketocarbene **140**, which then forms thiirene **141** that would then extrude a sulfur atom to form acetylene **139**. There are only two known literature reports of the extrusion of sulfur from thiirene to form an acetylene. Bis(trifluoromethyl)thiirene was found to photodecompose to to sulfur and perflourobutyne in the gas phase[3] and Barton[53] has postulated the extrusion of sulfur from thiirene intermediates as responsible for the formation of acetylenes formed on the gas phase pyrolysis of silylthioketenes. These findings seem to support the postulation of two energy surfaces for the rearrangement of silylated ketenes and thioketenes. When **173** was pyrolyzed at 800°C only a white polymeric material was formed.

The equilibrium established between **137** and **138** was unexpected from the behavior of the oxygen analogs, where the siloxyalkynes quantitatively rearrange to the corresponding silylketenes. Even more surprising was that the thioacetylene was the predominant isomer. Walton[4] reported that thioacetylene **120** isomerized quantitatively to thioketene **119** at 120°C, which has been found to be correct. That the energy gap between the silylated thioacetylene and thioketene isomers was smaller than that of the oxygen analogs was not unique to this system, however. Theoretical calculations on the isomerizations of the parent ketene and thioketene also find the difference between the ketene and acetylenic isomer to be smaller in the sulfur case (36 vs. 8 kcal/mol).[14,17]

Phenyl(t-butyldimethylsilylthio)ethyne (**142**) was pyrolyzed as it was to be a precursor for carbon-labelling studies. Flash vacuum pyrolysis of **142** at 600°C formed an 8% yield of the corresponding thioketene **143**, the remainder of the pyrolysate (quantitative recovery) recovered **142**. Pyrolysis of **142** at 650°C formed thioketene **143**, though in a moderate 13% yield, with 75% remaining unchanged. Another acetylene was formed, phenyl(t-butyldimethylsilyl)ethyne (**144**), in 5% yield. When the temperature is increased to 700°C still yet another acetylene is formed, 1-phenylpropyne (**145**). Both **144** and **145** have been identified by comparison with spectra of authentic samples. Acetylene **144** is most likely produced from thioketene **143** via a 1,2-silyl shift to form ketocarbene **146** that then forms thiirene **147** (Scheme 36). Thiirene **147** then would extrude sulfur to form **144**. Acetylene **145** would be formed from **143** by a 1,2-phenyl shift to form ketocarbene **148** which has been reported to undergo facile insertion into silicon-methyl and silicon-hydrogen bonds to form silylenes which cyclize and extrude acetylenes.[22,53]

A kinetic study of the thermal isomerization of thioacetylene **137** was then conducted, as done for the analogous oxygen compound. It was pleasing to find that thioacetylene **137** had sufficient vapor pressure to allow gaseous injection for studies using the SFR. Data for the isomerization was collected over the temperature range from 235 to 285°C at approximately 5°C intervals, yielding a nearly linear Arrhenius plot. The Arrhenius parameters, uncorrected for starting material returned in the equilibrium, were found to be 12.1+0.3 and 33.5+0.7 kcal/mol for log A and the energy of activation, respectively.

Scheme 36


PhC≡C–S SiMe2But
142
700°C
t-BuMe2Si
C=C=S
Ph
143
+
PhC≡CSiMe2But
144
+
Me C≡CPh
145
1,2-Ph
Ph
C=S
C
t-BuMe2Si
148
1,2-Me
Me
Ph
C–C
Si
S
t-Bu
Me
149
Me
Ph
C=C
Si–S
t-Bu
Me
150
1,2-Si
SiMe2But
C=S
C
Ph
146
S
Ph
SiMe2But
147
-S

Kinetic data was also gathered from 360 to 515°C, at approximately 25°C intervals, temperatures at which equilibrium was established and before substantial decomposition had occurred, so that a Van Hofft's plot could be constructed. This plot yielded values of 0.404+0.04 kcal/mol and 2.21+0.05 cal/°K mol for ΔH and ΔS, respectively. These values were then used to calculate the equilibrium constants at the temperatures used to construct the Arrhenius plot using the equation:

$$\ln Keq = -(\Delta H - T\Delta S)/RT$$

where Keq is the equilibrium constant, R is 1.9872 cal/°K mol and T is the temperature in degrees Kelvin. The equilibrium constant thus derived is then used in the equation:

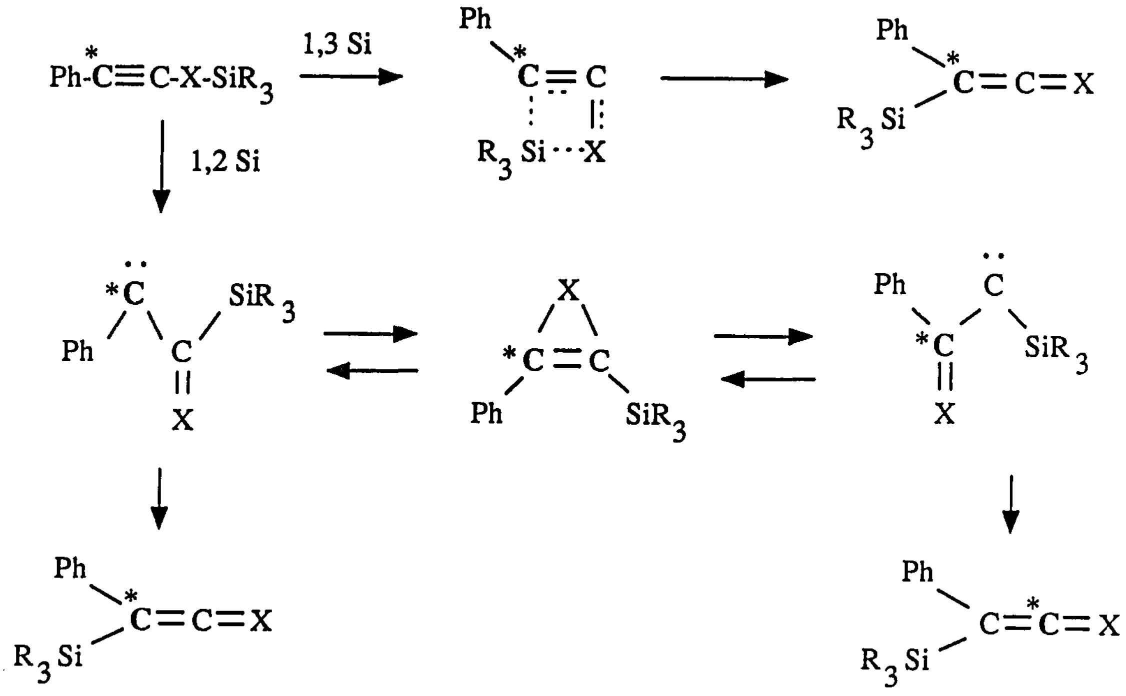
$$k = k'(1 + [(k \times t)/Keq])$$

where k is the actual rate constant, k' is the apparent rate constant (the sum of the forward and reverse reactions) and t is 2223.54/T. A new Arrhenius plot is then made utilizing the true rate constants. The new Arrhenius parameters are 12.9+0.3 and 35.4+0.7 kcal/mol for log A and the energy of activation, respectively, with the plot having a correlation coefficient of 0.998.

In an effort to gain insight into the degree of error introduced when using liquid injections instead of gaseous injections, as was necessary in the oxygen system, the kinetic studies of the aforementioned thioketene isomerization were repeated using liquid injections. At this time the sample size was varied from 0.01 to 0.5 microliters to establish the isomerization as unimolecular, which was concluded from the absence of any effect upon doing so. The uncorrected Arrhenius parameters obtained for the 249 to 291°C range were found to be 10.7 and 30.2 kcal/mol for the log A and energy of activation, respectively. When compared to the uncorrected values for gaseous injection of 12.1 and 33.5 kcal/mol one sees there is a significant difference, more so in the case of log A. Assuming one could extrapolate this effect to that of the ketene isomerization, which is the best that can be done in this case, one would expect the Arrhenius parameters for the siloxyacetylene to ketene isomerization to be on the order of 11.8 and 37 kcal/mol for the log A and energy of activation, respectively. This is also more in line with the slightly higher temperatures required to induce isomerization in the oxygen versus the sulfur system. In either case, it would appear that both the ketene and thioketene isomerizations go through similar mechanisms and that the low energy of activation for these isomerizations would seem to limit the possibility of the mechanism proceeding via 1,2-silyl shifts.

The possibility of experimentally differentiating between the 1,2- and 1,3-silyl shift mechanisms by pyrolysis of a silylated heteroacetylene with one of the acetylenic carbons carbon-13 enriched was then investigated. Determination of which carbon atom(s) was enriched in the isomeric silylketene would be expected to limit the mechanistic possibilities. This reasoning is illustrated in Scheme 37, where the position of the carbon label is followed throughout the isomerization by both mechanistic routes. It

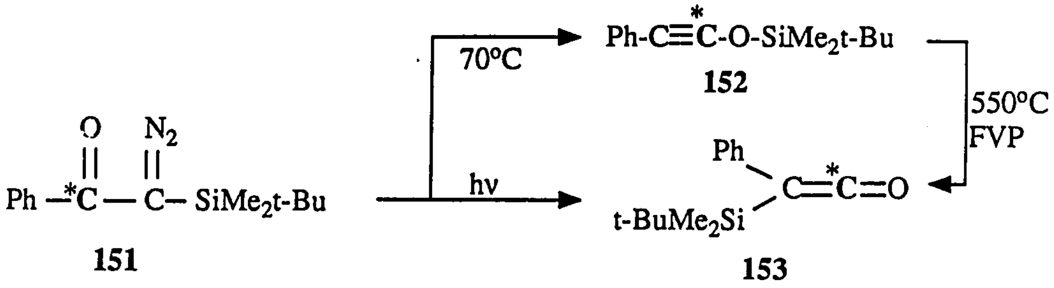
Scheme 37



can be seen that the carbon label will reside in only one of the carbons of the ketene when a 1,3-silyl shift is followed. But if the isomerization proceeds via 1,2-silyl shifts there is the potential for scrambling of the carbon label to both carbons of the ketene by passing through an oxirene intermediate. The amount of this scrambling is known to vary with the substituents of the oxirene,[3,8] so it would be best to have a standard with which to compare our results. There are two very important reasons to prepare our labelled siloxyacetylene from an alpha-silylated alpha-diazoketone. The first is that the same diazo precursor used to prepare the siloxyacetylene can also be used to prepare a labelled silylketene, and in doing so serve as a standard for the degree of carbon label scrambling expected when passing through an oxirene intermediate. The second reason is the ease of preparation of the starting material. All that was required was a carbonyl labelled benzoic acid, which was then easily converted to the acid chloride with thionyl chloride. The acid chloride was then converted to the desired diazo precursor **142** as outlined in Scheme 26.

Diazo precursor **151** has the carbonyl carbon enriched >99% so that calculations on the amount of scrambling would be easier. When **151** was heated to 70^{o}C in benzene siloxyacetylene **152** was formed with a single carbon peak at 96 ppm in the ^{13}C NMR showing enrichment (Scheme 38).

Scheme 38



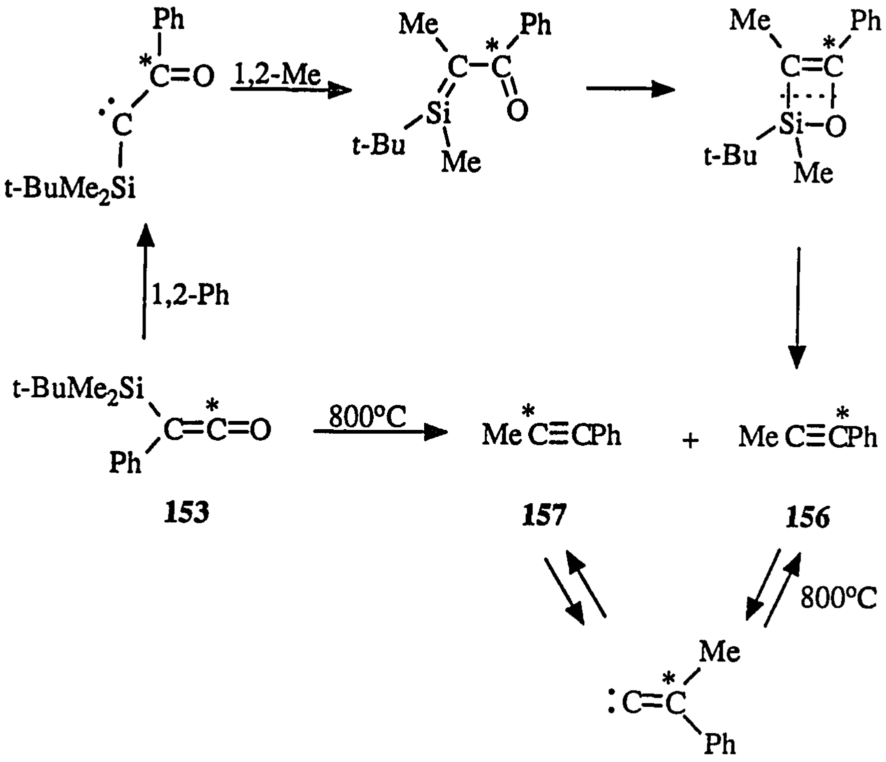
151

152

153

Siloxyacetylene **152** was then pyrolyzed at 550°C, forming silylketene **153**. Analysis by ^{13}C NMR revealed that only the carbonyl carbon of the silylketene was enriched (182 ppm), which was the carbon expected to be enriched should the isomerization proceed via a 1,3-silyl shift. Increasing the pyrolysis temperature to 800°C still caused no scrambling of the carbon label in silylketene **153**, but did show formation of another product. This compound has been identified as 1-phenylpropyne (**145**) by comparison of spectra with that of an authentic sample. Of note is that the carbon label is incorporated into both the acetylenic carbons of the propyne, but unequally. After accounting for the NOE it was found that 1-phenyl-1-^{13}C-propyne (**156**) was favored by a 7:1 ratio over 1-phenyl-2-^{13}C-propyne (**157**). Spectral assignment of the carbon peaks was collaborated by published data.[55] This result was consistent with the mechanistic pathway proposed by Barton and Groh[22] for the thermal decomposition of

Scheme 39



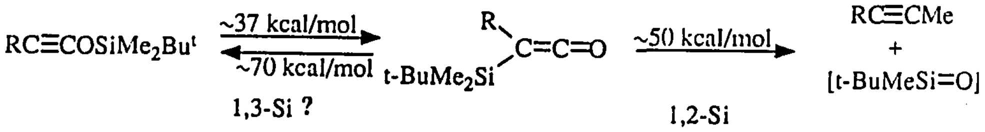
silylketenes, which proceed via a retro-Wolff rearrangement, and is illustrated in Scheme 39 for silylketene **153**. However, this would be expected to produce only propyne **156**. To show that indeed this was what occurred and that at these temperatures **156** isomerizes partially to **157**, **156** was prepared and subjected to pyrolysis at 800°C. Similar scrambling of the carbon label (8:1 ratio) was noted.

Compound **151** was then irradiated in benzene using a

Hanovia lamp and pyrex filter to form silylketene **153**. It was surprising to find that the carbon label resided in only the carbonyl carbon of the ketene, as was the case for the pyrolysis study. This would seem to eliminate the possibility of an oxirene intermediate, though it was still possible that it formed but opened preferentially back to the initial ketocarbene.

Using the accumulated kinetic and carbon labelling data a complete picture now emerges (Scheme 40). If it is assumed

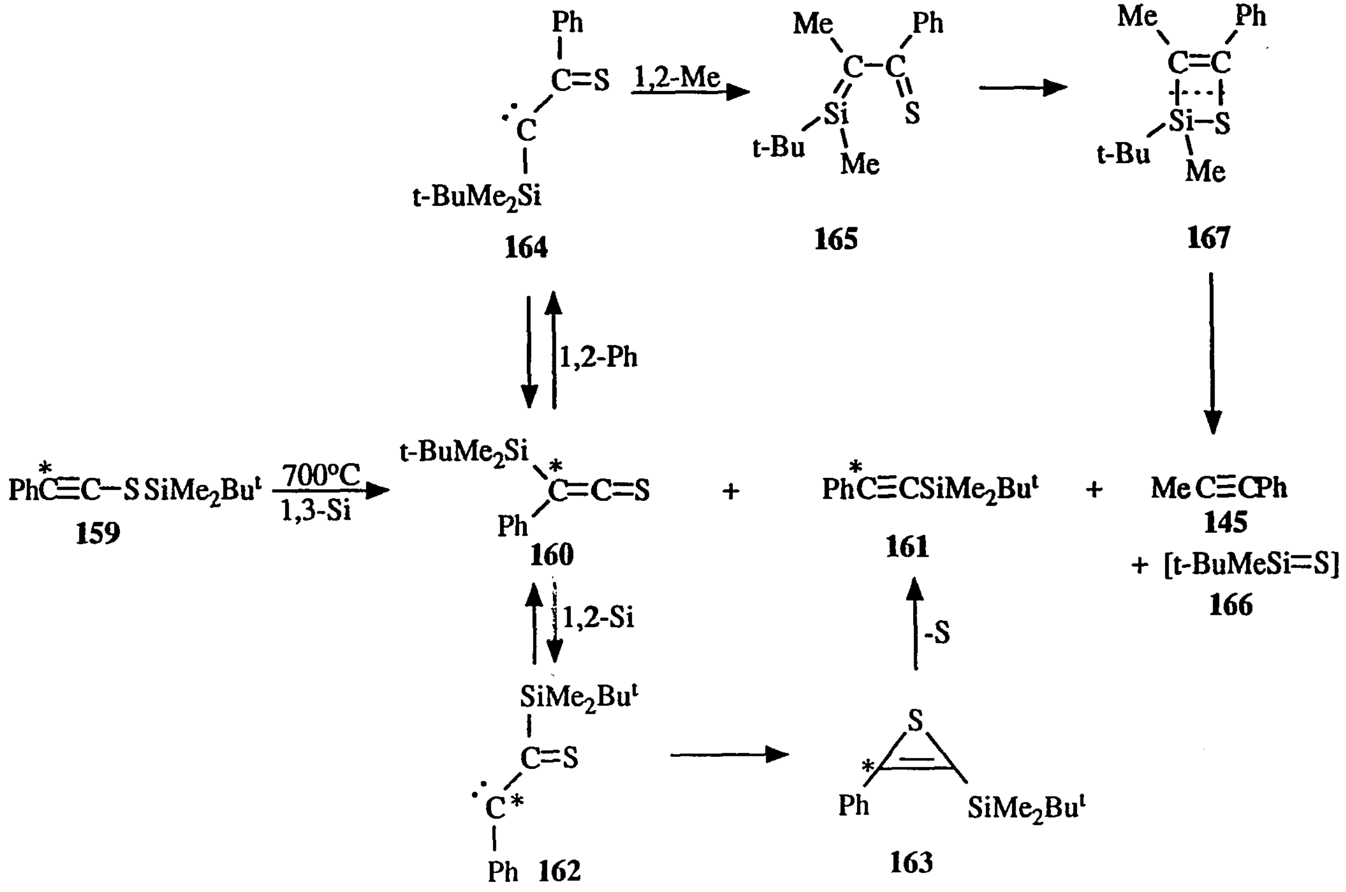
Scheme 40



siloxyacetylene **152** lies approximately 35 kcal/mol higher in energy than the isomeric ketene, which is where theoretical calculations by Radom et al.[14a] place hydroxyacetylene relative to ketene, then it would require approximately 70 kcal/mol for silylketene **153** to revert to siloxyacetylene **152** by the same mechanistic path. That this does not occur is explained by formation of **156** in the 800°C pyrolysis of **152**, via a retro-Wolff rearrangement of silylketene **153**, that has been found to require just over 50 kcal/mol a variety of silylketenes.[6] This demonstrates that once silylketene **153** forms it has an alternative mechanistic pathway, via either 1,2-silyl or 1,2-alkyl shifts, that requires approximately 20 kcal/mol less activation energy. This could also explain the lack of carbon label scrambling in the pyrolysis of **153**, which would be evidence of oxirene participation. It appears the alpha-ketocarbene has found the insertion into a silicon-methyl bond a lower energy path than formation of an oxirene, or at least kinetically faster. And with the 1,2-silyl shift already accounted for, the 1,3-silyl shift mechanism now must be greatly favored as responsible for the isomerization of siloxyacetylenes to silylketenes.

1-Phenyl-1-^{13}C-2-(t-butyldimethyl-silylthio)ethyne (**159**) was prepared for a similar study. Pyrolysis at 650°C then affords a 7:1 mixture of **159** and isomeric silyl-thioketene **160**, where the carbon label resides solely in the silylsubstituted ketenic carbon (68 ppm in ^{13}C NMR). This was the position expected should the isomerization have proceeded via a 1,3-silyl shift mechanism, just as was found in the oxygen analog. The only other product formed at this temperature has been identified as 1-phenyl-1-^{13}C-2-(t-butyldimethylsilyl)ethyne (**161**). These products are best explained by first postulating an initial 1,3-silyl shift of **159** to form **160**, which would not scramble the carbon label (Scheme 41). Acetylene **161** would then be formed by a

Scheme 41

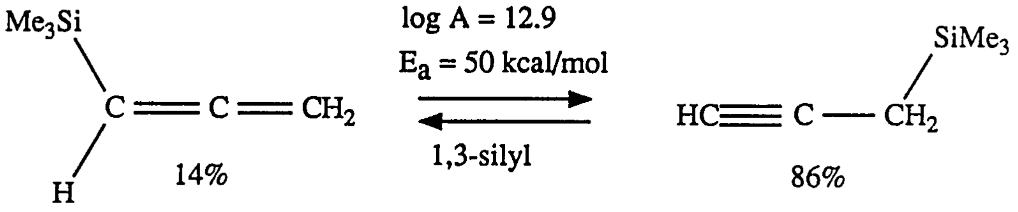

164
1,2-Me
165
167
1,2-Ph
PhC≡C−SSiMe2Bu^t
159
700°C
1,3-Si
t-BuMe2Si
160
+
PhC≡CSiMe2Bu^t
161
+
MeC≡CPh
145
+ [t-BuMeSi=S]
166
1,2-Si
-S
162
163

1,2-silyl shift in **160** to form ketocarbene **162** which can either return to reform **160** or form thiirene **163**. Thiirene **163** would then immediately extrude sulfur,[53] never opening to ketocarbene **164**, thus forming **161**. That thiirene **163** never opens to ketocarbene **164** is indicated by no enrichment of the thiocarbonyl carbon of **160** and the formation of still another acetylene, 1-phenylpropyne, when the pyrolysis temperature is increased to 700°C. 1-Phenylpropyne is believed to arise from a 1,2-phenyl shift of **160** to form ketocarbene **164** that then undergoes a 1,2-methyl shift to form silylene **165**, never passing through a thiirene intermediate as evidenced by the lack of scrambling of the carbon label in **162**, that then cyclizes and extrudes 1-phenylpropyne and silathione **166**, similar to that demonstrated to occur in higher temperature siloxyacetylene/silylketene pyrolyses and has literature precedent in both systems.[22,53] With both the 1,2-silyl and 1,2-phenyl shifts accounted for it would appear that the initial postulation of a 1,3-silyl shift forming **160** stands on solid ground.

Stereochemistry of the thermal rearrangement of siloxyacetylenes to silylketenes

With the isomerization of siloxyalkynes to silylketenes proceeding via a 1,3-silyl shift mechanism established, it was of interest to determine if this occurred with either retention or inversion of configuration of a chiral silicon center. The analogous rearrangement of allylsilanes and allenylsilanes has been shown by Kwart and Slutsky[21,56] to involve fully concerted, orbital symmetry controlled migration of silicon using a bridging 3p orbital. There are two bodies of evidence justifying this conclusion. The first was the complete insensitivity of the experimental activation parameters to variation in the substitution of silicon and in the allyl side chain.[56] The second was the complete inversion of configuration in the rearrangement of a chiral silicon substrate.[21]

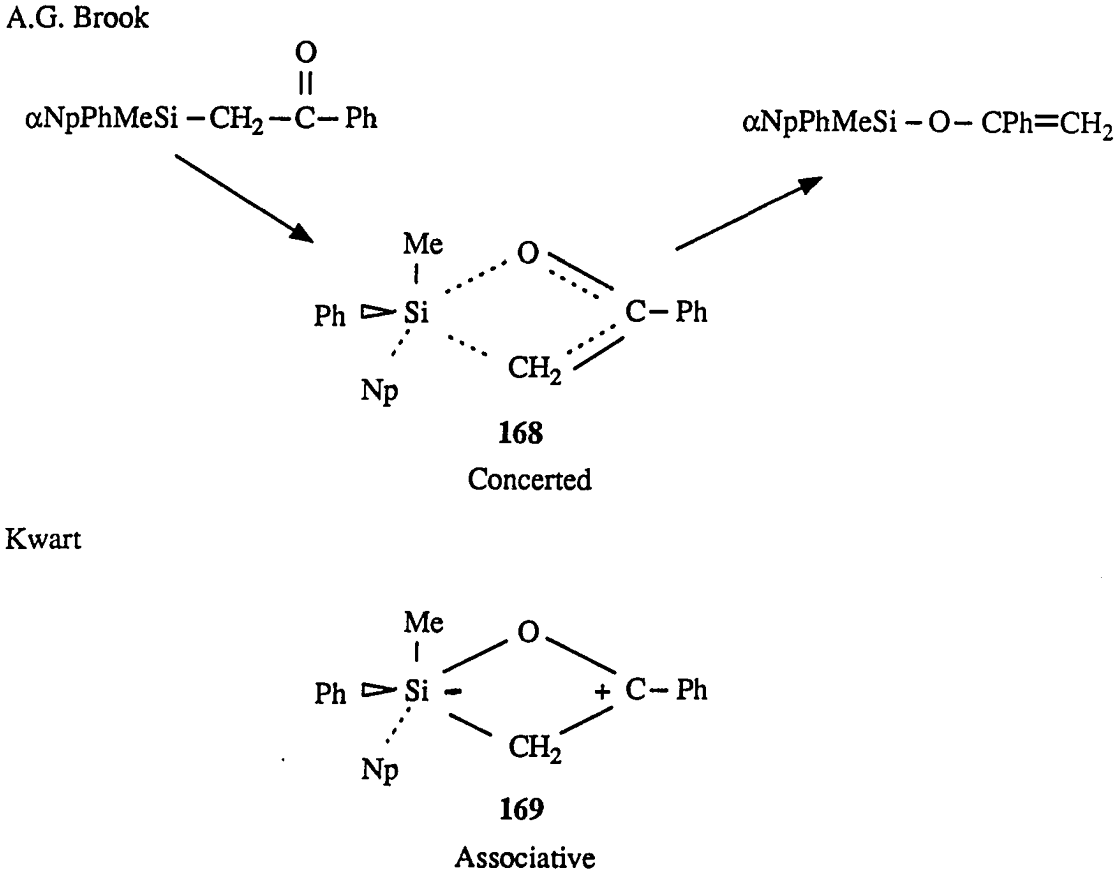
Scheme 42



Kwart, JACS, *95*, 8678 (1973)

Brook et al.[57] have presented evidence for a 1,3-silyl shift for the thermal rearrangement of beta-ketosilanes to siloxyalkenes which they claim to be fully consistent with an intramolecular, concerted four-center mechanism, though these

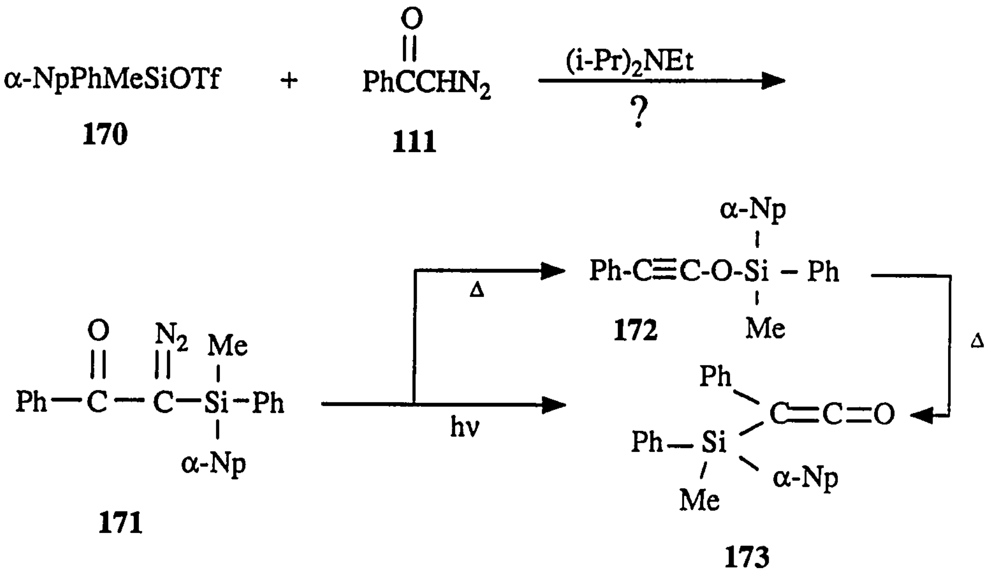
Scheme 43



rearrangements have been shown to go with retention of configuration at the chiral silicon center (Scheme 43). However, Kwart et al.[58] and Kwart and Silver[59] have attacked the contention that a fully concerted transition state exists based upon several arguments. First, they noted that the activation parameters are sensitive to substitution, the activation energy differing by two kcal/mol and the entropy by 10.5 eu when changing from triphenyl to trimethylsilyl groups. When R^1 is changed from phenyl to methyl the effect is even more pronounced, the activation energy changing by 3.5-5.0 kcal/mol and the entropy by about 3-8 eu.[58] They have also conducted solvent effect studies which also argue against a fully concerted transition state. A reaction involving development of a charge separated state from neutral molecules demands a significant decrease in activation energy and a more negative entropy value. They have found that a solvent change from benzene to nitrobenzene produces a 7.7 kcal/mol decrease in activation energy and lowers the entropy by 17.7 eu for silane **168**.[59] They favor an associative mechanism that requires a zwitterionic reaction intermediate like **169** that arises from octet expansion of the silicon.[58] They maintain that the central silicon is enabled to undergo octet expansion with the formation of a five-coordinate structure due to the favorable formation of a high energy silicon-oxygen bond. The concerted, sigmatropic process identified in the analogous sila-allylic rearrangement is abjured only when an axial bond to a highly electronegative substituent is possible to stabilize the trigonal bipyramid, thereby greatly lowering the activation requirements.

It is therefore of obvious interest to see which route the siloxyalkyne-silylketene isomerization takes. To this end the preparation of an optically active siloxyacetylene from an alpha-silyl alpha-diazoketone was attempted (Scheme 44). This approach would allow preparation of both the optically active silylacetylene desired, produced with

Scheme 44



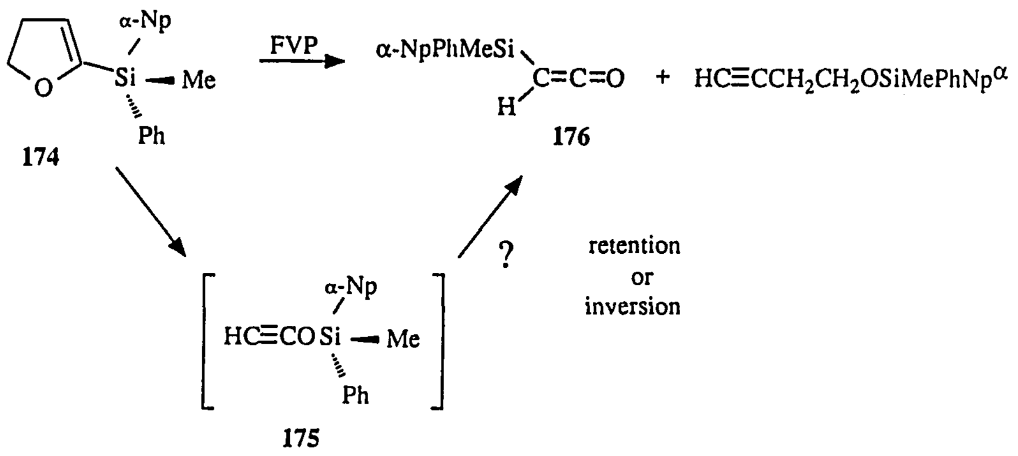
retained stereochemistry by a 1,3-silyl shift,[57] as well as a silylketene with retained stereochemical configuration, known from the carbon-labelling studies, to compare to the silylketene produced by silylacetylene rearrangement. This would allow determination of whether the rearrangement of silylacetylene proceeded with retention or inversion of configuration of the chiral silicon center by optical rotation measurements.

Before going to the expense of using an optically active compound, the chemistry was first attempted with the racemic silane. To prepare the necessary silyltriflate, silver triflate was reacted with alpha-napthylphenylmethylchlorosilane[60] in carbon tetrachloride, as reaction with triflic acid was found to racemize the optically active silanes.[61] Silyltriflate **170** is then reacted with diazoketone **111** to form the alpha-silylated diazoketone **171**, identified by a characteristic band in the IR at 2075 cm^{-1}. However, conversion of **171** to siloxyacetylene **172** did not occur. This was disappointing, though not surprising as there was a literature report of very similar substrates that possess an arylsilane undergoing intramolecular cyclopropanation of the aromatic system from the intermediate alkylidenecarbene.[62] This method was therefore abandoned as a route to an optically active silylalkyne.

There is another feasible route to producing an optically active silylalkyne, though it is not without drawbacks. This route requires the preparation of the optically active dihydrofuran **174**, which would then subjected to flow pyrolysis to induce decomposition to silylketene **176**. The crystal structures of both **174** and **176** would then be elucidated, thus allowing determination of whether retention or inversion of configuration had occurred (Scheme 45).

One problem with this route is that a previous attempt

Scheme 45



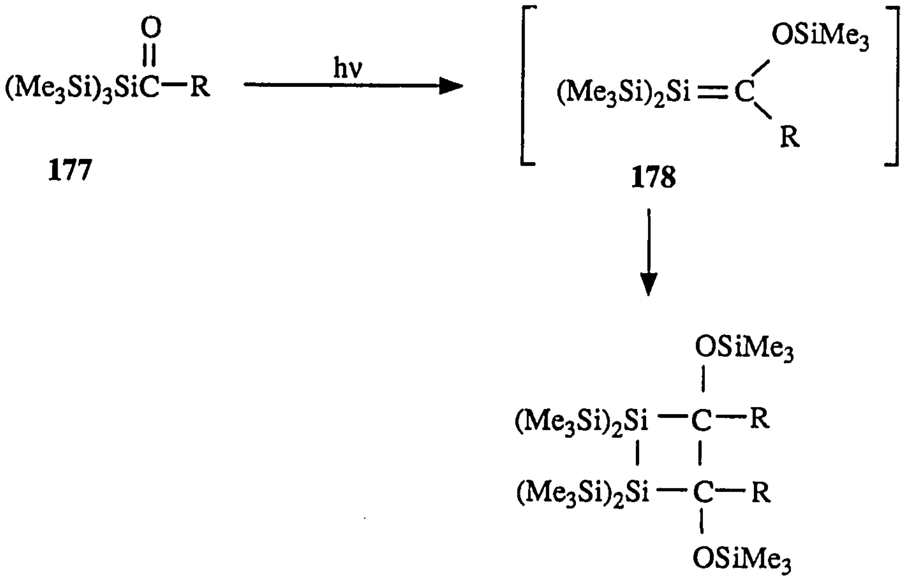
at determining the crystal structure of a silylketene was found to be impossible due to an imperfection in the crystal.[6] Another problem with this route is that the thermal decomposition of 5-silylated dihydrofurans has not been unequivocally established as going through a siloxyacetylene, only that if it did the siloxyacetylene would isomerize to a silylketene. However, evidence has been presented that infers a concerted reaction is responsible for the silylketene formation, not homolysis. Should the rearrangement proceed with inversion it could only mean that a siloxyacetylene had been formed and was responsible for the formation of the silylketene. If racemization or retention were found the precursor to silylketene could only be surmised.

Preparation of **174** has been accomplished by reaction of (-)alpha-naphthylphenylmethylchlorosilane[60] with an excess of 5-lithio-2,3-dihydrofuran in diethylether. Further work has been stalled by the inability to form crystals of **174**, which would be necessary for a crystal structure. Continued work on this procedure is in progress.

Attempted photochemical generation of siloxyalkynes from silylketenes

There are a number of reports[63-68] of photochemically induced 1,3-silyl migration. Brook et al.[63] and Brook and

Scheme 46

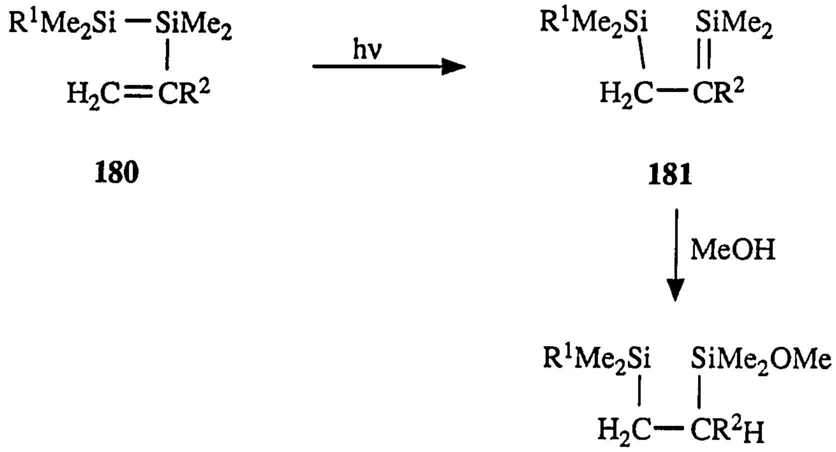


Baines[64] find that photolysis of acyltris(trimethylsilyl)-silanes form head to head dimers of the intermediate silenes (**178**) which are formed by a 1,3-silyl shift from silicon to oxygen (Scheme 46).

Kumada et al.[65,66] and Sakurai et al.[67] have reported that the photolysis of 1-alkenyldisilanes (**180**) afford silenes, which are trapped by methanol, by a 1,3-silyl shift from the silane to the carbon atom of the vinyl substituent (Scheme 47).

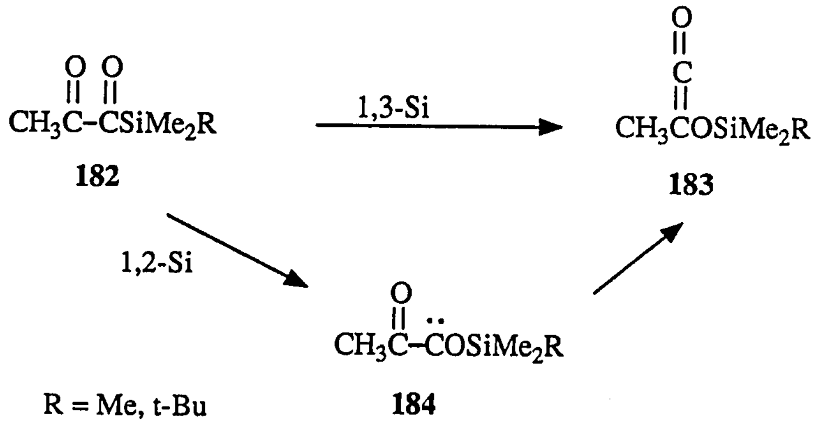
Wright[68] reported the possibility of a 1,3-silyl shift as responsible for the formation of siloxyketenes (**183**) from

Scheme 47



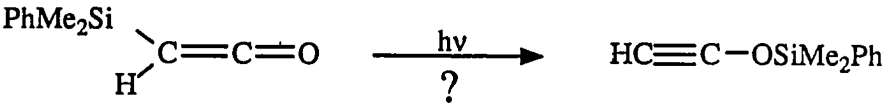
1-silyl-1,2-diones (**182**) (Scheme 48). He also notes that, in the absence of a trapping agent, the siloxyketenes thermally revert back to the initial acylsilane, but there is a substituent dependence. This is determined by comparing the rate of disappearance of the trimethylsilyl and t-butyldimethylsilyl transient siloxyketenes when irradiation is discontinued. In the trimethylsilyl case this is a few seconds, while with the t-butyldimethylsilyl group it was greater than five minutes.

Scheme 48



These reports implied that it may be possible to photochemically induce isomerization of silylketenes to siloxyalkynes, which could not be accomplished thermally. To this end dimethylphenylsilylketene (**185**) was prepared and

Scheme 49



185 186

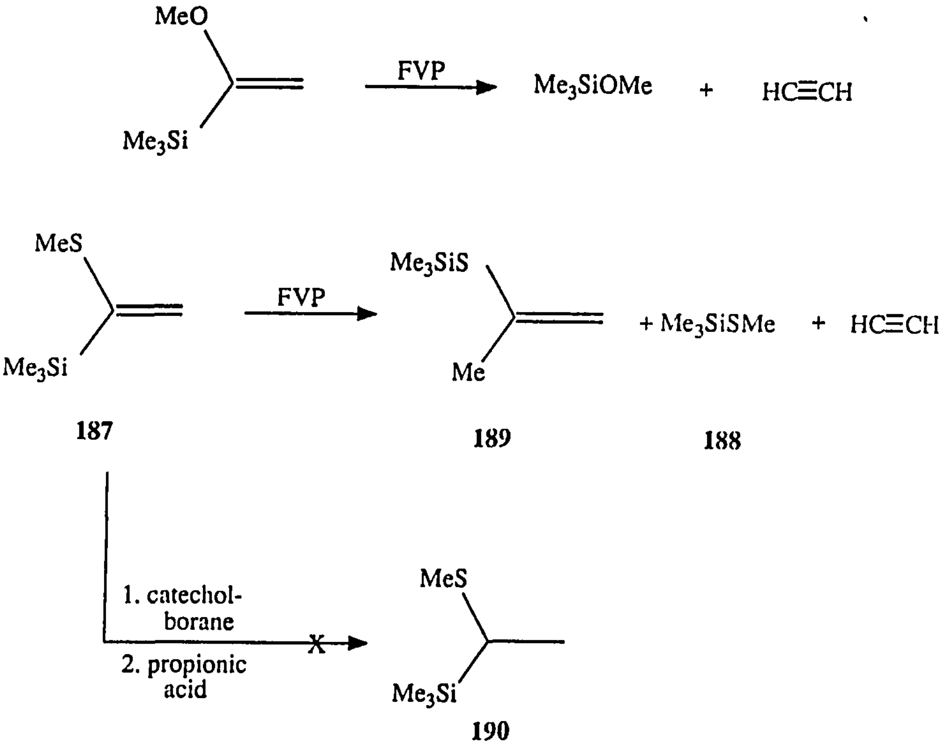
irradiated with a mercury arc lamp for up to 24 hours at room temperature under an argon atmosphere in dried pentane in a quartz tube. An aliquot of the reaction mixture was removed periodically and, after solvent evaporation, the IR spectrum checked to see if any siloxyacetylene had formed. Unfortunately, even when the solvent was changed to benzene and/or the irradiation carried out in pyrex glass, the formation of a siloxyacetylene was not detected, which has a characteristically strong band in the IR in the 2200 cm^{-1} region. Other bands were noted in the IR spectrum indicating a reaction was taking place, and, although the chemistry is assuredly interesting, it was decided to be outside the scope of this investigation and did not pursue further information on the irradiation products or the route of their formation.

Alkylidenecarbenes

Generation of alkylidenecarbenes by alpha-elimination of thiosiloxanes

Though thermally-induced alpha-elimination of siloxanes has already been shown to produce alkylidenecarbenes,[23,69] the same cannot be said for the analogous sulfur systems. For this reason vinylthioether **187** was prepared by the procedure of Takeda et al.[70] and subjected it to FVP (Scheme 50).

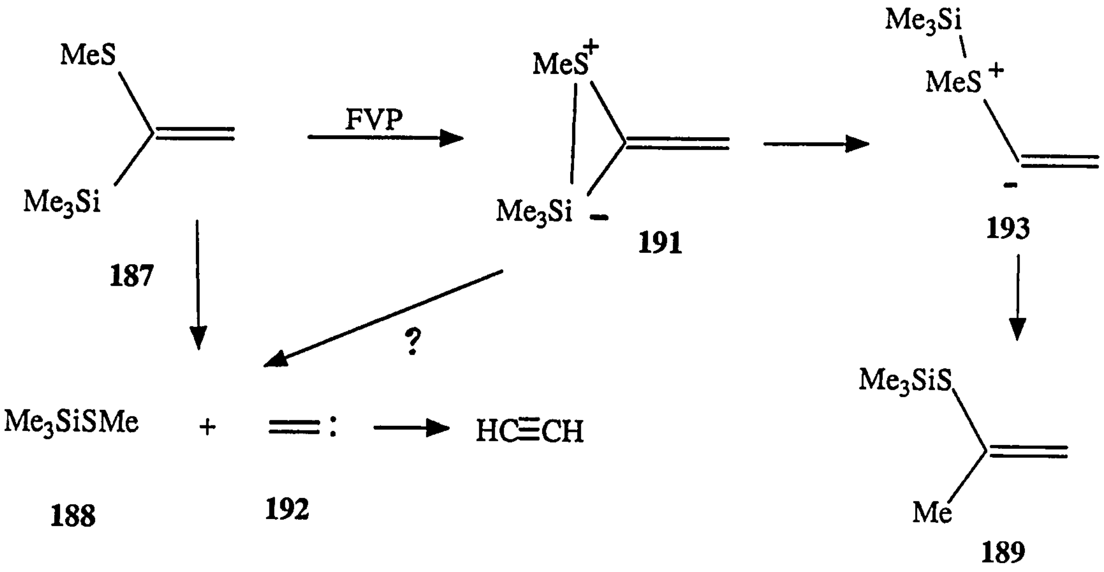
Scheme 50



At 650°C and 2x10^{-5}mm the pyrolysate was analyzed by both GCIR and GC/MS, care being taken to exclude moisture, as the expected thiosilane **188** is water sensitive. Both spectra indicated the formation of **188** when compared to those of an authentic sample. However, another major product was also formed, an isomer of the starting material. This compound has been identified as thiosilane **189**. This does not occur in the analogous oxygen system, which forms acetylene and trimethylmethoxysilane very cleanly.[69] This decomposition has also be studied utilizing the SFR and low-pressure pyrolysis (LPP) unit, which is connected to a quadrupole mass spectrometer to observe the formation of **188** and acetylene directly, without interference from possible moisture contamination. Clean formation of thiosilane **188** and acetylene was observed at 600°C, and interestingly, **189** was not. These results show that the reductive elimination of trimethyl-methoxysilane from alpha-silyl vinyl ethers to form a vinylidene is still operable when one substitutes a sulfur atom for the oxygen, but that at the elevated temperatures required to induce the elimination, most likely due to the greatly decreased gain in energy from formation of a silicon-sulfur bond (99 kcal/mol) instead of a silicon-oxygen bond (128 kcal/mol),[71] other routes for decomposition become feasible.

A possible mechanism to account for these results is presented in Scheme 51. Compound **187** could first form ylide **191**, which could then directly form **188** and vinylidene **192** (which would form acetylene) or rearrange to ylide **193**.

Scheme 51



Ylide **193** would then undergo a methyl shift to form **189**. [1,2]-Rearrangements have been found to occur in such ylides, but CIDNP evidence indicates that these reactions take place at least partly through a radical dissociation-recombination mechanism.[72] If this mechansim is operable, one would expect this isomerization to occur more readily in solution, an experiment that remains to be run.

Attempts to prepare the saturated analog to **187** for similar studies have as yet not been successful. Catalytic hydrogenation has been ruled out as a possible route from **187** due to known poisoning of catalysts by sulfur, especially when close to the reactive site.[73] It was decided hydroboration, followed by protonation with propionic acid, had the best chance for success.[74] Borane in THF was first attempted, stirring at room temperature for two hours then addition of the propionic acid with additional stirring for one hour. Workup afforded a complex mixture of products. It was later discovered that borinates of vinylthioethers disproportionate, with the sulfur migrating onto the boron atom.[75] It was hoped that the use of catechol borane with two oxygen atoms already attached to the boron would eliminate the disproportionation and allow preparation of **190** from **187**. Reaction of **187** with catecholborane at 100°C for two hours, followed by cooling and addition of propionic acid, resuming heating at 100°C for an additional two hours, then workup with aqueous sodium hydroxide and extraction with pentane also failed to form **190**, however. Being unable to prepare **190**, the precedent for gas phase reductive elimination of a thiosilane to form a carbene must rest solely on the results from the aforementioned study of the decomposition of **187**. Further study of this elimination is certainly warranted based upon these preliminary results and the general lack of knowledge of rearrangements involving organothiosilanes.

CONCLUSION

The formation of bis(silyl)ketenes on reaction of 2,3-dihydrofuran with n-BuLi was found to occur by the rearrangement of siloxyacetylene intermediates. Alternative use of 2,3-dihydro-2-phenylfuran allowed preparation of bis(trimethylsilyl)ketene in 65% yield. Similar decomposition of 2,3-dihydrothiophene was not detected, even when a variety of other bases were utilized.

4,5-Dihydro-3-methyl-2-(trimethylsilyl)furan and 2,3-dihydro-5-(trimethylsilyl)thiophene were both subjected to flash vacuum pyrolysis (FVP) and found to undergo reductive elimination to form vinylidenes, which then formed the corresponding acetylenes. The former did so exclusively, while the latter also formed 2-(trimethylsilyl)thiophene by hydrogen elimination and required higher temperatures to initiate decomposition. When 2,3-dihydro-2-phenyl-5-(trimethylsilyl)furan was subjected to FVP only fragmentation occurred. These results were found to be inconsistent with the formation of silylketenes by a biradical mechanism suggested for the the thermal decomposition of 2,3-dihydro-5-(trimethylsilyl)furan.[23]

Several new methods for preparing siloxyacetylenes, besides the dihydrofuran route, were reported but found to be unsuccessful.

Several siloxyacetylenes were subjected to FVP and found to undergo quantitative conversion to the corresponding silylketenes. Retro-Wolff rearrangement of the silylketenes produced was oberved at temperatures higher than those required for the siloxyacetylene-silylketene rearrangement. The kinetics of the thermal rearrangement of methyl(t-butyldimethylsiloxy)ethyne to the corresponding silylketene were followed in a stirred-flow reactor (SFR) and the activation parameters (E_a = 34.1 kcal/mol, log A = 10.4) were obtained. A siloxyacetylene with an acetylenic carbon ^{13}C-enriched was prepared and pyrolyzed. The resulting silylketene was found to have only a single ketenic carbon ^{13}C-enriched, that which one would expect if the rearrangement occurred via a 1,3-silyl shift. This data and theoretical calculations were used in arguments supportive of a 1,3-silyl shift mechanism for the siloxyacetylene-silylketene rearrangement.

Extension of the FVP studies to silylthioacetylenes produced isomerization to the corresponding silylthioketenes, but instead of quantitative conversion, the systems were found to establish an equilibrium. At increasingly higher pyrolysis temperatures the silylthioketenes were found to decompose to acetylenes which could be accounted for by 1,2-alkyl and 1,2-silyl shift mechanisms. The kinetics of the thermal rearrangement of methyl(t-butyldimethylsilylthio)-ethyne to the corresponding silylthioketene were followed in a stirred-flow reactor (SFR) and the activation parameters (E_a = 35.4 kcal/mol, log A = 12.9) were obtained after correction for returned starting material. A silylthioacetylene with an acetylenic carbon ^{13}C-enriched was prepared and pyrolyzed. The resulting silylthioketene was found to have only a single ketenic carbon ^{13}C-enriched, that which one would expect if the rearrangement occurred via a 1,3-silyl shift. This data was used in arguments supportive of a 1,3-silyl shift mechanism for the silylthioacetylene-silylthioketene rearrangement.

Attempts to determine the stereochemical outcome of a chiral silicon center in the thermal rearrangement of a siloxyacetylene to a silylketene have been thwarted.

Dimethylphenylsilylketene does not rearrange to the corresponding siloxyacetylene when photolyzed.

When 1-(thiomethyl)-1-(trimethylsilyl)ethene was pyrolyzed reductive elimination of trimethyl(thiomethyl)-silane occurred in competition with the formation of 1-methyl-1-(trimethylsilylthio)ethene. The formation of an ylide was suggested as a possible precursor to both products.

EXPERIMENTAL

All temperatures reported in this section are in degrees Celsius. Diethyl ether was dried over LAH before use for all reactions. All n-BuLi was purchased from Aldrich (2.5 M in hexanes) and titrated before use. All reported yields are GC yields, calculated as described below, unless otherwise noted.

Instrumentation

High resolution ^1H (300 MHz) and ^{13}C NMR (75.5 Hz) spectra were recorded on a Nicolet NT-300 spectrometer. All chemical shifts are reported as parts per million from tetramethylsilane and taken in $CDCl_3$ unless otherwise noted. Standard abbreviations are used to designate proton splitting. Mass spectra (MS) were recorded using a Finnigan 4023 (GC/MS) or a Hewlett Packard 5970B (GC/MS) operating at 70 eV and are reported as m/e (% relative intensity). Infrared (IR) spectra were recorded on a Beckman IR 4250 or an IBM 98 FT/IR spectrophotometer, which is coupled to a HP5880A capillary GC for GC/IR, and were taken as neat samples unless otherwise noted. Exact mass measurements were obtained on an AE1-MS-902 or a Kratos MS 50 spectrometer.

Gas chromatographic (GC) analyses were performed on a

Hewlett Packard 5790A or 5890 fitted with either a 15 or 30 meter nonpolar capillary column. Preparative GC was performed on a Varian 920 or Varian 1700 using 10 or 15 foot 10-15% SE-30 on chromosorb W packed columns.

GC yields were determined using internal standards and appropriate response factors and adjusted for consumed starting material. Elemental analyses were performed by Galbraith Laboratories, Inc. or by Mic Anal Organic Microanalysis.

A pulsed stirred-flow reactor (SFR) modeled after the design of Baldwin et al.[54] was used for kinetic analyses. The quartz sample chamber had a volume of 3 cm^3 and a tau of 2.39 s. The sample chamber was heated by an oven that was controlled by a Digi-Sense temperature controller. The SFR system used a 60 ml/min flow of helium to sweep the sample through the reactor into a Varian 6000 GC equipped with a 25 foot by 1/4 inch 25% SE-30 on chromosorb W packed column, which had the option of diverting the separated products, via a jet separator, into a quadrupole mass spectrometer (VG-SX300) for MS analysis. The GC (FID) signals were recorded on a chart recorder as well as a Magnum XT/Mark 2 microcomputer for precise determination of reactant and product areas. The SFR also enables one to determine the volatile hydrocarbon products which would have escaped detection under flash vacuum pyrolysis conditions.

Procedures and Results

General conditions for flash vacuum pyrolyses (FVP)

All samples were distilled from a bath at a temperature so as to allow 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 approximately 1.8 cm by 30 cm. Pyrolysates were collected in a cold trap cooled with liquid nitrogen. Pressures were measured by an ionization gauge located behind two liquid nitrogen traps and do not accurately reflect the actual pressure in the reaction zone, which is usually an order of magnitude greater.

General procedure for the synthesis of bis(silyl)ketenes

The general procedure for the preparation of bis(silyl)-ketenes from 2,3-dihydrofuran (**54**) has been published.[24] To THF (10 ml) precooled to -23°C is added **54** (10 mmol). To this was added 1 equiv. of n-BuLi at a rate to maintain the reaction temperature below -20°C. After 15 min. the mixture was warmed to room temperature and stirred for 24 hrs. At this time the mixture was cooled to -70°C and a second equiv. of n-BuLi is added slowly. After 15 min. the mixture was again warmed to room temperature and allowed to stir for an additional 10 hrs. The mixture was then cooled to -70°C and quenched with chlorosilane. After warming to room temperature and stirring for 1-2 hrs., 36 hrs. for t-butyldimethylchlorosilane, the mixture was diluted with pentane and washed with aqeous sodium bicarbonate. The organic layer was then dried over sodium sulfate and the solvent removed by distillation. Spectra of bis(trimethylsilyl)ketene matched that reported by Rathke et al.[27] The identity of bis(t-butyldimethylsilyl)ketene (**61**), formed in 21% yield by this procedure, was based upon spectra: ^{1}H NMR 0.12 (s, 6H), 0.91 (s, 18H); ^{13}C NMR 166.5 (=C=O), 26.5 (CMe_3), 19.4 ($Si-CMe_3$), -2.9 (Si-Me), -4.8 (-C=C); IR 2955, 2925, 2075, 1660, 1470, 1460, 1255, 1175, 875; MS 270 (M^+, 3), 213 (45), 172 (17), 171 (100), 157 (22), 100 (15), 97 (12), 73 (37); calc'd for $C_{14}H_{30}OSi_2$ m/e 270.18353, measured m/e 270.18331.

Bis(silyl)ketenes can also be prepared from 2,3-dihydro-2-phenylfuran[35] (**71**) instead of **54**. The same procedure described above was used except the reaction times at room temperature after addition of the first and second equivalents of n-BuLi are 11 hrs. and 4 hrs., respectively. When TMSCl was the electrophile a 65% yield of silylketene **55** was produced. When t-butyldimethylchlorosilane was the electrophile and the reaction mixture was allowed to stir for 36 hrs. a 40% yield of silylketene **61** is produced.

Synthesis of (t-butyldimethylsilyl)(t-butyldimethylsiloxy)-ethyne (62)

The same procedure for preparing the bis(silyl)ketenes from **54** just described was utilized here as well. After quenching with t-butyldimethylchlorosilane, care must be taken to workup the reaction mixture as described above within two hrs. or isomerization of **62** to **61** begins. The best yield of **62** by this method was 21%. The identity of **62** was based upon the spectra: ^{1}H NMR 0.03 (s, 6H), 0.27 (s, 6H), 0.90 (s, 9H), 0.96 (s, 9H); ^{13}C NMR 109.2 (sp C), 107.1 (sp C), 26.2 (CMe_3), 25.3 (CMe_3), 18.5 ($SiCMe_3$), 16.8 ($SiCMe_3$), -3.8 (SiMe), -5.6 (SiMe); IR 2960, 2934, 2185, 1631, 1594, 1471, 1463, 1390, 1363, 1255, 1176, 1093, 1061, 930, 840, 808, 784; MS 270 (M^+, 4), 213 (100), 171 (76), 157 (19), 100 (12), 73 (44); Anal. calc'd for $C_{14}H_{30}OSi_2$: C, 62.18; H, 11.1. Found: C, 62.16; H, 11.29.

Compound **62** can also be prepared from **71** as described for the preparation of the corresponding silylketene **61** by stirring the reaction mixture at -70°C for 30 min. after chlorosilane addition, then warming to 0°C for 1 hr. before allowing to come to room temperature for 30 min. A similar workup with pentane/sodium bicarbonate then affords a 43% yield of **62**.

Metallation of 2,3-dihydro-4-methylfuran (**63**)

To a solution of 10 ml THF and 8 mmol n-BuLi at -23°C is added **63**[38] (8 mmol) slowly dropwise so as to maintain the temperature below -15°C. After 45 min. the cooling bath was removed and the solution allowed to warm to room temperature, where it stirs for 24 hrs. The mixture was then cooled to -70°C and a second equiv. of n-BuLi was added. The mixture was again returned to room temperature and stirred for an additional 11 hrs. The mixture was then returned to -70°C and quenched with trimethylchlorosilane (TMSCl). After 30 min. the mixture was warmed to room temperature and after 1 hr. trap to trap distilled. This removed the volatile product 4,5-dihydro-3-methyl-2-(trimethylsilyl)furan (**65**) which was further purified by preparative GC, GC yield 21%. Furan **65** was identified by the spectra: ^{1}H NMR 0.13 (s, 9H), 1.70 (t, 3H, J=1 Hz), 2.52 (d of t, 2H, J=1 Hz, J=9.5 Hz), 4.13 (2H, J=9.5 Hz); ^{13}C NMR 158.2, 105.2, 69.1, 38.0, 11.6, -4.4; IR 3085, 2965, 2920, 2885, 2857, 1591, 1252, 1103, 933, 890, 862, 839, 770; GC/MS 156 (M^+, 29), 141 (13), 113 (13), 111 (51), 83 (22), 75 (42), 73 (100). Anal. calc'd for $C_8H_{16}OSi$: C, 61.5; H, 10.2. Found: C, 61.45; H, 10.4.

Another major product was isolated from the salts remaining after distillation by first dissolving the salts in water and extracting with ether. The ether layer was dried over sodium sulfate and solvent removed by rotary evaporation. This product was produced in 28% yield (GC) and identified as 1-(trimethylsiloxy)-1-(trimethylsilyl)-2-(4,5-dihydro-2-furanyl)propene (**66**) by the spectra: ^{1}H NMR 0.10 (s, 9H), 0.16 (s, 9H), 1.55 (s, 3H), 1.57 (s, 3H), 2.62 (t, 2H, J=10 Hz), 4.25 (t, 2H, J=10 Hz); ^{13}C NMR 148.0, 145.4, 116.8, 108.3, 67.6, 35.5, 16.1, 12.4, 0.6, -0.5; GC/MS 284 (M^+, 11), 269 (11), 146 (46), 122 (41), 79 (32), 75 (20), 73 (100), 45 (32).

FVP of **66**

Compound **66** (218 mg), distilled (2×10^{-5}mmHg) from a bath at 0°C, was pyrolyzed at 600°C. The pyrolysate (198 mg) was analyzed by GC and GC/MS. There was only one major product formed (68% isolated yield) that has been identified as 5-(trimethylsiloxy)-2-pentyne by the spectra: ^{1}H NMR 0.84 (s, 9H), 1.73 (t, 3H, J=2.5 Hz), 2.31 (m, 2H, J=2.5 Hz, J=7.3 Hz) 3.61 (t, 2H, J=7.3 Hz); ^{13}C NMR 76.7, 76.0, 61.8, 23.1, 3.4, -0.4; IR 2965, 2930, 2890, 2120, 1390, 1255, 1100, 1065, 915, 875, 840, 760; GC/MS 156 (M^+, 1), 155 (1), 141 (58), 111 (26), 103 (33), 75 (25), 73 (100).

Synthesis of 2,3-dihydro-2-phenyl-5-(trimethylsilyl)furan (85)

To a solution containing 20 ml ether and 2.5 mmol of 2,3-dihydro-2-phenylfuran that has been cooled to -70°C was added 5 mmol of n-BuLi slowly dropwise. After 30 min. this was warmed to -23^{o}C and allowed to stir for 4 hrs. The reaction was then quenched with TMSCl and warmed to room temperature after 15 min. The reaction mixture was then diluted with pentane, washed with aqueous sodium bicarbonate and the organic layer dried over sodium sulfate. After rotary evaporation crude **85** is obtained in a yield of 83%. Compound **85** is identified by the spectra: ^{1}H NMR 0.17 (s, 9H), 2.50 (d of d of d, 1H, J=7.8 Hz, J=2.4 Hz, J=16 Hz), 3.10 (d of d of d, 1H, J=10.8 Hz, J=2.4 Hz, J=16 Hz), 5.10 (t, 1H, J=2.4 Hz), 5.45 (d of d, 1H, J=10.8 Hz, J=7.8 Hz), 7.28 (s, 5H); GC/MS 216 (M^{+}, 6.2), 201 (7), 162 (23), 160 (34), 121, (19), 117 (13), 107 (24), 105 (19), 104 (38), 91(40), 77 (19), 73 (100) calc'd for $C_{13}H_{16}OSi$: 216.09705, found: 216.09738.

<u>FVP of **85**</u>

Compound **85** was distilled (2x10^{-5}mmHg) from a bath at 100^{o}C and was pyrolyzed at 500, 550, 600 and 650^{o}C. The pyrolysate was analyzed by GC, GC/MS and IR. No ketenes or acetylenes were formed based upon the IR spectra, and the only major product (10-25% yield) was identified as styrene by comparison of spectra with an authentic sample. No further effort was made to characterize the countless minor products.

Metalation of 3-phenylisoxazole (72)

Compound **72** was prepared and metalated as described by Hoppe and Schollkopf.[25] Quenching with TMSCl produces only the bis(silyl)ketene **55**, as identified by comparison with published spectra.[76] Quenching with t-butyldimethylchlorosilane produces both silylketene **61** and acetylene **62** in an approximately 8:1 ratio, respectively, based upon GC. Both compounds were identified by comparison with aforementioned spectra.

Metalation of 2,3-dihydrothiophene (73)

Compound **73**[39] (5 mmol) was added to THF (10 ml) at -23°C. Slow dropwise addition of 5 mmol of n-BuLi follows and the mixture was allowed to stir 30 min. before warming to room temperature. After 24 hrs. a second equivalent of n-BuLi was added after cooling the reaction mixture to -70°C. The reaction mixture was allowed to stir at this temperature for 30 min. before warming to room temperature for an additional 10 hrs. The mixture was then cooled to -70°C and TMSCl (11 mmol) added. The reaction mixture was then diluted with pentane and filtered through anyhydrous magnesium sulfate to remove the salts as thioketenes are water sensitive. Analysis by GC, GC/MS and IR failed to identify any thioketenes, and there was complete decomposition of the starting material. The GC trace was quite complex and no products were isolated. Similar results occurred when only one equivalent of n-BuLi was added to **73** in THF at -70°C and the reaction mixture stirred at room temperature for only 12 hrs. If, however, an equivalent of TMEDA was also added prior to the addition of n-BuLi and the reaction maintained at -70°C, one can prepare 2,3-dihydro-5-(trimethylsilyl)thiophene (**75**) cleanly. If the reaction mixture was allowed to warm to room temperature for 12 hrs. even this product was destroyed, and still there were no traces of a thioketene being formed. If instead one uses t-BuLi and maintains the reaction temperature at -70°C for 20 min before quenching with TMSCl, an 81% GC yield of **75** was produced. Warming to room temperature for 4 hrs. decreases this yield to 62% with no formation of a thioketene observed. If the reaction was allowed to stir at room temperature for 24 hrs. this yield decreases to 46% and other minor products are observed by GC. If a second equivalent was then added after cooling to -70°C, and then allowed to stir at room temperature for an additional 14 hrs. there was complete decomposition. Attempts at decomposition of **73** using LDA in hexane using a similar procedure. When the anion was made at -70°C and quenched after one hour with TMSCl, a 66% GC yield of **75** was formed. If this was then warmed to room temperature for 4 hrs. before quenching this yield was increased to 74%. Extending the reaction time at room temperature to 12 hrs. or greater begins to lower these yields, with no formation of thioketene observed. Compound **75** was identified by the spectra: ^{1}H NMR 0.18 (s, 9H), 2.80 (d of t, 2H, J=9 Hz, J=2.7 Hz), 3.15 (t, 2H, J=9 Hz), 5.75 (t, 1H, J=2.7 Hz); ^{13}C NMR 141.6, 130.8, 38.0, 33.0, -1.2; IR 3030, 2957, 2897, 1566, 1250, 960, 903, 841, 748; GC/MS 158 (M^+, 21), 143 (9), 109 (33), 97 (38), 85 (13), 75 (18), 73 (100), 45 (40), 43 (37); calc'd for $C_7H_{14}SSi$ m/e 158.05855, measured m/e 158.0583.

FVP of **75**

Compound **75** (ca. 100 mg avg.) was distilled ($2x10^{-5}$mmHg) from a bath at 0°C and pyrolyzed at various temperatures. At both 550°C and 650°C only starting material was recovered. When the temperature was increased to 750°C the pyrolysate was found to contain three major products with a 97% mass recovery. The products have been identified as 2-(trimethylsilyl)thiophene (**88**) (31% yield) and the cis and trans isomers of 1-(trimethylsilylthio)-1,3-butadiene (**89**) (62% yield). Compound **88** was identified by the spectra: ^{1}H NMR 0.29 (s, 9H), 7.15 (d of d, J=3.3 Hz, J=4.5 Hz), 7.23 (d of d, J=1 Hz, J=3.3 Hz), 7.55 (d of d, J=1 Hz, J=4.5 Hz); IR 3088, 2959, 2899, 1408, 1250, 1215, 1084, 993, 841, 756, 716; GC/MS 156 (M^+, 18), 142 (12), 141 (100), 75 (11), 73 (9), 53 (10), 45 (15).

The butadienes **89** were inseparable and identified by the combined spectra: ^{1}H NMR 0.32 (s, 18H), 5.1 (m, 4H), 6.2 (m, 3.5H), 6.8 (m, 0.5H); ^{13}C NMR 136.8, 136.0, 133.7, 132.5, 122.2, 120.0, 118.1, 115.3, 0.8; IR 3015, 2959, 2899, 1620, 1566, 1408, 1250, 1042, 843, 752, 631; GC/MS 158 (M^+, 9), 143 (2), 75 (12), 73 (100), 45 (38), 43 (15).

Synthesis of 4-(trimethylsilylthio)-1-butyne (91)

To a stirring mixture of THF (10 ml) and sodium hydride (9 mmol) cooled to 0°C was added 3-butyn-1-thiol (6 mmol), prepared by the method of Dupuy and Surzur[44] and identified GC/MS and by comparison of ^{1}H NMR and IR spectra, in 3 ml of pentane. Addition was controlled so as to produce a moderate rate of hydrogen evolution. Allow mixture to stir for 2 hrs. to insure complete reaction, then add 10 mmol of TMSCl and allow to stir an additional 1 hr. As **91** was water sensitive, the mixture was trap to trap distilled to remove salts, then purified further by preparative GC. Compound **91** was identified by the spectra: ^{1}H NMR 0.28 (s, 9H), 2.0 (t, 1H, J=2.7 Hz), 2.4 (d of t, 2H, J=2.7 Hz, J=7.5 Hz), 2.6 (t, 2H, J=7.5 Hz); GC/MS 158 (M^+, 13), 143 (23), 119 (37), 109 (35), 97 (58), 91 (10), 75 (31), 73 (100), 69 (11), 53 (12), 45 (20), 43 (37).

FVP of **91**

Compound **91** (83 mg) was distilled at 2×10^{-4}mmHg from a bath at 0°C and pyrolyzed at 750°C. The pyrolysate (69 mg) was analyzed by GC, GC/MS, IR and ^{1}H NMR and found to be composed of the same pyrolysate mixture as the decomposition of **75** when pyrolyzed under the same conditions, including 36% of **75**.

General procedure for metalation of bromoenol silyl ethers

The enol silyl ethers 1-bromo-2-(t-butyldimethylsiloxy)-ethene (**95**) and 1-bromo-2-(trimethylsiloxy)ethene (**97**) were prepared as described by Pirrung and Hwu[46] and identified by comparison of ^{1}H and ^{13}C NMR spectra. The enol ether was then added to a stirring solution of LDA (2 mmol) in THF cooled to 0°C. The reaction time was varied from 30 min. to 4 hrs. The reaction was then quenched by slow addition of the electrophile. After stirring for 30 min. at room temperature the solution was diluted with 25 ml of ether. This was then either washed with aqueous sodium bicarbonate or filtered through anyhydrous magnesium sulfate to remove salts. Products from both methods are compared to test for water stability. Products were formed from these reactions only when TMSCl was the quenching agent. These were identified as silylketene **55**, identified as previously reported, and (t-butyldimethylsilyl)(trimethylsilyl)-ketene

96, identified by the spectra: ^{1}H NMR 0.13 (s, 6H), 0.20 (s, 9H), 0.93 (s, 9H); ^{13}C NMR 167.0, 26.4, 19.0, 1.8, -1.8, -3.2; IR 2959, 2932, 2880, 2860, 2079, 1472, 1465, 1254, 910, 835, 800, 770 GC/MS 228 (M^+, 2), 213 (1), 173 (9), 172 (19), 171 (100), 73 (67), 59 18), 57 (27).

<u>FVP of 2,5-bis(trimethylsiloxy)bicyclo[2.2.2]triene (100)</u>

Triene **100** was prepared by the method of Gompper and Etzbach[49] and further characterized by the spectra: ^{1}H NMR 0.35 (s, 18H), 3.84 (d of d of d, J=1 Hz, J=3.6 Hz, J=3.9 Hz), 5.41 (d of d, J=1 Hz, J=3.6 Hz), 6.87 (d of d, J=3.6 Hz, J=3.9 Hz); IR 3085, 3072, 2991, 2960, 2902, 1728, 1645, 1624, 1415, 1310, 1296, 1271, 1254, 1222, 1197, 1178, 1089, 981, 914, 872, 847, 754; GC/MS 280 (M^+, 48), 279 (11), 265 (7), 239 (6), 166 (18), 151 (56), 147 (12), 75 (16), 73 (100), 45 (50). Triene **100** was distilled ($3x10^{-5}$mmHg) from a bath at 40°C and pyrolyzed at 300°C (162 mg) and found to undergo no decomposition. When pyrolyzed at 400°C (210 mg) there was an 81% mass recovery, with 50% starting material remaining by GC analysis. The product formed was isolated by preparatory GC and identified as p-bis(trimethylsiloxy)benzene (**101**) by the spectra: ^{1}H NMR 0.15 (s, 18H), 6.75 (s, 4H); IR 3040, 3015, 2963, 2908, 1261, 1134, 1065, 849, 748; GC/MS 254 (M^+, 75), 241 (10), 240 (23), 239 (100), 112 (9), 73 (57).

Synthesis of (α,α-dibromoacetyl)trimethylsilane (**109a**) and (α,α-dibromoacetyl)t-butyldimethylsilane (**109b**)

To acetyltrimethylsilane (**108a**)[52] (80 mmol), prepared in 66% yield and identified by comparison of ^{1}H NMR, IR, and MS spectral data, was added 50 ml of glacial acetic acid. This was cooled to 10°C and bromine (160 mmol) was added slowly via an addition funnel. Bromine was quickly consumed until near the end of the reaction, as evidenced by the disappearance of the dark brown color. It was allowed to stir an additional 30 min. after addition was complete, then diluted with 200 ml of chloroform. This was then washed with 3 x 100 ml of water, followed by 3 x 200 ml of aqueous sodium bicarbonate, caution being exercised that there was not a buildup of pressure. The organic layer was then separated and dried over sodium sulfate. A rotary evaporator was used to remove solvents, producing a 100% crude yield of **109a**. This was then vacuum distilled at 105°C/10mmHg to give a 84% distilled yield of pure **109a**. Compound **109a** was identified by the spectra: ^{1}H NMR 0.38 (s, 9H), 5.92 (s, 1H); IR 2961, 2885, 1740, 1668, 1647, 1366, 1252, 1042, 851, 768, 633; GC/MS 274 (M^+, 0.1), 203 (1), 139 (11), 137 (11), 122 (5), 120 (5), 73 (100).

Compound **109b** was prepared in a similar manner from the corresponding acetylsilane and identified by the GC/MS data: 316 (M^+, 0.3), 261 (1), 259 (2), 257 (1), 139 (11), 137 (10), 115 (15), 73 (100), 59 (8). However, other spectra were not collected due to the extreme ease with which this compound extruded t-butyldimethylbromosilane upon attempted purification with only slight heating (60°C).

Synthesis of 1,1-dibromo-2-(trimethylsiloxy)-2-(trimethylsilyl)ethene (110)

To a solution of diethyl ether (10 ml) and 3.8 mmol of sodium bis(trimethylsilyl)amide was slowly added 3.6 mmol of **109a**. This was allowed to stir at this temperature for 30 min., at which time 4.5 mmol of TMSCl was added. This was allowed to stir 1 hr. at this temperature before warming to room temperature. This was then diluted with 50 ml of diethyl ether and washed with 30 ml of aqueous sodium bicarbonate, followed by 30 ml of water. The organic layer was then separated and dried over sodium sulfate. The solvent was removed by rotary evaporation to produce a 85% crude yield of nearly pure **110**. Compound **110** was identified by the spectra: ^{1}H NMR 0.15 (s, 9H), 0.28 (s, 9H); GC/MS 348 (0.8), 346 (M^+, 1.6), 344 (0.8), 194 (15), 192 (15), 179 (17), 177 (17), 147 (11), 139 (8), 137 (8), 73 (100), 45 (27).

Metalation of 110

Compound **110** (0.5 mmol) was diluted with 10 ml of LAH dried hexane and cooled to -70°C, at which temperature 0.5 mmol of n-BuLi was slowly added dropwise via syringe. After 30 min. it was warmed to room temperature. This was diluted with 50 ml of pentane and washed with water. The organic layer was separated and dried over sodium sulfate. Analysis by both IR and GC/MS indicated no formation of either a silylketene or siloxyacetylene and no further attempts were made to isolate and identify remaining mixture.

Synthesis of 1-phenyl-2-(t-butyldimethylsiloxy)ethyne (113) and phenyl(t-butyldimethylsilyl)ketene (114)

Compounds **113** and **114** were both prepared by a modification of the method of Maas and Bruckmann.[45] To 2 mmol of 1-phenyl-2-diazo-1-ethanone (**111**),[77] was added 15 ml of freshly dried (LAH) diethyl ether and 3 mmol of ethyldiisopropylamine. This mixture was cooled to 0°C and the t-butyldimethylsilyltriflate (2.2 mmol) was slowly added via syringe, stopping addition for 5 min. every 1/5 portion of addition. The reaction mixture was kept at this temperature and the reaction followed by IR, monitoring the disappearance of starting material (2104 cm^{-1}) and formation of silylated diazoketone **112** (2070 cm^{-1}). When the reaction was complete, generally 2 hrs., the mixture was transferred and filtered through dried celite under an inert atmosphere due to the severe water sensitivity of **112**. The reaction mixture was then placed on a vacuum line and the solvents removed at room temperature and 1 mmHg pressure. This crude **112** was then diluted with 50 ml of dried benzene and warmed to 70°C for 2 hrs., forming **113** in 74% crude yields. Compound **113** was identified by comparison of with literature IR spectrum[45] and the following spectral data: ^{1}H NMR 0.54 (s, 6H), 1.2 (s, 9H), 7.4 (m), 7.5 (m); ^{13}C NMR 131.4, 128.0, 126.0, 124.1, 96.1, 48.5, 25.4, 18.5, -5.5; MS 232 (M^+, 31), 193 (27), 176 (19), 175 (93), 147 (100), 105 (14), 75 (31), 73 (89); calc'd for $C_{14}H_{20}OSi$ m/e 232.12835, measured m/e 232.12820.

Compound **114** was prepared in 58% yield by irradiation of **112** as reported by Maas and Bruckmann.[45] It was further identified by the spectra: ^{1}H NMR 0.27 (s, 6H), 0.90 (s, 9H), 7.3 (m), 7.4 (m); ^{13}C NMR 181.7, 131.0, 129.1, 128.8, 125.0, 26.7, 19.1, -2.5, -4.5; GC/MS 232 (M^+, 1), 194 (11), 193 (65), 91 (22), 77 (6), 75 (100), 73 (28), 65 (13).

<u>FVP of **113**</u>

Compound **113** (165 mg) was distilled at 1×10^{-5}mmHg from a bath at 110°C and was pyrolyzed at 400°C. The recovered pyrolysate (161 mg, 97% mass recovery) was analyzed by GC/MS and IR, which indicated that partial isomerization to **114** had occurred, by comparison to the spectra just presented. When **113** (147 mg) was pyrolyzed at 550°C the pyrolysate (144 mg, 98% mass recovery and yield) was similarly analyzed and found to contain only silylketene **114**.

General procedure for the synthesis of silylthioketenes and silylthioacetylenes

The method used for these reactions was a slight modification of the route used by Walton and Harris.[4] To prepare the thioacetylenes one adds 10 mmol of the desired acetylene to 50 ml of diethyl ether and cools the reaction mixture to -45°C and then slowly adds 10 mmol of n-BuLi. This order may be reversed in the case of gaseous acetylenes. After 30 min. 10 mmol of sulfur was added. Some warming (up to -15°C) may be required at this point to completely consume the sulfur. Once the sulfur was completely consumed, generally about 1 hr., the reaction mixture was cooled to -70°C and the TMSCl quench is added. This was allowed to stir for 1 hr., then allowed to warm to 0°C, at which point the mixture was diluted with pentane (200 ml). If t-butyldimethylchlorosilane was used as quench one needs only cool the mixture back to -45°C to add the chlorosilane and one allows the reaction mixture to warm to room temperature and stir for 1.5 hr. before diluting with pentane. The salts were then removed by filtering through anyhydrous magnesium sulfate, as the compounds are water sensitive, and the pentane removed by a rotary evaporator. (Trimethylsilyl)(trimethylsilylthio)-ethyne (**120**) was identified by comparison of IR and ^{1}H NMR spectral data with literature values[4] and by the spectra: ^{13}C NMR 92.0, 90.9, -4.2, -4.5; GC/MS 202 (M^+, 18), 187 (41), 98 (10), 97 (87), 75 (12), 73 (100). (Trimethylsilyl)(t-butyldimethylsilylthio)ethyne, formed in 88% yield, was identified by the spectra: ^{1}H NMR 0.11 (s, 9H), 0.38 (s, 6H), 0.98 (s, 9H); ^{13}C NMR 92.0, 91.1, 26.2, 19.7, 0.1, -4.2; IR 2957, 2932, 2903, 2865, 2098, 1472, 1464, 1250, 891, 842, 802, 760; GC/MS 244 (M^+, 8), 229 (4), 187 (83), 97 (76), 73 (100). Methyl(t-butyldimethylsilylthio)ethyne (**137**), formed in 76% yield, was identified by the spectra, which has the curiosity of no acetylenic stretch in the IR. ^{1}H NMR 0.33 (s, 6H), 0.95 (s, 9H), 1.81 (s, 3H); ^{13}C NMR 80.5, 63.3, 26.2, 19.4, 4.8, -4.0; IR 2955, 2930, 2850, 1470, 1462, 1250, 1005, 841, 822, 805, 779 GC/MS 186 (M^+, 14), 130 (11), 129 (70), 75 (22), 73 (100), 59 (32). Calc'd for $C_9H_{18}SSi$ m/e 186.18178, measured m/e 186.1814; Elemental anal. calc'd: C 58.0, H 9.66; found: C 58.11, H 9.80. The compound t-butyl(trimethylsilylthio)ethyne, formed in 68% yield, was identified by the spectra: ^{1}H NMR 0.37 (s, 9H), 1.17 (s, 9H); ^{13}C NMR 93.8, 62.8, 31.2, 28.6, 0.2; IR 2966, 2930, 2901, 1475, 1458, 1252, 1055, 845, 756; GC/MS 186 (M^+, 16), 171 (20), 75 (12), 73 (100). The spectra for ethyl(t-butyldimethylsilylthio)ethyne formed in 88% yield, were: ^{1}H NMR 0.34 (s, 6H), 0.96 (s, 9H), 1.10 (t, J=7.7 Hz), 2.15 (q, J=7.5 Hz); ^{13}C NMR 86.5, 63.7, 26.2, 19.5, 14.1, 13.7, -4.1;

IR 2957, 2932, 2857, 1472, 1464, 1252, 841, 822, 815, 781; GC/MS 200 (M^+, 18), 145 (5), 144 (9), 143 (57), 99 (12), 91 (60), 75 (18), 73 (100), 59 (28). The final thioacetylene formed by this method, phenyl(t-butyldimethylsilylthio)ethyne (**142**), was identified by the spectra: ^{1}H NMR 0.43 (s, 6H), 1.02 (s, 9H), 7.22 (m, 3H), 7.34 (m, 2H); ^{13}C NMR 131.4, 128.2, 127.5, 124.3, 84.4, 76.6, 26.2, 19.8, -3.9; IR 3080, 3062, 3031, 2956, 2929, 2896, 2883, 2860, 2173, 1596, 1487, 1469, 1463, 1252, 1004, 842, 821, 804, 781, 754, 690; GC/MS 248 (M^+, 25), 193 (10), 192 (22), 191 (91), 75 (14), 73 (100); calc'd for $C_{14}H_{20}SSi$ m/e 248.10551, measured m/e 248.10536.

Bis(trimethylsilyl)thioketene (**119**) was identified by comparison of the IR and ^{1}H NMR spectra with that of Walton and Harris[4] and additionally by the spectra: ^{13}C NMR 214.4, 52.3, 0.7; GC/MS 202 (M^+, 12), 188 (5), 187 (28), 114 (8), 99 (8), 98 (8), 97 (73), 75 (13), 73 (100), 45 (48).

<u>FVP of 137</u>

Compound **137** was distilled at 1×10^{-5}mmHg from a bath at 0°C and pyrolyzed at 500, 600, 700 and 800°C. The first two temperatures provided quantitative mass recovery and formed a 23% yield of methyl(t-butyldimethylsilyl)thioketene (**138**), the ratio of **137**:**138** at 3.2:1. This ratio remained the same at 700°C, but another compound was also produced, an 8% yield of methyl(t-butyldimethylsilyl)ethyne (**139**), which was identified by comparison of spectra with that of an authentic sample. Increasing the temperature to 800°C formed only a white polymeric material that was not characterized. Compound **138** was identified by the spectra: ^{1}H NMR 0.15 (s, 6H), 0.90 (s, 9H), 1.76 (s, 3H); ^{13}C NMR 237.2, 56.0, 26.6, 19.9, 9.6, -6.2; IR 2955, 2930, 2850, 1757, 1472, 1464, 1251, 1024, 839, 822, 803, 795; GC/MS 186 (M^+, 16), 131 (9), 130 (16), 129 (100), 101 (15), 85 (21), 75 (24), 73 (58), 43 (43).

Pyrolysis of 137 under SFR conditions

Compound **137** was pyrolyzed in an SFR from 249-291°C with injections of 0.01 microliters. Varying the sample size to 0.50 microliters had no measurable effect. Compound **137** was also studied by gaseous injections of 0.1 torr in the 235-285°C range for an Arrhenius plot. Pyrolyses were also carried out in the 360-515°C range to gather data to prepare a Van Hofft's plot using the gaseous injections.

FVP of 142

Compound **142** was distilled at $2x10^{-4}$mmHg from a bath at 120°C and pyrolyzed at 600, 650 and 700°C. At 600°C analysis of the pyrolysate indicates there was a 98% mass recovery and an 8% yield of thioketene **143**, the remainder starting material. At 650°C the pyrolysate was found to contain a 13% yield of thioketene **143**, with an 84% mass recovery (75% **142**). The pyrolysate was also found to contain another acetylene, phenyl(t-butyldimethylsilyl)ethyne (**144**), formed in 5% yield. When the temperature was increased to 700°C there was only a 67% mass recovery, the pyrolysate containing 53% recovered **142**, 13% thioketene **143**, 5% of acetylene **144**, and 20% of 1-phenylpropyne, identified by comparison of spectra with that of an authentic sample. Compound **143** was identified by the spectra: ^{1}H NMR 0.27 (s, 6H), 0.90 (s, 9H), 7.22 (m, 3H), 7.32 (m, 2H); ^{13}C NMR 221.5, 131.5, 128.4, 127.9, 124.3, 68.1, 26.9, 19.9, -4.1; IR 3082, 3063, 3031, 2956, 2929, 2885, 2858, 1716, 1598, 1489, 1471, 1256, 1070, 837, 781, 756, 690, 669; GC/MS 248 (M^{+}, 18), 193 (11), 192 (25), 191 (100), 115 (14), 75 (11), 73 (42). Compound **144** was identified by comparison of spectra with that of an authentic sample that were as follows: ^{1}H NMR 0.20 (s, 6H), 1.02 (s, 9H), 7.32 (m, 3H), 7.50 (m, 2H); ^{13}C NMR 132.0, 128.4, 128.2, 123.26, 105.8, 92.4, 25.4, 19.1, -4.4; IR 3080, 3060, 3030, 2955, 2930, 2885, 2855, 2150, 1487, 1470, 1460, 1360, 1252, 1025, 1000, 840, 805, 780, 750, 690; GC/MS 216 (M^{+}, 4), 161 (5), 160 (17), 159 (100), 129 (8), 105 (7), 43 (14).

FVP of **144**

Compound **144** was distilled at 1x10^{-4}mmHg at room temperature and pyrolyzed at 700°C and 750°C. The pyrolysate from both pyrolyses was analyzed by both GC and GC/MS and found to contain only **144**.

Synthesis of propyl(triisopropylsiloxy)ethyne (121) and methyl(t-butyldimethylsiloxy)ethyne (135)

Compound **121** and **135** were prepared by the method of Kowalski et al.[31] Compound **121** was prepared in 46% yield and purified by preparative GC. Compound **121** was further identified by the spectra: ^1H NMR 0.93 (t, 3H, J=7.5 Hz), 1.1 (d, 6H, J=6.6 Hz), 1.25 (m, 2H), 1.45 (heptet, 1H, J=6.6 Hz), 2.03 (t, 2H, J=7.8 Hz); ^{13}C NMR 86.9, 30.5, 23.4, 19.4, 17.4, 13.6, 11.9; IR 2960, 2947, 2895, 2280, 1464, 1296, 1254, 1016, 997, 883, 825, 692; GC/MS 240 (M^+,1), 211 (5), 197 (37), 156 (14), 155 (100), 127 (30), 113 (20), 85 (10), 73 (8), 71 (13), 59 (28).

Compound **135** was produced in 51% yield, purified by preparative GC and identified by the spectra: ^1H NMR 0.35 (s, 6H), 0.98 (s, 9H), 2.12 (s, 3H); ^{13}C NMR 89.2, 31.3, 25.3, 18.5, 5.0, -5.4; IR 2957, 2930, 2850, 2291, 1472, 1464, 1258, 1090, 1013, 839, 791; GC/MS 170 (M^+, 4), 155 (8), 131 (10), 113 (30), 99(9), 75 (32), 73 (100), 59 (66); calc'd for $C_6H_{18}OSi$ m/e 170.11269, measured m/e 170.1129.

FVP of **121**

Compound **121** is distilled at 1x10^{-5}mmHg at room temperature and pyrolyzed at 400, 500, and 600°C. At 400°C only a trace amount of propyl(triisopropylsilyl)ketene (**122**) was detected by a band in the IR at 2079 cm^{-1}. The mass recovery was 97%. At 500°C the stretches for both compounds were nearly of identical strength, the mass recovery being 94%. At 600°C the mass recovery was 98% and only a trace of starting material remained, as judged by the IR. No yields were possible as these compounds had nearly identical proton spectra and were inseparable by GC, which was necessary for the utility of this compound, desired for kinetic studies which required the ability to separate them by GC. Compound **122** was identified by the spectra: ^{1}H NMR 0.90 (t, 3H, J=7.5 Hz), 1.12 (d, 6H, J=6.6 Hz), 1.25 (m, 2H), 1.42 (heptet, 1H, J=6.6 Hz), 2.00 (t, 2H, J=7.8 Hz); IR 2961, 2945, 2895, 2079, 1464, 1256, 1007, 883, 675, 650; GC/MS 240 (M$^+$, 4), 198 (14), 197 (81), 156 (10, 155 (73), 141 (10), 113 (24), 101 (17), 99 (28), 97 (16), 85 (27), 84 (14), 83 (22), 75 (45), 73 (50), 71 (34), 70 (14), 69 (24), 67 (15), 59 (100).

FVP of **135**

Compound **135** was distilled at 1x10^{-5}mmHg from a bath at 0°C and pyrolyzed at 450°C and 550°C. At 450°C there was a 96% mass recovery containing only a trace of the isomeric methyl(t-butyldimethylsilyl)ketene (**136**), noted from the IR by a stretch at 2074 cm^{-1}, along with recovered starting material. At 550°C the mass recovery was 98% and contains only **135** and **136**. There was now a 72% yield of ketene **136**, which was identified by the spectra: ^1H NMR 0.28 (s, 6H), 0.98 (s, 9H), 1.98 (s, 3H); ^{13}C NMR 189.1, 26.7, 20.3, 9.8, -1.1, -5.4; IR 2957, 2930, 2852, 2074, 1473, 1464, 1257, 1090, 1014, 839, 791; GC/MS 170 (M^+, 3), 155 (43), 131 (13), 113 (22), 99 (10), 75 (35), 73 (100), 59 (48).

Pyrolysis of 135 under SFR conditions

Compound **135** was pyrolyzed in an SFR from 351.5-389.3°C with injections of 0.01 microliters. Varying the sample size to 0.10 microliters had no measurable effect. An impurity in the sample, which was found to be stable to the reaction temperatures, was measured by completely isomerizing **135** to ketene **136**. The ratio of the two was calculated and used to calculate the true area of the uncontaminated reactant.

Synthesis of 1-phenyl-2-diazo-2-(t-butyldimethylsilyl)-^{13}C-1-ethanone (151)

Benzoic-carboxy-^{13}C-acid (23.5 mmol), 99.1% ^{13}C enriched, was weighed into a dry 25 ml flask equipped with a magnetic stirrer and condenser. The system was nitrogen flushed and thionyl chloride (27.9 mmol) added rapidly. This was then heated at 90°C for 15 hrs. This mixture was then evacuated to 0.05 mmHg for 4 hrs. and the benzoylcarboxy-^{13}C-chloride used in this form for the next reaction. The benzoyl chloride just produced was then reacted with diazomethane as described by Bradley and Robinson[77] to produce a 78% recrystallized yield of 1-phenyl-2-diazo-1-^{13}C-1-ethanone. Compound **151** is then prepared in quantitative yield by reaction of this labelled diazo ethanone with t-butyldimethylsilyltriflate by the method described herein for the preparation of **113**. This moisture sensitive compound was identified by comparison of the IR spectrum with that of the unlabelled spectra in the literature[45] and used immediately.

Synthesis of 2-phenyl-1-^{13}C-1-(t-butyldimethylsiloxy)ethyne (152)

Compound **151** (3.9 mmol) was diluted with 50 ml of LAH dried benzene and warmed to 75°C for 2 hrs. after flushing the system with argon. This produced a quantitative crude yield of **152**, 78% on purification by vacuum distillation at 1×10^{-5}mmHg/110°C, which was identified by comparison of ^{1}H NMR, IR and GC/MS spectra with that of the unlabelled species. The only differences were a shift in the IR band at 2268 cm^{-1} to 2230 cm^{-1} and the ^{13}C NMR shows only enrichment at 96.1 ppm, the acetylenic carbon attached to the siloxy group.

Synthesis of phenyl-2-^{13}C-(t-butyldimethylsilyl)ketene (153)

Compound **151** (100 mg) was diluted with 20 ml of LAH-dried benzene and placed in a dry pyrex test tube and the system flushed with argon. This was irradiated for 1.5 hrs. using a Hanovia lamp. Evaporation of the benzene produced a quantitative crude yield of **153**, an 80% yield on purification by distillation at $1x10^{-5}$mmHg/110°C, identified by comparison of ^{1}H NMR, IR and GC/MS spectra with that of the unlabelled species. The only carbon showing enrichment in the ^{13}C NMR was that at 181.7, that of the carbonyl carbon of the ketene.

FVP of 152

Compound **152** was distilled at $1x10^{-5}$mmHg from a bath at 110°C and was pyrolyzed at 550°C. This produced a quantitative conversion to silylketene **153** (99% mass recovery), identified by carbon enrichment at only the carbonyl carbon (181.7) and comparison of ^{1}H NMR, IR and GC/MS spectra with that of the unlabelled ketene **113**. When the pyrolysis was carried out at 800°C a 82% yield of **153** is formed, along with a 7:1 ratio of 1-phenyl-1-^{13}C-propyne (**156**) and 1-phenyl-2-^{13}C-propyne (**157**), respectively, in 11% yield. Compounds **156** and **157** were identified by comparison of GC retention times, IR, ^{1}H and ^{13}C NMR spectra. The ^{13}C NMR allowed calculation of the ratios of **156** (85.8 ppm) to **157** (79.8 ppm), the assignments collabcrated by published spectra,[55] by accounting for the NOE effect determined from the ratio of the acetylenic carbons in ^{13}C NMR spectra of unlabelled 1-phenyl-1-propyne (**155**).

Synthesis of 156

To 1-lithio-2-phenyl-2-^{13}C-acetylide (> 99% ^{13}C enriched, 5 mmol) in 10 ml diethyl ether, prepared by the method of Brown et al.,[78] was added 5 mmol of dimethylsulfate. This is allowed to stir for 48 hrs, then diluted with 25 ml of diethyl ether and washed with aqueous sodium bicarbonate. This produced a 43% yield of **156** which was purified by preparative GC.

FVP of 156

Compound **156** was distilled at $1x10^{-5}$mmHg from a bath at 0°C and pyrolyzed at 800°C. The pyrolysate was analyzed by ^{1}H and ^{13}C NMR, which indicated, by the same means used in the pyrolysis of **152**, a ratio for the acetylenes **156** and **157** of 8:1, respectively.

Synthesis of 1-phenyl-1-^{13}C-2-(t-butyldimethylsilylthio)-ethyne (159)

To 1-lithio-2-phenyl-2-13C-acetylide (> 99% ^{13}C enriched, 5 mmol) in 50 ml of diethyl ether was added 5mmol of sulfur at -45°C. This was allowed to warm to -20°C for 45 min. (sulfur completely consumed at this time). This was then cooled to -70°C and 5 mmol of t-butyldimethylchlorosilane added dissolved in 4 ml of diethyl ether. After stirring for 10 min. at this temperature the reaction mixture was warmed to room temperature and allowed to stir for an additional 6 hrs. The reaction mixture was then diluted with 250 ml of pentane and filtered through a pad of anyhydrous magnesium sulfate. After vacuum distillation of the solvents, a 94% crude yield of **159** was obtained. Compound **159** was identified by comparison of IR, ^{1}H and ^{13}C NMR spectra with that of the unlabelled acetylene **142** and noting carbon enrichment at only 84.4 ppm in the ^{13}C NMR spectra, the acetylenic carbon bearing the phenyl group.

FVP of **159**

Compound **159** was distilled at 1×10^{-4}mmHg from a bath at 120°C and pyrolyzed at 650°C and 700°C. The pyrolysate (92% mass recovery) from the 650°C pyrolysis was analyzed by IR, GC, ^{1}H and ^{13}C NMR spectra and found to contain **159** (69% yield), 2-phenyl-2-(t-butyldimethylsilyl)-2-^{13}C-thioketene (**160**) (14% yield) and 2-phenyl-2-^{13}C-1-(t-butyldimethylsilyl)ethyne (**161**) (6% yield). Compound **160** was identified by comparison of GC retention time, IR, 1H and ^{13}C NMR spectra with that of the unlabelled thioketene **143**. The ^{13}C NMR spectra indicated only enrichment at 68.1 ppm, the phenyl-substituted ketenic carbon. Compound **161** was identified by comparison of GC retention time, IR, ^1H and ^{13}C NMR spectra with that of the unlabelled acetylene **144**. The ^{13}C NMR spectra indicated only enrichment at 105.8 ppm, the phenyl-substituted acetylenic carbon.

The pyrolysate from the 700°C pyrolysis (84% mass recovery) was found to contain **159** (61% yield), **160** (9% yield), **161** (12% yield) and 1-phenylpropyne (**145**) (3% yield), identified by comparison of GC retention time and GC/MS spectra to that of an authentic sample. Due to the low yield, the carbon label went undetected by ^{13}C NMR spectral analysis of the pyrolysate.

Synthesis of alpha-naphthylphenylmethylsilyltriflate (170)

Compound **170** is prepared using the general procedure of Schmeiser et al.[79] To 5.5 mmol of silver triflate, transferred in a dry box, is added 40 ml of phosphorous pentoxide dried carbon tetrachloride. This is cooled to 0°C and 5.6 mmol of alpha-naphthylphenylmethylchlorosilane[60] in 5ml of carbon tetrachloride is added via syringe. The flask is wrapped in aluminum foil to exclude light and allowed to stir 5 hrs. The reaction mixture is then transferred and filtered through dried celite under argon. The solvent is then removed at 23°C and 0.1 mmHg. This produced a quantitative crude yield of **170** which was used without further purification. Analysis by GC/MS was inconclusive, as no molecular ion peak was identified, although the GC trace was very clean and only a trace of clorosilane was detected. Other analyses were not performed as they would not conclusively identify **170** either.

Attempted synthesis of (alpha-naphthylphenylmethylsiloxy)-phenylethyne (172)

This reaction was conducted as previously described for the preparation of **113**. Compound **170** (2.4 mmol) was added to a stirring solution of diazoketone **111** (2 mmol) and ethyldiisopropylamine (6 mmol) in 20 ml of diethyl ether at $0^{o}C$. After 1 hr. an aliquot of the reaction mixture was analyzed by IR and bands at 2081 and 2031 cm^{-1} were observed and that of **111** was not. The reaction mixture was then transferred and filtered through dried celite under an argon atmosphere. The solvents and amine were removed by evacuating the flask to 0.1mm for 2 hrs. The remaining mixture was diluted with 25 ml of LAH-dried benzene and warmed to to $75^{o}C$ for 2 hrs. Analysis of an aliquot of the reaction mixture at this time by IR revealed that the bands at 2081 and 2031 cm^{-1} were both absent, indicating consumption of the silylated diazo compound **171**. However, there was no band indicating the presence of a siloxyacetylene either. Analysis of this aliquot by GC/MS also indicated that the desired siloxyacetylene **172** was not formed.

Synthesis of 2,3-dihydro-5-(α)-naphthylphenylmethylsilyl)-furan (174)

To a solution of 2,3-dihydrofuran (43 mmol) and 20 ml of diethyl ether cooled to -70°C was added 30 mmol of n-BuLi slowly dropwise, a modification of the method of Lukevics et al.[80] This was allowed to attain room temperature slowly, stir for 10 min. at this temperature, then again cooled to -70°C. Once cooled 7 mmol of (-)alpha-naphthylphenylmethylchlorosilane[60] was added dissolved in 5 ml of diethyl ether. After 15 min. the reaction mixture was allowed to warm to room temperature. After 1 hr. the reaction mixture was diluted with 50 ml of pentane and washed with aqueous sodium bicarbonate (3 x 50 ml) and then the combined aqueous layers extracted with 50 ml of pentane. The combined organic layers are dried over sodium sulfate. A rotary evaporator was used to remove most of the pentane, then warming to 80°C and evacuating the flask to 0.1 mm to remove any remaining entrained solvent. This produced an 89% crude yield of compound **174**, which was identified by the spectra: ^{1}H NMR 0.74 (s, 3H), 2.68 (d of t, 2H, J=2.7 Hz, J=9.6 Hz), 4.45 (t, 2H, J=9.6 Hz), 5.40 (t, 1H, J=2.7 Hz); IR 3056, 3053, 2959, 2928, 2856, 1740, 1610, 1506, 1429, 1256, 1146, 1111, 1053, 1024, 876, 825, 781; GC/MS 316 (M^{+}, 21), 265 (12), 264 (50), 250 (22), 249 (100), 231 (20), 202 (11), 171 (15), 169 (14), 165 (16), 127 (11); calc'd for $C_{21}H_{20}OSi$ m/e 316.12835, measured m/e 316.12763.

Synthesis of (dimethylphenylsilyl)ketene (185)

Compound **185** was prepared by the FVP of 2,3-dihydro-5-(dimethylphenylsilyl)furan[6] at 650°C and $1x10^{-5}$mmHg. Purification by preparative GC afforded a 22% yield of **185**, identified by the spectra: ^1H NMR 0.34 (s, 6H), 1.92 (s, 1H), 7.4 (m, 5H); IR 3071, 3051, 3010, 2956, 2870, 2085, 1632, 1495, 1454, 1429, 1254, 1175, 1117, 1067, 908, 827, 791, 733; GC/MS 176 (M^+, 31), 162 (16), 161 (100), 105 (13), 83 (34), 73 (5).

Irradiation of 185

Compound **185** (25 mg) was irradiated for 6 hrs. with a Hanovia lamp after dilution with 25 ml of dry pentane or benzene. Both pyrex and quartz tubes were used. Aliquots (0.5 ml) were removed every 2 hrs., the solvent evaporated and analyzed by IR.

Synthesis of 1-(methylthio)-1-(trimethylsilyl)ethene (187)

Compound **187** was prepared by the method of Takeda[70] and identified by the spectra: ^1H NMR 0.14 (s, 9H), 2.20 (s, 3H), 5.23 (s, 1H), 5.39 (s, 1H); ^{13}C NMR 147.8, 113.8, 13.6,

-1.5; MS 146 (M^+, 26), 131 (57), 105 (48), 73 (100), 59 (11); calc'd for $C_6H_{14}SSi$ m/e 146.05855, measured m/e 146.0584.

<u>FVP of **187**</u>

Compound **187** was distilled at $1x10^{-4}$mmHg from a bath at 0°C and pyrolyzed at 600 and 650°C. At 600°C only starting material was recovered. At 650°C the pyrolysate (86% mass recovery) contained starting material (67%), (methylthio)-trimethylsilane (**188**) and 2-(trimethylsilylthio)propene (**189**) (16%). Compound **188** was identified by comparison of GC/IR spectra, GC retention time and GC/MS spectra with that of an authentic sample. Due to the extreme volatility and water sensitivity of this compound the yield was not computed. Compound **189** was identified by the spectra: ^1H NMR 0.30 (s, 9H), 1.95 (s, 3H), 5.10 (t, 1H, J=1 Hz), 5.24 (t, 1H, J=1 Hz); GC/MS 146 (M^+, 25), 131 (21), 91 (30), 77 (10), 75 (25), 73 (100), 45 (29).

<u>Pyrolysis of **187** under SFR conditions</u>

Compound **187** was pyrolyzed in a SFR at 600°C using gaseous injections. The sample size was varied and found to change the number of products. With a 0.02 torr partial pressure of **187** only acetylene and **188** were observed. At higher partial pressures other products begin to form. Further studies are in progress.

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