

PHOTOLYSIS OF ORGANOPOLYSILANES. THE REACTION OF TRIMETHYLSILYLPHENYLSILYLENE WITH OLEFINS AND CONJUGATED DIENES *

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Summary

The photolysis of tris(trimethylsilyl)phenylsilane (I) in the presence of olefins and dienes has been investigated. Irradiation of I in the presence of 1-butene, *cis*- and *trans*-2-butene, isobutene and trimethylvinylsilane with a low-pressure mercury lamp bearing a Vycor filter afforded the respective silacyclopropanes (A–C). These compounds could be trapped by methanol as the corresponding methoxysilanes. In no case were alkenyldisilanes, which can be expected from photoisomerization of the silacyclopropanes, observed. Photolysis of silacyclopropanes A and B with a high-pressure mercury lamp afforded a mixture of the silylalkenes arising from both 1,2- and 1,3-hydrogen shift, while that of silacyclopropane C gave no volatile products. Irradiation of I in the presence of 2,3-dimethylbutadiene gave 1-phenyl-1-trimethylsilyl-3,4-dimethyl-1-silacyclopent-3-ene, in addition to methoxysilanes arising from methanolysis of the alkenylsilacyclopropane (D). The reaction of trimethylsilylphenylsilylene with 1,3-cyclooctadiene produced 9-phenyl-9-trimethylsilyl-9-silabicyclo[6.1.0]nona-2-ene (E) as the sole product. Photolysis of E with a high-pressure mercury lamp having a quartz filter afforded two isomers of 9-phenyl-9-trimethylsilyl-9-silabicyclo[4.2.1]nona-7-ene.

Introduction

Considerable attention has been focused in recent years on the chemical behavior of reactive silylene species and many papers that deal with the insertion of these intermediates into single bonds and with their addition to multiple bonds have been reported [1–3]. The reaction of the silylene inter-

* Dedicated to Professor E.G. Rochow on the occasion of his seventieth birthday.

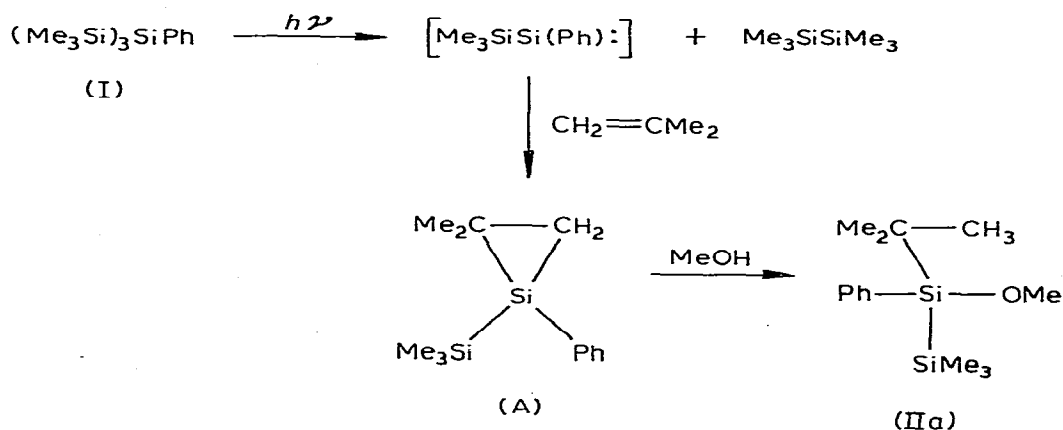
mediates generated by photolysis of polysilanes has been found to proceed simultaneously by two different pathways; one involves polymerization of the silylene itself, the other comprises the reaction with a trapping agent which is added to intercept the species. The fate of the silylene and the structure of reaction products will depend on the relative rates of these two processes. We felt that the silylene bearing bulky substituents on the central silicon atom might reduce the rate of polymerization and have different chemical properties toward unsaturated compounds from those of sterically less hindered silylenes. Indeed, we already found that trimethylsilylphenylsilylene generated by photolysis of tris(trimethylsilyl)phenylsilane reacted readily with alkynes such as 3-hexyne and bis(trimethylsilyl)acetylene to give the respective silacycloprenes [4]; whereas neither photochemically generated dimethylsilylene nor methylphenylsilylene did. In this paper, we report the formation and chemical properties of silacycloprenes arising from the reaction of trimethylsilylphenylsilylene with olefins and conjugated dienes.

Results and discussion

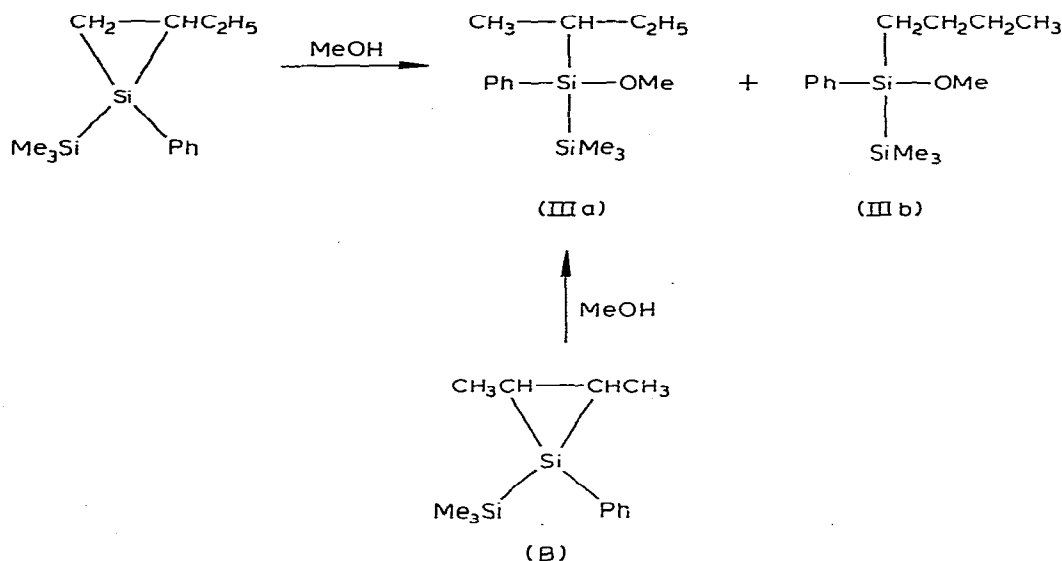
Reaction of trimethylsilylphenylsilylene with olefins

Photochemically generated trimethylsilylphenylsilylene has been found to readily add to the carbon-carbon double bonds of many types of olefin. Thus, the photolysis of a hexane solution of tris(trimethylsilyl)phenylsilane (I) in the presence of isobutene by irradiation with a low-pressure mercury lamp for 2 h produced, after subsequent treatment of the photolysis mixture with dry methanol, tert-butylphenyl(trimethylsilyl)methoxysilane (IIa) in 52% yield, as the sole methanolysis product, in addition to 23% of unchanged I (Scheme 1). The structure of IIa was confirmed by mass, IR and ^1H NMR spectrometric analysis. Direct evidence for the formation of 1-trimethylsilyl-1-phenyl-2,2-dimethyl-1-silacyclop propane (A) was obtained by the NMR spectroscopic analysis. Thus, distillation of the photolysis product under reduced pressure provided silacyclop propane A which was contaminated with ca. 30% of the starting

Scheme 1



compound. The proton NMR spectrum of the distillate in C_6D_6 displayed signals at δ 0.21 (Me_3Si , s, 9 H), 0.67 and 0.96 (H_2C in C_2Si ring, AB quart. J_{gem} 9.5 Hz, 2 H), 1.31 (MeC, broad s, 3 H), 1.39 (MeC, broad s, 3 H) *, together with those due to the starting I. Treatment of this solution with dry methanol resulted in the disappearance of the signals at δ 0.21, 0.67, 0.96, 1.31 and 1.39, and the appearance of new signals at δ 0.29 (Me_3Si , s, 9 H), 1.11 (Me_3C , s, 9 H) and 3.50 (MeO, s, 3 H). The chemical shifts of the new signals were identical with those of methoxysilane IIa in deuterobenzene solution. Trimethylsilylphenylsilylene also reacted with 1-butene under the same conditions to give, after treating with methanol, the methoxysilane in 47% yield which showed a single peak by GLC analysis. The proton NMR spectrum of the methoxysilane isolated by preparative GLC, however, indicated the presence of two isomers, butyl- and 2-butyl(trimethylsilyl)phenylmethoxysilane in a ratio of 1/3.7. This indicates that both the silicon-carbon bonds in the silacyclopropane ring were cleaved by methanol. The structure of the abundant species was determined to be the 2-butylmethoxysilane derivative (IIIa) arising from cleavage of the less substituted silicon-carbon bond in the three membered ring system. The minor one was identified as butyl(trimethylsilyl)phenylmethoxysilane (IIIb).

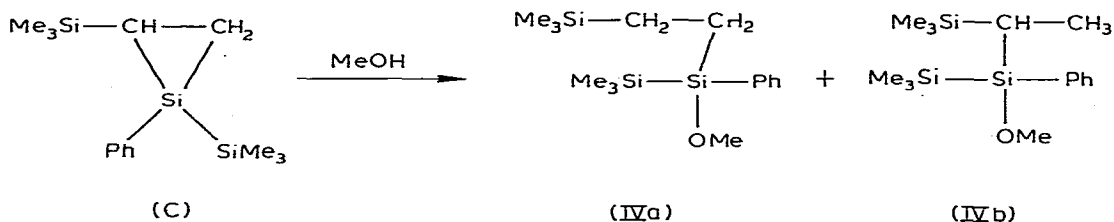


Trimethylsilylphenylsilylene also added to internal olefins such as *cis*- and *trans*-2-butene to give the silacyclopropane (B). Thus, irradiation of I in the presence of *trans*-2-butene in hexane with a low-pressure mercury lamp, followed by distillation under reduced pressure, afforded silacyclopropane B whose purity was determined to be ca. 70% by GLC analysis of a methanol-quenched aliquot. The 1H NMR spectrum of B in deuterobenzene displayed signals at δ 0.27 (Me_3Si , s, 9 H), 0.6–1.3 (HCM_e , m, 2 H), 1.39 (CH_3CH , d, 3 H, J 6.5 Hz), 1.46 (CH_3CH , d, 3 H, J 6.5 Hz) and 7.1–7.7 (C_6H_5 , m). Irradiation of methyl protons (δ 1.40) on the silacyclopropane ring changed the multiplet signals at 0.6–1.3 into an AB quartet. Treatment of B thus obtained with

* Values of δ are given in ppm relative to TMS.

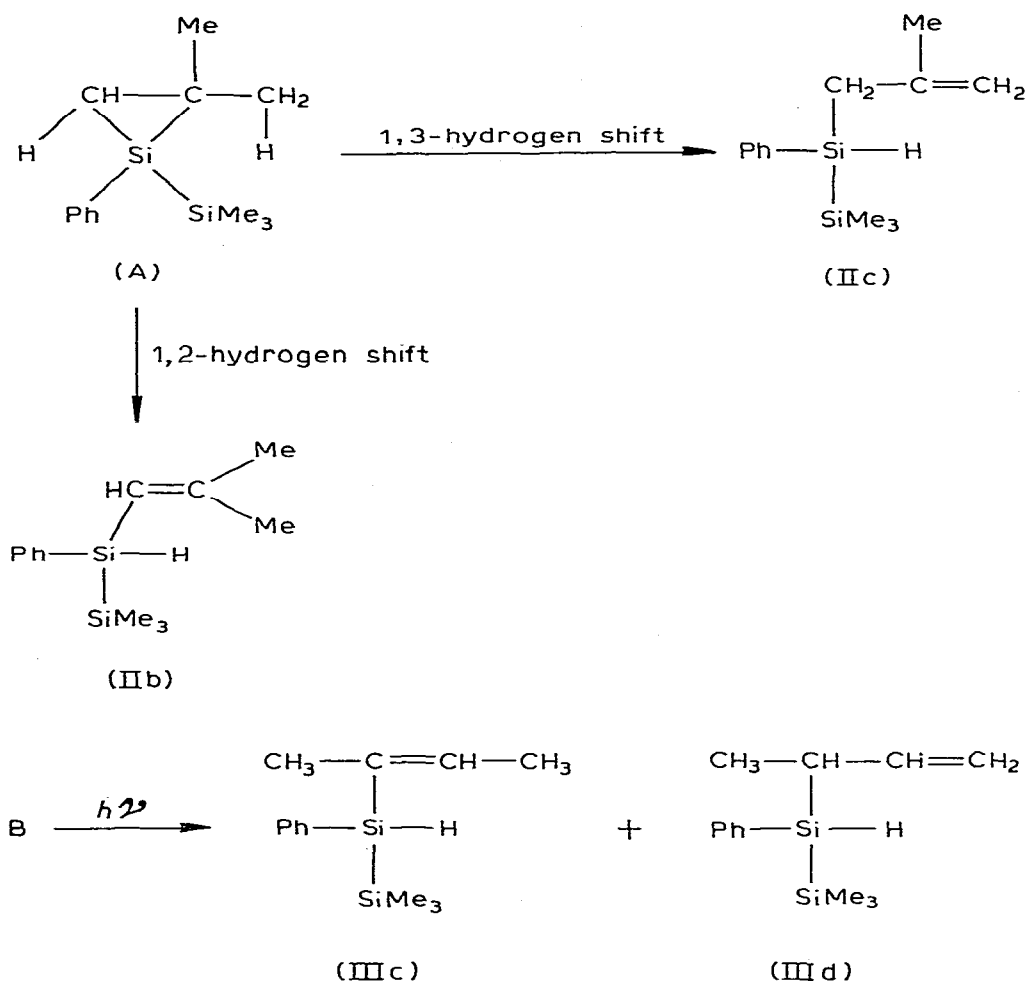
dry methanol afforded methoxysilane IIIa as the sole volatile product. These results indicate that the addition of trimethylsilylphenylsilylene to the olefin proceeds with high stereoselectivity giving the silacyclop propane. Similar irradiation of I with *cis*-2-butene gave also a silacyclop propane. The ^1H NMR spectrum of this silacyclop propane in deuterobenzene showed two singlets at δ 0.18 and 0.31 ppm in a ratio of 6/4, indicating the presence of two stereoisomers [0.18 (Me_3Si , s), 0.31 (Me_3Si , s), 1.1–1.3 (HCMe , m, 2 H), 1.43 (CH_3CH , m, 6 H) and 7.1–7.7 (C_6H_5 , m)]. Addition of methanol to this solution resulted in the disappearance of the signals at 0.18 and 0.31 ppm, and the appearance of a new signal at δ 0.26 due to the methylsilyl protons of methoxysilane IIIa.

It was reported previously that photochemically generated methylphenylsilylene does not add to the double bond of vinyltrimethylsilane [5,6]. In contrast, the present silylene reacted readily with vinyltrimethylsilane to afford the silacyclop propane (C) which could be detected by GLC-mass spectrometric analysis of the photolysis mixture (m/e 278). Treatment of the photolysis product with dry methanol gave two methoxysilanes IVa and IVb in 53 and 9% yields, respectively. It is interesting to note that the abundant product IVa was a methoxysilane arising from bond scission between the trimethylsilyl substituted carbon atom and the silicon atom in the silacyclop propane ring, because in all reactions which we investigated to date [6] the methoxysilanes derived from the cleavage of the less substituted carbon-silicon bond in the silacyclop propanes were obtained as main products. In the present case, presumably, a steric interaction between the two bulky trimethylsilyl substituents, which is significant enough to make the ring Si—CH bond weaker, as well as stabilization of the carbanion α to the silyl group [7], is responsible for the preferential formation of IVa.



In the photolysis of silacyclop propanes produced from methylphenylsilylene and various olefins [6], the photochemical 1,3-hydrogen shift giving the 3-silylalkenes only has been observed. However, the photolysis of silacyclop propanes A and B by irradiation with a high-pressure mercury lamp proceeded simultaneously by two different routes, one leading to the formation of a 1-alkenyl-substituted silane via a 1,2-hydrogen shift which has never been observed in the photolysis of the silacyclop propane system, and the other involving the usual 1,3-hydrogen shift. Thus, irradiation of a hexane solution of A with a high-pressure mercury lamp having a quartz filter gave photorearranged products, 1-(1'-phenyl-2',2',2'-trimethyldisilanyl)-2-methylpropene (IIb) and 3-(1'-phenyl-2',2',2'-trimethyldisilanyl)-2-methylpropene (IIc) in 10 and 13% yield, respectively (Scheme 2). The IR, mass and ^1H NMR spectra of IIb and IIc were identical with those of the authentic samples prepared by an independent route. That compound IIb is an initial photoproduct was confirmed by the fact that

Scheme 2



irradiation of IIc under identical conditions produced none of the isomers. Furthermore, the isomerization of IIb to IIc was never observed in the photolysis of IIb. These results clearly indicate that IIb and IIc came directly from silacyclop propane A via a 1,2- and a 1,3-hydrogen shift, respectively.

A similar photochemical 1,2-hydrogen shift in the silacyclop propane was found in the photolysis of B. In the early stages of this photolysis, both 2-(1'-phenyl-2',2',2'-trimethyldisilanyl)-2-butene (IIIc) and 3-(1'-phenyl-2',2',2'-trimethyldisilanyl)-1-butene (IIId) only were produced as the volatile products. After 1 h irradiation, IIIc and IIId were obtained in 13 and 16% yield, respectively, on the basis of the starting B, in addition to small amounts of three isomers (less than a 7% combined yield), which could be detected by GLC-mass spectrometric analysis.

In contrast to the photolysis of A and B, silacyclop propane C did not afford any disilanylalkenes analogous to IIb and IIc under the same photolysis conditions. Only non-volatile products were obtained after evaporation of the solvent from the photolysis mixture.

TABLE 1

PHOTOLYSIS OF TRIS(TRIMETHYLSILYL)PHENYLSILANE (I) IN THE PRESENCE OF OLEFINS AND DIENES IN HEXANE (LOW-PRESSURE MERCURY LAMP)

I g (mmol)	Olefin or diene (ml)	Time (h)	Products and yield (%) after methanolysis	Recovered I (%)
1.0027 (3.087)	isobutene (10)	2.0	IIa (52)	23
0.3261 (1.004)	1-butene (2)	1.5	IIIa (37), IIIb (10)	21
0.3263 (1.005)	<i>cis</i> -2-butene (5)	1.5	IIIa (35)	17
0.3263 (1.005)	<i>trans</i> -2-butene (5)	1.0	IIIa (40)	28
1.0006 (3.081)	trimethylvinyl- silane (3)	2.5	IVa (53), IVb (9)	12
1.0291 ^a (3.168)	isobutene (20)	2.0	IIb (10), IIc (13)	12
0.9797 (3.016)	2,3-dimethyl- butadiene (17.6) ^b	2.7	V (21), VI (13), VII (6), VIII (8)	12
0.9949 (3.063)	cyclooctadiene (13.9) ^b	3.2	IXa (16), IXb (8), X (16)	18
0.9807 ^{a c} (3.017)	cyclooctadiene (15.9) ^b	3.3	XIa (5), XIb (13)	23

^a High-pressure mercury lamp. ^b mmol.

Reaction conditions and product yields in the photolysis experiments are summarized in Table 1. The ¹H NMR, analytical, mass and IR spectral data for the isolated compounds are shown in Tables 2 and 3.

Reaction of trimethylsilylphenylsilylene with conjugated dienes

The addition of silylene species to acyclic 1,3-butadiene derivatives has been found to produce silacyclopent-3-enes. These apparent 1,4-addition products have been assumed to form from a 1,2-addition of the silylenes to the dienes, followed by rearrangement [8–10].

Recently, we have reported that the addition of phenylmethylsilylene to 2,3-dimethylbutadiene affords 2-phenylmethylsilylmethyl-3-methyl-1,3-butadiene arising from photoisomerization of the 1,2-adduct, in addition to the silacyclopentene [11]. We have now found that trimethylsilylphenylsilylene reacts with 2,3-dimethylbutadiene to give the 1,2-adduct which can be quenched by methanol, in addition to 1-trimethylsilyl-1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene (V). Thus, irradiation of a hexane solution of I in the presence of 2,3-dimethylbutadiene with a low-pressure mercury lamp for 5 h, followed by treating the resulting photolysis product with methanol, afforded V and two methoxysilanes, 1-(1'-methoxy-1'-phenyltrimethyldisilanyl)-2,3-dimethyl-2-butene (VI) and 4-(1'-methoxy-1'-phenyltrimethyldisilanyl)-2,3-dimethyl-1-butene (VII), in 21, 13 and 6% yield, respectively, in addition to VIII arising from the reaction of a silicon-carbon double-bonded intermediate [12] with 2,3-dimethylbutadiene (Scheme 3).

Fig. 1 illustrates the observed yields of products plotted against time for the

TABLE 2
PROTON NMR CHEMICAL SHIFTS FOR PRODUCTS

Compound	Chemical shifts (δ , ppm) in CCl_4
IIa	0.25 (Me_3Si , s, 9 H), 0.94 (Me_3C , s, 9 H), 3.57 (MeO, s, 3 H), 7.2–7.5 (ring protons, m, 5 H)
IIb ^a	0.18 (Me_3Si , s, 9 H), 1.80 ($\text{CH}_3\text{—C=C}$, broad s, 6 H), 4.98 (HSi, d, 1 H, J 6 Hz), 5.65 (HCSi, broad d, 1 H, J 6 Hz), 7.3–7.8 (ring protons, m)
IIc ^a	0.14 (Me_3Si , s, 9 H), 1.65 ($\text{CH}_3\text{—C=C}$, broad s, 3 H), 1.98 (H_2CSi , d, 2 H, J 5 Hz), 4.57 (HSi, t, 1 H, J 5 Hz), 4.80 ($\text{H}_2\text{C=C}$, broad s, 2 H), 7.2–7.8 (ring protons, m)
IIIa	0.17 (Me_3Si , s, 9 H), 0.85–1.80 (EtMeCH, m, 9 H), 3.52 (MeO, s, 3 H), 7.2–7.5 (ring protons, m, 5 H)
IIIb	0.14 (Me_3Si , s, 9 H), 0.85–1.80 (BuSi, m), 3.48 (MeO, s, 3 H)
IIIc	0.20 (Me_3Si , s, 9 H), 1.74 ($\text{CH}_3\text{—C=C}$, broad d, 3 H, J 7 Hz), 1.83 ($\text{CH}_3\text{—C=C}$, broad s, 3 H), 4.56 (HSi, s, 1 H), 6.18 (HC=C , broad quart, 1 H, J 7 Hz), 7.2–7.5 (ring protons, m, 5 H)
IIId	0.16 (Me_3Si , s, 9 H), 1.20 (CH_3CSi , d, 3 H, J 7 Hz), 2.13 (HCSi, m, 1 H), 4.02 (HSi, d, 1 H, J 3.2 Hz), 4.7–4.9 ($\text{H}_2\text{C=C}$, m, 2 H), 5.7–6.0 (HC=C , m, 1 H), 7.2–7.5 (ring protons, m, 5 H)
IVa	0.00 (Me_3Si , s, 9 H), 0.14 (Me_3Si , s, 9 H), 0.3–1.0 (CH_2CH_2 , m, 4 H), 3.47 (MeO, s, 3 H), 7.2–7.5 (ring protons, m, 5 H)
IVb ^b	A, –0.10 (Me_3Si , s, 9 H), 0.20 (Me_3Si , s, 9 H), 1.02 (MeC, d, 3 H, J 7.3 Hz), 3.53 (MeO, s, 3 H), 7.2–7.6 (ring protons, m); B, –0.15 (Me_3Si , s, 9 H), 0.16 (Me_3Si , s, 9 H), 1.22 (MeC, d, 3 H, J 8.0 Hz), 3.62 (MeO, s, 3 H), 7.2–7.6 (ring protons, m)
V	0.12 (Me_3Si , s, 9 H), 1.72 (CH_3 and CH_2 , broad s, 10 H), 7.2–7.5 (ring protons, m, 5 H)
VI	0.12 (Me_3Si , s, 9 H), 1.53 (CH_2 , broad s, 2 H), 1.60 ($\text{Me}_2\text{C=C}$, broad s, 6 H), 1.89 (MeC=C , broad s, 3 H), 3.47 (MeO, s, 3 H), 7.2–7.5 (ring protons, m, 5 H)
VII	0.13 (Me_3Si , s, 9 H), 1.05 (MeCH, broad d, J 7 Hz), 1.70 (MeC=C , broad s, 3 H), 2.35 (HC, m, 1 H), 3.48 (MeO, s, 2 H), 7.2–7.5 (ring protons, m, 5 H)
VIII	0.17 (Me_3Si , s, 9 H), 0.20 (Me_3Si , s, 9 H), 0.37 ($\text{Me}_3\text{SiC}_6\text{H}_4$, s, 9 H), 1.05 (Me—CH, d, 3 H, J 7 Hz), 1.43 ($\text{CH}_2\text{—Si}$, d, 2 H, J 7 Hz), 1.73 (MeC=C , broad s, 3 H), 2.2–2.6 (CH, m, 1 H), 4.57 (HC=C , broad s, 1 H), 4.66 (HC=C , broad s, 1 H), 7.0–7.6 (ring protons, m, 4 H)
IXa	0.14 and 0.17 (Me_3Si , s, 9 H, ratio of the diastereomers = 2 : 1 respectively), 1.1–1.9 ($(\text{CH}_2)_4$, m, 8 H), 1.9–2.5 (allylic protons, m, 3 H), 3.54 and 3.51 (MeO, s, 3 H, ratio 2 : 1), 5.3–5.8 (vinyl protons, m, 2 H), 7.2–7.6 (C_6H_5 , m, 5 H)
IXb	0.18 (Me_3Si , s, 9 H), 1.0–1.9 ($(\text{CH}_2)_3\text{CHSi}$, m, 7 H), 1.9–2.5 (allylic protons, m, 4 H), 3.53 (MeO, s, 3 H), 5.54 (CH=CH , m, 2 H), 7.2–7.5 (C_6H_5 , m, 5 H)
X	0.20 (Me_3Si , s, 9 H), 0.22 (Me_3Si , s, 9 H), 0.38 ($\text{Me}_3\text{SiC}_6\text{H}_4$, s, 9 H), 1.3–2.5 (cyclo-octenyl ring, m, 13 H), 5.3–5.9 (CH=CH , m, 2 H), 7.0–7.6 (C_6H_4 , m, 4 H)
XIa	–0.09 (Me_3Si , s, 9 H), 1.2–1.6 (CH_2 at C-3 and C-4, m, 4 H), 1.6–1.9 (CH_2 at C-2 and C-5, m, 4 H), 2.08 (HCSi, m, 2 H), 6.00 (CH=CH , m, 2 H), 7.2–7.4 (ring protons, m, 5 H)
XIb	0.11 (Me_3Si , s, 9 H), 1.4–2.0 (ring methylenes, m, 8 H), 2.16 (HCSi, m, 2 H), 5.87 (HC=CH , m, 2 H), 7.1–7.3 (ring protons, m, 5 H)

^a In deuterobenzene. ^b Mixture of diastereomeric isomers (A and B) in a ratio of 52/48.

photolysis of I in the presence of 2,3-dimethylbutadiene. As can be seen there, the alkenylsilacyclopropane (D) determined as methanolysis products, VI and VII, forms slightly faster than silacyclopentene V. The amounts of VI and VII in the system level off after about 2 h, then decrease with time, whereas the amount of V continues to increase, showing that V comes from photoisomerization of the alkenyl-substituted silacyclopropane. That the ratio of silacyclopentene V to methoxysilanes VI and VII does not depend on the reaction temperature was confirmed by low temperature photolysis. Thus, a hexane solution of I in the presence of 2,3-dimethylbutadiene was photolyzed at -70°C

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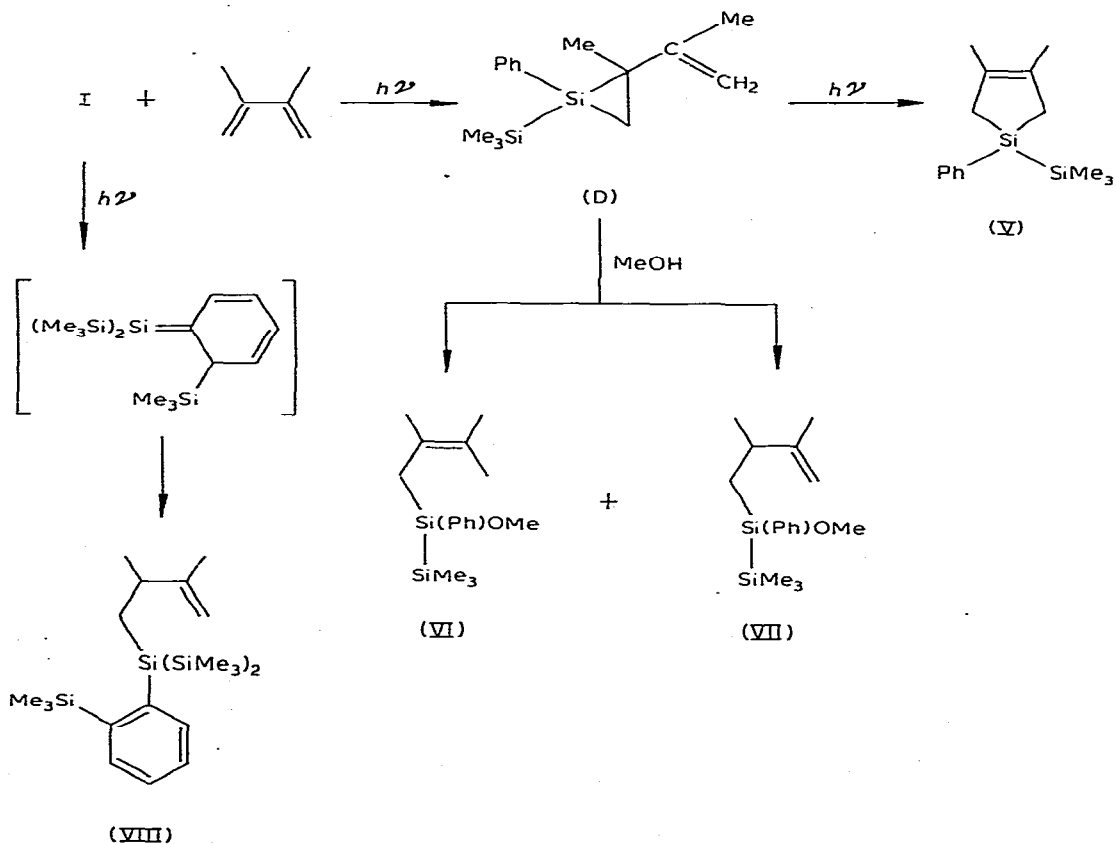
TABLE 3

ELEMENTAL ANALYSIS, MASS AND IR DATA FOR ISOLATED COMPOUNDS

Compound		Found (calcd.) (%)		IR (cm ⁻¹)	M ⁺
		C	H		
IIa	C ₁₄ H ₂₆ OSi ₂	62.94 (63.09)	9.93 (9.83)	1085	266
IIb	C ₁₃ H ₂₂ Si ₂	66.48 (66.59)	9.69 (9.46)	2090	234
IIc	C ₁₃ H ₂₂ Si ₂	66.48 (66.59)	9.66 (9.46)	2090	234
IIIa	C ₁₄ H ₂₆ OSi ₂	62.99 (63.09)	9.78 (9.83)	1080	266
IIIc	C ₁₃ H ₂₂ Si ₂	234.1262 (234.1260) ^a		2090	
IIId	C ₁₃ H ₂₂ Si ₂	66.66 (66.59)	9.72 (9.46)	2090	234
IVa	C ₁₅ H ₃₀ OSi ₃	57.70 (57.99)	9.75 (9.73)	1085	310
IVb	C ₁₅ H ₃₀ OSi ₃	58.39 (57.99)	10.03 (9.73)	1090	310
V	C ₁₅ H ₂₄ Si ₂	68.89 (69.15)	9.49 (9.29)		260
VI	C ₁₆ H ₂₈ OSi ₂	65.32 (65.69)	10.01 (9.65)	1080	292
VII	C ₁₆ H ₂₈ OSi ₂	65.46 (65.69)	9.64 (9.65)	1080	292
VIII	C ₂₁ H ₄₂ Si ₄	406.2377 (406.2364) ^a			
IXa	C ₁₈ H ₃₀ OSi ₂	67.74 (67.86)	9.65 (9.49)	1080	318
IXb	C ₁₈ H ₃₀ OSi ₂	67.56 (67.86)	9.62 (9.49)	1080	318
X	C ₂₃ H ₄₄ Si ₄	432.2520 (432.2520) ^a			
XIa	C ₁₇ H ₂₆ Si ₂	286.1569 (286.1573) ^a			
XIb	C ₁₇ H ₂₆ Si ₂	71.16 (71.25)	9.30 (9.15)		286

^a Exact molecular weight.

Scheme 3



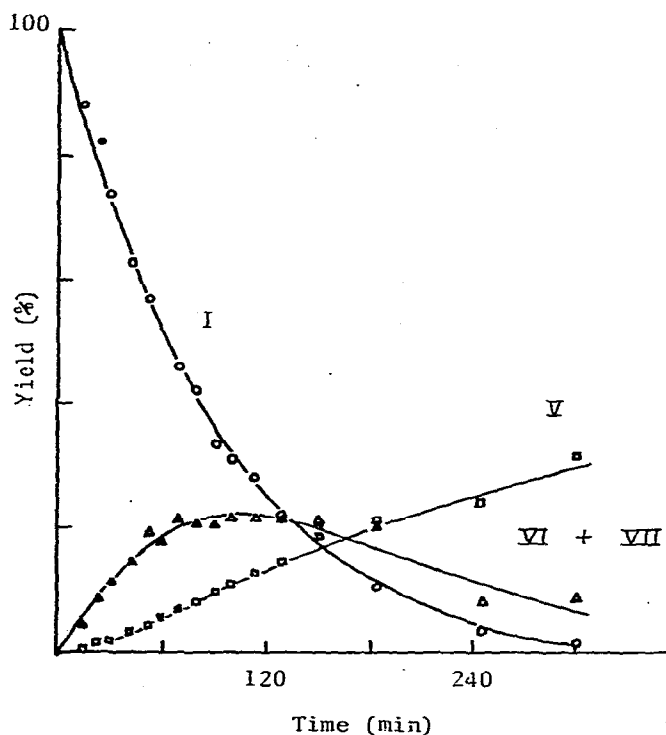
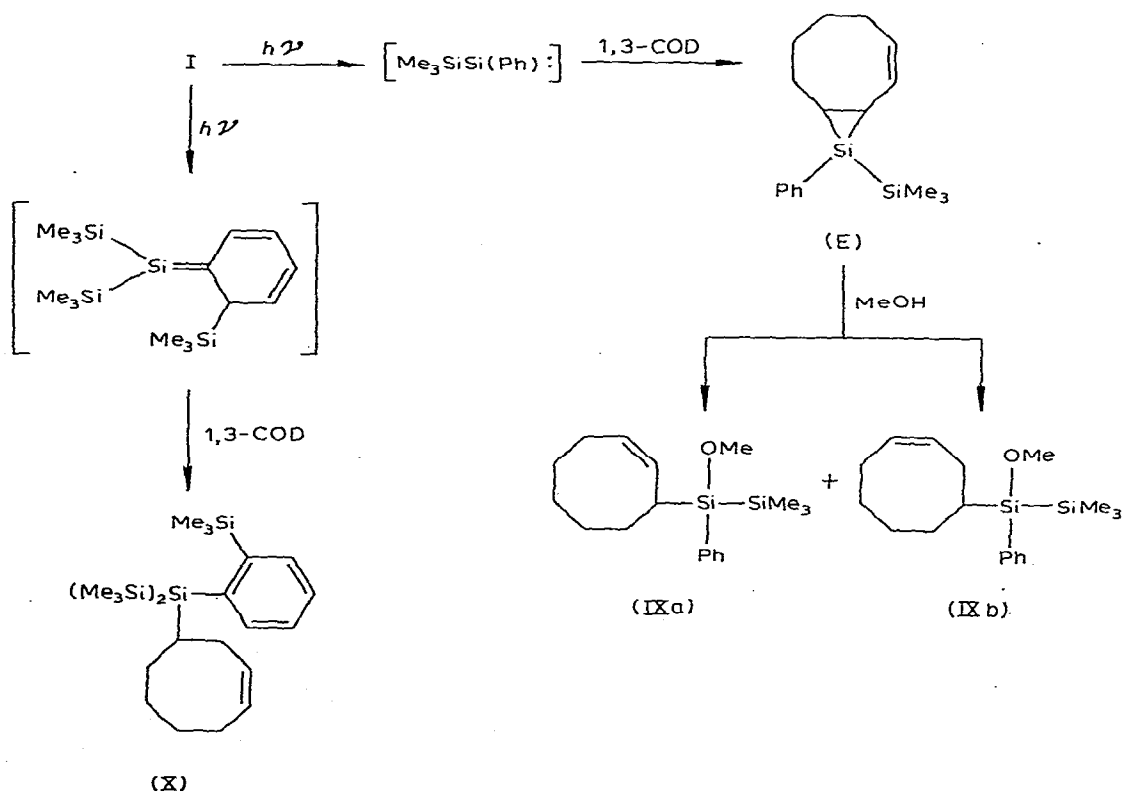


Fig. 1. Photolysis of tris(trimethylsilyl)phenylsilane (I) in the presence of 2,3-dimethylbutadiene.

Scheme 4



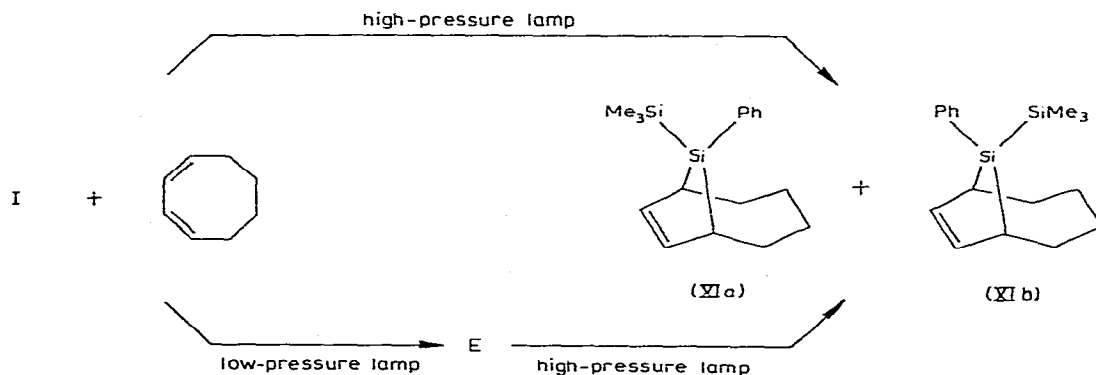
for 6.5 h. At this stage, 86% of the starting I was photolyzed. Treatment of the resulting solution with dry methanol at the same temperature afforded V, VI and VII in 20, 8 and 6% yield, respectively.

Interestingly, the present silylene added to 1,3-cyclooctadiene (1,3-COD) to give 9-phenyl-9-trimethylsilyl-9-silabicyclo[6.1.0]nona-2-ene (E) as the sole silylene insertion product which could be trapped as methoxysilanes IXa and IXb in 16 and 8% yield, respectively, by treatment of the resulting photolysis product with dry methanol (Scheme 4). In this photolysis, compound X derived from the reaction of a silicon-carbon double-bonded intermediate [12,13] with 1,3-cyclooctadiene was also produced in 16% yield. The structure of X was identified by its mass and ^1H NMR spectra. The location of the silyl group on the cyclooctenyl ring of compound X was confirmed by the well-known test that follows. Treatment of X with trifluoroacetic acid in carbon tetrachloride gave none of the cyclooctene, indicating that the silyl group is not located on the allylic carbon atom in the ring. The silyl group on an allylic carbon atom can readily be cleaved under the conditions used [6,14].

The reaction of thermally generated silylene species with cyclic 1,3-dienes has been reported [15,16]. In these reactions, the ring-expanded compounds expected from 1,2-adducts were obtained.

In order to obtain direct evidence for the transformation of a 1,2-adduct, which is always assumed as an initial product in the reaction of the silylenes with a conjugated diene, into the 1,4-isomer, we examined the photolysis and thermolysis of the silabicyclonona-2-ene (E).

Prior to these experiments, we carried out the photolysis of I in the presence of 1,3-cyclooctadiene using a high-pressure mercury lamp. Thus, a hexane solution of I was irradiated in the presence of 10-fold excess of 1,3-cyclooctadiene with a 100-W high-pressure mercury lamp bearing a quartz filter. Two isomers of 9-phenyl-9-trimethylsilyl-9-silabicyclo[4.2.1]nona-7-ene (XIa and XIb) were obtained in 5 and 13% yield as the volatile product. The structures of both isomers were determined by mass and ^1H NMR spectroscopic analyses. The ^1H NMR spectrum of one isomer showed an upfield shift for trimethylsilyl protons and methylene protons at C-3 and C-4 atoms due to the shielding effects of the olefinic group and the phenyl ring, respectively. Irradiation of the methine protons in this isomer changed the multiplet signal of the olefinic protons at δ 6.00 into a sharp singlet. Therefore we assign this isomer to XIa and the other to XIb.



Next we carried out the photolysis of silacyclopropane E. Irradiation of a hexane solution of E with a high-pressure mercury lamp gave XIa and XIb in a 39% combined yield. The results clearly indicate that the formal 1,4-adducts come from photoisomerization of E.

The thermolysis of E in a sealed glass tube at 200°C for 1 h resulted in the complete decomposition of the starting E; neither of compounds XIa and XIb nor 1-phenyl-1-trimethylsilyl-1-silacyclonona-2,8-diene could be detected by GLC and mass spectrometric analyses. Four compounds whose molecular ions appeared at 394, corresponding to $C_{25}H_{38}Si_2$, were produced. However, attempts to separate these products by preparative GLC were unsuccessful.

Experimental

General procedure

All photolyses were carried out under an atmosphere of purified nitrogen.

Proton NMR spectra were determined at ambient temperature with a JEOL Model JNM-MH-100 spectrometer using carbon tetrachloride solutions containing cyclohexane (δ 1.44 ppm) as an internal standard. Mass spectra were obtained on a JEOL Model JMS-D 300 equipped with a JMA-2000 data processing system. Ionizing 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" $\times$ 20' column containing Silicone DC 550 oil (30%) on Celite 545. Yields were determined by GLC using an internal standard on the basis of unrecovered tris(trimethylsilyl)phenylsilane.

Materials

1-Butene, *cis*- and *trans*-2-butene, isobutene were dried by passing the gases through a column containing $CaCl_2$ and silica gel. Trimethylvinylsilane, 2,3-dimethylbutadiene and 1,3-cyclooctadiene were dried over lithium aluminum hydride and distilled before use.

Preparation of tris(trimethylsilyl)phenylsilane (I)

In a 1-l three-necked flask fitted with a stirrer, reflux condenser and dropping funnel was placed 18 g (2.6 g-atom) of a finely cut lithium metal and 200 g (1.84 mol) of trimethylchlorosilane in 250 ml of THF. To this was added 84 g (0.40 mol) of phenyltrichlorosilane dissolved in 100 ml of THF over a period of 3 h at room temperature. The mixture was then refluxed for 3 h. The mixture was filtered to remove the unreacted lithium metal. Then the filtrate was hydrolyzed with water. The organic layer was separated and washed with water. The solvent was evaporated, and approximately 100 ml of acetone was added to the residue of the flask. The resulting crystalline by-products were filtered off, and the filtrate was dried over potassium carbonate. After evaporation of acetone, the residue was distilled under reduced pressure to give 19.0 g (15% yield) of white solid (I) [17], b.p. 135–137°C/3 Torr, m.p. 84–85°C; NMR (δ , ppm in deuterobenzene) 0.30 (Me_3Si , s) and 7.1–7.8 (ring protons, m).

Preparation of 1-(1'-phenyl-2',2',2'-trimethyldisilanyl)-2-methylpropene (IIb)

A THF solution of 2-methyl-1-propenylmagnesium bromide (2.0 mmol, 4.2 ml of 0.48 M) was added to 0.5 g (2.0 mmol) of 1,1-dichloro-1-phenyl-trimethyldisilane in 5 ml of dry THF with ice cooling. The mixture was stirred overnight at room temperature. It was added to 0.08 g of LiAlH_4 suspended in ether at 0°C and stirred at room temperature for half an hour. The mixture was hydrolyzed and the organic layer was dried over potassium carbonate. Distillation under reduced pressure gave 0.18 g (38% yield) of crude IIb, b.p. 105–120°C/15 Torr. Pure IIb was isolated by preparative GLC, n_D^{20} 1.5239.

Preparation of 3-(1'-phenyl-2',2',2'-trimethyldisilanyl)-2-methylpropene (IIc)

An ether solution of β -methallylmagnesium chloride (4.5 mmol) was added to 1.05 g (4.22 mmol) of 1,1-dichloro-1-phenyltrimethyldisilane in 10 ml of dry ether at –78°C. The mixture was stirred at room temperature for 1 h. It was then added to 0.20 g of LiAlH_4 in ether and stirred for 1 h at room temperature. After hydrolysis of the mixture, the organic layer was distilled under reduced pressure to give crude IIc. Pure IIc was isolated by preparative GLC, n_D^{20} 1.5236.

Photolysis of tris(trimethylsilyl)phenylsilane (I) in the presence of an olefin with a low-pressure mercury lamp

The following is typical of the procedures used. In a 100-ml reaction vessel fitted internally with a 10-W low-pressure mercury lamp (Fuji glass Co., Ltd.) having a Vycor filter was placed a solution of 1.0027 g (3.09 mmol) of I and 0.1011 g (0.359 mmol) of eicosane in 80 ml of dry hexane. To this solution, ca. 10 ml of dry isobutene was added through a nitrogen inlet tube. The solution was irradiated at 0°C for 2 h with a slow stream of nitrogen bubbling through the mixture. At this stage, GLC analysis of the mixture showed that 77% 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 was distilled off, and the residue was then analyzed by GLC. After distillation of the residue under reduced pressure, pure *tert*-butylphenyl(trimethylsilyl)methoxysilane (IIa) was isolated by preparative GLC. The reaction conditions and yields of the products obtained from the photolysis experiments are listed in Table 1.

Isolation of crude 1-trimethylsilyl-1-phenyl-2,2-dimethylsilacyclopropane (A)

A mixture of 0.6489 g (2.00 mmol) of I and ca. 10 ml of isobutene in 90 ml of dry hexane was irradiated for 5 h with a low-pressure mercury lamp as described above. After evaporating the hexane solvent and unchanged isobutene under reduced pressure (ca. 20 Torr), the residue was distilled to give a volatile product boiling up to ca. 120°C/2 Torr. The ^1H NMR spectrum of the distillate in deuterobenzene displayed signals at δ 0.21 (Me_3Si , s, 9 H), 0.67 and 0.96 (silacyclopropane ring protons, AB quart, 2 H, J_{gem} 9.5 Hz), 1.31 and 1.39 (Me_2C , broad s, 6 H), 7.1–7.7 (phenyl ring protons, m), in addition to resonances assignable to the starting I. Addition of 5 μl of dry methanol resulted in the disappearance of the signals at δ 0.21, 0.67, 0.96, 1.31 and 1.39, and the appearance of new signal at δ 0.29 (Me_3Si , s, 9 H), 1.11 (Me_2C , s, 9 H)

and 3.50 (MeO, s, 3 H). Chemical shifts of the new signals were identical with those of methoxysilane IIa in deutero benzene.

Photochemical rearrangement of silacyclopentane A to disilanyl-substituted alkenes

A hexane solution of 0.73 mmol of A prepared as above and 0.0898 g (0.318 mmol) of eicosane was irradiated with a 100-W high-pressure mercury lamp (Fuji glass Co., Ltd.) surrounded by a quartz cooling jacket for 3 h. At this stage, approximately 100% of the starting A was photolyzed. Most of the solvent was evaporated. The residue was analyzed by GLC as being 1-(1'-phenyl-2',2',2'-trimethyldisilanyl)-2-methylpropene (IIb) (13% yield) and 3-(1'-phenyl-2',2',2'-trimethyldisilanyl)-2-methylpropene (IIc) (10% yield). Pure IIb and IIc were isolated by preparative GLC as colorless liquids.

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

The following is typical of the procedures used. A solution of 0.9797 g (3.016 mmol) of I, 0.1570 g (0.695 mmol) of cetane and 1.44 g (17.6 mmol) of 2,3-dimethylbutadiene in 100 ml of dry hexane was irradiated at room temperature with a low-pressure mercury lamp for 2.7 h as described above. After the irradiation was stopped, 5 ml of dry methanol was added to the reaction mixture through the condenser by a syringe. After distilling off the hexane solvent and 2,3-dimethylbutadiene, the residue was analyzed by GLC as being 1-trimethylsilyl-1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene (V) (21% yield), 4-(1'-methoxy-1'-phenyltrimethyldisilanyl)-2,3-dimethyl-2-butene (VI) (13% yield), 4-(1'-methoxy-1'-phenyltrimethyldisilanyl)-2,3-dimethyl-1-butene (VII) (6% yield) and adduct VIII (8% yield). The products, V–VIII, were isolated by preparative GLC.

Plots of observed yields of the products against time for the photolysis of I in the presence of 2,3-dimethylbutadiene

A mixture of 0.9743 g (3.000 mmol) of I, 0.1182 g (0.558 mmol) of pentadecane and 2.618 g (31.9 mmol) of 2,3-dimethylbutadiene in 100 ml of dry hexane was irradiated at 0°C with a low-pressure mercury lamp bearing a Vycor filter. At suitable intervals small aliquots (ca. 0.2 ml) of the solution were extracted by a syringe and added to 0.1 ml of dry methanol under nitrogen atmosphere. The reaction products were analyzed by GLC. The results obtained are illustrated in Fig. 1.

Low temperature photolysis of I in the presence of 2,3-dimethylbutadiene

A mixture of 0.4479 g (1.38 mmol) of I, 1.2867 g (15.7 mmol) of 2,3-dimethylbutadiene and 0.0722 g (0.339 mmol) of pentadecane in 120 ml of hexane was irradiated with a low-pressure mercury lamp surrounded by a Vycor vacuum jacket for 6.5 h at -70°C. At this stage, 86% of I was photolyzed. After the irradiation was stopped, 1 ml of dry methanol was added to the photolysis mixture. The mixture was allowed to stand overnight, and then analyzed by GLC, as being silacyclopentene V (20% yield), methoxysilane VI (8% yield) and methoxysilane VII (6% yield).

Photochemical rearrangement of 9-trimethylsilyl-9-phenyl-9-silabicyclo[6.1.0]nona-2-ene (E)

A solution of 0.9732 g (3.00 mmol) of I, 0.1799 g (0.796 mmol) of cetane and 1.6770 g (15.52 mmol) of 1,3-cyclooctadiene in 100 ml of dry hexane was irradiated at room temperature for 5 h with a low-pressure mercury lamp having a Vycor filter. At this stage, 93% of the starting I was photolyzed. Treating a small aliquot (ca. 1 ml) of the solution, extracted from the photolysis vessel using a syringe, with methanol produced IXa and IXb, as determined by GLC. The amounts of IXa and IXb determined by analytical GLC were used to determine the yield (23%) of the 9-silabicyclo[6.1.0]nona-2-ene (E). The photolysis of a hexane solution containing 0.45 mmol of E with a high-pressure mercury lamp having a quartz filter for 1.5 h gave the photorearranged products, XIa and XIb, in a 39% combined yield, in a ratio of 1/2. After evaporating the hexane solvent, the residue was distilled under reduced pressure giving XIa and XIb. Pure XIa and XIb were isolated by preparative GLC.

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