PHOTOLYSIS OF ORGANOPOLYSILANES. GENERATION AND REACTIONS OF SILICON-CARBON DOUBLE-BONDED INTERMEDIATES

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Abstract — The photochemical formation of silicon-carbon double-bonded intermediates from phenyl, tolyl, naphthyl, 1-alkenyl and phenylethynyl substituted disilanes and their reactions are described. The silicon-carbon double-bonded intermediates generated from phenyl, tolyl and 2-naphthyldisilanes reacted with many organic substances to give 1:1 adducts; the mode of their addition reaction is very different from that of a hitherto reported dimethylsilaethene type of silicon-carbon double-bonded intermediates. Photolysis of 1-naphthyldisilane derivatives in the presence or absence of trapping agents led only to an isomer, 1-hydro-silyl-2-silylnaphthalene. The chemical nature of intermediates from vinyl- and α-styryldisilanes was rather similar to that of the thermally generated dimethylsilaethene-type intermediates. Photolysis of (penta-methyldisilanyl)phenylacetylene gave 1-silacyclopropene and 1-sila-1,2-propadiene which could be trapped by acetone or an alcohol.

INTRODUCTION

One of the fascinating areas of organosilicon chemistry in the last several years is the formation and reactions of silicon-carbon double-bonded intermediates.
In 1967 Russian chemists reported that gas-phase pyrolysis of 1,1-dimethylsilacyclobutane produces a reactive silicon-carbon double-bonded intermediate, dimethylsilaethene $Me_2Si=CH_2$, which, in the absence of suitable substrates, dimerizes yielding 1,1,3,3-tetramethyl-1,3-disilacyclobutane (1). Evidence for the transient existence of this unsaturated silicon compound has been shown by kinetic studies and also by trapping reactions (2). Since that time many papers concerning the formation and reactions of the thermally generated silicon-carbon double-bonded intermediates of the silaethene type have been published (3). Photochemical generation of reactive intermediates of such a type has also been shown (4-9). However, very little systematic investigation along these lines has been done until recently. It is my purpose to review our recent efforts in the area of photochemistry of aryl, 1-alkenyl and alkynyl derivatives of disilane, which has proved to offer a very convenient approach to the generation of a variety of silicon-carbon double-bonded species.

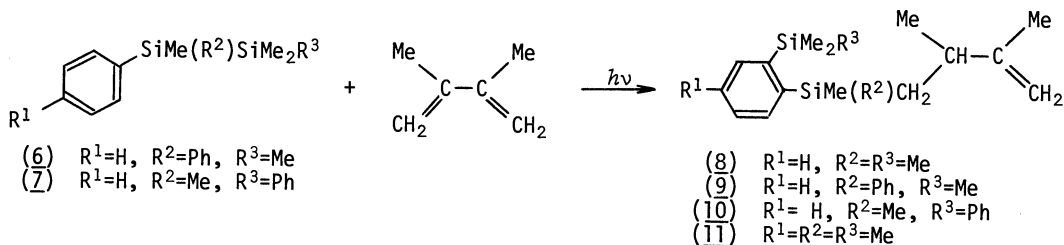PHOTOLYSIS OF BENZENOID AROMATIC DERIVATIVES OF DISILANE

In 1975, during the course of studies on the photolytic generation of phenylmethylsilylene from phenyl substituted polysilanes (10), we found that when a benzene solution of phenyl-pentamethyldisilane (1) containing an olefin such as isobutylene or trimethylvinylsilane was irradiated with a low-pressure mercury lamp at room temperature, 1:1 addition products of a novel type, 1,2-disilyl substituted benzenes (3), were produced (11). Also, irradiation of p-tolylpentamethyldisilane (2) with isobutylene under the same conditions produced a similar adduct (4) in high yield. We postulated a mechanism for their production involving

(1) R¹=H
(2) R¹=Me

(3a) R¹=H, R²=R³=Me (59%)
(3b) R¹=R²=H, R³=Me₃Si (49%)
(4) R¹=R²=R³=Me (58%)
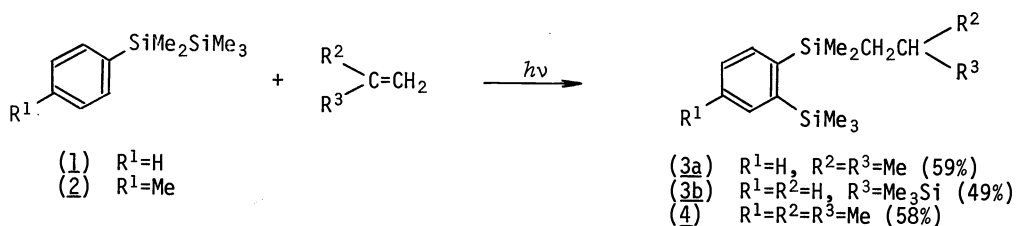
photoisomerization of the disilane to a silicon-carbon double-bonded intermediate such as A, followed by addition to an olefin. A transient formation of the reactive intermediate could be confirmed by trapping experiments (12). Thus, the photolysis of $\underline{2}$ in the presence of methanol-d_1 afforded 1,4- and 1,6-adducts, 1-methoxydimethylsilyl-4-methyl-5-deuterio-6-trimethylsilyl-1,3-cyclohexadiene ($\underline{5a}$) and 1-methoxydimethylsilyl-3-deuterio-4-methyl-6-trimethylsilyl-1,4-cyclohexadiene ($\underline{5b}$), in 27 and 28% yield, in addition to small amounts of deuterio and non-deuterio methoxydimethylsilyltoluene and trimethylsilyltoluene. The production of monodeuterio methoxydimethylsilyltoluene is thought to involve another type of silicon-carbon double-bonded intermediate, p-$CH_3C_6H_4Si(Me)=CH_2$. An intermediate of this type, diphenylsilaethene, has been reported by Sommer et al. who observed it in the photolysis of pentaphenylmethyldisilane (4).
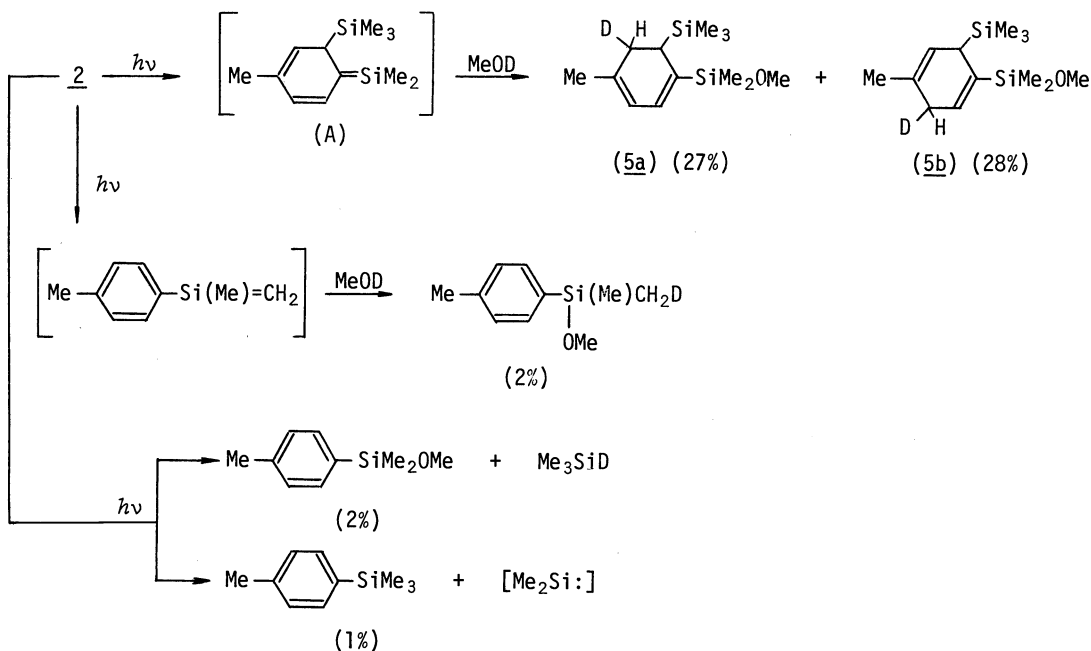

In contrast to the thermally generated silicon-carbon double-bonded intermediates of the silaethene type hitherto studied widely, the intermediates of type A are thought to polymerize in the absence of a trapping agent. No products that might be expected from dimerization of the intermediates have been observed. The photochemical formation of the silicon-carbon double-bonded intermediates from the benzenoid aromatic derivatives of disilane is quite a general reaction. All of such aryldisilanes bearing a hydrogen atom on the ortho carbon in the benzene ring, for instance, 1,1- and 1,2-diphenyltetramethyldisilane ($\underline{6}$ and $\underline{7}$), 1,1,1-triphenyltrimethyldisilane, 1,1,2,2-tetraphenyldimethyldisilane, and o-tolyl and o-anisylpentamethyldisilane, were also readily photolyzed upon irradiation with a low-pressure mercury lamp in n-hexane or in benzene to give the respective silicon-carbon double-bonded intermediates analogous to A, which could be trapped similarly (13,14).
Irradiation of the aryldisilanes ($\underline{1,2,6}$, and $\underline{7}$) with 2,3-dimethylbutadiene in benzene (13) afforded adducts ($\underline{8-11}$) whose structures are similar to those of compounds $\underline{3}$ and $\underline{4}$. In no case, [2+4] cycloaddition products were observed, whereas such cycloaddition occurs when thermally generated silaethenes are allowed to react with the conjugated diene (3).


($\underline{6}$) R^1=H, R^2=Ph, R^3=Me
($\underline{7}$) R^1=H, R^2=Me, R^3=Ph

($\underline{8}$) R^1=H, R^2=R^3=Me
($\underline{9}$) R^1=H, R^2=Ph, R^3=Me
($\underline{10}$) R^1= H, R^2=Me, R^3=Ph
($\underline{11}$) R^1=R^2=R^3=Me

Interestingly, the photolysis of phenyl- and tolyl-substituted disilanes bearing a silicon-hydrogen bond, $H(Ph_2)SiSiMe_3$, $H(Me)(p\text{-}MeC_6H_4)SiSiMe_3$ and $(p\text{-}MeC_6H_4)SiSiMe_2H$, in the presence

of 2,3-dimethylbutadiene under similar conditions gave analogous results to those of the above-mentioned system. No hydrodisilanylation products which might be derived from the reaction of the starting hydrodisilanes with the diene were observed. The reaction of 1-(p-tolyl)-1,1,2,2-tetramethyldisilane (12) with 2,3-dimethylbutadiene is exemplified in the following Scheme.
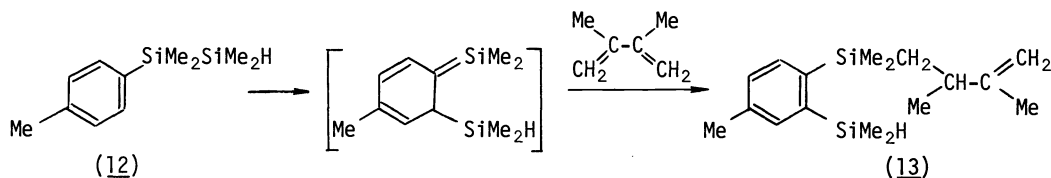
Butadiene and isoprene also reacted with the reactive intermediates to give the expected adducts. With isoprene, two possible isomers, 14 and 15, were obtained in the ratio of 2.3/1. The abundant isomer in this reaction was 14 resulting from addition of the reactive
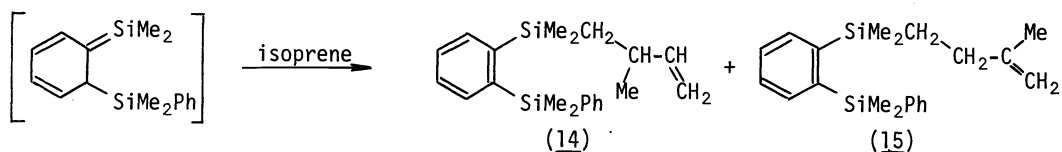
intermediate across the double bond bearing the methyl group. An analogous trend was observed when olefins were used as trapping agents (15). Both isobutylene and 1,1-bis(tri-methylsilyl)ethylene reacted more easily with the intermediates than ethylene or propylene did. These results suggest that the addition of the reactive intermediates to olefins or dienes may proceed by a pathway of radical nature.
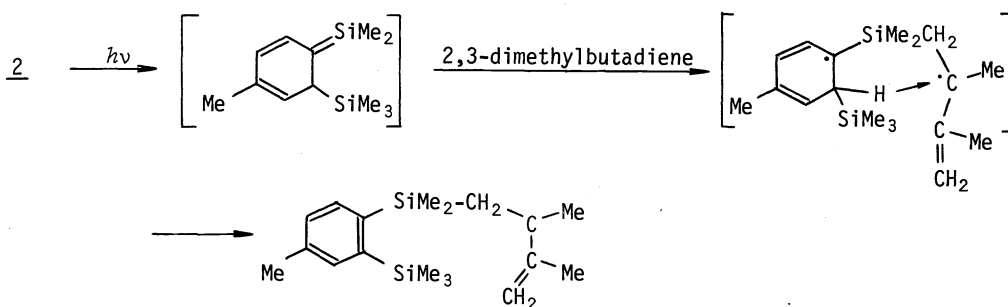
Similar irradiation of 1 and 2 with 1-hexyne or trimethylsilylacetylene in benzene led to the formation of (E)-olefins (16-18) in moderate yields, as the normal adducts. In no case (Z)-isomers were detected. However, the quenching ability of the acetylenic compounds seems

(16) R^1=H, R^2=n-Bu (21%)
(17) R^1=H, R^2=Me$_3$Si (15%)
(18) R^1=Me, R^2=n-Bu (23%)
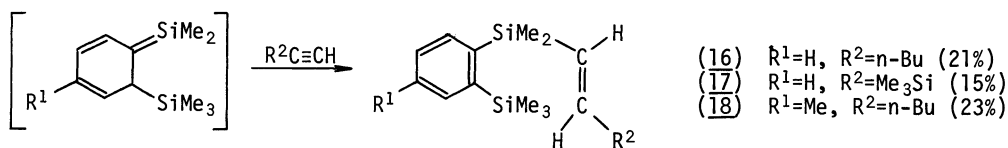
lower than that of olefins or dienes which gave the adducts in higher yields. In all cases, non-volatile products arising from polymerization of intermediate A were observed to form. When phenylacetylene or bis(trimethylsilyl)acetylene was used as a substrate in the photoly-sis of 1, both (E)- and (Z)-olefins (19 and 20) were formed. Control experiments showed that both (E)- and (Z)-isomers are produced as initial products of the photolysis (16). When vinylsilanes such as dimethylvinyl-, trimethylvinyl- and ethyldimethylvinylsilane were used as trapping agents in the photolysis of compounds 1 and 2, silepin derivatives (21-24) were always formed in 5-9% yield, in addition to the normal adducts (17). Likewise, the photochemical reaction of the aryldisilanes 1 and 2 with 1-hexyne gave silepins in 9-12% yields. The production of the silepins in these reactions can be best explained in terms of initial formation of 7-silabicyclo[4.1.0]heptadiene intermediate (B), which then undergoes

(19) R^1=R^2=SiMe$_3$
(20) R^1=H, R^2=Ph
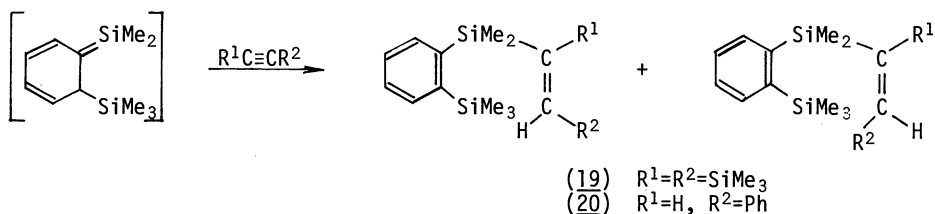
the Walk rearrangement to the sterically favored isomer (C), followed by ring expansion to the silepin (17).

(21) R^1=H, R^2=Me (7%)
(22) R^1=Me, R^2=H (9%)
(23) R^1=R^2=Me (7%)
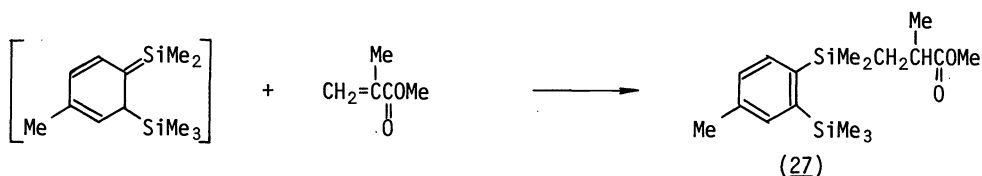(24) R^1=H, R^2=Et (5%)
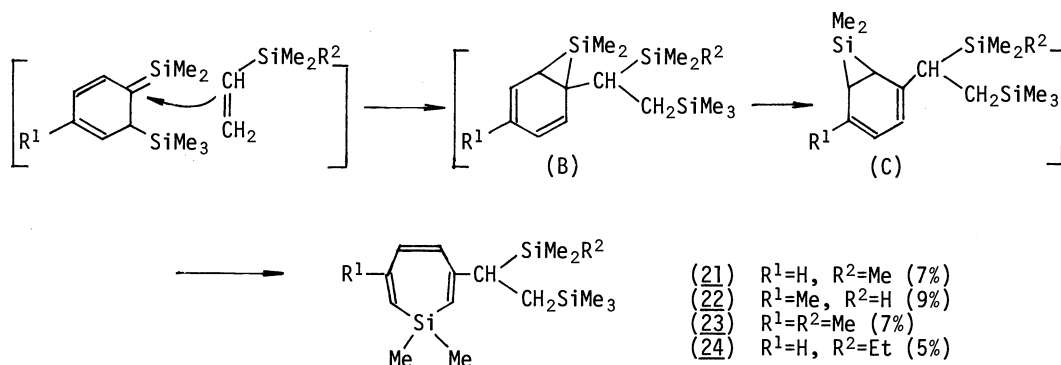
In marked contrast to copyrolysis of the silacyclobutanes (18) or silylphenyldiazomethanes (19) with ketones at high temperature, the reaction of all the silicon-carbon double-bonded intermediates generated from the arylpentamethyldisilanes with either enolizable or non-enolizable ketones yielded 2-trimethylsilyl(alkoxydimethylsilyl)benzene derivatives (20). No silyl enol ethers which can be expected to form O-H addition of enol form of enolizable ketones to the silicon-carbon double bond, as observed by Sommer and his co-workers (18), were produced. Likewise, the mode of the reaction of intermediate A with non-enolizable
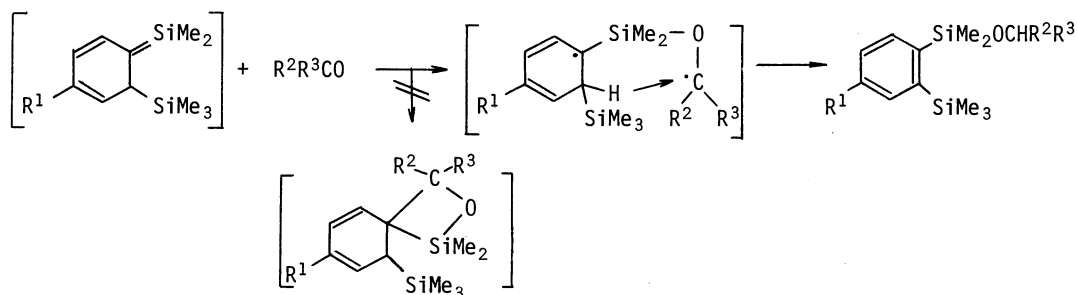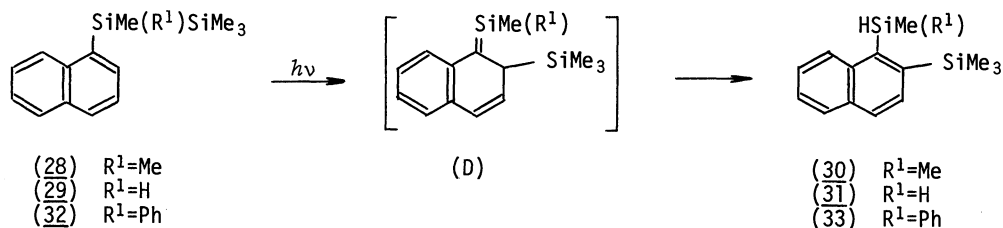

ketones is different from that observed in the copyrolysis of silacyclobutanes with such ketones, where [2+2] cycloaddition took place to give unstable silaoxetane derivatives (18), followed by decomposition to afford the corresponding olefins and cyclic siloxanes (20). The absence of silaoxetane derivatives in our system is consistent with the fact that the reaction of intermediate A with methyl alcohol afforded no 1,2-adduct.
We next examined the reaction of our silicon-carbon double-bonded intermediates with conjugated carbonyl compounds (20). Irradiation of p-tolylpentamethyldisilane with methyl vinyl ketone under similar conditions produced 2-trimethylsilyl-4-methyl-(methylallyloxydimethylsilyl)benzene (25) in 51% yield as a single volatile product. No product that might be expected from [2+2] cycloaddition could be observed. Acrolein also reacted with phenylpentamethyldisilane to afford 2-trimethylsilyl(allyloxydimethylsilyl)benzene (26) in 40% yield.
Recently, Valkovich and Weber (21) have reported that copyrolysis of silacyclobutane with acrolein affords products which can be accounted for in terms of initial competing [2+2] and [2+4] cycloaddition reaction between the Si=C intermediate and acrolein. In our case, however, no [2+2] nor [2+4] cycloaddition product was found by spectroscopic analyses. The photolysis of 2 in the presence of methyl methacrylate proceeded by a different manner to give a product (27) that resulted from addition of the intermediate to the carbon-carbon bouble bond, but not to the carbon-oxygen double bond.
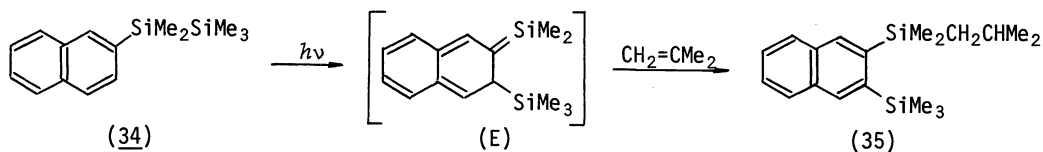
$$\left[\begin{array}{c} \text{SiMe}_2 \\ \text{Me} \quad \text{SiMe}_3 \end{array} \right] \; + \; \underset{\underset{\text{O}}{\overset{\|}{}}}{\overset{\text{Me}}{\underset{|}{\text{CH}_2=\text{CCOMe}}}} \quad \longrightarrow \quad \underset{\text{Me} \quad \text{SiMe}_3}{\text{SiMe}_2\text{CH}_2\overset{\text{Me}}{\underset{|}{\text{CHCOMe}}}} \underset{\overset{\|}{\text{O}}}{}$$

(27)

PHOTOLYSIS OF NAPHTHYLDISILANES

As an extention of the photochemical formation of the silicon-carbon double-bonded inter-
mediates to a naphthalene system, we have examined the photochemical behavior of 1- and 2-
disilanylnaphthalenes (22). UV-irradiation of 1-disilanyl substituted naphthalenes resulted
in formation of silicon-carbon double-bonded intermediates of type D. However, their
chemical behavior is quite different from that of intermediate A. Thus, photolysis of 1-
(pentamethyldisilanyl)naphthalene (28) and 1-(1'-hydrotetramethyldisilanyl)naphthalene (29)
in the presence or absence of a quencher afforded an isomer, 1-dimethylsilyl-2-trimethyl-
silylnaphthalene (30) and 1-methylsilyl-2-trimethylsilylnaphthalene (31), respectively, as
the sole volatile product. All of the 1-disilanyl-substituted naphthalenes so far investi-
gated afforded the photoisomerization products, but not adducts arising from the reaction
with trapping agents. These results are of considerable interest, because photochemically
generated silicon-carbon double-bonded intermediates from other aryldisilanes do not afford
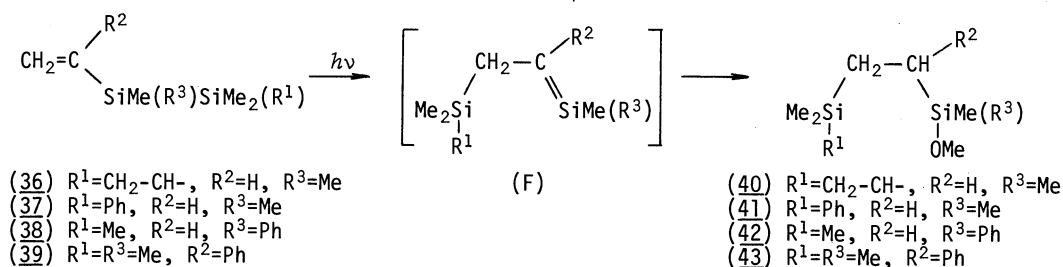any volatile products in the absence of quenchers.

$$\underset{\text{SiMe}(\text{R}^1)\text{SiMe}_3}{\text{[naphthyl]}} \xrightarrow{h\nu} \left[\underset{\text{SiMe}_3}{\overset{\text{SiMe}(\text{R}^1)}{\text{[naphthyl]}}} \right] \longrightarrow \underset{\text{SiMe}_3}{\overset{\text{HSiMe}(\text{R}^1)}{\text{[naphthyl]}}}$$

(28) $\text{R}^1=\text{Me}$	(D)	(30) $\text{R}^1=\text{Me}$
(29) $\text{R}^1=\text{H}$		(31) $\text{R}^1=\text{H}$
(32) $\text{R}^1=\text{Ph}$		(33) $\text{R}^1=\text{Ph}$

Next we turned our attention to investigation into the photolysis of 1-(1'-phenyltetramethyl-
disilanyl)naphthalene (32), because, in this system, there are two possible routes to the
photochemical formation of the silicon-carbon double-bonded intermediates. One involves
photorearrangement of a silyl group to the phenyl ring to give an intermediate of type A and
the other to the naphthyl ring to give intermediate D. Irradiation of 32 in benzene afforded
compound 33 as the sole product. On the other hand, photolysis of 2-(pentamethyldisilanyl)-
naphthalene (34) in the absence of quenchers did not produce any volatile products such as
2-(dimethylsilyl)-3-trimethylsilylnaphthalene. In the presence of isobutylene as a quencher,
however, 34 gave a 1:1 adduct, 2-(isobutyldimethylsilyl)-3-trimethylsilylnaphthalene (35) in
37% yield, as the sole volatile product, in addition to 13% of unchanged 34.

$$\underset{(34)}{\overset{\text{SiMe}_2\text{SiMe}_3}{\text{[naphthyl]}}} \xrightarrow{h\nu} \left[\underset{\text{SiMe}_3}{\overset{\text{SiMe}_2}{\text{[naphthyl]}}} \right] \xrightarrow{\text{CH}_2=\text{CMe}_2} \underset{(35)}{\overset{\text{SiMe}_2\text{CH}_2\text{CHMe}_2}{\underset{\text{SiMe}_3}{\text{[naphthyl]}}}}$$

(34)   (E)   (35)

PHOTOLYSIS OF ALKENYLDISILANES

We have shown that the photochemically generated silicon-carbon double-bonded intermediates
(A) from aryldisilanes react with many of substrates in a different fashion from the ther-
mally generated ones of silaethene type. We feel that such differences can be attributed
largely to a great tendency of intermediates of type A to stabilize themselves by restoring
the aromatic sextet and to the presence of a bulky substituent, such as Me$_3$Si group, adjacent
to the silicon-carbon double bond. Indeed, chemical behavior of intermediates of type F
generated by photolysis of 1-alkenyldisilanes is similar to that of silaethenes produced by
the thermal method. Thus, photolysis of 1,2-divinyl-, 1-phenyl-2-vinyl- and 1-phenyl-1-
vinyldisilane (36,37 and 38), and α-styrylpentamethyldisilane (39) led to intermediates F by
photorearrangement of a triorganosilyl group to the terminal carbon of a vinyl group, which
could be trapped by methanol in high yield (23). In the photolysis of 37 which contains

both phenyl-silicon and vinyl-silicon groupings in the molecule, we find that it is exclusively to the vinylic carbon atom (but not to the phenyl ring) that the migration of a silyl group occurs.

$$CH_2=C\begin{smallmatrix}R^2\\ \\SiMe(R^3)SiMe_2(R^1)\end{smallmatrix} \xrightarrow{h\nu} \left[\begin{smallmatrix}CH_2-C\diagdown R^2\\ \diagup \qquad \parallel\\ Me_2Si \qquad SiMe(R^3)\\ |\\ R^1\end{smallmatrix}\right] \longrightarrow \begin{smallmatrix}CH_2-CH\diagdown R^2\\ \diagup \qquad \diagdown\\ Me_2Si \qquad SiMe(R^3)\\ | \qquad\qquad |\\ R^1 \qquad\qquad OMe\end{smallmatrix}$$

(36) R^1=CH_2-CH-, R^2=H, R^3=Me
(37) R^1=Ph, R^2=H, R^3=Me
(38) R^1=Me, R^2=H, R^3=Ph
(39) R^1=R^3=Me, R^2=Ph

(F)

(40) R^1=CH_2-CH-, R^2=H, R^3=Me
(41) R^1=Ph, R^2=H, R^3=Me
(42) R^1=Me, R^2=H, R^3=Ph
(43) R^1=R^3=Me, R^2=Ph

The intermediates F reacted with both enolizable and non-enolizable ketones to give olefins. For instance, the photolysis of α-styrylpentamethyldisilane (39) in the presence of 1 mole equivalent of acetone afforded 1-trimethylsilyl-2-phenyl-3-methyl-2-butene (44) in 18% yield as a single product. No silyl enol ether which can be expected to form from the reaction of the intermediate with enol form of acetone was observed by GLC analysis. Similar irradiation of 39 with acetophenone gave (E)- and (Z)-1-trimethylsilyl-2,3-diphenyl-2-butene (45) in 10 and 13% yield, respectively. However, with benzophenone, unexpected adducts, (E)- and (Z)-1-benzhydroxydimethylsilyl-1-phenyl-2-trimethylsilylethene (47) (22% yield) in a ratio of 4/1 were obtained, together with 22% yield of an expected olefin (46). With vinyl ketone, 39 produced two types of products, (E)- and (Z)-3-methyl-4-phenyl-5-trimethylsilyl-1,3-pentadiene (48a and b) and 2,6,6-trimethyl-5-trimethylsilylmethyl-5-phenyl-1-oxa-6-sila-cyclohexene-2 (49) in 8 and 18% yield, respectively (24). The compounds, 48a and 48b, may
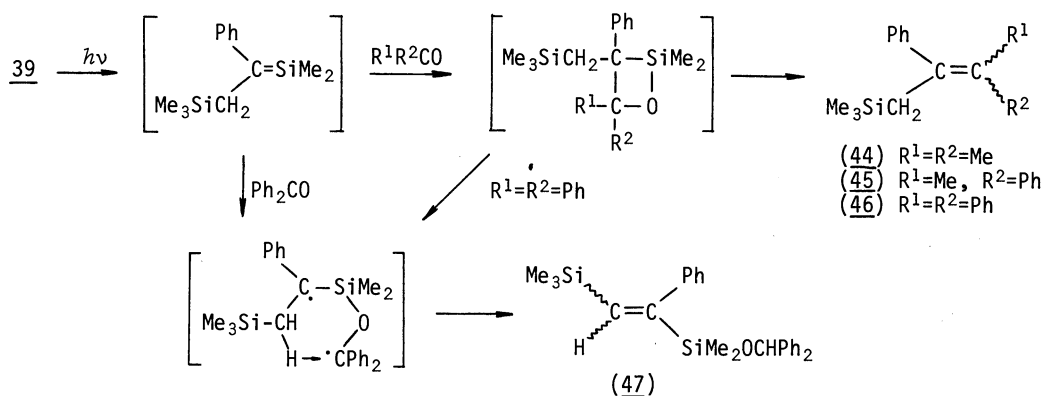
be formed by an initial [2+2] cycloaddition reaction, while the formation of 49 can be explained by a direct [2+4] cycloaddition reaction.
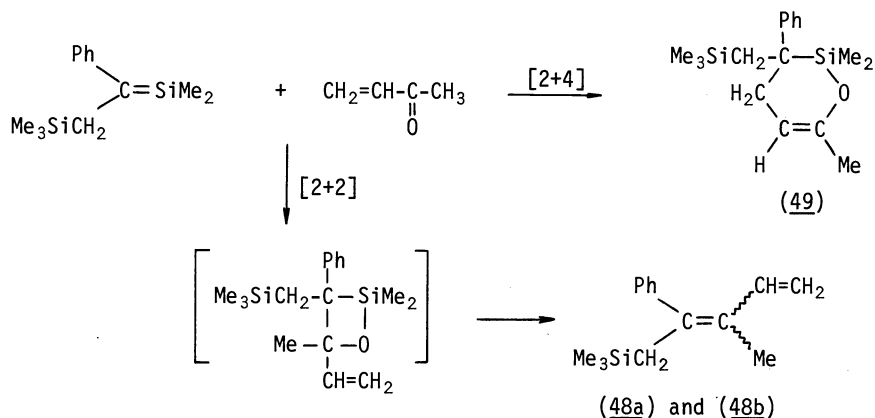
Photochemical behavior of β-styrylpentamethyldisilane (50a) is different from that of the above-mentioned α-isomer (25,26). Irradiation of 50a with methanol in benzene afforded an equilibrium mixture of cis and trans isomers in a ratio of 1/1. However, prolonged irradiation of this solution produced 1-methoxydimethylsilyl-1-trimethylsilyl-2-phenylethane (51) and 1,1-dimethyl-2,3-benzo-5-trimethylsilyl-1-silacyclopentene (52), in addition ot cis- and trans-β-styrylpentamethyldisilane.
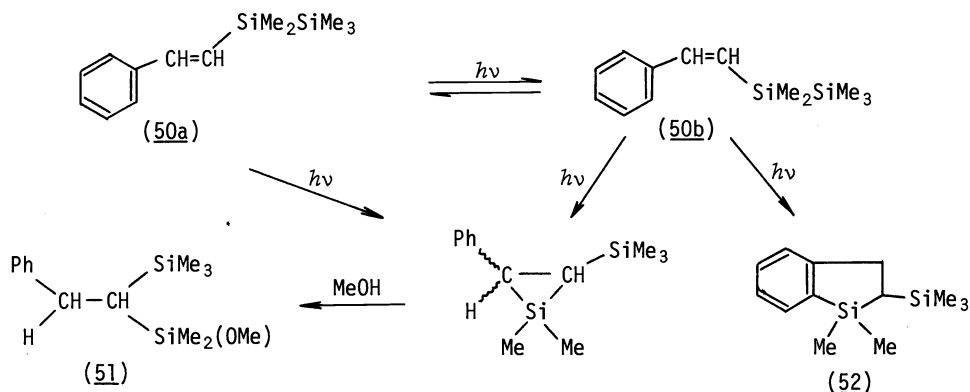
PHOTOLYSIS OF (PENTAMETHYLDISILANYL)PHENYLACETYLENE

In marked contrast to vinyldisilanes, the photolysis of (pentamethyldisilanyl)phenylacetylene (53) has been found to proceed simultaneously by two different routes, one of which, a main route, involves the production of 1-silacyclopropene (54), and the other, a minor one, comprises the transient formation of a new type of silicon-carbon double-bonded intermediate (G). Irradiation of 53 with acetone in dry benzene under a purified nitrogen atmosphere, four products, 2,2,5,5-tetramethyl-3-trimethylsilyl-4-phenyl-1-oxa-2-silacyclo-3-pentene (55), 2,2,5,5-tetramethyl-3-phenyl-4-trimethylsilyl-1-oxa-2-silacyclo-3-pentene (56), phenyl-trimethylsilylacetylene (57), and 1-phenyl-1-trimethylsilyl-3-methyl-1,2-butadiene (58) were obtained in 51, 2, 10 and 5% yield, respectively, with 81% conversion of the starting disilane. The formation of 55 and 56 can be explained by insertion of acetone into sila-cyclopropene 54. Liberation of dimethylsilylene species from either direct photolysis of 53 or decomposition of 54 results in the formation of 57. Compound (58) can be rationalized in terms of cycloaddition of acetone to intermediate G to afford silaoxetane, followed by loss of the Me$_2$SiO moiety. Intermediate G can also be trapped by methanol as (Z)- and (E)-1-phenyl-1-trimethylsilyl-2-methoxydimethylsilylethylene (27).
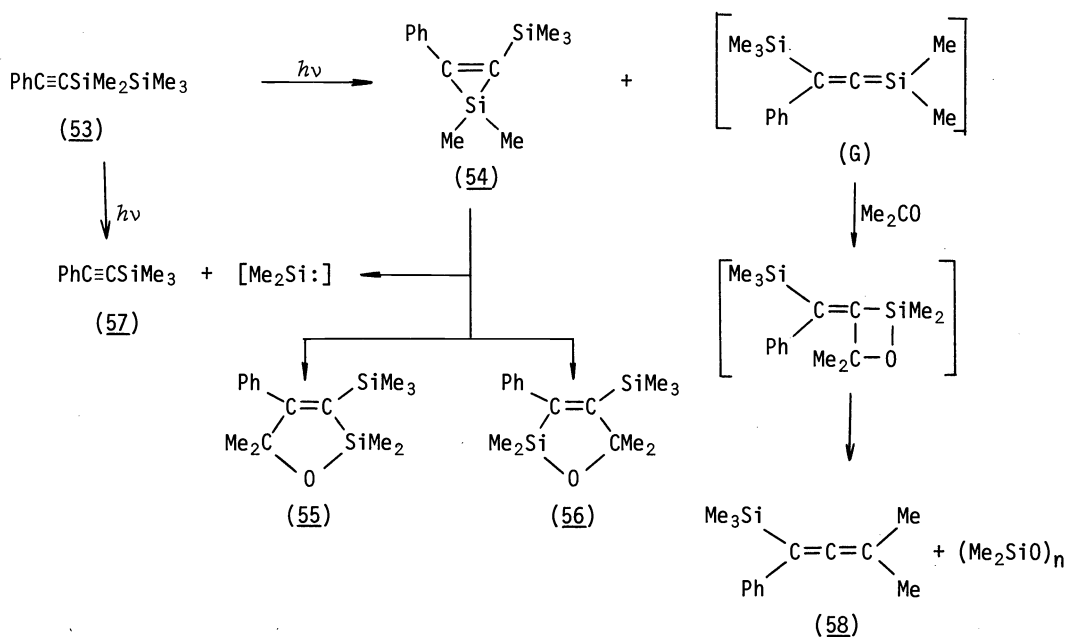
Irradiation of <u>53</u> in the absence of acetone produced a highly air-sensitive silacyclopropene which could be isolated by either ,distillation or GLC technique, in addition to a small amount of <u>57</u>.

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