

SILICON-CARBON MULTIPLE-BONDED ($p_\pi-p_\pi$) INTERMEDIATES

I. REACTIONS OF KETONES AND ALDEHYDES WITH INTERMEDIATES FROM THERMOLYSIS OF SILACYCLOBUTANES*

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Summary

The reactions of $R_2Si=CH_2$ ($R = Me, Et, \text{ or } Ph$), generated by thermolysis of the corresponding 1,1-disubstituted silacyclobutane at 611° , with a variety of ketones and aldehydes, are described. Two major reaction pathways were observed: olefin formation, postulated to occur via a pseudo Wittig reaction; and silyl enol ether formation. Olefin formation predominated in reactions involving aromatic carbonyls in contrast to the reactions involving aliphatic ketones which afforded silyl enol ethers as the major products. Heptanal reacted to give comparable yields of each class of products.

Introduction

In 1967 Gusel'nikov and Flowers pyrolyzed 1,1-dimethylsilacyclobutane (I) in the vapor phase and trapped an intermediate, postulated to be $Me_2Si=CH_2$ (II), with water [1]. It was later reported [2,3] by these workers that II could be trapped with ammonia, ethylene and propene. In the reactions of II with water and ammonia the positive part of the reagent added to the terminal methylene and the negative part to silicon. Because of these results, some of our recent work [4-6] involving photochemically generated species of the type $R_2Si=CH_2$, and some recently reported calculations [7], it appeared to us that the $p_\pi-p_\pi$ multiple bond between silicon and carbon is polarized in the sense $Me_2\overset{\delta+}{Si}\cdots\cdots\overset{\delta-}{CH_2}$ and hence might show considerable zwitter-ionic character. In turn, this reasoning led us to conceive that $Me_2Si=CH_2$ might behave similarly to $R_3P=CH_2$ toward carbonyl compounds and yield Wittig-type products.

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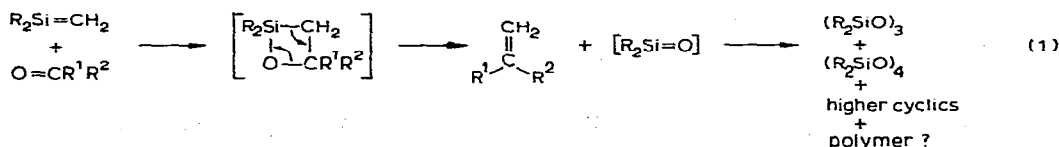
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In a recent brief report [8] we have shown that this occurs when a non-enolizable ketone is used. Benzophenone, for example, gives a high yield of 1,1-diphenylethylene. A moderate yield of 1-octene was also reported [8] for the reaction between II and heptanal. Reaction of II with potentially enolizable ketones afforded moderate yields of silyl enol ethers indicating that a second major reaction pathway was available to these compounds.

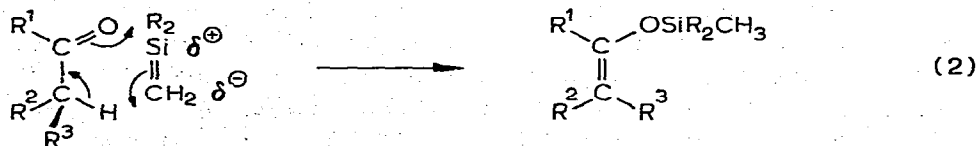
Since our initial report we have learned much more about the scope and nature of the reaction of $\text{Me}_2\text{Si}=\text{CH}_2$ with carbonyl compounds and these results are reported in detail in the present paper.

The major reaction pathways of $\text{R}_2\text{Si}=\text{CH}_2$, generated by pyrolysis of the corresponding silacyclobutane at 611° in a stream of nitrogen, are outlined first.

The mechanism of a pseudo Wittig reaction of a carbonyl compound with $\text{R}_2\text{Si}=\text{CH}_2$ is tentatively given in eqn. 1; formation of the postulated 4-ring intermediate may not be a concerted process.



The mechanism for formation of silyl enol ethers from the reaction of $\text{R}_2\text{Si}=\text{CH}_2$ with carbonyl compounds containing alpha hydrogen atoms is more difficult to formulate and we suggest in eqn. 2 a preliminary hypothesis based on the initial results of a series of experiments currently in progress. The postulate that II reacts with potentially enolizable aldehydes and ketones by a mechanism involving proton abstraction (eqn. 2) is supported by our recent observation [9] of the reaction of II with acetonitrile (or acetonitrile- d_3) to give moderate ($\approx 34\%$) yields of trimethylsilylacetonitrile [or $\text{Me}_2(\text{CH}_2\text{D})\text{SiCD}_2\text{C}\equiv\text{N}$]. This reaction, like that of II which yields silyl enol ethers, is most simply formulated as involving proton abstraction from an α -carbon by II. However, alternative mechanism paths, including prior enolization followed by addition, cannot be rigorously excluded at this time.



The nature of the carbonyl compound has a profound effect on the course of these two reactions (eqn. 1 vs. eqn. 2) and in some cases, notably heptanal, comparable yields of olefin and silyl enol ether are obtained.

Results

The yield of 1,1,3,3-tetramethyl-1,3-disilacyclobutane in reactions in which 1,1-dimethylsilacyclobutane (I) was the limiting reagent (most of the

TABLE 1

PYROLYSIS OF 1,1-DISUBSTITUTED SILACYCLOBUTANES IN THE PRESENCE OF KETONES AND ALDEHYDES AT 611°

Silacyclobutane (mmol)	Trapping Reagent (mmol)	Yield (%)					
		Silyl Enol Ether		Pseudo Wittig Olefin		(Me ₂ SiO) ₃	(Me ₂ SiO) ₄
		Uncorr.	(Corr.)	Uncorr.	(Corr.)	Uncorr.	Uncorr.
Me ₂ Si(CH ₂) ₃ I (9.93)	Me ₂ C=O (34.5)	25	(32) ^a	1.7 ^b	(3.9) ^c	1.4	<1
I (11.5)	(CH ₂) ₅ C=O (33.7)	34	(62) ^a	~6 ^d	(~9) ^a	<5 ^d	~0
I (11.1)	Ph(C=O)Me (33.8)	14	(22) ^a	49	(65) ^e	9.5	22
I (11.0)	<i>m</i> -FC ₆ H ₄ (C=O)Me (29.0)	22	(34) ^f	52	(69) ^e	14	24
I (11.7)	Ph ₂ C=O (6.15)			73	(97) ^e	28 ^d	5.5
I (21.6)	Me(CH ₂) ₅ CHO (37.6)	5.5	(26) ^a	19	(26) ^e	10.8	2.3
I (10.2)	PhCHO (30.2)			40	(54) ^e	4.4	32
Et ₂ Si(CH ₂) ₃ (10.1)	Ph ₂ C=O (6.85)			49	(65) ^e	8 ^g	~0
Ph ₂ Si(CH ₂) ₃ (5.37)	Me(CH ₂) ₅ CHO (12.3)	<i>h</i>		33	(44) ^e	trace ⁱ	<i>h</i>

^aCorrection based on yield of pure material recovered after pyrolysis and preparative GLC (see text and Table 2). ^bIsolated as the corresponding dibromide. ^cCorrection based on the yield of 1,2-dibromoethane in this reaction, see experimental. ^dIsolated as a mixture and identified on the basis of IR and NMR spectra. ^eCorrection made assuming that compound was thermally stable and that a 25% mechanical loss was incurred. ^fCorrection calculated assuming that this product had the same thermal stability as the trimethylsilyl enol ether of acetophenone. ^gHexaethylcyclotrisiloxane. ^hAnalysis was not performed for this product. ⁱHexaphenylcyclotrisiloxane.

reactions studied fall into this category) was generally less than 5%, indicating that Me₂Si=CH₂ (II) reacted efficiently with the trapping reagent, which was normally present in a 3-fold molar excess. The uncorrected yields in Table 1, unless otherwise noted, are based on amounts of material actually isolated by preparative GLC, and the corrected yields given in Table 1 were calculated using two different methods (see Experimental).

Table 1 shows that II exhibits different reactivity patterns with aliphatic as opposed to aromatic carbonyl compounds, with the exception of heptanal, which shows intermediate behavior.

In the reactions of II with acetone and cyclohexanone the major products, using either isolated or corrected yields, are the corresponding silyl enol ethers. These were obtained in at least a 6-fold molar excess over the olefins arising via the pseudo Wittig reaction pathway*.

To make certain that the pyrolysis of I in the presence of acetone did not produce significant quantities of isobutylene the volatile products of this reac-

* In preliminary experiments similar results were obtained in the reactions of II with 2-pentanone, 2,4-dimethyl-3-pentanone, and 3,3-dimethyl-2-butanone. In these reactions the yields of silyl enol ether were low (ca. 10%) and the reaction mixtures were complex.

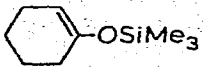
tion were trapped as the corresponding dibromides (see Experimental for details). A 44% yield of 1,2-dibromoethane as opposed to only a 1.7% yield of 1,2-dibromo-2-methylpropane demonstrates that the trapping technique is moderately efficient and also that no appreciable quantity of isobutylene was produced.

Additional evidence supporting the observation that reaction of $\text{Me}_2\text{Si}=\text{CH}_2$ (II) with enolizable aliphatic ketones produces only low yields of pseudo Wittig products is the fact that either low (< 5%) or negligible yields of $(\text{Me}_2\text{SiO})_3$ and $(\text{Me}_2\text{SiO})_4$ are obtained in these reactions. We have isolated $(\text{Me}_2\text{SiO})_3$ and $(\text{Me}_2\text{SiO})_4$ in modest (32 - 38%) combined yields from reactions of II with aromatic carbonyl compounds using identical reaction conditions. Because of this it seems reasonable to assume that they are not formed in appreciable quantities in the reactions of II with aliphatic ketones.

The reaction of II with heptanal, in contrast to the results obtained with the aliphatic ketones, yielded the pseudo Wittig product, 1-octene, as the major isolated product. However, when the corrected yields are used, the yields of 1-(trimethylsiloxy)-1-heptene and 1-octene are comparable. Since the corrected yields are probably maximum yields, in the pyrolysis of I in the presence of heptanal, either a third major or, more likely, a multiplicity of minor reaction pathways are operative. The combined 13.1% yield of $(\text{Me}_2\text{SiO})_3$ and $(\text{Me}_2\text{SiO})_4$ obtained from the reaction of II with heptanal is in accord with the 19% yield of 1-octene obtained in this reaction. We presently have no explanation as to why the pseudo Wittig pathway predominates in the reaction between II and heptanal. The thermal instability of both heptanal and its silyl enol ethers (see Table 2 and Experimental), indicates that caution should be used in interpreting the product ratios obtained for this reaction. The fact that the reaction of II with heptanal produces roughly equivalent amounts (a slight predominance of the *trans* isomer was observed) of *cis*- and *trans*-1-(trimethylsiloxy)-1-heptene may indicate that II is a highly reactive chemical species which shows little discrimination between these two reaction pathways. Furthermore, the predominance of *trans*-1-(trimethylsiloxy)-1-heptene is tentatively interpreted to mean that formation of the silyl enol ethers of heptanal is kinetically controlled since preparation of these compounds under reaction conditions reported [10] to allow equilibration of the *cis* and *trans* isomers leads to a predominance of the *cis* isomer.

From examination of the reactions of $\text{Me}_2\text{Si}=\text{CH}_2$ (II) with aromatic carbonyls (see Table 1) it is immediately evident that olefinic products are, in every instance, isolated in high (40 - 73%) yields. In the reaction between II

TABLE 2
PYROLYSIS OF TRIMETHYLSILYL ENOL ETHERS AT 611°

Compound	% Recovered ^a
$\text{CH}_2 = \text{C}(\text{Me})\text{OSiMe}_3$	78
	55
$\text{CH}_2 = \text{C}(\text{Ph})\text{OSiMe}_3$	65
$\text{Me}(\text{CH}_2)_4\text{CH} = \text{CHOSiMe}_3^b$	21

^aYields based on material isolated by preparative GLC. ^bA mixture of ca. 60/40 *cis/trans* isomers used. Recovered material had the same *cis/trans* ratio as the starting material.

and acetophenone both of the possible products, α -methylstyrene (49% uncorr. yield) and α -(trimethylsiloxy) styrene (14% uncorr. yield) are obtained. Since the same results (65% olefin and 22% silyl enol ether) are obtained when the corrected yields are used, in this case the pseudo Wittig reaction pathway clearly predominates. Even in the reactions between II and either benzophenone or benzaldehyde in which only one major reaction pathway is available, the high (40 - 73%) isolated yield of pseudo Wittig products and also the absence of appreciable quantities of the dimer of II indicate that this reaction must be an energetically favored one.

In most of the reactions between II and aromatic carbonyls the combined yield of $(\text{Me}_2\text{SiO})_3$ and $(\text{Me}_2\text{SiO})_4$ is lower, probably due to formation of higher cyclic or linear polymers which were not isolated, but roughly parallels that of the olefinic product. Except for the reaction between II and benzophenone, in which an excess of I was used, $(\text{Me}_2\text{SiO})_4$ was the major cyclic siloxane produced. The predominance of $(\text{Me}_2\text{SiO})_4$ is probably due to rearrangement of the strained $(\text{Me}_2\text{SiO})_3$ molecule under the rather severe reaction conditions used*. This, and also the possibility that $(\text{Me}_2\text{SiO})_3$ and $(\text{Me}_2\text{SiO})_4$ arise via different reaction pathways (i.e., $\text{Me}_2\text{Si}=\text{O}$ dimer + $\text{Me}_2\text{Si}=\text{O}$ versus $\text{Me}_2\text{Si}=\text{O}$ dimer + $\text{Me}_2\text{Si}=\text{O}$ dimer) are currently under investigation.

The reaction between II and *m*-fluoroacetophenone gives product yields and distributions similar to those observed for acetophenone (see Table 1) indicating that the direction of the reaction is not extremely sensitive to electronic effects. However, in this reaction a small (ca. 8%) increase in the yield of silyl enol ether, relative to that obtained for acetophenone itself, indicates that electronic effects may be of some importance.

The reactions discussed above are not limited to $\text{Me}_2\text{Si}=\text{CH}_2$; similar preliminary results have been obtained with $\text{Et}_2\text{Si}=\text{CH}_2$ and $\text{Ph}_2\text{Si}=\text{CH}_2$ produced by thermolysis of the corresponding 1,1-disubstituted silacyclobutanes (see Table 1).

We are currently carrying out additional research on the reactions and reaction mechanisms of multiply-bonded silicon intermediates.

Experimental

Melting points were taken in capillary tubes. NMR spectra were taken at $\approx 35^\circ$ on a Varian A-60A Spectrometer using dilute carbon tetrachloride solutions with tetramethylsilane as an external reference unless noted otherwise. Infrared spectra were obtained with a Beckman IR-8 infrared spectrometer using dilute carbon tetrachloride solutions and polystyrene calibration. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Starting silacyclobutanes

1,1-dimethyl-, 1,1-diethyl-, and 1,1-diphenyl-silacyclobutane were all prepared using conventional procedures, all of which have been recently reviewed [11].

* Treatment of $(\text{Me}_2\text{SiO})_4$ using the standard pyrolysis conditions resulted in recovery of only $(\text{Me}_2\text{SiO})_4$; no appreciable quantity of $(\text{Me}_2\text{SiO})_3$ was produced.

General pyrolysis procedure

$R_2Si=CH_2$ (R = Me, Et, or Ph) was generated from the corresponding 1,1-disubstituted silacyclobutane by vapor phase pyrolysis at 611°C in a stream of nitrogen using the apparatus and procedure outlined below. A cylindrical quartz tube 26 mm O.D. × 23 mm I.D. × 34 cm., inclined 10° from the horizontal was heated in a 750 watt furnace (Multiple unit no. 70-T). The portion of the tube actually heated to 611° was 30 cm. The higher end of this quartz tube was equipped with a nitrogen inlet (the nitrogen flow rate was 25 ml/min unless otherwise noted) and a small opening covered by a rubber serum cap through which the material to be pyrolyzed could be added via syringe. Commercial 99.996% nitrogen (Liquid Carbonic Hi-Pure) was passed through a 30 cm tube packed with anhydrous $CaSO_4$. One experiment when repeated using helium in place of nitrogen gave identical results. The lower end of the pyrolysis tube was attached to two cylindrical traps which were cooled to either 0° or -80° depending upon the volatility of the expected pyrolysis products. The temperature of the pyrolysis tube was measured by a iron-constantan thermocouple placed against the outside of the tube at the center of the oven. While the observed temperatures were probably slightly higher than the temperatures inside of the pyrolysis tube this method gave entirely reproducible results and allowed rapid detection of temperature variations as small as 0.5°.

Particular care must be taken to exclude air from the pyrolysis tube. On one instance when this precaution was not taken, an explosion, of sufficient force to break off one end of the pyrolysis tube, occurred.

The pyrolysis procedure consisted of first mixing weighed quantities of silacyclobutane, chemical trapping agent, and, where necessary to produce a homogeneous solution, a solvent (generally benzene). The resulting solution was then injected into the upper end of the pyrolysis tube and allowed to flow downward into the heated portion of the tube where it would immediately vaporize. The reaction solutions were generally added at the fastest possible rate which would not cause an appreciable temperature drop in the pyrolysis tube. For a reaction solution of 4 - 5 ml, addition times were generally 15 - 20 min.

Analysis and separation of reaction mixtures

Reaction mixtures were analyzed by GLC using a HP 7620A (FID) with either a 6 ft. × 1/8 in. 10% UC-W98 column or a 20 ft. × 1/8 in. 3% OV-1 column at temperatures ranging from 40 - 260°. Similar results were obtained with either column; however, better separations were generally obtained with the UC-W98 column and it was used for most of the work discussed below.

Since most of the pyrolysates obtained contained at least 3, and generally more, components, all separations were carried out by preparative GLC using a Varian 920 (TCD) with a 14 ft. × 3/8 in. 20% SE-30 column at temperatures ranging from 70° to 200°. In some instances it was necessary to resort to manual programming of the preparative GLC column, i.e. the lower boiling components of a mixture were collected at one temperature (generally about 100°), the oven was then raised to a higher temperature (generally about 200°), and the higher boiling components were collected. Unless otherwise noted, the

yields reported were calculated using the weights of material actually isolated by preparative GLC and the amount of limiting reagent (generally the silacyclobutane) initially used. In some cases it was not necessary to resolve an entire reaction mixture to obtain sufficient quantities of material for analysis. In these instances the weights of material collected were adjusted accordingly, e.g. if 2.00 g of material was obtained from a pyrolysis but only 1.00 g was separated by preparative GLC then the weight of each component obtained would be multiplied by two.

Reactions were generally carried out on a small scale, usually with ca. 1 g. of silacyclobutane and 2 - 3 g of trapping reagent. Mechanical losses engendered by the small scale reactions due to wetting of surfaces or aerosol formation are believed to be at least partially responsible for the fact that a 10 - 15% weight loss was generally observed during pyrolysis. Other possible explanations for the weight losses observed are formation of volatile materials due to decomposition of the trapping reagents and formation of non-volatile, presumably polymeric, residues in the pyrolysis tube. In some cases a significant portion (> 25%) of the trapping reagent decomposed under the reaction conditions used, causing larger weight losses and significantly lower yields. In many instances the trapping reagents were pyrolyzed in the absence of silacyclobutane to determine their thermal stabilities. Any products which appeared to be due solely to decomposition of the trapping reagent were generally not considered. Since another 10 - 15% weight loss generally occurred during preparative GLC, percentage recoveries of stable trapping reagents (corrected for the amount which was known to be consumed by reaction with $R_2Si=CH_2$) are reported to give some indication of the amount of overall mechanical loss which occurred during the entire reaction sequence. At this point no systematic effort has been made to optimize yields by variation of parameters such as reaction temperature, amount of trapping reagent, etc.

For each experiment the major reaction products are discussed first, then the minor products. In general, the products obtained eluted from the SE-30 GLC column in order of increasing boiling point. All reaction products were characterized as fully as possible (IR, NMR, and in some cases mass spectra), satisfactory elemental analyses were obtained for all new compounds.

Calculation of product yields

The corrected yields given in Table 1 were calculated using two different methods. First, corrected yields for the silyl enol ethers and methylenecyclohexane were calculated by multiplying the observed yield by an empirical correction factor. These empirical correction factors are based on data obtained in separate control pyrolyses in which each of these compounds was separately pyrolyzed at 611° and then recovered by preparative GLC. The factor necessary to adjust the yield of a control pyrolysis to 100% was then used to correct the observed yield of the corresponding compound in Table 1. For example, the control pyrolysis of 2-(trimethylsiloxy)propene afforded a 78% recovery and 78% requires a correction factor of 1.28. Thus, the observed yield of 2-(trimethylsiloxy)propene of 25% given in Table 1 multiplied by 1.28 gives the corrected yield as 32%. These corrected yields should be considered as maximum values since in the control experiments the silyl enol ether traveled

the full length of the pyrolysis tube (maximum chance for thermal decomposition, hence maximum correction factor), whereas the formed product need not have traveled the full length of the pyrolysis tube.

In the second method, used to correct the yields of the other remaining pseudo Wittig products in Table 1, it was assumed that these materials were thermally stable but that 25% of the material was lost mechanically in the reaction sequence: 611° pyrolysis and then preparative GLC. A value of 25% for mechanical loss (most of this occurred during preparative GLC) was used because we have generally observed that thermally stable molecules are recovered in yields of 70 - 80% after pyrolysis at 611° and then isolation by preparative GLC.

Pyrolysis of 1,1-dimethylsilacyclobutane (I) in the presence of acetone

A solution consisting of 0.993 g (9.93 mmol) of I and 2.01 g (34.5 mmol) of reagent grade acetone (dried over 3A molecular sieves) was pyrolyzed using the general procedure (see above) yielding 2.47 g (82.5% of original wt.) of a light yellow solution. GLC analysis of the pyrolysate indicated, in addition to unreacted acetone (33% recovered by preparative GLC after correcting for the amount consumed by $\text{Me}_2\text{Si}=\text{CH}_2$) and a small amount of unreacted I (crudely estimated at about 5%), one major and at least four minor products.

Resolution of this mixture by preparative GLC gave 0.332 g (24.8%) of 2-(trimethylsiloxy)propene (major product) which displayed NMR and IR spectra identical to those of this material prepared by an independent route [12]. The structure of 2-(trimethylsiloxy)propene was further confirmed by its mass spectrum (m/e 130, 115, 75 and 73). Two of the minor products were identified as 1,1,3,3-tetramethyl-1,3-silacyclobutane, 0.0127 g, (0.9%) tentatively identified by its GLC retention time, and hexamethylcyclotrisiloxane (III), 0.0106 g (1.4%) identified by its IR and NMR spectra. GLC analysis indicated that octamethylcyclotetrasiloxane had been produced in less than 1% yield.

In a similar experiment [except that 1.09 g (10.9 mmol) of I and 2.51 g (43.2 mmol) of acetone were used] a third trap containing an excess of bromine (16.6 mmole) in carbon tetrachloride (20.3 g), maintained at -5° , was placed after the first two traps (both at -78°). The purpose of the third trap was to capture the more volatile, olefinic products, e.g. ethylene and isobutylene. This trap was arranged in such a manner that the effluent bubbled through the bromine solution. Upon completion of the reaction the excess bromine was removed by purging the solution with nitrogen for ca. 1.5 hr. NMR analysis of the remaining solution indicated that both 1,2-dibromoethane and 1,2-dibromo-2-methylpropane were present. This solution was resolved by preparative GLC yielding 0.90 g (44%) of 1,2-dibromoethane and 0.0406 g (1.7%) of 1,2-dibromo-2-methylpropane. Assuming that only 44% of the total amount of 1,2-dibromo-2-methylpropane formed was trapped, a corrected yield of 3.8% is calculated for isobutylene formation.

In a separate experiment a solution consisting of 1.08 g of 2-(trimethylsiloxy)propene and 3.02 g of benzene was pyrolyzed at 611° using the general procedure. GLC analysis of the pyrolysate indicated that very little decomposition had occurred. Preparative GLC afforded 0.843 g (78.3% recovery) of the starting silyl enol ether.

Pyrolysis of 1,1-dimethylsilacyclobutane (I) in the presence of cyclohexanone

A solution consisting of 1.15 g (11.5 mmol) of I and 3.31 g (33.7 mmol) of cyclohexanone (reagent grade dried over 3A molecular sieves) was pyrolyzed using the general procedure (see above) yielding 3.59 g (81.7% of original wt.) of a clear yellow solution. GLC analysis indicated, in addition to cyclohexanone (65% recovered by preparative GLC after correction for amount which reacted with $\text{Me}_2\text{Si}=\text{CH}_2$), a small amount of I (isolated as an impure mixture and estimated to be less than 5% of original wt.) and one major and at least four minor products.

Resolution of the mixture by preparative GLC gave 0.659 g (33.7%) of the major product identified as 1-(trimethylsiloxy)cyclohexene on the basis of its NMR and IR spectra which were identical to those of this material prepared by independent methods [12,13]. Methylene cyclohexane, collected together with at least two other components, was identified on the basis of the NMR and IR spectra of the mixture. The yield of methylene cyclohexane based on NMR integrations was ca. 6%. Hexamethylcyclotrisiloxane (III), identified only on the basis of its retention time and isolation as a mixture, could not have been formed in greater than 5% yield. Octamethylcyclotetrasiloxane (IV) was not detected by GLC analysis.

In a separate experiment a solution consisting of 1.06 g of 1-(trimethylsiloxy)cyclohexene and 3.05 g of benzene was pyrolyzed at 613° using the general procedure. GLC analysis of the pyrolysate indicated that some decomposition had occurred. Preparative GLC afforded 0.588 g (55.3% recovery) of the starting silyl enol ether.

A solution of 1.06 g of methylene cyclohexane (Aldrich 98% used as received) and 2.72 g of benzene was pyrolyzed at 611° using the standard procedure. GLC analysis of the pyrolysate indicated little, if any, decomposition. Preparative GLC afforded 0.704 g (66.4% recovery) of methylene cyclohexane.

Pyrolysis of 1,1-dimethylsilacyclobutane(I) in the presence of acetophenone

A solution consisting of 1.11 g (11.1 mmol) I and 4.05 g (33.8 mmol) acetophenone (dried over 4A molecular sieves) was pyrolyzed using the general procedure, yielding 4.65 g (90% of original wt.) of a yellow solution. GLC analysis of this solution indicated, in addition to unreacted acetophenone (81% recovered by preparative GLC after correcting for the amount known to react with $\text{Me}_2\text{Si}=\text{CH}_2$), at least five minor and one major peaks of shorter retention time and one major and one minor peaks with longer retention times than the unreacted ketone.

Resolution of the reaction mixture by preparative GLC allowed isolation of 0.82 g of a mixture of α -methylstyrene (the major lower boiling product) and octamethylcyclotetrasiloxane (IV), identified on the basis of its IR and NMR spectra which were identical to those of a mixture of the authentic compounds. Using the NMR integrations it was calculated that the mixture consisted of 0.64 g (49%) of α -methylstyrene and 0.18 g (22%) of IV.

Collection of the major higher boiling product, that which eluted directly after unreacted acetophenone, afforded 0.308 g (14.4%) of α -(trimethylsiloxy)styrene identified on the basis of its spectra. NMR (CCl_4): δ 0.20 (s, 9 H, MeSi), 4.32 (d, J 1.3Hz, 1 H, HC=C), 4.79 (d, J 1.3Hz, 1 H, HC=C), and

7.36 ppm (m, 5 H, Ph). IR (CCl_4): 1615 s (C=C), and 1018 s cm^{-1} (SiO). The spectra of this silyl enol ether were in complete agreement with those previously reported [12,14] for this material prepared by independent routes.

An attempt to collect the first three peaks to be eluted yielded only 0.0776 g (9.5%) of hexamethylcyclotrisiloxane, the NMR and IR spectra of which were identical to those of an authentic sample.

In a separate experiment a solution of 1.67 g of α -(trimethylsiloxy)styrene and 3.64 g of dry benzene was pyrolyzed using the general procedure. GLC analysis indicated that a minor amount of decomposition had occurred. Preparative GLC afforded 1.09 g (65.3% recovery) of the starting silyl enol ether.

Pyrolysis of 1,1-dimethylsilacyclobutane (I) in the presence of m-fluoroacetophenone

A solution consisting of 1.10 g (11.0 mmol) I and 4.01 g (29.0 mmol) *m*-fluoroacetophenone (Pierce Chemical Company, used as obtained) was pyrolyzed using the general procedure yielding 4.67 g (92.5% of original wt.) of a yellow solution. GLC analysis of the pyrolysate indicated, in addition to unreacted ketone (73% recovered by preparative GLC after correction for the amount known to react with $\text{Me}_2\text{Si}=\text{CH}_2$) two major and at least five minor peaks.

Separation of the pyrolysate by preparative GLC allowed isolation of 0.983 g of a mixture of *m*-fluoro- α -methylstyrene and octamethylcyclotetra-siloxane(IV) (the first major peak eluted) which were identified on the basis of their IR and NMR spectra. On the basis of NMR integrations this mixture consisted of 0.79 g (52%) of *m*-fluoro- α -methylstyrene and 0.20 g (24%) of IV.

Collection of the major higher boiling product, that which eluted directly after *m*-fluoroacetophenone, afforded 0.506 g (21.9%) of α -(trimethylsiloxy)-*m*-fluorostyrene (Found: C, 62.60; H, 7.21. $\text{C}_{11}\text{H}_{15}\text{OSiF}$ calcd.: C, 62.81; H, 7.19%). NMR (CCl_4): δ 0.22 (s, 9 H, SiMe), 4.38 (d, *J* 1.8 Hz, 1 H, HC=C), 4.85 (d, *J* 1.8 Hz, 0.9 H, HC=C), and 7.07 ppm (m, 4 H, C_6H_4). Infrared spectrum (CCl_4): 1608 s (C=C) and 1010 s cm^{-1} (SiO). Mass spectrum: *m/e* (rel. int.) 210 (77.3), 209 (67.8), 195 (100), 153 (29), 147 (74), 75 (100), 73 (59.6). Accurate mass measurement carried out on *m/e* 210 peak: (Found 210.0893, $\text{C}_{11}\text{H}_{15}\text{OSiF}$ Calcd.: 210.0876).

Collection of the first minor product to be eluted yielded 0.0113 g (14%) of hexamethylcyclotrisiloxane, the IR spectrum of which was identical to that of the authentic material.

Pyrolysis of 1,1-dimethylsilacyclobutane (I) in the presence of benzophenone

A solution consisting of 1.17 g (11.7 mmol) I, 1.12 g (6.15 mmol) benzophenone (reagent grade, used as received), and 2.00 g of benzene (dried over 3A molecular sieves) was pyrolyzed using the general procedure yielding 5.37 g (90% of original wt.) of a yellow solution. GLC analysis of this solution indicated one major and at least six minor products. Preparative GLC allowed isolation of 0.810 g (72.8%) of the major product, subsequently identified on the basis of its NMR and IR spectra as 1,1-diphenylethylene. The benzene and the first minor peaks were collected together yielding 2.90 g of a mixture,

which (on the basis of NMR integrations using an internal standard) contained 1.35 g (68% of original wt.) of benzene, 0.18 g (21%) of 1,1,3,3-tetramethyl-1,3-silacyclobutane and 0.13 g (28%) of hexamethylcyclotrisiloxane (the two preceding compounds were identified only on the basis of the NMR spectrum and were not isolated). Collection of the following peak afforded 0.0252 g (5.5%) of octamethylcyclotetrasiloxane, the IR of which was identical to that of the authentic material. Except for a low recovery of benzophenone (ca. 2% of the original wt.) only small quantities (< 0.025 g) of the other minor products were collected and these were not identified.

Pyrolysis of 1,1-dimethylsilacyclobutane (I) in the presence of heptanal

A solution consisting of 2.16 g (21.6 mmol) of I and 4.29 g (37.6 mmol) of heptanal (Eastman white label, dried over 3A molecular sieves but not additionally purified) was pyrolyzed using the general procedure yielding 5.08 g (79.0% of original wt.) of a yellow solution. GLC analysis of this solution indicated a complex mixture with at least five low boiling peaks which appeared to be due to decomposition of the heptanal (see below), three major peaks with longer retention times, a large peak due to unreacted heptanal (37.4% recovery after correction for the amount known to react with II), and finally at least six additional peaks. Separation of this solution by preparative GLC yielded ca. 0.21 g (10%) of unreacted I, 0.464 g (19.2%) of 1-octene, 0.174 g (10.8%) of hexamethylcyclotrisiloxane, 0.0363 g (2.3%) of octamethylcyclotetrasiloxane, and 0.220 g (5.5%) of 1-(trimethylsiloxy)-1-heptene which was obtained as a ca. 40/60, *cis/trans* mixture. All of these compounds were completely characterized by comparison of their IR and NMR spectra with those of authentic samples.

In an experiment conducted under the same conditions, pyrolysis of heptanal in a stream of nitrogen and ethylene (20 ml/min N₂ and 20 ml/min ethylene) did not produce quantities of 1-octene or hexamethylcyclotrisiloxane which could be detected by GLC analysis.

Pyrolysis of neat heptanal using these reaction conditions resulted in a 60% wt. loss and yielded a mixture containing three major and at least two minor components in addition to unreacted aldehyde. NMR analysis of a weighed aliquot of this solution containing a known wt. of internal standard (benzene) indicated that only 28% of the original amount of heptanal was present. The NMR spectra did show a vinylic absorption pattern characteristic of a linear terminal olefin which presumably was 1-hexene since GLC analysis indicated the presence of this material and also the complete absence of 1-octene.

In a separate experiment a solution of 1.77 g of 1-(trimethylsiloxy)-1-heptene (a ca. 60/40 *cis/trans* mixture prepared using the procedure of House [10] b.p. 89.5 - 90.5/26 mm [lit. [15] b.p. 87°/28 mm]) and 3.21 g anhydrous benzene was pyrolyzed at 611° using the general procedure. GLC analysis of the bright yellow pyrolysate indicated a complex mixture which did contain a substantial amount of the starting silyl enol ether. Preparative GLC afforded 0.372 g (21%) of 1-(trimethylsiloxy)-1-heptene which contained the same ratio of *cis* to *trans* isomers present in this material prior to pyrolysis.

Pyrolysis of 1,1-dimethylsilacyclobutane (I) in the presence of benzaldehyde

Pyrolysis of a solution consisting of 1.03 g (10.2 mmol) of I and 3.20 g (30.2 mmol) of benzaldehyde (freshly opened analytical reagent grade, used without additional purification) using the general procedure yielded 3.26 g (79.2% of original wt.) of a yellow solution. GLC analysis of this pyrolysate indicated that in addition to unreacted benzaldehyde (28% recovered by preparative GLC after correcting for amount consumed by $\text{Me}_2\text{Si}=\text{CH}_2$, 47% recovered if loss due to decarbonylation is included), two major and three minor peaks with shorter retention times and a single minor peak with a longer retention time than benzaldehyde. Collection of the major peaks by preparative GLC yielded 0.279 g (35%) of benzene and 0.429 g (40.3%) of styrene which were positively identified on the basis of their GLC retention times and NMR spectra. Collection of two of the minor peaks yielded 0.033 g (4.4%) of hexamethylcyclotrisiloxane and 0.240 g (32%) of octamethylcyclotetrasiloxane which were positively identified on the basis of their IR and NMR spectra and GLC retention times.

Pyrolysis of 1,1-diethylsilacyclobutane in the presence of benzophenone

Pyrolysis of a solution consisting of 1.30 g (10.1 mmol) of 1,1-diethylsilacyclobutane, 1.25 g (6.85 mmol) of benzophenone, and 2.02 g of benzene using the standard procedure yielded 3.78 g (76% of original wt.) of a yellow solution. GLC analysis of this solution indicated in addition to solvent (58% recovered by preparative GLC) one major and at least six minor peaks. Preparative GLC yielded 0.598 g (48.5%) of the major product, identified as 1,1-diphenylethylene on the basis of its NMR spectrum and GLC retention time. Collection of the second minor product to be eluted yielded 0.0622 g (6.2% if pure, ca. 4% based on the high field singlet in the NMR spectrum) of a material, tentatively identified as 1,1,3,3-tetraethyl-1,3-disilacyclobutane, based on the NMR spectrum [(CCl_4) : δ -0.15 (s, 2.6 H, SiCH_2Si) and 0.90 ppm (complex multiplet, 20 H, EtSi)], and the IR spectrum, which was very similar to that of authentic 1,1,3,3-tetramethyl-1,3-disilacyclobutane, showing a strong band at 921 cm^{-1} characteristic of the cyclic $\text{Si}-\text{CH}_2\text{Si}$ linkage [16] and bands at 1225 m , 1005 m , and 955 m cm^{-1} characteristic of an ethyl group attached to silicon [17]. The incorrect NMR integrations (EtSi was too large) and a medium IR band at 1078 cm^{-1} may possibly be due to the presence of some hexaethylidisiloxane.

Collection of the minor peak which eluted immediately prior to 1,1-diphenylethylene yielded 0.084 g (8%) of hexaethylcyclotrisiloxane, identified by the NMR spectrum (complex multiplet centered at δ 0.8 ppm characteristic of EtSi) and the IR spectrum which was identical to that of the authentic material [18].

Pyrolysis of 1,1-diphenylsilacyclobutane in the presence of heptanal

Pyrolysis of 1.20 g (5.37 mmol) 1,1-diphenylsilacyclobutane and 1.40 g (12.3 mmol) heptanal was effected using the standard procedure except that the temperature of the pyrolysis tube was 600° . Preparative GLC afforded 0.20 g (33%) of 1-octene identified by its IR and NMR spectra which were identical to those of the authentic material. A small [$\sim 2\text{ mg}$ ($< 0.1\%$)] quantity of a solid,

m.p. 182 - 185° (lit. [19] m.p. 188 - 189°) which precipitated from the reaction solution was tentatively identified as hexaphenylcyclotrisiloxane.

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