

PHOTOCHEMICALLY GENERATED SILICON—CARBON DOUBLE-BONDED INTERMEDIATES

VII*. A NEW ROUTE TO SILAETHENE DERIVATIVES FROM 1-ALKENYLDISILANES

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Summary

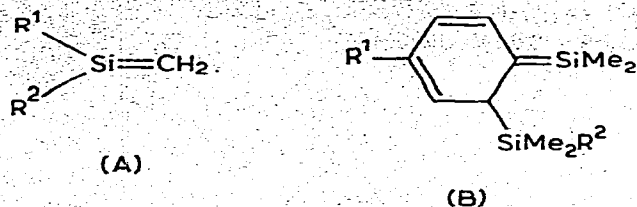
Photolysis of 1-alkenyldisilanes, with one exception, afforded silaethene type of silicon—carbon double-bonded intermediates via photorearrangement of a silyl group to the carbon atom of a vinyl substituent. These intermediates reacted with methanol and methanol- d_1 to give the corresponding methoxy-silanes in high yields. With *E*-2-phenylethenylpentamethyldisilane, UV-irradiation in the presence of methanol gave 1-methoxydimethylsilyl-1-trimethylsilyl-2-phenylethane and a novel photorearranged product, 1,1-dimethyl-2,3-benzo-5-trimethylsilyl-1-silacyclopentene, in addition to *E* and *Z* isomers of the starting substance. Irradiation of 1-phenyl-2-vinyltetramethyldisilane in the absence of a quencher led to dimerization of the silicon—carbon double-bonded intermediate to give *cis*- and *trans*-1,1,3,3-tetramethyl-2,4-bis(dimethylphenylsilylmethyl)-1,3-disilacyclobutane in moderate yield. The intermediate produced from 1-phenylethenylpentamethyldisilane reacted with both non-enolizable and enolizable ketones to give silyl-substituted olefins. With methyl vinyl ketone, however, [2 + 2] and [2 + 4] adducts were produced.

Introduction

Although the chemistry of silaethenes (A) generated thermally from silacyclobutanes has extensively been investigated [1], much less interest has been shown in the chemistry of photochemically generated silicon—carbon double-bonded intermediates [2–5]. In 1975 we initiated a systematic investigation into a novel type of silicon—carbon double-bonded intermediates (B) generated photo-

* For a preliminary communication see ref. 9; for Part VI, ref. 8.

chemically from aryldisilanes [6] and have shown that they are appreciably



different from silaethenes A in their mode of reaction with alkenes [6], conjugated dienes [7], alkynes [8] and carbonyl compounds [2]. Reasons for the different chemical behavior of intermediates B from that of A are probably not due to the difference in methods of generation, but are to be found largely in the following facts: (1) a great tendency of the intermediates B to stabilize themselves by restoring the aromatic sextet via addition to an unsaturated substrate with a simultaneous hydrogen shift from ring to substrate, and (2) the presence of a bulky substituent, such as a Me_3Si group, adjacent to the silicon-carbon double bond in B. With the aim of providing deeper insight into the nature of photochemically generated reactive silicon intermediates, we have now examined the photolysis of a variety of 1-alkenyldisilanes.

Results and discussion

The results obtained in the present study are summarized in Table 1. The refractive indices, melting points, and analytical and proton NMR data for isolated products are shown in Tables 2 and 3.

Photolysis of 1-alkenyldisilanes in the presence of methanol

The UV irradiation of 1,2-divinyltetramethyldisilane (Ia) in the presence of methanol in benzene with a low-pressure mercury lamp afforded a 1/1 adduct which was identified as 1-methoxydimethylsilyl-2-dimethylvinylsilylethane (IIa) in high yield. Similar photolysis of 1-phenylethenylpentamethyldisilane (Ib) in the presence of methanol gave 1-methoxydimethylsilyl-2-trimethylsilyl-1-phenylethane (IIb) in 43% yield, with 22% of unchanged Ib, while with methanol- d_1 as a quencher, under identical conditions, 1-deuterio-1-methoxydimethylsilyl-2-trimethylsilyl-1-phenylethane (IIc) was obtained in 47% yield as the sole volatile product, in addition to 6% of unchanged Ib. The isotopic purity of IIc was determined to be 80% from its ^1H NMR spectrum. The fact that the deuterium from methanol becomes bonded to the benzylic carbon atom substantiates that a silicon-carbon double-bonded intermediate (C) is formed transiently via a photochemical 1,3-shift of a silyl group to the carbon atom of a vinyl group. In the photolysis of 1-phenyl-2-vinyltetramethyldisilane (Ic) which contains both phenylsilyl and vinylsilyl groupings in the molecule, we find that the migration of a silyl group occurs exclusively to the vinylic carbon atom. Thus, irradiation of Ic with methanol afforded 1-methoxydimethylsilyl-2-phenyldimethylsilylethane (IIId) in 82% yield. Similarly, 1-phenyl-1-vinyltetramethyldisilane (Id) was converted upon photolysis in the presence of methanol into 1-methoxymethylphenylsilyl-2-trimethylsilylethane (IIe) in 57% yield, with 20% of unchanged Id. Again, no product arising from a 1,3-shift of

TABLE 1
PHOTOLYSIS OF ALKENYLDISILANE IN BENZENE

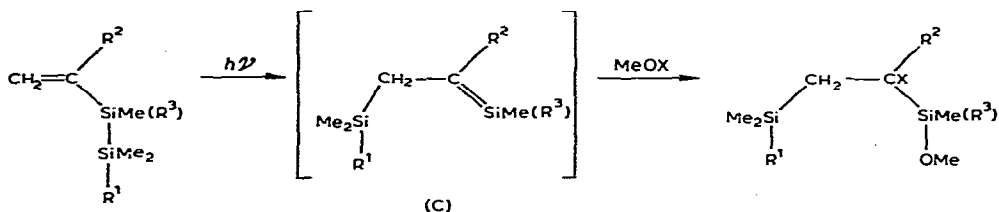
Disilane g (mmol)	Substrate g (mmol)	Time (h)	Products (yield (%))	Recovered disilane (%)
(CH ₂ =CHSiMe ₂) ₂ 0.959 (5.63)	MeOH 4.75 (148)	18	IIa (72)	17
CH ₂ =C(Ph)SiMe ₂ SiMe ₃ 1.054 (4.49)	MeOH 0.79 (25)	12	IIb (43)	22
CH ₂ =C(Ph)SiMe ₂ SiMe ₃ 0.610 (2.60)	MeOD 0.158 (4.94)	10	IIc (47)	6
CH ₂ =CHSiMe ₂ SiMe ₂ Ph 0.429 (1.94)	MeOH 0.317 (9.88)	1.5	II d (82)	18
CH ₂ =CHSiMe(Ph)SiMe ₃ 0.416 (1.89)	MeOH 0.317 (9.88)	1.5	IIe (57)	20
PhHC=CHSiMe ₂ SiMe ₃ 0.405 (1.73)	MeOH 1.58 (50)	22	Z-Ie, (15)	III, (17)
CH ₂ =CHSiMe ₂ SiMe ₂ Ph ^a 0.855 (3.88)	—	2	Va, (21)	IV (7)
CH ₂ =CHSiMe ₂ SiMe ₂ Ph ^b 0.979 (4.44)	—	2	VIc, (42)	Vb (10)
(CH ₂ =CHSiMe ₂) ₂ 0.919 (5.39)	H ₂ O 0.094 (5.33)	17	VIa, (11)	VIb (60)
CH ₂ =C(Ph)SiMe ₂ SiMe ₃ 1.033 (4.41)	Me ₂ C=O 0.279 (4.80)	15	VII (13)	29
CH ₂ =C(Ph)SiMe ₂ SiMe ₃ 0.983 (4.19)	PhCOMe 0.512 (4.26)	27	VIII (19)	17
CH ₂ =C(Ph)SiMe ₂ SiMe ₃ 0.960 (4.10)	Ph ₂ C=O 0.757 (4.15)	28	IX, (16)	X (16)
CH ₂ =C(Ph)SiMe ₂ SiMe ₃ 0.918 (3.91)	CH ₂ =CHCOMe 0.293 (4.17)	24	XI, (14)	XII (18)
CH ₂ =C(Ph)SiMe ₂ SiMe ₃ 0.974 (4.16)	CH ₂ =C(Me)C- (Me)=CH ₂ 0.509 (6.20)	18	XIII (27)	7

^a In n-hexane. ^b In insufficiently dried benzene.

the silyl group to the phenyl ring, followed by addition of methanol, was detected.

Interestingly, the irradiation of *E*-2-phenylethenylpentamethyldisilane (Ie) in the presence of methanol in benzene for 1 h gave an equilibrium mixture con-

SCHEME 1



(Ia) R¹ = CH₂=CH, R² = H, R³ = Me

(Ib) R¹ = R³ = Me, R² = Ph

(Ic) R¹ = Ph, R² = H, R³ = Me

(Id) R¹ = Me, R² = H, R³ = Ph

(IIa) R¹ = CH₂=CH, R² = H

R³ = Me, X = H

(IIb) R¹ = R³ = Me, R² = Ph, X = H

(IIc) R¹ = R³ = Me, R² = Ph, X = D

(IId) R¹ = Ph, R² = H, R³ = Me,

X = H

(IIe) R¹ = Me, R² = H, R³ = Ph,

X = H

TABLE 2
REFRACTIVE INDICES, MELTING POINTS AND ANALYTICAL DATA FOR ISOLATED PRODUCTS

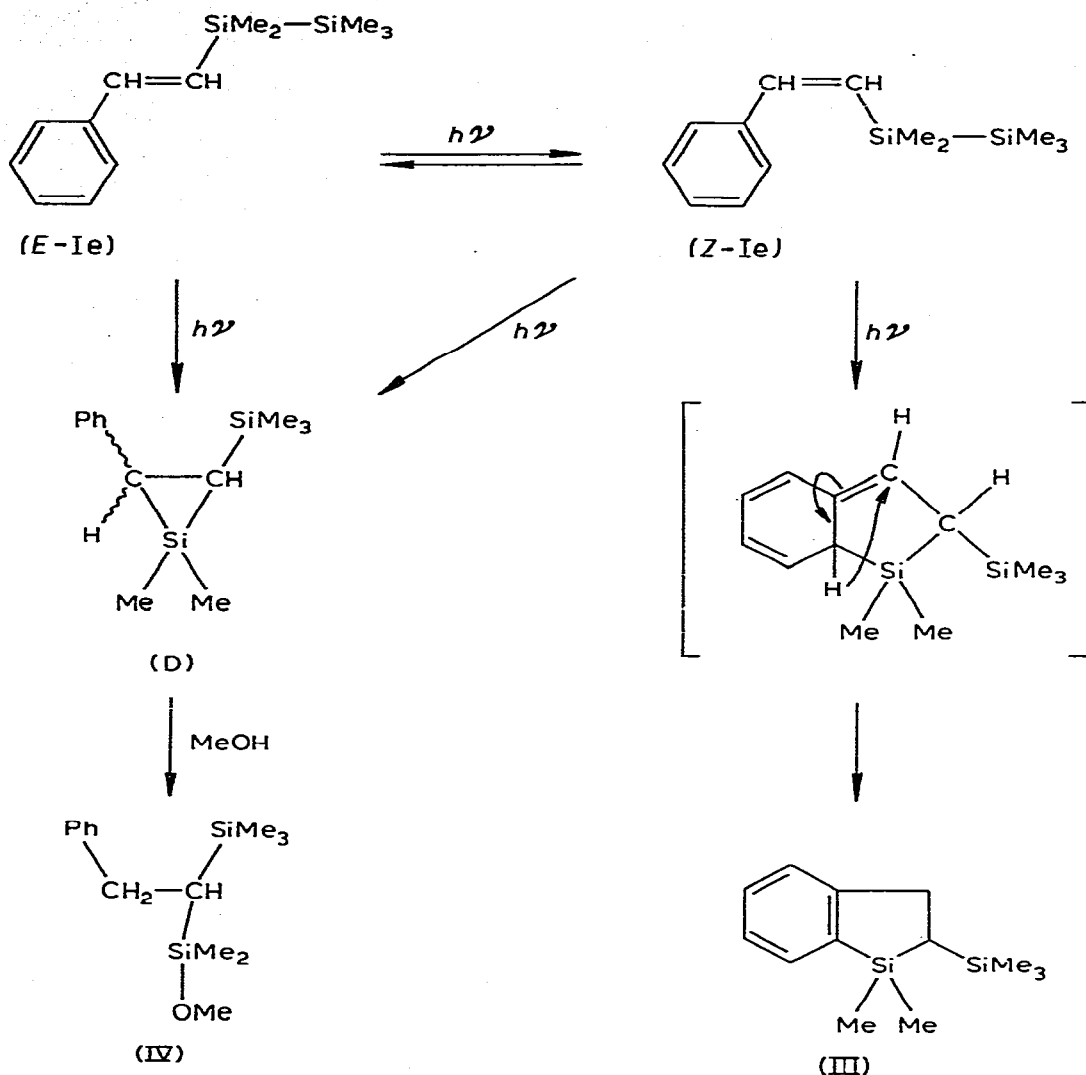
Product	n_D^{20}	M^+	Analysis (Found (calcd.) (%))	
			H	C
IIa	1.4353	202	10.66 (10.95)	53.51 (53.40)
IIb	1.4899	266	10.10 (9.83)	63.19 (63.09)
IIc	1.4889	252	9.60 (9.58)	61.76 (61.84)
IId	1.4856	252	9.66 (9.58)	61.67 (61.84)
IIe	1.4856	252	9.66 (9.58)	61.67 (61.84)
Z-Ie	1.5189	234	9.42 (9.46)	66.42 (66.59)
III	<i>b</i>	234	9.61 (9.46)	66.47 (66.59)
IV	<i>b</i>	266	9.76 (9.83)	63.25 (63.09)
Va (M.p. 50°C)		440	9.39 (9.14)	65.16 (65.38)
Vb (M.p. 45°C)		440	9.44 (9.14)	65.12 (65.38)
VIa	1.4503	188	10.92 (10.67)	53.83 (53.56)
VIb	1.4493	358	10.74 (10.70)	51.27 (51.00)
VII	<i>b</i>	218	10.35 (10.15)	76.40 (76.99)
VIII ^a	1.5535	280	8.75 (8.62)	81.57 (81.36)
IX (M.P. 111°C)		342	7.54 (7.65)	84.38 (84.15)
X ^a	<i>b</i>	416	7.73 (7.74)	74.82 (74.94)
XI ^a	<i>b</i>	230	9.88 (9.62)	77.37 (78.19)
XII	1.5207	304	9.48 (9.27)	66.77 (67.04)
XIII	1.5264	316	10.48 (10.19)	71.88 (72.07)

^a A mixture of *E* and *Z* isomers. ^b Not determined.

sisting of *E* and *Z* isomers in the ratio of 1.3/1. That the reaction reaches a true equilibrium was confirmed by the observation that about equal amounts of *E* and *Z* isomers also were obtained by the photolysis of the pure *Z* isomer. In this case, no product arising from the reaction of the silicon-carbon double-bonded intermediate with methanol could be observed at all. Instead, after prolonged irradiation of the solution two products were obtained in 17 and 7% yields, in addition to the *Z* (15% yield) and *E* (12% yield) isomers. The more abundant product was identified as 1,1-dimethyl-2,3-benzo-5-trimethylsilyl-1-silacyclopentene (III), a novel photo-rearranged product. Compound III was also produced in the photolysis of Ie in the absence of methanol. The minor product was 1-methoxydimethylsilyl-1-trimethylsilyl-2-phenylethane (IV) whose formation can be understood by considering the intermediary formation of a silacyclopropane derivative (D), followed by reaction with methanol. When methanol was used as solvent in this photolysis, IV was obtained in higher yield (14%), along with III in 11% yield. Sakurai et al. recently have reported that the photolysis of Ie in methanol gave IV in 5.9% yield, along with the *E* and *Z* isomers of the starting olefin [10]. However, they overlooked the novel photochemical pathway leading to compound III. The photochemical formation of a silicon-incorporated three-membered ring has been unambiguously established in recent photolysis studies of phenylethynylpentamethyldisilane [11].

The mechanism for the production of III in the prolonged photolysis of Ie is not fully understood at the present time, but is tentatively given in Scheme 2.

SCHEME 2



Photolysis of 1-phenyl-2-vinyltetramethyldisilane (Ic) in the absence of a quencher

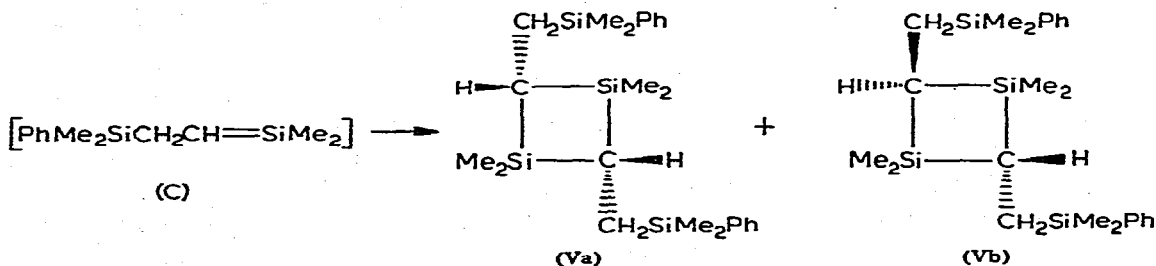
In a sharp contrast to the silicon-carbon double-bonded intermediates (B) produced from the photolysis of phenyl and *p*-tolylpentamethyldisilanes, which never afford any volatile products in the absence of a suitable substrate, the intermediate C derived from 1-phenyl-2-vinyltetramethyldisilane (Ic) has been found to undergo dimerization to give a head-to-tail dimer. Thus, when a solution of Ic in *n*-hexane was photolyzed for 2 h, *cis*- and *trans*-1,1,3,3-tetramethyl-2,4-bis(dimethylphenylsilylmethyl)-1,3-disilacyclobutane (Va and Vb) could be obtained in 21 and 22% yield, respectively.

The IR spectra of both the *cis*-Va and *trans*-Vb isomers showed a sharp band at 1050 cm^{-1} assignable to C-H deformation of the SiCHSi grouping, indicating

TABLE 3
¹H NMR DATA FOR ISOLATED PRODUCTS

Compound	Chemical shift from TMS in CCl ₄ (δ, ppm)
IIa	0.04 (MeSi, s, 12H), 0.47 (CH ₂ CH ₂ , s, 4H), 3.34 (MeO, s, 3H), 5.5–6.3 (vinylic protons, ABX, 3H)
IIb	–0.17 (Me ₃ Si, s, 9H), 0.05 (Me ₂ Si, s, 6H), 1.00 (CH ₂ , m, 2H), 2.19 (CH, dd, 1H), 3.35 (MeO, s, 3H), 6.9–7.3 (ring protons, m, 5H)
IIc	–0.17 (Me ₃ Si, s, 9H), 0.05 (Me ₂ Si, s, 6H), 1.02 (CH ₂ , m, 2H), 3.36 (MeO, s, 3H), 6.9–7.3 (ring protons, m, 5H)
IId	0.03 (Me ₂ Si, s, 6H), 0.25 (Me ₂ Si, s, 6H), 0.55 (CH ₂ CH ₂ , m, 4H), 3.33 (MeO, s, 3H), 7.2–7.5 (ring protons, m, 5H)
IIe	–0.01 (Me ₃ Si, s, 9H), 0.34 (MeSi, s, 3H), 0.58 (CH ₂ CH ₂ , m, 4H), 3.45 (MeO, s, 3H), 7.1–7.7 (ring protons, m, 5H)
Z-Ie	0.01 (Me ₃ Si, s, 9H), 0.08 (Me ₂ Si, s, 6H), 5.79 (vinylic proton, d, J 15 Hz, 1H), 7.23 (ring protons, s, 5H), 7.34 (vinylic proton, d, J 15 Hz, 1H)
III	0.07 (Me ₃ Si, s, 9H), 0.24 (MeSi, s, 3H), 0.32 (MeSi, s, 3H), 0.40 (CH, ABX, 1H), 3.05 (CH ₂ , ABX, 2H), 7.0–7.5 (ring protons, m, 4H)
IV	–0.06 (MeSi, s, 3H), –0.01 (Me ₃ Si, s, 9H), 0.03 (MeSi, s, 3H), 0.41 (CH, t, J 7 Hz, 1H), 2.26 (CH ₂ , d, J 7 Hz, 2H), 3.30 (MeO, s, 3H), 7.0–7.3 (ring protons, m, 5H)
Va	–0.03 (MeSi, s, 6H), –0.01 (MeSi, s, 6H), 0.06 (CH, t, J 7 Hz, 2H), 0.18 (Me ₂ Si, s, 12H), 0.71 (CH ₂ , d, J 7 Hz, 4H), 7.1–7.5 (ring protons, m, 10H)
Vb	–0.01 (Me ₂ Si, s, 12H), 0.18 (Me ₂ Si, s, 12H), 0.22 (CH, t, J 7 Hz, 2H), 0.79 (CH ₂ , d, J 7 Hz, 4H), 7.1–7.5 (ring protons, m, 10H)
VIa	0.05 (Me ₂ Si, s, 6H), 0.06 (Me ₂ Si, s, 6H), 1.66 (HO, s, 1H), 5.5–6.3 (vinylic protons, ABX, 3H)
VIb	0.03 (Me ₂ Si, s, 12H), 0.04 (Me ₂ Si, s, 12H), 0.43 (CH ₂ CH ₂ , s, 8H), 5.4–6.3 (vinylic protons, ABX, 6H)
VII	–0.18 (Me ₃ Si, s, 9H), 1.58 (Me, s, 3H), 1.74 (Me, s, 3H), 1.85 (CH ₂ , s, 2H), 6.9–7.3 (ring protons, m, 5H)
Z-VIII	–0.33 (Me ₃ Si, s), 1.78 (CH ₂ , s), 1.85 (CH ₃ , s)
E-VIII	–0.12 (Me ₃ Si, s), 2.07 (CH ₂ , s), 2.08 (CH ₃ , s), 6.7–7.5 (ring protons, m)
IX	–0.18 (Me ₃ Si, s, 9H), 2.04 (CH ₂ , s, 2H), 6.8–7.5 (ring protons, m, 15H)
E-X	–0.24 (Me ₃ Si, s), 0.07 (Me ₂ Si, s), 5.66 (CH, s), 6.34 (vinylic proton, s)
Z-X	–0.20 (Me ₃ Si, s), 0.14 (Me ₂ Si, s), 5.71 (CH, s), 6.36 (vinylic proton, s), 6.7–7.4 (ring protons, m)
XIa	–0.15 (Me ₃ Si, s, 9H), 1.73 (Me, s, 3H), 2.01 (CH ₂ , s, 2H), 4.73, 4.95, 6.32 (vinylic protons, ABX, 3H), 7.0–7.4 (ring protons, m, 5H)
XIb	–0.15 (Me ₃ Si, s, 9H), 1.66 (Me, s, 3H), 2.06 (CH ₂ , s, 2H), 5.00, 5.15, 6.75 (vinylic protons, ABX, 3H), 7.0–7.4 (ring protons, m, 5H)
XII	–0.28 (Me ₃ Si, s, 9H), –0.21 (MeSi, 3H), 0.29 (MeSi, s, 3H), 1.22 (CH ₂ , s, 2H), 1.74 (CH ₃ , s, 3H), 2.21 (CH, m, 1H), 2.77 (CH, m, 1H), 4.12 (vinylic proton, m, 1H), 6.9–7.3 (ring protons, m, 5H)
XIII	–0.28 (MeSi, s, 12H), 0.07 (MeSi, s, 3H), 1.09 (CH ₂ , bs, 2H), 1.18 (CH ₂ , AB, 2H), 1.74 (Me, bs, 6H), 2.51 (CH ₂ , bAB, 2H), 6.9–7.3 (ring protons, m, 5H)

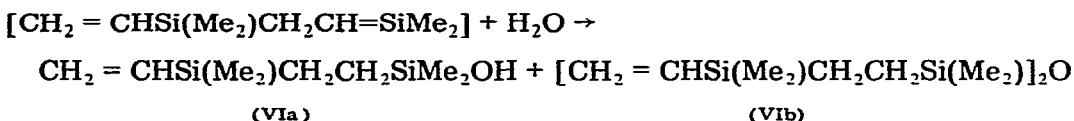
that these two must have the head-to-tail structure [12,13]. The assignment to *cis* and *trans* configuration could be made by means of ¹H NMR spectroscopy. Two different resonances of equal intensity from the protons of two different



CH₃-Si groups in the ring are found at δ -0.03 and -0.01 ppm for the *cis* isomer. On the other hand, the *trans* isomer shows a single CH₃-Si proton resonance at δ -0.01 ppm.

All attempts to prepare a 1,3-disilacyclobutane from either Ib or Id failed; always non-volatile products were obtained. Presumably, the bulky phenyl substituent on the unsaturated silicon or carbon atom prevents the [2 + 2] cycloaddition. Sommer and his coworkers have reported that photochemically generated diphenylsilaethene, Ph₂Si = CH₂, affords no [2 + 2] adduct in the absence of a quenching agent [6].

Unlike the intermediates of type B, the intermediates C react very readily with water producing adducts in high yields. For instance, the photolysis of Ia in the presence of approximately 1 molar equivalent of water yielded two compounds, (2-vinyldimethylsilylethyl)dimethylsilanol (VIa) and its condensation product VIb, in 11 and 60% yield, respectively. Therefore, a rigorously dried solvent had to be used for obtaining the dimeric products. Indeed, the photolysis of Ic in



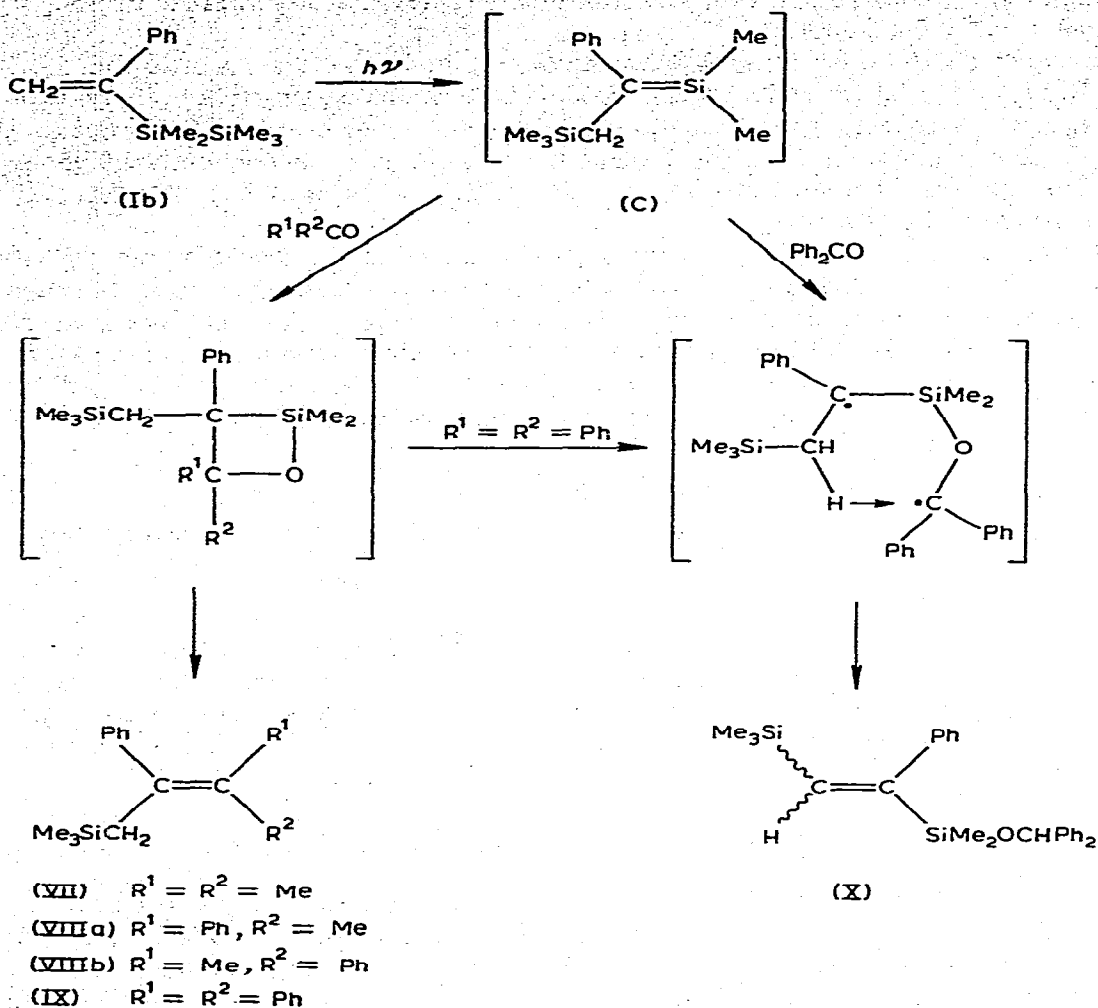
the absence of a substrate using an insufficiently dried solvent afforded only a low yield of the dimer, along with a large amount of the siloxane. Thus, irradiation of Ic in benzene used in the usual photolysis of arylsilylanes as solvent gave only 20% yield of a 1/1 mixture of the *cis*- and *trans*-1,3-silacyclobutane; production of the siloxane analogous to VIb amounted to 42% yield.

Photolysis of 1-phenylethenylpentamethyldisilane (Ib) in the presence of carbonyl compounds and dienes

Recently we reported that the photochemically generated silicon-carbon double-bonded intermediates from phenyl- and *p*-tolylpentamethyldisilane react with both enolizable and non-enolizable ketones in a different fashion than do the thermally generated silaethenes [18]. Therefore, it was of interest to examine the behavior of the intermediates C toward carbonyl compounds. With enolizable ketones such as acetone and acetophenone, it was found that a pseudo-Wittig reaction takes place, as in the case of the silaethene reaction, to give olefins. Thus, the photolysis of Ib in the presence of 1 molar equivalent of acetone afforded 1-trimethylsilyl-2-phenyl-3-methyl-2-butene (VII) in 13% yield as a single product. No silyl enol ether of the type to be expected to be formed in the reaction of the intermediate with the enol form of acetone was observed by GLC analysis. Similarly, irradiation of Ib with acetophenone gave *E*- and *Z*-1-trimethylsilyl-2,3-diphenyl-2-butene (VIIIa and VIIIb) in 8 and 11% yield, respectively. Again, no other volatile products were produced. However, with benzophenone unexpected adducts, *E*- and *Z*-1-benzhydroxydimethylsilyl-1-phenyl-2-trimethylsilylethene (X) (16% yield) in the ratio of 4/1, were obtained, together with 16% yield of an expected olefin (IX) as shown in Scheme 3.

In order to learn if the photo-excited triplet state of benzophenone might be responsible for the formation of X, we carried out the photolysis of Ib in the

SCHEME 3



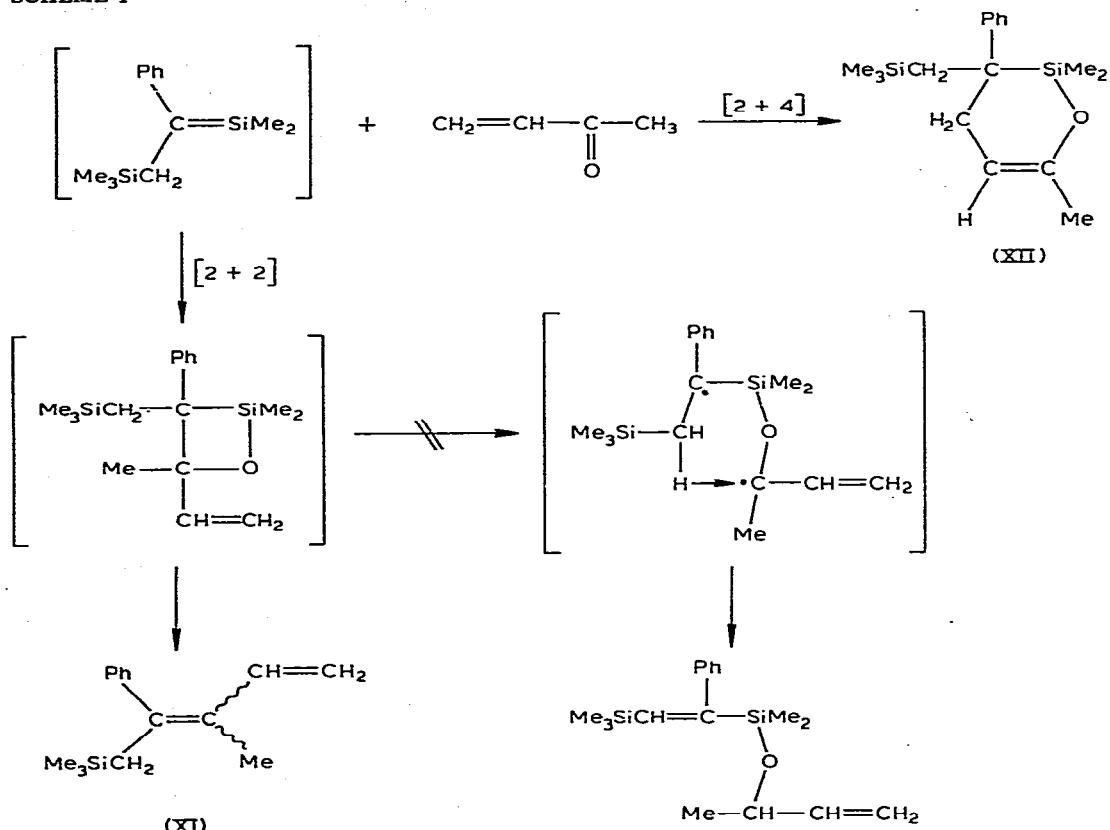
presence of benzophenone at various concentrations in benzene*. In no case did GLC analysis of the reaction mixture reveal a change in the product ratio (VIII/X = ca. 1). This finding indicates that compound X must be produced from the reaction of the ground state of benzophenone with the intermediate C. Therefore, the formation of X can be understood in terms of two possible pathways as shown in Scheme 3. One involves radical scission of the once-formed silaoxetane intermediate followed by a 1,5-hydrogen shift; the other the direct 1,5-hydrogen shift at the stage where the diradical intermediate is formed via radical addition of benzophenone to the silicon-carbon double bond, without the intermediacy of a silaoxetane.

Next, we examined the reaction of the intermediate C with an α,β -unsaturated

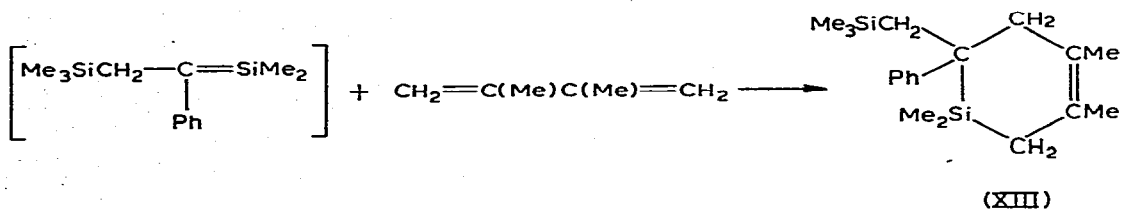
* At a high concentration of benzophenone, the relative rate of photochemical isomerization of Ib should be very small because benzophenone molecules absorb most of the incident radiation.

carbonyl compound and a 1,3-diene. Irradiation of Ib with methyl vinyl ketone under conditions similar to those above produced two types of compounds, *E*- and *Z*-3-methyl-4-phenyl-5-trimethylsilyl-1,3-pentadiene (XIa and XIb) and 2,6,6-trimethyl-5-trimethylsilylmethyl-5-phenyl-1-oxa-6-silacyclohexene-2 (XII), in 7, 7 and 18% yield, respectively. The isomers XIa and XIb may be formed by [2 + 2] cycloaddition, while the formation of compound XII can be explained by a direct [2 + 4] cycloaddition reaction. In this case, no product which might be expected from the radical scission of the carbon-carbon bond in the sila-oxetane derivative followed by intramolecular hydrogen shift, as observed in the photolysis of Ib in the presence of benzophenone, could be found.

SCHEME 4



Recently, Valkovich and Weber [14] have reported that the reaction of thermally generated silaethene derivatives with acrolein affords products which can be accounted for in terms of initial competing [2 + 2] and [2 + 4] cyclo-



addition reaction between intermediates and acrolein.

In contrast, reaction of the intermediate C with 2,3-dimethylbutadiene gave a [2+4] adduct XIII as the sole volatile product. No [2+2] cycloaddition product was detected by GLC and spectroscopic analysis [15].

Experimental

Materials

Benzene and n-hexane used as solvents were dried over lithium aluminum hydride and distilled from it just before use.

1,2-Divinyltetramethyldisilane (Ia) was prepared as reported in the literature [16,17]. Other vinyl-substituted disilanes were obtained as described below.

1-Phenylethenylpentamethyldisilane (Ib)

To a Grignard reagent prepared from 10.7 g (0.058 mol) of 1-phenylethenyl bromide and 1.6 g (0.066 g-atom) of magnesium in 50 ml of tetrahydrofuran (THF) was added 10 g (0.060 mol) of chloropentamethyldisilane dissolved in 50 ml of THF. The reaction mixture was heated at reflux for 10 h and hydrolyzed with dilute hydrochloric acid. The organic layer was washed to the neutral point with water and dried over potassium carbonate. Distillation gave 7.5 g (55% yield) of product Ib, b.p. 77–78°C/4 Torr, n_D^{20} 1.5179; NMR (δ , ppm) –0.01 (CH₃-SiMe₂, s, 9H), 0.22 (CH₃-SiMe, s, 6H), 5.51 (vinylic proton, d, J 3 Hz, 1H), 5.79 (vinylic proton, d, J 3 Hz, 1H), 6.9–7.4 (ring protons, m, 5H) (Found: C, 66.87; H, 9.75. C₁₃H₂₂Si₂ calcd.: C, 66.59; H, 9.46%).

1-Phenyl-2-vinyltetramethyldisilane (Ic)

In a 100-ml three-necked flask was placed a solution of 10.1 g (0.054 mol) of 1,2-dichlorotetramethyldisilane in 30 ml of dry THF. To this was added slowly a solution of phenylmagnesium chloride prepared from 1.36 g (0.056 g-atom) of magnesium and 6.1 g (0.054 mol) of chlorobenzene. The reaction mixture was refluxed for 2 h. Subsequently, it was cooled and vinylmagnesium chloride prepared from 2.0 g (0.082 g-atom) of magnesium and vinyl chloride in 30 ml of THF was added to it. After it had been refluxed for 3 h, the mixture was hydrolyzed with dilute hydrochloric acid. The organic layer was washed with water and dried over potassium carbonate. Distillation gave 6.0 g (50% yield) of compound Ic, b.p. 76°C/4 Torr, n_D^{20} 1.5141; NMR (δ , ppm) 0.15 (CH₃-SiMe, s, 6H), 0.37 (CH₃-SiMe, s, 6H), 5.58, 5.98, 6.14 (vinylic protons, ABX, 3H), 7.1–7.6 (ring protons, m, 5H) (Found: C, 65.61; H, 9.16. C₁₂H₂₀Si₂ calcd.: C, 65.38; H, 9.14%).

1-Phenyl-1-vinyltetramethyldisilane (Id)

A solution of 10.0 g (0.054 mol) of 1,1-dichlorotetramethyldisilane in THF was treated successively with the phenyl and vinyl Grignard reagents. The reaction and work-up was similar to that described above. Distillation gave 5 g (42% yield) of Id, b.p. 84°C/5 Torr, n_D^{20} 1.5168; NMR (δ , ppm) 0.09 (CH₃-SiMe₂, s, 9H), 0.39 (CH₃-Si, s, 3H), 5.71, 6.12, 6.26 (vinylic protons, ABX, 3H), 7.0–7.7 (ring protons, m, 5H) (Found: C, 65.37; H, 9.42. C₁₂H₂₀Si₂ calcd.: C, 65.38; H, 9.14%).

E-2-Phenylethenylpentamethyldisilane (Ie)

To the Grignard reagent prepared from 22 g (0.12 mol) of *E-2-phenylethenyl* bromide and 2.9 g (0.12 g-atom) of magnesium in 100 ml of dry THF was added 17 g (0.10 mol) of chloropentamethyldisilane dissolved in 20 ml of dry THF at room temperature for 5 min. The reaction mixture was refluxed for 5 h and then hydrolyzed with water. The organic layer was separated, washed with water, and dried over potassium carbonate. Distillation under reduced pressure gave 7 g (30% yield) of product *Ie*, b.p. 70–72°C/2 Torr, n_D^{20} 1.5276, NMR (δ , ppm) 0.08 (CH₃-SiMe₂, s, 9H), 0.20 (CH₃-SiMe, s, 6H), 6.37 (HC-Si, d, 1H, J 19 Hz), 6.75 (HC-Ph, d, 1H, J 19 Hz), 7.0–7.5 (ring protons, m, 5H) (Found: C, 66.86; H, 9.66. C₁₃H₂₂Si₂ calcd.: C, 66.59; H, 9.46%).

Photolysis of 1-alkenyldisilanes in the presence of methanol

The following is typical of the procedures used. A solution of 0.959 g (5.63 mmol) of 1,2-divinyldimethyldisilane (*Ia*) and 4.75 g (148 mmol) of dry methanol in 80 ml dry benzene was irradiated for 18 h with a low-pressure mercury lamp (10 Watt) having a Vycor filter under a purified nitrogen atmosphere at room temperature. Most of the solvent and unchanged methanol was evaporated and the residue was distilled under reduced pressure to give volatile products boiling up to 150°C/1 Torr. Yields of the products in the distillate were determined by GLC using *n*-undecane as an internal standard. The adduct *Iia* was then isolated by preparative GLC. Analytical and proton NMR data are listed in Tables 2 and 3.

Photolysis E-2-phenylethenylpentamethyldisilane (Ie) in the presence of methanol

A solution of 1.405 g (0.73 mmol) of *Ie* and 2 ml of dry methanol in 100 ml of dry benzene was photolyzed for 22 h at room temperature. Most of the solvent was evaporated and the residue was distilled under reduced pressure. Products were isolated by preparative GLC.

Photolysis of 1,2-divinyldimethyldisilane (Ia) in the presence of water

A solution of *Ia* (5.39 mmol) and water (5.33 mmol) in 80 ml of benzene was irradiated at room temperature for 17 h. GLC analysis of the reaction mixture showed that silanol *VIa* and siloxane *VIb* were formed in 60 and 11% yield, in addition to 29% of unchanged *Ia*. Pure *VIa* and *VIb* were isolated by preparative GLC.

Photolysis of 1-phenyl-2-vinyldimethyldisilane (Ic) in benzene

A solution of 0.979 g (4.44 mmol) of *Ic* in 80 ml of dry benzene was photolyzed with a low-pressure mercury lamp for 2 h. After evaporation of solvent, the residue was distilled under reduced pressure to give 42% yield of *sym*-bis(dimethylphenylsilylethyl)tetramethyldisiloxane (*VIc*), 10% yield of *cis*- and 10% yield of *trans*-1,1,3,3-tetramethyl-2,4-bis(dimethylphenylsilylmethyl)-1,3-disilacyclobutane (*Va* and *Vb*) in addition to 26% of unchanged *Ic*. Pure siloxane *VIc* was isolated by preparative GLC. M^+ 458 (mol. wt. 458.93); IR 1050 cm⁻¹; NMR (δ , ppm) 0.00 (CH₃-SiMe, s, 12H), 0.23 (CH₃-SiMePh, s, 12H), 0.49 (CH₂CH₂, m, 8H), 7.1–7.5 (ring protons, m, 10H) (Found: C, 63.11; H, 9.29. C₂₄H₄₂Si₄O calcd.: C, 62.81; H, 9.22%).

Photolysis of Ic in *n*-hexane

n-Hexane was refluxed over lithium aluminum hydride for 2 h. Approximately 80 ml of this solvent was distilled from the hydride directly into a reaction vessel. To this was added 0.855 g (3.88 mmol) of Ic and it was then photolyzed in the usual way. Distillation gave 21% yield of the *cis* isomer Va, m.p. 50°C, and 22% yield of the *trans* isomer Vb, m.p. 45°C, in addition to 28% of unchanged Ic.

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