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PHOTOLYSIS OF ORGANOPOLYSILANES. REACTIONS OF TRIMETHYLSILYLPHENYLSILYLENE WITH ALLYLIC HALIDES AND ALLYL ETHYL ETHER

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Summary

The photolysis of tris(trimethylsilyl)phenylsilane (I) in the presence of allyl chloride, allyl bromide, 2-cyclohexenyl chloride, 2-cyclohexenyl bromide and 2-methylallyl chloride resulted in formation of the respective 1-(2-alkenyl)-1-halo-1-phenyltrimethyldisilanes in moderate yields. Irradiation of I in the presence of crotyl chloride, 1-methylallyl chloride, prenyl chloride and 1,1-dimethylallyl chloride afforded the corresponding α- and γ-substituted chlorodisilanes. Photolysis of I in the presence of allyl ethyl ether produced 1-phenyl-1-trimethylsilyl-2-ethoxymethyl-1-silacyclopropane, although this product was not isolated. The reaction of this silacyclopropane with hydrogen chloride, methanol and boron trifluoride etherate is described.

Introduction

Although extensive studies have been done on the reactions of organosilylenes with various unsaturated hydrocarbons [1-8], much less interest has been shown in the reaction of the silylenes with unsaturated compounds bearing a heteroatom as a functional group in the molecule [9,11]. Recently, we have found that the reaction of photochemically generated trimethylsilylphenylsilylene with vinyl halides resulted in formation of products arising from formal insertion of the silylene into the carbon—halogen bond; however, with ethyl vinyl ether, the silylene added to the carbon—carbon double bond, not into the carbon—oxygen bond, giving a 2-ethoxy-1-silacyclopropane derivative which could be determined by ^{1}H NMR spectroscopic analysis [9].

These results prompted us to investigate the reactions of trimethylsilylphenylsilylene with functionally substituted allylic compounds.

Results and discussion

The photolysis of tris(trimethylsilyl)phenylsilane (I) in the presence of allylic chlorides (allyl, 2-methylallyl and 2-hexenyl chloride) afforded products of formal insertion of the silylene into the carbon—chlorine bond. Thus, when I was photolyzed with a 10-W low-pressure mercury lamp in the presence of allyl chloride in hexane, 1-allyl-1-chloro-1-phenyltrimethyldisilane was obtained in 45% yield as the sole volatile product. Interestingly, no silacyclopropane arising from addition of trimethylsilylphenylsilylene across the carbon—carbon double bond was detected in the photolysis mixture. Irradiation of I with 2-methylallyl chloride under similar conditions gave 1-(2-methylallyl)-1-chloro-1-phenyltrimethyldisilane. With 2-cyclohexenyl chloride, I produced 1-(2-cyclohexenyl)-1-chloro-1-phenyltrimethyldisilane (Scheme 1).

SCHEME 1

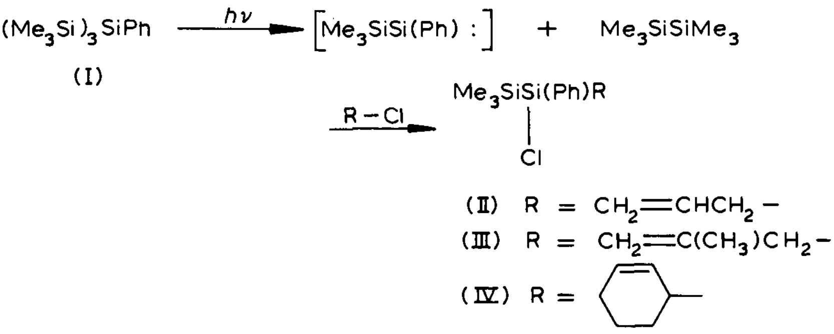


TABLE 1

PHOTOLYSIS OF I IN THE PRESENCE OF ALLYLIC HALIDES

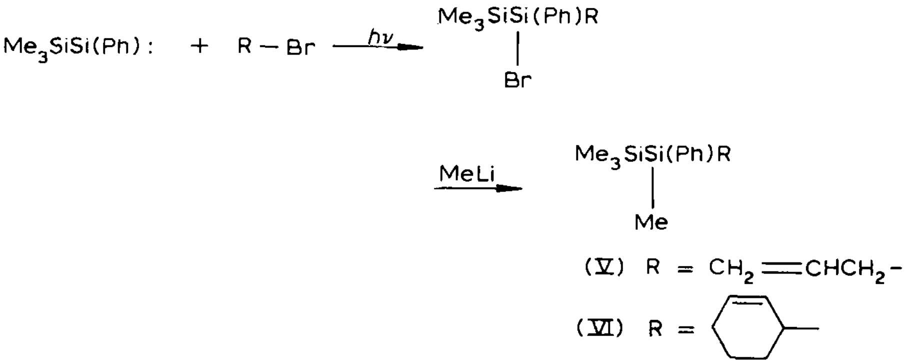
I (g (mmol))	Halide (mmol)	Time (h)	Products and yield (%)	Regioisomeric ratio (α : γ)
0.3346 (1.030)	allyl chloride (7.86)	1.5	II(45)	
0.3558 (1.095)	2-methylallyl chloride (8.39)	1.5	III(56)	
0.3261 (1.004)	2-cyclohexenyl chloride (8.66)	1.5	IV(33)	
0.3465 (1.067)	allyl bromide (9.38)	1.5	V(27) [a]	
0.3246 (0.999)	2-cyclohexenyl bromide (5.78)	1.5	VI(20) [a]	
0.3273 (1.008)	crotyl chloride [b] (7.91)	1.5	VIIa(33) [b], VIIb(10) [b] VIIc(3) [b]	28 : 72
0.3409 (1.050)	1-methylallyl chloride (8.23)	1.5	VIIa(5) [b], VIIb(32) [b] VIIc(10) [b]	11 : 89
1.0215 (3.145)	prenyl chloride (14.98)	1.5	VIIIa(23), VIIIb(14)	38 : 62
0.3286 (1.012)	1,1-dimethylallyl chloride (7.68)	1.5	VIIIa(9), VIIIb(21) IX(5)	30 : 70

[a] Methylated product. [b] Reduction product with lithium aluminium hydride.

Products II—IV could readily be isolated by preparative GLC. Reaction conditions and product yields in the photolysis experiments are summarized in Table 1.

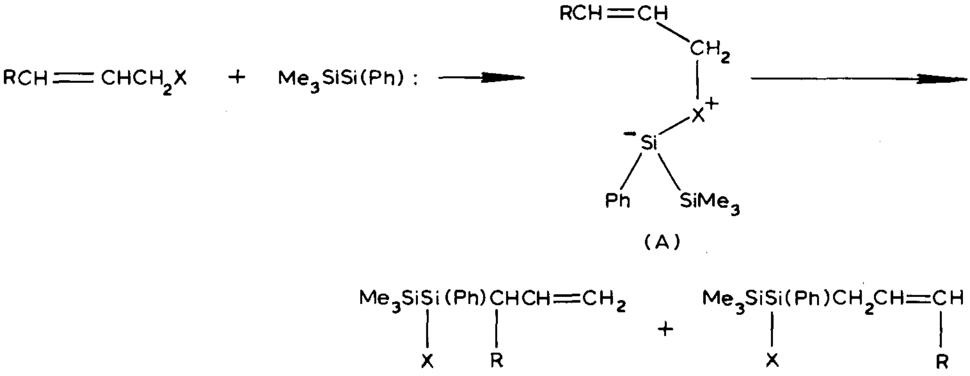
Allyl bromide and 2-cyclohexenyl bromide reacted with trimethylsilylphenylsilylene to give the products, which are probably of similar type to II and IV. However, the reactions were not clean and by-products arising from photochemical degradation of the bromo compounds were always produced. Attempts to separate the pure bromodisilanes using GLC were unsuccessful. Therefore, we methylated the photolysis mixture and isolated the products by preparative GLC. Thus, irradiation of I in the presence of allyl bromide in hexane followed by treatment with methyllithium afforded 1-allyl-1-phenyltetramethyldisilane (V) in 22% yield. Similar photolysis of I in the presence of 2-cyclohexenyl bromide followed by methylation gave 1-(2-cyclohexenyl)-1-phenyltetramethyldisilane (VI) (Scheme 2).

SCHEME 2



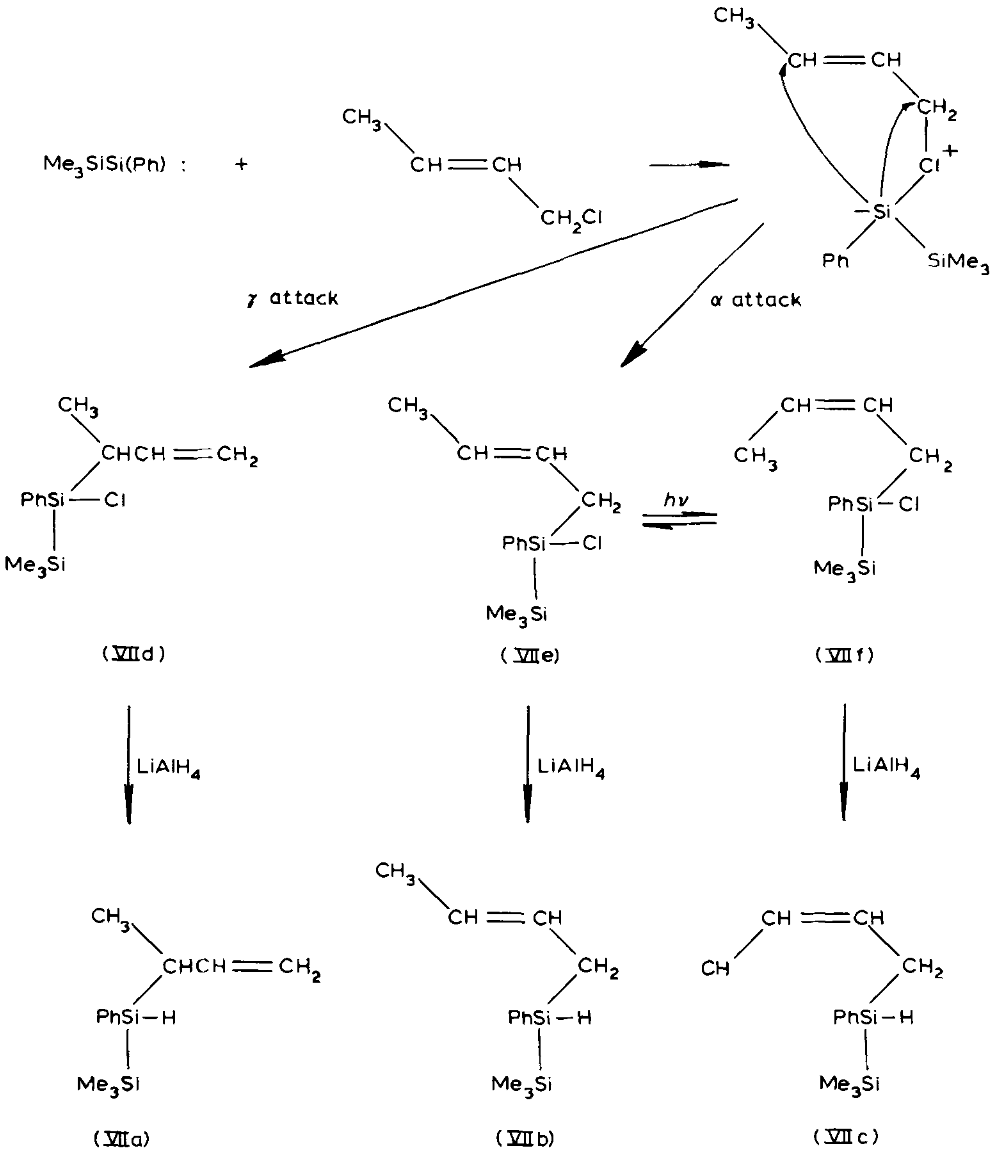
As discussed below, the low-temperature photolysis of I in the presence of phenyl chloride afforded no indication of the silacyclopropane expected to be produced from addition of trimethylsilylphenylsilylene to the carbon—carbon double bond. We thought that the reaction might proceed via a zwitterionic intermediate (A) as shown in Scheme 3. If this is so, one might expect to ob-

SCHEME 3



tain products of allylic rearrangement from the reaction of the silylene with unsymmetrically substituted allylic chlorides. In order to confirm this possibility, we photolyzed I in the presence of various substituted allylic chlorides. Irradiation of I in the presence of crotyl chloride led to the formation of three isomeric products. Unfortunately, all attempts to separate them using GLC were unsuccessful. Therefore the chlorodisilanes were reduced with lithium aluminum hydride. The resulting three hydrodisilanes, 1-(1-methylallyl)-1-phenyl-2,2,2-trimethyldisilane (VIIa) (33% yield), 1-(*trans*-2-butenyl)-1-phenyl-2,2,2-trimethyldisilane (VIIb) (10% yield) and 1-(*cis*-2-butenyl)-1-phenyl-2,2,2-trimethyldisilane (VIIc) (3% yield), could readily be isolated by

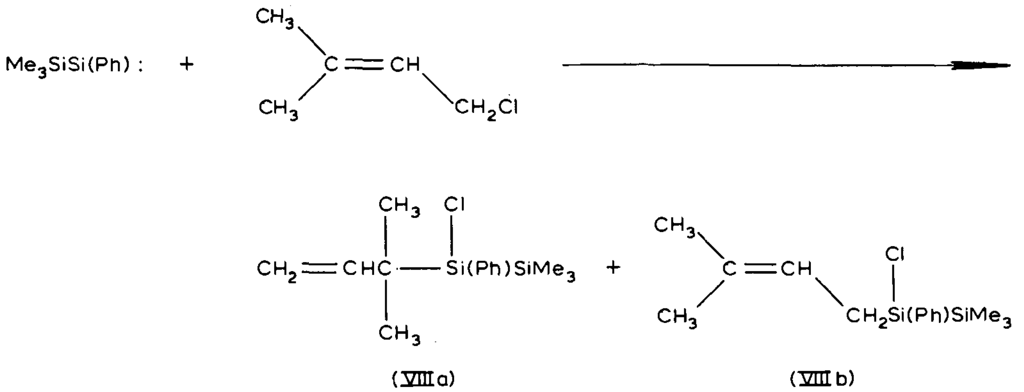
SCHEME 4



GLC. Chlorodisilane VIId (precursor of VIIa) must be formed by attack of the silyl anion on the γ carbon atom in the intermediate, while attack of the anion on the α carbon atom may produce chlorodisilane VIIe. The production of isomer VIIf may be ascribed to photochemical isomerization of VIIe (Scheme 4) *. A similar zwitterion mechanism has been postulated in the reaction of photochemically generated dimethylsilylene with 3,4-epoxy-1-butene [11].

Irradiation of I in the presence of 1-methylallyl chloride, followed by treatment with lithium aluminum hydride, afforded VIIa, VIIb and VIIc in 5, 32 and 10% yields, respectively. In all reactions with the substituted allylic chlorides, attack of the silicon nucleophile on the γ carbon was more favored than that on the α carbon atom. Thus, photolysis of I in the presence of prenyl chloride afforded only 1-(1,1-dimethylallyl)-1-chloro-1-phenyltrimethyldisilane (VIIIa) and 1-(3-methyl-2-butenyl)-1-chloro-1-phenyltrimethyldisilane (VIIIb) in 23 and 14% yields, respectively, as the volatile products (Scheme 5). Irradiation of I with 1,1-dimethylallyl chloride under similar conditions gave VIIIa and VIIIb in 9 and 21% yields, respectively. In this photolysis, an unexpected compound, 1-chloro-1-phenyltrimethyldisilane (IX), also was obtained in 5% yield. The formation of IX may be rationalized in terms of abstraction of a ptoron from a methyl carbon in the dimethylallyl group by the silyl anion as shown in Scheme 6. In no case was a change in the isomeric purity of the recovered allylic chlorides observed.

SCHEME 5



In order to establish whether or not the products VIIIa and VIIIb were formed as the initial products in the photolysis of I in the presence of prenyl chloride, we followed the progress of the reaction by GLC. Figure 1 illustrates a profile for the formation of VIIIa and VIIIb as a function of time. As can be seen from the figure, both VIIIa and VIIIb must be the initial products of the photolysis.

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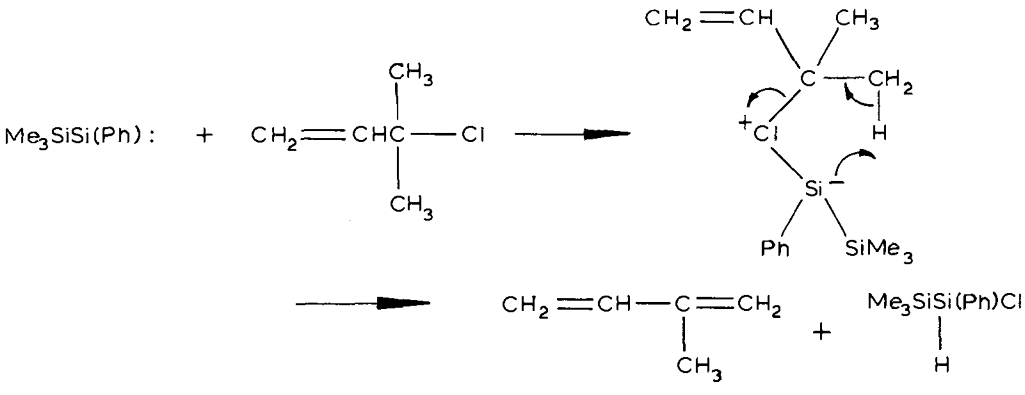
* For the production of VIIa, VIIb and VIIc, one referee suggested an alternative mechanism involving a radical pair that is produced from the homolytic scission of the initially formed zwitterion [10]. However, the fact that the reaction of trimethylsilylphenylsilylene with cyclopropylcarbinyl chloride afforded 1-chloro-1-cyclopropylcarbinyl-1-phenyltrimethyldisilanes, but not a ring-opened product, indicates the absence of such radical species [12].

SCHEME 6



(IX)

Next, we attempted to trap the silacyclopropane by low temperature photolysis of I in the presence of prenyl chloride. It is well known that the silacyclopropanes react with oxygen to give non-volatile substances. If 1-phenyl-1-trimethylsilyl-2-chloromethyl-3,3-dimethyl-1-silacyclopropane were present long enough in the photolysis mixture to react with oxygen, different yields of VIIIa and VIIIb would be observed before and after treatment of the mixture with oxygen. First, a hexane solution of I and prenyl chloride was irradiated with a low-pressure mercury lamp at —70° C for 4.5 h. GLC analysis of an aliquot which was extract from the photolysis mixture and warmed to room temperature under nitrogen showed the production of VIIIa and VIIIb in 23 and 12% yields. Secondly, dry oxygen was introduced into the original photolysis mixture at —70° C to decompose the silacyclopropane which might be present. Analysis of the mixture indicated that no difference was observed in the yields of VIIIa and VIIIb. All of the results obtained so far suggest the mechanism shown in Scheme 3.

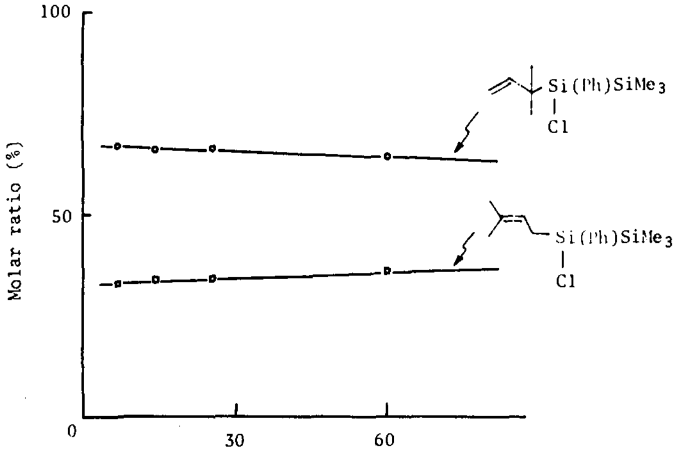
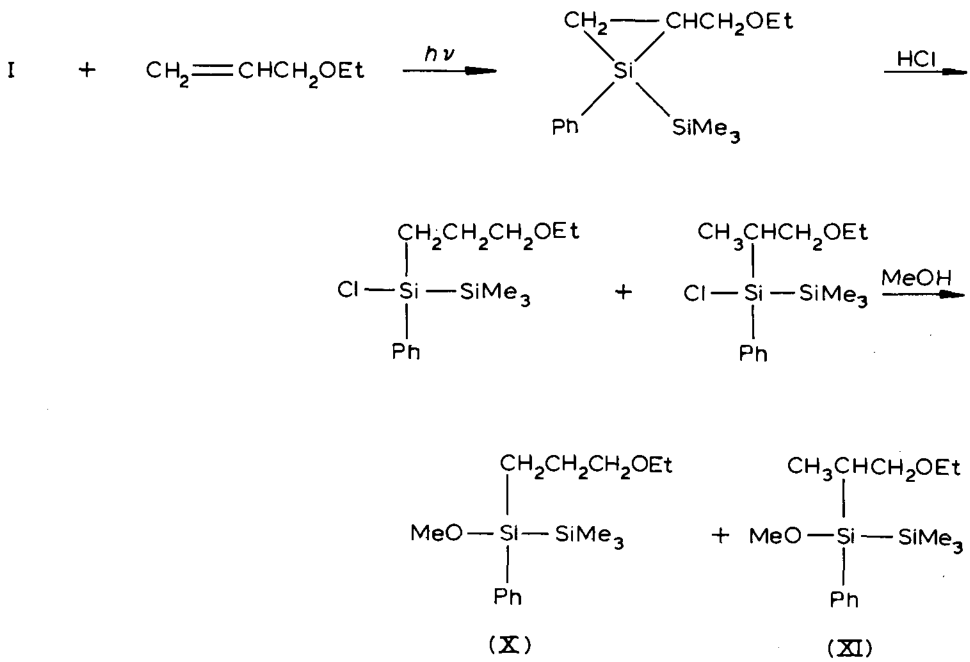


Fig. 1. Photolysis of tris(trimethylsilyl)phenylsilane in the presence of prenylchloride.

SCHEME 7



Interestingly, the photolysis of I in the presence of allyl ethyl ether is believed to give rise to 1-phenyl-1-trimethylsilyl-2-ethoxymethyl-1-silacyclopropane as a definite intermediate in solution, as evidenced by the following facts. Introduction of dry hydrogen chloride gas into the mixture obtained from the photolysis of I in the presence of allyl ethyl ether, followed by methanolysis of the resulting products, gave 1-(3-ethoxypropyl)-1-methoxy-1-phenyltrimethyldisilane (X) and 1-(2-ethoxy-1-methylethyl)-1-methoxy-1-phenyltrimethyldisilane (XI) in 7 and 8% yield. The reaction may involve the ring opening of the silacyclopropane by hydrogen chloride, followed by methanolysis of the resulting chlorodisilanes (Scheme 7).

SCHEME 8

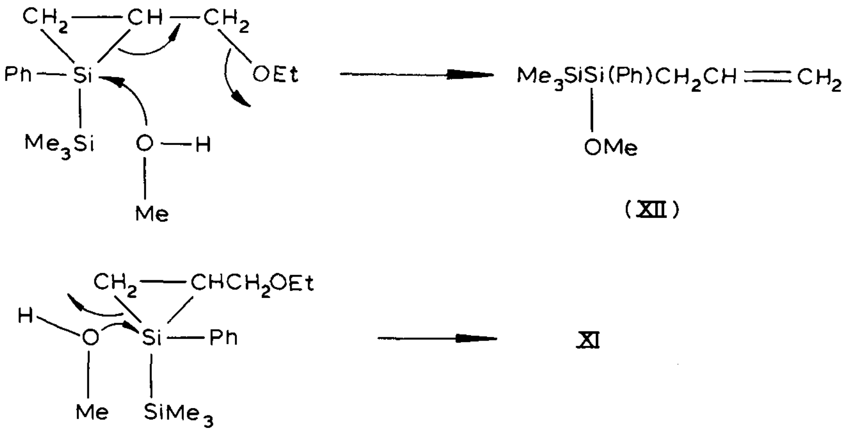


TABLE 2

^{1}H NMR CHEMICAL SHIFTS OF PRODUCTS

Compound	Chemical shifts (δ, ppm) in CCl_4
II	0.20 (Me_3Si, s, 9 H), 2.12 (H_2C, broad d, 2 H, J = 7.5 Hz), 5.5—5.9 (C=CH—C, m, 1 H), 7.2—7.6 (C_6H_5, m, 5 H)
III	0.20(Me_3Si, s, 9 H), 1.67 (H_3C—C, broad s, 3 H), 2.12 (H_2C—C=C, broad s, 2 H), 4.62 (HC=C, broad s, 1 H), 4.69 (HC=C, broad s, 1 H), 7.3—7.7 (C_6H_5, m, 5 H)
IV	0.20 and 0.21 (Me_3Si, unequivalent due to diastereomerism, s each, 9 H), 1.4—2.2 (saturated ring protons, m, 7 H), 5.71 (HC=CH, broad s, 2 H), 7.3—7.7 (C_6H_5, m, 5 H)
V	0.05 (Me_3Si, s, 9 H), 0.30 (MeSi, s, 3 H), 1.87 (H_2C—C=C, broad d, 1 H, J = 8 Hz), 4.90 (H—CH=C, broad d, 1 H, J = 17 Hz), 4.92 (H—CH=C, broad d, 1 H, J = 11 Hz), 5.6—6.0 (C—HC=C, m, 1 H), 7.3—7.6 (C_6H_5, m, 5 H)
VI	0.11 and 0.21 (Me_6Si, unequivalent due to diastereomerism, s each, 9 H), 0.32 (MeSi, s, 3 H), 1.4—2.2 (saturated ring protons, m, 7 H), 6.67 (HC=CH, m, 2 H), 7.3—7.6 (C_6H_5, m, 5 H)
VIIa	Mixture of diastereoisomers ca. 3 : 2, major isomer; 0.16 (Me_3Si, s), 1.20 (H_3C—C, d, J = 7 Hz), minor one; 0.14 (Me_3Si, s), 1.17 (H_3C—C, d, J = 7 Hz), common signals; 2.10 (HC—C=C, m, 1 H), 4.03 (H—Si, broad t, 1 H, J = 4 Hz), 4.70—5.0 (H_2C=C, m, 2 H), 5.7—6.1 (HC=C, m, 1 H), 7.2—7.5 (C_6H_5, m, 5 H)
VIIb	0.11 (Me_3Si, s, 9 H), 1.61 (H_3C—C=C, broad d, 3 H, J = 6 Hz), 1.82 (H_2C—Si, m, 2 H), 4.11 (H—Si, broad t, 1 H, J = 4.5 Hz), 5.31 (HC=CH, m, 2 H), 7.2—7.5 (C_6H_5, m, 5 H)
VIIc	0.13 (Me_3Si, s, 9 H), 1.51 (H_3C—C=C, broad d, 3 H, J = 6 Hz), 1.85 (H_2C—Si, m, 1 H), 4.11 (H—Si, broad t, 1 H, J = 4 Hz), 5.37 (HC=CH, m, 2 H), 7.2—7.5 (C_6H_5, m, 5 H)
VIIIa	0.24 (Me_3Si, s, 9 H), 1.07 and 1.16 (diastereotopic Me_2C, s each 6 H), 4.82 (HC=C, broad d, 1 H, J = 18 Hz), 4.99 (H—CH=C, broad d, 1 H, J_{cis} = 11 Hz), 5.90 (HC=C, dd, 1 H, J = 17 and 11 Hz), 8.2—7.6 (C_6H_5, m, 5 H)
VIIIb	0.18 (Me_3Si, s, 9 H), 1.50 (H_3C—C=C, broad s, 3 H), 1.67 (H_3C—C=C, broad s, 3 H), 1.96 (H_2C—Si, broad d, 2 H, J = 8 Hz), 5.12 (HC=C, broad t, 1 H, J = 8 Hz), 7.2—7.5 (C_6H_5, m, 5 H)
IX	0.23 (Me_3Si, s, 9 H), 5.20 (H—Si, s, 1 H), 7.3—7.6 (C_6H_6, m, 5 H)
X	0.11 (Me_3Si, s, 9 H), 0.77 (H_2C—Si, m, 2 H), 0.96 (H_3C—C, t, 3 H, J = 7 Hz), 1.5—1.8 (C—CH_2—C, m, 2 H), 3.33 (O—CH_2—CH_2, t, 2 H, J = 7 Hz), 3.34 (O—CH_2—CH_3, q, 2 H, J = 7 Hz), 3.50 (H_3C—O, s, 3 H), 7.3—7.6 (C_6H_5, m, 5 H)
XI	Mixture of diastereoisomers ca. 1 : 1, 0.16 and 0.18 (Me_3Si, s, each, 9 H), 1.04 (H_3C—C—Si, d, 3 H, J = 7 Hz), 1.15 (H_3C—C—O, t, 3 H, J = 7 Hz), 1.45 (HC—Si, m, 1 H), 3.37 (C—CH_2—O, q, J = 7 Hz), 3.39 (H_2C—OEt, d, overlapped with the former signals, 4 H, J = 7 Hz), 3.51 and 3.53 (H_3C—O, s each, 3 H), 7.2—7.5 (C_6H_5, m, 5 H)
XII	0.16 (Me_3Si, s, 9 H), 1.97 (H_2C—C=C, broad d, 2 H, J = 8 Hz), 3.50 (H_3C—O, s, 3 H), 5.6—6.0 (HC=C, m, 1 H), 7.2—7.5 (C_6H_5, m, 5 H)
XIII	0.18 (Me_3Si, s, 9 H), 2.01 (C—CH_2—Si, broad t, 2 H, $J_H = J_F$ = 7 Hz), 4.92 (H—CH=C, broad d, 1 H, J = 10 Hz), 4.95 (H—CH=C, broad d, 1 H, J = 17 Hz), 5.6—6.0 (C—CH=C, m, 1 H), 7.3—7.5 (C_6H_5, m, 5 H)

In contrast, direct methanolysis of the photolysis mixture caused the formation of 1-allyl-1-methoxy-1-phenyltrimethyldisilane (XII), in addition to XI (Scheme 8). It should be noted that no volatile product could be detected by GLC analysis before addition of methanol. Presumably the silacyclopropane is thermally unstable.

Similar elimination of the ethoxy group has been found in the methanolysis of 1-phenyl-1-trimethylsilyl-2-ethoxy-1-silacyclopropane obtained from trimethylsilylphenylsilylene and vinyl ethyl ether [9]. In marked contrast to our findings, Tortorelli and Jones [10] recently have reported that they obtained allylethoxydimethylsilane as a primary photo-product in the photolysis of dodecamethylcyclohexasilane in the presence of allyl ethyl ether.

TABLE 3

ELEMENTAL ANALYSES, IR AND MASS DATA FOR ISOLATED COMPOUNDS

Compound		Found (calcd.) (%)			IR (neat) (cm^{-1})	Exact mass, M^+ (calcd.)
		C	H	Cl		
II	$C_{12}H_{19}Si_2Cl$	56.54	7.36	14.03	1630	254.0707
		(56.54)	(7.51)	(13.90)		(254.0714)
III	$C_{13}H_{21}Si_2Cl$	57.77	8.03	12.80	1640s	268.0916
		(58.06)	(7.87)	(13.18)		(268.0870)
IV	$C_{15}H_{23}Si_2Cl$				1640w	294.1027
						(294.1027)
V	$C_{13}H_{22}Si_2$	66.84	9.35	—	1630s	234.1284
		(66.59)	(9.46)			(234.1260)
VI	$C_{16}H_{26}Si_2$			—	1640w	274.1565
						(274.1573)
VIIa	$C_{13}H_{22}Si_2$	66.61	9.71	—	2090s	234.1239
		(66.59)	(9.45)		1625s	(234.1260)
VIIb	$C_{13}H_{22}Si_2$	66.34	9.74	—	2090s	234.1251
		(66.59)	(9.45)		960m	
VIIc	$C_{13}H_{22}Si_2$			—	2090s	
					1650w	
VIIIa	$C_{14}H_{23}Si_2Cl$	59.17	8.16	12.32	1630m	282.0994
		(59.43)	(8.19)	(12.53)		(282.1027)
VIIIb	$C_{14}H_{23}Si_2Cl$	59.41	8.26	12.59		282.1036
		(59.43)	(8.19)	(12.53)		
IX	$C_9H_{13}Si_2Cl$	50.70	7.16		2125s	214.0390
		(50.32)	(7.04)			(214.0401)
X	$C_{15}H_{28}O_2Si_2$					
XI	$C_{15}H_{28}O_2Si_2$				1080s	281.1405 [a]
						(281.1393)
XII	$C_{13}H_{22}OSi_2$	62.26	9.09	—	1630s	
		(62.34)	(8.85)		1080s	
XIII	$C_{12}H_{19}FSi_2$	60.41	8.17	7.62 [b]	1630s	238.1004
		(60.44)	(8.03)	(7.97)		(238.1009)

[a] M^+—CH_3. [b] Fluorine content.

Interestingly, addition of boron trifluoride etherate to the silacyclopropane afforded 1-allyl-1-fluoro-1-phenyltrimethyldisilane (XIII) as the sole volatile product.

(XIII)

The structures of the products reported here were confirmed by ^{1}H NMR, IR and mass spectrometric analyses as summarized in Tables 2 and 3.

Experimental

General procedure

All photolyses were carried out under an atmosphere of purified nitrogen at 0° C using a 10-W low-pressure mercury lamp bearing a Vycor filter. Proton

NMR spectra were determined at ambient temperature with a JEOL Model JNM-MH-100 spectrometer using carbon tetrachloride solutions containing cyclohexane 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. IR spectra were measured on a Hitachi Model EPI-G3 grating spectrometer. Identification of the products by GLC was done using two different columns (Silicone SE-30 and Silicone DC-550). Yields were determined by GLC using internal standard method based on unrecovered I. An Aerograph Model 920 gas chromatograph with a thermal conductivity detector was used for separating the products. All compounds reported here were separated as colorless liquids by using a 3/8 in × 10 ft column containing Silicone DC-550 (30%) on Chromosorb P.

Materials

Tris(trimethylsilyl)phenylsilane [13], 2-chlorohexenyl chloride [14], prenyl chloride [15], 1,1-dimethylallyl chloride [13] and allyl ethyl ether [16] were prepared as reported in the literature. Allyl halides were dried over potassium carbonate and distilled from a small amount of sodium bicarbonate. Solvent hexane was dried over lithium aluminum hydride and distilled before use.

Photolysis of I in the presence of allylic chlorides

The following is typical of the procedure used. A mixture of 0.3346 g (1.030 mmol) of I, 0.6010 g (7.86 mmol) of allyl chloride and 0.0310 g (0.146 mmol) of pentadecane as an internal standard in 25 ml of dry hexane was photolyzed with a low-pressure mercury lamp for 1.5 h with ice cooling. GLC analysis of the reaction mixture showed the presence of 1-allyl-1-chloro-1-phenyltrimethyldisilane (II) in 45% yield, in addition to 32% of recovered I. Pure II was isolated by preparative GLC.

Photolysis of I in the presence of allyl bromide

A mixture of 0.3465 g (1.067 mmol) of I, 1.135 g (9.38 mmol) of allyl bromide and 0.0256 g (0.0908 mmol) of eicosane as an internal standard in 25 ml of hexane was irradiated for 1.5 h with ice cooling. After irradiation was stopped, the solvent and unreacted allyl bromide were distilled off. The residue in the flask was dissolved in 10 ml of dry ether. To this was added 10 ml of a 1.1 *M* methyllithium/ether solution with ice cooling and the mixture was stirred for 15 min at room temperature. It was then hydrolyzed with water. The organic layer was separated and washed with water, and dried over potassium carbonate. The mixture was analyzed by GLC as being V (27% yield) and 32% of the starting compound I. Pure V was isolated by preparative GLC.

Photolysis of I in the presence of crotyl chloride

A mixture of 0.3273 g (1.008 mmol) of I, 0.7158 g (7.91 mmol) of crotyl chloride and 0.0393 g (0.198 mmol) of tetradecane as an internal standard was photolyzed for 1.5 h with ice cooling. The solvent and unreacted crotyl chloride were evaporated. The remaining material was dissolved in 10 ml of dry ether and then was added to a suspension of lithium aluminum hydride (0.090 g, 2.4 mmol) in ether with ice cooling. After refluxing for 30 min, the mixture was hydrolyzed. The organic layer was separated and washed with water, and dried over potassium carbonate. The product was analyzed by GLC as being VIIa (33% yield), VIIb (10% yield) and VIIc (3% yield). Pure VIIa, VIIb and VIIc were separated by preparative GLC.

Plots of observed yields of the products against time for the photolysis of I in the presence of prenyl chloride

A mixture of 0.9875 g (3.040 mmol) of I, 2.406 g (23.0 mmol) of prenyl chloride and 0.0490 g (0.231 mmol) of pentadecane as an internal standard in 100 ml of hexane was photolyzed. At suitable intervals small aliquots of solution were extracted and analyzed by GLC (Silicone DC-550). The results obtained are illustrated in Fig. 1.

Low temperature photolysis of I in the presence of prenyl chloride

A mixture of 0.9863 g (3.067 mmol) of I, 2.218 g (21.1 mmol) of prenyl chloride and 0.0763 g (0.359 mmol) of pentadecane as an internal standard in 130 ml of hexane was photolyzed with a low-pressure mercury lamp surrounded by a Vycor vacuum jacket for 4.5 h at —70° C. At this stage, 83% of I was photolyzed. An aliquot (2 ml) of the reaction mixture was extracted by means of a syringe and warmed up to room temperature under an atmosphere of nitrogen. GLC analysis of this solution showed the formation of VIIIa and VIIIb in 23 and 12% yields. Dry oxygen was introduced into the original photolysis mixture for 10 min at —70° C, which was then warmed to room temperature. The mixture was analyzed by GLC as being VIIIa and VIIIb in 23 and 12% yields.

Treatment of 1-phenyl-1-trimethylsilyl-2-ethoxymethyl-1-silacyclopropane with hydrogen chloride, followed by methanol

A mixture of 0.3354 g (1.033 mmol) of I, 0.5692 g (6.62 mmol) of allyl ethyl ether and 0.0260 g (0.131 mmol) of tetradecane as an internal standard was photolyzed for 1.8 h with ice cooling. Into this was introduced dry hydrogen chloride admixed with nitrogen for 10 min at the same temperature. After the solvent was distilled off, 0.15 ml of triethylamine in 10 ml of dry ether was added to the residue. Addition of 1 ml of methanol was followed by reflux for 30 min. The mixture was then analyzed by GLC as being X (7% yield) and XI (8% yield). Distillation under reduced pressure gave crude X and XI, which were isolated pure by preparative GLC.

Reaction of 1-phenyl-1-trimethylsilyl-2-ethoxymethyl-1-silacyclopropane with methanol

A mixture of 0.3252 g (1.001 mmol) of I, 0.4900 g (5.70 mmol) of allyl ethyl ether and 0.0235 g (0.11 mmol) of tetradecane was photolyzed for 1.5 h. To this was added 1 ml of dry methanol. The mixture was analyzed by GLC as being XI (8% yield) and XII (11% yield). After the solvent was evaporated, the residue was distilled under reduced pressure to give crude XI and XII. Pure XI and XII were isolated by preparative GLC.

Reaction of 1-phenyl-1-trimethylsilyl-2-ethoxymethyl-1-silacyclopropane with boron trifluoride etherate

A mixture of 0.3445 g (1.061 mmol) of I and 0.6893 g (8.02 mmol) of allyl ethyl ether and 0.097 g (0.346 mmol) of eicosane in 25 ml of hexane was photolyzed for 1.5 h with ice cooling. To this was added 40 μl of boron trifluoride etherate and the mixture was allowed to stand at room temperature for 2 h. GLC analysis showed XIII in 14% yield.

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References

1 W.H. Atwell and D.R. Weyenberg, Angew. Chem. Intern. Ed., 8 (1969) 469.
2 E.A. Chernyshev, N.G. Komalenkova and S.A. Bashkirova, Usp. Khim., 45 (1976) 1782.
3 R.T. Conlin and P.P. Gaspar, J. Amer. Chem. Soc., 98 (1976) 3715.
4 D. Seyferth, D.C. Annarelli and S.C. Vick, J. Amer. Chem. Soc., 98 (1976) 6382.
5 D. Seyferth and S.C. Vick, J. Organometal. Chem., 125 (1977) C11.
6 M. Ishikawa, K. Nakagawa and M. Kumada, J. Organometal. Chem., 131 (1977) C15.
7 M. Ishikawa, K. Nakagawa, M. Ishiguro, F. Ohi and M. Kumada, J. Organometal. Chem., 152 (1978) 155.
8 C.S. Liu and T. Hwang, J. Amer. Chem. Soc., 100 (1978) 2577.
9 M. Ishikawa, K. Nakagawa, S. Katayama and M. Kumada, J. Amer. Chem. Soc., in press.
10 V.J. Tortorelli and M. Jones, Jr., J. Chem. Soc. Chem. Commun., (1980) 785.
11 D. Tzeng and W.P. Weber, J. Amer. Chem. Soc., 102 (1980) 1451.
12 M. Ishikawa, K. Nakagawa and M. Kumada, J. Organometal. Chem., in press.
13 M. Ishikawa, K. Nakagawa and M. Kumada, J. Organometal. Chem., 178 (1979) 105.
14 C.A. Grob, H. Kny and A. Ganeux, Gelv. Chim. Acta, 40 (1957) 130.
15 A.J. Ultee Sr., Rec. Trav. Chim., 68 (1949) 125.
16 R. Sjrabal, Z. Physik. Chem., A, 185 (1940) 92.