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PHOTOLYSIS OF ORGANOPOLYSILANES. THE REACTION OF PHOTOCHEMICALLY GENERATED METHYLPHENYLSILYLENE WITH OLEFINS

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Summary

The photolysis of 2-phenylheptamethyltrisilane (I) in the presence of trapping agents such as terminal, internal, and cyclic olefins has been investigated using both a high-pressure mercury lamp with a quartz filter and a low-pressure mercury lamp with a Vycor filter. Irradiation of I with a high-pressure mercury lamp in the presence of 1-butene, *cis*-2-butene, isobutene, tetramethylethylene, 1-octene, cyclohexene, cyclooctene, allyltrimethylsilane or isopropenyltrimethylsilane afforded the respective methylphenylsilyl-substituted alkene as the main product. Irradiation of I with a low-pressure mercury lamp in the presence of 1-butene, *cis*-2-butene, 1-octene, cyclohexene or cyclooctene, followed by treating the products with methanol, gave mostly a methoxysilane arising from the methanolysis of the corresponding silacyclopropane and a small amount of the silylalkene product. However, irradiation of I with either isobutene or tetramethylethylene using a low-pressure mercury lamp under similar conditions gave a silylalkene as the main product. A rearranged addition product was produced when I was irradiated with trimethylvinylsilane using the low-pressure and the high-pressure lamp systems.

Introduction

Inorganic silylenes [1] have been known for many years, with difluorosilylene [2] in particular having been studied quite extensively. However, little interest had been shown in the chemistry of silylenes bearing organic substituents until 1966 when Atwell and Weyenberg [3] reported a convenient synthetic route to organic silylene species by the thermolysis of alkoxydisilanes. Since that time, considerable attention has been devoted to investigations of the chemistry of these interesting intermediates and many papers that deal with the insertion of thermally generated organic silylenes into single bonds and with their addition to multiple bonds have been reported [4—6].

In 1970 we found that dodecamethylcyclohexasilane undergoes ring contraction upon photolysis with UV light, producing permethylated cyclic tetra- and penta-silanes with the concurrent generation of dimethylsilylene [7,8]. Subsequently, we demonstrated that the photolytic generation of organic silylenes from cyclic and acyclic polysilanes is a quite general reaction which offers a novel and convenient route to divalent silicon intermediates [9,10].

Recently, we have shown that the irradiation of 2-phenylheptamethyltrisilane (I) in the presence of a large excess of cyclohexene with a high-pressure mercury lamp bearing a quartz filter gives 3-methylphenylsilylcyclohexene, while analogous irradiation of the system with a low-pressure mercury lamp having a Vycor filter affords 7-methyl-7-phenyl-7-silabicyclo[4.1.0]heptane [11—13]. The latter compound readily undergoes photoisomerization to the 3-silylcyclohexene upon irradiation with a high-pressure mercury lamp. Since our initial findings, we have learned much more about the scope and nature of the reaction of I with olefins and these results are reported in detail in the present paper.

Results and discussion

Photolysis of 2-phenylheptamethyltrisilane (I) in the presence of diethylmethylsilane

The photolysis of I was carried out in the presence of a large excess of diethylmethylsilane to determine how much methylphenylsilylene could be obtained in the reaction. When a high-pressure mercury lamp with a quartz filter was used in this photolysis, 1,1-diethyl-1,2-dimethyl-2-phenyldisilane (II) was produced in 35% yield. When a low-pressure mercury lamp with a Vycor filter was used, 47% yield of II was obtained as the sole insertion product.

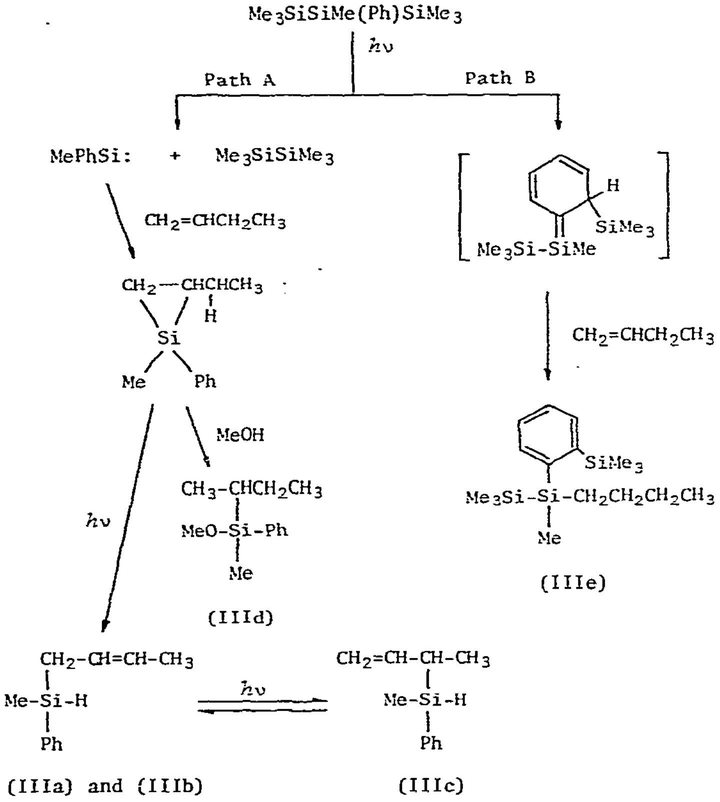
$$\underset{\text{(I)}}{\mathrm{Me_3SiSiMe(Ph)SiMe_3}} \xrightarrow{h\nu} \mathrm{MePhSi\colon} \xrightarrow{\mathrm{Et_2MeSiH}} \underset{\text{(II)}}{\mathrm{Et_2MeSiSiMe(Ph)H}}$$

The absence of homo-coupling products such as 1,2-dimethyl-1,2-diphenyldisilane, expected if the silylene abstracted hydrogen and underwent radical coupling, suggests that the methylphenylsilylene is present in a singlet state electronic configuration [14,15].

Photolysis of I in the presence of olefins with a high-pressure mercury lamp

Photochemically generated methylphenylsilylene adds readily to the carbon—carbon double bonds of many types of olefin. For example, the photolysis of a hexane solution of I in the presence of 1-butene for 2.1 h produced, after subsequent treatment of the reaction products with 2 ml of dry methanol, *trans*- and *cis*-1-methylphenylsilyl-2-butene (IIIa and IIIb) and 3-methylphenylsilyl-1-butene (IIIc) in 17, 6 and 4% yields, respectively. Other materials obtained were 4% yield of 2-(methylphenylmethoxysilyl)butane (IIId) and 4% of unreacted I. The *trans* configuration assigned to IIIa is based on the 15 Hz *J*(HC=CH) coupling constant observed for its proton-decoupled NMR spectrum. The corresponding 11 Hz coupling constant observed for IIIb is consistent with a *cis* configuration. As will be discussed below, the formation of both IIIa and IIIb can be accounted for by the photorearrangement of a 1-silacyclopropane intermediate involving a 1,3-hydrogen shift from carbon to the ring silicon atom. Methanolysis of the silacyclopropane accounts for compound IIId [16]. The reactions are summarized in path A of Scheme 1.

SCHEME 1



Careful product analysis in the early stages of the reaction indicated that compound IIIc is not an initial product, but is produced in the photoisomerization of IIIa and IIIb as shown in Fig. 1. This was confirmed by the observation that the photolysis of pure IIIa in hexane for 1 h gives an equilibrium mixture consisting of IIIa, IIIb and IIIc in the ratio of 3/1/5.

The formation of IIIc is of considerable interest because it involves a photochemically induced 1,3-shift of a silyl group. Recently it has been found that the photolysis of vinyl-substituted disilanes proceeds with a 1,3-shift, from silicon to carbon, of the silyl group that is not bonded directly to the vinyl system, forming silicon—carbon double-bonded intermediates [17]. However, the present reaction is to our knowledge the first example of a photochemically induced 1,3-shift of the silyl group from one carbon atom to the other in a silyl-substituted allylic system *.

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* Thermally induced 1,3-shift of the silyl group in allylsilane has been reported previously [22].

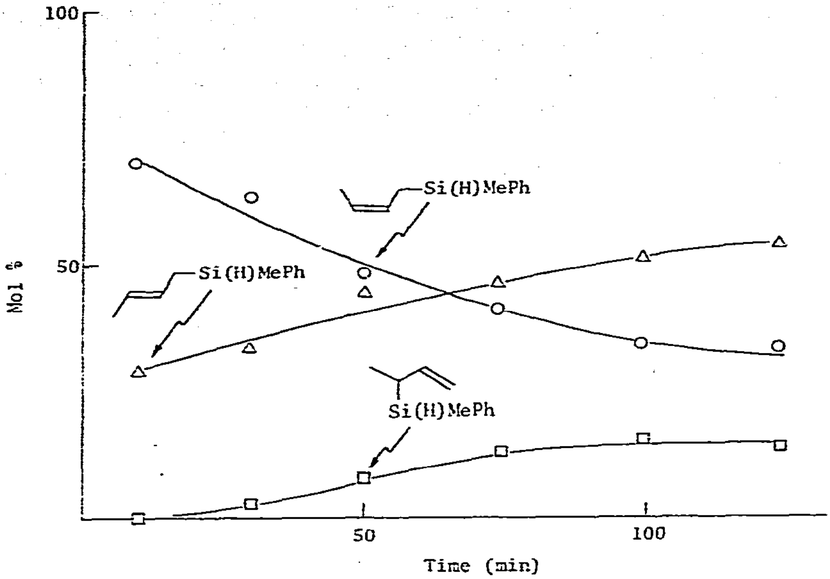
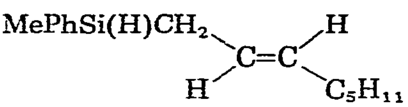
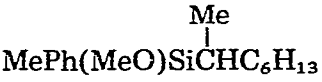


Fig. 1. Photoisomerization of *trans*- and *cis*-1-methylphenyl-2-butene.

Irradiation of I in the presence of 1-octene, followed by the addition of methanol to the resulting mixture, afforded *trans*-methylphenylsilyl-2-octene (IVa) and 2-(methylphenylmethoxysilyl)octane (IVb) in 20 and 14% yields, respectively. The 15 Hz coupling constant observed for olefinic protons of IVa clearly indicates that the structure is of *trans* configuration. No *cis* isomer was detected at any point in the reaction, either by GLC analysis of the reaction mixture in the early stages of the photolysis, or ^{1}H NMR spectroscopic analysis of the product. On the other hand, irradiation of I with isobutene under the same conditions afforded 2-methyl-3-methylphenylsilyl-1-propene (Va) in 39% yield. The fact that methoxysilane Vb was not formed on treating the products of this reaction with methanol indicated that if a silacyclopropane derivative were present, it would be photochemically unstable.



(IVa)



$$\mathrm{MePh(MeO)Si\overset{\displaystyle Me}{\overset{|}{C}}HC_6H_{13}}$$

(IVb)

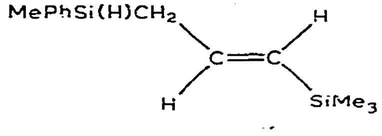
$\mathrm{MePhSi(H)CH_2C(Me)=CH_2}$

(Va)

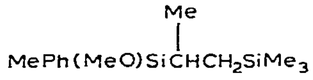
$\mathrm{MePh(MeO)SiCMe_3}$

(Vb)

Photochemically generated methylphenylsilylene also reacts with silyl-substituted olefins. Thus, the photolysis of I in the presence of a 30-fold excess of allyltrimethylsilane in hexane for 2 h, followed by methanolysis, produced *trans*-1-trimethylsilyl-3-methylphenylsilyl-1-propene (*J* 19 Hz) (VIa) in 20% yield and 1-trimethylsilyl-2-(methylphenylmethoxysilyl)propane (VIb) in 5% yield. Irradiation of I with isopropenyltrimethylsilane under similar conditions afforded 23% yield of 2-trimethylsilyl-3-methylphenylsilyl-1-propene (VII) as the sole product derived from the silylene species *.

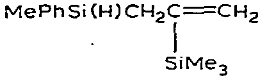


(VIa)



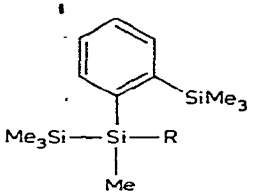
$$MePh(MeO)Si\overset{Me}{C}HCH_2SiMe_3$$

(VIb)



$$MePhSi(H)CH_2\underset{SiMe_3}{C}{=}CH_2$$

(VII)



(IVd) R = C_8H_{17}

(Vc) R = CH_2CHMe_2

(VId) R = $CH_2CH_2CH_2SiMe_3$

In all of the reactions that used terminal olefins as substrates, rearranged addition products (such as IVd, Vc and VId) of I and olefin were always produced in 6—11% yields. The formation of the addition product can best be understood in terms of the formation of a silicon—carbon double-bonded intermediate, followed by its addition to the substrate present (path B, Scheme 1). The generation of such reactive silicon—carbon double-bonded intermediates recently has been found in the photolysis of various aryldisilanes [18].

The location of the silyl group on the allylic carbon for compounds, IIIa, IIIb, IVa, Va, VIa and VII, was confirmed by the following general reaction. Protodesilylation of IVa with trifluoroacetic acid [19,20] in chloroform at 55°C for 3 h gave 1-octene in essentially quantitative yield. The fact that the silyl group can be cleaved from the allylic position under these conditions, but not from the vinylic position, was confirmed by the reaction of VII with trifluoroacetic acid. In this case, isopropenyltrimethylsilane was obtained as the sole product in 92% yield.

$$IVa + CF_3COOH \rightarrow CH_2{=}CHCH_2C_5H_{11} + [MePhSi(H)OCOCF_3]$$

$$VII + CF_3COOH \rightarrow CH_2{=}C(Me)SiMe_3 + [MePhSi(H)OCOCF_3]$$

All attempts to produce a silacyclopropane derivative in the photolysis of I in the presence of trimethylvinylsilane were unsuccessful. Thus, treating the reaction products of this photolysis with methanol did not afford any of the methoxysilane expected from the methanolysis of the 1-silacyclopropane. The rearranged addition product arising from reaction of the silicon—carbon double-bonded intermediate with trimethylvinylsilane always was obtained as the sole volatile product in 10—14% yield. In a previous communication, we reported the addition product to be a monosubstituted benzene derivative, 1,2-bis(trimethylsilyl)-1-(1′-phenyltetramethyldisilanyl)ethane [13]. This has turned out to be

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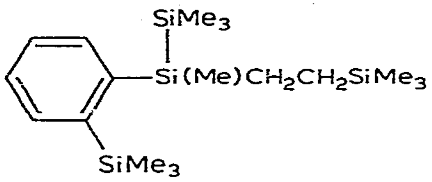
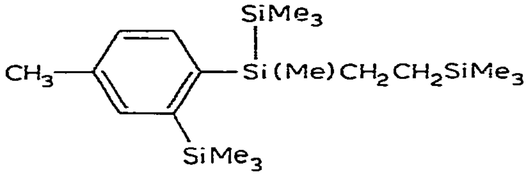
* In this reaction, methanolysis was not carried out after the photolysis.

an erroneous structural assignment. Careful studies of IR, mass and ^{1}H NMR data indicated that it must be a disubstituted benzene derivative, *o*-(trimethylsilyl)[1-(2'-trimethylsilylethyl)tetramethyldisilanyl]benzene (VIII). Supporting this is the fact that the ^{1}H NMR spectrum of the aryl ring protons in the addition product (IX), produced from the photolysis of 2-(*p*-tolyl)heptamethyltrisilane with trimethylvinylsilane, showed a typical pattern of a 1,2,4-trisubstituted benzene.

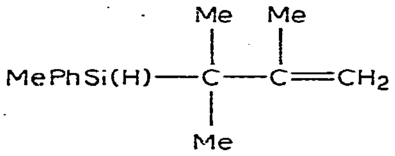


(VIII)



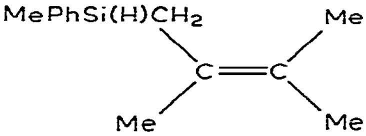
(IX)

Internal olefins and cyclic olefins also react with methylphenylsilylene to give silyl-substituted olefins. Thus, the irradiation of I with *cis*-2-butene in hexane for 1.6 h produced compound IIIc in 29% yield. Small amounts of IIIa and IIIb (less than 3%), expected from the photorearrangement of IIIc, also were detected. In this reaction, however, the addition of methanol to the product mixture did not produce any methoxysilane, indicating that complete photoisomerization of the silacyclopropane to the silylalkene took place during the photolysis. In a similar manner, the photolysis of I in the presence of tetramethylethylene gave two compounds, 2,3-dimethyl-3-methylphenylsilyl-1-butene (Xa) and an isomer, 2,3-dimethyl-1-methylphenylsilyl-2-butene (Xb), in 20 and 11% yield, respectively. Again, no methoxysilane was found after methanolysis of the reaction mixture. The irradiation of either pure Xa or Xb in hexane for 1 h gave an equilibrium mixture consisting of Xa and Xb in 51/49 ratio, showing that Xb came from photoisomerization of Xa via a 1,3-silyl shift.



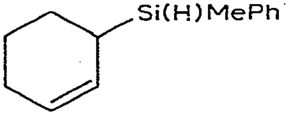
$$\mathrm{MePhSi(H)\!-\!\underset{Me}{\overset{Me}{C}}\!-\!\overset{Me}{C}\!=\!CH_2}$$

(Xa)

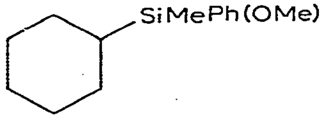


(Xb)

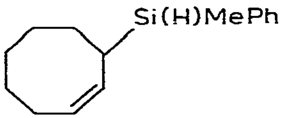
In contrast to the above results, photolysis of I in the presence of cyclohexene followed by methanolysis afforded 3-(methylphenylsilyl)cyclohexene (XIa) and cyclohexylmethylphenylmethoxysilane (XIb) in 27 and 7% yield, respectively. Irradiation of I with cyclooctene followed by methanolysis produced cyclooctylmethylphenylmethoxysilane (XIIb) in 34% yield, and 3-(methylphenylsilyl)cyclooctene (XIIa) in only 4% yield. None of the photolysis experiments carried out in the presence of cyclic and internal olefins gave the rearranged addition products. These results with the internal and cyclic olefins are consistent with those observed in the photolysis of aryldisilanes in the presence of dienes reported previously [18].



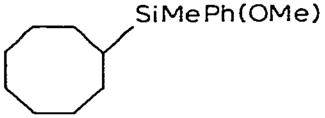
(XIa)



(XIb)



(XIIa)



(XIIb)

Reaction conditions and product yields for the various olefins investigated in these photolysis experiments are summarized in Table 1. The ^{1}H NMR, analytical, mass spectral and IR data for the isolated compounds are shown in Tables

(continued on p. 165)

TABLE 1

PHOTOLYSIS OF 2-PHENYLHEPTAMETHYLTRISILANE (I) IN THE PRESENCE OF OLEFINS IN HEXANE (HIGH-PRESSURE MERCURY LAMP)

I	Olefin	Time	Products and yield (%)		
g (mmol)	(ml)	(h)	Silyl alkene	Methoxysilane	Adduct
1.002 (3.76)	1-butene (20)	2.1	IIIa (17) IIIb (6) IIIc (4)	IIId (4)	IIIe (10)
1.000 (3.76)	1-octene (15)	2.0	IVa (20)	IVb (14) IVc (trace)	IVd (6)
1.009 (3.78)	isobutene (20)	2.0	Va (39)	—	Vc (10)
1.002 (3.76)	allyltrimethylsilane (15)	2.1	VIa (20)	VIb (5)	VId (13)
1.100 (4.13)	isopropenyltrimethylsilane (15)	2.0	VII (23)	—	—
0.957 (3.59)	trimethylvinylsilane (20)	2.0	—	—	VIII (14)
1.342^a (4.78)	trimethylvinylsilane (20)	2.3	—	—	IX (10)
1.005 (3.77)	*cis*-2-butene (20)	1.6	IIIc (29) IIIa (trace) IIIb (trace)	IIId (trace)	—
1.006 (3.78)	tetramethylethylene (15)	1.6	Xa (20) Xb (11)	—	—
0.0515 (0.19)	cyclohexene (1)	5.5^b	XIa (27)	XIb (7)	—
0.4350 (1.63)	cyclooctene (6)	0.5	XIIa (4)	XIIb (37)	—

[a] 2-*p*-Tolylheptamethyltrisilane. [b] Externally irradiated.

TABLE 2

PROTON NMR CHEMICAL SHIFTS FOR SILYL ALKENES

Compound	Chemical shifts (δ, ppm) in CCl_4
IIIa	0.34(CH_3-SiH, d, 3H, J=4 Hz), 1.62-1.84(CH_3-C=C-CH_2-, m, 5H), 5.42(vinylic protons, m, 2H, J=15 Hz), 4.21(H-Si, m, 1H), 7.35-7.65(C_6H_5, m, 5H)
IIIb	0.34(CH_3-SiH, d, 3H, J=4 Hz), 1.50(CH_3-C, broad d, 3H, J=5 Hz), 1.75(CH_2-Si, m, 2H), 4.35(H-Si, m, 1H), 5.15-5.55(vinylic protons, m, 2H, J=11 Hz), 7.20-7.60(C_6H_5, m, 5H)
IIIc	0.32(CH_3-SiH, d, 3H, J=4 Hz), 1.14(CH_3-CH, broad d, 3H, J=7 Hz), 1.95(HC-SiH, m, 1H), 4.31(H-Si, m, 1H), 4.88(H-CH=C, broad d, 1H), 4.92(H-CH=C, broad d, 1H), 5.88(HC=CH_2, m, 1H, J_{trans}=18 Hz, J_{cis}=10 Hz), 7.30-7.65(C_6H_5, m, 5H)
IVa	0.38(CH_3-SiH, d, 3H, J=4 Hz), 0.96(CH_3-C, broad t, 3H, J=6 Hz), 1.32(C-$CH_2CH_2CH_2$-C, broad s, 6H), 1.77(CH_2-Si, m, 2H), 1.98(CH_2-C=C, m, 2H), 4.73(H-Si, m, 1H), 5.70-4.95 (vinylic protons, m, 2H, J=15 Hz), 7.20-7.60(C_6H_5, m, 5H)
Va	0.27(CH_3-SiH, d, 3H, J=3.5 Hz), 1.62(CH_3-C=C, broad s, 3H), 1.72(CH_2-SiH, broad d, 2H, J=3.5 Hz), 4.57(H-Si, m, 1H), 4.62(H-CH=C, m, 1H, J_{gem}=2 Hz), 4.70(H-CH=C, m, 1H, J_{gem}=2 Hz), 7.10-7.55(C_6H_5, m, 5H)
VIa	0.01(CH_3-$SiMe_2$, s, 9H), 0.35(CH_3-SiH, d, 3H, J=4 Hz), 1.90(CH_2-SiH, m, 2H), 4.37(H-Si, m, 1H), 5.40[HC($SiMe_3$)=C, d, 1H, J=19 Hz], 5.95-6.14(HC=CHSi, m, 1H), 7.25-7.60(C_6H_5, m, 5H)
VII	0.00(CH_3-$SiMe_2$, s, 9H), 0.26(CH_3-SiH, d, 3H), 1.85(CH_2-SiH, broad d, 2H), 4.38(H-Si, m, 1H), 5.27(H_2C=C, broad d, J_{gem}=3 Hz), 7.15-7.50(C_6H_5, m, 5H)
Xa	0.30(CH_3-SiH, d, 3H, J=4 Hz), 1.10(CH_3-CMe, s, 6H), 1.70(CH_3-C=C, s, 3H), 4.25(H-Si, q, 1H, J=4 Hz), 4.64(H_2C=C, d, 2H, J_{gem}=1.5 Hz), 7.10-7.60(C_6H_5, m, 5H).
Xb	0.32(CH_3-SiH, d, 3H, J=4 Hz), 1.50(CH_3-C, s, 3H), 1.61(CH_3-CMe, s, 6H), 1.76(CH_2-SiH, broad d, 2H, J=4 Hz), 4.36(H-Si, m, 1H), 7.10-7.60(C_6H_5, m, 5H)
XIa	0.36(CH_3-SiH, d, 3H, J=4 Hz), 1.35-2.15(ring protons, m, 7H), 4.26(H-Si, m, 1H), 5.63 (vinylic protons, m, 2H), 7.15-7.60(C_6H_5, m, 5H)
XIIa	0.30(CH_3-SiH, d, 3H, J=4 Hz), 1.30-2.43(ring protons, m, 11H), 4.30(H-Si, m, 1H), 4.45 (vinylic protons, m, 2H), 7.25-7.65(C_6H_5, m, 5H)

TABLE 3

ELEMENTAL ANALYSIS, MASS AND IR DATA FOR ISOLATED COMPOUNDS

Compound		Found (calcd.) (%)		IR (neat)	M+	Exact mass
		C	H			(calcd.)
IIIa	$C_{11}H_{16}Si$	74.72(74.93)	9.39(9.15)	965(s) 1590(w) 2120(s)	176	
IIIb	$C_{11}H_{16}Si$	—	—	1610(w) 2120(s)		176.1100 (176.1021)
IIIc	$C_{11}H_{16}Si$	74.94(74.93)	8.94(9.15)	1630(s) 2120(s)	176	
IIId	$C_{12}H_{20}OSi$	69.31(69.17)	9.81(9.67)	1090(s)	208	
IIIe	$C_{17}H_{34}Si_3$	—	—	740(m)		322.1940 (322.1968)
IVa	$C_{15}H_{24}Si$	77.37(77.59)	10.15(10.34)	965(m) 2120(s)	232	
IVb	$C_{16}H_{28}OSi$	72.87(72.66)	10.66(10.67)	1090(s)	264	
IVc	$C_{16}H_{28}OSi$	—	—	1090(s)		249.1626[a] (249.1675)
IVd	$C_{21}H_{42}Si_3$	—	—	745(m)		378.2619 (378.2594)
Va	$C_{11}H_{16}Si$	75.04(74.93)	9.31(9.15)	1640(s) 2125(s)	176	
Vb	$C_{12}H_{20}OSi$	69.32(69.17)	9.88(9.67)	1090(s)	208	
Vc	$C_{17}H_{34}Si_3$	63.37(63.27)	10.59(10.62)	740(m)	322	
VIa	$C_{13}H_{22}Si_2$	66.33(66.59)	9.39(9.46)	1610(m) 2120(s)	234	
VIb	$C_{14}H_{26}OSi_2$	63.23(63.09)	9.68(9.83)	1090(s)	266	
VIc	$C_{14}H_{26}OSi_2$	—	—	1090(s)		266.1523 (266.1522)
VId	$C_{19}H_{40}Si_4$	60.09(59.96)	10.44(10.59)	740(s)	380	
VII	$C_{13}H_{22}Si_2$	66.77(66.59)	9.61(9.46)	1590(s) 2125(s)	234	
VIII	$C_{18}H_{38}Si_4$	58.78(58.94)	10.37(10.44)	730(s)	366	
IX	$C_{19}H_{40}Si_4$	59.99(59.96)	10.82(10.59)	860(s)	380	
Xa	$C_{13}H_{20}Si$	76.13(76.47)	9.98(9.80)	1640(m) 2120(s)	204	
Xb	$C_{13}H_{20}Si$	—	—	1590(w)		204.1345 (204.1354)
XIa	$C_{13}H_{18}Si$	77.08(77.22)	8.83(8.91)	2110(s)	202	
XIb	$C_{14}H_{22}OSi$	71.56(71.73)	9.31(9.46)	1090(s)	234	
XIIa	$C_{15}H_{22}Si$	78.02(78.26)	9.62(9.57)	2110(s)	230	
XIIb	$C_{16}H_{26}OSi$	73.52(73.22)	9.97(9.99)	1090(s)	262	

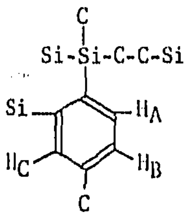
[a] $M^+ - 15$.

TABLE 4

PROTON NMR CHEMICAL SHIFTS FOR ADDUCTS

Compound	Chemical shifts (δ, ppm) in CCl_4
IIIc	0.07(CH_3-$SiMe_2Si$, s, 9H), 0.35(CH_3-$SiMe_2$, s, 9H), 0.48(CH_3-SiC_6H_4, s, 3H), 0.81-1.08 (CH_3-C and CH_2-Si, m, 5H), 1.14-1.45(CH_2CH_2, m, 4H), 7.10-7.65(ring protons, m, 4H)
IVd	0.07(CH_3-$SiMe_2Si$, s, 9H), 0.35(CH_3-$SiMe_2$, s, 9H), 0.47(CH_3-SiC_6H_4, s, 3H), 0.70-1.00 (CH_2-Si and CH_3-C, m, 5H), 1.28[(CH_2)$_6$, broad s, 12H), 7.10-7.60(ring protons, m, 4H)
Vc	0.06(CH_3-$SiMe_2Si$, s, 9H), 0.30(CH_3-$SiMe_2$, s, 9H), 0.52(CH_3-SiC_6H_4, s, 3H), 0.87 (CH_3-CMe, dd, 6H), 0.94(CH_2-, m, 2H), 1.78(CH-, m, 1H), 7.10-7.60(ring protons, m, 4H)
VId	-0.05(CH_3-$SiMe_2CH_2$-, s, 9H), 0.08(CH_3-$SiMe_2Si$, s, 9H), 0.35(CH_3-$SiMe_2C_6H_4$, s, 9H), 0.48(CH_3-Si, s, 3H), 0.60-1.55($CH_2CH_2CH_2$, m, 6H), 7.15-7.65(ring protons, m, 4H)
VIII	-0.02(CH_3-$SiMe_2CH_2$, s, 9H), 0.07(CH_3-$SiMe_2Si$, s, 9H), 0.34(CH_3-$SiMe_2C_6H_4$, s, 9H), 0.46 (CH_3-SiC_6H_4, s, 3H), 0.66-0.99(CH_2CH_2, m, 4H), 7.00-7.55(ring protons, m, 4H)
IX^a	-0.02(CH_3-$SiMe_2CH_2$, s, 9H), 0.07(CH_3-$SiMe_2Si$, s, 9H), 0.34(CH_3-$SiMe_2C_6H_3$, s, 9H), 0.46 (CH_3-SiC_6H_3, s, 3H), 0.26-1.28(CH_2CH_2, m, 4H), 1.33(CH_3-C_6H_3, broad s, 3H), 7.37(H_A, d, J=8 Hz), 7.35(H_B, dd, J=8 Hz), 7.04(H_C, s, J_{BC}=2 Hz)

a



2 and 3. The chemical shifts for the addition products are summarized in Table 4.

Photolysis of I in the presence of olefins with a low-pressure mercury lamp

In a previous communication [12], we reported that when a cyclohexane solution of I is photolyzed in the presence of cyclohexene using a low-pressure mercury lamp bearing a Vycor filter, 7-methyl-7-phenyl-7-silabicyclo[4.1.0]-heptane is produced in solution. We have now prepared various silacyclopropane derivatives by using this method. All attempts to isolate these silacyclopropanes by distillation and by GLC techniques were unsuccessful, undoubtedly because of their extreme kinetic instability. However, direct evidence for the formation of the silacyclopropane was obtained by NMR spectroscopy.

Figures 2A—2D show the typical ^{1}H NMR spectra in the methylsilyl regions, which were obtained on photolysis of a hexane solution of 2,3-diphenyloctamethyltetrasilane (XIII) and cyclooctene in a quartz tube. Two resonances at δ —0.04 and 0.48 ppm in Fig. 2A are consistent with the Me_3Si protons and Me—Si(Ph) protons, respectively, of the starting tetrasilane XIII. Irradiation of the solution with a low-pressure mercury lamp leads to the decay of XIII (see the signal at δ 0.48 ppm), and the growth of trisilane I (δ 0.37 ppm; Me—SiPh) and the silacyclopropane (δ 0.36 and 0.39 ppm; *syn*- and *anti*-methyl protons in silacyclopropane XIIIc). The starting XIII decreases with increasing irradiation time, while the amounts of I and the two peaks at δ 0.36 and 0.39 ppm continue to increase, as shown in Fig. 2B—2D. Treatment of the photolysis product after 3 h irradiation with methanol resulted in the disappearance of the signals at δ 0.36 and 0.39 ppm, and the appearance of a new signal at δ 0.29 ppm due to the methylsilyl protons of methoxysilane XIIb (Fig. 2E).

Recently, Seyferth and Annarelli have reported the reaction of dimethylsilylene species, generated by the thermolysis of hexamethylsilirane, with various olefins [21]. Their results indicate that no methoxysilanes are obtained from the reaction of dimethylsilylene with terminal olefins such as 1-decene or allyltrimethylsilane, followed by methanolysis. Presumably, the silacyclopropane produced from such olefins is thermally unstable under the reaction conditions [21]. In contrast, the present photochemically generated silylene reacts readily with terminal olefins to give silacyclopropanes, as indicated by the formation of their methanolysis products. The reaction conditions and product yields for the systems studied are summarized in Table 5; ^{1}H NMR data for the methoxysilanes produced are listed in Table 6.

As can be seen from Table 5, the yield of silacyclopropane produced is highly dependent on the structure of the olefins used. In general, substrates bearing one or two methyl groups on an olefinic carbon atom afford appreciable amounts of photorearranged silylalkenes and low yields of silacyclopropanes. Thus, the photolysis of I in the presence of *cis*-2-butene in hexane using a low-pressure mercury lamp, followed by methanolysis, gave methoxysilane IIId in 26% yield and the silylalkene IIIc in 10% yield. With isobutene as substrate in the reaction, methoxysilane Vb and silylalkene Va were obtained in 18 and 22% yield, respectively. When tetramethylethylene was used as a quencher, only a trace of the methoxysilane was found together with small amounts of Xa and

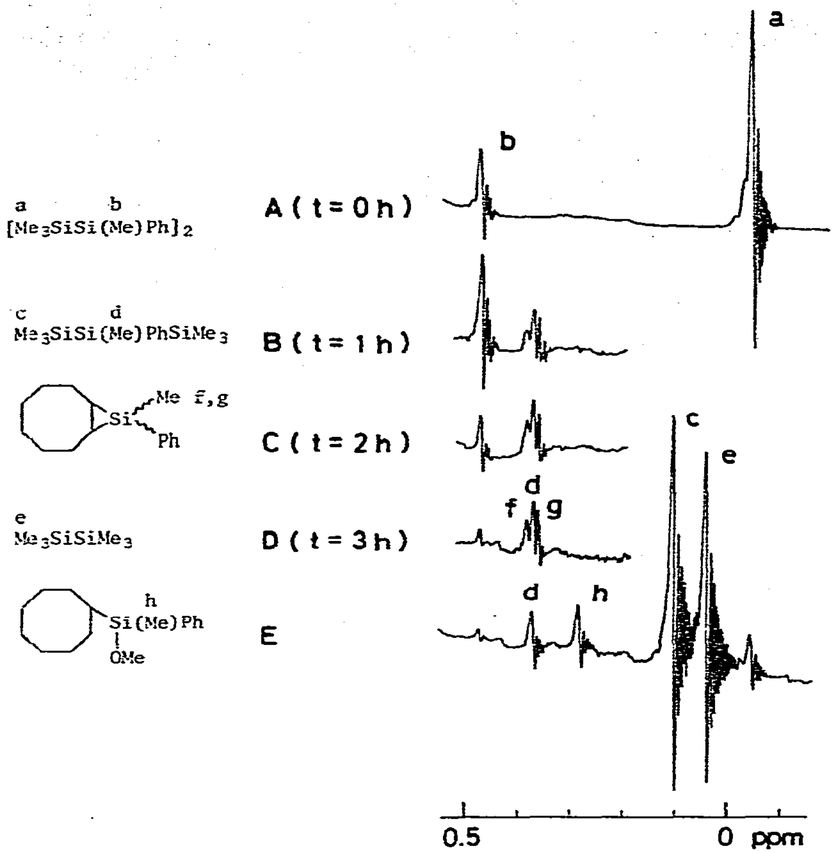


Fig. 2. ^{1}H NMR spectra of the products in the photolysis of 2,3-diphenyloctamethyltetrasilane in the presence of cyclooctene in hexane.

Xb (less than 4% combined yield). Photolysis of I in the presence of compounds that do not have methyl groups on an olefinic carbon atom, such as 1-butene, 1-octene, allyltrimethylsilane, cyclohexene and cyclooctene, produced the respective silacyclopropanes in moderate yield (27—50% yield) and only small amounts of the silylalkenes (3—4% yield) were formed.

That the ratio of methoxysilane to olefinic product does not depend on the reaction temperature was confirmed by low temperature photolysis. Thus, a hexane solution of I in the presence of a large excess of isobutene was photolyzed at −78°C for 8 h. At this stage, 93% of the starting I was photolyzed. Treatment of the resulting solution with dry methanol at the same temperature afforded methoxysilane Vb and silylalkene Va in 15 and 21% yield, respectively. The ratio of methoxysilane to rearranged olefin obtained from the quenching studies provides some insight into the relative photochemical stability of the silacyclopropanes investigated. Thus, the silacyclopropanes produced from allyltrimethylsilane, 1-octene, cyclohexene and cyclooctene are photochemically more stable than those derived from olefins bearing a methyl group on an unsaturated carbon atom.

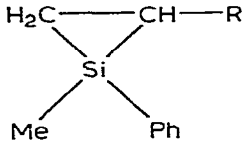
It is of interest to note that in the reaction of the silacyclopropanes with

TABLE 5

PHOTOLYSIS OF I IN THE PRESENCE OF OLEFINS IN HEXANE (LOW-PRESSURE MERCURY LAMP)

I	Olefin	Time	Products and yield (%)		
g (mmol)	(ml)	(h)	Silyl alkene	Methoxysilane	Adduct
1.003 (3.76)	1-butene (20)	2.5	IIIa (2) IIIb (1)	IIId (27)	IIIe (12)
1.016 (3.81)	*cis*-2-butene	2.5	IIIc (10)	IIId (26)	
1.004 (3.76)	1-octene	2.5	IVa (3)	IVb (28) IVc (4)	IVd (9)
1.020 (3.83)	isobutene (20)	3.0	Va (22)	Vb (18)	Vc (20)
1.000 (3.76)	allyltrimethylsilane (15)	2.5	VIa (4)	VIb (43) VIc (7)	VId (15)
1.230 (4.87)	cyclohexene (25)	7	XIa (4)	XIb (38)	—
1.002 (3.76)	cyclooctene (10)	2.5	XIIa (trace)	XIIb (35)	—

methanol, the less hindered carbon—silicon bond in the three membered ring is cleaved preferentially in giving the ring opening product. For example, treatment of a solution of silacyclopropane IVe produced from the photolysis of I and 1-octene with methanol gave methoxysilanes IVb and IVc in 28 and 4% yield, respectively. Similar treatment of VIe with methanol afforded VIb and VIc in 43 and 7% yield, respectively.



$MePh(MeO)SiCH_2CH_2R$

(IVc) R = C_6H_{13}

(VIc) R = CH_2SiMe_3

(IVe) R = C_6H_{13}

(VIe) R = CH_2SiMe_3

Photorearrangement of silacyclopropanes

Although attempts to isolate silacyclopropanes were unsuccessful, we found that the silacyclopropanes in solution could be used in further reactions. Thus, 7-methyl-7-phenyl-7-silabicyclo[4.1.0]heptane, produced from photolysis of I in the presence of cyclohexene upon irradiation with a low-pressure mercury lamp having a Vycor filter, undergoes photorearrangement to Xa when irradiated with a high-pressure mercury lamp with a quartz filter. As shown in Table 7, all of the silacyclopropanes investigated in this research with the exception of 1-methyl-1-phenyl-2-trimethylsilylmethyl-1-silacyclopropane (VIe) and 9-methyl-

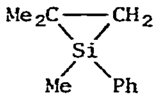
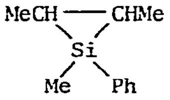
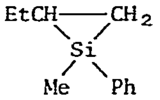
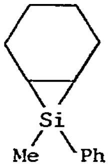
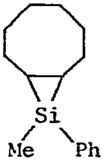
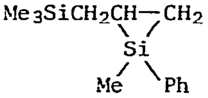
TABLE 6

PROTON NMR CHEMICAL SHIFTS FOR METHOXYSILANES

Compound	Chemical shifts (δ, ppm) in CCl_4
IIId	0.31(CH_3-Si, s, 3H), 0.85-1.25($CH_3CH_2CHCH_3$, m, 9H), 3.43(CH_3-O, s, 3H), 7.30-7.70(C_6H_5, m, 5H)
IVb	0.32(CH_3-Si, s, 3H), 0.70-1.05(CH_3CH-Si and CH_3-C, m, 7H), 1.26[$(CH_2)_5$, broad s, 10H], 3.44(CH_3-O, s, 3H), 7.25-7.55(C_6H_5, m, 5H)
IVc	0.31(CH_3-Si, s, 3H), 0.70-1.00(CH_2-Si and CH_3-C, m, 5H), 1.28[$(CH_2)_6$, broad s, 12H], 3.40(CH_3-O, s, 3H), 7.25-7.55(C_6H_5, m, 5H)
VIb	-0.01 and -0.04(CH_3-$SiMe_2$, two s, 9H), 0.31(CH_3-Si, s, 3H), 0.61-0.98(CH_3CHCH_2, m, 6H), 3.42(CH_3-O, s, 3H), 7.25-7.60(C_6H_5, m, 5H)
VIc	-0.07(CH_3-$SiMe_2$, s, 9H), 0.32(CH_3-Si, s, 3H), 0.47-1.50($CH_2CH_2CH_2$, m, 6H), 3.40(CH_3-O, s, 3H), 7.20-7.55(C_6H_5, m, 5H)
XIb	0.33(CH_3-Si, s, 3H), 0.82-1.94(C_6H_{11}, m, 11H), 3.42(CH_3-O, s, 3H), 7.18-7.62(C_6H_5, m, 5H)
XIIb	0.32(CH_3-Si, s, 3H), 0.80-1.98(C_8H_{15}, m, 15H), 3.42(CH_3-O, s, 3H), 7.25-7.55(C_6H_5, m, 5H)

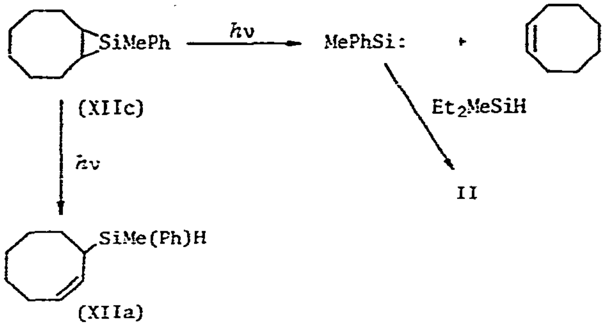
TABLE 7

PHOTOREARRANGEMENT OF SILACYCLOPROPANES (HIGH-PRESSURE MERCURY LAMP)

Silacyclopropane	(mmol)	Time (min)	Conversion (%)	Silyl alkenes (Yield %)
	(0.47)	30	68	Va (81)
	(0.72)	30	40	IIIc (98)
	(0.98)	100	66	IIIa (37), IIIb (16), IIIc (19)
	(0.83)	120	82	XIa (70)
	(0.54)	30	83	XIIa (9)
	(1.02)	45	68	VIa (24)

9-phenyl-9-silabicyclo[6.1.0]nonane (XIIc), undergo a similar photorearrangement to give silylalkenes in high yields. The photochemical behavior of VIe and XIIc is different from that of the others in that their photolysis under similar conditions produced low yields of isomeric olefins. In order to learn more about the photochemical degradation of XIIc, we photolyzed it in the presence of diethylmethylsilane. Interestingly, a 43% yield of 1,1-diethyl-1,2-dimethyl-2-phenyldisilane (II), arising from insertion of methylphenylsilylene into the hydrosilane, was obtained together with an 8% yield of the photoisomer (XIIa). This result indicates that the photochemical degradation of XIIc with a high-pressure mercury lamp proceeds by two different routes: one involving photorearrangement of XIIa, and the other proceeding via a silylene extrusion, a reaction which is the reverse of that involved in silacyclopropane formation (Scheme 2).

SCHEME 2



Similar photolysis of VIe with a high-pressure mercury lamp also produced methylphenylsilylene, but the yield of insertion product II could not be determined because II and VIa could not be separated by GLC analysis under the conditions used.

Experimental

General procedure

All reactions were carried out under an atmosphere of dry nitrogen. Photolysis was carried out using a 100 W high-pressure mercury lamp surrounded by a quartz cooling jacket, and a 10 W low-pressure mercury lamp bearing a Vycor filter. All photolyses were followed by GLC analysis using a 2 m × 0.5 cm stainless column with 20% Silicone DC oil, and irradiation was stopped when approximately 90% of the starting 2-phenylheptamethyltrisilane was photolyzed. Yields were determined by GLC using an internal standard on the basis of unrecovered trisilane I. The identification of the products by GLC method was done by using two different columns (30% Apiezon Grease on Celite 545 and 20% Silicone DC oil on Chromosorb W).

Proton NMR spectra were determined at ambient temperatures with a JEOL Model JNM-MH-100 spectrometer using carbon tetrachloride solutions containing methylene chloride as an internal standard. Mass spectra were obtained on a JEOL Model JMS-D 300 equipped with a JMA-2000 data processing system. Ionising voltage was 24 eV for all compounds.

An Aerograph Model 90-P gas chromatograph with a thermal conductivity detector was used for separating the reaction products. Most of the products were easily separated as colorless liquids by using a 3/8″ × 20′ column containing Silicone DC oil (30%) on Chromosorb W.

Materials

2-Phenylheptamethyltrisilane [NMR (δ, ppm, in hexane) 0.11 (s, 18H), 0.37 (s, 3H) and 7.2—7.4 (m, 5H)] [23], 2-chloroheptamethyltrisilane [23], trimethylvinylsilane [24], allyltrimethylsilane [25] and isopropenyltrimethylsilane [26] were prepared according to published procedures. 1-Butene, *cis*-2-butene and isobutene were dried by passing the gases through a column containing $CaCl_2$ and silica gel. Other olefins used were dried over lithium aluminum hydride. Hexane was dried over lithium aluminum hydride and distilled before use.

Preparation of 2-(p-tolyl)heptamethyltrisilane

To a solution of *p*-tolylmagnesium bromide, prepared from 2 g (0.08 g-atom) of magnesium and 15 g (0.08 mol) of *p*-bromotoluene in 50 ml of dry tetrahydrofuran (THF), was added 5.6 g (0.03 mol) of 2-chloroheptamethyltrisilane dissolved in 10 ml of THF. The mixture was refluxed for 8 h and hydrolyzed with water. The organic layer was dried over potassium carbonate. Distillation gave 2.7 g (45% yield) of 2-(*p*-tolyl)heptamethyltrisilane, b.p. 76—77°C/1.5 Torr, n_D^{20} 1.5245; NMR (δ, ppm) 0.01 (s, 18H), 0.35 (s, 3H), 2.32 (broad s, 3H), 7.05 and 7.20 (AB quartet, 4H, J_{AB} 8 Hz) (Found: C, 60.03; H, 10.23. $C_{14}H_{28}Si_3$ calcd.: C, 59.92; H, 10.06%).

Preparation of 2,3-diphenyloctamethyltetrasilane (XIII)

To an alloy prepared from 2.3 g (0.1 g-atom) of sodium and 20 g (0.51 g-atom) of potassium in 100 ml of heptane was added 100 ml of dry benzene. 1-Chloro-1-phenyltetramethyldisilane (99 g, 0.43 mol) dissolved in 100 ml of benzene was then added slowly to the alloy with stirring. The reaction mixture was refluxed for 10 h and decomposed by adding 100 ml of an ethanol/acetic acid mixture (1/1) and then water. The organic layer was washed with water and dried over calcium chloride. Fractional distillation gave 64 g (76% yield) of a mixture of *dl* and *meso* isomers in the ratio of 1/1, b.p. 159—161°C/2 Torr; NMR (δ, ppm) —0.03 (Me_3Si, s, 9H), —0.01 (Me_3Si, s, 9H), 0.45 (MeSiPh, s, 3H), 0.48 (MeSiPh, s, 3H), 7.1—7.4 (ring protons, m, 10H) (Found: C, 62.02; H, 8.58. $C_{20}H_{34}Si_4$ calcd.: C, 62.10; H, 8.86%). When the mixture was allowed to stand for one month at room temperature, one isomer was precipitated as white crystals, m.p. 52—54°C. NMR (δ, ppm) —0.03 (Me_3Si, s, 18H), 0.48 (MeSiPh, s, 6H), 7.1—7.4 (ring protons, m, 10H); NMR (δ, ppm, in hexane) —0.04, 0.48 and 7.1—7.4.

Photolysis of 2-phenylheptamethyltrisilane (I) in the presence of diethylmethylsilane with a high-pressure mercury lamp

In a 120 ml reaction vessel fitted internally with a high-pressure mercury lamp having a quartz filter was placed a solution of 1.005 g (3.77 mmol) of I and 10 g (0.10 mol) of diethylmethylsilane in 100 ml of dry hexane. The solution was irradiated at room temperature with a slow stream of nitrogen bubbling through the mixture. After 2 h of irradiation, 89% of the starting I was photolyzed. Most of the solvent and unchanged diethylmethylsilane were evaporated away. The residue that remained was distilled under reduced pressure to give a volatile product boiling up to 180°C/1 Torr. The amount of 1,1-diethyl-1,2-dimethyl-2-phenyldisilane (II) (35% yield) contained in the distillate was determined by analytical GLC techniques using cetane as an internal standard. Pure II was isolated by preparative GLC, n_D^{20} 1.5191; NMR (δ, ppm) 0.06 (Me—SiEt$_2$, s, 3H), 0.43 (Me—SiPh, d, 3H), 0.54—1.19 (Et—SiMe, m, 10H), 4.58 (H—SiMe, q, 1H), 7.12—7.72 (ring protons, m, 5H) (Found: C, 64.35; H, 9.87. $C_{12}H_{22}Si_2$ calcd.: C, 64.86; H, 9.91%).

Photolysis of I in the presence of an olefin with a high-pressure mercury lamp

The following is typical of the procedures used. A mixture of 1.005 g (3.77 mmol) of I and 0.202 g (0.89 mmol) of cetane in 100 ml of dry hexane was placed in a reaction vessel similar to that described above. To this solution, 20 ml of dry *cis*-2-butene was added through a nitrogen inlet tube. The mixture was maintained at 0°C and irradiated 2 h as described above. After the irradiation was stopped, 3 ml of dry methanol was added to the reaction mixture through the condenser by a syringe. After distilling off the hexane solvent and *cis*-2-butene, the residue was analyzed by GLC as being 3-methylphenylsilyl-1-butene (IIIc) (29% yield), traces of *cis*- and *trans*-1-methylphenylsilyl-2-butene, and 10% of the starting trisilane I. After distillation of the residue under reduced pressure pure IIIc was isolated by preparative GLC. The reaction conditions and yields of the products obtained from the photolysis experiments using a high-pressure mercury lamp as described above are listed in Table 1.

Photolysis of I with a low-presure mercury lamp

A mixture of 1.001 g (3.75 mmol) of I, 0.103 g (0.46 mmol) of cetane and 12 g (0.12 mol) of diethylmethylsilane in 80 ml of dry hexane was placed in a 100 ml reaction vessel, fitted with a low-pressure mercury lamp having a Vycor filter. The mixture was irradiated at room temperature for 2 h with a slow stream of nitrogen bubbling through the mixture. At this stage 90% of the starting I was photolyzed. After evaporating off the hexane solvent and unchanged diethylmethylsilane, the residue was distilled at reduced pressure giving II in 47% yield and 10% of unchanged I.

Low temperature photolysis of I in the presence of isobutene

A mixture of 1.1311 g (4.24 mmol) of I, 0.1010 g (0.45 mmol) of cetane and 20 ml of isobutene in 100 ml of hexane was irradiated with a low-pressure mercury lamp surrounded by a Vycor vacuum jacket for 8 h at —78°C. At this stage, 93% of I was photolyzed. After the irradiation was stopped, 5 ml of dry methanol was added to the reaction mixture through the condenser by a syringe. The solvent and isobutene were distilled off, and the residue was then analyzed by GLC as being silylalkene Va (21% yield), methoxysilane Vb (15% yield) and adduct Vc (4% yield).

The NMR study of the products in the photolysis of 2,3-diphenyloctamethyltetrasilane (XIII) in the presence of cyclooctene

A mixture of 12.2 mg (0.032 mmol) of crystalline XIII (see preparation of XIII) and 84.0 mg (0.76 mmol) of dry cyclooctene in 0.4 ml of hexane was placed in a quartz NMR tube. The solution was deoxygenated by bubbling dry argon for 20 min and the tube was sealed with a serum cap. It was then irradiated externally with a low-pressure mercury lamp with a Vycor filter at room temperature. After 3 h irradiation, 5 μl of dry methanol was added through the serum cap by means of a syringe. The results are illustrated in Fig. 2.

Photochemical rearrangement of silacyclopropanes to the silyl-substituted alkenes

A mixture of 1.016 g (3.81 mmol) of I, 0.1538 g (0.68 mmol) of cetane and 20 ml of *cis*-2-butene in 100 ml of hexane was placed in the 120 ml reaction vessel described above for experiments using a high-pressure mercury lamp. After bubbling nitrogen through the mixture to displace trace amounts of oxygen, the reaction mixture was irradiated with ice cooling for 3.5 h using a low-pressure mercury lamp equipped with a Vycor filter. Treating a small aliquot (ca. 2 ml) of product, removed from the flask using a syringe, with dry methanol produced IIId, as determined by GLC. The amount of IIId determined by analytical GLC was used to determine the yield (26%) of the silacyclopropane. The photolysis of a solution containing 0.98 mmol of 1,2,3-trimethyl-1-phenyl-1-silacyclopropane with a high-pressure mercury lamp having a quartz filter for 30 min, gave the photorearranged product IIIc in 98% yield at a stage where 40% of the silacyclopropane was photolyzed. The reaction conditions and the yields of photorearranged products are listed in Table 7.

Reaction of 1-methylphenylsilyl-2-octene with trifluoroacetic acid

A mixture of 1-methylphenylsilyl-2-octene (63 mg, 0.27 mmol) and trifluoroacetic acid (63 mg, 0.55 mmol) dissolved in 1 ml of chloroform was heated in a sealed ampoule at 55°C for 3 h. GLC analysis of the reaction mixture showed a single product, the retention time of which is consistent with that of 1-octene (quantitative yield).

Reaction of 3-methylphenylsilyl-2-trimethylsilyl-1-propene with trifluoroacetic acid

A solution of 2-trimethylsilyl-3-methylphenylsilyl-1-propene (59 mg, 0.47 mmol) and trifluoroacetic acid (49 mg, 0.47 mmol) in 1 ml of carbon tetrachloride was allowed to stand 2 h at room temperature. Isopropenyltrimethylsilane, identified by comparison of its GLC retention time with that of an authentic sample, was formed in 92% yield.

Attempted reaction of ethyldimethylvinylsilane with trifluoroacetic acid

A mixture of ethyldimethylvinylsilane (39 mg, 0.40 mmol) and trifluoroacetic acid (76 mg, 0.76 mmol) in chloroform was heated in a sealed tube at 55°C for 2 h. The GLC analysis of the reaction mixture showed that all of the starting vinylsilane remained unchanged.

Photoisomerization of 2,3-dimethyl-3-methylphenylsilyl-1-butene (Xa), 2,3-dimethyl-1-methylphenylsilyl-2-butene (Xb) and trans-(1-methylphenylsilyl)-2-butene (IIIa)

A solution of 20 μl of pure sample of each compound and 10 μl of cetane in 10 ml of dry hexane was placed in an approximately 10 ml carefully dried quartz tube. The solution was purged with dry nitrogen and the tube was sealed with a serum cap. It was then irradiated externally with a high-pressure mercury lamp fitted with a quartz filter at room temperature. The reaction products were analyzed by GLC. Irradiation of Xa and Xb individually afforded in each case an equilibrium mixture consisting of Xa/Xb 49/51 after 3 h irradiation. Irradiation of IIIa produced a mixture of IIIa, IIIb and IIIc in a ratio of 32/11/57 after a 2 h reaction.

Photolysis of 9-methyl-9-phenyl-9-silabicyclo[6.1.0]nonane (XIIc) in the presence of diethylmethylsilane

To a solution containing 0.45 mmol of XIIc, prepared from irradiation of a mixture of 1.93 mmol of I and 40.3 mmol of cyclooctene in dry hexane with a low-pressure mercury lamp having a Vycor filter for 2.5 h, was added 8 ml of diethylmethylsilane distilled from lithium aluminum hydride. The reaction mixture was then irradiated with a high-pressure mercury lamp for 20 min. Treating the products with dry methanol gave insertion product II, methoxysilane XIIb, and photoisomerization product XIIa, in 43, 43 and 8% yields, respectively.

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