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PHOTOLYSIS OF ORGANOPOLYSILANES. PHOTOCHEMICAL FORMATION AND REACTIONS OF 1-TRIMETHYLSILYL-1-PHENYL-1-SILACYCLOPROPENE DERIVATIVES *

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Summary

The photolysis of tris(trimethylsilyl)phenylsilane (I) in the presence of 1-hexyne, 3,3-dimethyl-1-butyne, trimethylsilylacetylene, 3-hexyne, 1-trimethylsilylpropyne, 1,2-bis(trimethylsilyl)acetylene and 2,2,5,5-tetramethyl-3-hexyne afforded the respective silacyclopropenes. The silacyclopropenes produced from monosubstituted acetylenes underwent photochemical isomerization to give disilanylacetylene derivatives, via a 1,2-hydrogen shift in the silacyclopropene ring. Irradiation of I in the presence of 3-hexyne, 1-trimethylsilylpropyne or 2,2,5,5-tetramethyl-3-hexyne gave the corresponding silacyclopropenes which could be isolated by preparative GLC. The silacyclopropene from 1,2-bis(trimethylsilyl)acetylene, however, readily underwent thermal rearrangement to give [bis(trimethylsilyl)phenylsilyl]trimethylsilylacetylene via a 1,2-trimethylsilyl shift. This type of rearrangement was also found in the photochemical process.

Introduction

The chemistry of silacyclopropenes has recently been developed by several research groups, and some of the silacyclopropenes have been isolated and characterized [1—5]. However, the chemical behavior of the silacyclopropenes is not as well understood as that of the cyclopropenes [6—10].

In 1970, we found that photolysis of cyclic and acyclic organopolysilanes affords a convenient route to divalent organosilicon intermediates [11]. We also reported that photochemically generated dimethylsilylene and methylphenylsilylene react with various olefins to give the silacyclopropanes [12,13].

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* For a preliminary communication see ref. 4.

However, all attempts to produce the silacyclopropenes by addition of these silylenes to the triple bond of alkynes were unsuccessful. We have now found that trimethylsilylphenylsilylene produced photochemically from tris(trimethylsilyl)phenylsilane adds to alkynes to give the silacyclopropenes. In this paper, we report the isolation and some reactions of the silacyclopropenes.

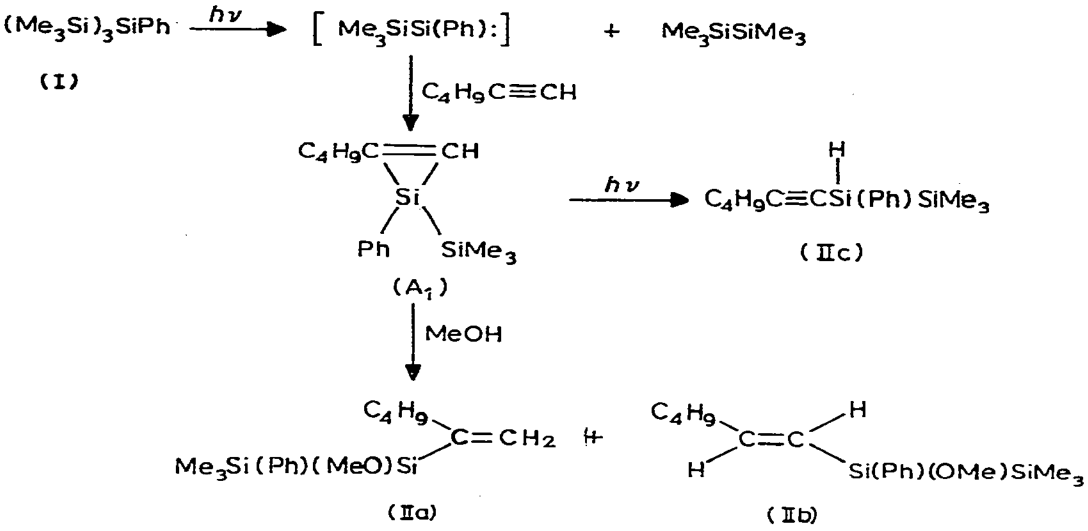
Results and discussion

Photolysis of tris(trimethylsilyl)phenylsilane in the presence of monosubstituted acetylenes

All of the silacyclopropenes produced from photolysis of tris(trimethylsilyl)-phenylsilane (I) in the presence of monosubstituted acetylenes were thermally unstable. Therefore, the GLC technique could not be used for determining directly the yields of the silacyclopropenes produced in the photochemical reactions. The silacyclopropenes always decomposed on the GLC column under the conditions used. For the purpose of estimating the yield, methanolysis was used and the resulting methoxysilanes were determined by GLC.

Irradiation of a hexane solution of I in the presence of 1-hexyne for 2 h produced a silacyclopropene (A_1). Treatment of this solution with dry methanol after irradiation was stopped afforded the two methoxysilanes to be expected from methanolysis of A_1, 2-(1′-methoxy-1′-phenyltrimethyldisilanyl)-1-hexene (IIa) and (*E*)-1-(1′-methoxy-1′-phenyltrimethyldisilanyl)-1-hexene (IIb) in 21 and 4% yield, respectively. The main product IIa was a methoxysilane arising from the scission of the less substituted silicon—carbon bond in the three-membered ring. In this photolysis, 1-(1′-phenyl-2′,2′,2′-trimethyldisilanyl)hexyne (IIc) derived from the photochemical isomerization of A_1, via a 1,2-hydrogen shift, also was obtained in 14% yield (Scheme 1). No other volatile products were detected by GLC analysis. Recently, we have reported such a photochemical 1,2-hydrogen migration in the photolysis of ethynyldisilane derivatives [14]. However, in the previous system, the silacyclopropene intermediates could not be detected by methanolysis of the photolysis mixture after irradiation was stopped.

In Fig. 1 the yields of the methoxysilanes IIa and IIb and the rearranged product IIc are plotted against time, which were obtained by treatment with methanol of the product from the photolysis of I in the presence of 1-hexyne. As can be seen from Fig. 1, methoxysilanes IIa and IIb are the only products in the early stage of the reaction. None of the rearranged product IIc can be observed. It is not until about 10 min. after irradiation with UV-light that IIc is formed in appreciable amount. The combined yield of IIa and IIb in the system passes through a maximum value (27%) after about 30 min and then decreases gradually to zero, whereas the yield of IIc continues to increase up to about 20%. These results clearly indicate that IIc is a secondary photoproduct arising from a 1,2-hydrogen shift in the silacyclopropene ring. Such a photochemical 1,2-hydrogen shift seems to be a general reaction for the compounds bearing hydrogen on the ring carbon atom in the silacyclopropene. Thus, photolysis of a hexane solution of I in the presence of 3,3-dimethyl-1-butyne, followed by methanolysis, afforded 2-(1′-methoxy-1′-phenyltrimethyldisilanyl)-3,3-dimethyl-1-butene (IIIa) derived from methanolysis of an initially formed sila-



SCHEME 1

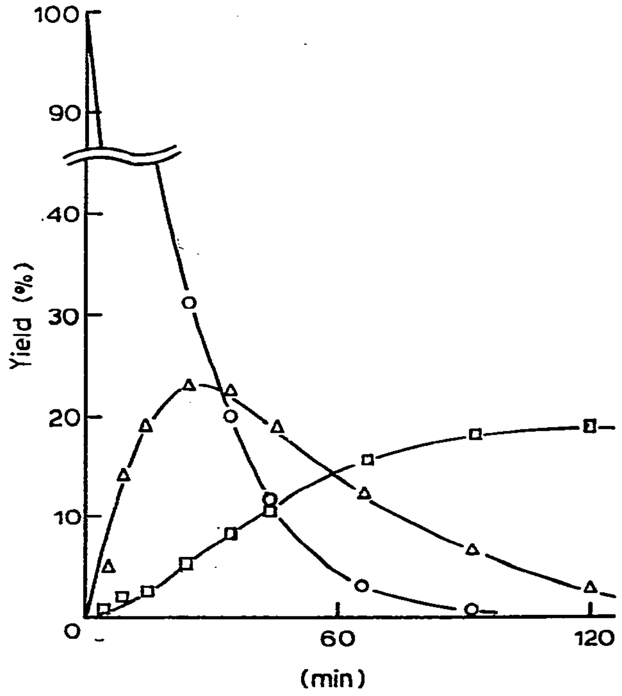
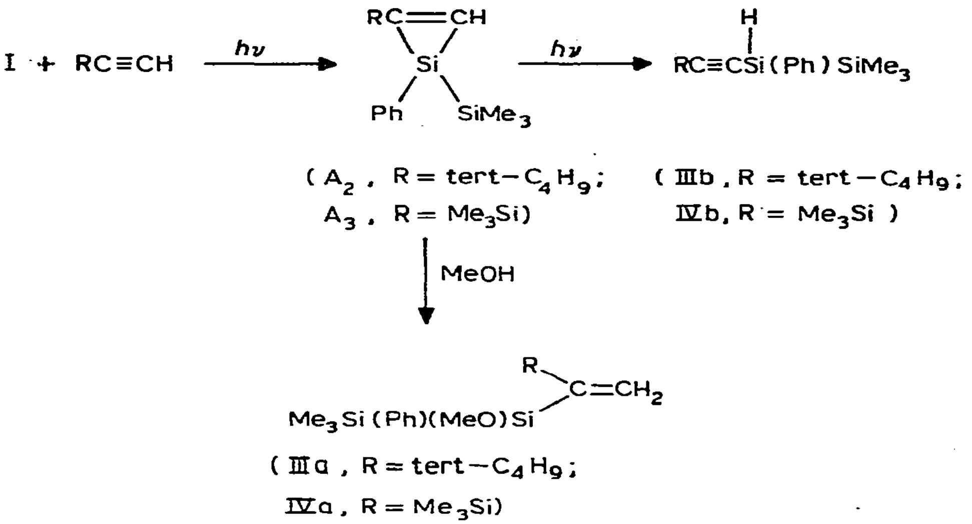


Fig. 1. Photolysis of tris(trimethylsilyl)phenylsilane (I) in the presence of 1-hexyne, followed by treatment with methanol, ○———○: I, △———△: IIa and IIb, □———□: IIc.

cyclopropene (A_2) and 1-(1′-phenyl-2′,2′,2′-trimethyldisilanyl)-3,3-dimethyl-1-butyne (IIIb) in 29 and 17% yield, respectively (Scheme 2).



SCHEME 2

Similar irradiation of I with trimethylsilylacetylene at 0°C and subsequent treatment with methanol produced trimethylsilyl(1′-phenyl-2′,2′,2′-trimethyldisilanyl)acetylene (IVb) in 40% yield, in addition to a 16% yield of 1-trimethylsilyl-1-(1′-methoxy-1′-phenyltrimethyldisilanyl)ethene (IVa). Again, no other volatile products were detected by GLC analysis. That IIIb and IVb are secondary photoproducts was also confirmed by monitoring the progress of the photolysis by GLC.

In order to learn whether or not such a 1,2-hydrogen shift in the silacyclopropene ring could involve a thermal process, we investigated the thermal behavior of silacyclopropene A_3 (Scheme 2). Thus, a hexane solution involving A_3 and IVb, prepared by photolysis of I in the presence of trimethylsilylacetylene, was allowed to stand for 4.5 h at 0°C. GLC analysis of the resulting solution showed that 50% of the silacyclopropene A_3 decomposed to give non-volatile substances, while the amount of IVb remained unchanged. This result clearly indicates that alkynyl-substituted disilanes IIc, IIIb and IVb must be produced by a photochemical process, but not thermal one. The formation of the silyl-substituted alkynes in the reaction of thermally generated silylene species with acetylene and propyne has been reported [15,16]. However, no chemical evidence for initial formation of silacyclopropenes was provided.

The reaction conditions and yields of the products are listed in Table 1, and the ^1H NMR, IR and mass spectral data and analytical results for the isolated compounds are shown in Tables 2 and 3.

Photolysis of I in the presence of disubstituted alkynes

It has also been found that the present silylene reacts with disubstituted

TABLE 1

PHOTOLYSIS OF TRIS(TRIMETHYLSILYL)PHENYLSILANE (I) IN THE PRESENCE OF ALKYNES [a]

I g (mmol)	Alkyne (mmol)	Time [b] (h)	Products and yields (%)	
			Methoxydisilane	Secondary product
1.003 (3.09)	$C_4H_9C{\equiv}CH$ (42)	2	IIa(21), IIb(4)	IIc(14)
0.325 (1.00)	tert-$C_4H_9C{\equiv}CH$ (9.2)	1.5	IIIa(29)	IIIb(17)
1.010 (3.11)	$Me_3SiC{\equiv}CH$ (42)	2	IVa(16)	IVb(40)
1.004 (3.09)	$C_2H_5C{\equiv}CC_2H_5$ (48)	2	Va(48)	Vb(3)
1.016 (3.11)	$Me_3SiC{\equiv}CMe$ (9.0)	2.5	VIa(26), VIb(7)	VIc(2), VId(2)
0.332 (1.02)	$Me_3SiC{\equiv}CSiMe_3$ (4.5)	1.2	VIIa(24)	VIIb(9)
1.000 (3.08)	tert-$C_4H_9C{\equiv}CC_4H_9$-tert (17.3)	2.5	B4(33)	—

[a] Dry methanol (3 ml) was added to the resulting photolysis mixture after irradiation was stopped. [b] Conversion of I was 80—90% in all experiments.

TABLE 2

PROTON NMR CHEMICAL SHIFTS FOR ISOLATED COMPOUNDS

Compound	Chemical shifts (δ, ppm) in CCl_4
IIa	0.14 (Me_3Si, s, 9H), 0.86(CH_3C, broad t, 3H), 1.32(CH_2CH_2, m, 4H), 2.11($CH_2C{=}C$, m, 2H), 3.48(CH_3O, s, 3H), 5.46(HC(H)=C, broad s, 1H), 5.78(HC(H)=C, broad s, 1H), 7.3—7.6 (ring protons, m, 5H).
IIb	0.11(Me_3Si, s, 9H), 0.94(CH_3C, m, 3H), 1.40(CH_2CH_2, m, 4H), 2.22($CH_2C{=}C$, m, 2H), 3.42(CH_3O, s, 3H), 5.76(HC(Si)=C, d, 1H, J = 19Hz), 6.22(HC=C(Si)H, ABX_2, 1H, J_{AX} = 6Hz), 7.2—7.6 (ring protons, m, 5H).
IIc	0.17(Me_3Si, s, 9H), 0.93(CH_3C, broad t, 3H), 1.54(CH_2CH_2, m, 4H), 2.33($CH_2C{\equiv}C$, m, 2H), 4.44(HSi, broad s, 1H), 7.2—7.6 (ring protons, m, 5H).
IIIa	0.15(Me_3Si, s, 9H), 1.08(Me_3C, s, 9H), 3.50(CH_3O, s, 3H), 5.36(HC(H)=C, AB_{quart}, 1H, J_{gem} = 1.6Hz), 5.83(HC(H)=C, AB_{quart}, J_{gem} = 1.6Hz), 7.2—7.5 (ring protons, m, 5H).
IIIb	0.15(Me_3Si, s, 9H), 1.29(Me_3C, s, 9H), 4.42(HSi, s, 1H), 7.2—7.6 (ring protons, m, 5H).
IVa	—0.02(Me_3Si, s, 9H), 0.15(Me_3Si, s, 9H), 3.50(CH_3O, s, 3H), 6.41(HC(H)C=C, AB_{quart}, J_{gem} = 5.0Hz), 6.49(HC(H)=C, AB_{quart}, J_{gem} = 5.0Hz), 7.2—7.6 (ring protons, m, 5H).
IVb	0.19(Me_3Si, s, 9H), 0.22(Me_3Si, s, 9H), 4.45(HSi, s, 1H), 7.3—7.6 (ring protons, m, 5H).
Va	0.15(Me_3Si, s, 9H), 0.88(CH_3C, t, 3H, J = 7.5Hz), 1.05(CH_3C, t, 3H, J = 7.5Hz), 2.02—2.37(CH_2, m, 4H), 3.48(CH_3O, s, 3H), 5.87 (HC=C, broad t, 1H), 7.3—7.6 (ring protons, m, 5H).
Vb	0.13(Me_3Si, s, 9H), 1.00(CH_3, t, 3H, J = 7Hz), 1.66($CH_3C{=}C$, d, 3H, J = 7Hz), 1.99(CH_2, m, 2H), 4.38(HSi, s, 1H), 4.79(HC=C, m, 1H), 7.2—7.5 (ring protons, m, 5H).
VIa	0.14(Me_3Si, s, 9H), 0.16(Me_3Si, s, 9H), 1.90(CH_3C, d, 3H, J = 1Hz), 3.48(CH_3O, s, 3H), 6.22(HC=C, q, 1H, J = 1Hz), 7.2—7.6 (ring protons, m, 5H).
VIb	—0.01(Me_3Si, s, 9H), 0.08(Me_3Si, s, 9H), 2.05(CH_3C, d, 3H, J = 6.5Hz), 3.50(CH_3O, s, 3H), 7.06(HC=C, q, 1H, J = 6.5Hz), 7.3—7.6 (ring protons, m, 5H).
VIc	0.07(Me_3Si, s, 9H), 0.17(Me_3Si, s, 9H), 4.00($CH_2C{=}C$, s, 2H), 4.41(HSi, s, 1H), 7.2—7.5 (ring protons, m, 5H).
VId	0.17(Me_3Si, s, 18H), 2.02(CH_3C, s, 3H), 7.2—7.5 (ring protons, m, 5H).
VIIa	0.04(Me_3Si, s, 9H), 0.13(Me_3Si, s, 9H), 0.24(Me_3Si, s, 9H), 3.50(CH_3O, s, 3H), 7.60(HC=C, s, 1H), 7.2—7.5 (ring protons, m, 5H).
VIIb	0.18(Me_3Si, s, 18H), 0.23(Me_3Si, s, 9H), 7.1—7.5 (ring protons, m, 5H).
VIII	0.09(Me_3Si, s, 9H), 1.15(Me_3C, s, 9H), 1.31(Me_3C, s, 9H), 3.55(CH_3O, s, 3H), 6.08(HC=C, s, 1H), 7.2—7.5 (ring protons, m, 5H).
IX	0.12(Me_3Si, s, 9H), 1.19(Me_3C, s, 9H), 1.32(Me_3C, s, 9H), 6.24(HC=C, s, 1H), 7.2—7.6 (ring protons, m, 5H).

TABLE 3

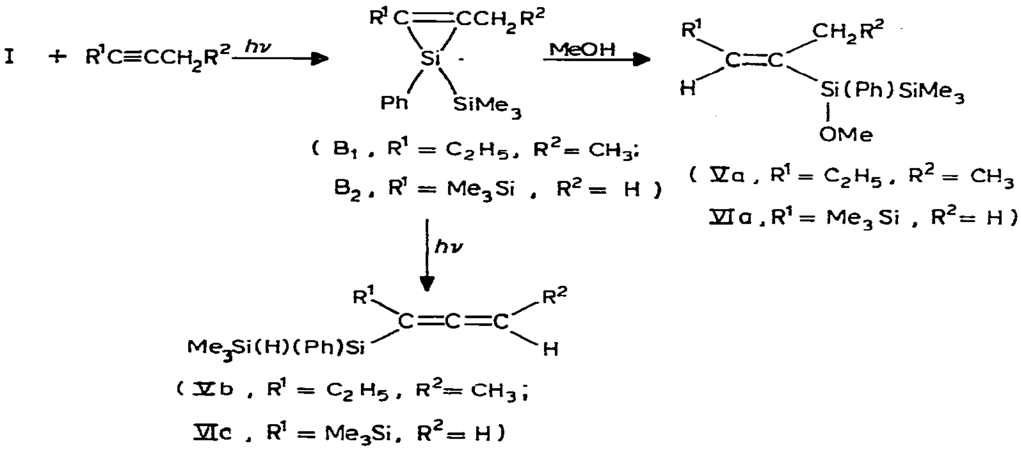
ELEMENTAL ANALYSES, REFRACTIVE INDICES, IR AND MASS SPECTRAL DATA FOR ISOLATED COMPOUNDS

Compound		Found (calcd.) (%)		n_D^{20}	IR (cm^{-1})	Mass (M^+)
		C	H			
IIa	$C_{16}H_{28}OSi_2$	65.69 (65.69)	9.93 (9.65)	1.5090	1080	292
IIb	$C_{16}H_{28}OSi_2$	—	—	—	1620	292.1705 (292.1679)
IIc	$C_{15}H_{24}Si_2$	69.10 (69.15)	9.57 (9.29)	1.5172	2170, 2110	260
IIIa	$C_{16}H_{28}OSi_2$	65.39 (65.69)	9.87 (9.65)	1.5182	1080	292
IIIb	$C_{15}H_{24}Si_2$	—	—	1.5042	2160, 2110	260.1411 (260.1417)
IVa	$C_{15}H_{28}OSi_3$	58.11 (58.37)	9.31 (9.14)	1.5100	1080	308
IVb	$C_{14}H_{24}Si_3$	60.98 (60.79)	8.89 (8.75)	1.5095	2100	276
Va	$C_{16}H_{28}OSi_2$	65.68 (65.69)	9.83 (9.65)	1.5138	1080	292
Vb	$C_{15}H_{24}Si_2$	—	—	—	1935, 2090	260.1380 (260.1417)
VIa	$C_{16}H_{30}OSi_3$	59.32 (59.56)	9.53 (9.37)	1.5090	1080	322
VIb	$C_{16}H_{30}OSi_3$	59.35 (59.56)	9.53 (9.37)	1.5179	1080	322
VIc	$C_{15}H_{26}Si_3$	—	—	—	1935, 2090	290.1379 (290.1342)
VId	$C_{15}H_{26}Si_3$	—	—	—	2108	290.1330 (290.1342)
VIIa	$C_{18}H_{36}OSi_4$	56.87 (56.77)	9.46 (9.53)	1.5136	1080	365 [a]
VIIb	$C_{17}H_{32}Si_4$	58.77 (58.54)	9.51 (9.25)	1.5131	2090	348
VIII	$C_{20}H_{36}OSi_2$	68.64 (68.89)	10.41 (10.41)	1.5169	1080	348
IX	$C_{19}H_{33}ClSi_2$ [b]	64.39 (64.63)	9.42 (9.42)	—	515, 1560	452

[a] M—15. [b] %Cl, Found: 9.90, calcd.: 10.04.

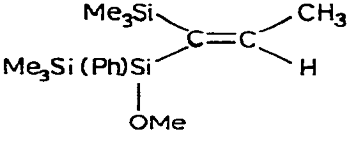
acetylenes such as 3-hexyne, 1-trimethylsilylpropyne, bis(trimethylsilyl)acetylene and 2,2,5,5-tetramethyl-3-hexyne to give the respective silacyclopropenes. The silacyclopropenes thus formed, with the exception of 1,2,3-tris(trimethylsilyl)-1-phenyl-1-silacyclopropene, could be distilled under reduced pressure without decomposition. Thus, photolysis of a hexane solution of I in the presence of 3-hexyne for 2 h gave a silacyclopropene (B_1) (Scheme 3). Treatment of this solution with dry methanol afforded 3-(1′-methoxy-1′-phenyltrimethyldisilanyl)-3-hexene (Va) in 48% yield, in addition to a trace of 4-(1′-phenyl-2′,2′,2′-trimethyldisilanyl)-2,3-hexadiene (Vb) and 10% of unchanged I. In contrast to silacyclopropene A's, compound B_1 is thermally stable and can be detected directly by GLC. Therefore we could isolate it in a pure form by distillation of the photolysis product, followed by preparative GLC. The structure of B_1 was confirmed by its ^1H NMR spectrum [δ (ppm) 0.30 (Me_3Si, s, 9H), 1.19 (CH_3C, t, 6H, $J = 7$ Hz), 2.12 (CH_2, q, 4H, $J = 7$ Hz) and 7.3—7.7 (ring protons, m)] and its exact parent peak (Found: m/e 260.1397. $C_{15}H_{24}Si_2$ calcd.: 260.1417). Silacyclopropene B_1 underwent isomerization upon irradiating with UV-light to give the rearranged product Vb, via a 1,3-hydrogen shift from the methylene carbon to the ring silicon atom in a good yield. A photochemical 1,3-hydrogen shift is always observed in the photolysis of silacyclopropanes, as reported previously [13].

Similar photolysis of I in the presence of 1-trimethylsilylpropyne produced, after subsequent treatment of the photolysis product with methanol, two

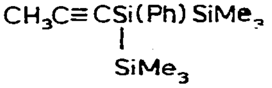


SCHEME 3

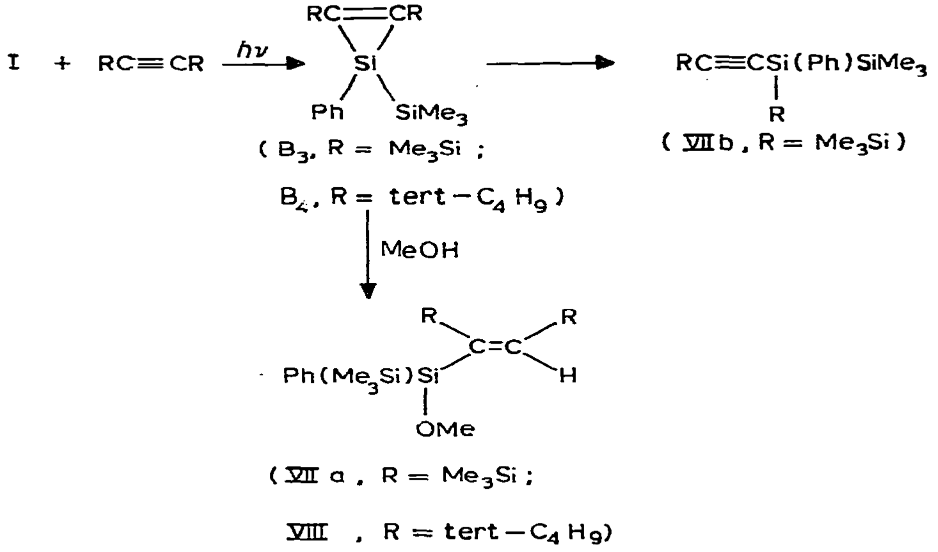
methoxysilanes, 1-trimethylsilyl-2-(1′-methoxy-1′-phenyltrimethyldisilanyl)-propene (VIa) and 1-trimethylsilyl-1-(1′-methoxy-1′-phenyltrimethyldisilanyl)-propene (VIb) in 26 and 7% yield, respectively. In this case, small amounts of two other compounds, 1-trimethylsilyl-1-(1′-phenyl-2′,2′,2′-trimethyldisilanyl)propadiene (VIc) (2% yield) arising from a 1,3-hydrogen shift of the initially formed silacyclopropene (B_2) and 1-bis(trimethylsilyl)phenylsilylpropyne (VId) (2% yield), were also obtained. Formation of the latter compound can be best explained in terms of another type of photochemical migration involving a 1,2-trimethylsilyl shift from carbon to the silicon atom in the three-membered ring. Attempts to isolate the silacyclopropene B_2 through the same preparative GLC column as that used for effective separation of B_1 failed. The ^{1}H NMR spectrum of a reaction mixture containing I, VIc and VId, however, gave a clear indication of B_2 [δ (ppm) 0.31 (Me_3Si, s, 18H), 2.42 (CH_3C, s, 3H) and 7.1—7.7 (ring protons, m)]. The GLC mass spectrometric analysis of crude B_2 showed an exact parent peak at 290.1328 (calcd.: 290.1342). A photochemical 1,2-silyl shift is also observed in the photolysis of I in the presence of bis(trimethylsilyl)acetylene. Thus, irradiation of I in the presence of a 4-fold excess of bis(trimethylsilyl)acetylene, followed by treatment with methanol gave two products in 24 and 9% yield, respectively. The main product was identified as 1,2-bis(trimethylsilyl)-1-(1′-methoxy-1′-phenyltrimethyldisilanyl)ethene (VIIa) produced from the methanolysis of a silacyclopropene (B_3), and the minor one was [bis(trimethylsilyl)phenylsilyl]trimethylsilylacetylene (VIIb) arising from isomerization of B_3 involving a 1,2-trimethylsilyl shift (Scheme 4). The fact that the ratio of VIIa to VIIb does not change in the low temperature photoly-



(VI b)


$CH_3C{\equiv}CSi(Ph)SiMe_3$ with $SiMe_3$ below the Si

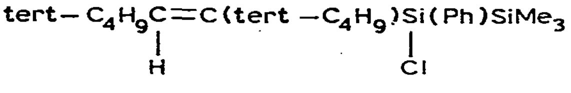
(VI d)



SCHEME 4

sis at —78°C indicates that VIIb must be produced by a photochemical process under the conditions used, not involving the thermal process. All attempts to isolate pure silacyclopropene B_3 under various conditions were unsuccessful because of its thermal instability. At high temperature, B_3 readily underwent thermal rearrangement to give VIIb. Attempts to isolate B_3 using preparative GLC (160°C) always afforded the rearranged product VIIb, although a yield of B_3 determined by analytical GLC was identical with that of methanolysis product VIIa. Thermal rearrangement of B_3 to VIIb could also be observed during distillation of the photolysis mixture under reduced pressure. Always, different ratios of B_3/VIIb were obtained before and after distillation of the product. The GLC mass spectrometric analysis of the distillate indicated an exact parent peak of B_3 at 348.1568, corresponding to the calculated molecular weight. When B_3 was heated in a sealed glass tube for 2 h at 200°C, the quantitative transformation of B_3 into VIIb was observed. None of the 1,4-disilacyclohexa-2,5-diene was detected by spectroscopic analysis.

Interestingly, the methanolysis of B_3 is very slow. The reaction rate was followed by GLC analysis using an internal standard method. The reaction of B_3 with a 50-fold excess of methanol in hexane solution for 30 min gave VIIa only in 42% yield, with 52% of B_3 remaining unchanged. The complete tranformation into VIIa was observed after 2 h. These results suggested that the introduction of the bulky groups onto the carbon atoms in the silacyclopropene ring would produce kinetically stable compounds. Therefore, we carried out the photolysis of I in the presence of 2,2,5,5-tetramethyl-3-hexyne in the hope of obtaining a stable silacyclopropene. Indeed, photochemically generated trimethylsilylphenylsilylene reacted with 2,2,5,5-tetramethyl-3-hexyne to give a rather stable silacyclopropene (B_4) which could be separated by distillation under reduced pressure, followed by preparative GLC. The ^{1}H NMR spectrum of B_4 thus obtained displayed two sharp singlets at δ 0.34 and 1.34 ppm with relative intensities of 1/2 attributed to Me_3Si and Me_3C protons, respectively. Silacyclopropene B_4 is less susceptible to methanolysis than that of B_3. For example, the reaction of B_4 with a large excess of methanol in hexane for 15 h afforded 3-(1′-methoxy-1′-phenyltrimethyldisilanyl)-2,2,5,5-tetramethyl-3-hexene (VIII) in only 15% yield, with 65% of the starting B_4 being recovered unchanged. Surprisingly, when a hexane solution of B_4 was allowed to expose to air for 5 min, 30% of B_4 was recovered unchanged. Such anomalous behavior may be attributed to the presence of the bulky substitutents on the carbon atoms in the silacyclopropene ring. Hydrogen chloride gas, however, reacted readily with B_4 to give a ring-opened chlorosilane, 3-(1′-chloro-1′-phenyltrimethyldisilanyl)-2,2,5,5-tetramethyl-3-hexene (IX), quantitatively.



$$\text{tert}-C_4H_9\underset{\displaystyle H}{\underset{|}{C}}=C(\text{tert}-C_4H_9)\underset{\displaystyle Cl}{\underset{|}{Si}}(Ph)SiMe_3$$

(IX)

The UV spectrum of B_4 in cyclohexane showed characteristic absorptions at 247 and 268 nm. When the solution was exposed to air, the absorbances of both absorptions decreased gradually with increasing time and finally disappeared, with a new absorption appearing at 243 nm.

Experimental

All reactions were carried out under an atmosphere of nitrogen purified by a method of Meyer and Ronge [17]. Photolysis was performed using a 10-W low-pressure mercury lamp surrounded by a Vycor filter. Identification of the products by GLC was done by using two different columns (30% Silicone SE-30 on Celite 545 and 30% Apiezon grease on Celite 545). Yields were determined by GLC using an internal standard (pentadecane, cetane or eicosane) on the basis of unrecovered tris(trimethylsilyl)phenylsilane.

Proton NMR spectra of methoxysilanes and rearranged products were determined with a JEOL Model JNM-MH-100 spectrometer using carbon tetrachloride solutions containing cyclohexane as an internal standard. For silacyclopropenes deuterobenzene was used as a solvent. IR spectra of thin liquid films were determined by a Hitachi Model EPI-G3 grating spectrometer. 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 20 ft × 3/8 in column containing Silicone SE-30 (30%) on Chromosorb W.

Materials

3,3-Dimethyl-1-butyne [18], 2,2,5,5-tetramethyl-3-hexyne [19,20], trimethylsilylacetylene [21], 1-trimethylsilylpropyne [22], bis(trimethylsilyl)-acetylene [21] and tris(trimethylsilyl)phenylsilane [23,24] were prepared as reported in the literature.

Photolysis of tris(trimethylsilyl)phenylsilane (I) in the presence of alkynes

The following is typical of the procedures used. In a 100 ml reaction vessel fitted internally with a low-pressure mercury lamp was placed a solution of 1.00 g (3.09 mmol) of I [23], 3.42 g (42 mmol) of 1-hexyne and 0.107 g (0.50 mmol) of pentadecane in ca. 100 ml of dry hexane. The solution was irradiated for 2 h with a slow stream of nitrogen bubbling through the mixture with ice cooling. At this stage, 91% of I was photolyzed. After irradiation was stopped, 3 ml of dry methanol was added to the reaction mixture. The mixture was then analyzed by GLC as being 2-(1'-methoxy-1'-phenyltrimethyldisilanyl)-1-hexene (IIa) (21% yield), (*E*)-1-(1'-methoxy-1'-phenyltrimethyldisilanyl)-1-hexene (IIb) (4% yield) and 1-(1'-phenyl-2',2',2'-trimethyldisilanyl)hexyne (IIc) (14% yield). After distilling off the hexane solvent and 1-hexyne, the residue was distilled under reduced pressure to give IIa, IIb and IIc. Pure compounds (IIa—IIc) were isolated by preparative GLC. The reaction conditions and yields of the products are listed in Table 1.

Plots of observed yields of products against time for photolysis of I in the presence of 1-hexyne

A mixture of 0.325 g (1.00 mmol) of I, 0.429 g (5.32 mmol) of 1-hexyne and 0.0225 g (0.11 mmol) of pentadecane in 25 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 are illustrated in Fig. 1.

Photoisomerization of silacyclopropenes

The following is typical of the procedure used. A mixture of 0.3250 g (1.001 mmol) of I, 0.369 g (4.50 mmol) of 3-hexyne and 0.0235 g (0.111 mmol) of pentadecane as an internal standard in 25 ml of dry hexane was irradiated at 0°C for 2 h. At this stage, 99% of I was photolyzed. GLC analysis of the mixture using a glass column (Silicone DC QF-1) showed the presence of B_1 (19% yield) and allenic isomer VIb (7% yield). This solution was irradiated for an additional 1 h at 0°C. GLC analysis of the mixture indicated that the yields of B_1 and VIb were 13 and 10%, respectively.

Attempted thermal isomerization of A_3

A mixture of 0.3196 g (0.984 mmol) of I, 1.529 g (15.60 mmol) of trimethylsilylacetylene and 0.0518 g (0.244 mmol) of pentadecane as an internal standard in 25 ml of dry hexane was irradiated at 0°C for 30 min. After irradiation was stopped, a small aliquot (1 ml) was taken from the photolysis mixture by means of a syringe, and it was treated with 50 µl of methanol. The mixture was analyzed by GLC as being methoxysilane IVa (23% yield) and trimethylsilylethynyldisilane IVb (34% yield), in addition to 37% of the starting I. The mixture was allowed to stand for 4.5 h at the same temperature. It was then treated with methanol. GLC analysis of the reaction mixture showed the presence of IVa (12% yield) and IVb (35% yield).

Low-temperature photolysis of I in the presence of bis(trimethylsilyl)acetylene

A mixture of 1.027 g (3.16 mmol) of I, 2.067 g (11.9 mmol) of bis(trimethylsilyl)acetylene and 0.1055 g (0.37 mmol) of eicosane in 130 ml of hexane was irradiated with a low-pressure mercury lamp surrounded by a Vycor vacuum jacket for 6 h at —78° C. At this stage, 73% of I was photolyzed. After the irradiation was stopped, 2 ml of dry methanol was added to the reaction mixture through the condenser by a syringe. Then the mixture was warmed up to room temperature and allowed to stand overnight. The mixture was analyzed by GLC as being 1,2-bis(trimethylsilyl)-1-(1′-methoxy-1′-phenyltrimethyldisilanyl)ethene (VIIa) (22% yield) and [bis(trimethylsilyl)phenylsilyl]trimethylsilylacetylene (VIIb) (5% yield). The ratio of 22/5 was identical with that obtained from the photolysis at 0° C, when conversion of I was 73%.

Isolation of silacyclopropenes

The following is typical of the procedure used. A mixture of 1.00 g (3.08 mmol) of I, 2.390 g (17.3 mmol) of 2,2,5,5-tetramethyl-3-hexyne and 0.1165 g (0.52 mmol) of cetane as an internal standard in 100 ml of hexane was irradiated with a low-pressure mercury lamp for 2.5 h at room temperature. The reaction mixture was analyzed by GLC as being 1-trimethylsilyl-1-phenyl-2,3-di(tert-butyl)-1-silacyclopropene (B_4) (33% yield). The solvent hexane and 2,2,5,5-tetramethyl-3-hexyne were evaporated and the residue was distilled under reduced pressure to give crude B_4. Pure B_4 was isolated by preparative GLC (Silicone SE-30, 200° C) as colorless crystals, m.p. ca. 40° C. ^1H NMR (δ, ppm) 0.34 (Me_3Si, s, 9H), 1.31 (Me_3C, s, 18H) and 7.2—7.7 (ring protons, m); exact mass, Found: 316.2068. $C_{19}H_{32}Si_2$ calcd.: 316.2043.

Pyrolsysis of 1,2,3-tris(trimethylsilyl)-1-phenyl-1-silacyclopropene (B_3)

A mixture of 0.24 mmol of silacyclopropene B_3 containing 0.30 mmol of I and 0.11 mmol of [bis(trimethylsilyl)phenylsilyl]trimethylsilylacetylene was heated in a sealed glass tube at 200° C for 2 h. GLC analysis of the reaction product showed quantitative formation of VIIb. Pure VIIb was isolated by preparative GLC.

Reaction of 1-trimethylsilyl-1-phenyl-2,3-di(tert-butyl)-1-silacyclopropene (B_4) with hydrogen chloride

A mixture of 1.0001 g (3.08 mmol) of I, 1.1696 g (8.48 mmol) of 2,2,5,5-tetramethyl-3-hexyne and 0.1479 g (0.65 mmol) of cetane as an internal standard in 100 ml of dry hexane was irradiated for 2.5 h at room temperature. At this stage, GLC analysis of the mixture showed that 95% of I was photolyzed and 0.86 mmol (28% yield) of silacyclopropene B_4 was produced. Into this solution was passed dry hydrogen chloride admixed with nitrogen for 10 min. The solvent hexane was evaporated and the residue was analyzed by GLC as being 3-(1′-chloro-1′-phenyltrimethyldisilanyl)-2,2,5,5-tetramethyl-3-hexene (IX) (quantitatively). Pure IX was isolated by preparative GLC.

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