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Thermochemical Decomposition and Isomerization of
Polysilacyclocdialkynes and Thermochemical and Photochemical
Decomposition of Cyclopolysilylketenes

by

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INTRODUCTION

Silacyclopropenes have been proposed in thermal- and photochemical silylene elimination from linear²¹⁻²³ and cyclic silylacetylenes²⁴⁻²⁶. However, to date, this intermediate has not been suggested for the parallel reaction for cyclic dialkynes. In fact, a free-radical mechanism has been suggested⁵. Investigation into the thermochemical silylene elimination of a dialkyne system has provided kinetic data that characterizes the transition state involved. Interpretation of this data will serve to either add support to current silylalkyne mechanistic theory or identify a potentially enlightening deviation.

Silyl ketene research has been limited predominantly to ketene synthesis²⁹⁻³⁴. Barton et al^{37,38} broadened the scope of this research by investigating the thermochemistry of monosilyl-substituted ketenes. Unfortunately, others have not followed this example and the scope of the research still remains rather narrow. Though not the original intent of this research, the thermal- and photochemical reactions of bis(polysilyl) and cyclic polysilylketenes were investigated. Beyond testing the current mechanism for thermal decomposition of silylketenes, this work expanded silylketene research to focus more on polysilyl-substituted compounds.

LITERATURE SURVEY

Photochemical and Thermochemical Reactions of Polysilylalkynes

In 1980, Sakurai¹ published a review espousing σ - π conjugation via the overlap of a Si-Si σ orbital with an adjacent π orbital of a C-C unsaturated bond. Experimental evidence for this theory was based predominantly on the ultraviolet, charge transfer, and photoelectron spectra of pentamethyldisilanyl-substituted π systems. Interest in this proposed phenomenon resulted in an investigation of the tetrasilacyclooctadiyne, **1**, for characteristics that supported σ - π through conjugation in the ring.

Several procedures for the synthesis of **1** have been published. In 1985, Kloster-Jensen and Eliassen² reacted 1,2-dichlorotetramethyldisilane with the diGrignard reagent, bis(bromomagnesium)acetylide, producing **1** and the hexasilacyclododecatriyne, **2**, with a total

overall yield of 5%. This was followed in 1988 by the patented procedure³ of Iwahara and West⁴, who reacted 1,2-dichlorotetramethyldisilane with the diGrignard reagent from 1,2-diethynyltetramethyldisilane, to afford **1** in a 63% yield with no other products reported. The

communication does warn, however, that dilithium reagents are not a suitable substitute for the diGrignard. Dilithium reagents result in the formation of ethynylene-disilanylene polymers.

However, the first synthesis of **1**, reported by Sakurai et al⁵ and patented by Hitachi, Ltd.⁶, was through the ring contraction of the pentasilacyclonona-1,5-diyne, **3**. Precursor **3** was prepared by the procedure that was later adopted and patented by West and Iwahara, for **1**, cited above. Substituting 1,3-dichlorohexamethyltrisilane for 1,2-dichlorotetramethyldisilane, **3** was produced in a 37% yield. The purified product was photolyzed and flash vacuum pyrolyzed in an effort to produce **1**. The photolysis yield was only 10%, but the pyrolysis yielded 63% **1** and, unexpectedly, 3.6% of a second silacyclodiyne, **4**. Flash vacuum pyrolysis of **1** confirmed **4** as a thermolysis product of **1**. This communication, as well as other papers^{7,8} concerned with **1**, focused on identifying

σ - π through conjugation. Mechanistic analysis was limited to referring to the synthesis as a ring-contraction method and citing two papers reporting the photolytic ring contraction of 1,2,3-trisilacycloheptane, reviewed below.

In 1971, Sakurai et al⁹ reported the synthesis of 1,2,3-trisilacycloheptane derivatives and the elimination of the central silicon in the trisilane, as a silylene, when irradiated with a low-pressure mercury arc lamp. By selective substitution of the central silicon atom, new silylene derivatives were prepared. Further investigation of this reaction¹⁰ revealed that the stereochemistry of the adjacent silicons was preserved in the elimination reactions. The

author interpreted the results as indicative of a concerted elimination reaction, but was quick to note that homolytic scission of a Si–Si bond followed by elimination of a silylene through an S_H2 mechanism (Scheme 1) could not be ruled out. Sakurai and Nakadaira¹¹ and Sakurai and Hosomi^{12,13} had previously published papers proposing an S_H2 mechanism for organosilicon reactions.

Scheme 1

The initial electronic transitions in the photochemistry of 1,2,3-trisilacycloheptane and other silicon compounds have been studied with various theories proposed. Ramsey¹⁴, proposed a $\sigma-\sigma^*$ transition, citing that the transition was in agreement with experimental evidence and allowed under the Woodward-Hoffman rules while a $\sigma-\pi$ transition was not. Halevi et al¹⁵ criticized Ramsey's work, citing that d-orbitals were excluded in his analysis, and proposed a transition to the a_1 orbital of trisilane, "a diffuse, loosely bonding, orbital with a large 4S component." Analysis of ESR results of the decamethylcyclopentasilane radical anion indicated a $\sigma-\pi^*$ transition. However, in reference to Ramsey's work, West¹⁶ does state that the σ^* transition might also be applicable, depending on the model used.

Regardless, a mechanism involving the homolytic scission of a Si-Si bond is generally accepted.

Although a parallel example of silylene elimination from pyrolysis of 1,2,3-trisilacycloheptane derivatives was not located in the literature, there is evidence for homolytic scission of the Si-Si bond in permethylpolysilanes. Shiina and Kumada¹⁷ proposed a homolysis of the Si-Si bond as the initial reaction in pyrolysis of hexamethyldisilane in 1958. Davidson and Howard¹⁸, in studying the kinetics of this reaction, determined the Arrhenius parameter, $\log A/s^{-1} = 17.2 \pm 0.3$, and the activation energy, 81 kcal/mol. Parallel reactions have been proposed in the kinetic studies of octamethyltrisilane¹⁹ and decamethyltetrasilane²⁰.

The reactivity of the permethylpolysilane portion of **3** was exclusively cited by Sakurai et al⁵ in the 1,2,3-trisilacycloheptane references^{9,10}. No reference alluded to the involvement of the alkyne functional group in the ring-contraction mechanism. Silacyclopropene intermediates have been isolated in the photolysis of silylalkynes and when photolyzed independently have subsequently eliminated silylene. In systems that have small substituents, e.g. Me, Et, Me₃Si, the silacyclopropene has not been observed, however, the photolysis of such systems results in products consistent with a silacyclopropene intermediate. In 1980, trisilanylacetylene, **5**, was photolyzed by Ishikawa et al²¹ and found to rearrange in the absence of a trapping agent. In the presence of the trapping agent, diethylmethylsilane, silylene was eliminated forming disilanylacetylene and the trapped silylene adduct. A silacyclopropene was not proposed as an intermediate in the silylene elimination, but could be applied as later proposed by Petrich²² in the thermolysis of trisilanylacetylene.

The thermochemical formation of a silacyclopentene intermediate was first proposed by Barton²³ in 1991. Since allene was known to isomerize through cyclopentene to form propyne, silylacetylene was studied for a similar rearrangement. Isotope labeling of the silylacetylene allowed the isomerization to be followed. A silacyclopentene was not isolated.

but was proposed in explanation of the isomerization. Petrich²² expanded on this precedent in a mechanism for the thermochemistry of disilanylacetylene, **6**. A silacycpropene

intermediate was proposed in the formation of the isomer, 7, the eliminated product, 8, and the insertion product, 9. An analogous mechanism was applicable to the thermochemistry of trisilanylacetylene, 5.

Polysilacycloalkynes have recently been isolated and have been thermolytically and photolytically studied. In 1990, Ando et al²⁴ reported the synthesis of the hexasilacyclooctyne, 10, and the results of its subsequent photolysis and pyrolysis reaction producing the ring-contraction product, pentasilacycloheptyne, 11. A more complete account was later published²⁵ with a mechanism that proposed a silacyclopropene intermediate for the ring contraction (Scheme 2).

The silacyclopropene intermediate mechanism for the photochemical ring contraction of a polysilacycloalkyne has since been supported by experimental evidence²⁶.

Bicycloheptene, 12, was synthesized by reaction of tetrasilacyclohexyne, 13, with

Scheme 2

dimesitylsilylene. When photolyzed, **12** both eliminated dimesitylsilylene, reforming **13**, and isomerized to the ring-enlarged pentasilacycloheptyne, **14**. The latter product demonstrates

that formation of the silacyclopropene intermediate can be reversible. A parallel reaction was undertaken with heptasilabicyclo[6.1.0]nonene with similar results.

Evidence in this paper also revealed that a second mechanism may compete. When hexasilacyclooctyne, **15**, was photolyzed, the two pentasilacycloheptynes, **16** and **17**, were produced. The pyrolysis reaction was not reported. The product **17** involves elimination of a dimethyl-substituted silicon, none of which are adjacent to the ethynyl functional group. Only an adjacent silicon would be expected to form silylenes from silacyclopentene, indicating an alternative mechanism. However, the experimental section does not indicate that the remaining starting material was completely characterized. This does not preclude the isomerization of **15** to **18**, resulting in the elimination product **17**.

Assuming that the isomerization proves incorrect, **17** could be accounted for by the precedented elimination of silylene from the polysilane functionality. Cyclohexasilane, **19**, has been reported to eliminate silylene when photolyzed²⁷, but has not when pyrolyzed. Barring more data, an alternative mechanism need not be proposed in explanation of pyrolysis products under study.

Thermochemistry of Silyl-Substituted Ketenes

Schukovskaya et al²⁸, in 1965, were the first to report a silyl-substituted ketene.

Thermochemical decomposition of trimethylsilylethoxyacetylene at 120-130°C resulted in a 90% yield of trimethylsilylketene. In the interim, a variety of syntheses for mono- and disubstituted silylketenes have been reported in the literature. A sampling of these reactions is presented below. The principle characteristics of the silylketenes are a very strong IR

absorption in the range of 2050-2150 cm^{-1} corresponding to the $\text{C}=\text{O}$ stretch and ^{13}C NMR peaks in the range of 160 to 180 ppm for $(\text{C})=\text{O}$ and -5 to 5 ppm for $(\text{C})=\text{C}=\text{O}$.

In 1987, Barton et al³⁵ published an innovative one-pot synthesis for bis(silyl)ketenes. Utilizing the readily available starting materials of $n\text{-BuLi}$, 2,3-dihydrofuran, and the chlorosilane corresponding to the desired silyl substituents, symmetrical ketenes were prepared. Monosilyl-substituted dihydrofuran was identified as the other major product in the synthesis. Modification of the synthesis to workup one hour after quenching with butyldimethylsilyl chloride, however, resulted in only siloxyacetylene. Workup 8 and 20 hours after quenching yielded a mixture of siloxyacetylene and ketene and workup 36 hours after quenching yielded only the ketene. Based on this data, the siloxyacetylene was designated as the ketene precursor and the following reaction mechanism (Scheme 3) was proposed.

Scheme 3

Efforts to optimize the reaction yields identified the necessity of adding each of the two $n\text{-BuLi}$ equivalents twenty-four hours apart. A single addition of both equivalents results in reaction of $n\text{-BuLi}$ with the solvent, tetrahydrofuran. Replacing 2,3-dihydrofuran with 2-

phenyl-2,3-dihydrofuran also improved ketene yields, 27% higher for bis(trimethylsilyl)ketene. Instead of ethene, styrene, which polymerizes, extrudes in the formation of lithium alkynolate and silyl-substituted dihydrofuran is no longer formed, simplifying product purification.

Silicon compounds are usually worked up with acidic water to avoid cleavage of the Si-Si bond by base. Silylated ketenes have proven to be an exception to this general procedure. In 1976, Lebedev et al³⁶ reported that acid-catalyzed hydrolysis resulted in quantitative formation of the corresponding carboxylic acid. Aqueous sodium bicarbonate solution has proven an effective wash without affecting the silicon substituents or hydrolyzing the ketene functional group.

The thermochemistry of silyl-substituted ketenes has been limited to the study of bis(monosilyl)ketenes. In 1985, Barton and Groh³⁷ demonstrated that (trimethylsilyl)-(dimethylsilyl)ketene thermally decomposed, when flash vacuum pyrolyzed at 650°C, forming dimethylsilanone and trimethylsilylacetylene. Analogous decomposition was observed for bis(dimethylsilyl)ketene and bis(trimethylsilyl)ketene³⁸. Three mechanistic pathways (Scheme 4) were proposed for the thermal reactions. PATH A was the least favored by the authors. Although the oxasilacyclopropene has been reported in the literature³⁹, there is no precedent for the reaction steps. PATH B has a precedent for each mechanism step and, as the most favored, will be reviewed at length. PATH C was attractive, due to its similarity to PATH B, but the lack of a precedent for the initial 1,3-Me shift argued against the mechanism overall.

Scheme 4

The first step of PATH B, the 1,2-silyl shift, was proposed as the first example of a Retro-Wolff rearrangement. The Wolff rearrangement was named for Ludwig Wolff who proposed a ketenocarbene intermediate in the formation of ketenes from the decomposition of dicarbonyldiazo compounds in 1912⁴⁰. The mechanism has been extensively studied for α -diazoketones, which are known to eliminate nitrogen followed by or with concomitant rearrangement to ketene. Whether a ketocarbene actually forms or a concerted reaction takes place has been the focus of debate. Carey and Sundberg⁴¹ assert that a carbene is an

intermediate in photochemistry, but the thermal rearrangement is concerted. The concerted mechanism has recently been reinforced by the theoretical calculations of Tsuda et al⁴². The lowest energy pathways of 2-diazobenzen-1-one and 2-diazoethan-1-one Wolff rearrangements to their respective ketenes were determined. A ketocarbene was not identified on either energy surface, but rearrangement through a 3-centered structure followed the weakening of the carbon-diazo bond in both cases.

The premise of a Retro-Wolff rearrangement was recently reinforced by Bender et al⁴³. In explanation of diazofulvenone, **20**, isomerization to isocyanate, **23**, a mechanism (Scheme 5) involving the initial formation of a ketocarbene, **21**, was proposed. Nguyen et al⁴⁴ sought to justify the mechanism with ab initio molecular orbital calculations. Although a ketocarbene and a bicyclic intermediate were examined, both systems were found to

collapse to the minima, ketene **20** or isocyanide, **22**. Instead, a three-center transition state was elucidated that supports a concerted mechanism and parallels the previously cited calculations for the Wolff Rearrangement. The carbonyl group apparently migrates into an adjacent N–C bond, leading to N–C bond cleavage, while forming a bond between the carbonyl carbon and the now adjacent nitrogen. The highest level calculations MRCISDQ/6-31G**, defined the energy pathway for the isomerization. Although the energy barrier from the ketene **20** to the Retro-Wolff transition state, **24**, may appear to be high, it is quite feasible for a FVP reaction.

In 1983, Ando and Sekiguchi⁴⁵ proposed the remainder of PATH B (Scheme 6) for the photochemical decomposition of the (pentamethyldisilanyl-diazomethyl) ketones, **25**. Although the silene-ketone intermediate, **26**, was not identified beyond supposition, the 1,2-siloxetene, **27**, was characterized to a degree by IR, MS and ¹³C NMR. Intermediate **27** was isolated in 1988⁴⁶ by low temperature crystallization from pentane. The reaction was shown to proceed analogously with adamantyl and t-butyl substituents. The t-butyl substituent is

Scheme 6

comparable in size to that of trimethylsilyl. The paper notes that in the absence of such a large functionality dimerization was found to occur followed by decomposition of **28** to the expected alkyne and silanone.

RESULTS AND DISCUSSION

Kinetics of Polysilacyclodialkyne Ring-Contraction

A biradical, 29, and a silacyclopropene, 30, intermediate each has precedent for silylene elimination and either could be proposed in the ring-contraction mechanism of the dialkyne 3. (The vinylidene intermediate, a possible precursor to the silacyclopropene intermediate, will be omitted from this discussion for the sake of simplicity.) In an effort to

elucidate information regarding the transition state in pyrolytic ring contraction, a kinetic study was undertaken that determined rate constants for the reaction at 10°C intervals, two runs at each temperature. Regression analysis of the straight-line plot, $\ln k$ (s^{-1}) versus $1/T$ (K^{-1}) (Figure 1 and 2), defined by the Arrhenius equation, $\ln k = (-E_a/R)(1/T) + \ln A$, yielded the Arrhenius parameter, A , usually reported as $\log A$, and the energy of activation, E_a . With and without butadiene (as a silylene trap), $\log A/\text{s}^{-1}$ for the reaction was 10.2 and 7.4, and the E_a was 39.7 kcal/mol and 31.2 kcal/mol, respectively.

The kinetic data does not prove that either of the two proposed pathways plays a role in the ring-contraction mechanism. Instead, the determined values, characteristic of the actual transition state, can only support or reject the two mechanisms currently in question. The transition state entropy, $\Delta S^\ddagger$, is especially significant in the current case. The biradical 29

Figure 1. Arrhenius plot for the formation of dialkyne 1 in the presence of 2,3-dimethylbutadiene.
 $\text{Log } A/\text{s}^{-1} = 10.2$, $E_a = 39.7 \text{ kcal/mol}$

Figure 2. Arrhenius plot for the formation of dialkyne **1** in benzene.
 $\text{Log } A/\text{s}^{-1} = 7.4$, $E_a = 31.2 \text{ kcal/mol}$

should have a positive entropy due to the ring opening of the starting material increasing the degrees of freedom. In contrast, the transition state forming the silacyclopropene **30**, composed of two joined rings, each more strained than the starting material, would be expected to have a more rigid structure, characterized by a negative entropy. The transition state entropy can be calculated from the Arrhenius parameter by the identity, $A = [(ekT_m)/h]\exp(\Delta S^\ddagger/R)$, where T_m is the mean temperature of the kinetic study, k is Boltzmann's constant, h is Planck's constant, and R is the gas constant. For the reaction with and without butadiene, $\Delta S^\ddagger$ was -15.8 kcal/mol·K and -17.9 kcal/mol·K. Although the entropy may be calculated, $\log A$ is preferentially reported.

A median value for $\log A$, representative of no entropy change in the formation of the transition state, may be calculated from the identity used to calculate $\Delta S^\ddagger$. Entering 773 K for T_m and setting $\Delta S^\ddagger$ equal to 0, the median $\log A/s^{-1}$ is 13.6. From this value, the relative change in $\log A$ for the transition state parallels that of the entropy. A negative entropy corresponds to a $\log A/s^{-1}$ lower than 13.6, whereas a positive entropy corresponds to a larger $\log A$. $\log A$ and $\Delta S^\ddagger$ each support a "tighter" transition, favoring formation of the silacyclopropene intermediate.

The energy of activation defines the energy difference between the starting material and the transition state. The formation of silacyclopropene **30** involves breakage of a Si-Si bond and a π -bond of the C≡C bond, with concerted formation of two Si-C bonds. The activation energy expected for this process would be relatively low, due to the balance of energy from the endothermic cleavage of two bonds and the exothermic formation of two bonds. In contrast, the biradical **29**, formed by homolytic cleavage of a Si-Si bond, an endothermic process, should have an activation energy comparable to the dissociation energy of the Si-Si bond. The dissociation energy of hexamethyldisilane, **31**, was experimentally

determined by Davidson and Howard¹⁸ to be 80.5 kcal/mol. The energy of activation for the ring-contraction lends further support for the silacyclopropene **30**.

The difference in the kinetic values determined for the reaction with and without butadiene has been attributed to a back reaction from **1** to **3**. The presence of butadiene inhibits the back reaction by trapping the eliminated silylene. There is no way of ensuring the back reaction has been stopped completely, however, the kinetic data for the reaction with butadiene is assumed to be more accurate.

Although the kinetic data supports the silacyclopropene pathway, Petrich's work with linear systems suggests that two silacyclopropene intermediates, **29** and **31**, could form, each yielding a unique tetrasilacyclodiyne, **1** and **32**, respectively. Disilanylacetylene **5** and

trisilanylacetylene **5** were each proposed to eliminate silylene through a silacyclopropene. However, experimentally, only the diyne **1** was isolated and identified. The diacyne **33** was

synthesized to determine if the absence of the isomer was due to the thermal instability of **33** compared to **1**. Flow pyrolysis of **33** at 610°C yielded a mixture of the starting material and the isomerization product **1** in a ratio of 9:1, and thus **33** was demonstrated to be thermally unstable with respect to **1**.

Collectively, the experimental data supports a silacyclopropene transition state. Although the biradical **29** is simultaneously disfavored, the results do not deny that to some degree a biradical mechanism may occur. However, if the biradical pathway is followed, it is negligible with respect to the mechanism with the silacyclopropene intermediate.

Thermal- and Photochemistry of Cyclopolysilylketenes

In recent years, an interest has developed in the synthesis of strained permethylcyclopolysilylalkynes. A series of rings with silicon chains ranging from four to seven silicons have been synthesized using a variety of synthetic methods. However, at present, the five-membered ring with a three-silicon chain has remained synthetically elusive. In reviewing the

thermochemical decomposition of silyl-substituted ketenes, a new synthetic method was proposed, assuming an analogous decomposition of cyclopolysilylketene (Scheme 7).

Scheme 7

Utilizing the synthetic method reported by Barton et al³⁵, cyclic ketenes were prepared and characterized with silicon chains of four and five atoms in yields of 49% and 40%, respectively. Attempts to make a cyclic ketene with three silicon atoms led to no

identifiable ketene products, whereas dichlorodisilane yielded two different ketene products. Ketenes **34** and **35** were characterized by infrared and mass spectrometry, but attempts to isolate the products were unsuccessful and product ratios were not recorded due to the instability of **35**.

The six-membered cyclic ketene, **36**, was flow pyrolyzed at 600°C , but unexpectedly produced no cyclic alkynes. The exclusive product was the five-membered cyclic ketene, **37**, from elimination of silylene. Thermolysis of **37** was studied with a qualitative stir-flow reactor

(SFR). This instrument allows for in-line mass spectral and infrared analysis of the pyrolysis products. Only a trace of what was believed to be the four-membered cyclic ketene was detected. Experience with this instrument has shown that results from the flow pyrolyses are usually poorer than with the SFR. A full scale pyrolysis was not undertaken since the product ketene was expected to be too minimal for separation and subsequent characterization.

With no precedent for pyrolysis of a bis(polysilyl)ketene, there was no basis for attributing the unexpected product to ring strain or to the multiple-silicon substituent. Bis(disilyl)ketene, **38**, was synthesized to differentiate between the two suspected causes.

Pyrolysis of **38** did result in elimination of silylene, resulting in the product ketene, **39**. The cyclic ketene products were thus not considered the result of possible ring strain effects.

The pyrolysis mechanism proposed by Barton and Groh³⁷ is the keystone of this work. Recent theoretical work⁴⁴, however suggests that the Retro-Wolff rearrangement does not involve a ketocarbene, but that the rearrangement is concerted, via a three-centered transition state. Although this mechanism has merit for the diazofulvenone **20** which was the subject of the theoretical work, a similar application of the proposed concerted mechanism to bis(monosilyl)ketenes results in a very strained bimolecular, five-centered transition state, **40**.

The complexity of the transition state, in conjunction with the documented β -silicon stabilizing effect on carbenes⁴⁸, suggests that the mechanism proposed by Barton and Groh should be maintained in its original form (Scheme 8).

Scheme 8

For the polysilyl-substituted ketenes currently under study (Scheme 9 and 10), the ketocarbenes formed, **41** and **43**, possess two β -silicons, which may serve to enhance the stabilization of the intermediate. However, in contrast to the bis(monosilyl)ketene systems, where a 1,2-Me or H shift from the α -silicon was observed, the carbenes can insert into the Si-Si bond of the β -silicon substituent, forming the silacyclopropanone, **42** or **44**.

Scheme 9

Scheme 10

Carbene insertion into a Si–Si bond is precedence. In 1987, Fritz⁴⁹ reported that the carbene, :CF_2 , inserts into a Si–Si bond if an electron-withdrawing group, such as F, Cl, Br, or OMe, was a substituent of one of the silicons. The author argued that the requisite

substituent weakened the Si–Si bond favoring carbene insertion. The carbonyl functionality in the present cases could act as the electron-withdrawing substituent.

More recently, Petrich²² proposed an intramolecular insertion of a vinylidene into a Si–Si bond, forming a silacyclop propane. This mechanism can be generally applied to the thermochemistry of linear- and cyclic polysilanylacetylenes.

An example of an isolated silacyclop propane-containing molecule was not found in the literature, but two theoretical studies were reported that examined silacyclop propaneones. In 1989, Sudhakar and Chandrasekhar⁵⁰ optimized the geometry of silacyclop propaneone, 45, utilizing the MNDO method, and in 1990, Cioslowski et al⁵¹ furthered the theoretical characterization of silacyclop propaneone by determining the atomic charges of 2-methyl-2-silacyclop propaneone, 46, from generalized atomic polar tensor (GAPT) population analysis. Neither study supports or denies the existence of a silacyclop propaneone, but the fact that the structures have been taken into consideration suggests that a silacyclop propaneone-containing molecule is reasonable.

DZP/DZ SCF		DZP/DZ SCF	
O1	-0.8915	H7	0.0084
C2	0.7347	H8	-0.3052
C3	-0.4121	H9	0.0046
Si4	1.1119	H10	-0.0061
C5	-0.2684	H11	0.0111
H6	0.0127		

The silacyclopropanones, 42 and 44, each eliminate silylene in the final step. The reformation of the resulting ketene is believed to be the driving force for the reaction.

Photolysis of the ketene 36 resulted in 37, with a yield exceeding that observed in the pyrolysis, and a second ring-contraction product, 47, identified solely by GC/IR/MS. The photolysis of silylketenes has not been previously studied, so a priori the thermochemical

TIME (min)	%		
	36	37	47
INIT	100		
10	50.0	30.0	
20	37.4	41.6	
31	28.8	50.6	3.1
50	11.9	48.1	5.0
70	5.5	41.2	6.9
90	2.5	29.9	7.4

and photochemical reaction pathways were initially considered to be synonymous. However, photolysis of bis(pentamethyldisilanyl)ketene, 38, deviated from the pyrolysis results when the

starting material decomposed, but no products were observed. Repeat of the reaction in the presence of an excess of triethylsilane did not result in a silylene-trapped product. However, photolysis of ketene **38** in the presence of carbon tetrachloride, a free radical trap, reduced decomposition from 64% to 14%, over a comparable time period. Although there is no data beyond that already cited, it seems likely that the silylene elimination observed with the cyclic ketene results from a biradical process (Scheme 11 and 12). Homolytic cleavage of a Si–Si bond followed by elimination of silylene through an S_H2 mechanism was discussed previously. When applied to **38**, there would be no tether to keep the two radical pieces together and decomposition of the starting material would be expected. Further research into this proposal will be necessary to justify application of this precedented mechanism to the photolysis of silylketenes.

Scheme 11

Scheme 12

CONCLUSION

The kinetic data for the elimination of silylene supports formation of a "tighter" transition state, indicative of a silacyclopropene intermediate. This data serves to extend the silacyclopropene mechanism to the cyclicdialkyne system and validates the consistency of the mechanism for silylakynes, in general. Investigation into the other possible silacyclopropene product established the instability of the product, removing the possibility that the absence was a result of a deviation from the proposed mechanism instead of kinetic and thermodynamic.

The work with silylketenes proved that an inherent difference exists between the thermal reactivity of monosilyl-substituted ketenes and polysilyl-substituted ketenes. Although the mechanism for thermal decomposition of bis(silyl)ketenes can be modified to account for the unexpected silylene elimination products, reasons for the difference are limited to speculation.

The photochemistry of silylketenes has not been previously studied, so a model system does not exist for comparison with our polysilylketene work. The photochemical experimentation, in the limited form presented here, serves only to suggest that the photochemistry and thermochemistry of polysilylketenes is not the same. A more extensive study of the mechanism of the systems covered in this research as well as with monosilyl-substituted systems needs to be undertaken before the diversity in the reactions can be understood and explained.

EXPERIMENTAL

Instrumentation

High resolution ^1H , NMR (300 Hz), ^{13}C NMR (75.5 Hz), and ^{29}Si NMR (59.5 MHz) spectra were recorded on a Varian VXR-300 spectrometer. All chemical shifts are reported as parts per million from tetramethylsilane and taken in deuterated chloroform. Standard abbreviations are used to designate proton splitting. Mass spectra (MS) were recorded using a Hewlett Packard 5970B (GC/MS) operating at 70 eV and are reported as m/e (% relative intensity). Exact mass measurements were recorded using a Kratos MS 50 GC/MS operating at 8 kV, 10,000 resolution, and are reported as m/e . Infrared (IR) spectra were recorded using a Hewlett Packard 5965A (GC/IR) and are reported as wave numbers (cm^{-1}).

Gas chromatograph (GC) analyses were performed on a Hewlett Packard 5790A or Hewlett Packard 5890 Series II using a 30 meter DB-5 capillary column. Preparative GC was performed on a Varian 1400 using 14% SE-30 on Chrom WHP 100/120.

A pulsed stirred-flow reactor (SFR) modeled after the design of Davidson et al⁵² was used for kinetic studies. The SFR was calibrated by following the well-established thermal isomerization of cyclopropane to propylene. (Lit.: $\log A/\text{s}^{-1} = 15.45$, $E_a = 65.63 \text{ kcal/mol}$; Exp.: $\log A/\text{s}^{-1} = 14.51 \pm 0.38$, $E_a = 63.39 \pm 1.58 \text{ kcal/mol}$) The quartz reaction vessel has a volume of 4 cm^3 and a τ of 3.30 s. The reaction vessel was heated by an oven that was controlled by a Digi-Sense temperature controller. The SFR used a 30 ml per minute flow of helium to sweep the sample through the reactor into a Varian 6000 GC fitted with a 30 meter DB-5 megabore column which had the option of diverting the separated products into a VG-SX300 quadrupole mass spectrometer for MS analysis. The GC (FID) signals were recorded on a Hewlett Packard 3390A integrator as well as a Magnum XT/Mark 2 microcomputer for determination of the reactant and product areas.

Procedures and Results

General setup for flow pyrolyses

A vertical quartz tube, ca. 1.8 cm $\times$ 30 cm, packed with quartz chips, was suspended with the packed area of the column within, the septumed outer joint above, and the inner joint below a Lindberg 800 watt oven. Open area around the column at each end of the oven was filled with insulation and the oven door was closed, encapsulating the packed area. The inner joint of the column was fitted with a vacuum adapter, with a side hose connection and drip tip. A 5 or 10 mL round-bottom flask was fitted to the vacuum adapter. The pyrolyses was conducted in a flow of argon. The argon flow entered through the septum via a needle-tipped gas line and exited from the side hose connection of the vacuum adapter. Tubing from the connection to a U-shaped, oil-filled, bubble tube prevented air contamination. Temperature was controlled by a Digi-Sense temperature controller. Pyrolysates were trapped by immersing the round bottom flask in an isopropanol/dry ice bath.

General setup for photolyses

Photolyses were conducted with a 450 watt Hanovia medium pressure mercury arc lamp in a water-cooled quartz immersion well fitted with a surrounding reaction vessel. The reaction vessel had a vertical and angled neck. After filling the reaction vessel with the reaction solution, the angle neck was septumed and used for sampling. The vertical neck was fitted with a septumed dry ice condenser filled with dry ice or an isopropanol/dry ice bath to prevent solvent loss. An argon flow entered the system through a gas frit at the bottom of the reaction vessel and exited through the condenser septum via a needle-tipped gas line. Argon flow was initiated at a minimum of thirty minutes prior to initiation of the photolyses to degas the reaction vessel and was continued throughout the reactions to agitate the degassed solution.

Synthesis of 1,2-dichlorohexamethyltrisilane and 1,4-dichlorooctamethyltetrasilane

The synthetic method used to prepare these compounds is a modification of the free radical halogenation of hydrido-substituted silanes reported by Stolberg⁵³. The 1,3-dihydrido-hexamethyltrisilane or 1,4-dihydrido-octamethyltetrasilane was weighed directly into a round-bottom flask. A thirty-fold molar excess of carbon tetrachloride was added to the flask followed by a catalytic amount of benzoyl peroxide, ≈ 0.021 g (8.7×10^{-2} mmol). The flask was equipped with a magnetic stir bar and fitted with a septum condenser. An argon balloon was fitted to the condenser, water flow to the condenser was initiated, and the magnetic stirrer was turned on. The oil bath temperature was increased slowly until the solution began to reflux. This condition was maintained overnight. The flask was then removed from the bath to cool. The carbon tetrachloride was removed by rotoevaporation and the product was purified by vacuum distillation. Products were identified by GC/MS and reaction yields ranged from 79-92%.

Synthesis of 3,3,4,4,7,7,8,8,9,9-decamethyl-3,4,7,8,9-pentasilacyclonona-1,5-diyne (3)

This compound was prepared following the synthetic method reported by Sakurai et al⁵. A 10 mL solution of 2.0 M ethylmagnesium bromide (20 mmol) in THF was added to a 10 mL solution of 1,2-diethynyltetramethyldisilane (10 mmol) in THF cooled to 0°C. The system, fitted with an argon balloon and equipped with a magnetic stirrer, was allowed to warm to room temperature while stirring. An aliquot was removed and quenched with chlorotrimethylsilane. The analytical GC identified a ratio of 1:2 between mono- and diGrignard reagent. An additional 2.5 mL of the 2.0 M ethylmagnesium bromide (5.0 mmol) increased the ratio to 1:8. The system was cooled to -23°C and 2.42 g of 1,3-dichlorohexamethyltrisilane (9.9 mmol) was slowly added via syringe. After warming to room temperature

while stirring, the solution was washed three times with water, separating the organic layer after each wash. After drying over sodium sulfate, the solution was decanted into a round-bottom flask. The solvent was removed by rotoevaporation, leaving a solution of 18% product by analytical GC trace. The remaining solvent and low-molecular weight impurities were pumped off. The mixture was vacuum distilled at 0.5 torr with a bath temperature of 140°C resulting in a colorless white solid. The product was sublimed repeatedly and the best cuts were purified by preparative GC (8 ft, 14% SE-30, col. temp. 175°C). The product was characterized as follows: ^1H NMR 0.160 (s, 6H), 0.219 (s, 12H), 0.23 (s, 12H); ^{13}C NMR - 7.517, -3.350, -2.737, 115.950, 116.733; ^{29}Si NMR -45.370, -35.667, -34.070; GC/MS 338 (M^+ , 38), 323 ($\text{M}^+ - \text{Me}$, 95), 265 ($\text{M}^+ - \text{SiMe}_3$, 15), 183 (16), 73 (SiMe_3 , 100); IR 2961 (m), 2899 (w), 1252 (m), 831 (vs), 769 (s). NMR data was very similar to that reported⁵, but only Raman IR results were reported preventing a second basis for comparison.

Synthesis of 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasilacycloocat-1,5-diyne (1)

This compound was prepared following the synthetic method reported by Iwahara and West⁴. A 10 mL solution of 2.0 M ethylmagnesium bromide (20 mmol) in THF was injected into a round-bottom flask, equipped with a magnetic stirring bar and fitted with an argon balloon, cooled to 0°C, and containing a 10 mL solution of 1,2-diethynyltetramethyldisilane (10 mmol) in THF. After warming to room temperature while stirring, an aliquot was removed and quenched with chlorotrimethylsilane. The analytical GC trace indicated a ratio of 1:2 between mono- and diGrignard product with some starting material remaining. The 1,2-dichlorotetramethyldisilane, 1.93 g (10 mmol), was added slowly via syringe. The mixture was washed three times with water, separating the organic layer after each separation. After drying over sodium sulfate, the solution was decanted into a round-bottom flask and the solvent removed by rotoevaporation. The crude product was vacuum distilled with the

product subliming as a colorless crystalline solid in the area around the thermometer. The product was scraped out and resublimed. Final product yield was 3.6%. The product was characterized as follows: ^1H NMR 0.242 (s, 24H); ^{13}C NMR -2.979, 119.518; ^{29}Si NMR 33.579; GC/MS 281 (18), 280 (M^+ , 54), 267 (18), 266 (32), 265 (M^+ -SiMe₃, 100), 83 (16), 73 (SiMe₃, 84); IR 2963 (w), 1901 (w), 1253 (m), 831 (vs), 769 (s). NMR data was comparable to that reported in the communication⁴ and no IR data was reported.

Pyrolysis of dialkyne 3 in the kinetic SFR

A solution of 3 diluted in benzene, 0.036 M, was pyrolyzed in the SFR, at 10°C intervals, from 450-550°C. A 1 μL solution of starting material was syringe injected into the SFR. The formation of the elimination product, 1, was followed by GC. The GC temperature program was 60°C for 2 minutes, 20°C/minute, 250°C for 5 minutes.

Pyrolysis of dialkyne 3/2,3-dimethylbutadiene in the kinetic SFR

A solution of 3 diluted in pentane, 0.071 M, was pyrolyzed in the SFR, at 10°C intervals, from 450-520°C. A 0.5 μL solution of starting material was syringe injected into the SFR. The formation of the elimination product, 1, and the trapped silylene adduct were followed by GC. The GC temperature program was 50°C for 1 minute, 20°C/minute, 250°C for 5 minutes.

Synthesis of 3,3,6,6,7,7,8,8-octamethyl-3,6,7,8-tetrasilacycloocta-1,4-diyne (33)

Approximately 70-100 mL of THF was distilled over LiAlH₄ directly into a flask containing 0.44 g of 1,3-diethynylhexamethyltrisilane (1.98 mmol) and a magnetic stirring bar. Two equivalents of 2.0 M ethylmagnesium chloride in diethyl ether was initially injected into

the system at 0°C, but based on the ratios of the mono- and diGrignard product and starting material, additional ethylmagnesium chloride was added. A total of 5.3 mL of ethylmagnesium chloride (10.6 mmol) was injected in all. The system was allowed to warm to room temperature while stirring for 1-2 hours after each addition. The mixture was cooled to -73°C and 0.24 mL of dichlorodimethylsilane (1.98 mmol) was injected dropwise. After warming to room temperature, the solution was worked up with several acid washes, separating the organic layer after each wash, and dried over sodium sulfate. The solution was decanted into a round-bottom flask and the solvent was removed by rotoevaporation. Crude product yield was 38.9%. The product was purified by preparative GC (8 ft, 14% SE-30, col. temp. 130°C) and characterized as follows: ¹H NMR 0.173 (s, 6H, SiSiMe₂Si), 0.226 (s, 12H, Me₂SiSiSiMe₂), 0.242 (s, 6H, CSiMe₂C); ¹³C NMR -8.322 (SiSiMe₂Si), -3.043 (Me₂SiSiSiMe₂), -1.220 (CSiMe₂C), 123.600 ((Me₂Si)₃C≡), 124.384 (≡CSiMe₂); ²⁹Si NMR -64.627 (SiSiSi), -35.839 (SiSiSi), -33.333 (CSiC); GC/MS 280 (M⁺, 44), 265 (M⁺-Me, 100), 97 (17), 83 (18), 73 (SiMe₃, 99); exact mass calculated for C₁₂H₂₄Si₄ 280.09468, measured 280.09552; IR 2962 (w), 2899 (w), 1256 (m), 835 (vs), 777 (m).

Flow pyrolysis of dialkyne 33

A solution of 33 in hexane was pyrolyzed at 610°C in a flow of argon (~30 mL/min). Solvent was removed by rotoevaporation and vacuum. The ¹³C NMR had peaks in addition to the starting material at -3.157 and 119.369, characteristic of the isomer 1.

Synthesis of bis(dimethylsilyl)ketene dimer (34) and 2.2.3.3.5.5.6.6-octamethylcyclotetrasiloxylketene (35)

Approximately 15-20 mL of THF was distilled from LiAlH₄ directly into the reaction flask, containing a magnetic stir bar. Fitted with an argon balloon, the flask was cooled to -30

°C by an ethylene glycol/dry ice bath and 1 mL of 2,3-dihydrofuran (13.2 mmol) was injected into the system. A 6 mL solution of 2.5 M n-butyllithium (15 mmol) in hexanes was injected dropwise and the bath was removed 15 minutes after completion of addition. The system was stirred for 24 hours and was then cooled to -73°C by an isopropanol/dry ice bath. A second equivalent of 6 mL of 2.5 M n-butyllithium (15 mmol) in hexanes was injected dropwise and the bath was removed 15 minutes after completion of addition. The system was stirred for 6 hours and then an aliquot was quenched with dimethylchlorosilane to confirm the presence of the dianion. The system was recooled to -73°C and 2.60 g of 93% 1,2-dichlorotetramethyl-disilane (13 mmol) was injected dropwise. The bath was removed 15 minutes after completion of addition. The system was stirred for 2 hours and then 10 mL of pentane was injected into the system. Two products were detected by GC/IR/MS. The reaction mixture was not washed since doing so seemed to result in decomposition of **35**. The products appeared to decompose in the preparative GC and attempts to separate by column chromatography proved ineffective. Ketene **34** was characterized as follows: GC/MS 312 (M^+ , 9), 297 ($M^+ - \text{Me}$, 27), 269 (33), 211 (16), 73 (SiMe_3 , 100); IR 2084 (vs), 897 (w), 810 (w). Ketene **35** was characterized as follows: GC/MS 288 (M^+ , 6), 273 ($M^+ - \text{Me}$, 29), 245 (16), 229 ($M^+ - \text{SiMe}_2\text{H}$, 15), 73 (SiMe_3 , 100); IR 2086 (vs), 1256 (w), 1011 (m), 886 (w), 810 (w).

Synthesis of 2,2,3,3,4,4,5,5,6,6-decamethylpentasilacycloketene (**36**)

Approximately 15-20 mL of THF was distilled over LiAlH_4 directly into the reaction flask. Fitted with an argon balloon, the system was cooled to -30°C by an ethylene glycol/dry ice bath and 1 mL of 2,3-dihydrofuran (13.2 mmol) was injected into the system. A 6 mL solution of 2.5 M n-butyllithium (15 mmol) in hexanes was injected dropwise and the bath was removed 15 minutes after completion of addition. The system was stirred for 24 hours and

was then cooled to -73°C by an isopropanol/dry ice bath. A second 6 mL solution of 2.5 M *n*-butyllithium (15 mmol) in hexanes was injected dropwise and the bath was removed 15 minutes after completion of addition. The system was stirred for 6 hours and then an aliquot was quenched with dimethylchlorosilane to confirm the presence of the dianion. The system was recooled to -73°C and 5.46 g of 85% 1,5-dichlorodecamethylpentasilane (15 mmol), obtained from Dr. Yi Pang, was injected dropwise. The bath was removed 15 minutes after completion of addition. The system was stirred for 2 hours and then 10 mL of pentane was injected into the system. The reaction mixture was subsequently washed three times with aqueous sodium bicarbonate, separating the organic layer after each wash, and dried over sodium sulfate. The solution was decanted into a round-bottom flask and the solvent removed by rotoevaporation. The crude yield was 49%. The ketene was purified by preparative GC (8 ft, 14% SE-30, col. temp 180°C) and further purified by sublimation. The product, a colorless, crystalline solid was characterized as follows: ^1H NMR 0.242 (s, 12H, $\text{Me}_2\text{SiSiC=}$), 0.160 (s, 6H, $\text{Me}_2\text{SiSiSiC=}$), 0.127 (s, 12H, $\text{Me}_2\text{SiC=}$); ^{13}C NMR -6.911 ($\text{Me}_2\text{SiSiC=}$), -6.591 ($\text{Me}_2\text{SiSiSiC=}$), -1.726, -0.885 (C=C=O), 165.313 (C=O); ^{29}Si NMR -46.278 (SiSiC=), -44.289 (SiSiSiC=), -15.427 (SiC=); GC/MS 330 (M^+ , 9), 315 (M^+-Me , 14), 257 (M^+-SiMe_3 , 12), 229 (15), 73 (SiMe_3 , 100), 59 (SiMe_2H , 11); exact mass calculated for $\text{C}_{12}\text{H}_{30}\text{OSi}_5$ 330.11431, measured 330.11393; IR 2955 (w), 2894 (w), 2083 (vs), 1254 (w), 893 (w), 806 (w). The product melting point was $100-104^{\circ}\text{C}$.

Flow pyrolysis of ketene 36

A solution of 0.116 g of ketene 36 (0.35 mmol) and 3 mL of hexane (23 mmol) was pyrolyzed at 600°C in a flow of argon (30 mL/min). The column was washed with an additional 2 mL of hexane (15 mmol). The solvent was removed by rotoevaporation. The crude yield, calculated from the mixture mass and GC trace percent, was 25% starting

material and 25% ketene **37**. The elimination product **37**, a colorless, crystalline solid, was isolated by preparative GC (8 ft, 14% SE-30, col. temp. 160°C) and characterized as follows: ^1H NMR 0.255 (s, 12H, $\text{Me}_2\text{SiSiC=}$), 0.157 (s, 12H, $\text{Me}_2\text{SiC=}$); ^{13}C NMR -7.367 ($\text{Me}_2\text{SiSiC=}$), -6.156 ($\text{Me}_2\text{SiSiC=}$), -0.614 (C=C=O), 164.772 (C=O); ^{29}Si NMR -44.412 (SiSiC=), -4.840 (SiC=); GC/MS 272 (M^+ , 17), 257 (M^+-Me , 27), 213 ($\text{M}^+-\text{SiMe}_2\text{H}$, 14), 155 (14), 73 (SiMe_3 , 100); exact mass calculated for $\text{C}_{10}\text{H}_{24}\text{OSi}_4$ 272.09043, measured 272.09000; IR 2956 (w), 2896 (w), 2086 (vs), 1253 (w), 877 (w), 811 (w).

Synthesis of 2,2,3,3,4,4,5,5-octamethyltetrasilacycloketene (**37**)

The procedure is the same as that described for ketene **36** except 4.64 g of 93% 1,4-dichlorooctamethyltetrasilane (14.3 mmol) was used to quench the dianion. The crude yield was 40%. The product was isolated by preparative GC (8 ft, 14% SE-30, 160°C) and identified by comparison of GC/IR/MS spectra with the spectra of an authentic sample isolated from the pyrolysis of **36**.

Synthesis of chloropentamethyldisilane

This compound was prepared following the synthetic method reported by Sakurai et al.⁵⁴. The aluminum chloride, 80.03 g (602 mmol), was weighed directly into an argon-purged three-necked flask. The hexamethyldisilane, 120.9 mL (604 mmol), was poured into the flask and a condenser, mechanical stirrer, and an addition funnel were fitted to the three necks. Argon flow was initiated and continued throughout the reaction. A cannula was used to transfer 43.0 mL of acetyl chloride (605 mmol) to the addition funnel. The system was cooled to 0°C by an ice bath, the mechanical stirrer was started, and dropwise addition of acetyl chloride was initiated. The ice bath was removed periodically to monitor the flask temperature/rate of addition. Upon completion of addition, the ice bath was removed and the

system was stirred overnight. The product mixture was removed from the reaction vessel by cannula and the product was isolated from the pale yellow solution by trap-to-trap distillation. The product, trapped in a round-bottom flask immersed in an isopropanol/dry ice bath, was a colorless, crystalline solid, which when warmed to room temperature was a colorless liquid. The crude yield was 63%. The product was identified by GC/MS spectra: 166 (M^+ , 5), 74 (11), 73 (SiMe_3 , 100).

Synthesis of bis(pentamethyldisilanyl)ketene (38)

The procedure is the same as that described for **36** except 5.29 g of chloropentamethyldisilane (27 mmol) was used to quench the dianion. The crude yield was 40%. The product, a colorless liquid, was isolated by preparative GC (8 ft, 14% SE-30, 130°C) and characterized as follows: ^1H NMR 0.102 (s, 18H, $\text{Me}_3\text{SiSiC=}$), 0.208 (s, 12H, $\text{Me}_2\text{SiC=}$); ^{13}C NMR -4.525 ($\text{Me}_3\text{SiSiC=}$), -2.666 ($\text{Me}_2\text{SiC=}$), -1.099 (C=C=O), 165.470 (C=O); ^{29}Si NMR -18.227 (SiSiC=), -16.974 (SiC=); GC/MS 302 (M^+ , 2), 229 ($M^+-\text{SiMe}_3$, 13), 171 ($M^+-\text{SiMe}_2\text{SiMe}_3$, 22), 147 (13), 131 ($\text{SiMe}_2\text{SiMe}_3$, 18), 73 (SiMe_3 , 100); exact mass calculated for $\text{C}_{12}\text{H}_{30}\text{OSi}_4$ 302.13738, measured 302.13719; IR 2955 (w), 2898 (w), 2078 (vs), 1256 (w), 835 (m), 792 (m).

Flow pyrolysis of ketene 38

A solution of 0.124 g of ketene **38** (0.38 mmol) and 3 mL of hexane (23 mmol) was pyrolyzed at 550°C in a flow of argon (~30 mL/min). The column was washed with an additional 2 mL of hexane (15 mmol). The solvent was removed by rotoevaporation. The crude yield, calculated from the mixture mass and GC trace percent, was 40% starting material and 13% ketene **39**. The elimination product **39**, a colorless liquid, was isolated by preparative GC (8 ft, 14% SE-30, 130°C) and characterized as follows: ^1H NMR 0.098 (s,

9H, $Me_3SiSiC=$), 0.178 (s, 9H, $Me_3SiC=$), 0.204 (s, 6H, $Me_2SiC=$); ^{13}C NMR -2.368 ($Me_3SiSiC=$), -1.641 ($C=C=O$), -1.057 ($Me_2SiC=$), 1.471 ($Me_3SiC=$), 166.455 ($C=O$); ^{29}Si NMR -13.573 ($SiSiC=$), -13.179 ($SiSiC=$), 4.909 ($SiC=$); GC/MS 244 (M^+ , 5), 172 (17), 171 (M^+-SiMe_3 , 100), 73 ($SiMe_3$, 85); exact mass calculated for $C_{10}H_{24}OSi_3$ 244.11350, exact mass measured 244.11406; IR 2957 (w), 2085 (vs), 1258 (w), 905 (w), 841 (m), 797 (w).

Photolysis of ketene 36

Using decane as an internal standard, 0.159 g of **36** (0.48 mmol) in hexane was photolyzed by a medium pressure mercury arc lamp in a water-cooled quartz immersion well. The photolysis was monitored by GC/IR/MS and analytical GC at ten minute intervals for the first thirty minutes and at twenty minute intervals for the following sixty minutes. Percents were based on the analytical GC. Ketene **37** was identified by comparison of spectra with authentic spectra collected on the same instrument using the same temperature program. The second ketene **47** was speculated based on the following spectra: GC/MS 214 (M^+ , 41), 200 (18), 199 (M^+-Me , 85), 171 (35), 156 (15), 155 (M^+-SiMe_2H , 93), 73 ($SiMe_3$, 100), 59 ($SiMe_2H$, 23); IR 2091 (vs), 1319 (w), 1249 (w), 846 (w). The ketene **47** was not isolated. The reaction was suspended when the reaction starting material was consumed, resulting in a limited amount of this product.

Photolysis of ketene 38

Using decane as an internal standard, 0.167 g of **38** (0.55 mmol) in hexane was photolyzed by a medium pressure mercury arc lamp in a water-cooled quartz immersion well. The photolysis was monitored by GC/IR/MS and analytical GC at ten minute intervals for the first thirty minutes, at twenty minute intervals for the following hour, and finally for a single

twenty-six minute interval. Decomposition of starting material with no resulting products detected was observed. Addition of 2.6 mL of triethylsilane (16 mmol) prior to the final interval did not result in any observable products.

Photolysis of ketene 38 with triethylsilane

Using decane as an internal standard, 0.216 g of **38** (0.71 mmol) and 5.6 mL of triethylsilane (35 mmol) was photolyzed in hexane by a medium pressure mercury arc lamp in a water-cooled quartz immersion well. The photolysis was monitored by GC/IR/MS and analytical GC at ten minute intervals for the first thirty minutes, twenty minute intervals for the next forty minutes, a twenty-five minute interval, a fifteen minute interval, and finally at thirty minute intervals for the last hour and a half. Decomposition of ketene **38** occurred with no resulting products detected.

Photolysis of ketene 38 with carbon tetrachloride

Using pentadecane as an internal standard, 0.200 g of **38** (0.66 mmol) and 6.4 mL of carbon tetrachloride (66 mmol) was photolyzed in hexane by a medium-pressure mercury arc lamp in a water-cooled immersion well. The photolysis was monitored by GC/MS and analytical GC at ten minute intervals for the first thirty minutes, twenty minute intervals for sixty minutes, thirty minute intervals for sixty minutes, and finally, at the end of a sixty minute interval. Decomposition of **38** occurred, but any products observed were not attributed to the decomposition. A control, composed of all materials except the ketene **38**, produced the products observed with the carbon tetrachloride-ketene **38** photolysis.

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