1988

Kinetic and mechanistic aspects of the thermal decomposition of silyketenes, -thioketenes and -ketenimines

Gitendra Chandra Paul
Iowa State University

Recommended Citation

Paul, Gitendra Chandra, "Kinetic and mechanistic aspects of the thermal decomposition of silyketenes, -thioketenes and -ketenimines " (1988). *Retrospective Theses and Dissertations*. 9713.
https://lib.dr.iastate.edu/rtd/9713

INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the original text directly from the copy submitted. Thus, some dissertation copies are in typewriter face, while others may be from a computer printer.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyrighted material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each oversize page is available as one exposure on a standard 35 mm slide or as a 17″ × 23″ black and white photographic print for an additional charge.

Photographs included in the original manuscript have been reproduced xerographically in this copy. 35 mm slides or 6″ × 9″ black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I
Accessing the World's Information since 1938

300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA

Order Number 8825434

Kinetic and mechanistic aspects of the thermal decomposition of silylketenes, -thioketenes and -ketenimines

Paul, Gitendra Chandra, Ph.D.

Iowa State University, 1988

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

Kinetic and mechanistic aspects of the thermal decomposition of silylketenes, -thioketenes and -ketenimines

by

Gitendra Chandra Paul

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

1988

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

DEDICATION

To my parents

INTRODUCTION

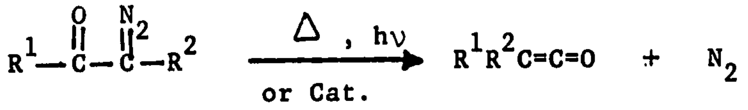
The chemistries of ketenes, thioketenes and other heterocumulenes have been comprehensively reviewed.[1] Almost all of the work that has appeared in the literature is limited to alkyl- and arylheterocumulenes.

Most of these heterocumulenes are very reactive and hence complicated experimental set-ups are required for their studies. Most often they are generated in situ, in solution, and, therefore, limits full understanding of the chemistry of these compounds. Silylsubstituted ketenes, -thioketenes, etc., being relatively stable, are of recent interest.[2] The thermochemistry of these heterocumulenes are almost unexplored and it deserves exploration.

This dissertation will, therefore, examine the kinetic and mechanistic aspects of 1,2-silyl migration on silylketenes, -thioketenes and -ketenimines. The reactivity of some of these cumulenes with other reactive molecules such as silylene and silene will be examined.

HISTORICAL

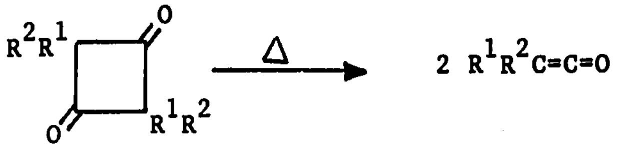
Ketenes, thioketenes and other heterocumulenes are important both from synthetic and mechanistic points of view. A great body of work which appeared in the literature was recently reviewed.[1] Ketenes are perhaps the most important because of their extensive use in organic synthesis. Most often, they are generated in situ and are reacted with alkenes, alkynes and other unsaturated compounds intra-/or intermolecularly. A number of methods are available for synthesis of ketenes and interestingly, many of the methods widely used today to prepare stable ketenes were developed by Staudinger and others at the beginning of the present century. Some important general methods are outlined below:[3]

1. 

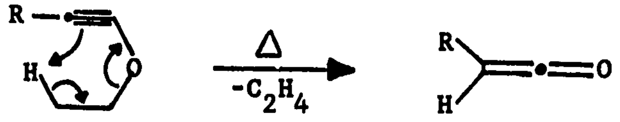
$$R^1-\overset{O}{\overset{\|}{C}}-\overset{N_2}{\overset{\|}{C}}-R^2 \xrightarrow[\text{or Cat.}]{\Delta\ ,\ h\nu} R^1R^2C{=}C{=}O \ + \ N_2$$

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

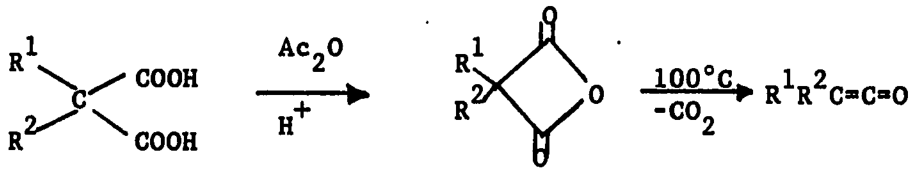
3. $R^1R^2CBr\text{-}COBr \xrightarrow{Zn} R^1R^2C{=}C{=}O \ + \ ZnBr_2$

4. 

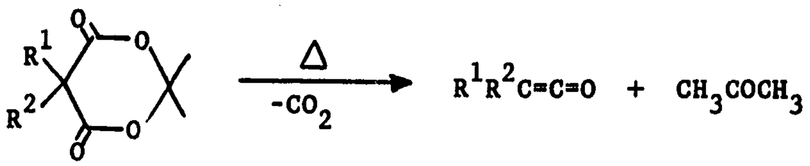
5.



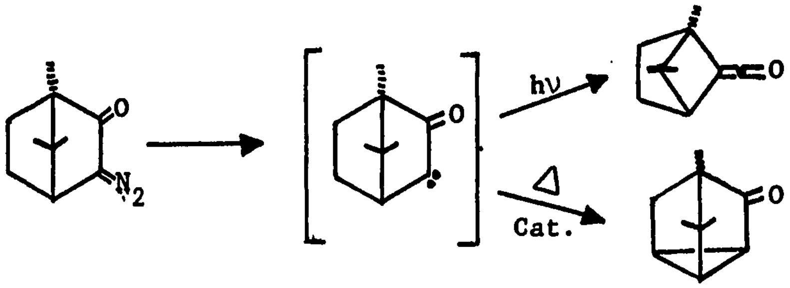
6. $R^1R^2CHCO)_2O \xrightarrow{550°C} R^1R^2C{=}C{=}O + R^1R^2CH\text{-}COOH$



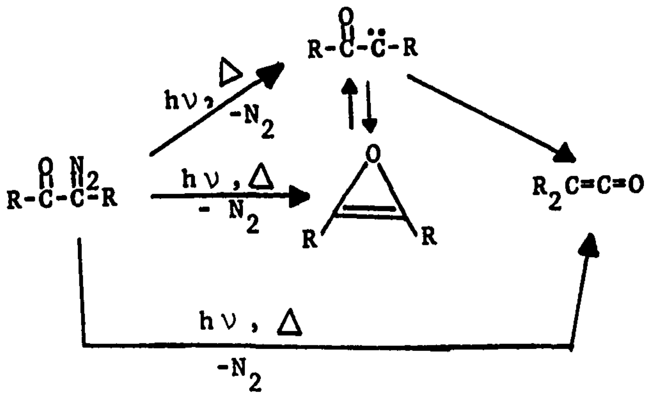
7.



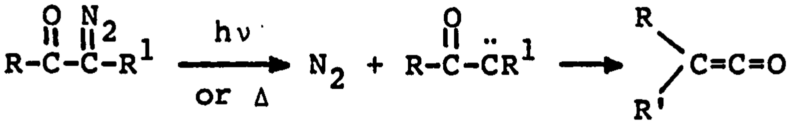
Because of its relevance, the Wolff rearrangement (WR) of α-diazocarbonyl compounds leading to ketenes will be discussed. This rearrangement is particularly useful for preparation of arylketenes. The WR can be brought about by thermolysis, photolysis and by catalysis.[4,5] Photochemically induced WR is frequently superior to other methods where C-H insertion by the intermediate carbene is avoided.



Several different mechanisms have been proposed for WR[4] and are summarized below.



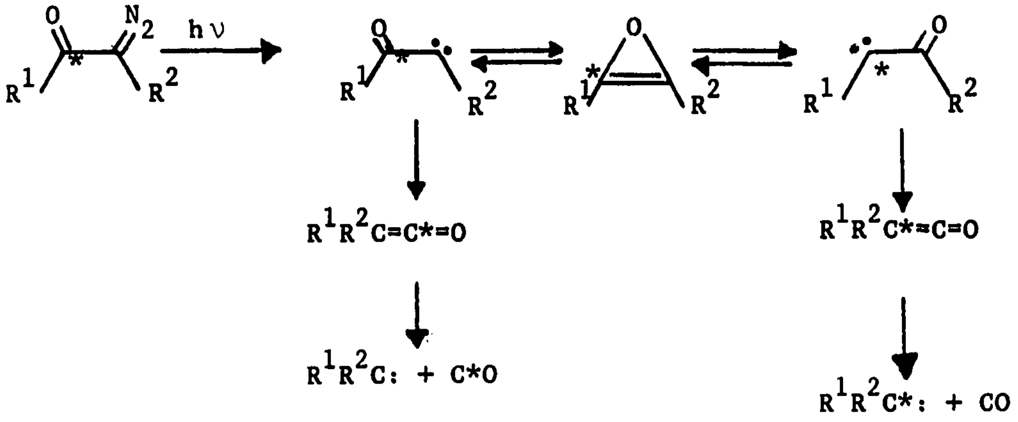
For a long time, the commonly accepted mechanism[4] was the formation of ketocarbene in spite of the lack of direct evidence at that time for its intermediacy. Later, the intermediacy of ketocarbene (as a precursor of ketene) has been determined by ESR spectra and by trapping experiments.[5] Very recently, spectroscopic characterization (through UV-vis, and IR in addition to ESR) of α-ketocarbenes (from



$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{N_2}{\|}}{C}\text{-}R^1 \xrightarrow[\text{or } \Delta]{h\nu} N_2 + R\text{-}\overset{\overset{O}{\|}}{C}\text{-}\ddot{C}R^1 \longrightarrow {}^{R}_{R'}\!\!>C{=}C{=}O$$

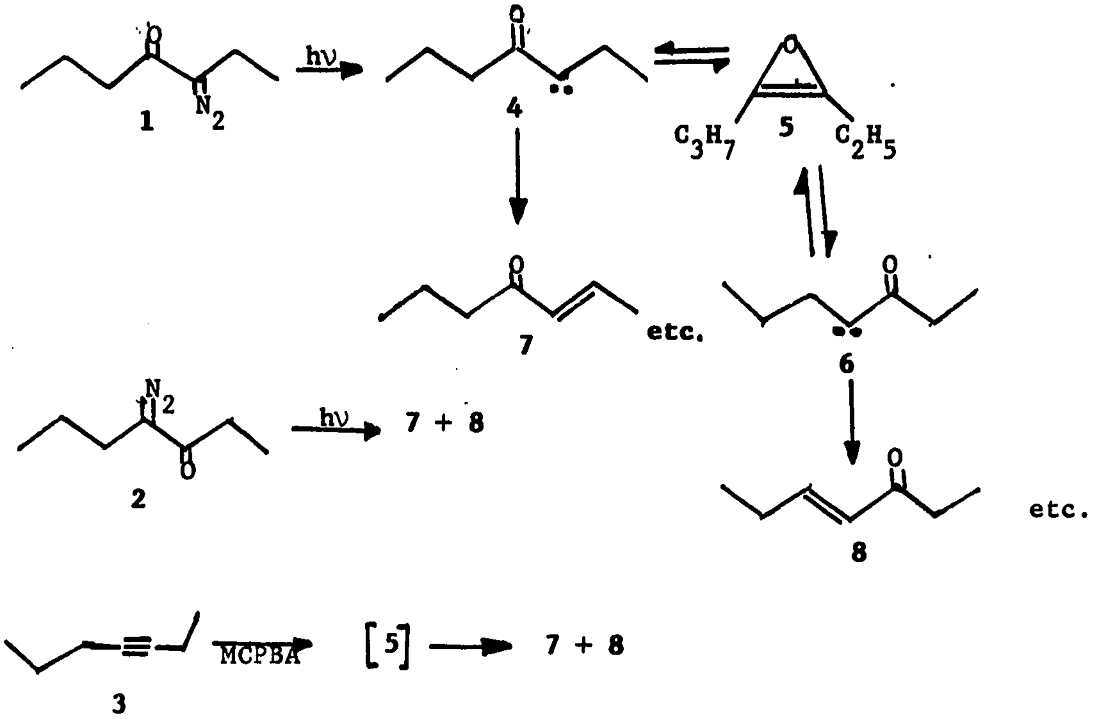
conformationally rigid α-diazoketones) and their trapping adducts with carbon monoxide and dioxygen have been reported.[6] It is claimed to be the first direct observation of nonconcerted Wolff rearrangements which proceed through α-ketocarbene intermediates.

The involvement of a species with the symmetry of an oxirene has been established from carbon-13 labeling experiments.[5,7] Thus, the gas phase photochemical WR of ^{13}C labeled 3-diazo-2-butanone and diazoacetone led to scrambling in the products, from which the extent of oxirene participation was calculated to be 100 and 16% respectively.[7]



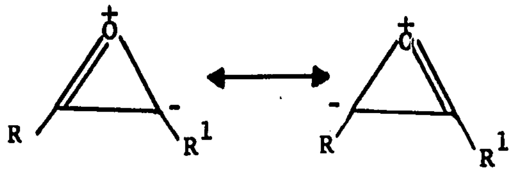
Ketocarbene-ketocarbene interconversion through oxirene intermediate or oxirene like transition state, has also been established from both thermal and photochemical studies of unsymmetrically substituted diazoketones (Scheme 1).[5]

Scheme 1



Participation of oxirene in the thermal decomposition of α-diazoketones is also observed and this is found to be strongly temperature dependent, higher temperature favoring oxirene formation.[5] Numerous theoretical calculations predict oxirene itself to be an energy minimum with a low barrier (2-8 kcal/mol) to rearrange to ketene. Singlet formylcarbene () rearranges to ketene with almost no barrier.[5]

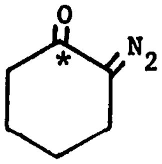
Ogata and coworkers found that peracid epoxidation of alkynes which professly proceeds through an oxirene, gave products which were inconsistent with a ketocarbene intermediate.[8] The authors concluded that oxirenes do not interconvert with ketocarbenes, and proposed that ketocarbene-ketocarbene interconversion proceeds through an ylide.



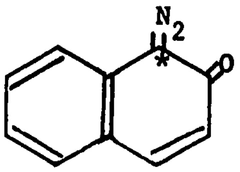
Lewars' recent example, however, suggests that isomerization of an oxirene to ketocarbene does occur.[9]

Thus, oxirene participation in both photochemical and thermal WR of a number of α-diazoketones has been demonstrated. Evidence suggests that ketocarbene-oxirene interconversion takes place on a singlet surface and only when ketocarbene is vibrationally excited.[5] Oxirene participation is more common in photochemical processes as excess vibrational energy is readily available. The required vibrational excitation is also accessible by thermal means and as expected, oxirene participation increases with increasing temperature.

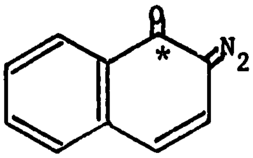
The extent of oxirene involvement in the WR of α-diazoketones depends on a number of factors, the major one being relative rates of substituent migration and ring closure, the nature of the substituent, the phase, the solvent and the rate of S_1-T_0 intersystem crossing in ketocarbenes. Possible effects of ring strain on the WR of ketocarbenes were also investigated. Photolysis ($\lambda > 290$ nm) of the ^{13}C labeled diazoketones **9** to **12** in dioxane-water



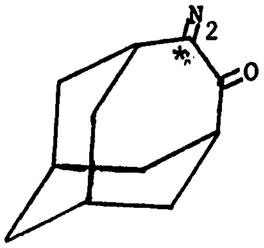
9



10



11



12

(10:1) led to no scrambling in the products and it was concluded that cyclic or annelated oxirenes are not formed because of high ring strain.[5]

In spite of great effort, direct experimental evidence for oxirene formation is rather weak. Recently, Torres et al. reported infrared characterization of both bis(trifluoromethyl)oxirene and trifluoroacetyl(trifluoromethyl)-carbene $(CF_3-\overset{O}{\ddot{C}}-CCF_3)$ under matrix isolation condition.[10] Leganis and coworkers, however, demonstrated that the species originally assigned as α-ketocarbene($CF_3CO\ddot{C}CF_3$) is actually the α-keto-diazirine isomer of the starting diazoketone.[11] Also, they failed to generate oxirene under irradiation conditions which were similar with those of Torres et al.

Oxirene formation also takes place in the gas phase photolysis of ketenes though to a lesser extent.[5b] This participation is 4% for phenylketene but 30% for diphenylketene. Mercury sensitized photolysis of ketene or of ketene generated from CH_2 ($^3B_2$) and CO did not show any scrambling. Ketenes produced from $CH_2(^1A)$ + CO reaction, however, showed oxirene formation. Once again, oxirene formation in the photochemical decomposition of ketenes, as in the WR, takes place on a singlet surface. A plausible mechanism for its formation was proposed.[12] This

rearrangement occurs in parallel and in competition with decomposition to CO and CH_2.

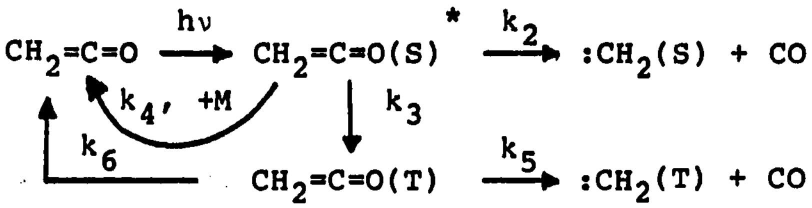
The photochemistry of ketenes has been reviewed.[4a] Ketene absorbs in the region 370-260 nm with λ_{max} = 330 nm and ε = 12. The major products in the photolysis of ketene are ethylene and carbon monoxide ($CO:C_2H_4 \geq 2:1$). This is accompanied by small amounts of cyclopropane, propene, ethane and acetylene. Ethane and acetylene result from radical side reactions. The photochemistry of ketene is observed to be wavelength dependent.

At ~270 nm, ketene dissociates to give carbon monoxide and methylene, the latter reacts with another molecule of ketene to produce ethylene and carbon monoxide.

$$CH_2{=}C{=}O \xrightarrow{h\nu} CH_2{=}C{=}O^* \longrightarrow :CH_2 + CO \qquad (1)$$

$$:CH_2 + CH_2{=}C{=}O \longrightarrow CH_2{=}CH_2 + CO \qquad (2)$$

At longer wavelength (~370 nm) excited ketene molecules react not only by dissociation (eq. 1), but also by collisional deactivation. The intervention of a triplet state of ketene is indicated from quenching experiment with cis-2-butene. A mechanism[13] that can account for the experimental results is as follows:



where "S" denotes a singlet state and "T" a triplet state. At short wavelengths, ketene in its excited state contains excess energy and k_2 will be larger than k_3 and k_4 (M). At long wavelengths, the situation is reversed.

Triplet methylene predominates in the mercury-sensitized decomposition of ketene.

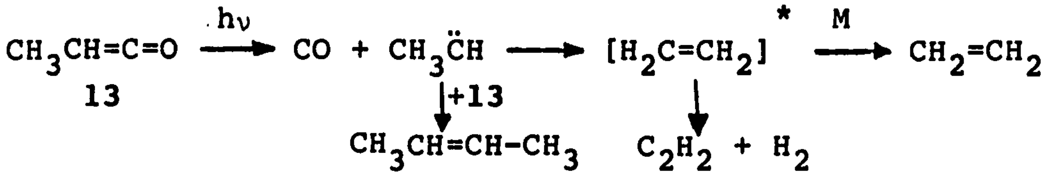
$$Hg\ (^3P_1) + H_2C{=}C{=}O \longrightarrow Hg\ (^1S_0) + H_2C{=}C{=}O\ (T)$$

$$H_2C{=}C{=}O\ (T) \longrightarrow :CH_2\ (T) + CO$$

Unlike singlet methylene, the triplet species appears to be rather long-lived. Combination of two triplet methylene molecules gives rise to "hot" ethylene which has been suggested as a source of acetylene and other secondary products of the mercury-sensitized decomposition of ketene.[14]

$$2\ CH_2\ (T) \longrightarrow CH_2{=}CH_2^{*} \longrightarrow HC{\equiv}CH + H_2$$

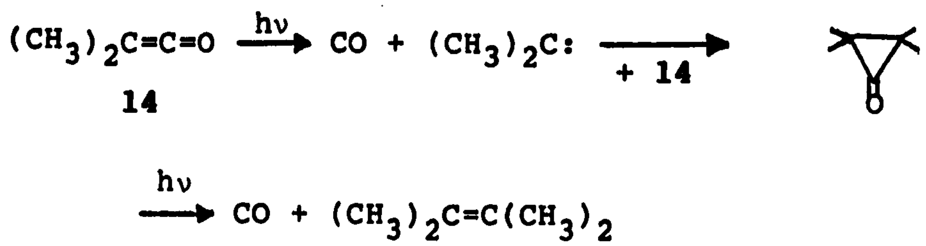
Photochemical behavior of alkyl ketenes in the vapor phase is somewhat similar to that of ketene. Thus major products in the photolysis of methyl- and dimethylketene are respectively ethylene and propene in addition to carbon monoxide. Ethylene and propene result from the unimolecular rearrangement of intermediate alkyl carbenes.[4a,5b] These intramolecular reactions are fast and consequently bimolecular products, 2-butene (from methylketene) and 2,3-dimethyl-2-butene (from dimethylketene) are minor only.



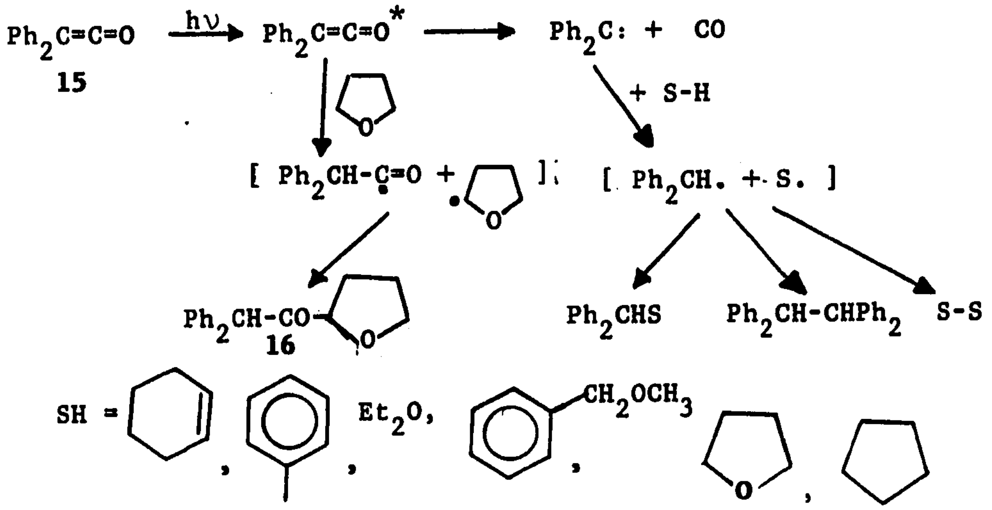
$$\begin{array}{ccccccc} \underset{13}{CH_3CH{=}C{=}O} & \xrightarrow{h\nu} & CO + CH_3\ddot{C}H & \longrightarrow & [H_2C{=}CH_2]^{*} & \xrightarrow{M} & CH_2{=}CH_2 \\ & & \downarrow{+13} & & \downarrow & & \\ & & CH_3CH{=}CH{-}CH_3 & & C_2H_2 + H_2 & & \end{array}$$

The "hot" ethylene either decomposes to acetylene and hydrogen or is stabilized by collisional deactivation. Increased yield of acetylene with photon of higher energy is in agreement with this proposal.

In cyclohexane solution, dimethylketene under photolysis at 253.7 nm, gave carbon monoxide and 2,3-dimethyl-2-butene as major products.[15] Formation of olefin is suggested to occur from the photolysis of intermediate tetramethyl cyclopropanone.



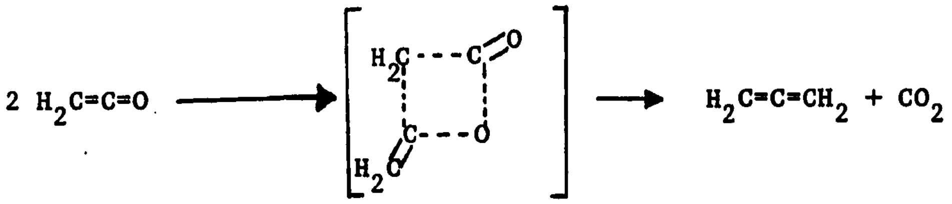
The photolytic behavior of diphenylketene in different solvents has been studied.[16,17] Some of the products originate from abstraction of hydrogen from solvent by diphenylcarbene, but the formation of acyloin product **16** can be attributed to photochemically excited ketene molecules.



Recent studies on the thermal decomposition of ketene itself can be divided into two classes:[18] (a) those at around 500°C in a static system and (b) those in the range 900-2000°C in a shock tube.

At lower temperature two groups[19,20] observed that the disappearance of ketene followed a second-order rate law, the Arrhenius equation being $k = 10^{10.0} e^{(-3500 \text{ cal/RT})} \text{ l mol}^{-1}\text{s}^{-1}$. At lower temperature and small extents of decomposition, the principal products are allene and carbon dioxide but at a relatively higher temperature or more extent of decomposition, carbon monoxide, ethylene and methane dominated. Addition of allene has been observed to increase the rate of formation of carbon monoxide. Carbon dioxide formation is also observed to follow a second order rate law with an activation energy of 35 kcal/mol.

It is, therefore, proposed that allene and carbon dioxide form in a bimolecular process through a transition state having some resemblance to the diketene structure. Mechanism of carbon monoxide formation is rather complex and



probably produced in a chain reaction initiated by radicals produced in the decomposition of allene.[19]

$CH_2{=}C{=}CH_2 \longrightarrow :CH_2 + C_2H_2$ etc.

The initial step in the high temperature decomposition of ketene is unimolecular with the formation of carbene and carbon monoxide. Tsuda and Kuratani,[21] for example, in shock tube experiments (1140-1530 K) obtained an order of 1.5 for formation of carbon monoxide, i.e., for disappearance of ketene with rate constant $k = 10^{14.2} e^{(-65000\ \mathrm{cal/RT})} l^{-1/2} mol^{-1/2} s^{-1}$. The initially formed carbene ($:CH_2$) reacts readily with ketene and a chain reaction follows. The rate of ketene disappearance was not

$CH_2{=}C{=}O \longrightarrow :CH_2 + CO$

$:CH_2 + CH_2{=}C{=}O \longrightarrow C_2H_4 + CO$

$:CH_2 + CH_2{=}C{=}O \longrightarrow {}^{\bullet}CH_3 + H\underset{\bullet}{C}{=}C{=}O$

${}^{\bullet}CH_3 + CH_2{=}C{=}O \longrightarrow CH_4 + H\underset{\bullet}{C}{=}C{=}O$

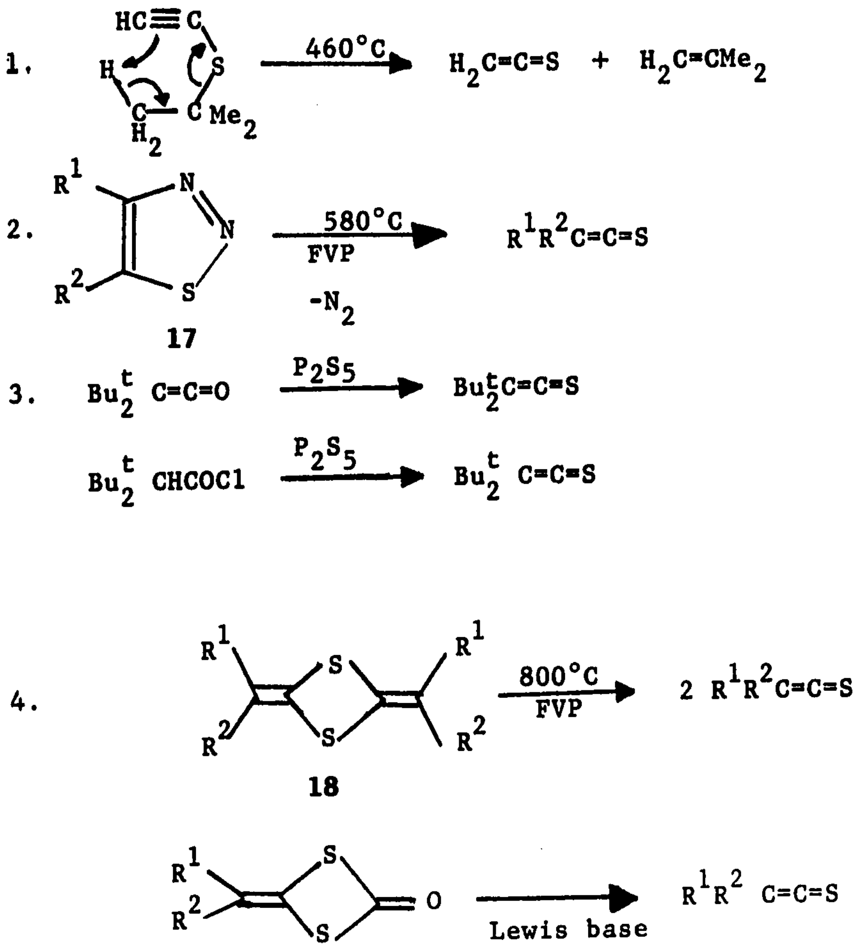
$CHCO \longrightarrow CH + CO$

$CH + CH_2CHO \longrightarrow CH_2 + CHCO$ etc.

affected by the addition of C_2H_4 or NO.

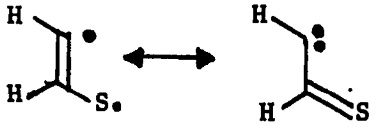
The decomposition kinetics of methylketene are similar in nature to that of ketene.[22] Carbon dioxide and penta-2,3-diene formed in equal amounts are the main initial products at 360°C, but carbon monoxide and 2-butene, and 1,3-butadiene and methane, increase with increasing temperature and extent of reaction. The order for both carbon monoxide and carbon dioxide is found to be 1.5. Productions of both CO and CO_2 are inhibited by added isobutene and affected by vessel surface. This, therefore, complicates the situation and a distinction between the mechanisms producing CO and CO_2 could not be made.[22]

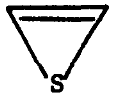
Thioketenes are more unstable than the corresponding ketenes. Only a few sterically hindered thioketenes such as bis(trifluoromethyl)- and di-t-butylthioketene are stable at room temperature. Thioketenes can be synthesized by different methods - a few are outlined below.[3]

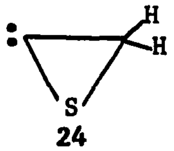


Flash vacuum pyrolysis (FVP) of 1,2,3-thiadiazoles (**17**) and 1,3-dithietane derivatives (**18**) constitute a general method for synthesis of thioketenes.[23] In the formation of thioketenes from 17, the intermediacy of thiirenes has been proposed.

Unlike oxirene, transient thiirene and its derivative are now well characterized spectroscopically at low temperature.[5b,24] Thiirene itself (**21**) was first invoked as the spin and symmetry allowed primary adduct in the S (^1D) plus acetylene reaction. Several possible isomeric forms of C_2H_2S species are shown.

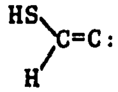

19 **20**


21


24

$HC\equiv C\text{-}SH$ $H_2C{=}C{=}S$

22 **23**

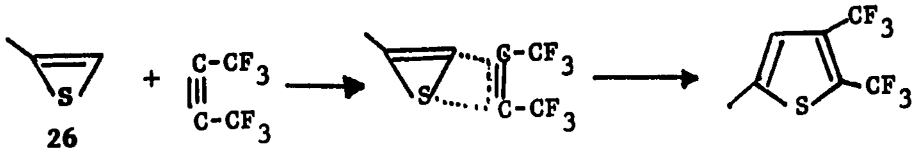

25

In the search for thiirene, the photochemistry of 1,2,3-thiadiazoles (**17**) was examined. One would expect nitrogen extrusion and the formation of singlet state diradical species **19** equivalent to **20**, a thioketocarbene. By analogy with the known reactions of ketocarbenes, WR to thioketene (**23**) could occur possibly via thiirene **21**.

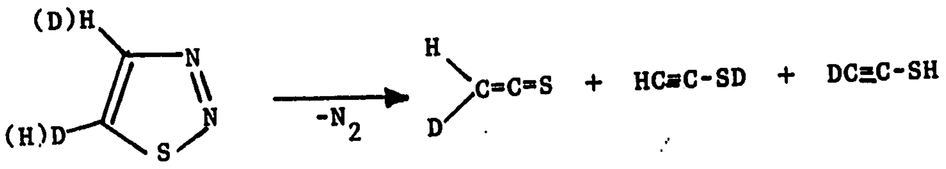
17 **19** **20** **21** **23**

Rearrangements to **22**, **24**, and **25** are also possible. Photolysis of either 4-methyl- or 5-methyl-1,2,3-thiadiazole in the presence of perfluoro-2-butyne led to only one thiophene, 5-methyl-2,3-bis(trifluoromethyl)thiophene.

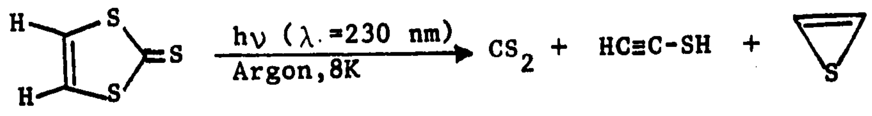
These results have been best explained as due to the reaction of common intermediate methylthiirene (**26**) and perfluorobutyne.

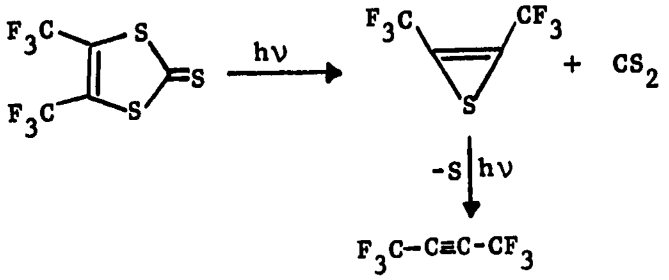


Analysis of the photolysis ($\lambda > 290$ nm) products of argon matrix isolated 1,2,3-thiadiazole by infrared spectroscopy indicated that only ethynyl mercaptan and thioketene had formed.[5b,24] Photolysis of either 4-deutero- or 5-deutero-1,2,3-thiadiazole produced monodeuterated thioketene and two isomeric mercaptans, implying a



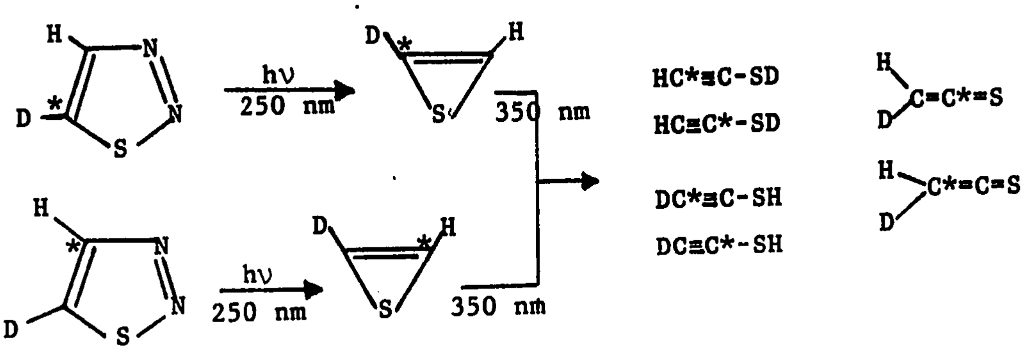
symmetrical precursor, most likely thiirene. Conducting photolysis at $\lambda = 230$-280 nm of 1,2,3-thiadiazole showed a new transient spectrum in addition to ethynyl mercaptan and thioketene. The same transient spectrum was obtained also in the photolysis ($\lambda = 230$-280 nm) of either 4-deutero- or 5-deutero- as well as 4-^{13}C- or 5-^{13}C-1,2,3-thiadiazoles. It was, therefore, concluded that the transient spectrum was due to thiirene.[24] A number of substituted thiirenes are also characterized by IR spectroscopy from photolysis of argon matrix isolated substituted thiadiazoles. Vinyltrithiocarbonate is observed to be an excellent source of thiirene generator.[5b]



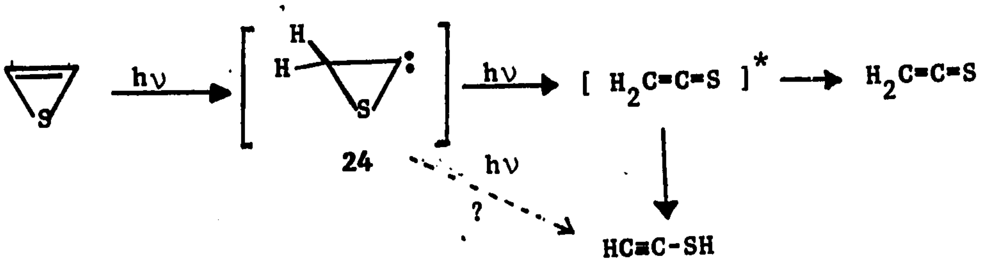


Bis(trifluoromethyl)thiirene is observed to be the most photostable of all the derivatives synthesized to date, presumably because, owing to the low migratory aptitude of CF_3, the thiirene-thioketocarbene rearrangement can not take place. Hence, perfluorobutyne and S atoms are photodecomposition products. Alkynes produced in the gas phase photolysis of 17 are probably formed via this mechanism.

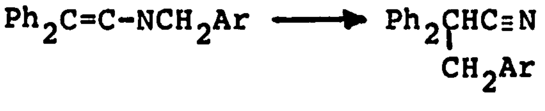
In order to understand more clearly the pathway leading to ethynyl mercaptan, photolysis was performed with doubly labeled (^2H, ^{13}C) 1,2,3-thiadiazoles.[24] Scrambling of labels was observed in the products. Careful irradiation of matrix isolated doubly labeled thiirene isomers gave the same four ethynyl mercaptans. It was concluded from these



labeling studies that there were two pathways originating from 1,2,3-thiadiazole (**17**) which gave rise to thioketene and ethynyl mercaptan. One stems from **17** without intervention of thiirene and does not scramble hydrogen or carbons; the other is mediated by thiirene which necessarily makes C-H bonds equivalent. Formation of all four possible ethynyl mercaptans from irradiation of doubly labeled thiirene, indicates one exchange of hydrogens between carbon atoms must occur. A plausible hypothesis would involve an intermediate in which both hydrogens reside on the same carbon at some point during photoisomerization of thiirene to ethynyl mercaptan.[24] Thiirenylidene (**24**) which is computed to differ from thiirene by ~0.3 kcal/mol, is considered as a candidate.

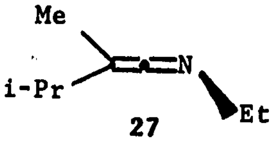


Ketenimines, like ketenes are very reactive and except arylsubstituted ketenimines, most of them are unstable at room temperature. The structure, preparation and properties of ketenimines have been reviewed.[1,25] The kinetics of the thermal rearrangement of some ketenimines are discussed here. Lee and coworkers[26] studied the kinetics of thermal rearrangement of a series of diphenyl-N(arylmethyl)-ketenimines to the corresponding nitriles at 25-65°C.

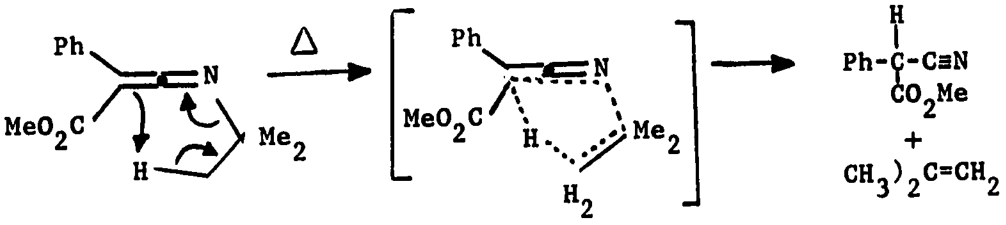


$$Ph_2C{=}C{-}NCH_2Ar \longrightarrow Ph_2\underset{\displaystyle CH_2Ar}{\underset{|}{C}}HC{\equiv}N$$

The reaction rates are found to be relatively insensitive to solvent polarity ($k_{CH_3CN}/k_{CCl_4} \leq 2.5$) and substituents in aryl group. These results along with free radical scavenging experiments indicate that the reaction occurs through a rate determining homolytic decomposition to a caged radical pair which subsequently efficiently recombines to nitrile. The effect of substituents on the free energy barrier to racemization of various ketenimines has been studied by NMR spectroscopy.[27] Substituents which can stabilize a negative charge on the carbon end of the heterocumulene lower the barrier. The highest barriers of about 14 kcal/mol were obtained with aliphatic substituents such as with **27**. Pyrolysis of ketene-N-butylimines at 140-160°C in solution gave isobutene and nitrile.[28] The reaction follows a first order kinetics having an activation energy of 30 kcal/mol and entropy of activation of -8.0 e.u. A retroene reaction forming a cyclic six-centered transition state is proposed.

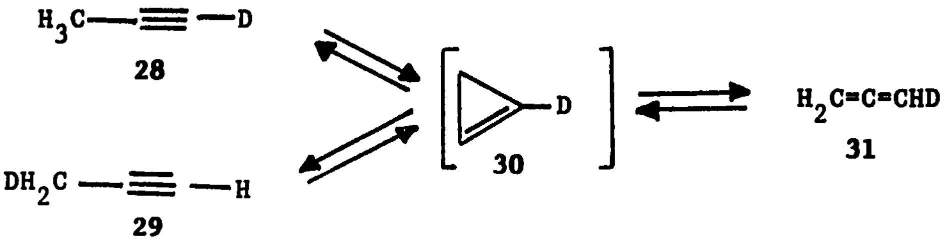


27

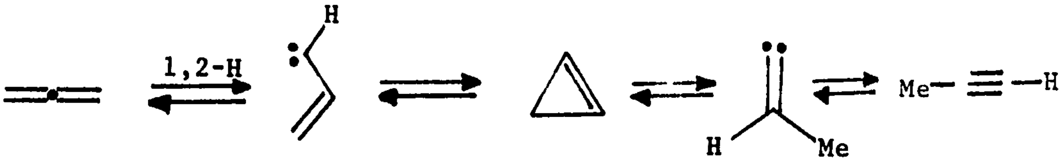


The thermochemistry of cumulenes such as allene is now being studied. Until recently, the thermal isomerization of allene to propyne was suggested to occur by 1,3-hydrogen shift in a concerted manner.[18] Recent evidence[29] suggests a two-step process involving cyclopropene as an intermediate. Thus, when 1-deuteriopropyne (**28**) is pyrolyzed in a flow of nitrogen at 500-700°C it isomerizes more rapidly to 3-deuteriopropyne (**29**) than to 1-deuterioallene (**31**).[29]

This is rationalized by postulating intermediacy of cyclopropene **30**. A 1,2-H shift is required to form



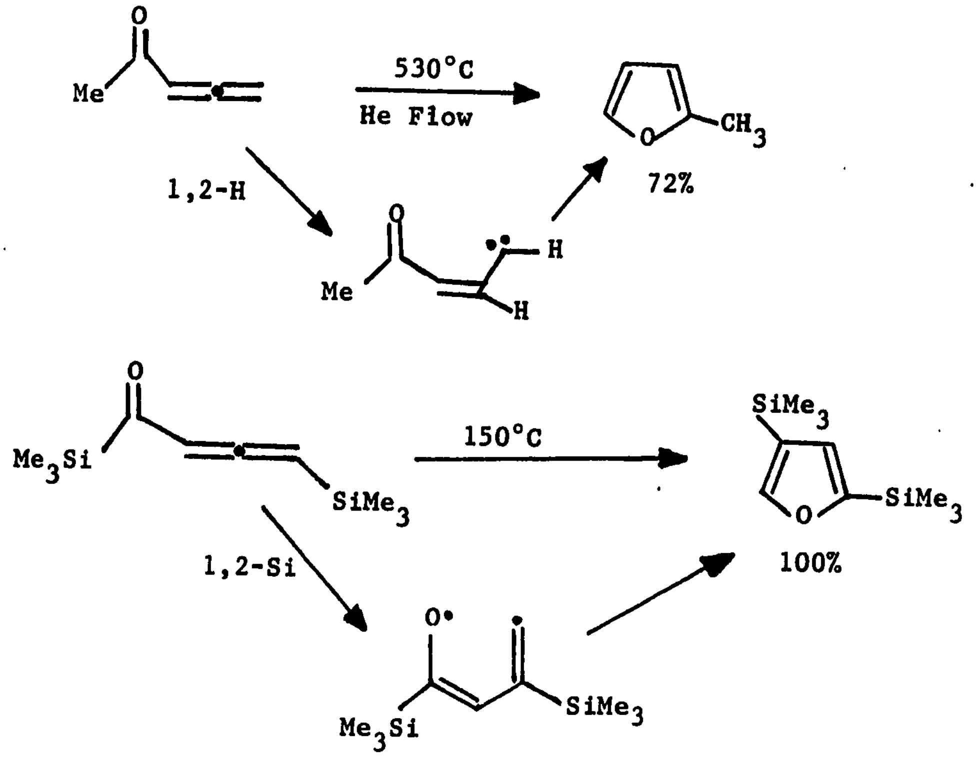
cyclopropene intermediate. This postulate has been confirmed by ab initio calculations of Honjou et al.[30] who have shown that the most favorable pathway for interconversion of allene to propyne involves an initial 1,2-H shift to form vinylcarbene and that cyclopropene is indeed, an intermediate in this rearrangement. Among the several intermediates, cyclopropene is calculated to be the lowest energy species in this rearrangement. The proposed pathway for allene to propyne conversion is shown below.



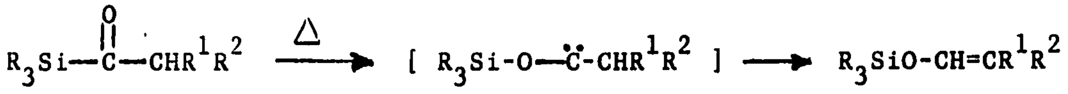
A rather general observation is that silyl groups migrate more readily than those of carbon groups or hydrogens.[31] Comparison of the results in the thermal isomerization of methyl allenylketone to 2-methylfuran[32] at 530°C and trimethylsilyl-3-(trimethylsilyl)-allenylketone to

2,5-bis(trimethylsilyl)furan[33] at 150°C suggests that 1,2-silyl shifts are more facile than 1,2-hydrogen shifts (Scheme 2).

Scheme 2



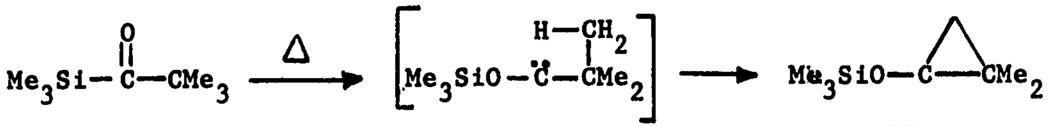
A variety of acylsilanes on thermal decomposition (>200°C, sealed tube) rearrange via 1,2-silyl shifts to give siloxyalkenes.[34] The reactions have been proposed to proceed through the intermediacy of a siloxycarbene which



$$R_3Si{-}\overset{O}{\overset{\|}{C}}{-}CHR^1R^2 \xrightarrow{\Delta} [\ R_3Si\text{-}O{-}\ddot{C}\text{-}CHR^1R^2\ ] \longrightarrow R_3SiO\text{-}CH{=}CR^1R^2$$

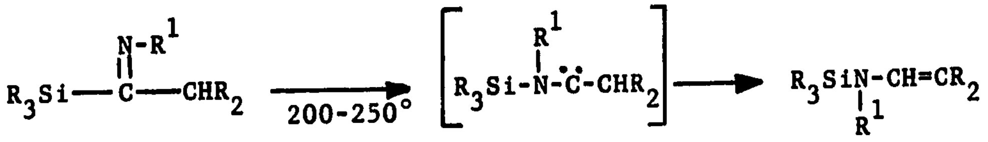
subsequently undergoes insertion into an adjacent C-H bond. Pivaloyltrimethylsilane (**32**) lacking α-hydrogen, on heating gave 2,2-dimethylcyclopropyloxytrimethylsilane (**33**) in 98%

yield. This, therefore, strongly supports the intermediacy of a siloxycarbene.

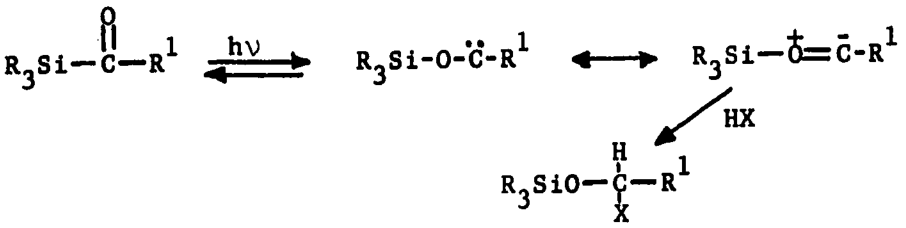


32 33

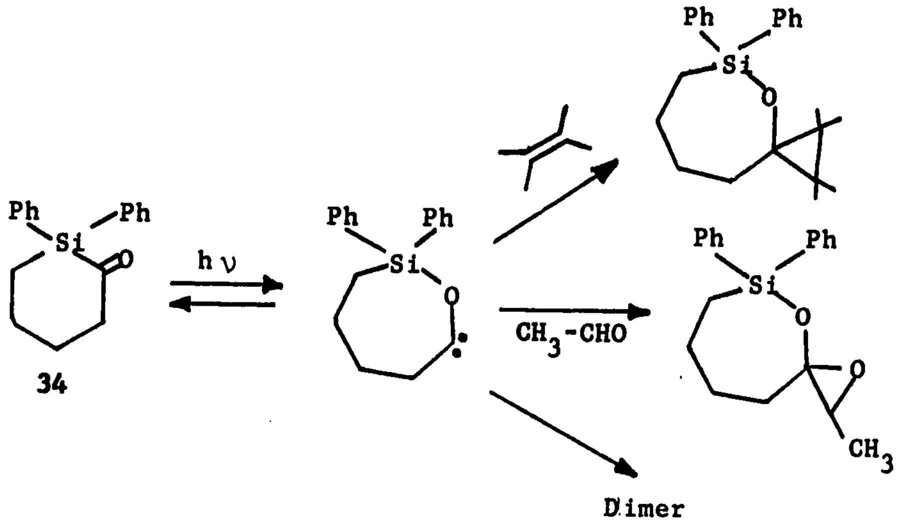
C-silylimines bearing α-hydrogen are reported to undergo similar rearrangement.[35]



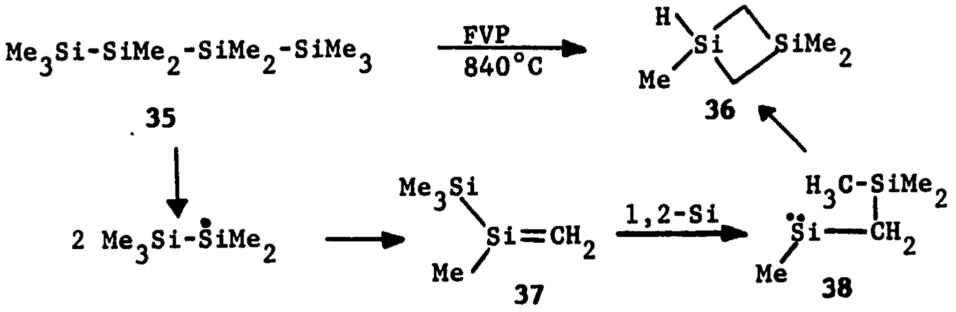
A 1,2-shift of a silyl group is also observed in the photochemical rearrangement of acylsilanes.[31] Intermediate



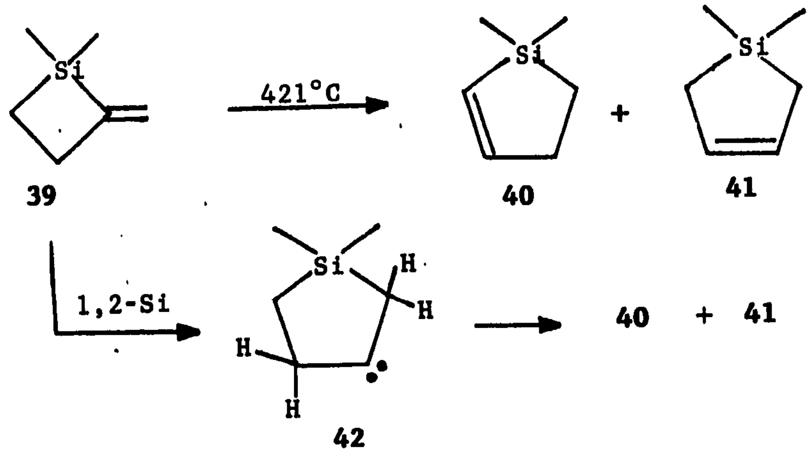
siloxycarbenes react readily with any molecule containing kinetically acidic hydrogen (alcohols, HCN, pyrrole, etc.) but, if not trapped, they revert to the parent acylsilane. Some trapping products from intermediate siloxycarbene are shown.[31]



Barton and coworkers[36] have reported formation of 1,3-disilacyclobutane **36** as the only volatile product in the FVP of several silanes. For example, formation of **36** in the FVP of decamethyltetrasilane (**35**) has been invoked through the intermediacy of silene **37**, followed by 1,2-silyl shift to give **38** which then inserts into γ-CH bond to produce **36**.

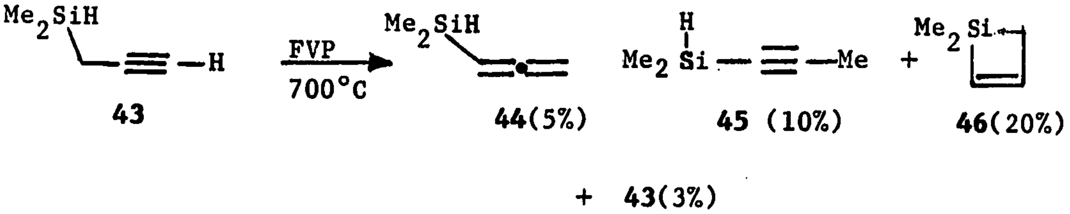


Conlin and coworkers[37] have observed formation of silacyclopentene isomers **40** and **41** (> 95%) in the pyrolysis of 2-methylene-1,1-dimethylsilacyclobutane (**39**). Results are best explained by the intermediacy of carbene **42** and its



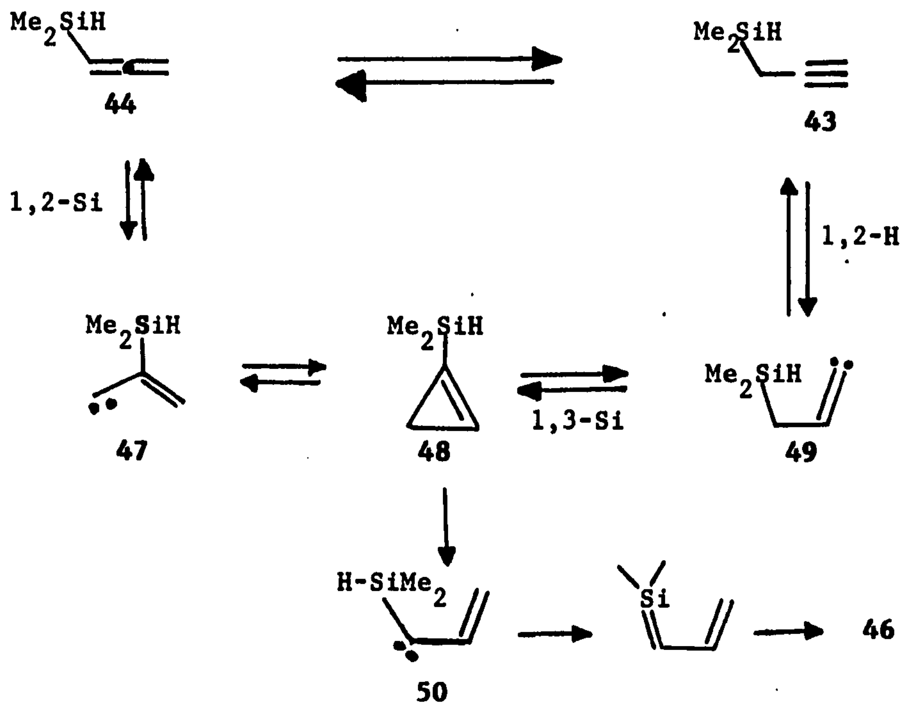
subsequent C-H insertion on either side to give **40** and **41**.

FVP of 3-(dimethylsilyl)propyne (**43**) at 700°C has been reported to give three isomeric products **44-46**.[38] Silanes **43** and **44** are expected to equilibriate,[39] and at higher



temperatures this equilibrium is considered[38] to bleed to **45**. Although a number of mechanistic possibilities exist for the formation of **46**, one initiated by a 1,2-silyl shift is shown here (Scheme 3).[38] Equilibration of **44** and **43** by

Scheme 3



such a pathway involving 1,2-silyl shifts is in agreement with the recent ab initio calculations on allene-propyne isomerization[30] discussed before. (Trimethylsilyl)allene-propargylsilane isomerization which has been presented as a concerted 1,3- migration of silicon,[39] is suggested[38] to follow the pathway shown in Scheme 3.

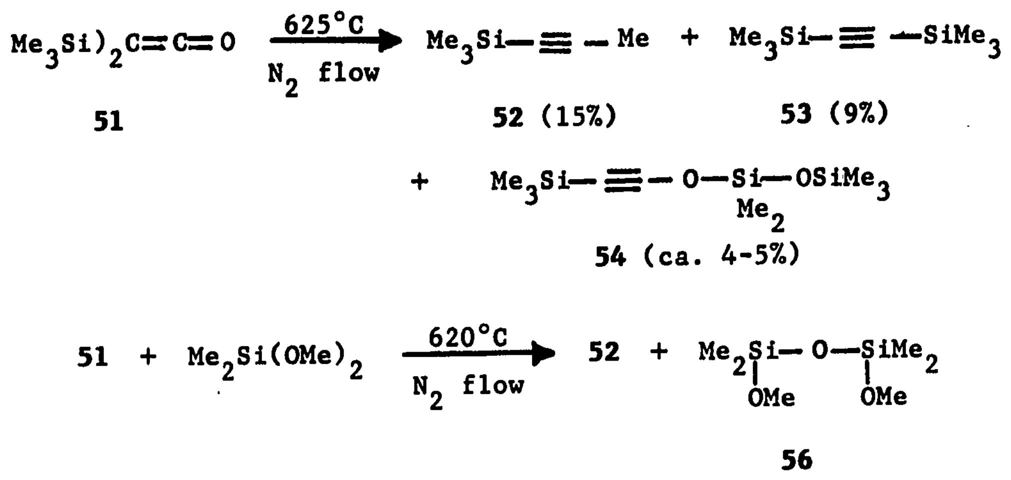
RESULTS AND DISCUSSION

Silylketenes, unlike alkyl- and arylketenes, are remarkably stable at room temperature. The stability of silylketenes led to investigate their reactivity with a few reactive intermediates. While studying the reactivity of dimethylsilene (generated thermally from 1,1-dimethyl-1-silacyclobutane) with bis(trimethylsilyl)ketene (**51**) under flow-pyrolysis conditions, it has been observed that **51** itself undergoes rearrangements. Recently Barton and Groh observed a remarkable extrusion of dimethylsilanone in the thermal decomposition of some hydridosilylketenes.[40] These observations inspired us to conduct a detailed study on the thermal decomposition of silylketenes.

Gas-phase thermal decomposition of silylketenes

Nitrogen-flow pyrolysis of **51** at 625°C led to three products. The products identified were 1-trimethylsilylpropyne (**52**, 15%) and bis(trimethylsilyl)acetylene (**53**, 9%) with an 89% mass recovery. A third product having a M^+ of m/e = 260 was detected in the GCMS. Attempts to isolate this compound by preparative GC were unsuccessful. The product based on GCMS data was tentatively assigned structure **54**. The presence of **52** and **54** warranted examination of the possible intermediacy of dimethylsilanone ($Me_2Si=O$). Thus, copyrolysis of **51** and dimethyl-

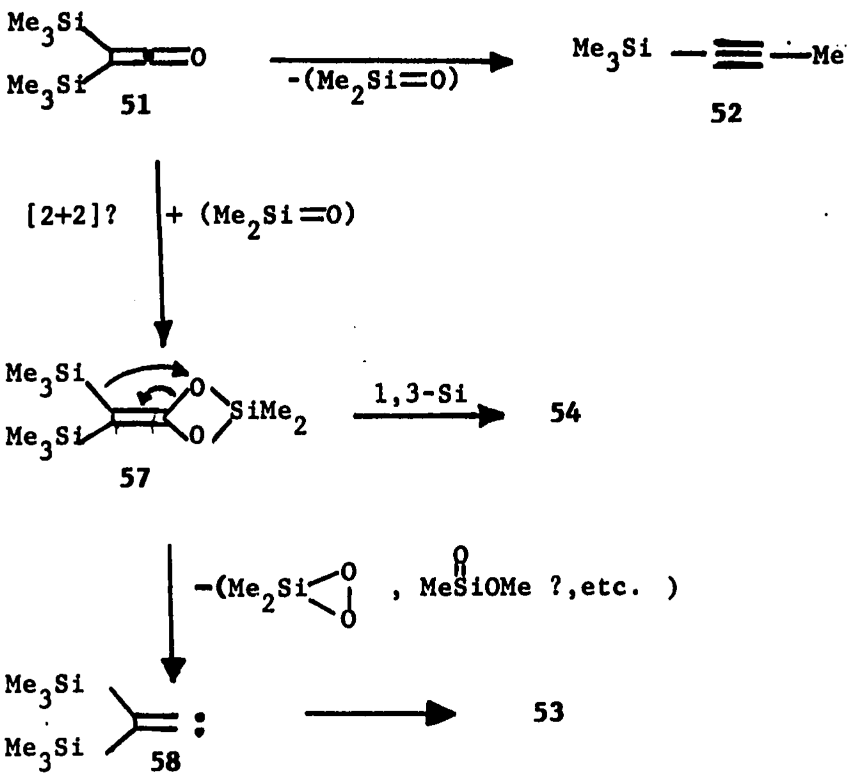
Scheme 4



(dimethoxy)silane (**55**) (a trap for $Me_2Si=O$) under the same experimental conditions led to only **52** along with the usual silanone trapped product **56** (Scheme 4).

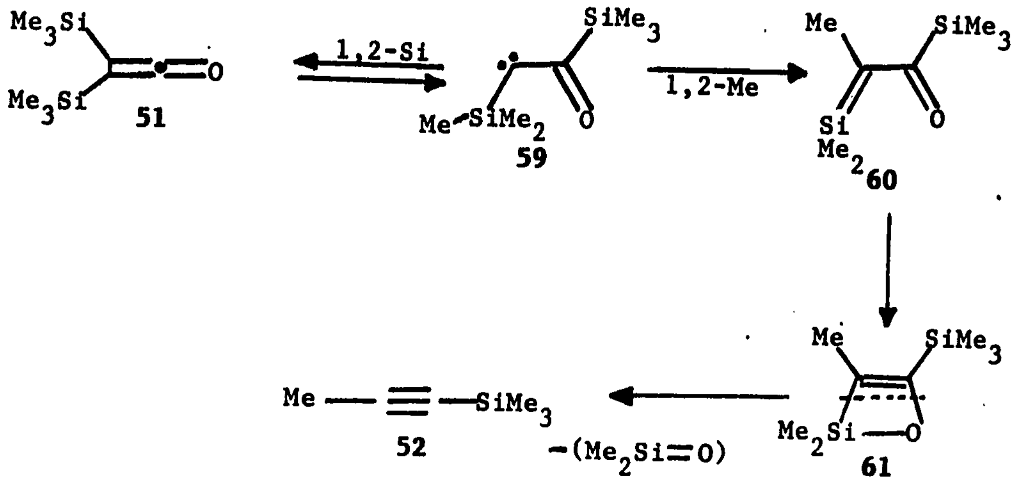
It appeared from these experiments that both **53** and **54** are derived possibly from a common intermediate; the intermediate is conceivably an adduct of ketene **51** and dimethylsilanone. It is reasonable to propose structure **57** as an intermediate, which can undergo 1,3-silyl shift to give **54** and/or it may lose Me_2SiO_2[41] species to give vinylidene **58**, the rearrangement of which affords **53** (Scheme 5). Dimethylsilanone, which is required for the production of **53** and **54**, is presumably extruded in the course of formation of **52** from **51**. Although several mechanistic pathways are possible for the formation of **52**, one involving

Scheme 5



a retro-Wolff rearrangement will be first considered. The first step is a 1,2-shift of a silyl group to the central carbon of the ketene **51** to produce ketocarbene **59**, followed by 1,2-Me migration to give silene **60** which then closes to **61**, and a retro 2+2 of **61** to **52** (Scheme 6). Conversion of **59** to **60** via a 1,2-Me shift is well precedented[43] and steps **60** to **52** are also well documented in the work of Sekiguchi and Ando.[44]

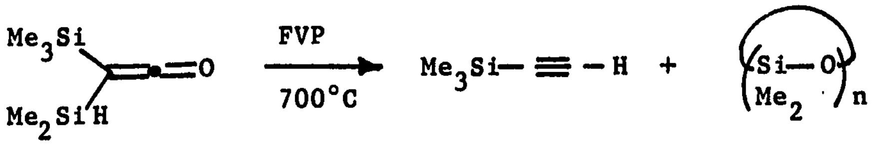
Scheme 6



Flash vacuum pyrolysis (FVP) of **51** at 834°C afforded, rather cleanly, 1-trimethylsilylpropyne (**52**) in 42% yield along with a trace of D_3 (mass recovery 76%). The yield was based on a 53% recovery of **51**. Ketene **51** was then pyrolyzed in a stirred-flow reactor (SFR) at 730.4°C. The apparent first-order rate constants for the formation of **52** from **51** were measured in an SFR both in the absence and in the presence of toluene (10- to 15-fold excess). Although small amounts of CH_4 and C_2H_6 were formed, the rate constants were found to be the same in both the cases indicating a nonhomolytic cleavage process for formation of **52**.

$$\mathbf{51} \xrightarrow[834^{\circ}C]{FVP} \underset{42\%}{\mathbf{52}} + \underset{\mathbf{62}}{D_3}$$

As has been pointed out, extrusion of dimethylsilanone in the thermal decomposition of certain hydridosilylketenes was observed.[40] For example, FVP of trimethylsilyl-(dimethylsilyl)ketene (**63**) at 700°C (67% completion) afforded (trimethylsilyl)acetylene (**64**, 76%) along with D_3 (22%) and D_4 (16%); D_3 and D_4 are usual products from oligometization of dimethylsilanone. In this preliminary study it was thought that an Si-H is required for this



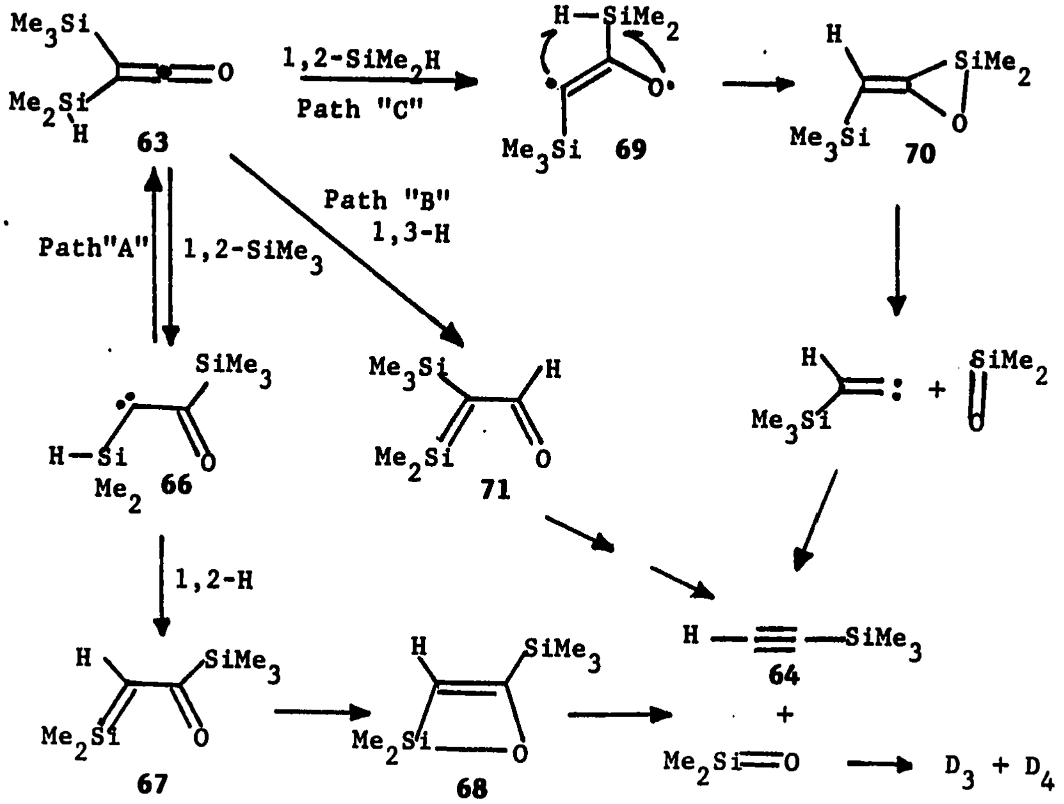
63 **64** (76%) **62**. n=3, D_3 (22%)

65. n=4, D_4 (16%)

decomposition and accordingly a few mechanistic possibilities were considered (Scheme 7).[40] It now appears that the presence of an Si-H is not a requirement as ketene 51 undergoes similar decomposition. Very recently we have reported similar results in the thermal decomposition of silylthioketenes.[45]

It is reasonable to assume that a single general mechanistic route is responsible for thermal decomposition of silylketenes. Among the several mechanistic possibilities (Scheme 7), pathway B involving a 1,3-H shift from silicon to central carbon of ketene **63** is unprecedented

Scheme 7



and will not be considered further. The high yield of trimethylsilylacetylene (**64**) can be better accounted for by pathway A than by pathway C. One would not expect abstraction of a hydrogen and recombination in **69** to give **70** to be a high yield process. On the other hand, rearrangement of carbene **66** to **67** is expected to be a high yield process and in fact both experimental and theoretical works are supportive of this. We will favor mechanistic path A largely because there are excellent precedents for each of the steps from **66** to dimethylsilanone. Conversion of **66** to **67** via a 1,2-H shift is well precedented on both experimental[43] and theoretical[46] works. Step **67** to **68** leading to products is well documented in the work of Sekiguchi and Ando.[44] As has been mentioned, a step similar to **63** -> **66** is supported by recent ab initio calculations on allene to propyne isomerization.[30] It became of great interest then to see whether such a step initiated by a 1,2-silyl migration directly leading to ketocarbene **66** (a retro-Wolff rearrangement) is involved in the decomposition of silylketenes. This was tested by studying the decomposition kinetics of **63** in an SFR from 506-580°C with reactant partial pressures of 0.18 to 0.20 torr. The first-order rate constants for the formation of trimethylsilylacetylene (**64**) were measured at different temperatures and the results are summarized in Table 1. The Arrhenius plot for the formation of **64** is shown in Figure 1, from which the activation parameters are evaluated and are included in Table 1. The activation parameters clearly rule out any process(es) involving bond homolysis and, therefore, support a retro-Wolff process. The decomposition of ketene **51** leading to products can be reasonably described by a retro-Wolff process as shown in Scheme 6.

In order to trap a ketocarbene such as **59** or **66** intramolecularly, isopropyl(trimethylsilyl)ketene (**72**) was synthesized.[47] FVP of **72** at 750°C afforded six products

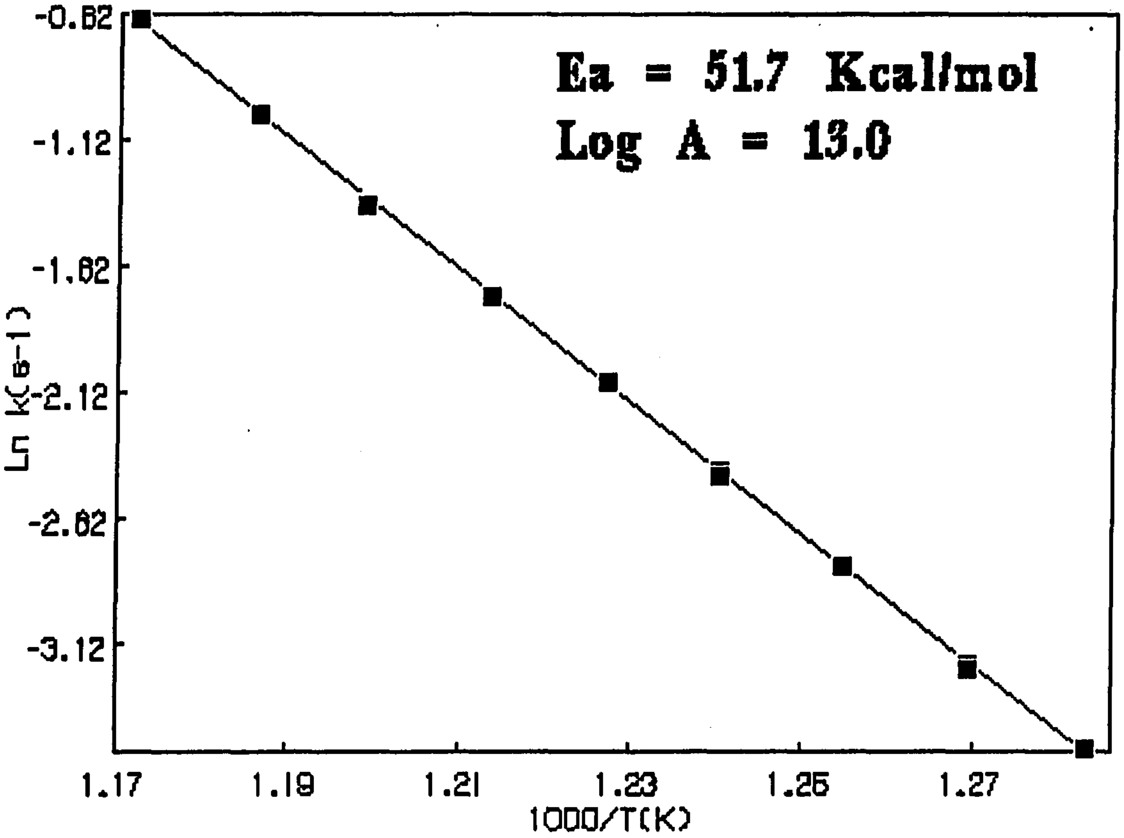


Figure 1. Arrhenius plot for formation of **64** in the decomposition of **63**

Table 1. Rate constants (k) for the formation of trimethylsilylacetylene (**64**) in the decomposition of trimethylsilyl(dimethylsilyl)ketene (**63**)

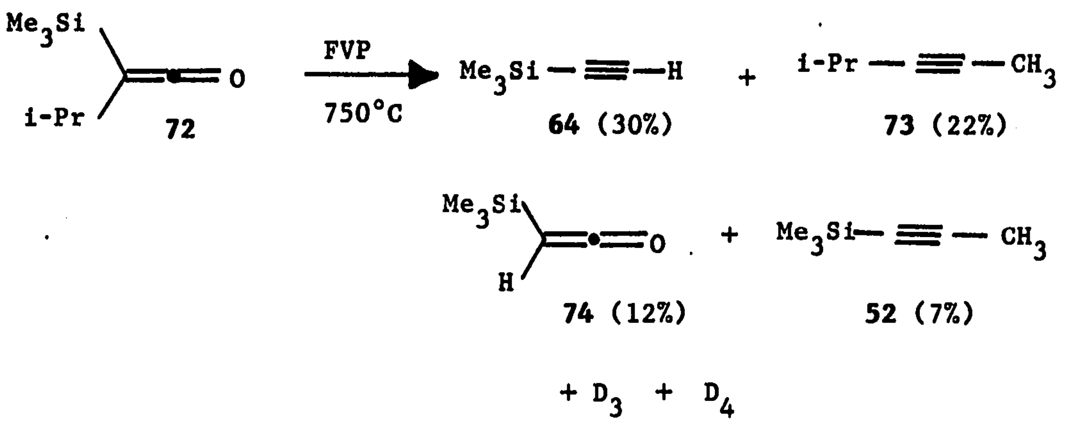
Run	k, sec^{-1}	temp, °C	Run	k, sec^{-1}	temp, °C
1	0.53218	580.1	9	0.12517	541.9
2	0.36019	570.0	10	0.08869	533.1
3	0.36255	570.0	11	0.08678	533.1
4	0.25515	561.0	12	0.06141	524.0
5	0.25367	561.0	13	0.06077	524.0
6	0.17494	551.2	14	0.04121	514.9
7	0.17724	551.2	15	0.04044	514.9
8	0.12654	541.9	16	0.02948	506.4

log A (s^{-1}) = 12.97 ± 0.06 ΔS# (e.u.) = -3.18 ± 0.27

Ea (Kcal/mol) = 51.7 ± 0.22.

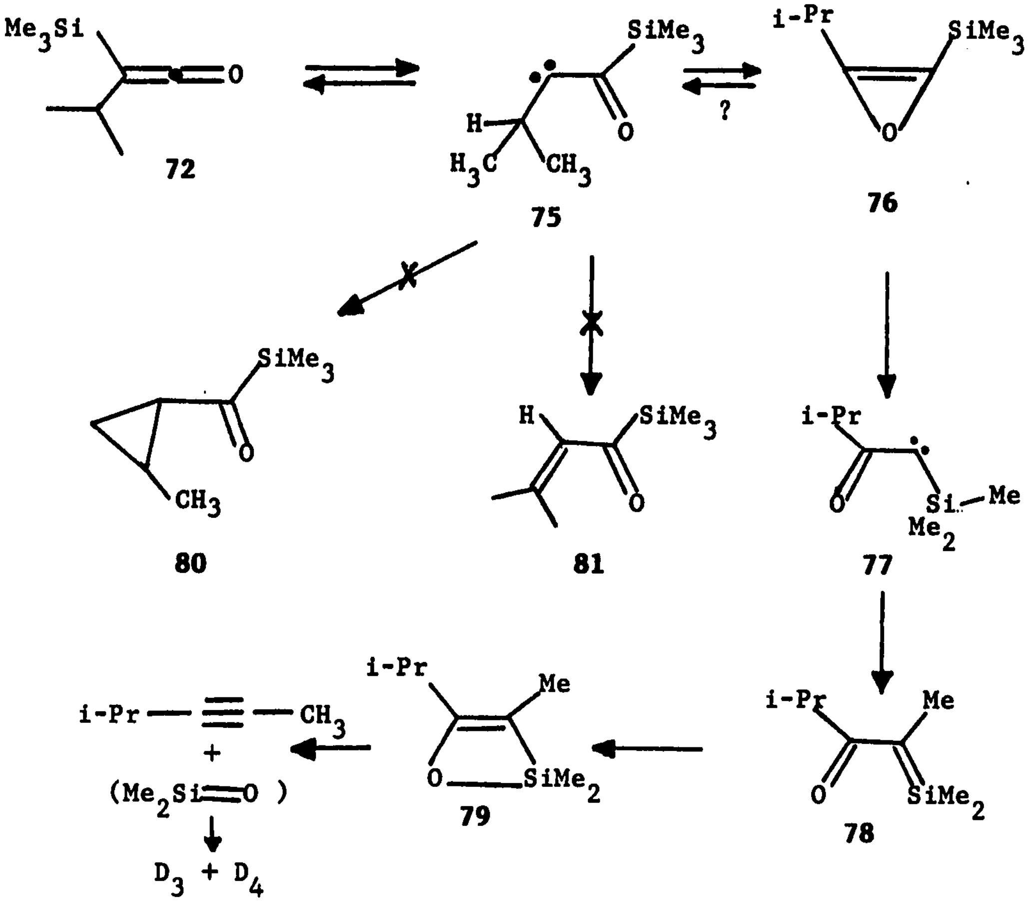
with a mass recovery of 78%. The products were identified as trimethylsilylacetylene (**64**, 30%), 4-methyl-2-pentyne (**73**, 22%), trimethylsilylketene (**74**, 12%), 1-trimethylsilylpropyne (**52**, 7%), in addition to trace amounts of D_3 and D_4. The yields were corrected for recovered starting material (**51**, 27%) (Scheme 8). Compound **72** was also pyrolyzed in an SFR at 660.8°C. In addition to the above-mentioned

Scheme 8



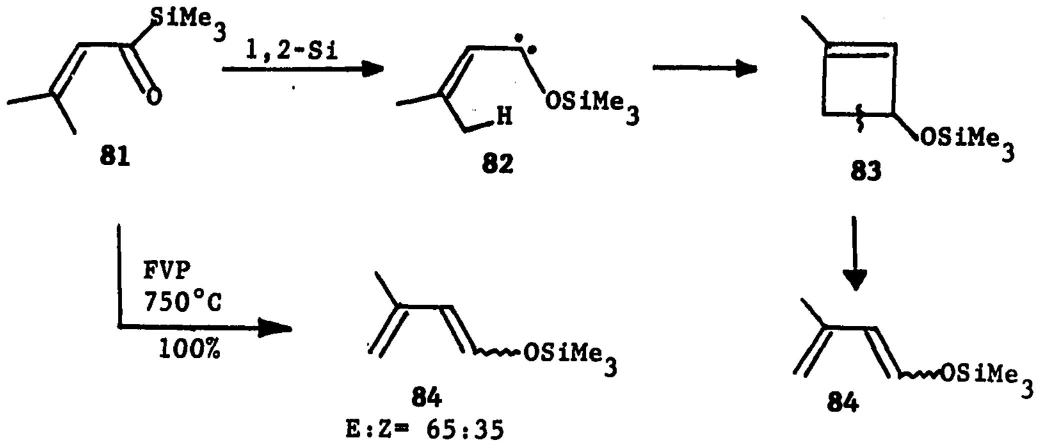
products, methane, ethane and propene were observed. It could be demonstrated that this product mixture did not simply arise from a single intermediate, rather a few competitive pathways were involved. One of the principal products, **73**, can be explained by invoking a 1,2-Si shift to produce carbene **75** which then interconverts to carbene **77** through oxirene **76**[5] (Scheme 9). Steps leading to products analogous to **77** to **79** were discussed before and are precedented.[43,44] The α,β-unsaturated silyl ketone **81**,[48] one of the most expected intramolecular carbene trapped products, was not formed in the FVP of **72** and this was demonstrated by pyrolyzing **81** under similar experimental conditions.

Scheme 9

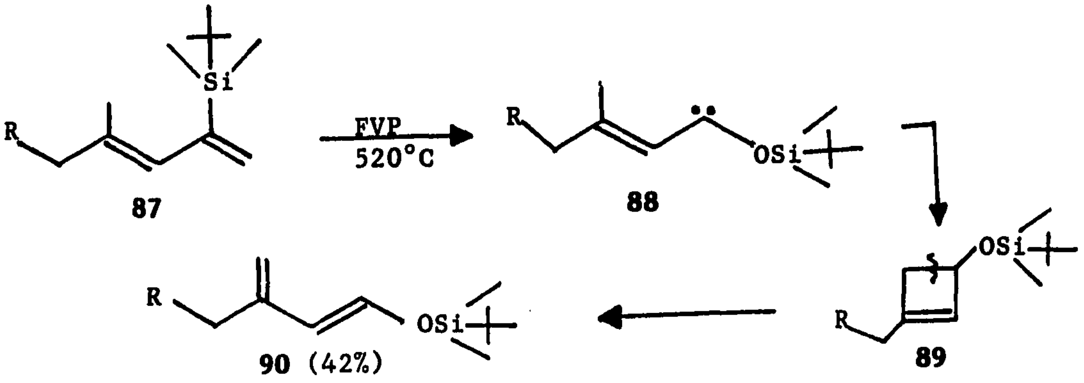


FVP of **81** at 750°C (100% conversion) afforded almost quantitatively 3-methyl-1-(trimethylsiloxy)butadiene (**84**, E:Z = 65:35) (Scheme 10). This remarkable transformation presumably involves a 1,2-silyl shift to oxygen[31] to form carbene **82** which then inserts into the allylic C-H bond to give cyclobutene **83**, ring opening of the latter leads to **84**. Formation of both cis- and trans- forms of **84** is perhaps a result of thermal equilibration. Similar thermal rearrangements of α,β-unsaturated silyl ketones have been

Scheme 10

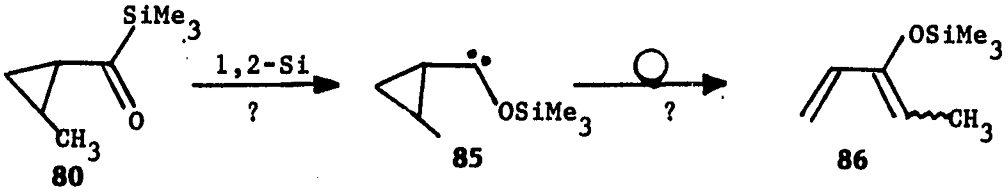


recently reported.[49] For example, silyl ketone **87** on FVP at 520°C (100% conversion) afforded **90** in 42% yield, and at



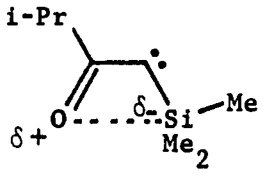
350°C (76% conversion) produced **90** in 32% yield along with isomerization of starting material (E:Z ≈ 5:1).[49a] Vinyl siloxycarbenes are unique in the sense that they do not undergo ring closure reactions to cyclopropenes as typically observed for vinyl carbenes.[50] Cyclopropene under the experimental conditions is expected to isomerize to allene and propyne derivatives which are totally absent in the present case.

It could also be shown that carbene **75** does not produce silyl ketone **80**. Ketone **80** is expected to undergo a 1,2-silyl shift to form carbene **85** which in an analogous fashion as suggested by Barton and Groh,[51] could ring expand



and open to give **86**. However, **86** was not a product in the FVP of **72**.

The rationale for **75** not being the precursor of **81** and **80** is as follows: Oxocarbene **75** which is presumably in rapid equilibrium with starting ketene **72** and perhaps also with oxirene **76**, has a very short lifetime as a free carbene to undergo 1,2-H shift and C-H insertion products **81** and **80** (Scheme 9). Carbene **77** once formed from **76** can be stabilized by Si-O interactions as shown by **77a**. This, therefore, allows a 1,2-Me shift from silicon to carbon to produce silene **78** which then goes on to the products. It is

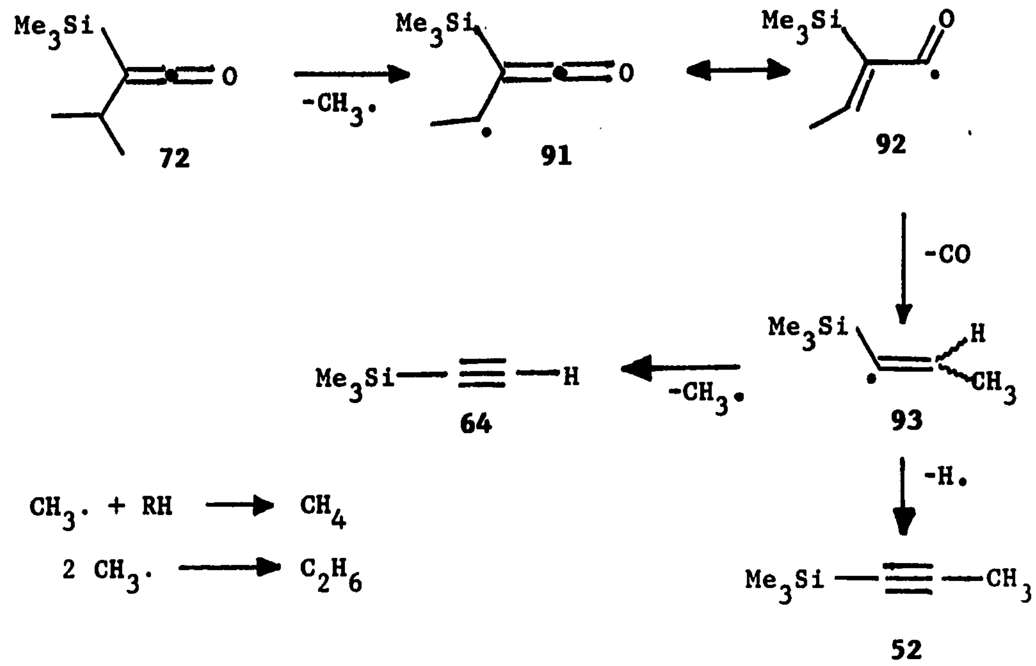


77a

possible that step **76** to **77** is essentially irreversible because of silicon-oxygen interaction as in **77a**, and **77** may then act as a siphon for product formation.

The retro-Wolff rearrangement mechanism discussed above (Scheme 9) accounts for only one of the major products. Several mechanistic paths were then considered for trimethylsilylacetylene (**64**, major product) and most of them were found inconsistent with the data. Production of CH_4 and C_2H_6 in the pyrolysis of **72** implies intermediacy of CH_3 radicals. It is quite likely that at such a high temperature (750°C) the isopropyl group of ketene **72** undergoes bond homolysis to produce methyl radicals. Ketene **72** was, therefore, subjected to copyrolysis with toluene at 660.8°C in an SFR. Copyrolysis of **72** and toluene-do (1:10 to 14) at 660.8°C led to a large increase in the yield of methane whereas the yield of ethane was reduced drastically. Other products were almost unaffected. Copyrolysis of **72** and toluene-d_8 (1:10) afforded CH_3D and CH_4 ($CH_3D:CH_4 \approx 9:1$) along with a small amount of C_2H_6. Hydrocarbons CH_3D and CH_4 were monitored by GCMS for their peak intensities respectively at $M^+ = 17$ and 16. These experimental results confirmed the production of CH_3 radicals in the pyrolysis of **72**. A homolytic cleavage mechanism can be put forward to explain the formation of **64** and **52** (Scheme 11). Ketene **72** can lose a methyl radical to form **91**. Hot radical **92** may then lose CO to give **93**. Subsequent loss of methyl and hydrogen radicals can afford **64** and **52** respectively.

Scheme 11



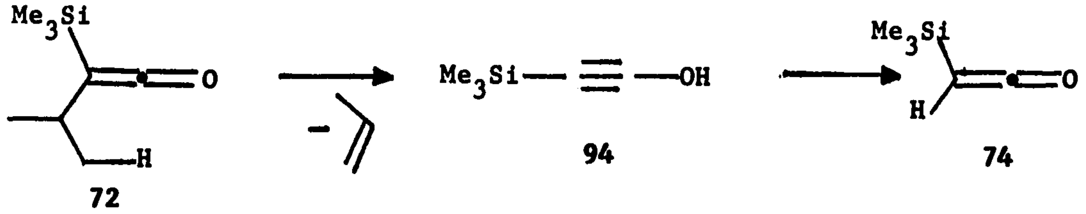
$CH_3\cdot + RH \longrightarrow CH_4$

$2\ CH_3\cdot \longrightarrow C_2H_6$

Formation of methane and ethane then can be explained respectively as due to abstraction of hydrogen from a substrate by methyl radical and by its dimerization. Although our experimental set-up did not allow us to detect CO, it is quite reasonable to lose CO from **92**. Similar mechanisms involving loss of methyl radicals and CO have been proposed for lower alkyl isocyanates such as isopropyl isocyanate.[52]

Formation of trimethylsilylketene (**74**) and propene in the pyrolysis of **72** can be rationalized by invoking a retro-ene process (Scheme 12). Intermediate **94** should

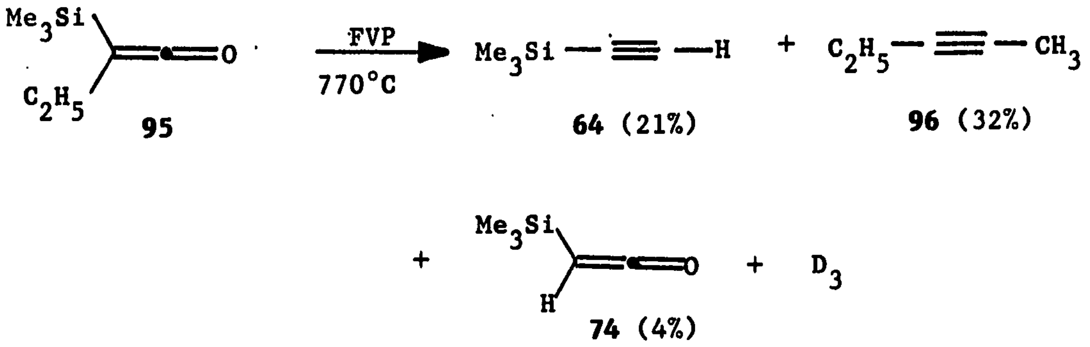
Scheme 12



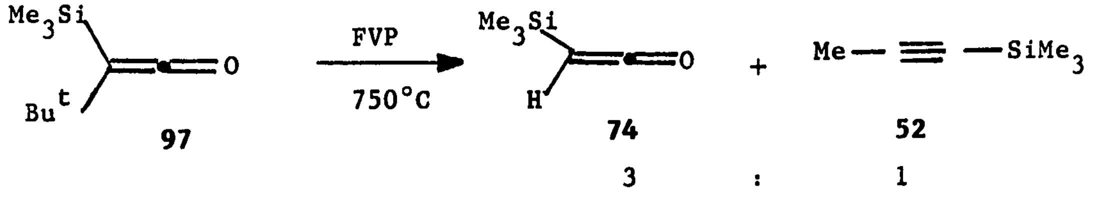
readily tautomerize to the ketene **74**.[53] For alkyl isocyanates a similar mechanism has been proposed.[52] In order to get further insight into this unimolecular mechanism attempts were made to study the kinetics of decomposition of **72**. The complex nature of the product mixture did not allow us to separate either propene and/or **74** from other components completely and hence, reliable kinetic data could not be obtained. As will be discussed, supportive evidence for this retro-ene mechanism came from the kinetic studies of the thermal decomposition of t-butyl(trimethylsilyl)ketene where formation of **74** (one of the products) could be monitored.

Thus, FVP products of isopropyl(trimethylsilyl)ketene are accounted for by three independent mechanistic pathways viz. (i) a retro-Wolff process, (ii) a homolytic cleavage process, and (iii) a retro-ene process.

In order to study the generality of alkyl(trimethylsilyl)ketene decomposition, ethyl(trimethylsilyl)ketene (**95**) and t-butyl(trimethylsilyl)ketene (**97**) were synthesized using analogous procedures[47] as used for ketene **72** (see experimental section). FVP of ethyl(trimethylsilyl)ketene (**95**) at 770°C (at 47% conversion) gave rise to **64**, 2-pentyne (**96**) and **74** in yields of 21%, 32%, and 4% respectively along with a small amount of D_3. Volatile C_1,C_2, etc., hydrocarbon products were not examined. The products obtained here are those which could be expected if the three mechanistic pathways discussed above were operative. Formation of **96** and D_3 follows a carbene mechanism (a retro-Wolff process), that of **64** follows a homolytic cleavage mechanism and that of **74** follows a retro-ene process.



FVP of ketene **97** at 750°C (ca. 70% conversion) afforded **74** and **52** in ca. 3:1 ratio. Pyrolysis of **97** in an SFR in the temperature range of 555-620°C produced **74** and **52**; in addition C_1, C_2 and C_4 hydrocarbon products CH_4, C_2H_6 and



isobutene were identified. Production of **52** from **97** can be accounted for by a homolytic cleavage mechanism (scheme analogous to 11) and that of **74** and isobutene can be explained by a retro-ene process. The expected carbene mechanism product (Bu^t-≡-Me), however, was not observed in the pyrolysis of **97**. This is perhaps due to the fact that homolytic cleavage mechanism and retro-ene process are energetically more favorable and carbene route can not compete.

A kinetic analysis of the thermal decomposition of t-butyl(trimethylsilyl)ketene (**97**) was performed in an SFR in the temperature range 552.4°-620.5°C with reactant partial pressures of 0.035-0.05 torr. The first-order rate constants for formation of trimethylsilylketene (**74**) were measured at different temperatures and are reported in Table 2. The Arrhenius plot is shown in Figure 2, from which the evaluated kinetic parameters are included in Table 2. Similar kinetic parameters were obtained for the thermal decomposition of t-butyl isocyanate (log A (s^{-1}) = 13.35 ± 0.08, Ea (Kcal/mol) = 51.7 ± 0.3).[52] The value of A ($10^{13.35}s^{-1}$) in t-butyl isocyanate does not distinguish between a 4-centered and a 6-centered transition state (**98** and **99**);[52] two rotations are lost in both types. Because of

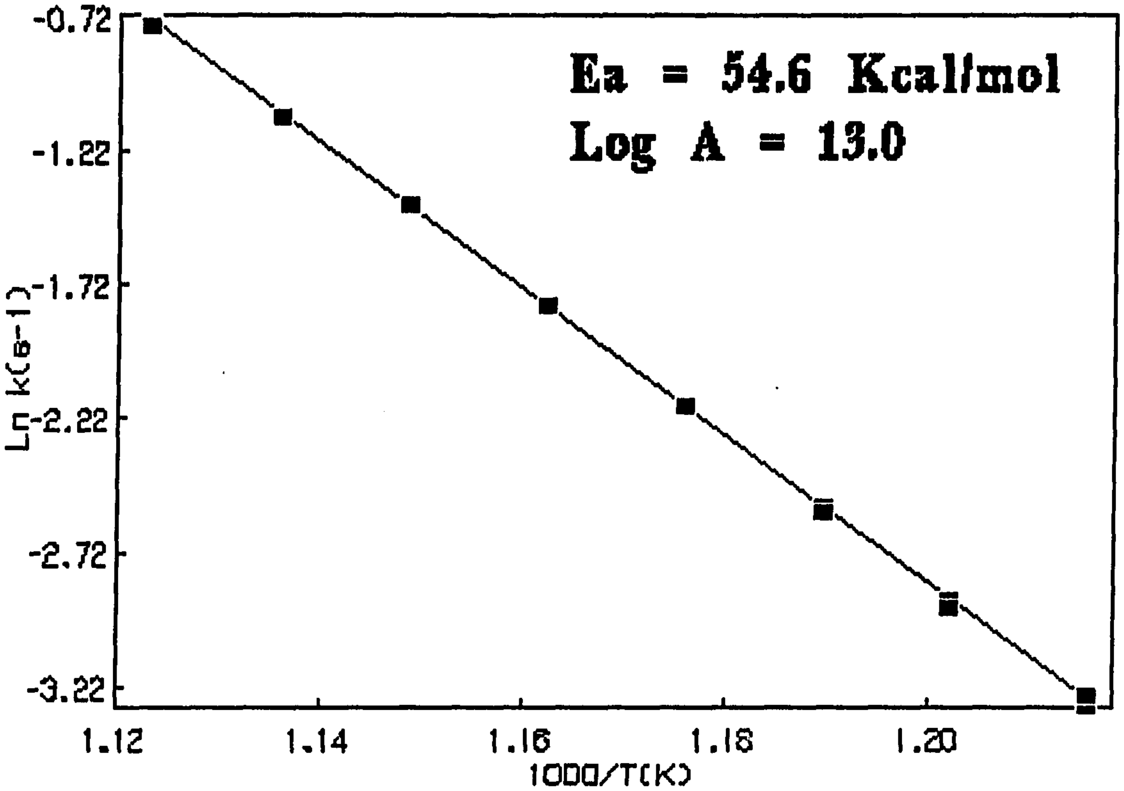


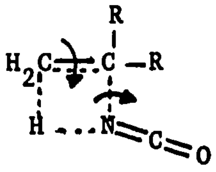
Figure 2. Arrhenius plot for formation of **74** in the decomposition of **97**

Table 2. Rate constants (k) for trimethylsilylketene formation (**74**) in the decomposition of tert-butyl(trimethylsilyl)ketene (**97**)

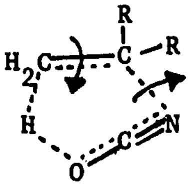
Run	k,sec^{-1}	temp; °C	Run	k,sec^{-1}	temp; °C
1	0.4795	620.5	9	0.1162	580.4
2	0.4742	620.5	10	0.1150	580.4
3	0.3365	610.4	11	0.0785	570.5
4	0.3385	610.4	12	0.0778	570.5
5	0.2435	600.6	13	0.0556	561.8
6	0.2430	600.6	14	0.0540	561.8
7	0.1661	590.4	15	0.0375	552.4
8	0.1673	590.4	16	0.0388	552.4

log A (s^{-1}) = 13.04 ± 0.06 $\Delta S^{\ddagger}$(e.u.) = −2.96 ± 0.28

Ea (Kcal/mol) = 54.6 ± 0.28.



98



99

the fact that isothiocyanates decompose much more readily than isocyanates, implying oxygen or sulfur are directly rather than indirectly involved, a six-centered transition state is indicated.[54]

The value of A ($10^{13}s^{-1}$) for ketene **97** also will not distinguish between 6-centered and 4-centered transition state structures but in accordance with isocyanate results a 6-centered transition state is preferred. In other words, a retro-ene mechanism can be proposed. A more definitive decision can be made from the synthesis and pyrolytic studies of t-butyl(trimethylsilyl)thioketene.

The results of FVP studies of silylketenes discussed above are summarized in Table 3. Several features are evident from the results in Table 3. For persilyl substituted ketenes (**51**, **63**) decomposition solely occurs by the retro-Wolff process. The lower thermal requirement for **63** (R = Me_2SiH) as compared with **51** (R = Me_3Si) could be ascribed to the greater migratory aptitude of hydrogen over methyl in Si-R (R = H, Me) to the generated carbenes (Schemes 6 and 7). For monosilylated ketenes with R equal to different alkyl groups, other mechanistic routes become increasingly important, and for R = Bu^t case, the retro-Wolff process does not compete with other routes. It is also evident that a retro-ene process is the predominant pathway for R = t-butyl compound, and this route becomes less important as R changes from Bu^t to i-Pr to Et group. This perhaps can be attributed to the number of available β-hydrogens to the ketene (a statistical factor). For ketene **97** the number of β-hydrogens (9) greatly facilitates

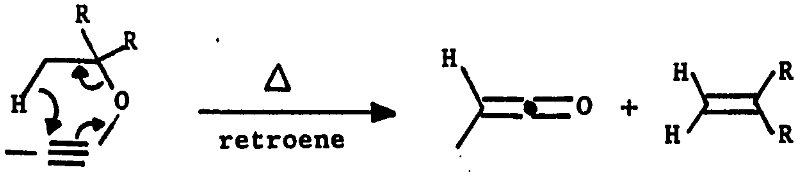
Table 3. FVP results of several silylketenes

Compounds	Products			
$Me_3Si\underset{R}{C}=C=O$	retro-Wolff	Homolytic	Retro-ene	Temp °C (% conv)
R = Me_2SiH[a] **63**	$Me_3Si-\equiv-H$ **64** (76%) D_3, D_4	-	-	700 (67)
R = Me_3Si **51**	**52** (42%) D_3	-	-	834 (47)
R = Et **95**	$C_2H_5-\equiv-Me$ **96** (32%) D_3	**64** (21%)	$Me_3SiCH=C=O$ **74** (4%)	770 (47)
R = i-Pr **72**	i-Pr-$\equiv$-Me **73** (22%) D_3, D_4	**64** (30%) $Me_3Si-\equiv-Me$ **52** (7%)	**74** (12%)	750 (73)
R = Bu^t **97**	-	**52** (ca. 15%)	**74** (ca. 46%)	750(70)

[a] FVP results of **63** were taken from ref. 40.

the retroene process. A similar trend has been observed for the related acetylenic ethers (e.g., **100** and **101**) having hydrogen atoms β to oxygen. These ethers decompose readily

Scheme 13

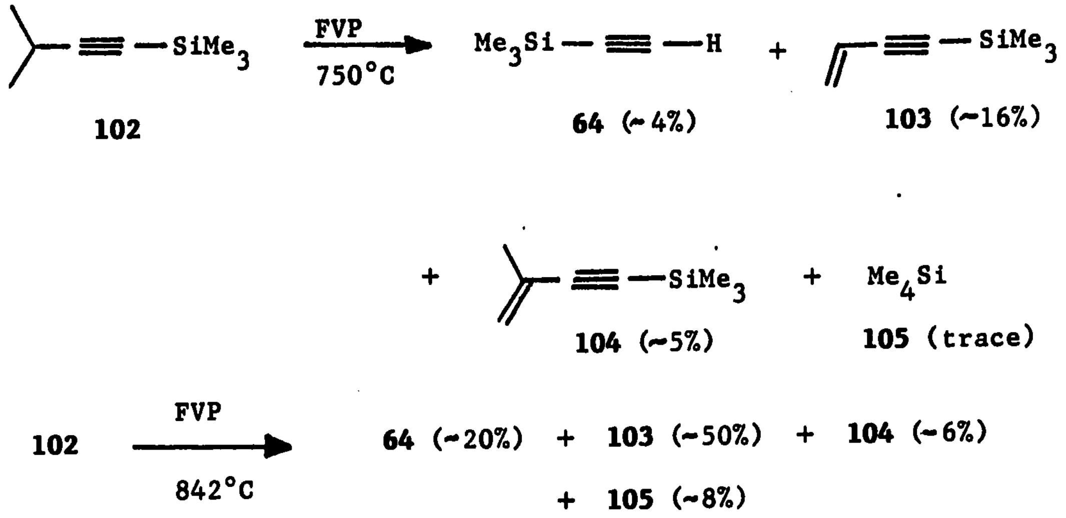


100. R= H, 120°C
101 . R= Me, 40°C

with loss of olefins leading to ketenes (Scheme 13).[55] Thus, t-butoxyacetylene (**101**) decomposes at a much lower temperature than the corresponding ethoxyacetylene (**100**).

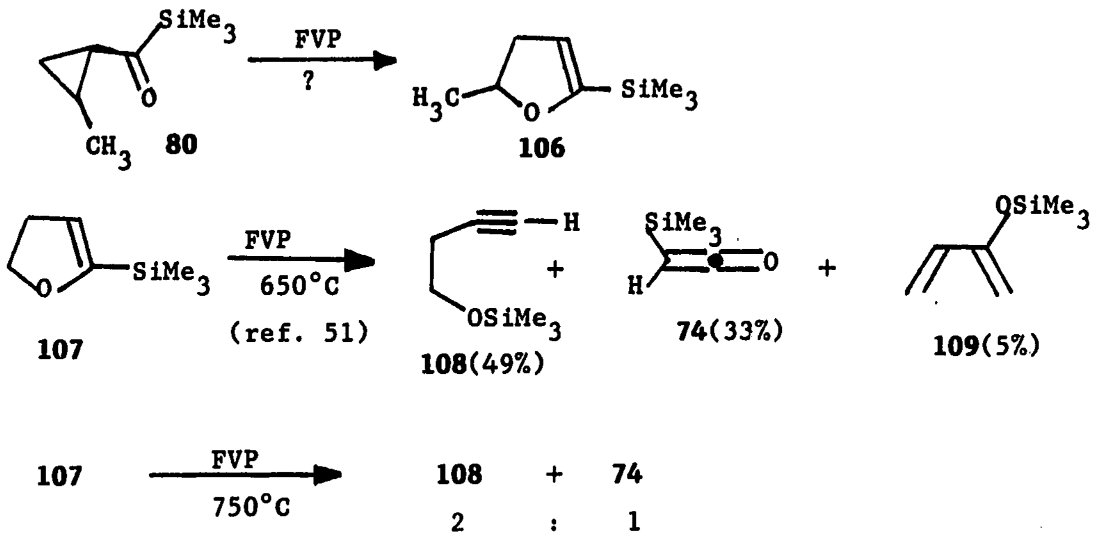
While investigating the mechanistic paths for the decomposition of **72** to **64** (Scheme 8), the possible intermediacy of isopropyl(trimethylsilyl)acetylene (**102**) was examined. FVP of **102** at 750°C (~30% conversion) afforded **64** (~4%), vinyl(trimethylsilyl)acetylene **103** (~16%), 4-methylvinyl(treimthylsilyl)acetylene **104** (~5%) and a trace of tetramethylsilane (**105**). The yields are relative GC yields and are uncorrected. Pyrolysis of **102** at 842°C led to the same products but in a different ratio (Scheme 14). It is clear from these results that **102** was not an intermediate in the decomposition of **72**.

Scheme 14



The possibility of insertion-product ketone **80** undergoing a vinyl cyclopropane type rearrangement to afford **106** was also scrutinized. The FVP of 2-(trimethylsilyl)-4,5-dihydrofuran (**107**) at 650°C has been reported,[51] and in the present study, results at 750°C have been examined (Scheme 15). Dihydrofuran **106** would also be expected to give similar products, and clearly the results do not support the intermediacy of **106**.

Scheme 15

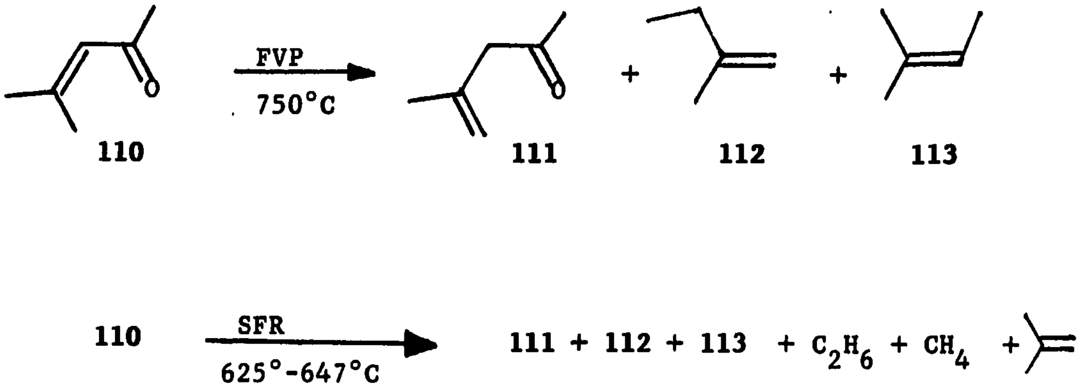


Thermal decomposition of α,β-unsaturated ketones

While assessing the possibility of the intermediacy of α,β-unsaturated silyl ketone **81** in the gas phase decomposition of **72**, it was deemed necessary to study the thermal decomposition of corresponding α,β-unsaturated ketones. Hence mesityl oxide (**110**) and methyl vinyl ketone were examined and the results are reported below.

FVP of mesityl oxide (**110**) at 750°C (55% conversion) afforded 2-methyl-1-butene (**112**) and 2-methyl-2-butene (**113**) in a combined yield of 47% (**112**:**113**≈9:1) along with its isomer **111**. The yields were corrected for recovered starting material and its isomer (45% total). Volatile C_1-C_4 hydrocarbon products were determined by conducting the pyrolysis in an SFR from 625°-647°C. In addition to the above mentioned products, CH_4, C_2H_6 and isobutene were characterized (Scheme 16). Under SFR conditions a component having an M^+ of m/e = 96 was also observed. This component was present even at below the decomposition temperature of **111**. And during decomposition, the amount of this component increased. Formation of methane and ethane suggests the

Scheme 16



intermediacy of methyl radical. Enone **110** was, therefore, copyrolyzed with 10- to 20-fold excess of toluene in the SFR at 647°C. This resulted in a considerable decrease in the amount of **112** and **113**, while the yield of methane increased dramatically with a concomitant decrease in ethane formation. Isobutene yields were almost unaffected by these copyrolysis experiments. The rates of formation of **112** were measured and were observed to decrease by ca. 34% with a 10-fold excess and by 55% with a 20-fold excess of toluene. Almost no effect was found on the rate of formation of isobutene.

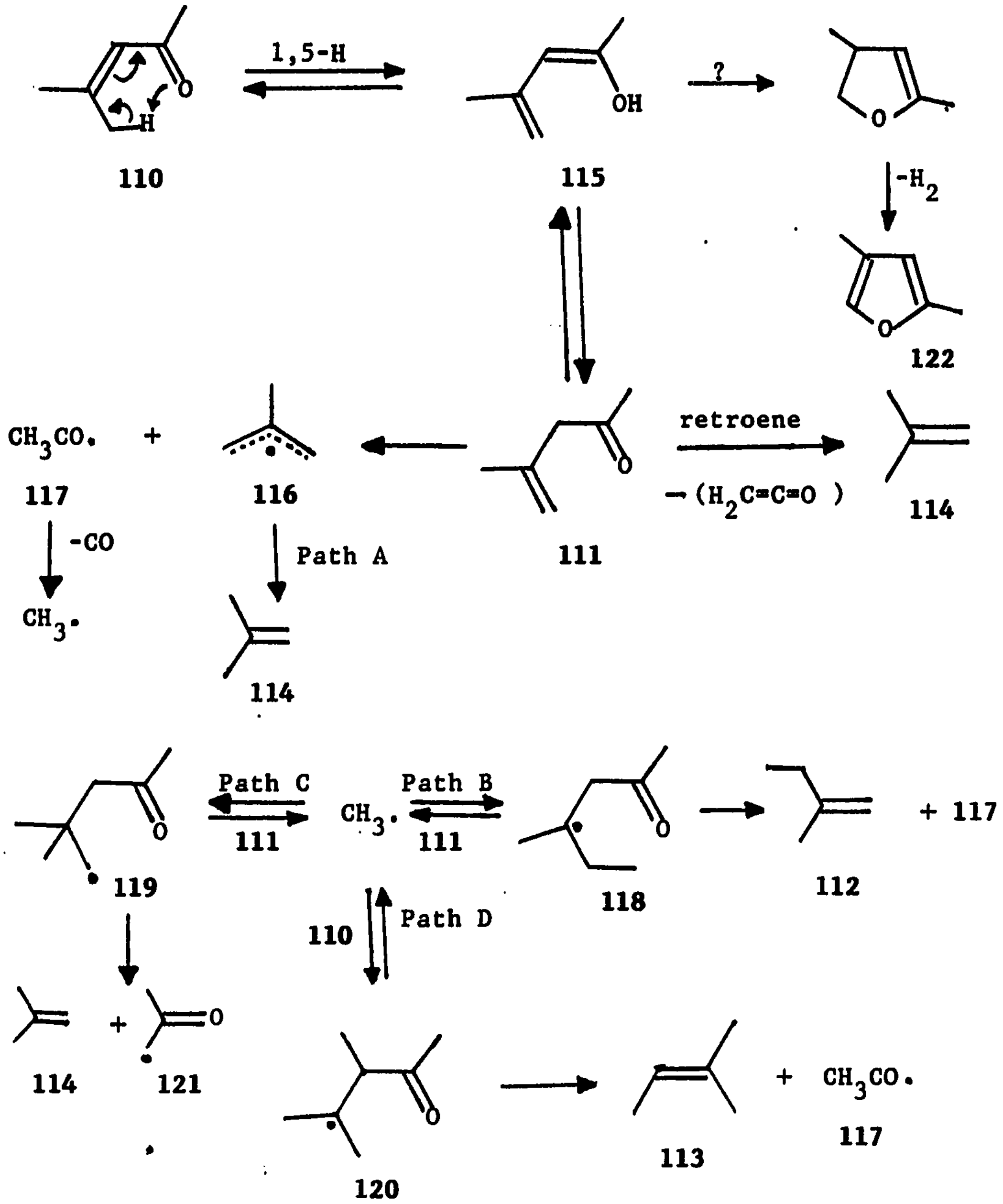
FVP of **110** at a lower temperature such as 660°C (at 10% conversion) gave only its isomer **111**. Compound **111** also has been observed to isomerize thermally back to **110**. For example, pyrolysis of **111** up to 500°C under SFR conditions led to mixture of **110** and **111**.

These experimental results can be reasonably explained by the mechanisms shown in Scheme 17. Isomerization of **110** to **111** can be explained by the well known 1,5-H shift of allylic hydrogen to form dienol **115** which then tautomerizes to **111**.[56] Component M^+ of m/e = 96 may be assigned structure **122**. Enone **111** can be assumed to decompose by a homolytic cleavage to produce two stable radicals **116** and **117**. Radical **116** can abstract a hydrogen to give **114**. Acyl radical **117** can lose CO to generate CH_3 radicals, which can either add to the terminal position of the double bond in **111** to form **118** (path B) or can add to the internal position to give **119** (path C).

Radical **118** can undergo a homolytic cleavage to produce **112** and regenerate **117**. Homolysis of **119** gives isobutene and radical **121**. The fate of **121** is not clear. Methyl radicals can also add to **110** to form **120** which then produces **113** and acyl radical **117** (path D).

The decreases in **112** and **113** in the copyrolysis experiments are in good agreement with the proposed mechanisms. The almost constant yield of isobutene in the

Scheme 17


110
1,5-H
115
OH
?
O
-H2
122
CH3CO•
+
117
116
111
retroene
-(H2C=C=O)
114
-CO
CH3•
Path A
114
119
Path C
111
CH3•
Path B
111
118
112
+ 117
110
Path D
114
+
121
120
113
+ CH3CO•
117

copyrolysis experiments implies that pathway A and/or a retro-ene process are mainly involved. The larger yield of **112** as compared with that of **113** suggests preferential addition of methyl radicals to the terminal position of **111** (path B). Formation of carbon monoxide has been observed by pyrolyzing **110** in a low pressure pyrolysis (LPP) condition and monitoring $M^+ = 28$ by MS.

An obvious experiment is to generate CH_3 radicals at a temperature where both **110** and **111** are stable. A mixture of **110** plus **111** (9:1) and dimethylmercury was pyrolyzed at 502°C in the SFR. The identified products were **112**, **113** and **114**. Starting materials were stable under at 502°C except that the ratio changed from ~9:1 to 2.3:1. Despite a larger amount of **110**, **112** and **113** were formed in about equal amounts. The preferential addition of methyl radicals to **111** over **110** is again evident.

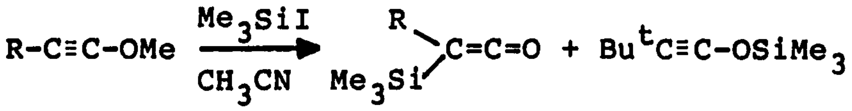
Formation of isobutene in the methyl radical induced reaction perhaps can be explained by invoking addition of CH_3 radicals to the internal position of the double bond in **111** to form **119**, homolysis of which leads to **114** (path C).

Attention was then turned to an α,β-unsaturated ketone having no β-alkyl group. Methyl vinyl ketone (**123**) was chosen as a model compound. Pyrolysis of **123** in the SFR even at 730°C did not afford any product. This is what one can expect from the mechanisms shown in Scheme 17.

Syntheses of alkyl(trimethylsilyl)ketenes

Alkyl(trimethylsilyl)ketenes were synthesized from the corresponding alkyl methoxy acetylenes.[47] Methoxyacetylenes were obtained according to the general procedure of Nooi and Arens.[57] When alkyl methoxy acetylenes were treated with trimethylsilyl iodide in CH_3CN, the corresponding alkylsilylketenes were obtained (Scheme 18). It is interesting to note that when R = t-butyl group, siloxyacetylene **127** is also obtained.

Scheme 18



127

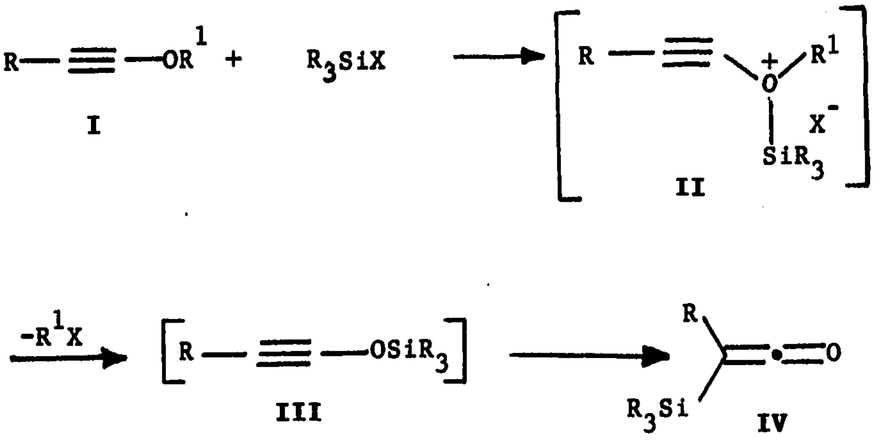
124 R = Et   **95** R = Et

125 R = iPr   **72** R = iPr

126 R = Bu^t **97** R = Bu^t

Efimova and coworkers[47,58] reported that reaction of trialkylsilyl halides with alkyl alkoxyacetylenes bearing primary alkyl groups gave addition products whereas reactions with sterically hindered ynol ethers (e.g., **125**) led to the corresponding ketenes. It was concluded that steric hindrance at the most nucleophilic site of the ynol ether apparently directed electrophilic attack to the oxygen atom to acquire oxonium character. Subsequent intra- or intermolecular alkylation of the halide ion afforded an ynol ether which rapidly rearranged to the corresponding ketene (Scheme 19).[47] In the present study it has been observed

Scheme 19



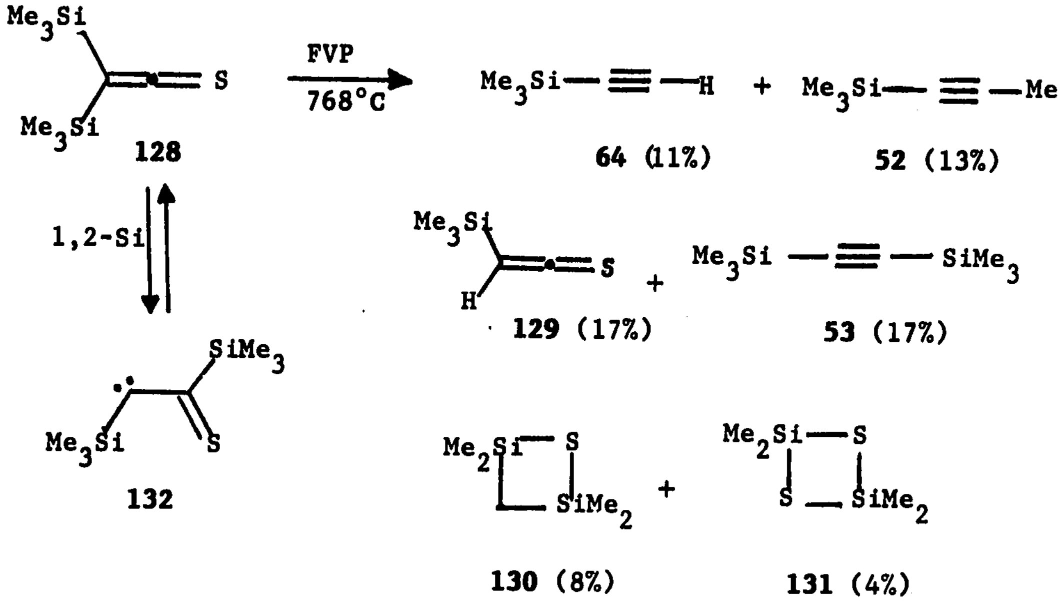
that even with a primary alkyl group (**124**) only ketene **95** is obtained. Steric effects do not seem to be a factor although it is possible that an initially-formed addition product is converted to the ketene. Isolation of t-butyl-(trimethylsiloxy)acetylene (**127**) in the present study supports the mechanism shown in Scheme 19. Because of the bulky t-butyl group, intermediate III becomes isolable. Presumably **127** slowly isomerizes to ketene **97**. It is not clear at this time as to what factors are responsible for this isomerization. In the case of less bulky alkyl groups (R = Et, i-Pr) form III is not observed rather only form IV is isolated (Scheme 19). It could be suggested that in these latter cases, initially-formed silyl ynols III readily isomerize to ketenes IV. Recently a few reports on the preparation and properties of siloxyalkynes have appeared in the literature.[59-61] Although bulky stable siloxyalkynes have not been observed to isomerize thermally to ketenes,[59] Kowalski and coworkers,[61] however, suggested this isomerization for less bulky siloxyalkynes. Results in the present study are in agreement with this suggestion. Our results also agree with the recent report of Jabry and coworkers who observed silylketenes in FVP of ethenoanthracenic silylated enol ethers.[53] Intermediate siloxyalkynes isomerized thermally to the stable silylketenes (Scheme 29).

Gas-phase decomposition of silylthioketenes

In an effort to extend the decomposition studies from silylketenes to other heterocumulenic systems, silylthioketenes were examined. Results in these studies are described below.

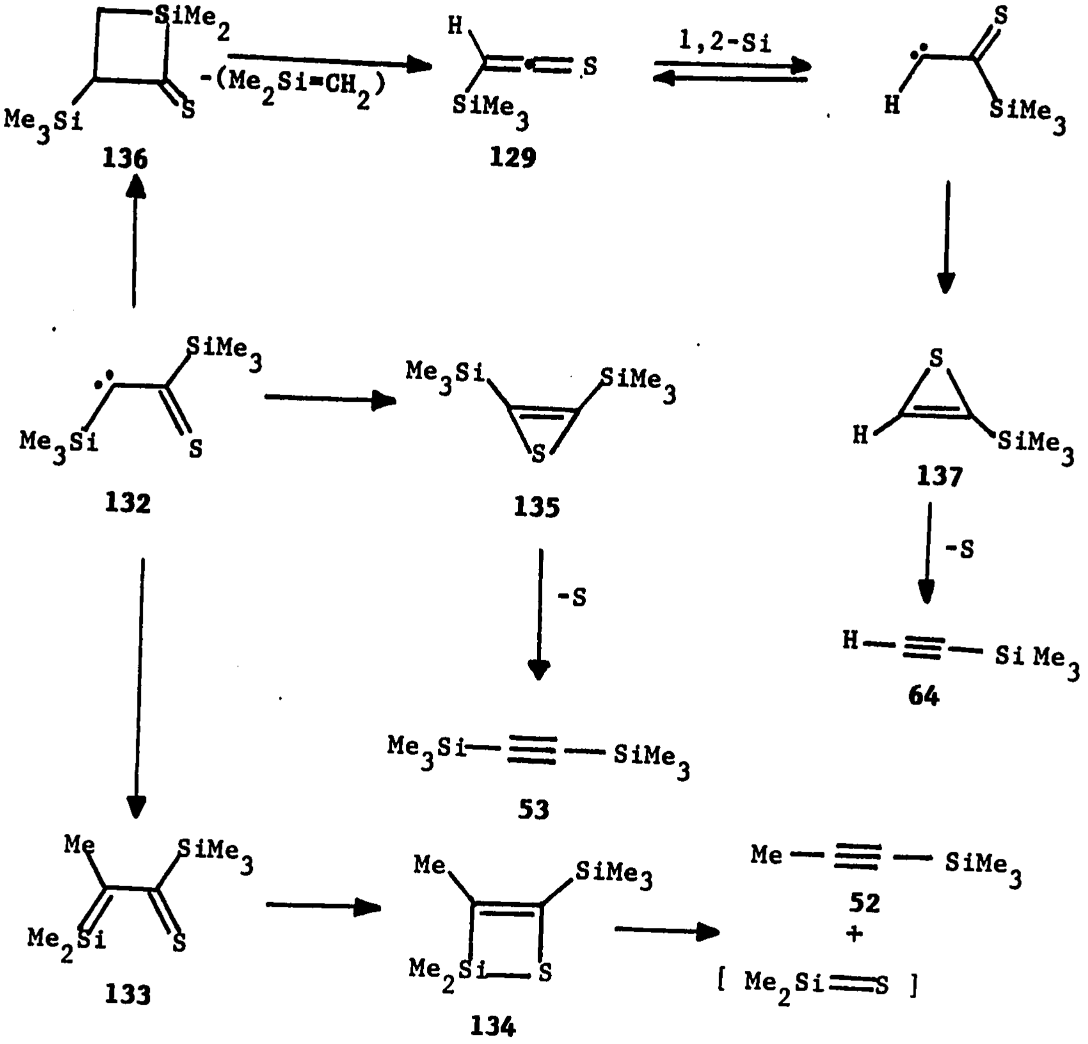
FVP of bis(trimethylsilyl)thioketene[62] (**128**) at 768°C resulted in 47% conversion and the formation of the seemingly complex mixture of six products for which the yields have been corrected for unreacted starting material (Scheme 20). The complexity of product mixture from **128** is considerably reduced when it is recognized that every one of the six products can be mechanistically rationalized by processes each initiated by isomerization of **128** to

Scheme 20



α-thioketocarbene **132** via a 1,2-shift of Me_3Si group. Rearrangement of **128** to **132** via 1,2-silyl shift corresponds to what is the first example of a retro-thio Wolff rearrangement. The proposed route for six products all originating from carbene **132** are incorporated into Scheme 21. Rearrangement of **132** by 1,2-methyl migration from silicon produces silene **133** which would, in analogy to the mechanism proposed for silylketenes, be expected to close and decompose to acetylene **52** and dimethylsilanethione ($Me_2Si{=}S$). Isomerization of **132** to thiirene **135** affords a path to acetylene **53** by extrusion of atomic sulfur.

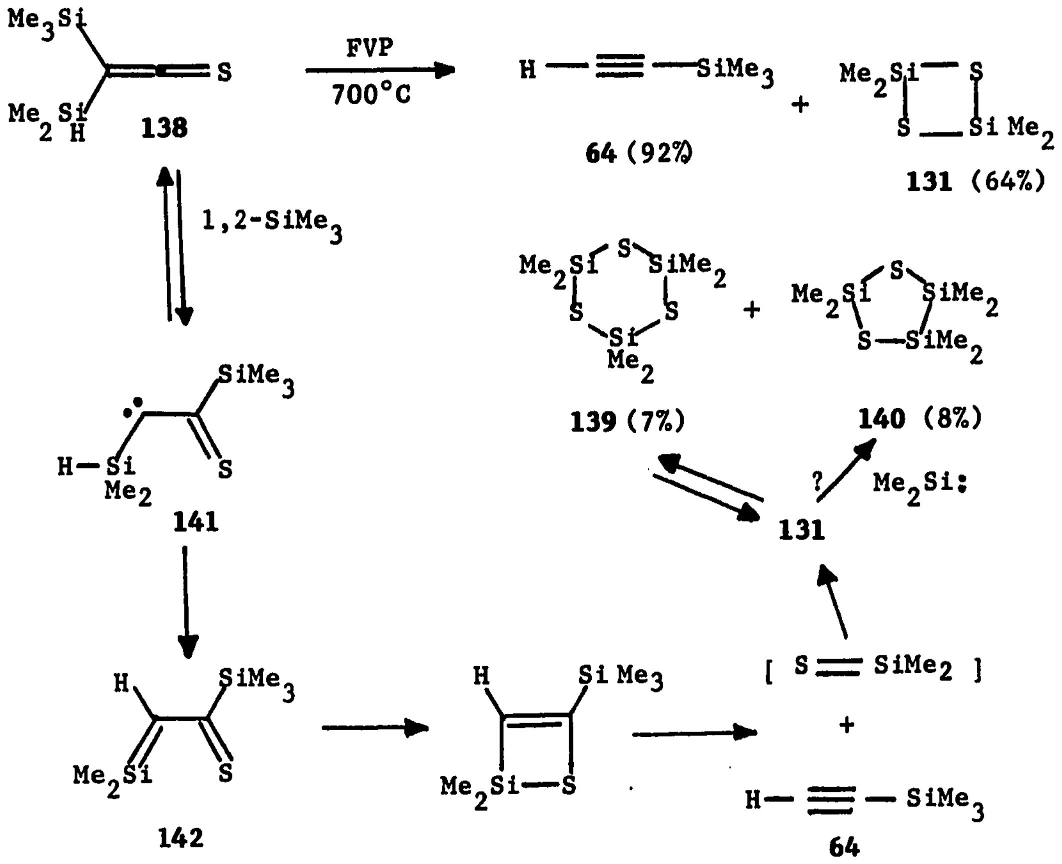
Scheme 21



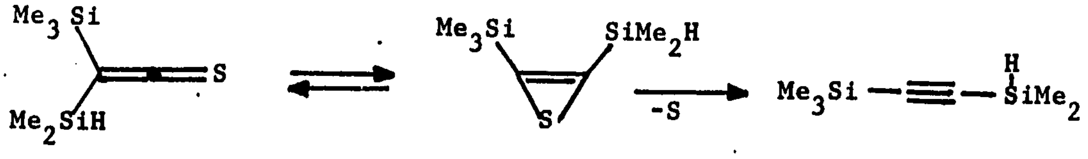
Photochemical decomposition of thiirene to alkyne and sulfur has been reported by Torres and coworkers.[5b] Thus matrix isolated bis(trifluoromethyl)thiirene photodecomposes to perfluorobutyne. As mentioned before, alkyne formation in the gas phase photolysis of 1,2,3-thiadiazole is presumed to form from intermediate thiirene. These authors also noted the gas phase thermal decomposition of thiirene to the alkyne but this was reported to be a minor process. Recently by MNDO calculations McKee[63] have directly linked $S(^1D)$ and acetylene to thiirene. Thus, our proposal for formation of **53** from thiirene **135** is reasonable both from theoretical and experimental grounds. Formation of thioketene **129** can be explained by intramolecular C-H insertion by carbene **132** to produce silacyclobutane **136** followed by dimethylsilene extrusion. Thioketene **129** would be expected, by analogy to the **132** to **53** transformation, to isomerize to thiirene **137** and extrude sulfur to afford product **64**. Cyclic products 2,2,4,4-tetramethyl-2,4-disilathietane (**130**) and tetramethylcyclodisilthiane (**131**) correspond to reaction of $Me_2Si{=}S$ with either $Me_2Si{=}CH_2$ or another molecule of silanethione. Thus, all products are readily rationalized as arising from a single initial intermediate, carbene **132**.

The apparent complexity of the product mixture arising from thermolysis of **128** is drastically reduced by the simple modification of replacing one methyl group in silicon by hydrogen. The desired dimethylsilyl(trimethylsilyl)-thioketene (**138**) was synthesized by a method analogous to that in reference 62. FVP of **138** at 700°C results in 100% conversion and formation of trimethylsilylacetylene (**64**) in a remarkable 92% yield accompanied by cyclosilthianes **131** and **139** in a combined yield of 71%. A minor product **140** (8%) was also observed (Scheme 22). Both **131** and **139** are thought to be the products of the cyclic oligomerization of dimethylsilanethione $Me_2Si{=}S$,[64] and are known to thermally equilibrate.[65] Once again all major products can be easily rationalized as originating from an initial 1,2-silyl migration on the π-framework of silylthioketene. Minor product **140** can only be speculated to arise from Me_2Si: (perhaps from reductive elimination in **138**) insertion into

Scheme 22



131 as has been suggested by Soyasa et al.[66] In an attempt to understand the origin of $Me_2Si:$ and/ **140**, two other possibilities were examined. One possibility is that thioketene **138** may lose sulfur through thiirene **143** to give acetylene **144** which perhaps under reductive



138 **143** **144**

$$\mathbf{144} \xrightarrow[-Me_2Si:]{FVP} Me_3Si-\equiv-H$$

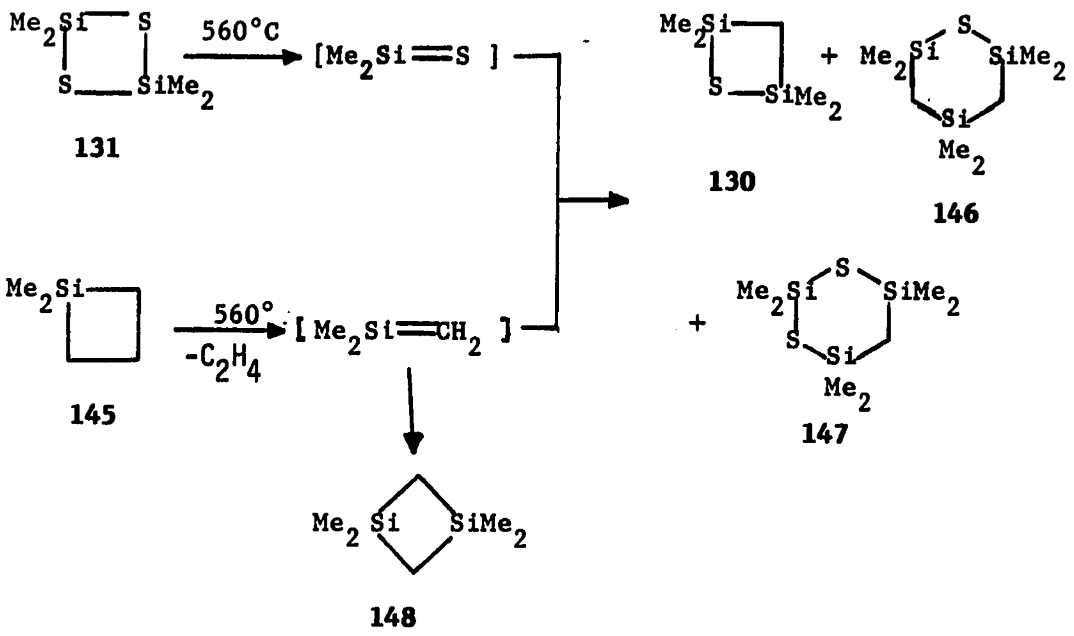
64

elimination of dimethylsilylene can give acetylene **64**. Acetylene **144** was, therefore, pyrolyzed under FVP conditions at 700°C and at 800°C. FVP of **144** at 700°C (9% conversion) gave only **64**. Even at 800°C only 72% of **144** was converted to **64**. If it is assumed that **144** formed from **138**, was in a vibrationally excited state, then complete conversion of **144** to **64** at 700°C is perhaps accountable. Such an assumption does not seem to be tenable as FVP of **138** at 600°C did not lead to any identifiable **144**. The possibility that **139** under pyrolytic conditions may lose sulfur leading to **140** was also sought. The pyrolysis of **139** (and **131**) did not afford **140** thus disproving the intermediacy of **139** as a source of **140**.

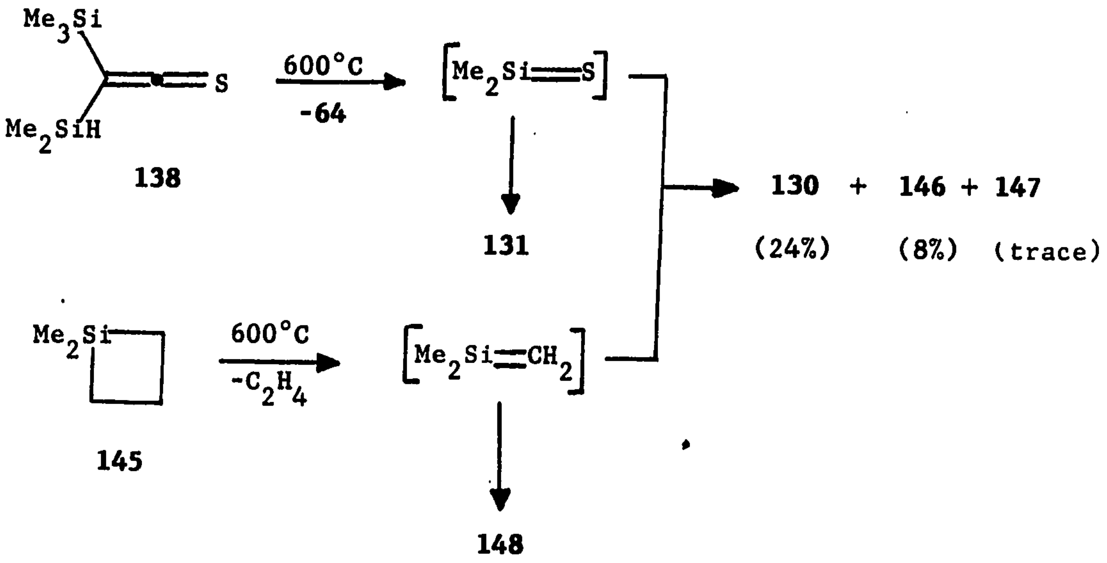
FVP of silylthioketene **138** even at 600°C results in 94% conversion and formation of the above mentioned products. Both the lower thermal requirements and the higher yield of silanethione extrusion products for **138** as opposed to **128** are paralleled in the thermochemistry of analogous silylketenes discussed earlier. This may be explained by the greater migratory aptitude of hydrogen (**141** -> **142**) as compared with methyl (**132** -> **133**, Scheme 21).

It is possible to test the assumption made above that FVP of **138** results in the extrusion of free $Me_2Si=S$. Although the evidence for transient silanethione is rather meager,[67] dimethylsilanethione has been trapped[68] by copyrolyzing 1,1-dimethyl-1-silacyclobutane (**145**, a well-established thermal generator of $Me_2Si=CH_2$) and tetramethylcyclodisilthiane **131**. The products **130**, **146**, **147** correspond to the mixed cyclic oligomers from $Me_2Si=CH_2$ and $Me_2Si=S$ (Scheme 23).[68] Thus, conducting a similar copyrolysis of **145** and thioketene **138** (4.2:1) under a flow of N_2 (35 ml/min) at 600°C also afforded adducts **130** (24%), **146** (8%), **147** (trace by GCMS) in addition to **64**, **131** and silene dimer **148** (Scheme 24).

Scheme 23



Scheme 24



The decomposition kinetics of hydridosilylthioketene **138** were examined in an SFR from 435-494°C. The rates of formation of **64** from **138** were measured in the range 435-494°C. The values obtained are reported in Table 4. The Arrhenius plot for the formation of **64** is shown below in Figure 3, from which the following kinetic parameters are obtained.

$\log A\ (s^{-1}) = 13.30 \pm 0.12$ $\Delta S^{\#}$ (e.u.) $= -1.47 \pm 0.55$

Ea (Kcal/mol) $= 44.8 \pm 0.4$

These parameters clearly rule out any process initiated by bond homolysis and, therefore, support the retro-thio Wolff rearrangement. These values are also similar to the activation parameters found for the thermal isomerization of $Me_3Si\text{-}CH{=}C{=}CH_2$ to $Me_3SiCH_2C{\equiv}CH$[39] ($Ea = 49.9 \pm 0.6$ kcal/mol, $\log A = 12.89 \pm 0.17$), suggesting that the two reactions are initiated by similar processes. This is in keeping with the recent suggestion[38] that trimethylsilylallene isomerizes by an initial 1,2-silyl shift and not by a concerted[39] 1,3-migration of silicon.

Several points should be mentioned here. Formation of **141** from **138** by the 1,2-shift of Me_3Si group has been invoked to explain products in the decomposition of **138**. The other possible carbene **149** that would be formed by the 1,2-shift of Me_2SiH group must also be produced. The two carbenes perhaps interconvert through thiirene **150**.[5b] It is

Table 4. Rate constants (k) for trimethylsilylacetylene (**64**) formation in the decomposition of trimethylsilyl(dimethylsilyl)thioketene (**138**)

Run	k, sec^{-1}	temp; °C	Run	k, sec^{-1}	temp; °C
1	3.5439	493.9	11	0.7571	458.2
2	2.3546	484.5	12	0.5754	450.9
3	2.3262	484.5	13	0.5702	450.9
4	1.7923	478.0	14	0.5754	450.9
5	1.7833	478.0	15	0.4542	445.4
6	1.3738	471.1	16	0.4567	445.4
7	1.3060	471.1	17	0.3689	439.9
8	1.0264	465.0	18	0.3643	439.9
9	1.0261	465.0	19	0.2918	434.8
10	0.7631	458.2	20	0.3014	434.8

log A (s^{-1}) = 13.3 ± 0.12 $\Delta S^{\#}$ (e.u.) = -1.47 ± 0.55

Ea (Kcal/mol) = 44.8 ± 0.4.

reasonable to assume that a 1,2-H shift from silicon to a carbene is energetically more favorable (perhaps with zero activation energy) than the corresponding 1,2-Me shift and hence, products derive solely from 1,2-H shift intermediate **142**. In fact theoretical calculations by Goddard et al.[46] have shown that the isomerization of silylmethylene ($H_3Si\text{-}\ddot{C}H$) to silaethylene ($H_2Si{=}CH_2$) is exothermic by 69

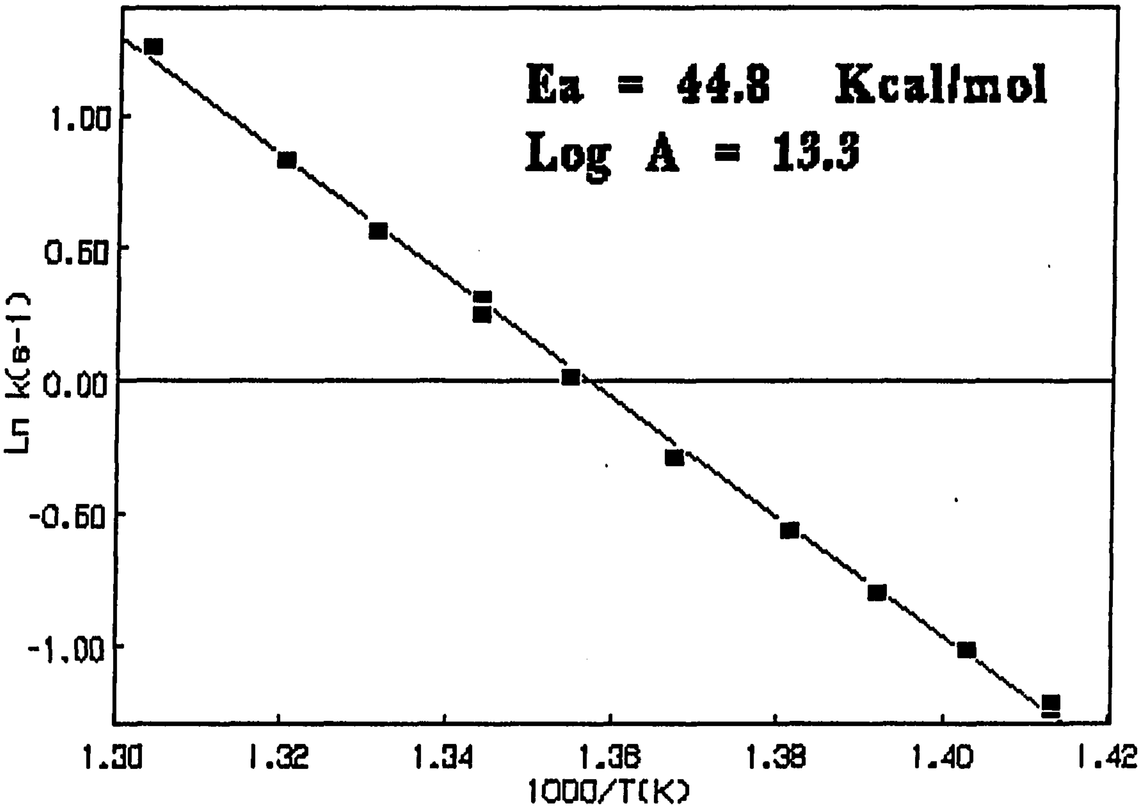
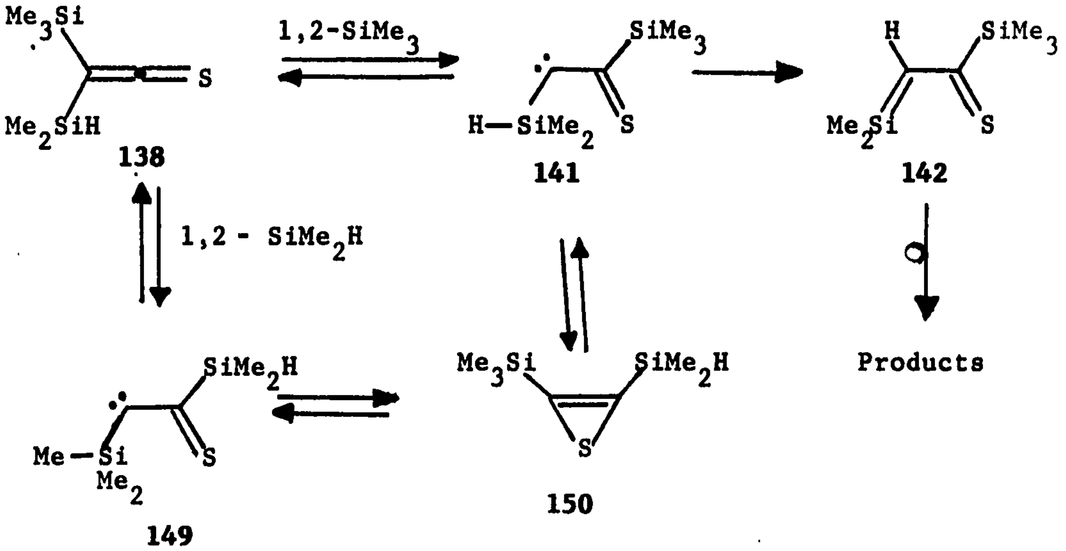


Figure 3. Arrhenius plot for formation of **64** in the decomposition of **138**

kcal/mol with a barrier of 0-<3 kcal/mol. The observed higher thermal requirements for bis(trimethylsilyl)-thioketene decomposition is in agreement with the above assumption.

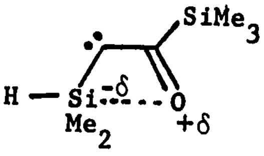


It was attempted to study the kinetics of decomposition of **128** from which evaluation of activation energy for 1,2-Me shift might have been possible. Because of complexities of product mixture and of separation difficulties, reliable kinetic data could not be obtained.

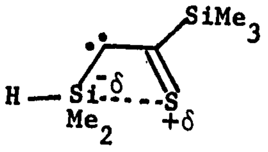
Situations discussed above for thioketene **138** are apparent in analogous hydridosilylketene **63** discussed earlier. Similar reasonings could be advanced for **63** where two keto carbenes that could form by 1,2-shifts of Me_3Si and Me_2SiH may interconvert through oxirene.[5]

It should be noted that the activation energy for the decomposition of hydridosilylketene **63** to **64** is about 7.0

kcal/mol higher than that of the corresponding hydridosilylthioketene **138**, decomposition. This difference in activation energy perhaps can be rationalized by postulating involvement of oxygen/sulfur in the transition state. Probable transition states for the two systems are most likely **151** and **152** shown below.



151

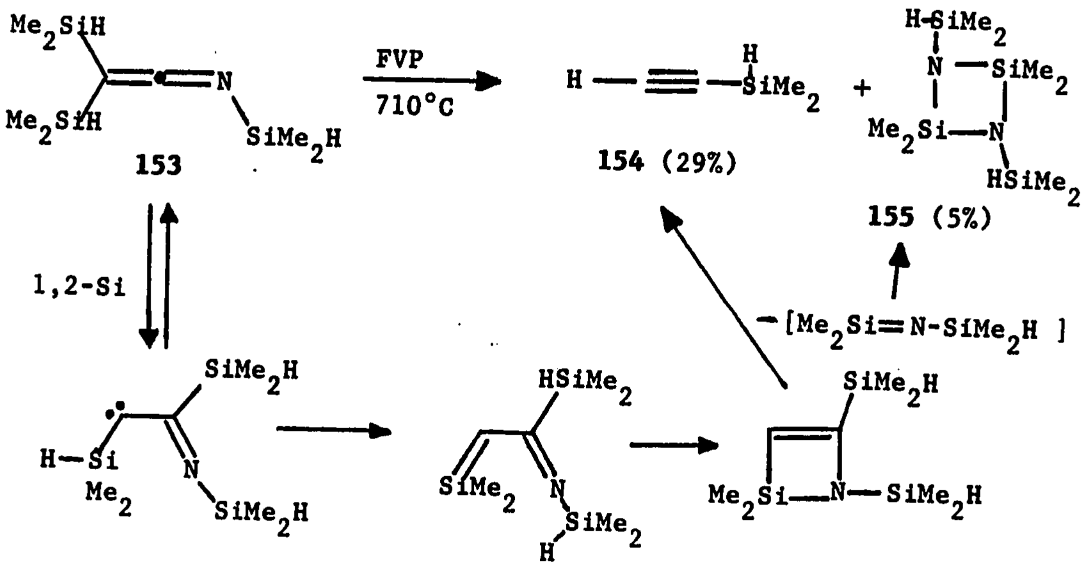


152

Thermal decomposition of silylketenimines

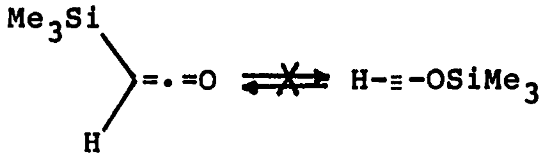
Gas-phase thermal decomposition of silylketenimines, another class of heterocumulenes, were briefly examined.

FVP of tris(dimethylsilyl)ketenimine[69] (**153**) at 710°C (80% mass recovery) resulted in 72% conversion of **153** and formation of dimethylsilylacetylene (**154**, 29%) and N,N-bis(dimethylsilyl)tetramethylcyclodisilazane (**155**, 5%). Formation of these products can be rationalized by a retro-Wolff type rearrangement as has been discussed for other heterocumulenes. Oligomerizations of silaimine to form cyclidisilazanes are well documented.[67] It should be noted that the decomposition temperature for silylketenimines is higher than the analogous hydridosilylketenes.[40]



Structure of silylketenes

Trimethylsilylketene (**74**), which was obtained by pyrolysis of trimethylsiloxyacetylene,[70] showed some interesting IR bands and rather unusual PMR spectrum. Based on these observations it was suggested[70] that a tautomeric equilibrium exists between ketene form (I) and acetylenic form (II). On the other hand, chemical properties such as



I II

addition reactions with water, ammonia, etc., giving products are in accord with ketene form only. In order to resolve this dilemma a number of silylketenes were synthesized and their PMR spectra and IR spectra were recorded.[71] For example, the NMR spectrum of $Et_2\underset{H_b}{Si}CH_a{=}C{=}O$ shows the proton H_a as a doublet at $\delta = 1.65$ ppm having $J_{ab} = 3$ Hz. Although this proton resonates in the region of acetylenic proton, the splitting supports ketenic structure I for in structural form II splitting of H_a by H_b would hardly be observed. Inspection of IR spectra of several silylketenes and comparison of these spectra with those of ketene and its derivatives led authors[71] to assign the origin of the curious band near 3370 cm^{-1} as due to the combination band as exemplified in Table 5. The difference between $(\nu_1+\nu_2)$ and combination band, is almost the same for compounds investigated. It is important to note that band near 3370 cm^{-1} is also retained in the spectrum of 51 where there is no proton at the unsaturated carbon to give C≡C-H form. Thus, it is concluded[71] that all ketenes made from pyrolysis of the corresponding silicon-containing alkoxyacetylenes exist only in ketene form.

^{13}C NMR spectra of silylketenes are very interesting and chemical shift values for some silylketenes along with diphenylketene are in Table 6.[72] The ketene carbon atoms are unusually screened by SiR_3 groups. In order to explain the upfield chemical shifts, it is proposed by Grishin et al.[72] that the polar structure $^{-}C{-}C{\equiv}O^{+}$ largely contributes to the ketene structure.

Table 5. Summary of IR bands of a few silylketenes

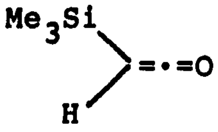
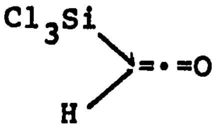
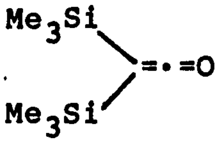
	 **74**	 **161**	 **51**
$_1$ C=C(=O)	1270 cm^{-1}	1296	1295
$_2$ O=C(=C)	2112	2165	2085
$_3$ H-C(=C)	3038	3067	--
($_1$+ $_2$)	3365	3444	3363
	17	17	17

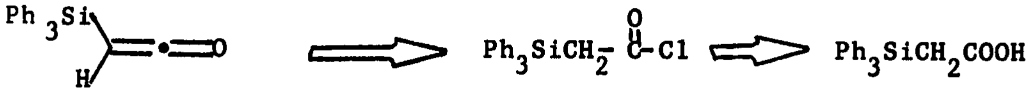
Table 6. ^{13}C chemical shifts of silylketenes (ppm relative to TMS)

4 3 2 1
C-C-Si-C=C=O

Compounds	C^1	C^2	C^3	C^4
$(CH_3)_3SiCH=C=O$	179.2	-0.1	0.9	-
$(C_2H_5)_3SiCH=C=O$	179.2	-4.9	7.5	6.1
$(CH_3)_3Si)_2C=C=O$	166.8	1.7	2.3	-
$Ph)_2C=C=O$	201.2	47.6	-	-

Rather unusual PMR, IR and ^{13}C NMR spectra of silylketenes prompted us to synthesize a stable crystalline silylketene and determine its structure by X-ray crystallography. To this end a few silylketenes were synthesized in an attempt to determine the structure of a bulky silylketene.

Triphenylsilylketene (162) Initial study in this area began with the synthesis of triphenylsilylketene (**162**). Although **162** was synthesized before as seen in the Chemical Abstract[73] its physical properties were not reported. It was hoped that **162** would be suitable for structural studies. Retrosynthetic steps for **162** are shown below.



$$Ph_3SiCH_2-\overset{O}{\overset{\|}{C}}-Cl \Longrightarrow Ph_3SiCH_2COOH$$

162 **163** **164**

Triphenylsilylacetic acid (164) There are contradictory reports about both the synthesis and the melting point of **164**. Because of this controversy, the acid was synthesized by two different methods and was completely characterized by spectroscopic means.

Method "A" This is a modification of the original method[74a] as shown below. Grignard reagent **166** was prepared carefully from **165**.

$$\underset{\textbf{165}}{Ph_3SiCH_2Cl} \xrightarrow[THF]{Mg} \underset{\textbf{166}}{Ph_3SiCH_2MgCl} \xrightarrow[2\ H^+(2\%)]{1\ CO_2(S)} \textbf{164}$$

Quenching **166** with CO_2 gas followed by hydrolysis afforded acid **164** in ~80% yield. In the original method,[74a] ether was used as a solvent; it was also claimed that one equivalent of EtBr was necessary to prepare **166**. The yield of acid was reported to be 34%. Brook and coworkers[74b] were unable to reproduce this result and hence they synthesized acid **164** by a different route (Method B). Furthermore, the melting point of the reported acid was found to be incorrect and it was assumed that Huang and Wang[74a] perhaps isomerized this acid to acetoxysilane, $Ph_3SiO\text{-}COCH_3$, during work up.

__Method__ __"B"__ Acid **164** was also synthesized by the method given by Brook et al.[74b] (Scheme 25). It was claimed

Scheme 25

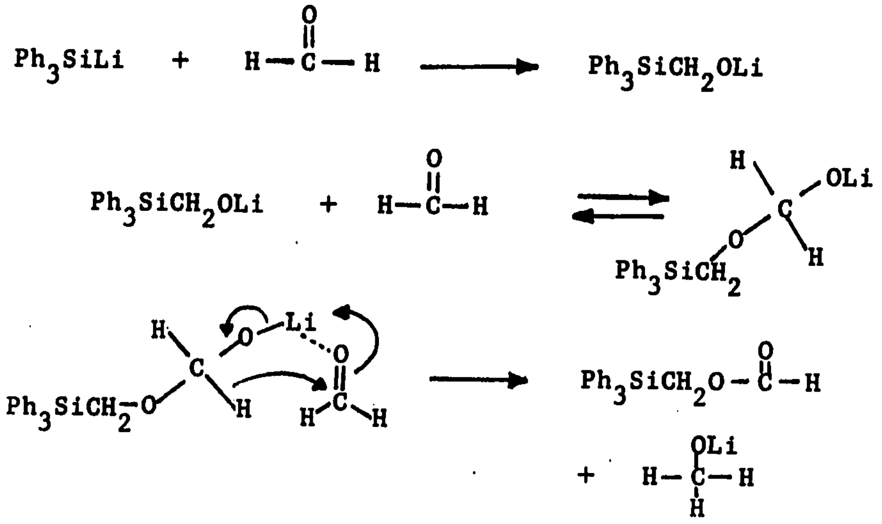
$$\underset{\textbf{167}}{Ph_3SiCl} \xrightarrow[THF]{Li(x's)} \underset{\textbf{168}}{Ph_3SiLi} \xrightarrow[H_2CO]{} \underset{\textbf{169}}{Ph_3SiCH_2OCOH}$$

$$\xrightarrow[Et_2O]{LiAlH_4} \underset{\textbf{170}}{Ph_3SiCH_2OH} \xrightarrow{PBr_3} \underset{\textbf{171}}{Ph_3SiCH_2Br} \xrightarrow[\substack{2\ CO_2(s) \\ 3\ H^+(2\%)}]{1\ n\text{-}BuLi} \textbf{164}$$

by the authors that **170** can be produced directly from **168** in good yield.[74c] Only in one occasion, **169** was produced in about 20% yield. Adoption of Brook's synthetic route always gave **169** as the major product, in yield up to 89%. Alcohol **170** if formed at all, amounts to about 4%. Formate **169** was then quantitatively reduced to alcohol **170** by $LiAlH_4$. Synthesis of acid **164** from **170** follows exactly the same steps as in the literature.[74b]

Formation of triphenylsilylmethylformate (**169**) may be explained by a Tishchenko type of reaction as has been suggested[74c] (Scheme 26). Properties of this compound made by both methods were identical and the observed melting point was 173°C (Lit. 175°C). The acid proton of **164** can not be seen in PMR. Furthermore, the OH-band of acid is weak at ~3050 cm^{-1} and can only be seen when the IR spectra is taken on a KBr pellet. Modified method "A" described here appears to be the best choice for synthesis of triphenylsilylacetic acid (**164**).

Scheme 26



Triphenylsilylketene (162) Triphenylsilylacetic acid was then converted to acid chloride **163** in about 95% yield.[73b] Treatment of the acid chloride with freshly distilled triethylamine at room temperature afforded ketene **162**[73a] in >90% yield (vide infra). Attempts to isolate **162** in pure form were unsuccessful for **162** quickly converts into anhydride **172**.

$Ph_3SiCH_2CO)_2O$

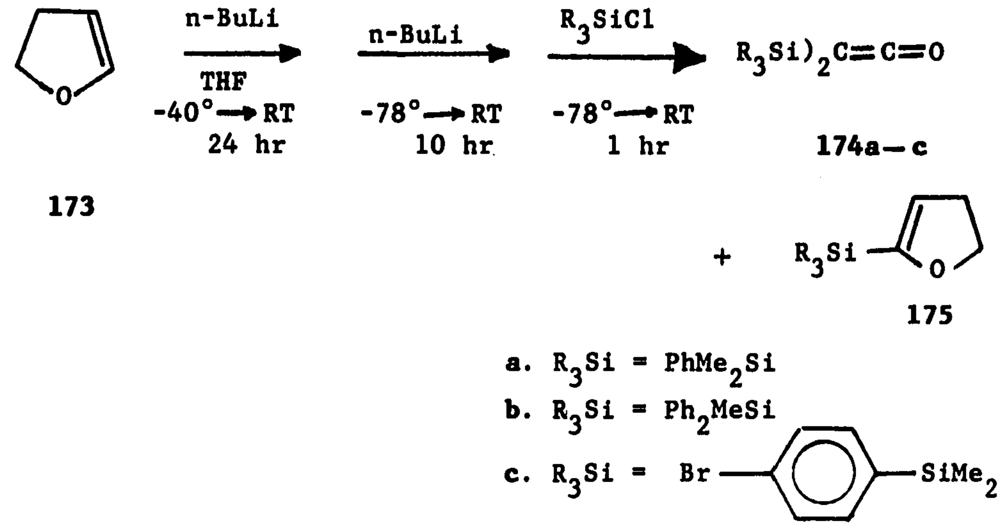
172

Presumably the moisture sensitive ketene reacts with water to form acid **164**, which then reacts with ketene forming anhydride **172**. The PMR of CH_2 protons in the literature is erroneous and is actually $\delta = 3.34$ ppm.

Syntheses of several bulky silylketenes

In a continuing effort to prepare a suitable crystal of stable silylketene, the procedure[75] for the synthesis of bis(silyl)ketenes was then adopted. The general synthetic steps for bis(silyl)ketenes are outlined in Scheme 27. Quenching with a few chlorosilanes afforded several bis(silyl)ketenes. As usual, silyl derivatives of 2,3-dihydrofuran were also observed. Ketenes **174a** and **174c** were viscous liquids and, therefore, were not suitable for structural studies. Bulky bis(diphenylmethylsilyl)ketene (**174b**) was separated by flash chromatography (silica gel, hexane eluent). Recrystallization from pentane afforded

Scheme 27



173

174a–c

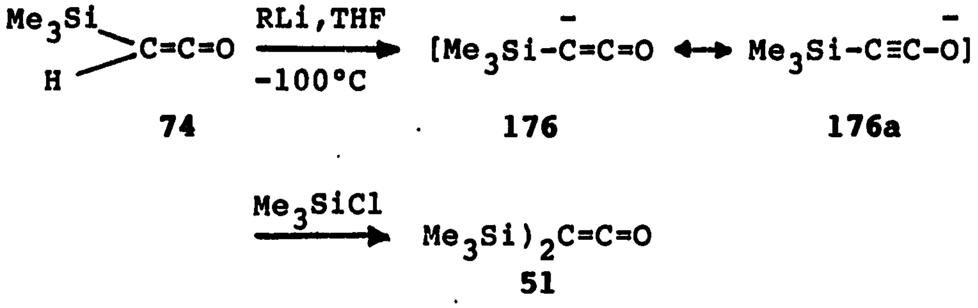
175

a. R_3Si = $PhMe_2Si$
b. R_3Si = Ph_2MeSi
c. R_3Si = Br–C_6H_4–$SiMe_2$

suitable crystals (m.p. 111.5°C) of **174b**. It was then subjected to X-ray crystallographic study[76] but its structure has not yet been solved.

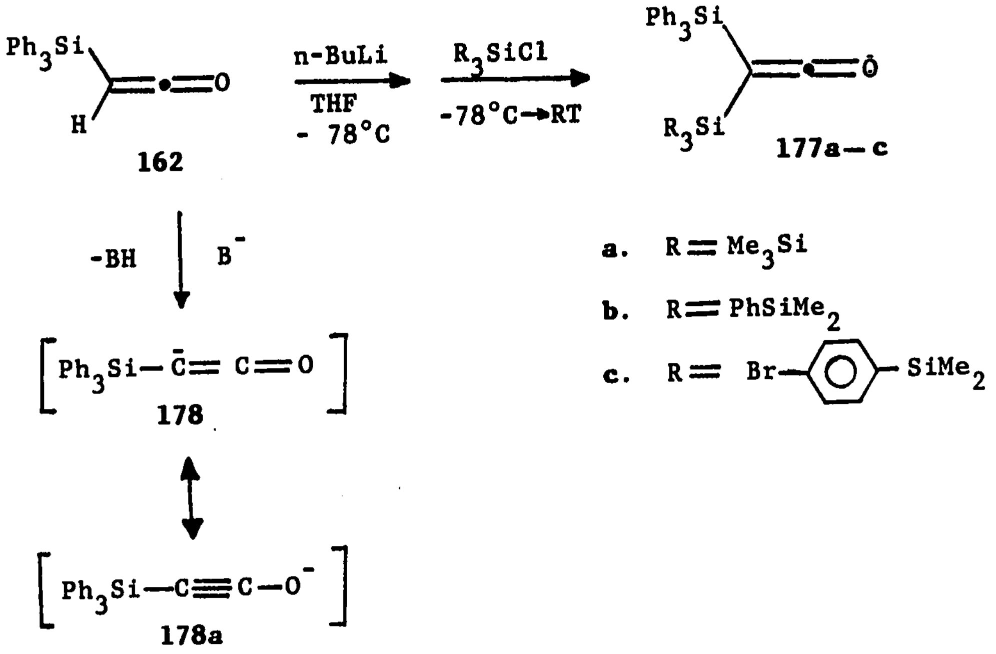
It should be noted that quenching with bulky chlorosilanes led to ketene products only. Formation of ketene from **173** has been explained by suggesting intermediacy of dilithioketene and/or its isomer dilithioalkynolate.[75] Thermodynamically stable ketene products may arise from the isomerization of initially formed silyl(siloxy)acetylenes.

There are few reports in the literature on the generation of alkynolates.[77-79] For example, Woodbury and coworkers[77] generated alkynolate **176** from trimethylsilylketene and a base at -78° to -100°C. Trapping with



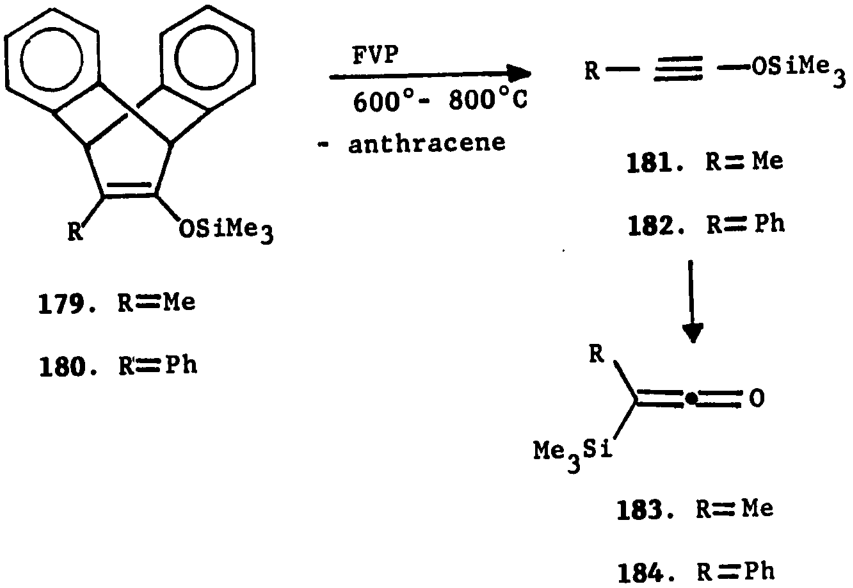
trimethylchlorosilane led to the isolation of ketene **51**. It was of great interest to see whether use of bulkier ynolate and trapping with rather bulkier chlorosilanes, isolation of siloxyalkynes is possible. Triphenylsilylketene (**162**) was chosen for this study. Freshly prepared ether solution of **162** was treated with n-BuLi at -78°C and then quenched with several different chlorosilanes. In each case only ketene product was observed (Scheme 28).

Scheme 28



Very recently two groups were able to trap alkynolate via O-silylation resulting in siloxyalkynes.[60,61] Kowalski and coworkers[61] from their observations, suggest that silylation occurs kinetically on oxygen to afford siloxyalkynes, but upon warming less bulkier siloxyalkynes rearrange thermally to the more stable ketene products. In our present study it is possible that initially formed siloxyalkynes rearrange to the corresponding ketenes. This is also in keeping with a recent report where it appears that siloxyalkynes rearrange thermally to the more stable silylketenes (Scheme 29).[53] In the case of compound **179**, the authors were able to detect siloxyalkyne **181** by IR at -196°C; this transient absorption at 2240 cm^{-1}, however, disappeared at -150°C.

Scheme 29



Reactions of silylenes with silylketenes and silylthioketene

Strained ring systems containing a silicon atom have attracted chemists, owing to their high reactivity.[80] Reactions of silylene with alkene, alkyne and carbonyl compounds leading to the strained rings of silacyclopropane,[81] silacyclopropene,[82] and oxasilacyclopropane[83] are known. In some cases the intermediate ring compound has been isolated. Conlin and Gaspar,[82] e.g., isolated tetramethyl-1-silacycloprop-2-ene at room temperature, as the addition product of dimethylsilylene to 2-butyne. The products obtained in the reaction of carbonyl compounds with thermally generated dimethylsilylene have been attributed to the addition of silylene to the C=O bond with the formation of oxasiliranes followed by rearrangement.[83] It was sought here to investigate the reactivity of silylenes with silylketenes and silylthioketenes.

Nitrogen-flow pyrolysis of bis(trimethylsilyl)ketene (**51**) and 1,2-dimethoxy-1,1,2,2-tetramethyldisilane (**185**) at 550°C resulted in the formation of bis(trimethylsilyl)-acetylene (**53**) and several silanone trapped products. Copyrolysis of methoxypentamethyldisilane (**186**) and **51** in a flow of N_2 (30 ml/min) at 550°C (50% conversion of **51**) resulted in **53** (15%), Me_3SiOMe and methoxy pentamethyldisiloxane (**189**, silanone trapped product). There were some other silanone trapped products too.

$$\mathrm{Me_3Si)_2C{=}C{=}O} + \mathrm{Me_3SiSi(OMe)Me_2} \xrightarrow[\text{Flow}]{550°\mathrm{C}} \mathrm{Me_3Si{-}{\equiv}{-}SiMe_3}$$

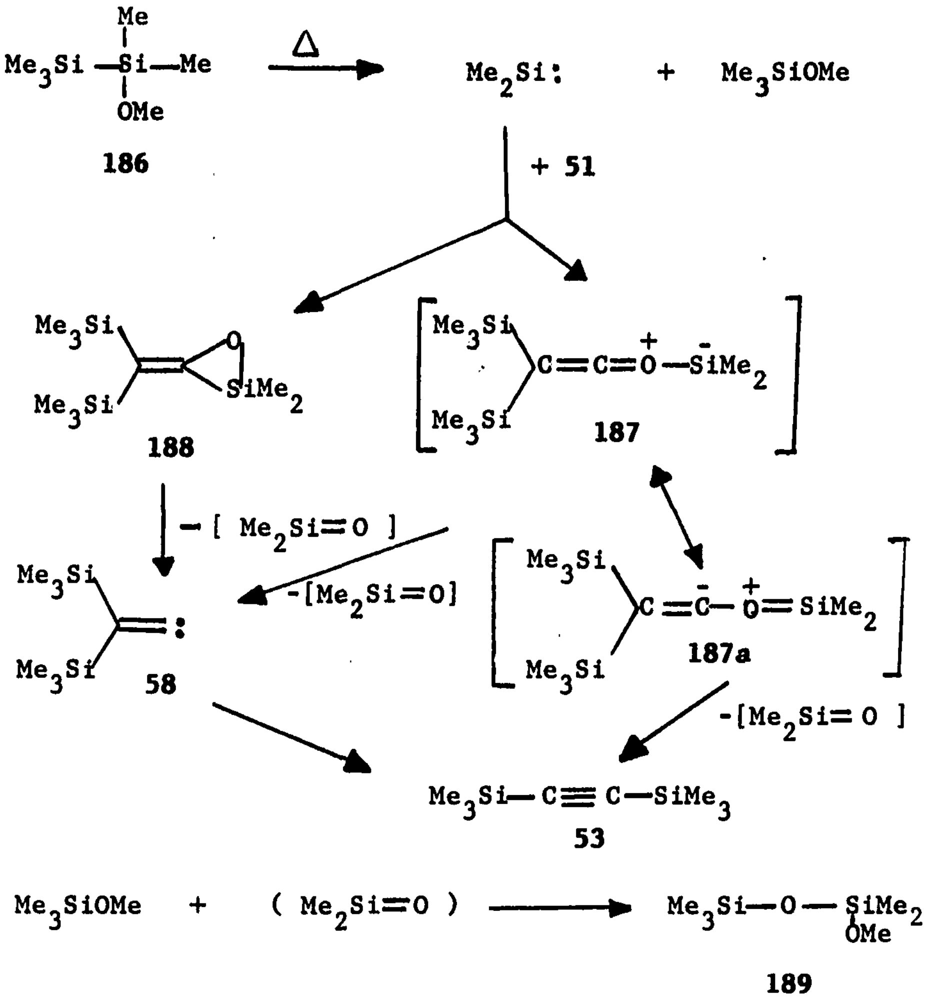
$$\mathbf{51} \qquad \mathbf{186} \qquad\qquad \mathbf{53}\ \mathbf{(15\%)}$$

$$+\ \mathrm{Me_3SiOMe} + \mathrm{Me_3SiOSiMe_2(OMe)}$$

$$\mathbf{189}$$

Formation of products can be rationalized by mechanisms shown in Scheme 30. Thermally generated dimethylsilylene may react with ketene to form ylide **187** which then collapses

Scheme 30



to give vinylidene **58** and dimethylsilanone. 1,2-Silyl migration in **58** results in **53**. Ylide **187** may directly decompose to **53** and dimethylsilanone. Alternatively, dimethylsilylene may add to ketene to form alkylidene oxasilirane **188**, which then may decompose to alkylidene carbene **58** leading to product **53**. Insertion of dimethylsilanone into Si-O bond of methoxytrimethylsilane leads to methoxy pentamethyldisiloxane (**189**). Similar mechanisms have been recently proposed for reaction of germylene ($:GeMe_2$) with thioketenes by Ando and coworkers.[84]

Copyrolysis of bis(trimethylsilyl)thioketene (**128**) and 1,2-dimethoxy,1,1,2,2-tetramethyldisilane (**185**) in an N_2 flow system (30 ml/min) at 346°C (59% conversion of **128**) results in bis(trimethylsilyl)acetylene (**53**) in yield of 31% (mass recovery 78%). Similar mechanisms can be proposed to explain the formation of products. No products

$$\underset{\mathbf{128}}{Me_3Si)_2C{=}C{=}S} + \underset{\mathbf{185}}{Me_2(OMe)Si{-}Si(OMe)Me_2} \xrightarrow[N_2\ \text{Flow}]{346°C} \mathbf{53}\ (31\%) + \underset{\mathbf{55}}{Me_2Si(OMe)_2}$$

$$\mathbf{128} + Me_2Si: \longrightarrow [Me_3Si)_2C{=}C{=}\overset{+}{S}{-}\overset{-}{Si}Me_2]$$

$$\mathbf{53} \longleftarrow \mathbf{58} \xleftarrow[-(Me_2Si=S)]{\qquad\qquad} [Me_3Si)_2C{=}\overset{-}{C}{-}\overset{+}{S}{=}SiMe_2]$$

corresponding to the oligomerization of dimethylsilanethione or its insertion into **185** and/or **55** were detected!

Although ketenes under photolytic conditions decompose to give CO and carbene,[4a] silylketenes such as **51** and **74** are found to be remarkably stable under photolytic conditions. Silylketenes **51** and **74** were recovered unchanged after photolyzing for several hours with light having λ = 254 nm.

Reactivity of photochemically generated silylenes were investigated with silylketenes **51** and **74**. Both ketenes were found to be unreactive toward silylenes generated photochemically.

$$\mathbf{51} \text{ or } \mathbf{74} + \underset{\mathbf{190}}{(Me_2Si)_6} \xrightarrow[C_6H_6/C_6H_{12}]{h\nu} \text{No reaction}$$

It appears that state and energetic of silylene are important for its reactivity with silylketenes.

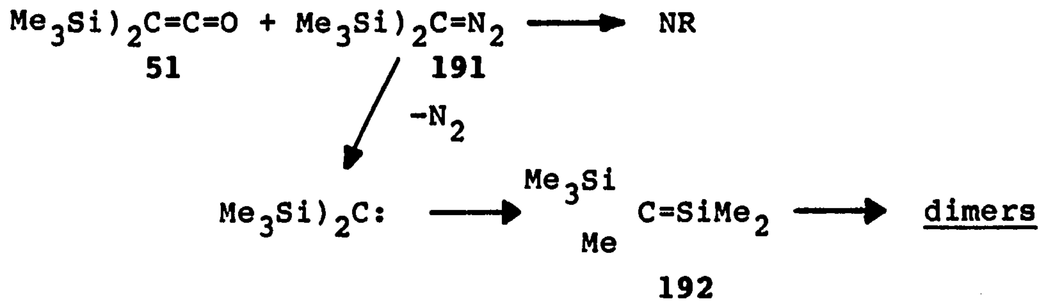
Reactivity of silene with silylketenes

Silenes react with both olefins and isolated carbonyl compounds in a 2+2 fashion. Ene reactions of silene with enolizable ketones are also observed.[63] It was attempted here to study the reactivity of silenes with silylketenes which possess both functionalities mentioned above.

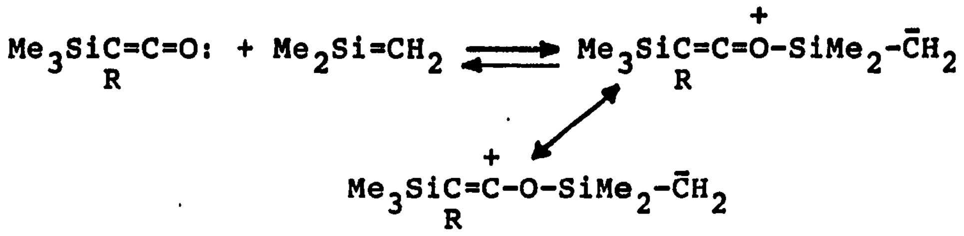
Nitrogen-flow pyrolysis of 1,1-dimethyl-1-silacyclobutane (**145**, a well-established thermal generator of $Me_2Si{=}CH_2$) with **51** at 516°C (where **51** is stable) did not afford any product resulting from interaction of dimethylsilene with ketene **51**. Only the head-to-tail dimer of silene along with unreacted starting material was observed.

Copyrolysis of trimethylsilylketene (**74**) with **145** at 570°C under SFR conditions was performed. Once again only dimer **148** of $Me_2Si{=}CH_2$ was observed along with unreacted **74** and **145**.

Reactivity of photochemically generated silene with ketene **51** was also investigated. Bis(trimethylsilyl)-diazomethane (**191**) is known to generate silene both thermally and photochemically.[43] Thus, a benzene solution of ketene **51** and diazomethane **191** was photolyzed in a Rayonet photochemical reactor with 253.7 nm lamps. Ketene **51** remained totally unchanged. Dimers of intermediate silene **192** were observed. A small amount of siloxane resulting from the reaction of moisture with silene was also formed. Dimers formation and/siloxane formation from **191** is in accord with literature report.[43]



Silenes generated both thermally and photochemically are thus found to be unreactive toward silylketenes. This unreactivity perhaps can be rationalized as follows:



$$Me_3Si\underset{R}{C}{=}C{=}O{:} + Me_2Si{=}CH_2 \rightleftharpoons Me_3Si\underset{R}{C}{=}C{=}\overset{+}{O}-SiMe_2-\bar{C}H_2$$

$$\leftrightarrow Me_3Si\underset{R}{C}{=}\overset{+}{C}-O-SiMe_2-\bar{C}H_2$$

Presumably the reaction is stepwise and reaction steps involve rather energetically unfavorable vinyl cation which, therefore, disfavors the reaction of ketene with silene.

The stability of α- and β-silicon-substituted alkyl radicals

The stability of alkyl radicals by α- and β-silyl substituents is a long standing question. Gas kinetic experiments have been used for determining the activation energies for primary reactions viz. radical forming homolysis and retroene elimination.[85] It was conceived that kinetic studies of suitable compounds might allow to determine α- and β-stabilization due to silylsubstituents. For this purpose, tert-butyl compounds 2,2-dimethyl-3-(trimethylsilyl)propane (**194**), 2,2-dimethyl-4-(trimethylsilyl)butane (**195**) and 2,2-dimethylbutane (**196**) were chosen. Hydrocarbon **196** is commercially available and is used as a reference compound. Compounds **194** and **195** were synthesized.

The only primary reaction of compounds **194-196** would be expected to be the homolysis of the tert-butyl-carbon bond.

Compounds **194-196** were pyrolyzed under low pressure pyrolysis (LPP) conditions with partial pressures of reactant between 0.005 and 0.04 torr. Pyrolyses with emphasis on product analysis were also carried out in an SFR, with reactant partial pressures of 0.08-0.8 torr in ca. 1000 torr of N_2. Kinetic results for the decomposition of these compounds appear in Table 7.[86]

The early stages of pyrolysis of **196** could be as shown in Scheme 31, followed by abstraction reactions by Me radicals to propagate a chain forming CH_4 and C_5H_{10}. All of these products were detected in the SFR, but $[Me_2C{=}CH_2] = [C_2H_4] > CH_4$; i.e., the chain did not develop.

Scheme 31

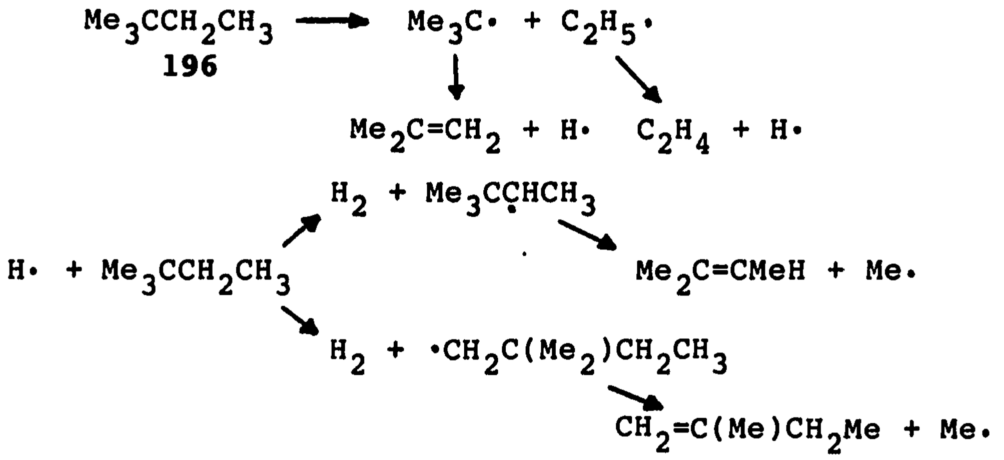
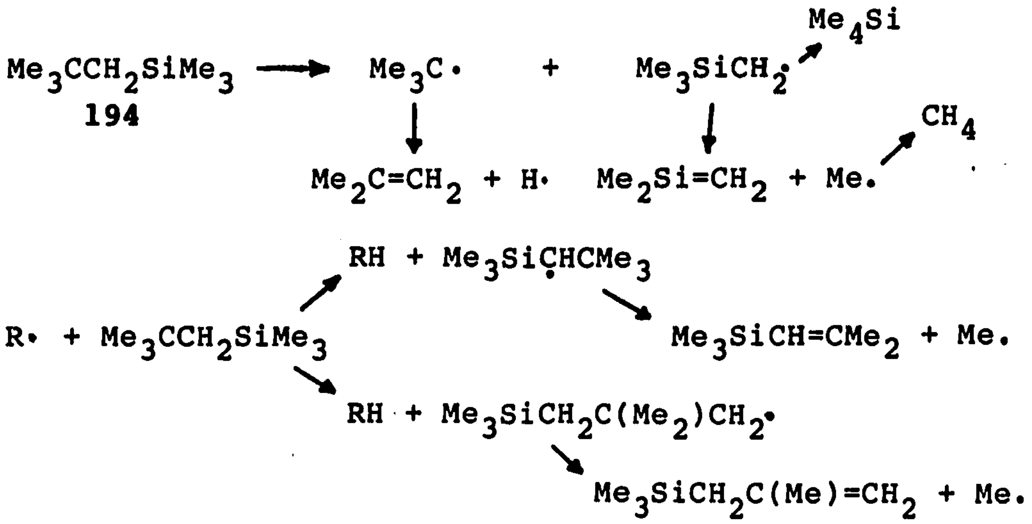


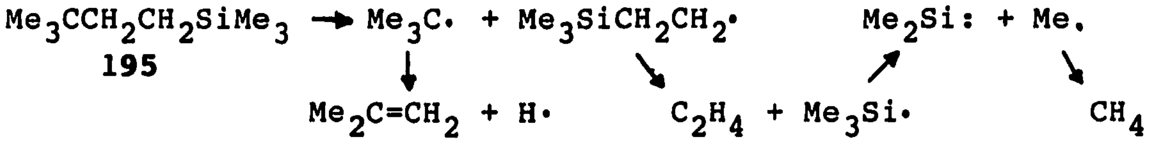
Table 7. Kinetic results by LPP (R = tert-butyl)

Compound	log A	Ea/kcal mol^{-1}	temp/°C
Me_3SiCH_2R (**194**)	16.2 ± 0.1	73.9 ± 1	600-653
$Me_3SiCH_2CH_2R$ (**195**)	16.1 ± 0.2	73.9 ± 1	606-668
CH_3CH_2R (**196**)	16.1 ± 0.1	76.5 ± 1	650-712

Scheme 32



Product analysis in the SFR: $[Me_2C=CH_2] > [CH_4]$



Product analysis in the SFR: $[C_2H_4] = [Me_2C=CH_2] > [CH_4]$

As the kinetic data in Table 7 were obtained by LPP at lower pressures of **196**, the Arrhenius parameters should relate to the initial dissociation of the tert-butyl ethyl bond. Similar arguments should apply to **194** and **195** as shown in Scheme 32. Kinetic data were unaffected by LPP experiments with added methylchloride or hydrogen chloride, strengthening our belief that the pyrolyses of **194-196** were nonchain under LPP conditions. Kinetic results in the SFR at 1000 torr indicated that the results in Table 7 were little affected by unimolecular fall-off; insofar as they were, the effect would be greater for **196**. The activation energy differences in Table 7 should, therefore, be a reasonable measure of the relative strengths of the bonds broken, especially as the A factors in Table 7 are essentially constant. It can be concluded that α- and β-silyl substituents appear to stabilize alkyl radicals equally by (76.5-73.9) kcal mol^{-1}, i.e., 2.6 ± 1 kcal/mol.

Kinetic experiments by Auner and coworkers led to an estimate of 3 ± 1 kcal mol^{-1} for the β-silyl stabilization energy,[87] but only 0.4 ± 1 kcal/mol for the α -stabilization.[88] Both methods are indirect, each with assumptions that are reasonable but not infallible. Consequently, while the agreement over β-stabilization is pleasing, the extent of α-stabilization remains an open question. Jackson and coworkers[89] found enhanced reactivity toward hydrogen abstraction at both the α- and β-carbons of Et_4Si; they considered the β-stabilization effect to be greater than the α-effect, but comparisons are complicated by uncertainty over the allowance that should be made for steric hindrance when Et_4Si was compared with hydrocarbon prototypes. From ESR studies on $\cdot CH_2SiMe_3$ radicals generated by hydrogen abstraction, Krusic and Kochi[90] concluded that these radicals might be more stable than their alkyl counterpart. Although their explanation for the nature of that stabilization has been challenged,[91] it remains an experimental fact that radicals could be generated from Me_4Si but not from Me_4C under the same experimental conditions. Similar enhanced reactivity in analogous circumstances was observed by Sakurai and coworkers.[92] Walsh has suggested that some of the "α-stabilization" we observed with compound **194** may simply result from release of gauche interactions[86] but these are believed[93] to be small in organosilanes because bonds to silicon are long. Measurements[86] are consistent with that and the two gauch interactions in **194** are calculated to be only 0.4 kcal.

Clearly, both the α- and β-silyl stabilization effects are small and elusive, but results indicate that they may be closer in magnitude to each other than has been supposed hitherto.

Possible intermediacy of silicon-carbon triple bond in the decomposition of cyclopropylmethylsilylene

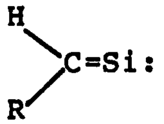
Although silicon-carbonl and silicon-silicon double bonded compounds are now well known, those containing triple bonds are still at the early level of theoretical calculations.[67] Calculations suggest that silynes (**197**)

$H{-}C{\equiv}Si{-}R$

197

a. $R = H$

b. $R = CH_3$



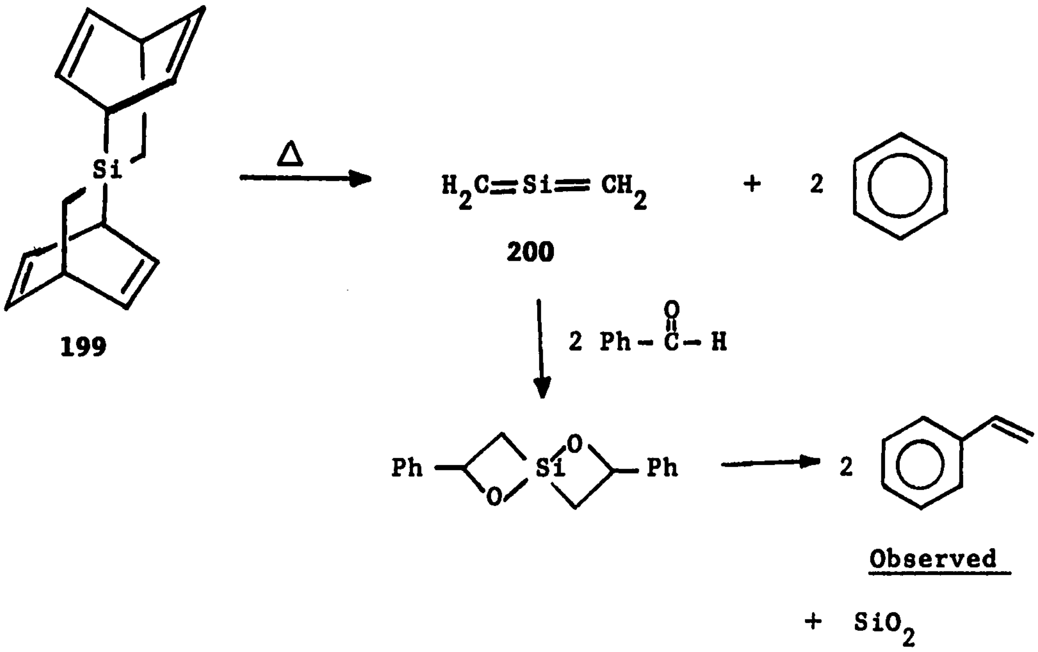
198

a. $R = H$

b. $R = CH_3$

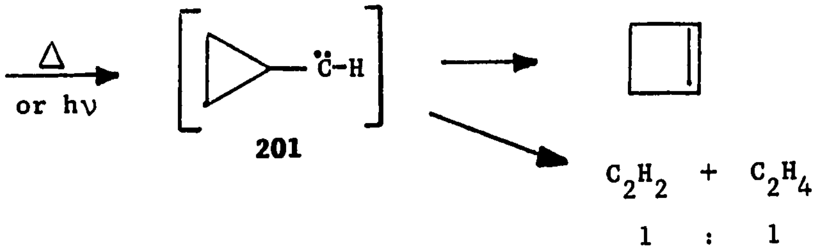
possess even higher degree of instability than those of silenes. Also isomeric 1-silavinylidene (**198**) is calculated to be more stable (~50 kcal/mol) than the linear isomer silyne (**197**). Furthermore, 2-silaallene (**200**) is calculated to be somewhat more stable than 1-methylsilyne (**197b**).[67]

2-Silaallene (**200**) has been proposed once as a possible intermediate in the copyrolysis of the adduct (2,8-dimethyl-3,9-dichloro-6-sila[5.5]spiroundecatetra-2,4,8,10-ene + methylacetylenedicarboxylate) and benzaldehyde.[94]



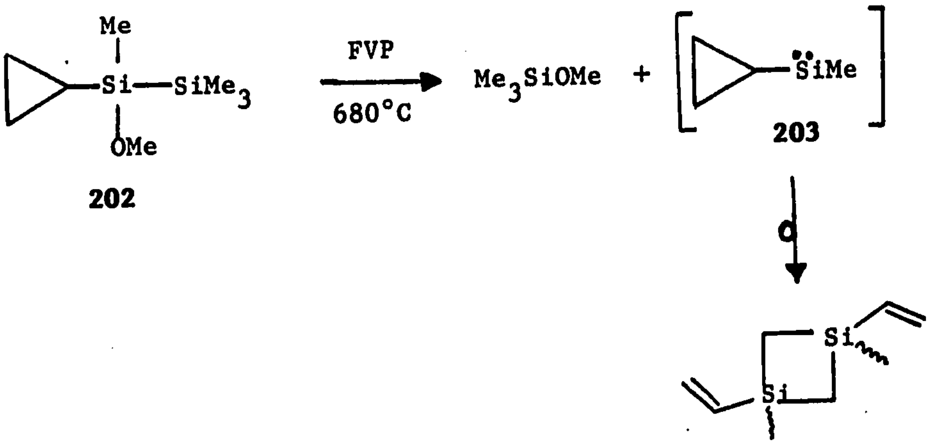
No other report regarding silyne or its isomer has appeared in the literature.

In an effort to gain insight into the possible intermediacy of silyne, it was decided to generate cyclopropylmethylsilylene (**203**). It is known that thermally or photochemically generated cyclopropylcarbene (**201**) gives both ring expansion product (cyclobutene) and fragmentation products (C_2H_2 and C_2H_4).[95] Distribution of products is dependent on both phase of the reaction and energy of the

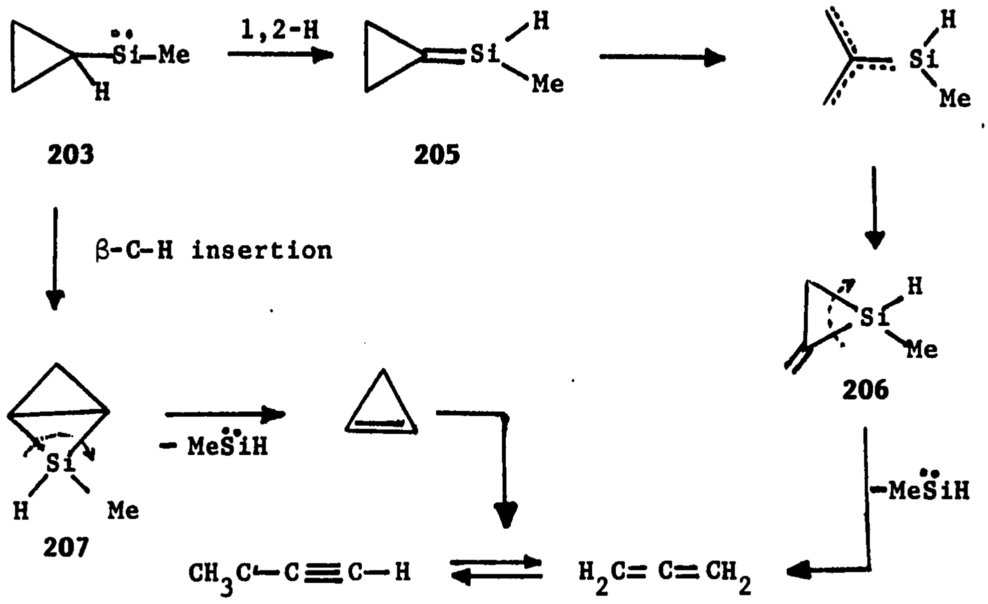


intermediate carbene **201**. Ethylene and acetylene are found to form in equimolar ratio.

In an earlier investigation,[96] silylene **203** has been generated, trapped with diene and in the absence of a trap ring expansion product **204** is characterized. Gaseous products, however, were not examined. It was decided to re-examine the decomposition of **202** with the intention of searching for C_2 hydrocarbons. FVP of **202** at 680°C afforded the previously mentioned products. In addition, gaseous hydrocarbon products formed in the process were examined by GCFTIR and GCMS. Products identified were acetylene, ethylene, allene and propyne. It should be mentioned that these products constitute only ca. 8-10% of the reaction. Formation of propyne and allene may be rationalized through the intermediacy of silylene **203** (Scheme 33). A 1,2-H

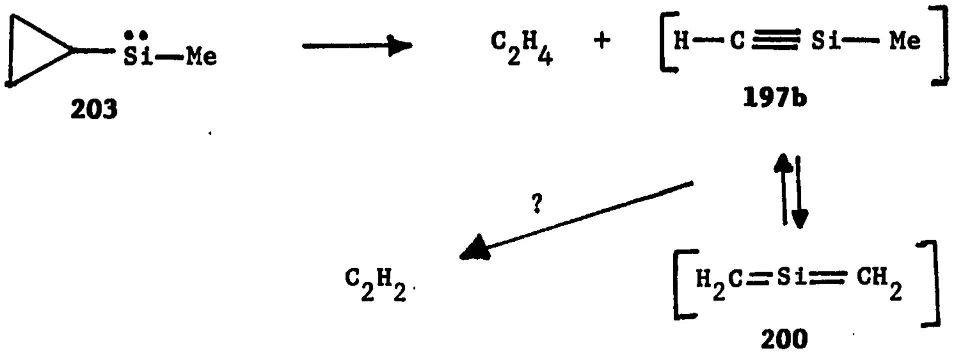


Scheme 33



migration from carbon to silicon in **203** gives cyclopropylidene silane **205** which then can isomerize to methylene silacyclopropane **206**. Extrusion of methylsilylene leads to allene, the latter is known to isomerize thermally to propyne. Alternatively, **203** can undergo C-H insertion to form silabicyclobutane **207** and extrusion of methylsilylene affords cyclopropene. Cyclopropene under experimental conditions is known to isomerize to allene and propyne.

Ethylene formation perhaps can be accounted for by fragmentation process analogous to that described for **201**,[95] as shown below.



The fate of transient silyne (**197b**) or its isomer **200** is not known. Silyne or its isomer may give rise to acetylene.

In addition, a few silylhydrides were observed by GCFTIR. In the GCFTIR fraction of allene and propyne, there were a few characteristic IR bands (Figure 4). These uncharacterized bands are marked U. Some of these bands do, however, correspond to terminal acetylenic compound (X≡C-H) and allene compound.

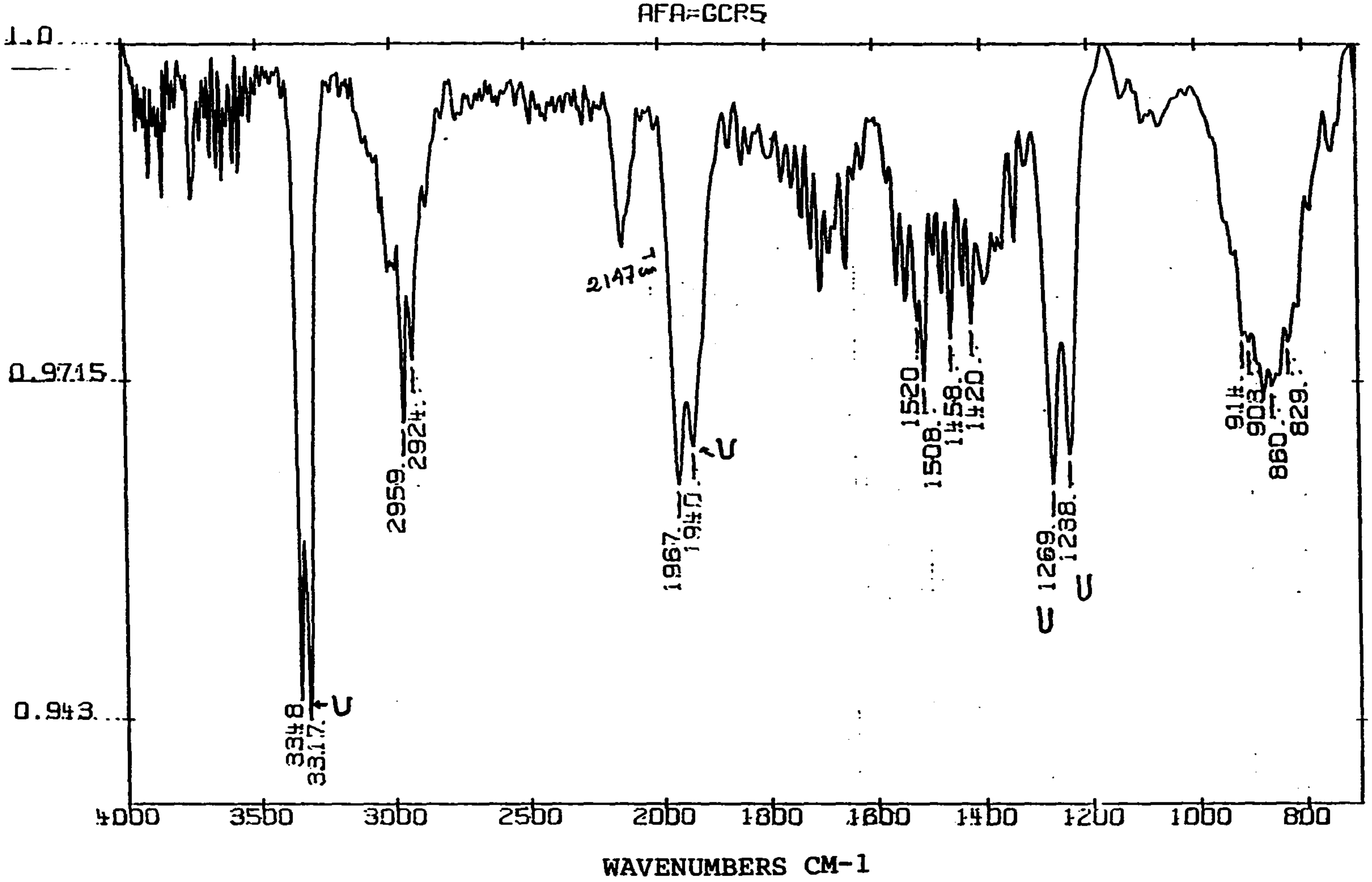


Figure 4. GCFTIR spectra of allene and propyne fraction

CONCLUSION

The products obtained in the thermal decomposition of persilylsubstituted ketenes were explained by invoking a 1,2-silyl shift to form an α-ketocarbene (a retro-Wolff process) which rearranged and decomposed to products. The activation parameters obtained from the decomposition kinetics of dimethylsilyl(trimethylsilyl)ketene were in accord with a retro-Wolff process.

The FVP products of alkyl(trimethylsilyl)ketenes were accounted for by three mechanistic routes viz., (i) a retro-Wolff process, (ii) a homolytic cleavage process and (iii) a retro-ene process. With bulkier alkyl groups such as t-butyl group, the predominant decomposition route was a retro-ene process, and the retro-Wolff products were not observed. The kinetic parameters obtained in the decomposition of t-butyl(trimethylsilyl)ketene to trimethylsilylketene were found to be consistent with a retro-ene process. The absence of intramolecular trapping products in the decomposition of the above alkyl-(silyl)ketenes has been rationalized.

The products obtained in the decomposition of bis(trimethylsilyl)thioketene and dimethylsilyl(trimethylsilyl)thioketene were also consistent with the intermediacy of an α-thioketocarbene formed by an initial 1,2-shift of silyl group (a retro-thio Wolff process). In the former case the presumed α-thioketocarbene underwent several modes of rearrangement to afford mixtures of products. The decomposition kinetics of the latter thioketene were measured in an SFR and the evaluated activation parameters were found to be consistent with the proposed 1,2-silyl shift mechanism.

Hydridosilylketenes and -thioketenes have been observed to decompose at a lower temperature than the corresponding bis(silyl)ketene and bis(silyl)thioketene. This could be attributed to the greater migratory aptitude of hydrogen over methyl. The observed higher activation energy for the decomposition of hydridosilylketene than that of hydridosilylthioketene implied that oxygen and sulfur were involved in the rate determining transition states.

Formation of dimethylsilylacetylene and cyclodisilazane in the FVP of tris(dimethylsilyl)ketenimine were also consistent with the 1,2-silyl shift mechanism to form inimocarbene and its subsequent rearrangements.

In an attempt to determine the structure of a silylketene, several bulky silylketenes were synthesized. Isolation of ketene products were rationalized through the intermediacy of silyl(siloxy)acetylenes and their isomerization.

Thermally generated dimethylsilylene has been observed to react with bis(trimethylsilyl)ketene and -thioketene resulting in bis(trimethylsilyl)acetylene. The reactions were proposed to proceed through ylide intermediates.

Both thermally and photochemically generated silenes were found to be unreactive toward silylketenes and this unreactivity has been rationalized.

Stabilization of α- and β-alkyl radicals due to silyl substituents were determined from collaborative kinetic studies of appropriate compounds and the values were found to be small and similar.

In an attempt to gain insight into the possible intermediacy of silylne, cyclopropylmethylsilylene was generated. Formation of ethylene and acetylene are suggestive of the transient formation of silyne or its isomer.

EXPERIMENTAL SECTION

Instrumentation

^1H NMR (300 MHz) and ^{13}C NMR (75.5 Hz) spectra were recorded on a Nicolet model NT-300 spectrometer. All chemical shifts are reported as parts per million (δ scale) from tetramethylsilane (TMS) and were taken in $CDCl_3$ solution unless otherwise noted. Infrared (IR) spectra and GCIR spectra were recorded on an IBM 98 FT/IR spectrometer coupled with an HP5880A capillary GC. All bands are reported in reciprocal centimeters (cm^{-1}). Mass spectra (MS) were recorded using a Finnigan 4023 (GC/MS) or a Hewlett Packard 5970 series (GC/MS) mass spectrometer and are reported as m/e (% relative intensity). 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 and/ 5890A series gas chromatograph fitted with a nonpolar 12.5 M or 30 M capillary column. Preparative GC was performed on a GOW MAC 550P or a Varian-Aerograph Series 1700 or a Varian 920 using 10 ft or 15 ft 10-15% SE-30 column on chromosorb W. Yields were determined by GC using internal standards after determination of appropriate response factors and are based on amount of starting material consumed. Elemental analyses were performed by Galbraith Laboratories Inc. or by Desert Analytics.

A pulsed stirred-flow reactor (SFR) modeled after the design of Baldwin et al.,[97] was used for kinetic analyses. The quartz sample chamber had a volume of 3 cm^3 and $\tau = 2.39$ s. The sample chamber was heated by an oven that was controlled by a Digi-Sense temperature controller. The SFR system used a 60 ml/min flow of helium to sweep the material (0.05-0.30 torr) through the reactor into a Varian 6000 GC, equipped with a 25 ft x 1/4 in, 25% SE-30 column on chromosorb W, 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 micro-computer (IBM-PC clone) for precise estimation of reactants and products. The SFR system enabled the determination of volatile C_1-C_4 hydrocarbon products which could have escaped detection under flash vacuum pyrolysis (FVP) conditions.

Procedures and results

General condition for flash vacuum pyrolysis (FVP)

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

General conditions for flow pyrolysis All samples were added slowly to a vertical quartz tube packed with quartz chips of the same dimensions used for flash vacuum pyrolysis. Pyrolysis was done in a flow of nitrogen (30-35 ml/min). The pyrolysate was collected in a cold trap cooled to -78°C.

Synthesis of bis(trimethylsilyl)ketene (51) Compound 51 was synthesized from 2,3-dihydrofuran following the procedure described by Groh.[75] In a 50 ml round-bottom flask containing THF (10 ml) at -40 to -50°C was added n-BuLi (11.5 mmol). 2,3-Dihydrofuran (0.70 g, 10 mmol) was added dropwise while keeping the bath temperature below -40°C, stirred for 45 minutes at this temperature and then allowed to warm up to room temperature. After stirring for 24 hours at room temperature it was cooled to -78°C and n-BuLi (11.5 mmol) was added. It was kept 40 minutes at this temperature and then warmed up to room temperature and stirred for 10 hours. After cooling to -78°C, excess trimethylchlorosilane was added and the mixture was gradually allowed to reach room temperature and stirred for another hour. Trap to trap distillation under vacuum, followed by preparative GC (10 ft 15% SE 30 column) led to **51** (46% based on 2,3-dihydrofuran). This is also accompanied by 2-trimethylsilyl-4,5-dihydrofuran (**107**). Spectra of **51** matched those reported by Woodbury et al.[77]

Flash vacuum pyrolysis (FVP) of 51 A sample of **51** (284.0 mg) was distilled (0-5°C, 10^{-4} torr) through a packed quartz tube at 834°C with a mass recovery of 76.4%. The products identified were 1-trimethylsilylpropyne (**52**, 42%) and D_3 (trace, by GCMS). Compound **52** was characterized by comparison of ^1H NMR, GCMS and GC retention time with an authentic sample. The yield was based on a 53% recovery of **51**.

Flow pyrolysis of 51 Nitrogen-flow pyrolysis of **51** (328 mg) at 625°C was carried out by dropwise addition of **51** to the pyrolysis tube over a period of 35 minutes. The pyrolysate (293 mg, 89%) was analyzed by GC and GCMS. Identified were 1-trimethylsilylpropyne (**52**, 15%) and bis(trimethylsilyl)acetylene (**53**, 9%). The yields were based on a 55% recovery of **51**. A third product having M^+ of m/e = 260 was detected by GCMS. Attempts to isolate this component by preparative GC were unsuccessful. Based on GCMS data the component was assigned structure **54** (ca. 4-5%): GCMS 260 (M^+, 0.6), 246 (4.5), 245 (16), 157 (5), 97 (19), 74 (8), 73 (100), 59 (13), 45 (24), 43 (9).

Pyrolysis of 51 in an SFR Ketene **51** was pyrolyzed in an SFR at 730.4°C. Apparent first order rate constants for the formation of **52** from **51** were measured both in the absence and in the presence of added 10- to 15-fold excess of toluene. Although small amounts of methane and ethane were detected, the rate constant for the formation of **52** was unaffected by added toluene (Table 8).

Copyrolysis of bis(trimethylsilyl)ketene (51) and dimethoxydimethylsilane (55) A mixture of **51** and dimethyldimethoxysilane (584 mg, 1:9) was pyrolyzed under N_2 flow pyrolysis at 620°C. The pyrolysate (464 mg, 79%) was collected in a cold trap at -78°C and analyzed by GC and GC/MS. Products identified were 1-trimethylsilylpropyne (**52**) and 1,3-dimethoxytetramethyldisiloxane (**56**). Yields were not calculated.

Synthesis of dimethylsilyl(trimethylsilyl)ketene (63) The compound **63** was synthesized from trimethylsilylketene (**74**) according to the general procedure of Woodbury et al.[77] The ynolate was quenched with dimethylchlorosilane to afford **63** (35%). Ketene **63** was isolated by preparative GC on a 15% SE-30 column (temperature programmed from 120°-200°C at 10° per minute). Spectral data of **63**: ^{1}H NMR 4.25 (sept, 1 H), 0.26 (d, 6 H), 0.20 (s, 9 H); ^{13}C NMR 166.60, 0.98, -1.34, -1.54; IR 3369, 2961, 2903, 2129, 2085, 2035, 1298, 1254, 918, 895, 841, 770, 633; MS 172 (M^+, 11), 158 (17), 157

Table 8. Apparent rate constants for formation of **52** from **51**

Compound Pressure **51** (torr)	Toluene (torr)	Temp, °C	k (s^{-1})
0.06	-	730.4	0.1069
0.07	-	730.4	0.1090
0.05	1.5	730.4	0.1154
0.14	1.4	730.4	0.1210
0.13	1.8	730.4	0.1205
0.29	-	730.4	0.1159

(100), 131 (17), 83 (34), 73 (85), 71 (13), 59 (35). The spectra of **63** matched those reported.[40,75]

Kinetics of decomposition of 63 Compound **63** was pyrolyzed in an SFR from 506-580°C. The products identified were trimethylsilylacetylene (**74**), D_3 and D_4. The first order rate constants for the formation of **74** were determined by pyrolyzing **63** at 506-580°C in an SFR (sample pressure 0.18-0.20 torr). The data along with the results of a linear least square calculation performed by a microcomputer, are summarized in Table 1. The kinetics of decomposition of **63** in the presence of D_3 (1:10 ratio) were measured at 560.5°C. The rate constant was found to be the same as it was in the absence of D_3.

Synthesis of isopropyl(trimethylsilyl)ketene (72) The method of Efimova et al.[47] was used to synthesize **72** in 80-85% yield. Isopropyl methoxyacetylene[57] and trimethylsilyl iodide[98] required for the synthesis of **72** were prepared according to literature procedures. Spectra of **72**: ^{1}H NMR 2.15 (sept, 1 H), 1.14 (d, 6 H), 0.15 (s, 9 H); ^{13}C NMR 183.06, 28.53, 25.72, 25.01, -0.32; IR 3364, 2961, 2872, 2081, 1460, 1385, 1366, 1288, 1252, 1167, 1001, 870, 839, 754, 633; MS 156 (M^+, 12), 141 (50), 99 (5), 83 (9), 75 (51), 73 (100), 59 (14), 45 (23), 43 (26).

FVP of 72 A sample of **72** (350 mg) was slowly distilled (10^{-3} torr) at 0°C through a quartz tube at 750°C with a mass recovery of 76%. By GC analysis, the pyrolysate showed four products which were isolated by preparative GC on a 15 ft 20% SE-30 column temperature programmed from 100-150°C at 2° per minute. The products identified were trimethylsilylketene (**74**, 12%), trimethylsilylacetylene (**64**, 30%), 4-methyl-2-butyne (**73**, 22%) and 1-trimethylsilylpropyne (**52**, 7%). The products were characterized by comparison of GCMS, ^{1}H NMR and IR data with those of authentic samples. The yields were based on recovered **72** (27%). Also formed were small amounts of D_3 and D_4 identified by GC retention times and GCMS data.

Pyrolysis of 72 under SFR conditions Ketene **72** was pyrolyzed in an SFR from 448-661°C with reactant partial pressures of 0.3-6.5 torr. At 610-661°C appreciable decomposition of **72** occurred. In addition to the above mentioned products, more volatile C_1-C_3 hydrocarbon products CH_4, C_2H_6 and propene were identified. Except methane and ethane, the ratio of other products were almost insensitive to the reactant pressures. At higher pressure, methane yield was observed to increase whereas yield of ethane decreased.

Copyrolysis of 72 and toluene under SFR conditions A mixture of **72** and toluene-d_0 (1:10 to 1:14) was pyrolyzed in an SFR at 660.8°C and products were analyzed. Except methane and ethane, all other products were unaffected by this copyrolysis experiments. Concentration of methane increased considerably with concomitant decrease in concentration of ethane. Pyrolysis was also conducted with a mixture of **72** and toluene-d_8 (1:10) where a large amount of CH_3D was observed in addition to CH_4 and ethane gases. Peak intensities corresponding to M^+ = 17 and 16 were monitored by MS which was connected to GC. From relative peak intensities the ratio of CH_3D and CH_4 was approximated to be 9:1. No deuterium incorporation appeared to be involved in any other product from 72.

Copyrolysis of 72 and dimethylmercury in an SFR Compound **72** (0.3 0.6 torr) was copyrolyzed with dimethylmercury (0.2-0.4 torr) at 508.8°C where **72** was stable. No product derived from **72** was observed. Only CH_4 and C_2H_6, the decomposition products of dimethylmercury were observed.

Synthesis of 2,2,5-trimethyl-2-silahex-4-en-3-one (81) The synthesis of **81** began with the synthesis of 1,1,3-trimethoxy-3-methylbutane (**210**) which was prepared from acetonedimethylketal and vinyl methylether using boron trifluorideetherate as catalyst.[99] Compound **210** was then converted into (E and Z)-1-methoxy-3-methyl-1,3-butadiene (**211**) in 50-60% yield using the $MgHPO_4 \cdot Na_2SiO_3$ catalyst according to the procedure described by Soderquist and Hassner.[48] The catalyst was made by mixing $MgHPO_4 \cdot 3H_2O$ (Sigma Chem. Co.) and water glass (Petrach System) as described in literature.[99] Compound **211** was transformed into (Z)-1-methoxy-3-methyl-1-trimethylsilyl-1,3-butadiene (**212**).[48] Hydrolysis of **212** led to **81** along with its minor isomer, which transforms into **81** on heating and/or on preparative GC. Spectral data for **81** matched published spectra.[48]

FVP of 81 A sample of **81** (134 mg) was slowly distilled (5°C, 1×10^{-4} torr) through the tube at 750°C. The pyrolysate (132 mg, 99% mass recovery) was analyzed by GC showing 100% conversion of **81** with almost quantitative formation of two isomeric products. The two products were separated by preparative GC on a 15 ft x 0.25 in 20% SE-30 chromosorb W column temperature programmed from 100-220°C at

4° per min. The products were identified as the (Z)- and (E)-isomers of 3-methyl-1-(trimethylsiloxy)butadiene (**84**) in a ratio of 35:65. The products were identified by GCMS, IR and ^{1}H NMR (300 MHz) data. **84** E: ^{1}H NMR 6.48 (d, 1 H, J = 12 Hz), 5.80 (d, 1 H, J = 12 Hz), 4.73 (broad s, 1 H), 4.67 (br s, 1 H), 1.79 (s, 3 H), 0.20 (s, 9 H); GCMS 156 (M^+, 17)., 141 (25), 113 (14), 101 (10), 75 (34), 74 (9), 73 (100), 59 (12), 55 (8), 47 (9), 45 (42), 43 (20). The NMR spectrum of **84** E is in close agreement with those reported by Trost et al.[100] **84** Z: ^{1}H NMR 6.12 (d, 1 H), J = 6.6 Hz), 4.93 (d, 1 H, J = 6.6 Hz), 4.97 (br s, 1 H), 4.72 (br s, 1 H) 1.97 (s, 3 H), 0.19 (s, 9 H); GCMS 156 (M^+, 18), 141 (26), 113 (14), 111 (10), 75 (35), 74 (9), 73 (100), 59 (13), 55 (8), 53 (6), 47 (9), 45 (44), 43 (20); IR **84** (Z and E): 3084, 3032, 2963, 2924, 1643, 1607, 1456, 1273, 1265, 1175, 1099, 1024, 924, 883, 847, 754 cm^{-1}.

<u>**Synthesis of ethyl(trimethylsilyl)ketene (95)**</u> Ketene **95** was synthesized from ethyl methoxyacetylene[57] and trimethylsilyl iodide[98] by an analogous procedure[47] as was used in the preparation of 72. The yield of **95** was 35%: ^{1}H NMR 1.94 (q, 2 H), 1.12 (t, 3 H), 0.14 (s, 9 H); ^{13}C NMR 182.82, 16.50, 15.82, 15.14, -0.87; IR 2964, 2935, 2085, 1788, 1252, 1018, 937, 843, 754, 653 cm^{-1}; GCMS 142 (M^+, 27), 127 (100), 99 (6), 83 (5), 73 (75), 59 (34); calcd for

$C_7H_{14}OSi$ m/e 142.0814, measured m/e 142.0812. An alternative synthesis of ketene **95** has been described.[101]

FVP of 95 A sample of **95** (134 mg) distilled (1 x 10^{-4} torr), from a bath at -12 to -15°C (dry ice/ethylene glycol) was pyrolyzed at 770°C with a mass recovery of 88%. The products were analyzed by GC. Four products were identified: trimethylsilylacetylene (**64**, 21%), 2-pentyne (**96**, 32%), trimethylsilylketene (**74**, 4%) and D_3 (trace by GCMS). The products were characterized by comparison of GCMS, ^1H NMR and IR data with those of authentic samples. The yields were based on a 53% recovery of starting material **95**.

Synthesis of 3,3-dimethyl-1-butanal (213) Compound **213** was prepared by oxidation of 3,3-dimethyl-1-butanol with pyridinium chlorochromate according to the general procedure of Corey and Suggs[102] in 85% yield. ^1H NMR 9.82 (t, 1 H), 2.24 (d, 2 H), 1.06 (s, 9 H). IR 2731, 1724 cm^{-1} (C=O).

Synthesis of tert-butylmethoxyacetylene (214) Following the general procedure of Nooi and Arens,[57] compound **213** was successively converted to 1-methoxy-1-chloro-3,3-dimethylbutane to 1-methoxy-1,2-dibromo-3,3-dimethylbutane which was then dehydrobrominated with diethylaniline in refluxing benzene to the corresponding 1-methoxy-2-bromo-3,3-dimethyl-1-butene **215** (E:Z = 98:2). The alkene **215** was then converted to compound **214** by heating with powdered potassium hydroxide at 140-150°C. The yield of **214** from **215** was >80%. Spectral data: **215** (E): ^{1}H NMR 6.24 (s, 1 H), 3.70 (s, 3 H), 1.16 (s, 9 H); ^{13}C NMR 141.64, 116.60, 60.03, 36.04, 29.50; GCMS 192 (M^+, 15), 179 (84), 177 (86), 125 (12), 123 (13), 113 (10), 98 (11), 83 (23), 82 (11), 81 (11), 79 (11), 67 (13), 66 (14), 65 (24), 55 (67), 53 (44), 51 (22), 50 (13), 43 (27), 41 (100). **214:** ^{1}H NMR 3.77 (s, 3 H), 1.16 (s, 9 H); ^{13}C NMR 90.32, 65.34, 44.94, 31.96, 26.32; IR 2968, 2947, 2868, 2282, 2241, 1477, 1458, 1362, 1308, 1198, 1132, 847 cm^{-1}.

Synthesis of tert-butyl(trimethylsilyl)ketene (97) and t-butyl(trimethylsiloxy)acetylene (127) In a 25 ml round bottom flask containing 0.017 mol of **214** and 6 ml dry acetonitrile was added 0.017 mol of trimethylsilyl iodide dropwise with constant stirring. The mixture was stirred for several hours at room temperature and the reaction was monitored by GCMS and IR. Finally it was gently refluxed (bath temperature 70-80°C) for several hours. Solvent was removed under low pressure and products were collected by distillation (b.p. 30-36°C at 1-2 torr). Identified were **97** and **127** in about equal ratio. Compounds **97** and **127** were separated by preparative GC on a 10 ft 15% SE-30 chromosorb W column temperature programmed from 100-200°C at 4° per min. The yields were low (ca. 8-10%). Spectral data: **97:** ^{1}H NMR 1.18 (s, 9 H), 0.18 (s, 9 H); ^{13}C NMR 183.38, 33.28, 32.32, 27.15, 1.22; GCMS 170 (M^+, 7), 156 (6), 155 (42), 99 (37), 75 (16), 73 (100), 69 (6), 67 (6), 59 (6), 57 (9), 55 (8), 53 (7), 45 (28), 43 (27), 41 (17); IR 3368, 2963, 2872, 2081, 2029, 1366, 1300, 1252, 1038, 978, 839, 756 cm^{-1}; calculated for $C_9H_{18}OSi$ m/e 170.11270, measured m/e 170.11250. **127:** ^1H NMR 1.15 (s, 9 H), 0.26 (s, 9 H); ^{13}C NMR 84.82, 40.85, 32.25, 26.48, -1.10; IR 2966, 2866, 2270, 1321, 1256, 1151, 868, 849, 725 cm^{-1}; GCMS 170 (M^+, 6), 155 (18), 99 (6), 75 (16), 73 (100), 45 (21), 43 (15), 41 (14); calculated for $C_9H_{18}OSi$ m/e 170.11270, measured m/e 170.11284.

FVP of tert-butyl(trimethylsilyl)ketene (97) A sample of **97** (46 mg) was slowly distilled (10^{-4} torr) through the quartz tube heated at 750°C. The pyrolysate was analyzed by GC. The products identified were trimethylsilylketene (**74**) and 1-trimethylsilylpropyne (**52**) in a relative ratio of ca. 3:1. About 30% of **97** was recovered. The products were identified by comparison with GCMS, IR and ^1H NMR data with those of authentic samples.

Pyrolysis of tert-butyl(trimethylsilyl)ketene (97) in an SFR Ketene **97** was pyrolyzed in an SFR from 550-650°C. In addition to products **74** and **52**, methane, ethane and isobutene were characterized. The kinetics of decomposition of **97** to trimethylsilylketene (**74**) were measured by pyrolyzing **97** in an SFR from 552.4-620.5°C with reactant partial pressures of 0.035-0.05 torr. The first-order rate constants for the formation of **74** at different temperatures were measured and they appeared in Table 2. The Arrhenius plot for this decomposition is shown in Figure 2; from which the kinetic parameters are evaluated and are included in Table 2.

Synthesis of isopropyl(trimethylsilyl)acetylene (102) Acetylene **102** was synthesized from commercially available 3-methylbut-1-yn-3-ol in three steps according to literature procedures.[103] It was accompanied by isomeric allenylsilane only (acetylene:allene = 24:1). Compound **102** was separated from isomeric allenylsilane by preparative GC. Acetylene **102** was also synthesized from isopropylacetylene in one pot as the sole product (Farchan Laboratory) by metallation with n-BuLi at -78°C followed by quenching with Me_3SiCl.[104]

FVP of 102 (i) Neat **102** (98 mg) was distilled (10^{-3} torr) slowly from a bath at 0°C, pyrolyzed at 750°C (~30% conversion). The pyrolysate (88 mg, 90% mass recovery) analyzed by GC and GCMS was found to contain trimethylsilylacetylene (**64**, ~4%), vinyl(trimethylsilyl)acetylene **103** (16%), 4-methyl-vinyl-(trimethylsilyl)acetylene **104** (~5%) and a trace of Me_4Si (**105**). The yields are relative GC yields and are uncorrected. (ii) FVP of **102** (140 mg) at 842°C (98% conversion) led to the above mentioned products in a different ratio (mass recovery 66%). The ratio of relative GC yields was **64**:**103**:**104**:**105** = 20:50:6:8.

FVP of mesityloxide (110) Mesityloxide (**110**, 0.305 g) distilled (10^{-2} torr) from a bath at 0-5°C, was pyrolyzed at 750°C (mass recovery 82%). The products identified were 2-methyl-1-butene (**112**) and 2-methyl-2-butene (**113**) in a combined yield of 47% (**112**:**113** ≈ 9:1) along with isomer 4-methyl-4-penten-2-one (**111**). The yield was based on recovered starting material **110** and isomer **111** (a total of 45%). The products were characterized by comparison of GCMS, GC retention times and ^{1}H NMR data with those of authentic samples. FVP of **110** at 660°C (10% conversion) gave only **111**.

Pyrolysis of 110 in the SFR Enone **110** was pyrolyzed in an SFR from 625-647°C with partial pressure of reactant 0.2-0.7 torr. More volatile hydrocarbon products CH_4, C_2H_6, and isobutene were obtained in addition to the products obtained under FVP conditions. A component having M^+ of m/e = 96 was also detected by GCMS. This component was present even below the decomposition temperature of **111**. Pyrolysis of either **110** or **111** from 400-500°C in the SFR results in mixture of **110** and **111**.

Enone **110** was pyrolyzed with 10- to 20-fold excess of toluene in an SFR at 647°C. The relative yields of methane, isobutene, **112** and **113** were measured. The yields of **112** and

113 decreased with increase in amount of toluene whereas isobutene concentration remained almost constant. The yield of methane increased dramatically. Apparent rate constants were evaluated for **112** and isobutene by pyrolyzing **110** and toluene (a few fold excess) at 646.9°C in an SFR. The results appear in Table 9.

Synthesis of bis(trimethylsilyl)thioketene (128) N-BuLi (10.0 mmol) was added to a stirred solution of trimethylsilylacetylene (10.0 mmol) in 20 ml dry ether (under N_2) at -40°C. After 45 minutes of stirring at -40°C sulfur (10 mmol) was added. Stirring was continued for 2-3 hours keeping temperatures below -30°C to form a yellow solution. Trimethylchlorosilane (11 mmol) was then added to the above solution at -40°C which was then gradually warmed to room temperature. Volatiles are removed under low vacuum. Distillation of the residue under vacuum gave **128** in about 80-90% yield (b.p. 60°C at 0.25 torr). ^{1}H NMR 0.23 (s, Me_3Si); ^{13}C NMR 214.42, 52.21, 0.67; IR 2959, 2899, 1758, 1252, 841, 760 cm^{-1}. Spectral data matched reported values.[62]

FVP of 128 Compound **128** (282 mg) distilled (10^{-4} torr) slowly from a bath at 5°C, was pyrolyzed at 768°C with a 75% mass recovery. The pyrolysate was analyzed by GC, GCMS, ^{1}H NMR and IR and found to contain a mixture of six

Table 9. Apparent rate constants for formation of isobutene and 2-methyl-1-butene

Compd. 110 (torr)	Pressure Toluene (torr)	Rate constants (k)		Temp. °C
0.60	-	0.1028	0.3727	649.9°C
0.57	5.34	0.1111	0.2466	649.9°C
0.60	8.16	0.1144	0.1958	649.9°C
0.62	12.32	0.0934	0.1788	649.9°C

products: 1-trimethylsilylpropyne (**52**, 13%), trimethylsilylacetylene (**64**, 11%), bistrimethylsilylacetylene (**53**, 17%), trimethylsilylthioketene (**129**, 17%), 2,2,4,4-tetramethyl-2,4-disilathietane (**130**, 8%) and tetramethylcyclodisilathiane (**131**, 4%). The products were separated by preparative GC on a 10 ft x 0.25 in. 15% SE-30 chromosorb W column temperature programmed from 100-200°C at 8° per minute. Compounds **52**, **53** and **64** were characterized by comparison of ^{1}H NMR, GCMS and IR data with those of authentic samples. **129** was collected by preparative GC along with **53** and because of instability of **129**, it was characterized by ^{1}H NMR 3.52 (s, 1 H), 0.20 (s, 9 H); ^{13}C NMR 220.87, 49.94, -0.032; IR (C=C=S) 1744 cm^{-1}; GCMS 130 (M^{+}, 18), 115 (79), 75 (33), 73 (97), 57 (32), 53 (38), 45

(80), 43 (100), 39 (36), 32 (36). **130:** ^{1}H NMR 0.62 (s, 2 H), 0.50 (s, 12 H); GCMS 162 (M^+, 14), 149 (12), 148 (16), 147 (100), 131 (5), 75 (4), 73 (7), 59 (12), 45 (10), 44 (6), 43 (17). MS data of **130** closely agree with literature values.[68] **131:** ^{1}H NMR 0.75 (s, 12 H); MS 180 (M^+, 24), 167 (15), 166 (14), 165 (100), 75 (8), 73 (14). Spectral data matched those reported.[65,68]

Synthesis of dimethylsilyl(trimethylsilyl)thioketene (138) Compound **138** was synthesized by a route analogous to that used for the synthesis of **128**. Trimethylsilylethynyl lithium was successively quenched with sulfur and dimethylchlorosilane (instead of Me_3SiCl) to afford **138** in 98% yield (b.p. 22-23°C at 0.25 torr). ^{1}H NMR 4.24 (sept, 1 H), 0.31 (d, 6 H), 0.23 (s, 9 H); ^{13}C NMR 213.66, 49.49, 0.17, -2.34; IR 2961, 2904, 2131, 1765, 1252, 943, 879, 839, 768, 625 cm^{-1}; MS 188 (M^+, 33), 173 (81), 159 (7), 133 (16), 115 (23), 97 (16), 90 (7), 83 (42), 73 (100), 59 (10), 53 (5); calcd for $C_7H_{16}SSi_2$ m/e 188.05113, measured m/e 188.05118. Anal. calcd for $C_7H_{16}S$: C, 44.62; H, 8.56; S, 17.01. Found: C, 44.41; H, 8.41; S, 16.63.

FVP of 138 (i) A sample of **138** (249 mg), distilled (1×10^{-4} torr) slowly from a bath at 0-5°C, was pyrolyzed at 700°C resulting in 100% conversion of **138**. The pyrolysate consisted of two parts: (i) solid materials that were condensed on the cool surface above the collection tube and (ii) liquid in the collecting tube at -196°C. Analysis of liquid (127 mg) by GC, GCMS and ^1H NMR showed only trimethylsilylacetylene (**64**, 92%). The solid materials were thawed, weighed (94 mg) and dissolved in $CDCl_3$. Analyses by GC, GCMS and ^1H NMR showed tetramethylcyclodisilthiane (**131**, 64%), hexamethylcyclotrisilthiane (**139**, 7%) and **140** (8%). Spectral data of **131**, **139** and **140** matched reported values.[65,68] Yields of **131**, **139** and **140** were calculated from integration of appropriate NMR peaks. (ii) FVP of **138** at 600°C resulted in 94% conversion of **138** with formation of the above mentioned products.

Copyrolysis of 138 and 1,1-dimethyl-1-silacyclobutane (145) A mixture of **138** and **145** (900 mg, 1:4.3) under a flow of N_2 (35 ml/min) was pyrolyzed slowly through a tube heated to 600°C. The pyrolysate was analyzed by GC, GCMS and ^1H NMR revealing three components: 2,2,4,4-tetramethyl-2,4-disilathietane (**130**, 24%), **146** (8%) and **147** (trace by GCMS) in addition to **64**, **131** and **148**. Compounds **130** and **146** were separated by preparative GC (10 ft 15% SE-30 on chromosorb W column temperature programmed from 100-150°C at 5° per min) and were characterized by GCMS and ^1H NMR data. Spectral data of these compounds matched those reported.[68]

Kinetics of decomposition of 138 The first-order rate constants for formation of trimethylsilylacetylene (**64**) were determined by pyrolyzing **138** at 435-494°C in an SFR with reactant partial pressures of 0.28-0.32 torr. The results are reported in Table 4. The Arrhenius plot for formation of **64** is shown in Figure 3, from which the kinetic parameters are evaluated and are included in Table 4.

Synthesis of tris(dimethylsilyl)ketenimine (153) Compound **153** was synthesized according to the procedure described by Gornowicz and West.[69] Pure sample of **153** was obtained by preparative GC on a 10 ft 15% SE-30 on chromosorb W column. ^{1}H NMR 4.57 (sept, 1 H), 4.22 (sept, 2 H), 0.28 (d, 6 H), 0.18 (d, 12 H); ^{13}C NMR 162.34, 10.19, -1.59, -1.78; MS 215 (M$^+$, 24), 214 (11), 201 (14), 200 (63), 157 (12), 156 (63), 140 (10), 131 (13), 130 (64), 116 (38), 115 (35), 100 (31), 86 (11), 73 (61), 70 (17), 59 (100), 45 (27), 43 (55).

FVP of 153 Neat **153** (90 mg) distilled (2-4 x 10^{-4} torr) from a bath (25°C) was pyrolyzed at 710°C (80% mass recovery). Analyses of the pyrolysate by GC, GCMS and ^{1}H NMR showed dimethylsilylacetylene (**154**, 29%) and N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane (**155**, 5%). Acetylene **154** was characterized by comparing GCMS and ^{1}H NMR data with those of an authentic sample. Cyclodisilazane **155** was characterized by comparing GC retention time and GCMS data with those of an authentic sample of **155** synthesized following the literature procedure.[105] The yields were based on a 28% recovery of **153**.

Synthesis of triphenylsilylacetic acid (164)

Method (A) Triphenylsilylchloromethane (**165**), needed for the synthesis of **164**, was prepared from phenylmagnesium bromide and trichlorosilylchloromethane in 73% yield.[106] Compound **165** was then converted to **164**. A typical procedure for the synthesis of **164** is as follows: In a flame-dried 3-neck flask (100 ml) fitted with a magnetic stirring bar, an addition funnel, a reflux condenser and a septum inlet, was introduced magnesium (0.4 g) under N_2. Dry **165** (3.08 g, 10 mmol) dissolved in THF (40 ml) was transferred to the additional funnel. The reaction was initiated by dibromoethane and then dropwise addition of the solution of **165** was continued. The temperature of the reaction mixture was maintained at 50-60°C. At the end of addition, the reaction mixture was stirred for 5 more hours at 50°C. Dry CO_2 gas was then passed through the Grignard solution overnight (12 hours) at which point white solid appeared. This was hydrolyzed with dilute HCl (2%), extracted with ether, dried over anhydrous $MgSO_4$, rotavaped to obtain white crystalline solid (2.82 g, >88%). This was associated with a small amount of triphenylsilylmethane. Recrystallization from a mixture of CH_2Cl_2 and skelly "B" led to pure acid **164** (2.42 g, 76%; m.p. 173°C (lit.[74b]

175°C)). ^{1}H NMR 7.25-7.65 (m, 15 H), 2.71 (s, 2 H); ^{13}C NMR 176.3, 135.6, 132.95, 130.0, 127.98, 24.0; IR 3068, 1686, 1427, 1298, 1113, 743, 737, 698, 501 cm^{-1}; MS 318 (M^{+}, 0.8), 276 (26), 260 (25), 259 (100), 241 (35), 240 (59), 200 (17), 199 (93), 181 (32), 155 (10), 122 (14), 105 (9), 77 (15); calcd for $C_{20}H_{18}O_{2}Si$ m/e 318.1076; measured m/e 318.1072.

Method (B) Triphenylsilyllithium in THF made from triphenylchlorosilane and excess lithium[107] was filtered from unreacted lithium metal. Passing formaldehyde through this solution led to acetoxysilane **169** (89% yield). This was then reduced with $LiAlH_4$ quantitatively to triphenylsilylmethanol **170**. This was then converted to acid **164** as has been reported.[74b] Spectral data for **169**: ^{1}H NMR 7.25-7.6 (m, 15 H), 4.6 (s, 2 H), 8.08 (s, 1 H); ^{13}C NMR 161.4, 135.76, 132.29, 130.15, 129.12, 54.06. Gated-decoupled spectra: 161.4 (d), 54.06 (t); IR 3060, 1720, 1170, 1115 cm^{-1}; MS 318 (M^{+}, 0.2), 261 (7), 260 (28), 259 (100), 241 (81), 181 (26), 105 (13), 91 (5).

Synthesis of triphenylsilylacetylchloride (163) Compound **163** was synthesized according to the literature procedure[108] in 95% (crude product) yield. ^{1}H NMR 7.25-7.6 (m, 15 H), 3.34 (s, 2 H). IR 3092, 3071, 3037, 1776-80, 1479, 1429, 1113, 1005, 995, 795, 741, 698, 675 cm^{-1}.

Synthesis of triphenylsilylketene[109] (162) In a flame-dried 3-neck flask fitted with a stirring bar, a reflux condenser, an addition funnel and a septum inlet was introduced **163** under N_2. The compound was dissolved in ether (dried from LAH). Triethylamine (1.4 eq.) diluted with ether was added dropwise from an addition funnel with continuous stirring at room temperature and the reaction was monitored by IR. A reaction run on a 2.0 mmol scale was found to be complete in 45 minutes. Moisture should be avoided, and the solvent and triethylamine should be distilled just before use. Yield of **162** is > 90% (vide infra). Attempts to isolate **162** in pure form were unsuccessful. It was characterized by IR and GCMS. Ketene **162** readily transforms into anhydride **172**. **162:** IR (C=C=O) 2110 cm^{-1}; MS 300 (M^+, 8.6), 273 (26), 272 (100), 259 (15), 224 (11), 223 (56), 181 (9), 117 (7), 105 (12). **172:** ^1H NMR 7.25-7.6 (m, 30 H), 2.40 (s, 4 H); ^{13}C NMR 166.74, 135.7, 132.4, 130.1, 128.0, 25.3; IR 3060, 2963, 1794, 1427, 1259, 1113, 1036, 797, 737, 698.

Synthesis of $Ph_3Si(R_3Si)$ketenes (177a-c) (i) A flame dried 50 ml flask containing THF (10 ml), septum inlet and a stirring bar was cooled to -78°C. A positive pressure of N_2 was maintained throughout the reaction. N-BuLi (0.65 mmol) was added dropwise to the flask and stirred for 10 minutes at -78°C. A freshly prepared ether solution of triphenylsilylketene (162) was added dropwise to the above solution. After 15 minutes of stirring, Me_3SiCl (R_3SiCl, 1.0 mmol) was added and allowed to stir at -78°C for 20 minutes. It was then allowed to warm up to room temperature and stirred for 20 more minutes. The procedure described here was adapted from Woodbury et al.[77] The solution was filtered, and filtrate briefly flash chromatographed through silica gel (hexane as eluent) to remove salt and other impurities. Analyses of the material by GCMS, IR and ^1H NMR showed the presence of triphenylsilyl(trimethylsilyl)ketene (**177a**) ^1H NMR 7.3-7.7 (m, 15 H), -0.03 (s, 9 H); IR 3358, 3071, 2957, 2083, 1429, 1252, 1111, 901, 841, 698; MS 372 (M^+, 51), 358 (32), 357 (100), 279 (82), 255 (46), 217 (9), 197 (13), 193 (12), 181 (8), 132 (9), 105 (8).

(ii) Following the above procedure and finally quenching with $PhMe_2SiCl$ (R_3SiCl) led to triphenylsilyl-(phenyldimethylsilyl)ketene (**177b**). ^1H NMR 7.3-7.7 (m, 20 H), 0.39 (s, 6 H); IR 3373, 3071, 3049, 2959, 2083, 1427, 1258, 1119, 908, 831, 790, 698; MS 434 (M^+, 31), 420 (40), 419 (100), 342 (31), 341 (91), 317 (60), 279 (20), 259 (19), 197 (13), 181 (12), 105 (14).

(iii) Following the above procedure and quenching with p-bromophenyldimethylchlorosilane afforded ketene **177c**. ^1H NMR 7.2-7.7 (m, 19 H), 0.215 (s, 6 H); ^{13}C NMR 166.16, 136.85, 135.78, 135.17, 133.84, 130.90, 129.96, 127.92, 124.23, -0.45, -0.82; IR 3350, 3070, 2959, 2926, 2083, 1429, 1377, 1258, 1111, 1069, 906, 835, 816, 779, 741, 708; MS 514

(M^++2, 52), 512 (M^+, 45), 500 (25), 499 (67), 497 (62), 475 (58), 473 (52), 452 (24), 421 (27), 409 (37), 397 (28), 395 (26), 339 (42), 331 (31), 317 (31), 316 (33), 315 (100), 259 (52), 257 (44), 255 (29), 197 (20), 195 (54), 181 (30), 165 (15), 127 (17), 105 (17); calcd for $C_{28}H_{25}BrOSi_2$ m/e 512.06273; measured m/e 512.06263.

Synthesis of p-bromophenyldimethylchlorosilane This compound was synthesized from p-dibromobenzene according to the literature procedure.[110]

Synthesis of bis(silyl)ketenes (174a-c) The procedure used to synthesize bis(trimethylsilyl)ketene (**51**) was adopted to synthesize several other bis(silyl)ketenes **174a-c**. Here instead of Me_3SiCl, other chlorosilanes were used to quench ketene-enolate intermediate to give bis(silyl)ketenes. (i) Thus quenching with $PhMe_2SiCl$ led to ketene **174a**. It was separated from salt by filtration and finally briefly chromatographed through silica gel. The liquid obtained was subjected to preparative GC (10% SE-30 column, 10 ft) to obtain pure ketene **174a**. ^1H NMR 7.25-7.6 (m, 10 H), 0.32 (s, 12 H); IR 3354, 3069, 3049, 3010, 2956, 2083, 1427, 1290, 1252, 1113, 908, 835, 802, 731, 698 cm^{-1}; MS 310 (M^+, 30), 296 (28), 295 (100), 279 (7), 217 (56), 197 (9), 194 (14), 193 (71), 135 (29), 105 (16), 101 (15), 73 (8), 43 (18). The IR spectra matched those reported.[111] Also formed was **175a**: ^1H NMR 7.3-7.7 (m, 5 H), 5.23 (t, 1

H), 4.287 (t, 2 H), 2.58 (d of t, 2 H), 0.40 (s, 6 H); IR 3088, 3071, 3049, 3022, 2961, 2885, 1693, 1427, 1250, 1115, 1086, 926, 835, 812 cm^{-1}; MS 204 (M^+, 100), 203 (13), 189 (27), 176 (23), 161 (32), 159 (87), 149 (17), 135 (58), 131 (16), 105 (18), 43 (15).

(ii) Ketene **174b** was prepared by quenching with $Ph_2MeSiCl$. It was separated from other components by flash chromatography on silica gel (hexane as eluent). Finally recrystallized from pentane to obtain suitable crystals of bis(diphenylmethylsilyl)ketene (**174b**) m.p. 111.5°C. ^1H NMR 7.2-7.5 (m, 20 H), 0.47 (s, 6 H); ^{13}C NMR 166.0, 135.87, 134.59, 129.64, 127.83, -0.81, -1.44; IR 3354, 3061, 2956, 2087, 1427, 1254, 1118, 906, 830, 695 cm^{-1}; MS 434 (M^+, 29), 420 (36), 419 (97), 342 (31), 341 (100), 317 (62), 279 (16), 259 (10), 255 (11), 197 (26), 195 (18), 163 (8), 105 (20); calcd for $C_{28}H_{26}OSi_2$ m/e 434.15223; measured m/e 434.15165; anal. calcd for $C_{28}H_{26}$: C, 77.40; H, 5.99. Found: C, 77.15; H, 5.97. **175b** was also formed. MS 266 (M^+, 100), 252 (7), 251 (29), 238 (26), 223 (49), 221 (68), 211 (11), 197 (57), 181 (13), 173 (14), 165 (13), 131 (10), 129 (10), 119 (12), 105 (61), 77 (9), 53 (19), 43 (17).

(iii) Ketene **174c** was formed when intermediate ketene-enolate was quenched with p-bromophenyldimethylchlorosilane. As before separation from other components was done first by filtration, then by flash chromatography to give **174c** (a viscous liquid): ^{1}H NMR 7.2-7.45 (2 d, 8 H), 0.33 (s, 12 H); ^{13}C NMR 166.58, 136.60, 135.08, 130.96, 124.38, 0.05, -0.42; IR 3358, 3034, 2959, 2083, 1574, 1479, 1377, 1290, 1256, 1107, 1069, 912, 835, 798, 785, 723, 662 cm^{-1}; MS 468 (M^++2, 56), 466 (M^+, 21), 456 (14), 455 (49), 454 (23), 453 (100), 452 (13), 451 (45), 429 (14), 425 (14), 423 (13), 373 (42), 371 (31), 359 (32), 357 (28), 349 (29), 291 (32), 275 (39), 273 (39), 269 (51), 267 (24), 215 (25), 213 (25), 195 (42), 165 (13), 135 (12), 107 (12), 105 (13), 99 (15), 91 (34), 73 (18); calcd for $C_{18}H_{20}Br_2OSi_2$ m/e 465.94194; measured 465.94198; **175c** was also produced: MS 284 (M^++2, 65), 282 (M^+, 65), 269 (26), 267 (26), 256 (26), 254 (28), 239 (100), 237 (71), 215 (69), 213 (69), 185 (15), 129 (22), 128 (12), 119 (16), 115 (18), 111 (20), 109 (28), 107 (28), 91 (36), 75 (17), 53 (30), 45 (23), 43 (59), 41 (17).

Synthesis of methoxypentamethyldisilane (186)

Compound **186** was synthesized according to the procedure of Atwell and Weyenberg.[112]

Synthesis of 1,2-dimethoxytetramethyldisilane (185)

Compound **185** was synthesized from the corresponding dichlorosilane by a route analogous to that used for the synthesis of **186**.

Flow pyrolysis of 51 and 186 A mixture of 51 and **186** (234 mg, 1:3.3) was pyrolyzed under a flow of nitrogen (30 ml per min) at 550°C. The pyrolysate was analyzed by GC and

GCMS and the products identified were bis(trimethylsilyl)acetylene (**53**, 15%), methoxytrimethylsilane and methoxypentamethyldisiloxane. The yield was based on 50% recovery of **51**. Products were identified by comparison of GC retention time, GCMS and ^{1}H NMR data with those of authentic samples. In the decomposition, a few other silanone-trapped products were obtained which actually derived from the decomposition of **186** alone.

Flow pyrolysis of 128 and 185 A mixture of **128** and **185** (380 mg, 1:3) was pyrolyzed with a flow of N_2 (30 ml per min) at 346°C with 78% mass recovery. The pyrolysate was analyzed by GC and GCMS. Identified were dimethoxydimethylsilane (**55**) and **53** (31%). In addition, several silanone-trapped products which usually derived from the decomposition of **185** alone were observed. Products were identified by comparison of GCMS, IR and ^{1}H NMR data with those of authentic samples. The yield of **53** was based on 41% recovery of **128**.

Synthesis of dodecamethylcyclohexasilane (190) Compound **190** was synthesized according to the procedure described by Laguerre and coworkers.[113]

Synthesis of trimethylsilylketene (74) Ketene **74** was synthesized from ethoxyacetylene according to the procedure described by Ruden.[114]

Photolysis of 51 A thoroughly degassed 5% cyclohexane solution of **51** in a quartz NMR tube was irradiated by a 450 W medium pressure Hanovia mercury arc lamp. The reaction was monitored by GC and GCMS. The compound **51** remained unchanged even after seven hours of irradiation.

Photolysis of 74 The photolysis of ketene **74** was performed exactly as described above. Ketene **74** remained unchanged even after 15 hours of irradiation.

Photolysis of 51 and 190 A benzene (2.5 ml) solution of **51** (150 mg, 0.80 mmol) and **190** (85 mg, 0.24 mmol) in a quartz tube, was thoroughly degassed by purging with a stream of dry nitrogen. The solution was then photolyzed in a Rayonet photochemical reactor equipped with 253.7 nm lamps. The progress of the reaction was monitored by GC and GCMS. After several hours of irradiation almost all of **190** disappeared while **51** remained unchanged. The products observed were the same as those derived from irradiation of **190** alone.[115] No product derived from the interaction of **51** and dimethylsilylene was observed.

The irradiation of **51** (30 mg) and **190** (22 mg) in a cyclohexane (1.5 ml) solution with a 450 W Hanovia mercury arc lamp gave the same results as above.

Photolysis of 74 and 190 A cyclohexane (1.5 ml) solution of a mixture of **74** (27 mg, 0.23 mmol) and 190 (22 mg, 0.06 mmol) was thoroughly degassed and sealed in a quartz NMR tube. It was then photolyzed using a 450 W Hanovia mercury arc lamp for 2.3 hours. Analyses of the reaction products by GC, GCMS did not reveal any product from reaction of **74** and dimethylsilylene; **74** remained unaffected. As usual, products derived from **190** were observed.[115]

Synthesis of 1,1-dimethyl-1-silacyclobutane (145) Compound **145** was produced in three steps starting from allylchloride according to the sequence allylchloride --> 3-chloropropylmethyldichlorosilane --> 1-chloro-1-methyl-1-silacyclobutane --> **145**. (3-Chloropropyl)dichloromethylsilane was synthesized in 50% yield by the hydrosilation of allylchloride with dichloromethylsilane in presence of catalyst chloroplatinic acid (CPA) according to the literature procedure (Method A).[116] This was then converted successively to 1-chloro-1-methyl-1-silacyclobutane (82% yield) and then to **145** (77%) according to the published procedures.[117]

Synthesis of trimethylsilyldiazomethane (193) Compound **193** was prepared according to the procedure of Mori et al.[118]

Synthesis of trimethylsilylacetic acid The acid was synthesized according to the procedure of Sommer et al.[119]

Synthesis of bis(trimethylsilyl)diazomethane (191) Diazomethane **191** was synthesized from **193** according to published procedure.[120] Pure **191** was obtained by preparative GC on a 10 ft 10% SE-30 column on chromosorb W temperature programmed from 100°-120° at 5° per min.

__Flow pyrolysis of 51 and 145__ A mixture of **51** and **145** (189 mg, 1:2.5) was pyrolyzed under a flow of N_2 (30 ml/min) at 516°C. The pyrolysate was analyzed by GC and GCMS. The only product identified was 1,3-tetramethyl-1,3-disilacyclobutane (**148**), the head-to-tail dimer of dimethylsilene. Ketene **51** was recovered unchanged along with some unreacted **145**.

__Copyrolysis of 74 and 145__ A mixture of **74** and **145** (1:4) was pyrolyzed under SFR conditions at 570°C. Again **74** was recovered unchanged along with some unreacted **145**. Only product, dimer of dimethylsilene, **148** was formed.

__Photolysis of 51 and 191__ A 4% solution of **191** in dry benzene containing a threefold molar excess of ketene **51** in a quartz tube (90 mg **191**, 2.4 ml benzene, 290 mg **51**), was thoroughly degassed by purging with a stream of dry N_2 while keeping the solution below -40°C. The solution was then irradiated in a Rayonet photochemical reactor equipped with 253.7 nm lamps at room temperature. The progress of the reaction was monitored by GC and GCMS. After irradiation for three hours GC and GCMS revealed unchanged ketene **51**, a small amount of **191** and dimers of silene **192**. A small amount of disiloxane derived from reaction of silene dimer and H_2O is also observed. No product derived from **51** and silene **192** is found. The products derived from the intermediate silene **192** are in accord with literature report.[43]

Synthesis of 2,2-dimethyl-3-(trimethylsilyl)propane (194) To a 250 ml 3-neck flask containing magnesium turnings (1.5 g, 61.0 mmol), THF (60 ml), magnetic stirring bar and equipped with addition funnel and septum inlet under nitrogen was slowly added a THF solution of 2,2-dimethyl-1-chloropropane (5.33 g). The reaction was initiated by the addition of 1,2-dibromoethane. In the meantime freshly distilled trimethylchlorosilane (6.5 g, 60 mmol) was added all at once. The addition of 2,2-dimethyl-1-chloropropane was continued for a period of two hours while gently refluxing the solution. The solution was then refluxed for two days and hydrolyzed with dil HCl. After usual work up, the organic layer was dried over anhydrous $MgSO_4$. The more volatile compounds were removed by distillation and liquid left was collected. Compound **194** in pure form was obtained by preparative GC on a 10 ft 10% SE-30 column on chromosorb W. ^1H NMR 0.96 (s, 9 H), 0.67 (s, 2 H), 0.02 (s, 9 H); ^{13}C NMR 34.28, 33.09, 31.12, 0.94; MS 144 (M^+, 0.1), 129 (23), 113 (.1), 103 (0.8), 85 (0.3), 73 (100), 57 (6.6); calcd for $C_8H_{20}Si$ m/e 144.13343; measured m/e 144.13361.

Synthesis of 2,2-dimethyl-4-(trimethylsilyl)butane (195)

Compound **195** was synthesized from the reaction of Grignard reagent made from 3,3-dimethyl-1-bromobutane (**216**) and magnesium and trimethylchlorosilane. Compound **216** was synthesized from 3,3-dimethyl-1-butene via hydroboration followed by bromination, according to the general procedure of Brown and Lane (Method A).[121]. The yield of **216** was 48%; this was accompanied by the isomeric product 3,3-dimethyl-2-bromobutane (<2%). **216**: ^{1}H NMR 3.45 (app. d of d t, 2 H), 1.9 (app. d of d t, 2 H), 0.98 (s, 9 H); MS 166 (M^++2, 0.1), 164 (M^+, 0.1), 151 (2.7), 149 (2.8), 109 (1), 107 (1), 85 (2), 70 (2), 69 (38), 58 (5), 57 (100).

The synthesis of **195** from **216** was as follows: In a flame dried, 250 ml 3-neck flask fitted with a condenser, a stirring bar, a pressure equalizing addition funnel, a septum inlet, was taken magnesium turnings (2.45 g, 100 mmol) and THF (60 ml) under nitrogen. The reaction was initiated by adding 1,2-dibromoethane and refluxing for few minutes. Freshly distilled trimethylchlorosilane (9.8 g, 90 mmol) was then added into the flask all at once. A THF solution of **216** (13.7 g, 83 mmol) was added dropwise over a period of two hours. The reaction mixture was stirred for several hours at room temperature and then gently refluxed for 12 hours. It was hydrolyzed with dil. HCl, extracted with pentane, dried over anh. $MgSO_4$ and solvent removed under reduced pressure. The liquid left was fractionally distilled to obtain **195** (5.9 g, 45%): b.p. 58-60°C (20 torr); ^{1}H NMR 1.11-1.18 (m, 2 H), 0.83 (s, 9 H), 0.36-0.41 (m, 2 H), -0.04 (s, 9 H); ^{13}C NMR 38.12, 31.05, 28.96, 10.90, -1.75; MS 158 (M^+, 0.5), 143 (3), 101 (17), 83 (1), 73 (100), 59 (14).

FVP of 195 Neat **195** (170 mg), distilled (2×10^{-4} torr) from a bath (5°C), was pyrolyzed at 790°C. The volatiles from the pyrolysate were separated by trap-to-trap distillation (-78°C and -196°C traps). The gaseous products from -196°C trap were identified by both GC and GCMS as ethylene, propene and isobutene. The liquid at -78°C trap was mostly **195** (>90%).

Flow pyrolysis of 195 A sample of **195** was slowly passed through a vertical quartz-chips packed quartz tube heated externally at 720°C under the flow of methylchloride gas (35 ml/min). The pyrolysate collected at -78°C trap was analyzed by GCMS showing trimethylchlorosilane as the major reaction product.

Synthesis of 202 Compound **202** was synthesized according to the procedure described by Burns.[122]

FVP of 202 A sample of **202** (140 mg), distilled (10^{-4} torr) from a bath (5°C), was pyrolyzed at 680°C. The pyrolysate collected at -196°C trap was warmed up to -78°C (dry ice/isopropanol bath) and more volatile components were collected at -196°C in a gas collecting bulb. The liquid from -78°C trap was analyzed by GC and GCMS and found to contain methoxy(trimethyl)silane and cis- and trans-isomer of **204** as has been reported previously.[96] The gaseous products were analyzed by FTIR, GCFTIR and by GCMS. The products identified were acetylene, ethylene, allene and propyne. A small amount of methoxy(trimethyl)silane was also observed. In addition, some silylhydrides were appeared to form as indicated by their characteristic Si-H bands. In the GCFTIR fraction of allene and propyne, some additional IR bands were noted (Figure 4). Some of these bands are indicative of allenic and terminal acetylenic compounds ($X{\equiv}C{-}H$).

BIBLIOGRAPHY

1. The Chemistry of Ketenes, Allenes and Related Compounds. Patai, S., Ed.; Wiley: New York, **1980**; Part *1* and *2*.
2. Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, **1981**; p. 174.
3. Ward, R. S. In "The Chemistry of Ketenes, Allenes and Related Compounds," Patai, S., Ed.; Wiley: New York, **1980**; Part 1, p. 221.
4. (a) Kirmse, W. "Carbene chemistry," 2nd edition; Academic Press: New York, **1971**. (b) Meier, H.; Zeller, K.-P. *Angew. Chem. Int. Ed. Eng.* **1975**, *14*, 32.
5. Oxirene literature has been comprehensively reviewed recently: (a) Lewars, E. G. *Chem. Rev.* **1983**, *83*, 519; (b) Torres, M.; Lown, E. M.; Gunning, H. E.; Strausz, O. P. *Pure Appl. Chem.* **1980**, *52*, 1623.
6. McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H.-P. *J. Am. Chem. Soc.* **1985**, *107*, 7597.
7. Csizmadia, I. G.; Font, J.; Strausz, O. P. *J. Am. Chem. Soc.* **1968**, *90*, 7360.
8. Ogata, Y.; Sawaki, Y.; Ohno, T. *J. Am. Chem. Soc.* **1982**, *104*, 216.
9. Lewars, E.; Siddiqui, S. *J. Org. Chem.* **1985**, *50*, 135.
10. Torres, M.; Bourdelande, J. L.; Clement, A.; Strausz, O. P. *J. Am. Chem. Soc.* **1983**, *105*, 1698.
11. Leganis, E. D.; Janik, D. S.; Curphey, T. J.; Lemal, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 7457.
12. Russell, R. L.; Rowland, F. S. *J. Am. Chem. Soc.* **1970**, *92*, 7508.
13. Strachan, N. A.; Thornton, D. E. *J. Phys. Chem.* **1966**, *70*, 952.
14. Frey, H. M.; Walsh, R. *J. Chem. Soc.* 'A' **1970**, 2115.

15. Haller, I.; Srinivasan, R. *J. Am. Chem. Soc.* **1965**, *87*, 1144.

16. Fenwick, J.; Frater, G.; Ogi, K.; Strausz, O. P. *J. Am. Chem. Soc.* **1973**, *95*, 124.

17. Nozaki, H.; Nakano, M.; Kondo, K. *Tetrahedron* **1966**, *22*, 477.

18. Blake, P. G. In "The Chemistry of Ketenes, Allenes and related compounds"; Patai, S., Ed.; Wiley: New York, **1980**; Part 1, p. 328.

19. Young, J. R. *J. Chem. Soc.* **1958**, 2909.

20. Guenther, W. B.; Walters, W. D. *J. Am. Chem. Soc.* **1959**, *81*, 1310.

21. Tsuda, M.; Kuratani, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 53.

22. Blake, P. G.; Hole, K. J. *J. Phys. Chem.* **1966**, *70*, 1464.

23. Seybold, G.; Heibl, C. *Chem. Ber.* **1977**, *110*, 1225; *Angew Chem. Int. Ed. Eng.* **1975**, *14*, 248.

24. Krantz, A.; Laureni, J. *J. Am. Chem. Soc.* **1981**, *103*, 486.

25. Krow, G. R. *Angew Chem. Int. Ed. Eng.* **1971**, *10*, 435.

26. Lee, K.; Horowitz, N.; Ware, J.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 2622.

27. Jochims, J. C.; Herzberger, S.; Gambke, B.; Anet, F. A. L. *Tetrahedron Lett.* **1977**, 2255.

28. Ciganek, E. *Tetrahedron Lett.* **1969**, 5179.

29. Hopf, H.; Prieb, H.; Walsh, R. *J. Am. Chem. Soc.* **1980**, *102*, 1210.

30. Honjou, N.; Pacansky, J.; Yoshimine, M. *J. Am. Chem. Soc.* **1984**, *106*, 5361; *J. Am. Chem. Soc.* **1985**, *107*, 5332.

31. Brook, A. G.; Bassindale, A. R. In "Organic Chemistry"; DeMayo, P., Ed.; Academic Press: New York, **1980**; Vol. 2, Essay No. 9.

32. Huntsman, W. D.; Yin, T.-K. *J. Org. Chem.* **1983**, *48*, 3813.

33. Barton, T. J.; Hussman, G. P. *J. Am. Chem. Soc.* **1983**, *105*, 6313.

34. Bassindale, A. R.; Brook, A. G.; Harris, J. *J. Orgamet. Chem.* **1975**, *90*, C6.

35. Brook, A. G.; Golino, C.; Matern, E. *Can. J. Chem.* **1978**, *56*, 2286.

36. Barton, T. J.; Burns, S. A.; Burns, G. T. *Organometallics* **1982**, *1*, 210 and references therein.

37. Conlin, R. T.; Huffaker, H. B.; Kwak, Y.-W. *J. Am. Chem. Soc.* **1985**, *107*, 731.

38. Barton, T. J.; Groh, B. L. *J. Am. Chem. Soc.* **1985**, *107*, 8297.

39. Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678.

40. Barton, T. J.; Groh, B. L. *J. Am. Chem. Soc.* **1985**, *107*, 7221.

41. R_2SiO_2 species has been recently invoked in the reaction of silylene with oxygen.[42]

42. Gasper, P. P.; Holten, D.; Konieczny, S.; Corey, J. Y. *Acc. Chem. Res.* **1987**, *20*, 329.

43. Barton, T. J.; Hoekman, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 1584 and references therein.

44. Sekiguchi, A.; Ando, W. *J. Am. Chem. Soc.* **1984**, *106*, 1486.

45. Barton, T. J.; Paul, G. C. *J. Am. Chem. Soc.* **1987**, *109*, 5292.

46. Goddard, J. D.; Yashioka, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1980**, *102*, 7644.

47. Efimova, I. V.; Kazankova, M. A.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1985**, *55*, 1647.

48. Soderquist, J. A.; Hassner, A. *J. Am. Chem. Soc.* **1980**, *102*, 1577.

49. (a) Scheller, M. E.; Iwasaki, G.; Frei, B. *Helv. Chim. Acta* **1986**, *69*, 1378. (b) Shih, C.; Swenton, J. S. *J. Org. Chem.* **1982**, *47*, 2668.

50. Hartzler, H. D. In "Carbenes"; Moss, R. A.; Jones, M., Eds.; Wiley: New York, **1975**; Vol. 2, p. 57.

51. Barton, T. J.; Groh, B. L. *J. Org. Chem.* **1985**, *50*, 158.

52. Blake, P. G.; Ijadi-Maghsoodi, S. *Int. J. Chem. Kinet.* **1983**, *15*, 609.

53. Jabry, Z.; Lasne, J.-C.; Ripoll, M.-L. *J. Chem. Res. (S)* **1986**, 188.

54. Barroeta, N. "The Chemistry of Cyanates and their Thio Derivatives," S. Patai, Ed.; Wiley: Chichester, **1977**, p. 549.

55. Pericas, M. A.; Serratosa, F.; Valenti, E. *Tetrahedron* **1987**, *43*, 2316 and references therein.

56. Conia, J. M.; LePerchec, P. *Synthesis* **1975**, 1.

57. Nooi, J. R.; Arens, J. F. *Rec. Trav. Chim.* Pay-Base **1959**, *78*, 284.

58. Efimova, I. V.; Kalganov, B. E.; Kazankova, M. A.; Lutsenko, I. F. *Otkrytiya Izobret.* **1984**, *41*, 87. *Chem. Abstr.* **1984**, *102*, 149521c.

59. Mass, G.; Bruckmann, R. *J. Org. Chem.* **1985**, *50*, 2801.

60. Stang, P. J.; Roberts, K. A. *J. Am. Chem. Soc.* **1986**, *108*, 7125.

61. Kowalski, C. J.; Lal, G. S.; Haque, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 7127.

62. Harris, S. J.; Walton, D. R. M. *J. Chem. Soc. Chem. Commun.* **1976**, 1008.

63. McKee, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 5059.

64. Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

65. Moedritzer, K. *J. Organomet. Chem.* **1970**, *21*, 315.

66. Soyasa, H. S. D.; Jung, I. N.; Weber, W. P. *J. Organomet. Chem.* **1979**, *171*, 177.

67. Michl, J.; Raabe, G. *Chem. Rev.* **1985**, *85*, 420.

68. Gusel'nikov, L. E.; Volkova, V. V.; Avakyan, V. G.; Volnina, E. A.; Zaikin, V. G.; Nametkin, N. S.; Polyakova, A. A.; Tokarev, M. I. *J. Organomet. Chem.* **1984**, *271*, 191.

69. Gornowicz, G. A.; West, R. *J. Am. Chem. Soc.* **1971**, *93*, 1714.

70. Shchukovskaya, L. L.; Pal'chik, R. I.; Lazarev, A. N. *Dokl. Akad. Nauk SSSR* **1965**, *164*, 357.

71. Shchukovskaya, L. L.; Kol'tsov, A. I.; Lazarev, A. N.; Pal'chik, R. I. *Dokl. Akad. Nauk SSSR* **1968**, *179*, 892.

72. Grishin, Yu. K.; Ponomarev, S. V.; Lebedev, S. A. *Zh. Org. Khim.* **1974**, *10*, 404 (Russ) *J. Org. Chem. USSR* **1974**, *10*, 402.

73. (a) Baukov, Yu. I.; Burlachenko, G. S.; Kostyuk, A. S.; Lutsenko, I. F. *Chem. Abstr.* **1973**, *79*, 78904y. (b) Kostyuk, A. S.; Boyadzhan, Zh. G.; Zaitseva, G. S.; Segreev, V. N.; Savel'eva, N. I.; Baukov, Yu. I.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1979**, *49*, 1543.

74. (a) Huang, C.-T.; Wang, P.-J. *Acta Chim. Sinica.* **1959**, *25*, 341; *Chem. Abstr.* **1960**, *54*, 16413. (b) Brook, A. G.; Duff, J. M.; Anderson, D. G. *Can. J. Chem.* **1970**, *48*, 561. (c) Brook, A. G.; Iachia, B. *J. Am. Chem. Soc.* **1961**, *83*, 827.

75. Groh, B. L. Ph.D. Dissertation, Iowa State University, 1985.

76. Dr. Jacobson's group (Ames Laboratory, Iowa State University) has been investigating the X-ray crystal structure of 174b for more than a year and a half.

77. Woodbury, R. P.; Long, N. R.; Rathke, M. W. J. Org. Chem. **1978**, 43, 376.

78. Hoppe, I.; Schollkopf, U. Justus Liebigs Ann. Chem. **1979**, 219.

79. Kowalski, C. J.; Haque, M. S. J. Am. Chem. Soc. **1986**, 108, 1325 and references cited therein.

80. Barton, T. J. In "Comprehensive Organometallic Chemistry"; Wilkinson, S. G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, **1982**; Vol. 2, p. 205.

81. Lambert, R. Jr.; Seyferth, D. J. Am. Chem. Soc. **1972**, 94, 9246.

82. Conlin, R. T.; Gaspar, P. P. J. Am. Chem. Soc. **1976**, 98, 3715.

83. Gaspar, P. P. In "Reactive Intermediates"; Jones, M. Jr.; Moss, R. A., Eds.; Wiley: New York, **1985**; Vol. 3, p. 362.

84. Ando, W.; Tsumuraya, T.; Goto, M. Tetrahedron Lett. **1986**, 27, 5105.

85. (a) Davidson, I. M. T.; Wood, I. T. J. Organomet. Chem. **1980**, 187, C65. (b) Barton, T. J.; Burns, S. A.; Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Wood, I. T. J. Am. Chem. Soc. **1984**, 106, 6367.

86. (a) Davidson, I. M. T.; Barton, T. J.; Hughes, K. J.; Ijadi-Maghsoodi, S.; Revis, A.; Paul, G. C. Organometallics **1987**, 6, 644. (b) LPP and SFR experiments were performed by the authors in The University, Leicester, Great Britain.

87. Auner, N.; Walsh, R.; Westrup, J. J. Chem. Soc., Chem. Commun. **1986**, 207.

88. Doncaster, A. M.; Walsh, R. J. Chem. Soc., Faraday Trans., 1, **1976**, 72, 2908.

89. Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazran, A. S. J. Am. Chem. Soc. **1985**, 107, 208.

90. Krusic, P. J.; Kochi, J. K. J. Am. Chem. Soc. **1969**, 91, 6161.

91. Lyons, A. R.; Neilson, G. W.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans.*, 2, **1972**, *68*, 807.

92. Sakurai, H.; Hosomi, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 568.

93. O'Neal, H. E.; Ring, M. A. *J. Organomet. Chem.* **1981**, *213*, 419.

94. Bertrand, G.; Manuel, G.; Mazerolles, P. *Tetrahedron* **1978**, *34*, 1951.

95. (a) Smith, J. A.; Shechter, H.; Bayless, J.; Friedman, L. *J. Am. Chem. Soc.* **1965**, *87*, 659. (b) Shevlin, P. B.; Wolf, A. P. *J. Am. Chem. Soc.* **1968**, *88*, 4735.

96. Barton, T. J.; Burns, G. T.; Goure, W. F.; Wulff, W. D. *J. Am. Chem. Soc.* **1982**, *104*, 1149.

97. Baldwin, A. C.; Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans.*, 1, **1975**, *71*, 972.

98. Jung, M. E.; Lyster, M. A. *Org. Syn.*, **1979**, *59*, 35.

99. Nazarov, S. M.; Makin, S. M.; Kruptsov, B. K.; Mironov, V. A. *Zh. Obshch. Khim.* **1959**, *29*, 111.

100. Trost, B. M.; McDougal, P. G.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 383.

101. Baigrie, L. M.; Seiklay, H. R.; Tidwell, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 5391.

102. Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

103. Bennetau, B.; Pillot, M.-P.; Dunogues, J.; Calas, R. *J. Chem. Soc. Chem. Commun.* **1981**, 1094.

104. Benkeser, R. A.; Burrous, M. L.; Nelson, L. E.; Swisher, J. V. *J. Am. Chem. Soc.* **1961**, *83*, 4385.

105. Wiseman, G. H.; Wheeler, D. R.; Seyferth, D. *Organometallics* **1986**, *5*, 146.

106. Wilt, J. W.; Kolewe, O.; Kraemer, J. F. *J. Am. Chem. Soc.* **1969**, *91*, 2624.

107. George, M. V.; Peterson, D. J. J. Am. Chem. Soc. **1960**, 82, 403.

108. Kostyuki, A. S.; Boyadzhan, Zh. G.; Zaitseva, G. S.; Sergeev, V. N.; Savel'eva, N. I.; Baukov, Yu. I.; Lutsenko, I. F. Zh. Obshch. Khim. **1979**, 49, 1543. English Translation **1979**, 1346.

109. Baukov, Yu. I.; Burlachenko, G. S.; Kostyuk, A. S.; Lutsenko, I. F. Chem. Abstr. **1973**, 79, 78904y.

110. Lewis, D. W.; Gainer, G. C. J. Am. Chem. Soc. **1952**, 74, 2931.

111. Shchukovskaya, L. L.; Pal'chik, R. I.; Petrushina, T. A. Zh. Obshch. Khim. **1971**, 42, 240.

112. Atwell, W. H.; Weyenberg, D. R. J. Organomet. Chem. **1967**, 7, 71.

113. Laguerre, M.; Dunogues, J.; Calas, R. J. Chem. Soc. Chem. Commun. **1978**, 279.

114. Ruden, R. A. J. Org. Chem. **1974**, 39, 3607.

115. Ishikawa, M.; Kumada, M. J. Organomet. Chem. **1972**, 42, 325.

116. Ryan, J. W.; Menzie, G. K.; Speier, J. L. J. Am. Chem. Soc. **1960**, 82, 3601.

117. Damrauer, R.; Davis, R. A.; Burker, M. T.; Karn, R. A.; Goodman, G. T. J. Organomet. Chem. **1972**, 43, 121.

118. Mori, S.; Sakai, I.; Aoyama, T.; Shioiri, T. Chem. Pharm. Bull. **1982**, 30, 3380.

119. Sommer, L. H.; Gold, J. R.; Goldberg, G. M.; Marans, N. S. J. Am. Chem. Soc. **1949**, 71, 1509.

120. Seyferth, D.; Flood, T. C. J. Organomet. Chem. **1971**, 29, C25.

121. Brown, H. C.; Lane, C. F. J. Am. Chem. Soc. **1970**, 92, 6660.

122. Burns, G. T. Ph.D. Dissertation, Iowa State University, 1981.

ACKNOWLEDGMENTS

I would like to thank my parents for their love and support throughout my education. I would also like to express my gratitude to my late uncle, Umesh Chandra Paul, who constantly encouraged me in the early part of my education.

I would also like to express my indebtness to Dr. Philip B. Shevlin who trained and inspired me in conducting basic research.

I would like to thank Dr. Thomas J. Barton under whose supervision works described in this thesis have been carried out. To him I am grateful.

Finally, I would like to thank Nancy Qvale for her skillful typing of this dissertation.